INTRODUCTION

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Corrosion can be defined as the reaction of a metallic material with its environment. The product of this reaction may be solid, liquid or gaseous. Both the physical and chemical natures of the products are of great importance since they frequently influence the subsequent rate of corrosion reactions.

Aqueous corrosion can take many forms. Apart from general corrosion which results in relatively uniform removal of the surface, specific features on a metal surface may be preferentially or selectivity attacked, such features include, grain boundaries, precipitates and metal/inclusion interface. The presence of films on a metal surface may give rise to highly localized region of attack, resulting, perhaps in pitting. With all of these forms of corrosion an anodic and cathodic reactions must occurs on the metal surface.

The thermodynamically possible process of metal transition into oxide or ionic state by reacting with surrounding medium i.e., the corrosion process can proceed by a chemical or electrochemical route, or by both taking place simultaneously. However it can be assumed that with electrical conducting media (electrolytes), the electrochemical mechanism prevails to such an extent that the purely chemical mechanism can be completely eliminated from consideration.

The basic difference of the electrochemical from the chemical mechanism is that the overall reaction of the metal with the surrounding environment. The former take place through two independent processes, namely, anodic and cathodic. It was found from many years ago that metals corrode in aqueous environment by an electrochemical mechanism(1-4). Any electrochemical corrosion process must be considered as a result of operation of local galvanic corrosion couple.

The driving force for the corrosion reaction is determined by the difference in potential between the anodic and cathodic sites on the surface of the metal. The corrosion process depends on various factors, namely, metallurgical and environmental factors which affect the rate as well as the rate of its distribution. The environmental factors that influence the corrosion process are:the nature of the medium,its chemical composition, pH of the solution,the presence of additives, the motion of the electrolyte relative to the metal, temperature and pressure. On the other hand, metallurgical factors are those connected with the metal itself as the chemical nature of the metal, its .heat treatment and the surface conditions.

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 the first sight, do not seem to take part. The work carried out by **Kolotyrkin et al.,**(5-7) has shown that changes in the anion composition can influence both the cathodic (Hydrogen evolution)(5,6) and the anodic process.(7,8) The influence of anions on the anodic process is connected frequently with their action on the state of the passivating film carried out by the metal surface i.e., on the diffusion barrier.(9) Evidence has been accumalted to indicate that anions contribute directly to the discharge reactions and to the formation of metallic ions.(7,8,10)

However, it was indicated that the corrosion process consists not only of oxidation reduction but also of acid-base reactions.(11) The anodic dissolution of metal is an oxidation process producing metal ions. The metal ions thus produced are transferred into aqueous solution to form hydrated aquo-metal ions or anino complexes of metal ions. Therefore, the acid-base character involved, that makes the corrosion process diversified, depends not only on the oxidizing agent and the electrode potential but also on the acid-base species present in the solution.

(A) Corrosion Benaviour of Steel and Nickel Alloys in Acidic Medium :

In acidic solutions, nickel is capable of passivation and the extent of passive range is considerable.(12) The passivation of nickel in acidic solutions is not predicted by the potential -pH equilibria digram.(12,13) Therefore, the corrosion resistance of the metal in acidic solutions is better than indicated from consideration of thermodynamic equilibria. A second and perhaps the more important reasons lies in the fact that in the active region the anodic polarization in acidic solution is considerably greater than that of most other metals. This together with the fact that in the electrochemical series nickel is only moderately negative with respect to the H^+/H_2 equilibrium, which indicate that the rate of dissolution of nickel in acidic solutions is slow in the absence of oxidants more powerful than H^+ or of substance capable of making the anodic reaction kinetically easy. The anodic dissolution current density of nickel in the active state as a function of potential does, however, depends on the rate at which the measurements were made(14,15) and the pH of the solution.(14)

Sato and Okamoto(16) suggested that the overall dissolution reaction of nickel in sulphuric acid solutions to Ni^{2+} proceeds in three steps involving $NiOH_{(ads)}$ and $NiOH^+$ species. Previous work(17) showed that the potential decay curve for passive nickel electrode consisted of three potential arrests, corresponding to the equilibrium potentials for NiO/Ni, Ni_3O_4/NiO and Ni_2O_3/Ni_3O_4. **Bockris**(18) **et al.** favoured a dissolution-precipitation mechanism for the formation of $Ni(OH)_2$ from $NiOH^+$. They suggested that, the cause of passivity is neithera monlayer nor a multi-layer of oxides but is the conversion of the multi-layer from an ionic to an electronic conductor at the passivation potential. On the other hand, **Ebersach et al.,**(19) suggested that passive film is formed by a solid, state mechanism rather than by a dissolution precipitation mechanism.

