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ON THE ELECTROCHEMICAL BEHAVIOUR OF ALUMINIUM IN ACIDIC CHLORIDE SOLUTION

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Abstract—The electrochemical behaviour of aluminium in 0.1 M hydrochloric acid solution positive of the open circuit potential (OCP) has been studied using open circuit potential measurements, linear sweep voltammetry and electrochemical impedance spectroscopy at stationary and rotating high purity aluminium disc electrodes. Freshly polished electrodes show an induction time before the OCP changes negatively towards its steady-state value. Steady-state current–voltage profiles show two distinct almost linear, non-Tafelian regions positive of the OCP. Evidence for pitting corrosion through a salt film and dissolution via ionic migration through the thin oxide film as parallel corrosion paths is discussed.

INTRODUCTION

THE PROTECTION of aluminium against corrosion in aqueous media by the easily formed protective oxide layer is affected by the presence of chloride ions, such as in marine environments owing to pitting corrosion type phenomena.[1–8] This type of corrosion is used to good advantage in the etching of aluminium in strong hydrochloric acid solution for use in dielectric capacitors.[9] Depending on the pH value, oxidation of aluminium can give rise to partially or fully hydrated aluminium oxide, to soluble hydroxo-complexes and other complexes in the presence of suitable anions. When pits are formed it is likely that the local environment consists of a salt film giving rise to a second type of surface film through which corrosion can occur,[10,11] similar to that found in the cases of iron and nickel corrosion.[12,13] The permeability of this salt barrier layer, together with the porosity of the oxide layer are thus crucial in determining the corrosion rate.[12]

In this work investigations on aluminium corrosion in 0.1 M hydrochloric acid solution in stationary and moving solution using various techniques are reported: measurements of open circuit potential, cyclic and linear sweep voltammetry and electrochemical impedance spectroscopy (EIS). This complementary information is then discussed with respect to corrosion mechanisms.

EXPERIMENTAL METHOD

A section of a 5 mm diameter aluminium (99.999% pure, Johnson Matthey) rod was glued to a brass rod with silver araldite epoxy resin (Johnson Matthey) and machined in order to fit into an Oxford Electrodes rotating assembly; a Teflon sheath left only the disc end of the Al rod exposed (area 0.20 cm^2). The electrode surface was prepared by abrading with silicon carbide paper (600×) and dry alumina powder of decreasing particle size down to 1 μm. The electrode was used in stationary mode or rotated at 4 Hz (almost no dependence on rotation speed above $W \sim 1$ Hz was found in the experiments described). A platinum foil counter electrode and a saturated calomel reference electrode (Radiometer K401) inserted into a Luggin capillary were employed.

Potentials were controlled using an analogue potentiostat of conventional design or a Solartron 1286

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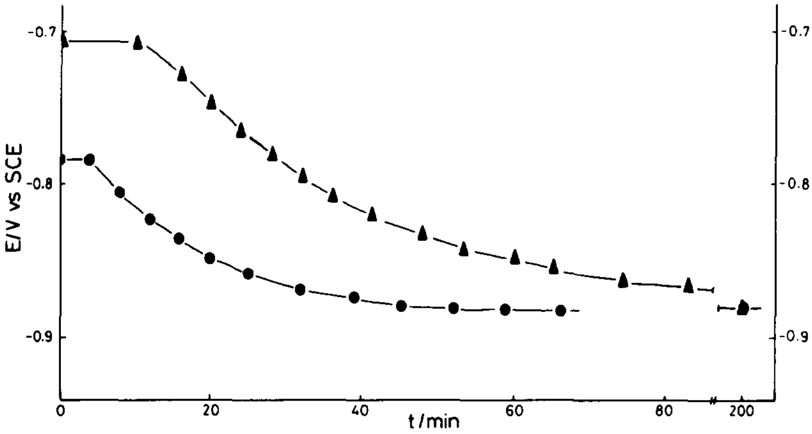

Fig. 1. Variation of open circuit potential of Al electrode with time in moving solution (rotation at 4 Hz) at freshly polished smooth (▲) and at polished then scratched (●) aluminium electrodes in 0.1 M HCl.

