

Effects of Fluoride Ions on the Corrosion and Passive Behaviour of Aluminium

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The title subject has been studied by stationary and transient polarization measurements on high-purity aluminium electrodes in deoxygenated solutions of 1 M ammonium acetate (pH 7.2) with ammonium fluoride additions of 0 to 5 mM at 25 °C and by Auger electron spectroscopic profile investigations of oxide films formed. It is found that fluoride ions strongly stimulate the anodic dissolution (and, hence, the corrosion) of passive aluminium without destroying its passivity. This seems to occur mostly by a transport limited formation of complexes with aluminium ions dissolving at the passive metal surface. However, fluoride ions to some extent also enter at least the outer and thickest part of a duplex oxide film on the metal. Neither the active/passive transition nor the cathodic hydrogen evolution reaction appears much affected.

Fluoride ions are known to increase the corrosion rate and the anodic passive current of aluminium in aqueous solutions,¹⁻³ but the underlying mechanism is not clear. Some authors² have ascribed the observed effects to fluoride ions weakening the protective properties of the passivating oxide film by substitutional incorporation. Other authors³ have ascribed them to fluoride ions stimulating the aluminium ion transfer at the oxide/solution interface by adsorption and complex formation.

In the present work, this subject is further studied by stationary and transient polarization measurements on high-purity aluminium electrodes in deaerated salt solutions (1 M $\text{NH}_4\text{Ac} + x$ mM NH_4F , $x=0$ to 5, pH=7.2, 25 °C) and by subsequent Auger electron spectroscopic (AES) investigations of passive films formed. The studies concern both anodic metal ion transfer (metal conversion and dissolution) and cathodic electron transfer (hydrogen evolution) at the aluminium electrode. This work is an extension of previous work in our laboratory on the corrosion and passive behaviour of aluminium.⁴⁻⁶

EXPERIMENTAL

Experiments and measurements have been performed with materials, equipment, instruments and procedures essentially as previously described.^{4,5} Deaerated aqueous solutions of 1 M $\text{NH}_4\text{Ac} + x$ mM NH_4F with x -values of 0, 0.2, 1 and 5 have been used as test solutions under a protecting nitrogen atmosphere. For stationary behaviour to be approached at a chosen electrode potential, a stabilization period of about 20 h was used throughout. The electrode was brought to the chosen potential by a linear sweep of 1 mV/s. After having

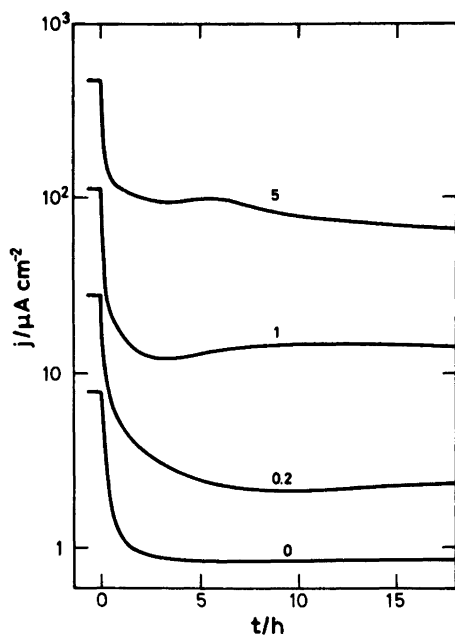


Fig. 1. Anodic current/time curves for aluminium at -0.5 V(sce) in 1 M $\text{NH}_4\text{Ac} + x$ mM NH_4F at 25 °C (after sweeping at 1 mV/s from the open-circuit corrosion potential). Values of x at the curves. No stirring.

disturbed a stationary state by a square potential (or current) pulse, one usually had to wait 10–15 min for the starting state to be well regained. All polarization measurements were performed at 25 °C in a thermostatted cell and with a thermostatted saturated calomel electrode (sce) as reference electrode.

RESULTS

Fig. 1 gives examples of potentiostatic current/time curves obtained for the aluminium electrode in the various test solutions after the chosen stabilization potential was reached by sweeping at 1 mV/s from the open-circuit corrosion potential. The curves illustrate that a rather long stabilization period is needed for stationary conditions to be approached, and

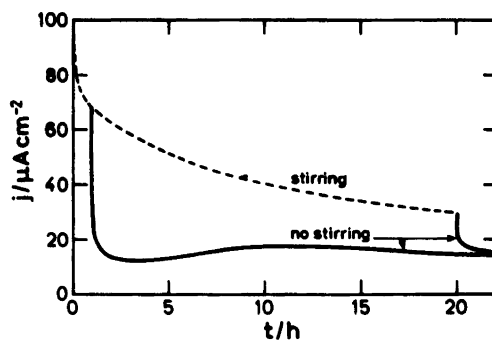


Fig. 2. Anodic current/time curves for aluminium at -0.5 V(sce) in stirred (---) and unstirred (—) solution of 1 M $\text{NH}_4\text{Ac} + 1$ mM NH_4F at 25 °C (after sweeping at 1 mV/s from the open-circuit corrosion potential).

that the stationary anodic current increases with increasing fluoride concentration in the test solution. The examples apply to a stabilization potential of -0.5 V(sce) for the aluminium electrode in unstirred solution.