Okamoto et al.(20) suggested that the passive nickel in sulphuric acid is covered by a compact pseudomorphic film. They showed that increasing the electrolyte temperature above 60°C resulted in crystallized film and the formation of "active patches" upon which the dissolution is concentrated. Metallographic studies by **Myers et al.**(21) supported the belief that "active patches" are generated in the transpassive dissolution region.

The potentiostatic current-potential curves of nickel in nitric acid solutions was classified into three categories according to the proportion of acid concentrations.(22) (i) At concentrations less than 8M the behaviour is similar to that of Fe in dilute HNO_3 and H_2SO_4 solutions for which the increase of potential increases the anodic current, (ii) in the concentration range between 8M and 10M the effect of cathodic reactions becomes greater. (iii) with acid concentrations more than 10M, the anodic curve of dissolution compeletely disappears and in the reverse direction only a negative current is observed which corresponds to the cathodic reaction.

Nickel metal and its alloys containing chromium become passive by anodic polarization in acid solutions containing no halide ions.(23)

XPS was used to investigate the composition and quality of the surface film formed on nickel and nickel-base alloy(24) (Inconel 600). The main constituent of the passive film formed on Ni in 0.3M H_3PO_4 and 0.5M H_2SO_4 was hydrated nickel oxyhydroxide in which the ratio of O^{2-} to OH^- increased when passivation occured. In 0.5M H_2SO_4 solution, S^{2-} ion was found in the surface film formed on both nickel metal and alloy 600 and its content varied with polarization potential. The sulfide ions seemed to be formed by the reduction of sulfate ions on the metal surface.

The composition of passive film formed on Inconel 600 in all acid solutions tested is not essentially different. The passive film consists of a mixture of hydrated chromium oxyhydroxide and hydrated nickel oxyhydroxide.

Trabanelli et al.(25) observed that the passivity of Inconel 600 was superior to that of nickel in acidic solutions in both the presence and absence of chloride ions and attributed this characteristic to the presence of chromium. **Bond and Uhlig**(26) investigated the critical current density of passivation for Ni-Cr alloys in H_2SO_4 solution. They observed that the critical current density decreased sharply with increase in chromium content and reached a constant value at approximately 15% chromium. It is quite evident that the chromium greately improve the passivation characteristics of nickel.

A comparative study of corrosion rates of commercial stainless steel and nickel base alloys containing chromium in phosphoric acid solution indicated that, the nickel base alloys are more corrosion resistant than stainless steels.**(27-29)** On the other hand "Wet phosphoric acids" containing water are more aggressive than "dry phosphoric acids" containing pyro and poly phosphoric acids without water, particulary for intergranular corrosion of sensitized austenitic stainless steel.**(30)**

The anodic polarization curves for the Fe-9Ni-Cr alloys with 3,11 and 18wt % chromium was studied in de-aerated 1N H_2SO_4.**(31)** The potential range of passivity increases and the passivation current density decreases when the chromium content is increased from 3 to 18%. This is consistent with previous results.**(32,33)** As the chromium content is increased, the galvanic current decreases gradually but suddenly undergoes a sharp decrease at a critical chromium content and finally goes to zero for the 18% Cr alloy.

Gouda et al.(34) studied the corrosion behaviour of steel in stagnant deaerated citric and oxalic acid solutions (10^{-5} - 10^{-1}M) in the pH range of 2-6. They reported that in dilute organic acid solutions (of pH 2-5), the corrosion behaviour of steel is similar to that obtained in neutral solutions. In these solutions the corrosion process is dependent on the break down of the pre-immersion oxide film. Thus the destruction of the film leads to an increase of the anodic areas at the expense of the cathodic ones. The corrosion process in these dilute acid solutions becomes controlled by the anodic reaction because there is a negative shift in the corrosion potential and an increase in the corrosion rate with the increase of acid concentration. But in concentrated acid solutions (10^{-2}, 10^{-1}M) the corrosion process is controlled by the cathodic reaction because there is a positive shift in the corrosion potential and an increase in the corrosion rate on increase of acid concentration.

(B) Corrosion Behaviour of Steel and Nickel Alloys in Alkaline Solutions :

When nickel metal becomes in contact with an alkaline hydroxide solution it spontaneously covered by a layer of $Ni(OH)_2$(35-41). The study of the electrochemical behaviour of nickel in this medium particularly under stationary conditions indicates that the metal behaves like a hydrated nickel hydroxide electrode. This sort of electrode used in different batteries.

