EVALUATION STUDY OF CORROSION AND INHIBITION OF SOME STAINLESS STEELS IN ACID MEDIA

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CHAPTER I

INTRODUCTION

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INTRODUCTION

Stainless steel equipment exposed in service to hydrochloric acid solutions during acid cleaning of deposits (e.g hard water scale) from metal surfaces. Hydrochloric acid is used for removing hard water deposits from heat exchangers made of different metals including stainless steel, which suffers general and stress corrosion due to the halide anions. At the same time, organic and inorganic inhibitors have been developed and used to minimize the acid attack on the metal during the operation. A number of investigations have been carried out to study the nature of corrosion of various types of stainless steel. The corrosion behaviour of stainless steel is dependent on the properties of the passive film. The composition of the film is determined by the composition of the alloy and by the environmental conditions to which stainless steel is exposed.

Binary Fe-Cr alloys are especially susceptible to localized attack. By alloying these steels with Ni and Mo, the resistance against localized attack is markedly improved.

The role of Mo has been discussed in the literature. It has long been known that additions of Mo to austenitic Cr-Ni stainless steels, to a marked degree, improve resistance to chloride pitting (1-13).

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Sugimoto et al (14,15) and Hashimoto et al (16,17) suggest that the stability of the oxide film in acid chloride solution is the result of hexavalent molybdenum oxide forming on the surface. Hashimoto explains the fact that Mo alloyed steels show a much lower current in the passive region by a model in which the passive film is not homogeneous, instead, it contains a high density of microcracks through which current can leak. The microcracks are filled with water, and this is responsible for the high current .

Increasing the molybdenum and nickel contents increased the resistance of pitting; however, decreasing the carbon and nitrogen content also increased the resistance to pitting. Nickel had little effect on critical current density, but did shift the primary passivation potential in the noble direction (18) . Thus, molybdenum facilitates the attainment of the passive state for these alloys in 0.1 N HCl, but nickel does not.

The surface composition of austenitic steel in hydrochloric acid were analayzed by ESCA technique (19) . The passive film formed on the surface consists mainly of a mixed Fe-Cr-Mo oxide. The average content of Cr^{3+} in the oxide is about 70%. The inner layer of the oxide product consists mainly of Cr oxide.

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The use of concentrated hydrochloric acid leads to the intensification of corrosion processes in the installations of extractive industries. For the protection of these installations, a large number of procedures against corrosion based on utilisation of inhibitors, cathodic protection, anticorrosion coating etc. are developed. The most convenient method was based on the utilisation of inhibitors. The advantage of this procedure is that the inhibitors can be easily introduced in the installations and can reach any part of the metallic surfaces where agressive fluids circulate.

On the basis of their chemical nature, inhibitors are divided into inorganic and organic categories. According to the nature of their polarizing action, they are classified as anodic, cathodic and general; or as surface-conversion inhibitors, adsorption inhibitors (amines),and diffusion inhibitors (gelatin). They are divided into brine inhibitors (sodium dichromate), pickling inhibitors (amines), water inhibitors (phosphates), etc., depending on the corrosive medium in which they are employed.

Organic inhibitors, called inhibitors of adsorption, control corrosion acting either on the anodic or cathodic reaction or influencing both of them. Inhibition in this

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case is the result of adsorption of organic compound on the metallic surface with the formation of an invisible thin layer of film of some molecules$^{(20)}$. This type of inhibitors are especially used in practice in the acid pickling of steel for the removal of furnace-and mill-scale, in certain acid rust-removing preparations designed for the rehabilitation of rusted ferrous articles and in acid scale-removing preparations designed for the removal of lime and other scales from ferrous systems. Other possible uses are as additives to acid preparations to allow their storage, transport, and even reaction, in mild steel vessels.

Kaesche$^{(21)}$ suggested that the observations of the shift of open-circuit potential in the presence of an inhibitor would permit the specification of which partial process is influenced by the inhibitor. Summing up the postulated that; (a) shifts of the open - circuit potential in the positive direction indicate predominant interference with the anodic partial process, (b) shifts in the negative direction show that the cathodic partial process is affected; and (c) no shift in open circuit petential means that both processes are affected to the same extent.