Electrochemical Interface. Cyclic voltammograms at high scan rates were registered on a Gould Advance OS4020 digital storage oscilloscope. Impedance spectra were recorded using a Solartron 1250 Frequency Response Analyser coupled to the Solartron 1286 Electrochemical Interface and controlled by an HP9816S microcomputer; a sinusoidal perturbation of 5 mV rms was employed in all cases.

Solutions were made using analytical grade hydrochloric acid (Merck pro analysi) and water distilled, distilled from alkaline permanganate and then redistilled. The majority of experiments were carried out under normal atmospheric conditions at an ambient temperature of 23 ± 1°C. When required, de-aeration was done with ultra-pure oxy-free nitrogen.

EXPERIMENTAL RESULTS

Open circuit potential (OCP)

The variation of the OCP with time can give an indication of the anodic and cathodic processes. The profile of OCP vs time is shown in Fig. 1 for a freshly polished smooth electrode and an electrode deliberately scratched with 600× abrasive paper; the final stable OCP is the same in both cases. An induction time is evident, longer for the smooth electrode. Visual inspection of the aluminium electrode shows that a dull covering of oxide is formed.

If the anodic process involves pitting corrosion then an induction time can be expected before pit formation, so long as the initial value of the potential is positive of the pitting potential, after which the OCP will become more negative.[13] This period depends on the initial state of the electrode surface and on solution movement relative to it. It has also been shown that induction times can be associated with the period before hydrogen evolution is detected.[14] As seen from Table 1, electrode rotation leads to a less negative OCP, the stable value of which is almost independent of rotation speed and is reached more quickly. If the aluminium is activated by cycling the potential at $10\,\mathrm{mV\,s^{-1}}$ to +0.0 V the OCP moves negative by about 40 mV. Removal of oxygen does not affect the final potential, merely increases the time to reach a stable value—thus, as expected at this low pH, it is concluded that the cathodic process is $H^+(aq)$ reduction; solution movement enables faster replacement of the protons consumed by hydrogen evolution, a higher cathodic current and thence a more positive OCP value.

Linear sweep voltammetry

The shape of voltammetric curves obtained from cyclic and linear sweep voltammetry depends significantly on the sweep rate.

Cyclic voltammetric studies at fast scan rate ($>10\ V\ s^{-1}$) between −2.0 V and +0.5 V(SCE) in 1 M HCl show the evolution of the surface over the first few cycles and the creation of pits, with pitting corrosion continuing on a long-term basis.[13] In 0.1 M HCl solution after approximately a minute a predominantly resistive behaviour is obtained, presumably since the oxide film is formed more readily (higher pH) and because of the lower chloride concentration.

A small sweep rate of $10\ mV\ s^{-1}$ at an electrode that has reached a stable OCP value gives a rather different type of behaviour, as shown in Fig. 2. Three regions positive of the OCP can be distinguished, the first two of which are approximately linear: that close to the OCP until −0.7 V(SCE), a second portion to −0.2 V(SCE) of higher slope, and a third where the slope of the *i–E* curve is significantly higher and curved. The linearity shows the resistive nature of the process. As will be discussed below, −0.7 V(SCE) may correspond to a salt formation potential,[11] and its value is independent of stationary/moving solution. Figure 3 is a Tafel plot representation of the data of Fig. 2. It is clear that the slopes are low and tend to a potential-independent value at potentials approching 0 V(SCE), which can be explained in terms of dissolution of aluminium through a passivating film.[15]

Figure 4 shows the *i–E* curve obtained using a staircase waveform of 10 mV steps each of 5 s duration with current sampling at the end of each step, corresponding to an effective steady-state (no hysteresis on inverting scan). The form of the curve is the same as Fig. 2, but higher currents are registered. Lack of hysteresis shows that oxide film breakdown is not a rate determining step. This linearity has been noted in studies undertaken of pure aluminium in potassium hydroxide solution.[15,16] It could be attributed either to a resistive film of constant thickness of oxide or to a mechanism involving chloride and proton transport through the film.