The first potentiodynamic anodization of Ni in 0.2N KOH showed that different reactions takes place within relatively well defined potential range.(36,38,41). The electrochemical anodization can be seperated into at least three main process (i) formation of $Ni(OH)_2$ [Equation (1)], (ii) oxidation of $Ni(OH)_2$ to NiOOH [Equation (2)].

$$Ni + 2OH^- ====== Ni(OH)_2 + 2e^- \quad (1)$$

$$Ni(OH)_2 + OH^- ====== NiOOH + H_2O + e^- \quad (2)$$

and (iii) oxygen evolution at higher anodic potential, and the peak at cathodic scan is for the reverse reactions.(42-45) Ellipsometric studies showed that $Ni(OH)_2$ and NiOOH are present in the potential range preceding oxygen evolution.(46)

Under a linear potentiodynamic perturbation, the formation of $Ni(OH)_2$ is characterized by an irreversible anodic current peak, which under certain circumstances has been assigned to a hydrogen electro-oxidation current.(47) As $Ni(OH)_2$ is gradually built up as a non conducting layer, a sort of prepassivation of the metal is observed prior to further oxidation of $Ni(OH)_2$ to B- NiOOH.(18,48,49)

The potentiodynamic polarization curves of Fe, Ni, Cr and Fe-Ni-Cr alloys in concentrated NaOH solutions at the temperature range 25°C to the boiling point, at sweep rate of 600 mV/hr was studied.(50)

Iron and nickel as well as the Fe-Ni-Cr alloys showed conventional active-passive transition which correlates very well with predictions of the pourbaix digram both with respect to M/HMO_2^- dissolution and oxide formation. Pure chromium on other hand, did not exhibit an active passive behaviour in caustic solutions but exhibits only the transpassive behaviour. The corrosion potential shifts to negative value with an increase in temperature and caustic concentration. The presence of nickel in iron or chromium alloys produce significant improvement in corrosion resistance but the addition of chromium to nickel or iron is generally deleterious.(50)

The stress corrosion behaviour of nickel-base alloys in high temperature caustics has been studied to a lesser degree than austentic stainless steel, although a summary of corrosion behaviour of both types of materials in industrial use is available. One of the few comparative evalutions of stainless steel and high nickel alloys was carried out by **Wilson and Aspdon.**(51) The susceptibility to stress corrosion cracking decreased with increasing nickel content of alloys.

The nickel content of the Ni-Cr-Fe alloys was found to be the most significant factor in determining resistance to stress corrosion penetration. It was found that the resistance of stress corrosion is decreased as the nickel content increased.(52) One more complex commercial alloy containing additional elements such as molybdenum, tungesten and niobium revealed that the presence of these element have no significant importance improving stress corrosion resistance in deareated 50% NaOH.

Truman and Perry(53) studied the behavior of various Fe-Cr-Ni alloys in oxygenated 50% NaOH at 300^{o}C. They found that increasing nickel content from 15 to 45% had a beneficial effect on stress corrosion resistance for alloys containing 10 to 15% chromium, but little influence for alloys containing 20 to 25% chromium. They also noted that high nickel content as in Alloy 600, impart higher resistance to cracking. In another investigation of the behaviour of 18 Cr-8Ni and 25 Cr-20Ni steels at 300^{o}C, **Snowden**(54) concluded that increasing the chromium and nickel content has less effect in improving stress corrosion resistance in NaOH and KOH solutions than in chloride solution.

X-ray photoelectron spectroscopy (xPS) has been used to investigate the composition of the surface film formed on Inconel 600 and Incoloy˙ 800 in 50 wt% NaOH at 120^{o}C as a function of polarization potential(55).

The high nickel alloy exhibit successively the active, primary passive, transpassive and secondary passive regions with increasing the potential. The primary passivation takes place by the formation of hydrated chromium oxyhydroxide, $CrO_x(OH)_{3.2x} \cdot nH_2O$ where x and n were dependent upon the composition and quality of underlying alloy and the condition of film formation. The transpassive reactions leads to abrubt decrease in the chromium content in the film with consequent enrichment of nickel. The secondary passive film occurs exclusively by the formation of nickel hydroxide which transformed to hydrated nickelous oxy-hydroxide with an increase in potential. This transformation is in agreement with the results of chemical analysis with aid of tritiated water for the passive film on austenitic stainless steel obtained by **Okamoto et al.** (56,57). They have suggested that the concentration of bound water depend upon the degree of development of the passive film.

The corrosion behaviour of AISI 304 and 316 stainless steel in hot concentrated caustic soda solutions was investigated under heat-transfer conditions.(58) The corrosion potential of the specimens was located in the active region, thus, the alloy were attacked in the form of general corrosion depending on the heat-transfer conditions. AISI 316 stainless steel was more susceptible than AISI 304. Such corrosion behaviour is attributed to the failure of the passive film formation on the heated surface caused by concentrated caustic solution next to the metal surface and erosion by gas bubbles.

