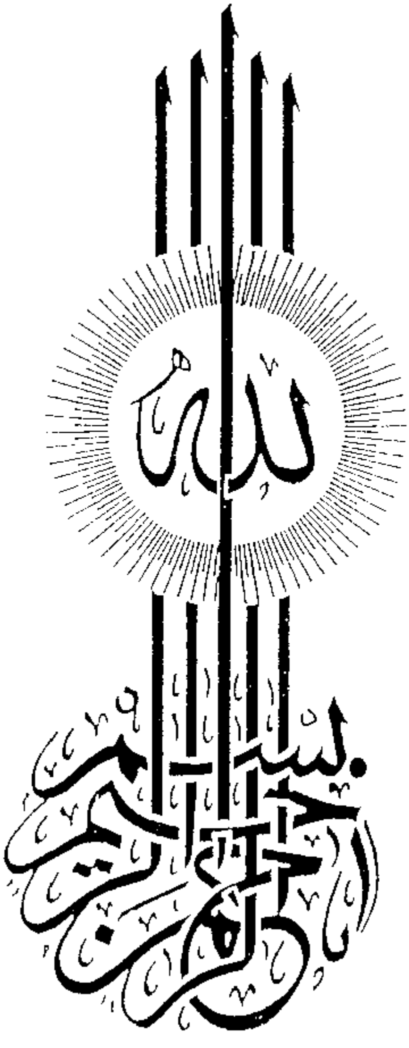
TO MY PARENTS
TO MY WIFE

PITTING CORROSION AND INHIBITION OF ALUMINIUM ALLOYS IN AQUEOUS AND AQUEOUS ORGANIC MEDIA

Thesis Advisers.	Approved
Prof. Dr. Ahmed Mohamed Azzam	Ahmed. Azzam
Prof. Dr. Mohamed Gamal El Din Khedr	Gamal Khedr
Prof. Dr. Salah Abd El Haleem	Salah. Abd. El. Haleem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INTRODUCTION

INTRODUCTION

Aluminium and aluminium alloys have a remarkable economic importance in view of their characteristics of low cost, light weight, high thermal conductivity good corrosion resistance at moderate temperatures and low neutron capture cross section. They are widely applied in industrial and household systems including the transfer and storage of fluids, solar thermal energy collectors, condensers, fuel rod cladding material in pressurized boiler water reactors ....etc.

From the point of view of corrosion susceptibility and resistance, aluminium represents in fact a particular case between the metals. While it lies among the most active metals in the electrochemical series with a standard oxidation potential of-1.66V, it is covered by a chemically inert film of a high electric resistance. These contradicting factors contribute to the observed corrosion aspects of , a) tendency to act as anode when aluminium is brought in galvanic contact with most of the common metals, b) cathodic control of corrosion of aluminium in neutral and acid media, c) severe anodic dissolution once the protective film is damaged, d) high tendency to undergo pitting corrosion if the film damage is localized.

In the following the current state of knowledge about the pitting corrosion of aluminium and the different mechanisms which explain its initiation and propagation, the role played by the metal cations in this process, and the corrosion behaviour at high temperatures are resumed.

I. PITTING CORROSION OF ALUMINIUM AND ALUMINIUM ALLOYS

Pitting corrosion is one of the most insidious and destructive forms of corrosion. It is usually defined as a concentrated anodic dissolution into a point in electrochemical equivalence to the cathodic reaction taking place over a much larger cathodic area on the surrounding passive film. This high cathodic/anodic area ratio is responsible about the rapid penetration of pits. The impurities in the metallic state and consequently in the film interfer usually with the pitting corrosion on the level of determination of the initiation points and with the subsequent propagation. It is evident that these views are mainly based on the work on iron and steel.

Among the questions to be considered by the present work are: to which extent these views are valid in the case of aluminium in presence of the already mentioned particular aspects, and where the film of Al_2O_3 represents a bad cathode in view of its resistance to electron transfer ? how would the metallic impurities in the inert film, interfer with the process ? and what would be the respective roles of the electrochemical reactions and the mechanical state of the film in inducing pitting corrosion ?

Several authors have observed that when aluminium corrodes in the pH range of 4-9, the predominant mode of corrosion is pitting (1). The factors influencing the initiation and propagation of pitting corrosion of aluminium are:-

A. COMPOSITION OF THE SOLUTION

Some workers reported that for potable water to cause pitting of aluminium, it must contain Cu^{2+} and Cl^- ions, Ca $(HCO_3)_2$ and O_2 (2,3). The effect of $CaSO_4$ (permanent hardness) was equivalent to a large increase in temporary hardness (3). SO_4^{2-} ion is usually referred to as devoid of pitting corrosion activity. Lunev and Lysaya (4), found that the addition of SO_4^{2-} ion leads to some acceleration of the cathodic process and a slowing down of the anodic process, and concluded that SO_4^{2-} ion additions in small amounts increase slightly corrosion. However when added in sufficient quantities SO_4^{2-} ion inhibits corrosion (4,5).