Fig. 2 illustrates the effect of stirring (by nitrogen bubbling). Two comparable current/time curves are there given, one for a case in which an initial stirring was stopped after 1 h stabilization, and one for a case in which the stirring was stopped first after 20 h stabilization. Stirring clearly increases the anodic current going through a positively polarized aluminium electrode in a fluoride containing solution. However, the relative stirring effect appears to decrease with time over the stabilization period. This decrease is stronger than can be explained by a consumption of free fluoride ions on complexing with dissolved aluminium ions. Most data of the present work apply to unstirred solutions.

Transient data. After 20 h stabilization at open circuit or at a chosen stabilization potential, the aluminium electrode responded to short-time (1–2 s) voltage pulses by giving current transients like those previously presented and discussed for similar (but fluoride free) conditions.^{4,5} Hence, fluoride ions do not affect the general shape of such potentiostatic transients very much. Hydroxyl ions do so more noticeably.⁵

Fig. 3 exemplifies initial polarization data revealed (as previously described⁴) by potentiostatic transients. It also illustrates how the measured current (j) can be decomposed into its components of metal-ion transfer (j_m) and electron transfer (j_e) at the metal/oxide interface by:⁴

$$j = j_m + j_e \quad (1)$$

Here, anodic currents are regarded as positive and cathodic ones as negative, a sign convention adopted in the present work.

The above treatment yields not only initial values of j_m and j_e (at various potentials), but also their stationary values (j'_m and j'_e) at the stabilization potential concerned (E'). This is notified in Fig. 3 and utilized below. At stationary open-circuit conditions (Fig. 4), one has (since $j=0$).

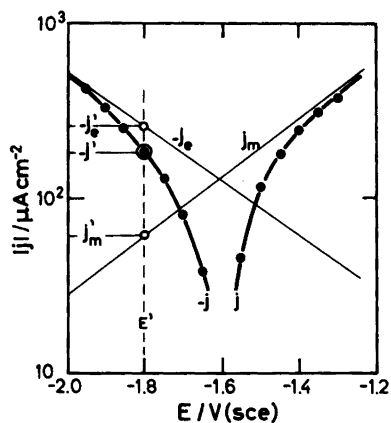


Fig. 3. Initial polarization data for aluminium electrode stabilized for 20 h at -1.8 V(sce) in 1 M NH_4Ac at 25 °C.

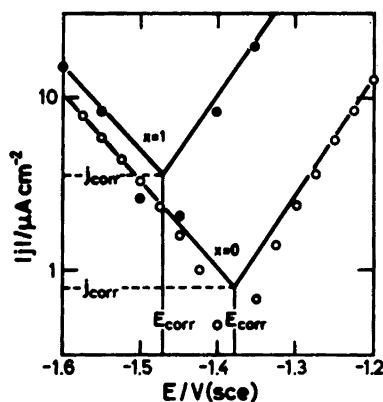


Fig. 4. Initial polarization data for aluminium electrodes stabilized for 20 h at open circuit in 1 M $\text{NH}_4\text{Ac} + x$ mM NH_4F at 25 °C. (○) $x=0$ and (●) $x=1$.

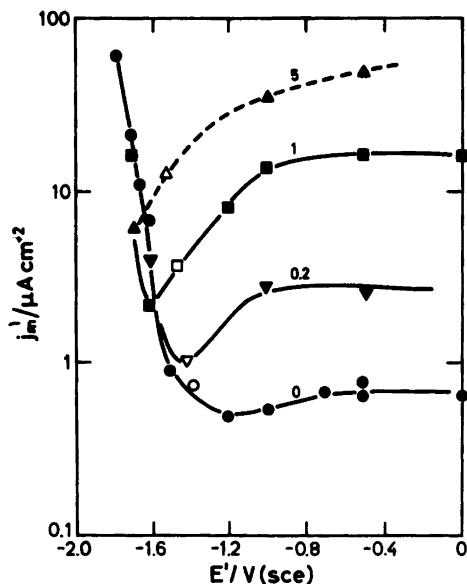


Fig. 5. Stationary rate of anodic metal-ion transfer (j'_m) vs. stabilization potential (E') at aluminium electrodes in 1 M $\text{NH}_4\text{Ac} + x$ mM NH_4F (values of x at the curves) at 25 °C. No stirring. Open symbols represent open-circuit conditions.

$$j'_m = -j'_e = j_{\text{corr}} \quad (2)$$

This has presently been used to determine the stationary open-circuit corrosion current (j_{corr}) or corrosion rate of aluminium in the various test solutions (see below).