Voltammetric studies(59,60) of steels in alkaline sulphide solutions indicated that, passivation is due to the presence of a defective oxide layer. The sulphide anions are apparently able to inhibit the oxide growth process by a competitive adsorption with the hydroxyl anions. This competitive adsorption between SH^- and OH^- anions for corrosion and passivation of steel in alkaline sulphide solution is based on their concentration. If the concentration of SH^- is much greater than OH^- anions, the mackinwaite layer is instantaneously formed on the electrode and the surface attack is mainly uniform. On the other hand if the concentration of SH^- is greater than OH^- anions, an oxide film with sulphide species is located at certain sites of the surface. Finally, when the SH^- and OH^- anions concentration are approximately like, the metal passivation or repassivation is then favoured.(61)

(C) Corrosion Behaviour of Steel and Nickel Alloys in Neutral Solutions :

The anodic oxidation of nickel in neutral sulphate solutions was studied using different physicochemical techniques and found to be highly dependent on the extent of coverage with perior surface oxide.(62) Electropolishing of nickel in sulphuric acid gives a thin (6-8°A) film of NiO which can be removed by cathodic reduction in sulphate solution. However, anodization of nickel in the same solution gives a thicker NiO film (9-12 °A) which can not be removed by cathodic reduction. The latter film is formed by a direct electrochemical reaction and although the oxide film on both electropolished and anodized nickel exhibit nickel dissolution, they differ with regard to their thickness, lattice parameters and cathodic reduction.The film on anodizing nickel being the passive oxide.

In-situ differential reflectometry in conjunction with ESCA techniques were used to identify various surface films formed electrochemically on nickel. The anodic film which primarily forms on pure Ni in 0.15N Na_2SO_4 is $Ni(OH)_2$.(63) At different of pH and potential values, NiO has been found to be formed simultaneously with $Ni(OH)_2$. In solutions of $pH > 8$ the $Ni(OH)_2$ film partially transforms into a third oxide, presumably, NiOOH, which can only be observed in-situ.

X-ray and electron diffraction studies indicated that the surface film formed on pure nickel in 0.1N Na_2SO_4 at 200-290°C is a mixture of NiO, $Ni(OH)_2$ and γ-NiOOH(64) and the surface film formed on Inconel 600 in simulated reactor water at 260-340 °C consists of NiO and $NiCr_2O_4$ or $(NiCrFe)_3O_4$.(65)

Electron diffraction studies(66) have indicated that the major corrosion product formed on stainless steel (Type 316) in air equilibrated dilute oleate solution after potentiostatic polarization at 210°C was Fe_3O_4 or magnetite, the formation of magnetite occurs according to :

$$3\ Fe + 4\ H_2O \longrightarrow Fe_3O_4 + 8\ H^+ + 8e^- \qquad (3)$$

This result is similar to that reported by **Fujii et al.**(67) they found a combination of α-Fe_2O_3 and Fe_3O_4 on stainless steel surface in 0.1N Na_2SO_4 solution at 210°C.

The presence of thiosulfate ions $(S_2O_3)^{2-}$ in aqueous environments containing other anions notably chloride and sulfate, impairs the localized corrosion resistance of stainless steel (SSs) and leads to more severe pitting(68-70) and crevice corrosion behaviour.(71)

Aqueous solutions containing $S_2O_3^{2-}$ also promote intergranular stress corrosion cracking (IGSCC) of sensitized stainless steel.(72-74) Similar studies on Ni-based alloy (alloy 600) have shown that $S_2O_3^{2-}$ species promote pitting corrosion of the unsensitized alloy in the presence of chloride ions and cause stress corrosion cracking (SCC) of the sensitized alloy.(75-76)

The pitting of stainless steels (SSs) in thiosulfate solutions containing chloride or sulfate ions was studied by **Newman**(69) who suggested that the thiosulfate ion is considered as an activating species in the anodic dissolution of nickel due to the reduction of the thiosulfates in the pit nuclei. Adsorbed sulfur (or sulfide) is produced on the bare metal surface and consequently, activating the anodic dissolution and hindering passivation. This behaviour is in agreement with that of the effect of adsorbed sulfur on Fe-Ni alloys suggested by **Marcus and Oudar.**(77) Following sulfur adsorption, the usual pitting mechanism occurs with the hydrolysis of the Cr^{3+} ions and the decrease in pH to a low value enough to sustain the very high rate of anodic dissolution. **Garner**(70) found that, very small additions (5 to 20 ppm) of $S_2O_3^{2-}$ to a saturated paper-machine white water (100ppm

SO_4^{2-} at pH 4.5 and 50°C) with or without chloride ions cause a pitting of AISI 304 SS.. Also, an increase of the solution pH values results in a little effect on the thiosulfate attack.

Occluded corrosion cell solutions was synthesized by a mixture of iron, nickel, and chromium chloride salts,(78) the concentration of which was proportionally the same as that of the alloy matrix. The overall chloride concentration varied between 0.01M and the one of these salts. The variation of open-circuit electrode potential and the potentiodynamic anodic polarization curves with increasing overall chloride concentration indicated that the corrosion behaviour of INCOLOY 800 and AISI304 steel changes from the passive to active dissolution corrosion mechanism. The threshold chloride concentration is close to 0.5 g. ion L^{-1} for both alloys. It was noticed, however, that even for a very concentrated medium, the dissolution rate was independent of mass transport. It was also found that the anodic behaviour of these alloys depended essentially on the chloride concentration and pH of the solution.