Böhni and Uhlig (6), found that the potential becomes more negative with higher Cl^- ion concentration but more positive when NO_3^-, CrO_4^{2-}, CH_3COO^-, $C_6H_5COO^-$ and SO_4^{2-} ions are present. The latter anions are effective as pitting inhibitors in the order listed. The rate of aluminium

Trials to inhibit the pitting corrosion of aluminium by inorganic inhibitors included individual and mixed inhibitors. $Na_2Cr_2O_7$ mixture with $ZnSO_4$, was found to be more effective than $Na_2Cr_2O_7$ with Na_2HPO_4, while Na_2SiO_3 was found to be effective in waters containing Cl^- and SO_4^{2-} ions, but its use is limited by a maximum value of the carbonate hardness of water. $(NaPO_3)_6$ was found to be effective also in the presence of Cl^- and SO_4^{2-} ions but requires chlorination of the circulating water to prevent biological growth in the system. $Na_2Cr_2O_7$ cannot be used alone as it causes pitting corrosion. Phosphate-chromate and phosphate-chromate-zinc mixtures were effictive at concentrations of Cl^- and SO_4^{2-} ions less than 1000 mg/l (12). Pryor et al. (13-17), reported that in CrO_4^{2-} ion solutions the anodic film on aluminium thinned uniformly down to the passive film thickness without any evidence of preferential attack. Air-formed films thickened slightly by anodic polarization appeared to have developed crystalline oxide on the outer surface. In F^- ion solutions a contaminating phase of nonuniformly distributed crystals of an oxyfluoride was detected on the metal surface. A continuous salt film was formed on immersion of high purity aluminium in concentrated $AlCl_3$ solution. At low salt concentrations and potentials the convection induced by simultaneous hydrogen evolution prevents continuous salt film formation (18).

Based on measurements of capacitance, Richardson et al.(19), confirmed the results of Pryor et al.,that in CrO_4^{2-} and $Cr_2O_7^{2-}$ ions solutions mechanical flaws originally present in air-formed films tend to be healed and anodic films are thinned to the passive film thickness. Little attack is detected in SO_4^{2-} ion solutions until after long periods. In Cl^- ion solutions on the other hand and to a lesser extent Br^- and I^- ions solutions, pitting commences rapidly by preferential dissolution of metal transiently exposed at flaws base in air-formed or anodic films, while in F^- ion solutions the oxide film is removed and replaced by a complex oxyfluoride. The general degree of agression of the anions increases in the order $Cr_2O_7^{2-}$, CrO_4^{2-}, SO_4^{2-}, I^-, Br^-, Cl^-, F^-. Similar views were expressed by Thompson et al.(20) .

In solutions containing an excess of NO_3^- ions together with Cl^- ions the existence of an unusually high passive current was observed(21) .

Some authors reported particular effects of certain anions on certain steps in the pitting corrosion mechanism (22); and found that the increase of free Cl^- ion concentration affected more the initiation of pitting than the propagation, while the increase of concentration of SO_4^{2-}; SiO_3^{2-} or PO_4^{3-} ions considerably accelerated the propagation of pitting. The rates of nucleation and growth of the crystalline oxide layer were found to be modified in presence of low concentrations of SiO_3^{2-}, PO_4^{3-} and MoO_4^{2-} ions in presence of Cl^- ion (23). NO_3^- and CrO_4^{2-} ions form $\gamma-Al_2O_3$ on the electrode surface as a thick film which inhibit the initiation and progress of attack (24,25). The conversion coating produced on aluminium surface on immersion in a CrO_4^{2-}/F^- solution is essentially amorphous chromium-containg material, probably largely hydrated chromic oxide (26). $Cr_2O_7^{2-}$ ion inhibits the corrosion of aluminium upon reduction and becomes incorporated in the existing surface film. On the other hand, MoO_4^{2-}ion has a higher tendency to become adsorbed on the surface rather than being incorporated in the surface film (27).

The potential of pitting formation Ep, for aluminium in presence of Cl^- ions remained the same on addition of organic inhibitors to the solution, while it shifts towards positive values on addition of organic and inorganic acid salts. The inhibitor efficiency drops in the order PO_4^{3-}, CrO_4^{2-}, NO_3^-, $HC_6H_5O_7^{2-}$, OAC^-, SO_4^{2-}. The organic compounds were found to decrease the pitting corrosion current (28).

Several classes of organic inhibitors were used with success for the inhibition of pitting corrosion of aluminium of which the most important are the amine derivatives (29-39). N-substituted anilines were found to be cathodic inhibitors(29,30). O-substituted anilines were reported to have the inhibitor efficiency which depends on the nature of the substituted group in the order $Cl^- > -CH_3 > -OCH_3$(31). Aromatic amines strongly inhibit the corrosion of aluminium in HCl acid due to the adsorption of there cationic active particles on aluminium surface and the formation of an inhibitor-oxide layer bond of the chemisorption nature(32). Mono-di-and triethanolamine were found to be effective inhibitors for aluminium in HCl acid and the most effective was monoethanoleamine(33-35). Methylamine, trimethylamine, mono-, di- and triethylamine were found to be cathodic inhibitors which increase the cathodic Tafel slope. Diethylamine gave the best results(35-37). Mono-, di-, and tributylamine were also used as corrosion inhibitors for aluminium alloys in HCl acid. Tributylamine was the most effective. Inhibition was found to depend on the electron density of the nitrogen atom(35). Aliphatic polyamines were investigated as corrosion inhibitors for aluminium alloys in HCl acid, and were also found to increase cathodic polarization mainly by adsorption(38,39). EDTA raises the anodic passive current of aluminium and stimulates the cathodic,(hydrogen evolution), electron transfer from the passive aluminium (40).