Under all conditions of the present work, initial j_m and j_e data essentially obey the Tafel law with slopes depending on the stabilization potential concerned. These results agree well with previous ones for a pH of 7.2.^{4,5} It seems that fluoride ions do not affect the initial anodic Tafel slope (b'_m) very much. Hydroxyl ions do so more noticeably.⁵

Steady-state data. Fig. 5 gives data obtained (as described above) for the stationary rate of anodic metal-ion transfer (j'_m) at various stabilization potentials (E') in the test solutions applied. Open symbols give the stationary open-circuit corrosion point (E_{corr} , j_{corr}) for aluminium in the respective solutions. Closed symbols apply to potentiostatically stabilized aluminium electrodes. All the data apply to stagnant conditions (no stirring). The results show that fluoride ions have little effect on the active/passive transition appearing at the most negative potentials applied, but an essentially first-order control of the essentially potential independent stationary passive current appearing at the highest electrode potentials applied.

The latter is better seen in Fig. 6, where the potential independent stationary passive current (j_p) approached in the test solutions is log-log plotted against the fluoride concentration to which it applies. A line has been drawn with unit slope (as prescribed for a first-order dependence) and seems reasonably well obeyed. Furthermore, the line extrapolates to a low-limit concentration of about 0.05 mM ($5 \cdot 10^{-5}$ M) for the fluoride-consuming process to be faster than the fluoride-free one (at $x=0$) under the conditions applying.

Fig. 7 gives data obtained (as described above) for the stationary rate of cathodic electron transfer (j'_e) at various stabilization potentials (E') in the test solutions. This electron transfer most likely occurs across a passive film to solvent water molecules,

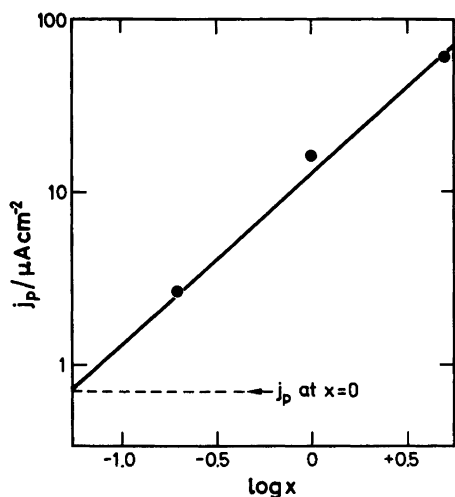


Fig. 6. The potential independent stationary passive current (j_p) vs. $\log x$ for aluminium in 1 M $\text{NH}_4\text{Ac} + x$ mM NH_4F at 25 °C. No stirring.

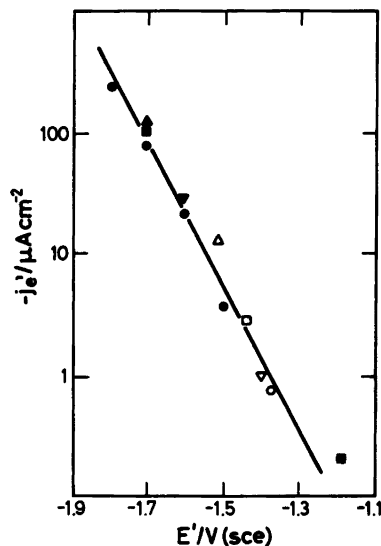


Fig. 7. Stationary rate of cathodic (hydrogen evolving) electron transfer (j_e) vs. stabilization potential (E') at aluminium electrodes in 1 M $\text{NH}_4\text{Ac} + x$ mM NH_4F at 25 °C. No stirring. Symbols as in Fig. 5.

reducing them to hydrogen molecules and hydroxyl ions. Gas evolution was generally observed at the cathodically polarized electrodes. Open symbols again apply to electrodes stabilized at open circuit and closed symbols to potentiostatically stabilized ones. The former symbols hence give stationary open-circuit corrosion points (the same as in Fig. 5). The results of Fig. 7 show little effect of fluoride ions on the stationary rate of cathodic electron transfer (hydrogen evolution) under the conditions applying. The Tafel line drawn has a slope of -0.17 V/decade.

Capacitance data. By the initial slope (dE/dt), galvanostatic transients yield electrode capacitance data (C):

$$C = \Delta j / (dE/dt) \quad (3)$$

at the starting potential concerned. Such determinations have presently been made for aluminium electrodes after 20 h stabilization at open circuit in the test solutions used. Capacitance values obtained are presented in Table 1 together with values hence emerging for the apparent barrier-layer thickness (d_C) from the approximate eqn. (4):

$$d_C = \epsilon \epsilon_0 / C \quad (4)$$

assuming the relative dielectric constant (ϵ) to be 12.