(D) Passive Film Formation :

In electrolytic solutions, passivity of metals results from the formation of an interface which makes the direct contact of the metal with the electrolyte. The behaviour of interface depends on its thickness, chemical composition, conductivities, potential maintained and rate of dissolution.(79) Measurements of metal tendency to be passive are important for determining the electrochemical corrosion characteristics of the metal. These measurements are available from the potential-current anodic polarization curves.

Several investigations have been performed on the passivation behaviour of nickel. **Sato and Okamoto**(17) proposed that the potential for the onset of passivity is the potential for the transformation from NiO to the higher oxide Ni_3O_4, when the concentration of the nickel in solution is small. This potential has been identified as the flade potential.(17) Polarization to the higher potentials leads to oxidation and covnersion of this oxide Ni_3O_4 to Ni_2O_3. Thus, the passive oxide film on nickel may considered to consist of either a single higher oxide Ni_3O_4 or the duplex oxide NiO and Ni_3O_4. The results of **Cowan and Satehle**(80) support the presence of a single oxide Ni_3O_4. In cases where the nickel electrode is directly subjected to a passive potential in H_2SO_4 solution, the passive film has been assumed(81) to be composed of NiO.

In a certain concentrated acidic solution e.g. H_2SO_4, nickel whilst not truly passive, but exhibit "pseudo passivity" owing to crystallization of a layer of nickel salt (in concentrated H_2SO_4 probably β-$NiSO_4.6H_2O$) on the surface.(82)

Ramman spectroscopy showed that the oxide film is responsible for the phenomena of passivity of nickel in sulphuric acid and that the composition of the anodic film changes with the electrode potential. In concentrated H_2SO_4 solution ranging from 10M to 1M, NiO is the main species responsible for the passivity.(83)

In alkaline solutions, galvanostatic measurements(84) suggested that passivation of nickel is due to formation of a monolayer of $Ni(OH)_2$. This is, probably, formed by a solid state process involving nucleation and growth of the film which proposed by **Armstrong et al.**(85). In some alkaline solutions, particularly concentrated ones, thicker films are undoubted by formed at high temperatures.

The corrosion resistance of stainless steel and nickel alloys is related to their passivation behaviour. Generally the higher the Cr-content, the more easier the passivation is facilitated and the chemical stability is also improved.(86,87) Other elements are usually added to modify the structure and mechanical properities of the alloy and/or to increase corrosion resistance such as Mo. Addition of Mo to austenitic stainless steel(87) and vanadium to 18% Cr ferrite stainless steel,(88) improve their resistance to pitting by chloride ions.

Chromium enrichment has been found in passive film on many kinds of chromium bearing alloys.(89) The major constituent of the passive films formed on many kinds of alloy containing certain amount of chromium was hydrated chromium oxyhydroxide.(90,91)

XPS studies of the passive films formed on stainless steel has indicated that, a Cr-rich film is responsible for maintaining passivity. Studies carried out by **Hashimoto et al.**(92) and by **Sugimoto et al.**(87) suggested that, the Cr-rich film consists of a hydrated form of CrOOH. While **Olefjord et al.**(93) suggestes that, Cr_2O_3 is the main passivating compound.

The anodic films formed on 304 stainless steel in 0.5M H_2SO_4 and 0.5M H_2SO_4 + 0.35 M NaCL is consisted of a Cr-rich inner layer and an Fe-rich outer layer.(94) The Cr-rich film results from the direct reaction of Cr with H_2O to form an initially non crystalline Cr_2O_3 film containing a trace of CrO_3. A highly hydrated amorphous $Cr(OH)_3.nH_2O$ is then formed. This phase deprotonates and recrystallizes during the first hours of passivation. The Fe-rich outer layer results from the direct interaction of Fe with water to form non-crystalline $Fe(OH)_2$, which subsequently recrystallizes and react in the solid state with SO_4^{2-} ions to form green rust compounds and, eventually transforms to β— FeOOH via a nucleation process. CrO_4^{2-} enriched below the Fe-rich layer and is formed in the solid state by the reaction of $Cr(OH)_3$ with lattice water. While the chromium oxide barrier layer is the primary means of passivation, the incorporation of SO_4^{2-} and CrO_4^{2-} bipolarizes the passive film and, therefore, enhances the deprotonation process, leading to further growth in the barrier layer as well as impeding the ingress of OH^- and Cl^- ions.

