CHAPTER (I)

Introduction

Corrosion can be defined in many ways. The most preferred one in literature is the loss of useful properties of a material as a result of its chemical or electrochemical reaction with the environment. The corrosion specialist is concerned with the study about the corrosion mechanism through which a better understanding is obtained of the causes about corrosion and the available means for preventing or minimizing damage.

Corrosion as a spontaneous process may occur predominantly without the application of an external current. A distinction is made between chemical, biochemical and electrochemical corrosion of metals. Chemical corrosion of metals is a spontaneous destruction governed by the laws of ordinary heterogeneous chemical reactions. Biochemical corrosion or biocorrosion, is caused by the vital activity of various micro-organisms using a metal as a culture medium or evolving products which attack the metal. Electrochemical corrosion is encountered more frequently than other types of corrosive destruction and is most dangerous to metals. It is governed by the kinetics of electrochemical reactions. Its rate can be determined on the basis of Faraday's law.

According to the mode of destruction accompanying electrochemical corrosion, a distinction is made between general corrosion, affecting the entire surface of a metal, and local corrosion, confined to definite parts of the metal surface. In the latter case corrosion may result in stains (stain corrosion) or pits (pitting corrosion). This corrosion may involve grains of a single component of a metal alloy (selective corrosion), penetrate all grains, thereby forming narrow cracks (transcrystalline corrosion) or, finally, concentrate along grain boundaries (intergranular or intercrystalline corrosion).

According to the theory of local cells, the actual metal which corrodes in a given medium must contain impurities of other metals, frequently nobler than the base metal. Therefore, the metal surface is consisting of anodes (base metal) and microscopic cathodes, which form a series of many short-circuited galvanic cells. A certain potential difference arises between cathodes and anodes, which lead to the flowing of electric currents, and metal is thus dissolved. The higher the potential difference between anodes and cathodes, the stronger are the current flowing in the local cells, and hence the higher is the rate of corrosion.

A logical consequence of the local cell theory is that a completely pure metal, whose surface is equipotential, that is, has the same electrode potential at all points, can't corrode. According to the kinetic theory of corrosion, ultrapure metal corrodes. The necessary and sufficient condition, for the corrosion to occur, is the simultaneous occurrence of metal dissolution reaction (anodic reaction) and some electronation reaction (cathodic reaction). Thus, impurities and, the fixed cathodic and anodic areas, are not essential for corrosion to occure. It could be a random distribution of local cells with respect to space and time.

A- Corrosion Behavior of Cadmium in Aqueous Solutions.

Cadmium and its alloys find extensive application in industry as a protective coating for iron, steel, and aluminum [1,2] and also in the fabrication of Ni-Cd and Cd-Ag alkaline batteries and other electrochemical technologies [3-10].

In spite of previous studies of cadmium electrode in alkaline solutions, there is uncertainty concerning the nature of the dissolved Cd species and its relationship to the formation of the passive film. There is also uncertainty concerning the character of the passive film and the mechanism whereby it is produced [11,12]. The formation of a layer of $Cd(OH)_2$ is responsible for the inhibition of metal dissolution [13,14] nevertheless, some experimental evidences suggest that the formation of CdO films is the cause of passivation and some suggesting that anodization in alkaline solutions comprises the formation of a passivating layer consisting of $Cd(OH)_2$ and CdO and simultaneous generation of soluble Cd(II) species going into solution [9,15-17]. The electrochemical behavior of cadmium in 1 M NaOH solution is studied using potentiodynamic and potentiostatic polarization techniques with the specific goal of identifying the probable mechanism of the corrosion and passivation process taking place at the electrode-electrolyte interface in alkaline solutions. An adsorbed layer represents the intermediate species for both active dissolution and passivation. The passive film formed on Cd is duplex in nature, consisting of an inner barrier layer and an outer porous layer. The passive film formation under potentiostatic conditions is believed to occur through a solid state mechanism [18].

The formation of the first hydroxide layer on the surface of cadmium electrode in dilute alkaline medium was studied by cyclic voltammetry. By resolution of the voltammetric peaks, it is possible to distinguish the different steps of the superficial oxidation of cadmium. The first step seems to be the formation of a labile type of hydroxide [19].

The anodic polarization of cadmium in alkaline solutions has been studied under constant-current conditions [20]. The potential may rise from about -0.9 V (vs. Hg |HgO| N KOH) to as much as + 1 V on passivation; there appears to be more than one arrest in the polarization curves. Preliminary study of the effect of stirring indicates that, it may hasten the transition in dilute solutions and delay it in concentrated solutions. Potentiostatic studies in the range -1·2 to +1·2 V (vs Hg |HgO| N KOH) have shown that, hydrogen is cathodically evolved at -1.0 V; then, in the first truly active region (-0·86 V), the main reaction is the formation of Cd^{2+}_{aq}; after passivation (+0·70 V) it changes to oxygen evolution. Potentiostatic techniques reveal intermediate stages, undisclosed by constant-current methods, of pseudo-passivation and current-plateau regions, in which the passivating layer thickness, controlled by high-field cation transport.

Anodic films were formed on smooth chemipolished Cd electrodes in alkaline electrolytes (0·1-5 M KOH) at constant electrode potential by stepping rapidly from -0·7 V to different potentials between 0·03 and 1·0 V referred to a hydrogen electrode in the same solution [21]. The film formation was followed by measuring the current as a function of time. Spectra of the films on the electrode were recorded after the electrodes were removed from the solution as a function of time and potential. The intensity of characteristic bands in the IR region gives an estimation of the amount of $Cd(OH)_2$ in the film. If the film is formed in the vicinity of the thermodynamic potential for $Cd(OH)_2$ formation, it contains a substantial amount of $Cd(OH)_2$. The $Cd(OH)_2$ formation decreases with increase of anodic polarization under the above conditions. UV spectra of the same films appear characteristic for cadmium oxide and may be a function of the electronic conductivity of the films.