Small amplitude cyclic voltammetry (SACV)

SACV[17] is a convenient method for determining the polarisation resistance of the electrode/electrolyte interface. It is essentially a differential technique, and relies on a time-independent measurement of the slope of the *i–E* curve near the corrosion potential. Very slow scan rates of the order of 0.1 $mV\ s^{-1}$ are necessary. The effect of scan rate is visibly demonstrated in Fig. 5 for stationary solution: from this

TABLE 1. OPEN CIRCUIT POTENTIAL VALUES IN STEADY STATE FOR ALUMINIUM ELECTRODE IN 0.1 M HCl

	OCP/V(SCE)	
	Stationary electrode	Rotating electrode*
Before activation†	−0.91	−0.83
After activation†	−0.95	−0.87

* $W = 4$ Hz.

† Activation was $10\ mV\ s^{-1}$ scan from OCP to OV and back.

$R_P \simeq 4.5$ kΩ (0.9 kΩ cm^{-2}) can be calculated. If the oxide film could be regarded as a true passive film then R_P would tend to infinity, as occurs with iron.[18]

Impedance measurements

Impedance spectra were recorded at potentials anodic of the OCP in the passive zone and after activation of the electrode surface. The effect of rotating the electrode on the form of the plots is small; a typical example is shown in Fig. 6. These types of spectra are similar to those found in other corroding media, and for aluminium in neutral chloride solution.[8] A short summary of the results obtained is given in the following paragraph: a detailed interpretation may be found elsewhere.[19]

Three loops can be identified: a high frequency capacitative loop depressed below the real axis, probably associated with a high field conduction mechanism through the oxide film, a medium frequency inductive loop typical of passivated metals and due to bulk or surface relaxation processes, and a low frequency capacitative branch linked possibly to a constant passive current in the steady state. Although it was not possible to obtain reliable data below a frequency of 10^{-2} Hz, due to changes in the structure of the interfacial region with time, the values of R_P determined by SACV (previous section) show that in reality there is a low frequency

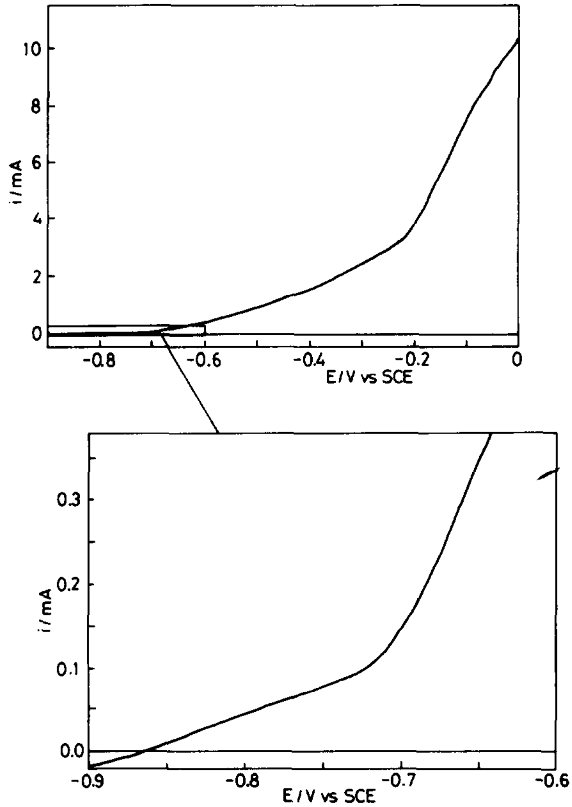

FIG. 2. Voltammetric curve at sweep rate of 10 mV s^{-1} of aluminium in 0.1 M HCl recorded with positive feedback compensation. Initial potential −0.90 V(SCE); rotation speed 4 Hz.