The passive film formed on the surface of Fe-19 Cr-9Ni and Fe-19Cr- 9Ni- 5Mo alloys in 0.1M HCl have been characterized by AES and variable angle XPS.(95) Addition of Mo to Fe-19 Cr-9Ni results in the formation of a passive film with a more highly developed interfacial barrier film composed mainly of Cr_2O_3 containing CrO_3 in solid solution which forms a glass phase. In addition, the passive films were found to contain more Fe. Molybdenum appears to be present as Mo^{4+}, and Mo^{6+} and was identified as hydrated MoO_2 and MoO_4^{2-} apparently $FeMoO_4$. The molybdate anions (MoO_4^{2-}) are formed in the solid state along with CrO_4^{2-}. These together are responsible for producing (in 0.1 M HCL) a bipolar film consisting of a cation selective outer layer containing CrO_4^{2-} and MoO_4^{2-} and an intrinsically anion selective inner layer. The ion selective property of this duplex film is considered to be largely responsible for the development of the $XCr_2O_3 . YCrO_3$ barrier layer and resisting Cl^- and OH^- ingress. Both of these properties provide greater resistance to breakdown of passivity in Cl^- ion media.

(E) Pitting Corrosion of Steel and Nickel Alloys :

Pitting of nickel and nickel alloys as other metals and alloys, occurs when passivity breakdown at local points (anodic sites) on the surface are exposed to the corrosive medium, whilst the major part remain passive since most of the cathodic reactions accompanying corrosion is distributed over the passive part of the surface, it follow that the fewer the number of sites of breakdown the more intense is the anodic dissolution at each site, i.e. the fewer the pits the faster the growth, at least in the early stage. Pitting of nickel has been shown to develop preferentially near structural feature in the metal such as grain boundaries, and also at imperfection in the surface such as scratches.(96)

Breakdown of passivity of stainless steel due to chloride attack has aroused considerable attention. Failure due to pitting corrosion has become more and more serious problem in applying this material to various practical fields. So many studies from pure acadmic to industrial one have been done extensively. Many mechanism have been proposed, but it is still uncertain which meachanism is correct. **Zahari et al.**(97) had show an interesting observation which suggests that both reactions of film breakdown and repair take place even without Cl^- during anodization of aluminium. Similar concepts had been proposed by **Okamoto and Shibata**(98) to explain the stability of stainless steel. It had been emphasized that the stable passivity is not at rest but "being alive" in a dynamical balance between breakdown and repair of the film at the sites distributed in the film.(99)

The corrosion resistance of high alloy steels and nickel alloys in many environments is due to their ability to produce an oxide film which keeps the alloy in a metastable state of passivity(100-102). The stability of this passive state is damaged and pitting corrosion occurs when these alloys are polarized above some electrode potentials in environments containing certain aggressive ions such as chloride ions.(103-105)

Pitting may be divided in two distinct steps namely, pit initiation or surface breakdown and pit propagation (growth) in depth and volume.

Some authors(98,106,107) claim that, there is no fundamental difference between initiation and propagation steps, since direct contact between the bare metal and the electrolyte occurs instantaneously upon the immersion of the passive metal. The aggressive electrolyte instantaneously penetrates the film at these flows and react with the bare metal giving rise to a rapid metal dissolution.

Janik-Czachor(108) distinguished between initiation and propagation steps in pitting process for iron. He stated that, halide ions agglomerate and adsorb on the oxide surface specially at the defects or inhomogeneties on the surface. The chemisorbed halide may replace oxygen ions on the passivating film. These adsorbed halide ions cause a localized decrease in the film thickness before the pit nucleation potential followed by complete local removal of the film at sufficiently high anodic potential (pitting potential). This potential was found to be decreased as the concentration of halide ions is increased. However, **Galvele**(109) stated that the main reason for passivity breakdown at the initial stages of pit growth is the localized acidification due to the metal hydrolysis.

The non metallic inclusions plays an important role in the initiation of pits,(110-112) but the influence of their nature and geometric shape has not yet been exhaustively considered in depth. In the case of stainless steel, pitting corrosion starts from the sulfide inclusions, both isolated and surrounding oxide or silicate particles.(110-113) The oxidized inclusions may nucleate pitting corrosion but only when no sulfides are present.(113) The pitting resistance of stainless steel can be improved by addition of metals which from sparingly soluble or insoluble sulfides. It should be noted, however, that not all soluble sulfides necessarily cause pits. since in the initiation stages of pitting the geometry of the micro-cavities left by the inclusion dissolution has a determining role.(112,113) In this respect the mixed inclusion, sulfide oxide or sulfide silicate, must be considered more dangerous since geometrically they are more prone to reach locally favourable conditions to pitting nucleation.(112,114)

Pitting may also be considered as a microcrevice which starts from the micro cavities left by the dissolution of the soluble inclusions.(114) Three stages, therefore,can be distinguished in the corrosion process i) dissolution of the active inclusions and initiation of micro cavities, ii) agglomeration of chloride ions in those micro cavities which are geometrically favourable (incubation stages) iii) initiation and growth of pits.

