

Thermodynamic and Kinetic Factors in Chloride Ion Pitting and Nitrogen Donor Ligand Inhibition of Aluminium Metal Corrosion in Aggressive Acid Media

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The corrosion behaviour of aluminium in 1.0 mol l⁻¹ solutions of HCl, H₂SO₄, HNO₃ and HClO₄ has been investigated in the presence and absence of added Cl⁻ ions. The rate of corrosion of the metal in HCl and in acid solutions containing Cl⁻, was significantly higher than in the other solutions studied and is attributed to Cl⁻ pitting. The rate of corrosion was found to be zero order overall with an observed rate constant dependence on Cl⁻ of the form $(k_{\text{obs}} - k_0) = kK_2[\text{Cl}^-]^2 / (K_1[\text{O}_2] + K_2[\text{Cl}^-])$ where K_1 and K_2 are, respectively, the equilibrium constants for O₂ and Cl⁻ adsorption on the metal surface. The addition of the sodium salts of *N*-*n*-butyl, *N*-ethyl and *N*-phenyl dithiocarbamates was found to have an accelerating effect on the corrosion rate, whereas the addition of the quadridentate macrocyclic amine cyclam (1,4,8,11-tetraazacyclotetradecane) and its open-chain analogue DND (3,7-diazanonane-1,9-diazine) was found to offer inhibition characteristics. These latter rates were investigated at 30, 35, 40, 45 and 50 °C in various amine concentrations. A mechanism involving three competitive equilibria, viz. molecular oxygen adsorption, Cl⁻ adsorption and inhibitor adsorption, followed by a rate-determining chloride ion catalysed dissociation step is proposed for the reaction. Finally, the pitting potentials of Al in aggressive acid solutions containing various Cl⁻ concentrations were determined from anodic polarization curves. These data were discussed and correlated to the overall mechanism of pitting corrosion.

The process of corrosion has both thermodynamic as well as kinetic implication. The thermodynamics are a direct consequence of the electrochemical nature of the reactions taking place, whereas the kinetics result from the energy barriers arising in a rate-determining step that controls the mechanism of corrosion. A glance at the electrochemical reduction potentials of metals would lead to the conclusion that aluminium ($E^\circ = -1.8$ V) is a very active metal and that, in the absence of other factors, the corrosion of the metal in aggressive acid media should proceed at a fast rate. It is, however, well known that aluminium possesses excellent corrosion resistance characteristics. This is attributed to the rapid formation of a coherent inert oxide layer.^{1,2} Thus, it has been estimated that a layer of the oxide 10–12 μm thick would render the metal inactive in the pH range 4–9.

Aluminium is, however, readily soluble in hydrochloric acid solutions or in other acid solutions containing Cl⁻ ions. The initiation of aluminium corrosion by Cl⁻ ions arises from damage to the protective oxide layer. Thus if the oxide film dissolves, the metal corrodes uniformly and for these cases it has been shown by Lorking and Mayne^{3,4} that the corrosion was associated with the initial rate of solution of the oxide layer. If, however, the film is damaged under conditions that prevent self repair, localized corrosion occurs.⁵ The process of partial or local oxide layer removal or dissolution has been termed pitting. Although there is still no general agreement concerning the exact mechanism of pit initiation,^{6–10} the following steps are plausible: (1) adsorption of chloride ions on the oxide surface under the influence of the electric field at the oxide/solution interface. The preferential adsorption sites may be oxide defects where the surface film is thinner, (2) formation of a basic aluminium hydroxochloride salt, which readily goes in solution, (3) dissolution of the oxide, mainly where the film is thinner because of a strong local electric field which stimulates step (1) above. The propagation of pitting then occurs with the dissolution of the underlying metal. It is thus obvious that these steps have both kinetic as well as thermodynamic implications. Thus one could view the process as simply a dynamic one, where

the metal interface is constantly being subjected to oxide film formation and to dissolution.¹¹

The present study was thus initiated with the objective of studying the characteristics of acid corrosion of aluminium in the presence of Cl⁻ and the effects of added chelating agents as possible inhibitors for the process. We thus present data for the corrosion of aluminium in 1.0 mol l⁻¹ solutions of the mineral acids HCl, H₂SO₄, HNO₃ and HClO₄, as well as the effect of varying concentrations of Cl⁻ ions on the corrosion rate in H₂SO₄ acid media. In addition, data are presented for the effects of added dithiocarbamates and the quadridentate amines, cyclam and DND (see Scheme 1).

Experimental

Chemical Tests

The specimens used in the chemical test were in the form of strips 1 cm × 10 cm × 0.07 cm. The samples were prepared from aluminium strips (99.99% from BDH). The samples were mechanically polished with a series of emery papers of variable grades, starting with a course one and proceeding in steps to the finest (1000) grade available and then etched in an alkaline solution of 15 g l⁻¹ Na₂CO₃–15 g l⁻¹ Na₃PO₄ before use.¹² Etching was conducted at 80–85 °C for 30 s. This was followed by rinsing with distilled water and drying. The aluminium specimens were bent in a U-form and placed in a sample vessel containing the test solution. The vessel has the same form as that described by Mylius¹³ [Fig. 1(a)], with a volume capacity of 100 ml. The evolved hydrogen gas is collected through the side arm A connected by flexible polyethylene tubing to a gas burette B thermostatted by circulating water from a constant-temperature bath through the jacket C. In addition, the reaction cell is immersed up to level 2 in the temperature bath adjusted at the desired temperature. The volume of the evolved hydrogen was measured as a function of time and the rate determined from the slope of the obtained curve. The experiments were carried out with