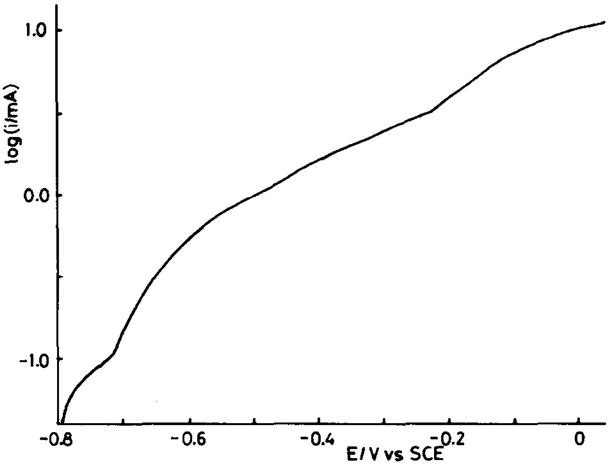

FIG. 3. Tafel plot of data from Fig. 2.

capacitative loop. The frequency associated with a particular point on the impedance spectrum increases as the potential increases.

DISCUSSION

Previous work on aluminium has highlighted the different corrosion mechanisms and reaction products according to the medium. Depending on the pH, $Al(H_2O)_6^{3+}$ ions, oxide or hydrated oxide or $Al(OH)_4^-$ are formed as predominant species. In this work at low pH, it was confirmed that hydrogen evolution is the predominant cathodic process using solutions containing oxygen and those with oxygen removed. In the presence of chloride other complexes can be formed.

There are two distinct types of corrosion mechanism to consider: through the oxide film and/or localised (pitting) corrosion. A thin oxide layer can give rise to a high electric field strength permitting the occurrence of ionic migration across the layer. This is the basis of the mechanism proposed by Drazic *et al.*[3] of

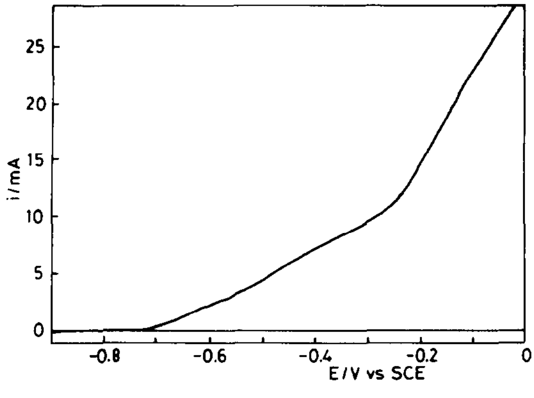

FIG. 4. Voltammetric curve obtained with 10 mV steps of 5 s duration each; current sampled at end of step. Other conditions as in Fig. 2.

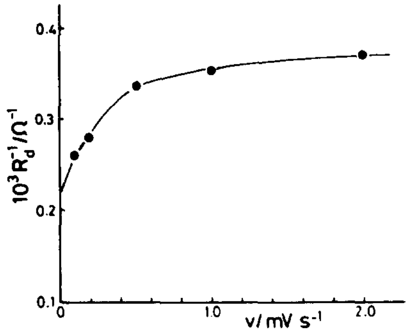

Fig. 5. Resistance of Al electrode in 0.1 M HCl determined from small amplitude cyclic voltammetry near the OCP (OCP ± 20 mV) for various scan rates. At very slow scan rate R_d, the diagonal resistance equals R_P, the polarisation resistance.

Al/oxide interface	$Al \rightarrow Al^+$
Oxide/electrolyte interface	$Al^+ \rightarrow Al(III)$

with the formation of hydroxo complex ions etc. which diffuse into bulk solution. The data obtained in this work support this type of mechanism, at least in the passive region, in particular the high frequency loop found in impedance studies.