The influence of the nature and shape of non metallic inclusions on the nucleation and growth of the pits in aqueous 3% NaCl solutions of different pH values on 18 Cr-9Ni and 17 Cr-11 Ni- 2Mo stainless steels was examined.(115) Pits are always localized on sulfide and mixed inclusions. The potential – pH field which determines the preferential dissolution of the sulfide inclusions are drawn. Sulfide dissolution is a condition necessary but not sufficient for the nucleation of pits since not only the nature of inclusions but also the shape is effective in determining the probability of pitting nucleation. The higher reactivity of the transverse sections of stainless steel in comparison with the longitudinal ones is explained by the more unfavourable inclusion shape is that direction. The influence of the inclusion shape become less and less important as the bulk solution pH is lower or the etching potentials is higher.

The pitting potential is an important characteristic of the pitting of passive metals, is of practical significance because its value give some indication about the pitting resistance of the metal in corrosive environment. It was found that, the pitting potential considered as the minimum potential at which localized acidity could be maintained a pit.(116) On the other hand **Strehblow**(117) defined the pitting potential as the potential corresponds to a critical coverage of film by halide ions above which there are sufficient aggressive ion at the surface to breakdown the film.

The potentiokinetic method has been used to produce a pitting potential, which is .a function of the scan rate, **Leckie**(118), **Bernnert**(119) and **Broli et al.**(120) founded that high scanning rate more noble pitting potential. **Pessal and Liu**(121) have demonstrated that it is possible to obtain accurate pitting potential values by rapid anodic polarization during which the extermely small area of the specimen surface are removed at frequent intervals. At the pitting potential the bare surface fails to repassivate and the occurance of an abrubt permanent increase in current then define the pitting potential. The value of critical pitting potentials obtained using this technique were independent of the polarization rate and surface treatment. These value depend only on the composition and structure of the metal and the test environment.

Pitting corrosion of stainless steel in chloride solutions starts when the applied potentials exceed a certain value, E_b. (breakdown potential).(122) Anodic polarization curves in the potential range preceding pitting exhibit current oscillations which are attributed to breakdown and repair events at the passive layer.(123) These events were recently, correlated with the degree of non stationarity of the passive layer in the presence of chloride ions, and finally lead to microscopic, pitting. The passivity breakdown depends strongly on both the properties of the passive film thickness(124), degree of protection(125) and the electrolyte composition [aggressive anion, inhibitor concentration,(122) solution pH(126), and temperature(122)].

The pitting potential (E_p) of 316 stainless steel in 0.5 M NaCl is more positive than that of other metals and alloys such as iron,(126) carbon steel(127) and nickel(128) in the same solution. The high positive values of E_p is related to the presence of chromium in the alloy.(129)

Alloying nickel with other elements has a marked influence on the susceptibility to pitting. The variation of the breakdown potential with chromium concentration of binary Ni-Cr alloys indicates that breakdown become significantly less probable as the chromium increases above 10%. Alloying with iron in addition to chromium yields a further improvement. The Ni-15 Cr-8 Fe alloy (Inconel 600)exhibits a little tendency to pitting even in acidic solution containing 10% NaCl. In practice Ni-Cr-Fe alloy exhibits a degree of pitting resistance and as stainless steel, the addition of few percent Mo improve their resistance.(87)

The effect of temperature on the rate of development of pitting was studied(130) by measuring the corrosion current in an acidic solution containing Cl^-. It was found that, the influence of temperature is of considerable significance, when metals and alloys act as heat transfer surface and are heater than the corrosive environment with which they are in contact. In these circumstances deep pointed pits may develop rather than the shallower rounded pits usually found when there is no thermal gradient. A possible explantion is that anodic dissolution becomes connected at the base of the growing pit in preference to its sides under the influence of the thermal gradient in the metal.

The influence of pH on the breakdown potential of nickel in alkaline solutions containing Cl^- ions was studied by **Postethawit.**(131) He found that the breakdown potential becomes more positive as the pH increases.

(F) Inhibition of Pitting Corrosion :

A corrosion inhibitor has been defined as(132) a material which when added in small amount to the corrosive environment of a metal or alloy effectively decreases the corrosion rate by retarding reactions at the electrode. More Formal definitions based on inhibitor function, have been proposed.(133) These definitions would seem to depend, to some extent, on assumptions concerning mechanisms which are not yet generally accepted. Furthermore, when initially bright metal is "inhibited" in neutral solution it remains bright, thus behaving as a noble metal, the inhibitor then called a "passivating inhibitor".

Inhibitors may be classified according to whether they act by supressing the anodic or the cathodic reactions or both. This is true for inhibitors employed in both acid and neutral solutions.