The mechanism of corrosion as early described by Evans$^{(22)}$, Whitman$^{(23)}$, Hoar$^{(24)}$ and Uhlig$^{(25)}$

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related corrosion to a galvanic cell on the metal surface. Metal ions go into solution at anodic areas in amounts equivalent to the reaction occuring at the cathodic areas thus,

Anodic reaction : $Fe \longrightarrow Fe^{2+} + 2e$ (1)

Cathodic reaction : $2H^{+} + 2e \longrightarrow 2H \longrightarrow H_2$ (2)

The magnitude of the temperature effect for the acid corrosion reaction has been studied by a number of workers (26-33), most often in sulfuric and hydrochloric acids. Machu (29), in his studies of the influence of temperature on inhibitor action, concluded that with "powerful" inhibitors, the activation energy is lower for the inhibited than for the uninhibited reaction. This type of behaviour, which means that an inhibitor becomes more effective as the temperature increases (27), was explained by Putilova (32) as due to an "increase in surface area of the metal covered by inhibitor molecules as the temperture rises".

Dhirendra and Co workers (34) showed that the dissolution of stainless steel [A ISI 321] in 1N HCl was progressively decreased with rise in the concentration of hexamine (10^{-5} to 4%). Protection was more than 80% at above 0.1% concentration of hexamine. The potential ennobled as the concentration of the inhibitor is increased

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in the acid solution. Hexamine remained effective at higher temperature (up to 80 °C), which may attributed to increase chemisorption of the inhibitor at the higher temperatures but became less effective in longer test durations. The activation energies calculated from the Arrhenius plots are 15-18 Kcal/mole for HCl and 6.74 Kcal/mole for Hcl + 0.1% hexamine. This indicate that the presence of hexamine lowers both the activation energy and the rate of reaction.

Also the effect of hexamethylenetetramine in comparison with other organic inhibitors on the corrosion of steel C-95 was studied in aqueous solutions of Hcl of different concentrations by Viorel Branzoi, Ahmed Kabir and Mihai Ciopec (35). Kinetic parameters determined from the polarization curves suggest a dissolution mechanism of the type Mccafferty-Hackerman (36). Use of some of the organic inhibitors led to a considerable reduction of corrosion process. At 25 °C hexamethylenetetramine got the maximum efficiency.

The corrosion behaviour of mild steel was examined by Gentaro Kano and Tutuk Subowo (37) in hydrochloric acid solution with hexamethylenetetramine and N, Ǹ-dicyclohexyl-thiourea by means of hydrogen - evolution measurements and surface observation of corroded specimen. The evolution - rate of hydrogen by the steel was kept constant in the acid

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solution with thiourea. In contrast, the evolution - rate reduced with time in the acid solution with the other inhibitors. The surface of corroded specimens was much smoother in the acid solution with hexamethylenetetramine than in the acid solution with thiourea.

The inhibition effect of hexamethylenetetramine on the corrosion of mild steel in 5% Hcl solution was examined by means of the electrochemical polarization method (38). The magnitude of corrosion current density was reduced in presence of hexamethylenetetramine. It can be concluded that the charge transfer reactions i.e $Fe \longrightarrow Fe^{2+} + 2e$ and $H^{+} + e \longrightarrow H$ are inhibited simultaneously and individually by the organic adsorption film at metal/solution interface and consequently the corrosion-rate of steel is reduced effectively in Hcl solution.

The dissolution of mild steel by 5% (w/v) sulphuric acid at 70 °C and 40 °C with and without two families of inhibitors quinoline and some substituted quinolines, and thiourea and some substituted thioureas have been examined by T.P. Hoar and R.D. Holliday (39). The results show that quinoline and substituted quinolines are anodic inhibitors, at high concentrations of inhibitor they inhibit the cathodic reaction also, though to a less

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