

INTRODUCTION

The word corrosion is usually used to cover all transformations in which a metal passes from the elementary to the combined condition by chemical or electrochemical reaction with the surroundings. It includes reactions leading to a solid crust of oxide or sulphide, and also those resulting in a clear solution of chloride or sulphate, although here evaporation is needed to isolate the compound in the solid state. This differs from erosion, galling or wear which are caused by physical deterioration of metals. In some instances, chemical attack accompanies physical deterioration as described by the terms: corrosion-erosion, corrosive wear, or fretting corrosion⁽¹⁾.

Corrosion changes may be divided into two classes: those which produce a solid film and those which do not. Film-forming reactions usually become increasingly slow as the film thickens, whereas, in the absence of film formation, the velocity of attack is unlikely to slow down with time, except as a result of the exhaustion of a reactant.

Corrosion rate depends not only on the usual variables of chemical kinetics, concentration and temperature, but also on the electrochemical parameters of the

system.⁽²⁾ The electrode potential and the structure of the electric double layer at the metal/solution interface are another factors which affect the corrosion reaction.

The electrochemical study of a corrosion reaction is simplified considerably when it occurs uniformly over the electrode surface. However, in uniform corrosion, the microscopic sites for oxidation and reduction are distributed randomly. A site does not influence the neighbouring ones. Reduction sites change over to oxidation sites and vice versa in a random fashion. Few corrosion reactions satisfy all of these conditions. For example, while dissolution of amalgams is uniform, that of solid metal is not strictly uniform even when the metals are pure. The concept of uniform corrosion can be branched to include dissolution of most metals without any change in the basic electrochemical equation describing the reaction.⁽³⁾ Dissolution is considered to be uniform except when there is evidence of localized corrosion e.g. pitting, etching, etc.

Wagner and Traud⁽⁴⁾ gave a detailed account of uniform corrosion based on the principle of superposition of partial current-potential curves. They provided an experimental proof of the validity of this principle for

the dissolution of zinc amalgams in acid solutions.⁽⁴⁾ They also gave general relations applicable to dissolution of solid metals although they were unable to get proof in this case.

Bonhoeffer and Jenna⁽⁵⁾, Petrocelli⁽⁶⁾ and Stern⁽⁷⁻⁹⁾ discussed these reactions further and showed that they held true for a number of dissolution reactions.

The rate at which electrochemical corrosion proceeds, depends directly on two factors; namely degree of thermodynamic instability and the magnitude of the over-all kinetic kinderence in the given corrosion system.⁽³⁾ At a given thermodynamic instability, which is determined by the E.M.F. of the corrosion couple, corrosion rate is simply determined by the over-all kinetics (over-all resistance) in the corrosion system.

Of all the factors that control the dissolution of metals in aqueous environment, stand the type and concentration of the present anions as the most important. There are, however, many cases where the dissolution rate of metals in acid solutions depends not only on the concentration of hydrogen ions directly participating in the process, but also on the nature and concentration of anions which, at first sight, do not seem to take part.