Inhibitors for acid solution: It was formerly considered that acid or pickling inhibitors function primarily by suppressing the cathodic reaction(134,135) or more specifically they raise the hydrogen overvoltage at the cathode.(136). Recent polarization studies by **Hoar and Holliday**(137) have, however, shown that inhibitors in acid solutions may, in some cases, affect the anodic process also.

Inhibitors for neutral solution: In neutral solutions inhibitors fall more easily into anodic or cathodic types. **Chyzewski and Evans**(138) were able to distinguish anodic from cathodic inhibitors (of ferrous metal corrosion) by their effect on the iron electrode in a divided cell, in which the iron electrode was made either the anode or the cathode (with a second electrode of Zn). Cathodic inhibitors, in neutral solutions, comprise mainly those materials that can supress the cathodic reaction by forming insoluble deposits with hydroxyl ions formed at the cathode by the reaction process. Such materials include: a) salts of metals such as Zinc,(139) magnesium, manganese or nickel. b) calcium salts which can precipitate as $CaCO_3$ in water containing CO_2 at those points where the alkalinity is sufficiently high. Inhibitors of this class probably act by increasing the cathodic resistance polarization, and are not true passivators, they usually form visible films on the metals. A large number of inorganic inhibitors such as the sodium salts of chromate, nitrite, phosphate, carbonate, silicate and benzoate are generally referred to as anodic inhibitors (for ferrous metals) because the potential of the metal (iron or steel) become more noble in these solutions.(140)

The inhibition of pitting corrosion of stainless steel and nickel base alloys in chloride solution containing carbonate and bicarbonate was studied.(141) It was found that inhibitor is more efficient in centre for the establishment of chemisorption process. In such case the adsorption bond strength is determined by the electron density of the atom acting as the reaction centre and by the polarizability of the function group (143,144).

Machu(145) attributed inhibition by organic compounds to physical adsorption over the entire metal surface. **Fink**(146,147) also suggested that general adsorption of the inhibitors may occur. This adsorption is chemical in nature and leads to polarization of both anodes and cathodes with subsequent surface "equipotentialization" that diminishes corrosion.

Kuznetsov and Iofa(148) noted that, nitrogenous compounds produce anodic as well as cathodic inhibition. **Hackerman and Sudburg,**(149), showed that both anodic and cathodic areas might be affected by amine inhibitors. Correlation of inhibitors efficiency with molecular structure has not yet been an outstanding process. **Mann et al.**(150) Stated that the inhibitor becomes more effective with increasing the hydrocarbon chain length. They added that, as the number of substituents on functional group of the inhibitor increased the inhibitive power also increases.

Nathan(151,152) showed that, branching of the alkyl chain decreased inhibitor efficiency as it decreased the ease of adsorption from solution. In addition, depending on the basicity(153) and solubility of aliphatic amines, they were arranged as inhibitors according to their relative effectiveness.(154)

The effect of addition of some aniline, benzaldhyde, azomethines and furylacrolines on the pitting corrosion of 18/8 stainless steel in sulphuric, formic, acetic and propionic acid solutions was reported by **Grigoriev et al.**(155). The additives used did not affect the pitting potential but reduced the rate of attack. **Ahmed**(156) showed that the pitting of 18/8 stainless steel in H_2SO_4 by quinoline-chloride mixtures was inhibited as a result of synergtic adsorption due to interaction between the quinoline cation and Cl^- ion. The results were supported by electrochemical and metallurgical studies.

The inhibition of nickel corrosion in solution of CH_3OH and HCL was studied in presence of organic inhibitors.(157) The efficiency of these inhibitors decreases in the order of aniline > aliphatic amine > hexamethyleneimine > thiourea > urea > O-phenylendiamine. The inhibition process was attributed to the developed a theory for inhibition in the presence of a series of secondary aliphatic amines and cyclicimines as inhibitors for iron in acid media.(161) They concluded that, the greater the precentage of π-orbital of the free electron on the nitrogen atom the more effective is the corresponding inhibiting action. Therefore, cyclicimines would be of more inhibiting efficiency than the corresponding aliphatic amines.

Phthalocyanines are used as corrosion inhibitors for steel in 1% NaCl solution of pH=2.(162) Water soluble tetra-sulfophthalocyanines are very poor corrosion inhibitors.Water insoluble tetraaminophthalocyanines serve as better corrosion inhibitors than water soluble ones when the metal surface is coated with an adsorbed layer of the phthalocyanine. The inhibitor efficiency was still or too low to be of any significance water insoluble polymeric phthalocyanine coated based on Fe (III) centres give inhibition efficiencies as high as 82% as confimred by both slow potentiodynamic technique and A.C. impedance analysis. Polymerization was achieved by simple dip coating followed by heat treatment of the coated surface at 450^{o}C in any inert atmosphere. The resulting coating is adherent and electrically conducting thereby providing a unique set of conducting polymer inhibitors that can be used in acid environments.