Auger data. Auger electron spectroscopic measurements and depth profile studies (using argon ion etching at a rate of 60 Å/min) have been performed on aluminium specimens both after 20 h stabilization at open circuit and after 20 h stabilization at -0.5 V(sce) in the test solutions applied. The depth profiles all showed a rather broad transition zone between

Table 1. Differential capacitance (C) and oxide film thickness from capacitance (d_C) and from AES depth profiles (d_A) for high-purity aluminium electrodes in deaerated solutions of 1 M $\text{NH}_4\text{Ac} + x$ mM NH_4F at 25 °C. No stirring.

x	0	0.2	1	5
After 20 h at open circuit				
$C/\mu\text{F cm}^{-2}$	12.9	13.2	16.3	28.1
$d_C/\text{Å}$	8.2	8.0	6.3	3.8
$d_A/\text{Å}$	130	50	20	15
After 20 h at -0.5 V(sce)				
$d_A/\text{Å}$	70	110	170	3000 ^a

^a Dark (almost black) appearance.

metal and oxide. Use had then to be made of points of half the full response to roughly locate the metal/oxide interface.⁵ Rounded thickness values (d_A) obtained from such determinations are presented in Table 1.

The Auger spectra revealed that fluoride ions were present in oxide films formed in fluoride containing solutions. The atomic F/O ratio in such films increased a little with the fluoride concentration of the solution used and approached 0.1 at the highest fluoride concentration tested (5 mM). It did not seem to change much with depth. The Al/O ratio in the films generally appeared rather low (around 0.5 as for $\text{AlO}(\text{OH})$).

DISCUSSION

Fluoride ions clearly effect the corrosion and passive behaviour of aluminium in neutral acetate solution. Their main effect is to raise the anodic passive current of the metal (Figs. 4–6). This fully occurs first well into the passive region [above -1 V(sce)]. At lower potentials, the effect is smaller, and it disappears in the active/passive transition occurring at the lowest potentials applied. This gives a dip in the stationary passive current at low potentials in the passive region (Fig. 5). The cathodic electron transfer (hydrogen evolution) at passive aluminium electrodes appears little affected by fluoride ions (Figs. 4 and 7). In all these aspects, fluoride ions to some extent resemble hydroxyl ions.⁵

Fluoride ions seem to introduce some fast and transport limited process of fluoride-ion consuming metal-ion dissolution at the passive aluminium surface. This is indicated both by stirring increasing the dissolution rate (Fig. 2) and by the stationary passive current in unstirred solution being close to expectations for a diffusion limited participation by fluoride ions (Fig. 6). The latter needs some elaboration.

Assuming the overall anodic dissolution reaction under stationary conditions (constant passive film) in fluoride containing solution to be as represented by eqn. (5):



one should expect the limiting anodic diffusion current to be as given by eqn. (6):

$$j_d = (3/n)FDc/\delta \quad (6)$$

Assuming, furthermore, the average ligand number \bar{n} to approach 4,⁷ the diffusion coefficient D to be about $8 \cdot 10^{-6}$ cm²/s for fluoride ions, and the diffusion-layer thickness δ to be about 0.04 cm at natural convection, one obtains $j_d/x = 14 \mu\text{A}/\text{cm}^2$ (where x is the dimensionless fluoride-ion millimolarity of the bulk solution). This is only a little higher than obtained for the stationary passive current by the straight line in Fig. 6 ($j_p/x = 12 \mu\text{A}/\text{cm}^2$).

From the results of Table 1, the oxide film formed on aluminium under the present conditions appears to be duplex. It apparently has an inner barrier part (whose stationary thickness decreases with increasing fluoride concentration in the solution) and an outer non-barrier part (whose stationary thickness increases with increasing fluoride concentration in the solution). The latter parenthetical remark applies to potentiostatic conditions [-0.5 V(sce)], but not to open-circuit conditions (where the electrode potential changes with the fluoride concentration). AES data clearly reveal that fluoride ions to some extent enter at least the non-barrier part of the oxide film. This apparently makes the film less protective, since it grows thicker, but provides less protection the higher the fluoride concentration [see at -0.5 V(sce) in Table 1 and Fig. 5].

The duplex nature of the oxide film on aluminium prevents a simple treatment of the passive behaviour of this metal. For instance, the general theory for passive metals by Vetter⁸ does not directly apply to such a case. The kinetics of the interaction by fluoride ions is moreover hidden by the transport control exhibited. This may be overcome by rotating-disc electrode measurements,³ which should be pursued.

Acknowledgement. The authors are grateful to siv.ing. A. Grande (E-lab, NTH, Trondheim) for measuring Auger spectra and depth profiles on our specimens.

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Received May 2, 1985.