It is well known that chloride is important in determining the corrosion rate, postulated to be via adsorption on[3] or absorption within the oxide film due to the high electric field, eventually reaching the metal/oxide interface and starting dissolution there.[7] Very recently, work using radioactively labelled chloride has shown that chloride does not enter into the oxide film but that it is chemisorbed onto the oxide surface and acts as a reaction partner, aiding dissolution via the formation of oxy-chloride complexes.[5] The relaxation manifested in the inductive loop of the impedance spectra is a reflection of these oxide film processes, but does not distinguish which mechanism. The chemical nature of the rate-determining step in dissolution is supported by the lack of dependence on electrode rotation rate; this phenomenon has been noted in other media.[20]

The almost linear nature of the *i–E* curves in the first two sections suggests at first sight a constant oxide film thickness. This is, however, contrary to experimental

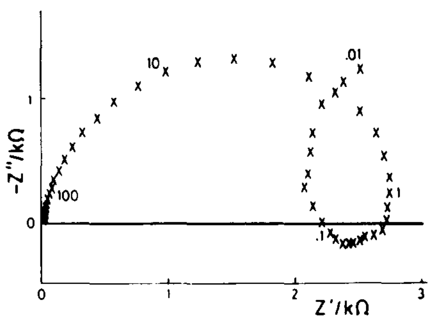

Fig. 6. Impedance spectrum obtained at −0.80 V(SCE) at stationary Al electrode in 0.1 M HCl.

observation especially as it has been shown that the variation of film thickness with applied potential is of the order of 1 nm V^{-1} in chloride-containing solutions.[6] In pore-forming electrolytes a linear relation between current and potential has been suggested[21] arising from the low-potential limiting case of Palibroda's equation:[22,23]

$$j = j_0 + \frac{j_c}{V_c}(V_s - V_0). \tag{1}$$

Here j_s is the steady-state current density. The first term on the right-hand side, j_0, is the current density due to all reactions, such as chemical dissolution, except ionic conduction. The second term represents ionic conduction: j_c is a constant, V_c is a critical potential of the order of 100 V, $(V_s - V_0)$ is the potential difference across the oxide film. Although the experimental examples studied were sulphuric and propanedioic acid solutions,[21] it is possible that an equation of this kind can be applied to the present acid solution.

The *i–E* curves and OCP data show the importance of pitting corrosion at more positive potentials. The three sections in the anodic part of the linear sweep curve have not been seen before, and may be a property of this type of acidic chloride solution in contact with aluminium. As remarked above, the potentials where there is a discontinuity in the slope of the *i–E* curve can be tentatively identified with the commencement of a region of salt formation (salt formation potential[11]) and pitting potential respectively. According to this model,[11] significant pitting can occur positive of the salt formation potential, and positive of −0.2 V(SCE) there is a contribution from active dissolution. Visual observation of the electrode surface with an optical microscope shows an oxide layer in the passive region and confirms the commencement of pitting of the oxide positive of −0.7 V(SCE), the bottom of the pits appearing as black points. For potentials positive of −0.2 V(SCE) the pit density increases, and bare metal is visible inside the pits.

It is to be recalled that the impedance spectrum recorded at the beginning of the second linear portion already begins to show different characteristics,[19] losing the low frequency loop attributed to the passive current.

It has been proposed[11,12] that a salt barrier layer is formed within pits on their formation, in this case $AlCl_3$, which could then form $AlCl_4^-$ and diffuse into bulk solution. If this is so, the induction time observed in OCP measurements can be associated with the time necessary to dissolve the oxide film and chloride reach the bulk metal for pit initiation. Pit cessation is probably due to migration of water through the salt film of the pit to the metal surface,[9] which occurs when the salt film reaches a certain thickness. As to why pitting should occur preferentially in certain active sites, when chloride could dissolve the oxide film all over the metal, the explanation must lie in the non-uniform thickness of the oxide film and in the microheterogeneity of the surface exposed to solution.

Finally, it is noted that it is not easy to separate the many factors that affect the rate and mechanism of aluminium corrosion. For example, variation of pH means altering the solution buffer capacity; buffer anions can alter the structure of the interface. Such criteria must be taken carefully into consideration when proposing and discriminating between mechanisms.

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