CHAPTER (I)

Introduction

Aluminium is a reactive metal that attributes its corrosion resistance to the environmental attack, which leads to the formation of a passive film on its surface. Pure aluminium is soft and weak but can be alloyed and heat-treated to provide a broad range of mechanical properties. Alloy composition is also one of the most important variables, which affect the corrosion behaviour of the metal.

Corrosion resistance of aluminium [1] is excellent in many corrosive conditions. Bare aluminium performs a resistance to corrosion better than other metals coated or protected. The potential to a great extent depends on the insulating properties of the oxide film; thus, the characteristics of the film are paramount importance to the corrosion resistance. Any factor that improves the tightness, thickness and insulating ability of the film tends to improve the corrosion resistance. Conversely, any factor that reduces the effectiveness of the film either mechanically or chemically, may drastically reduce the corrosion resistance. This dependence of corrosion resistance on a surface film, rather than on a low electronegative potential of the bulk material increases the variability of response of aluminium to corrosive conditions.

Hurlen and Haug [2] have found an inner thin Al_2O_3 oxide film and non-barrier outer layer for aluminium metal immersed in NaOH for 80 days. Similar film consists of an outer crystalline layer of $Al_2O_3.3H_2O$ and relatively inner gelatinous layer of $Al_2O_3.3H_2O$ was observed by Tabrizi et. al, [3].

The excellent corrosion resistance of aluminium and its wide speared use is attributed to the air formed film that is bounded strongly to its surface and when damaged, it reforms quickly in most environments. However, alkalis seem to destroy the protective film very quickly, possibly due to the adsorption of OH^- ions which interact with Al_2O_3 [4].

The standard electrode potential of aluminium is –1.66V vs. NHE. Its resistance against corrosion can be attributed to a rapid formation of thin and highly protective barrier oxide film, which separate the bare metal from the corrosive environment. This film can be formed directly in hummed air or by exposure to natural aqueous electrolytic solutions [5]. Protection by this film is very good in environments with pH between 4 and 9, while above and below this range aluminium exhibits uniform attack. In contrast, a porous and poorly protecting oxide film is formed in non-oxidizing acid solution [6].

Anodization of aluminium is largely dependent on the type of electrolyte. Thus, while a porous film possessing low ionic resistance is formed in several acids, a non porous film of high ionic resistance results in borate, phosphate and carbonate solutions. It was proved that, the basic process of the oxide growth is the same for the two types of oxides [7, 8]. Later evidences in the literature indicate that the mode of film growth for the two oxides is different [9].

There is some evidence [10] that when aluminium dissolves anodically both Al^{3+} and Al^+ are formed initially, the univalent ion then reducing water to form the trivalent ion in accord with

$$Al^+ + 2H_2O \longrightarrow Al^{3+} + H_2 + 2OH^- \qquad (1)$$

Hence, when aluminium is anodized for the purpose of intentionally building a thicker surface oxide film, hydrogen is evolved at the anode as well as at the cathode. On the other hand, some investigators explain that, the hydrogen evolution at the anode [10] to be due to increased local-action corrosion during anodic dissolution.

A-Corrosion Behaviour of Aluminium in Aqueous Solutions

A porous oxide film is produced by local action of electrolyte when aluminium is anodized in acid solutions. According to Evans [11] anodic dissolution of aluminium involves a series of reactions:

$$Al \longrightarrow Al^{3+} + 3e^- \qquad (2)$$

$$Al + H_2O \longrightarrow Al(OH)^{2+} + H^+ + 3e^- \qquad (3)$$

$$Al + 2H_2O \longrightarrow Al(OH)_2^+ + 2H^+ + 3e^- \qquad (4)$$

$$Al + 3H_2O \longrightarrow Al(OH)_3 + 3H^+ + 3e^- \qquad (5)$$

Reaction (2) is the main anodic reaction occurring during the dissolution of aluminium in acidic media.

The presence of an alkali metal ion such as Cs^+ improves the hardness and the coating ratio of the film [12], since an alum, is deposited tightly on the porous film shortly after the beginning of the anodic oxidation. The stability of the alum increases in the order of the ionic radii of alkali metal ions [13].

The anodic oxidation of aluminium in sulfuric acid containing Cs^+ ions [14] contributes to the decrease of the frequency factor of the barrier layer dissolution. Cs-alum is probably deposited at the upper part of the inner surface of pores and not at the bottom since the recovery time never changes with the prolongation of the initial oxidation when Cs-alum is deposited.

The corrosion of 99.8% aluminium with 0.2% Mg in solution of chloro-substituted acetic acid has been studied [15]. It was found that the extent of corrosion increases with the increase in the acid concentration and the period of immersion.

The electrochemical behaviour of aluminium in hydrochloric acid solutions was studied using cyclic voltammetry, square-wave chronoamperometry and square-wave chronopotentiometry [16]. High-speed cyclic voltammetry of aluminium was studied in HCl solution, and the effect of temperature, HCl concentration, potential sweep rate and cathodic potential limit were also examined. Relevant parameters that can be determined from the cyclic voltammetry I-V curves include the breakdown and protection potential for aluminium, the onset potential for hydrogen evolution and the magnitude of the anodic and cathodic currents are calculated. The degree of passivation, which is reflected in the anodic breakdown potential and the magnitude of the anodic current, are decreased with increasing the solution temperature and HCl concentration, and increased with higher sweep rates. The nature of aluminium passivation that occurs during the cathodic half-cycle depends on the cathodic potential limits.

The electrochemical behaviour of aluminium in 0.1M hydrochloric acid solution has been studied [17] using open-circuit potential measurements (OCP), linear sweep voltammetry and electrochemical impedance spectroscopy at stationary and rotating high purity aluminium disc electrodes. Freshly polished electrodes showed an induction time before the (OCP) changes negatively towards its steady-state value. Steady-state current-voltage profiles showed two distinct almost linear, non-Tafel line regions positive of the (OCP).

Corrosion behaviour of 1060 (0.12Si, 0.02Fe and 0.04Mn), 1100 (0.13Si, 0.52Fe, 0.068Mn and 0.01Cu) and 5052 (0.17Si, 0.04Fe and 2.3Mg) aluminium alloy in orthophsphoric acid of different concentrations has been studied [18] by weight loss and potentiostatic polarization technique at various temperatures. Corrosion rate was found to increase with increasing acid concentration, temperature and immersion period. The corrosion resistance may be regraded as 1100 > 1060 > 5052. The alloying element plays an important role in the corrosion resistance of aluminium alloy. It is true that highly pure aluminium has greater corrosion resistance. When alloy surface comes in contact with the phosphoric acid it forms $Mg_3(PO_4)_2$ and $Al_2(PO_4)_3$ as corrosion products. The solubility of $Mg_3(PO_4)_2$ is higher than that of $Al_2(PO_4)_3$. This causes an increase in the corrosion rate of 5052 aluminium alloys. Further, its lower corrosion resistance may be also explained in view of the structure of oxide film.

Due to its amphoteric nature, Al-oxide cannot protect aluminium in alkaline solutions and the metal corrodes. Some applications of aluminium depend on its behaviour in alkali. In practice caustic alkali is usually employed for pickling and cleaning processes of aluminium [19, 20].

The mechanism of aluminium corrosion in concentrated alkaline solutions involves four steps [21-23]. A series of three single electron transfer reactions involve $(OH)^-$ addition leading to the final trihydroxide oxidation state, $Al(OH)_3$.

$$Al_{(s)} + OH^- \longrightarrow Al(OH)_{ads} + e^- \quad (6)$$

$$Al(OH)_{ads} + OH^- \longrightarrow Al(OH)_{2ads} + e^- \quad (7)$$

$$Al(OH)_{2ads} + OH^- \longrightarrow Al(OH)_{3ads} + e^- \quad (8)$$

where (s) represent a bare aluminium surface site (SS). The final step is believed to be corresponding to the chemical dissolution of aluminium trihydroxide in