INTRODUCTION

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Nickel is one of the transition metals which exhibits a typical active-passive phenomenon in aqueous solutions. It is active in the E.M.F series with respect to hydrogen, but it is noble with respect to iron. It does not react rapidly with dilute non-oxidizing acids unless dissolved oxygen is present. Nickel is thermodynamically inert to deareated water at room temperature in which $Ni(OH)_2$ forms the corrosion product. It is passive in contact with many areated aqueous solutions, but the passive film is not so stable.

According to the potential-pH equilibrium diagram,(1) nickel would be stable in neutral and moderately alkaline solutions and it would not be stable in acidic and strongly alkaline media. In acidic solutions, the metal would be expected to dissolve as Ni^{2+} ions with the evolution of hydrogen, while in strong alkaline solutions, it would dissolve to form $HNiO_2^-$ ions.

Passive Film-Formation on Nickel :-

Regarding the nature of passive film-formation on metals there are in general two commonly expressed points of view. The first view holds that the passive film is always a diffusion-barrier layer of reaction products, (e.g., metal oxide or other compound), which separates the metal from its environment and which slows down the rate of anodic-reaction. This is sometimes referred to as "the oxide-film theory". The second view holds that passive metals are covered by a chemisorbed film of oxygen. Such a layer displaces the normally adsorbed H_2O molecules and slows down the rate of anodic dissolution involving the hydration of metal ions. Expressed in another way, adsorbed oxygen decreases the exchange current density corresponding to the reaction.

$$M \rightleftharpoons M^{2+} + ze^- \text{ ....} \qquad \textbf{(1)}$$

Even less than a monolayer on the surface is observed to have a passivating effect,(2,3) hence it is suggested that such a film cannot act primarily as a diffusion-barrier layer. This second point of view is called the "adsorption theory of passivity".

The electrochemical passivation of metals has been generally ascribed to the presence of a thin film of some sort on the surface of electrode.(4,5) The mechanism, whereby this film is formed, has been the subject of much discussion. **Muller**(6) as well as several authors suggest that an initial film may be produced by a dissolution-precipitation process. The metal dissolves until a critical concentration C^* is reached in the vicinity of the anode where a precipitate, which blocks the metal surface is formed. The other means of producing this film involves a solid-state reaction. Anions, which may be derived from the solvent, e.g. O^{2-} from H_2O, could react with the metal directly without metal cations entering the solution. This is analogous to the gas phase oxidation of metals. In principle, these two mechanisms could be distinguished by determining whether or not the metal cations have entered the solution prior to the film formation. However, when metal dissolution occurs in parallel with a solid-state reaction, (i.e. metal dissolution occurs in the active region and during the onset of passivity), distinction could not be easily made. Therefore, it is necessary to consider the various models of passive film-formation on metals in more detail.

Dissolution-Precipitation Model :-

In this model, it is recognized that the metal could dissolve as metal cations or as complex species, which means that[4] homogeneous reactions may well as several authors suggest that an initial film may be produced by a dissolution-precipitation process. The metal dissolves until a critical concentration C^* is reached in the vicinity of the anode where a precipitate, which blocks the metal surface is formed. The other meansof producing this film involves a solid-state reaction. Anions, which may be derived from the solvent, e.g. O^{2-} from H_2O, could react with the metal directly without metal cations entering the solution. This is analogous to the gas phase oxidation of metals. In principle, these two mechanisms could be distinguished by determining whether or not the metal cations have entered the solution prior to the film formation. However, when metal dissolution occurs in parallel with a solid-state reaction, (i.e. metal dissolution occurs in the active region and during the onset of passivity), distinction could not be easily made. Therefore, it is necessary to consider the various models of passive film-formation on metals in more detail.

Dissolution-Precipitation Model :-

In this model, it is recognized that the metal could dissolve as metal cations or as complex species, which means that homogeneous reactions may play a part. This metal dissolution may be totally irreversible, as in the case with most of the transition metals, or it may be reversible to some extent (as in the case of Zn- Cd- Hg- Ag). It is assumed that the mass transport of metal cations within the precipitated film to the surface of the metal is unimportant. The concentration value C^* will be generally in excess of that thermodynamically in equilibrium with the precipitated material because supersaturation should occur before precipitation. The precipitate is assumed to be formed in some way close to the electrode surface causing the rate of the metal dissolution reaction to be lowered. It should be noted that the nuclei of the precipitated-material will always be three dimensional and accordingly this mechanism would not expecte to lead to a monomolecular passivating film. It must also be recognized that a precipitate will be formed "near" the electrode surface and not on it, otherwise precipitation would be indistinguishable from solid-state reaction. "Near" the electrode should probably be taken to mean a distance from the surface which is much greater than the thickness of the electrical double layer.

Determination of the rate constants for the precipitation reaction have been made to obtain the nucleation rate and the crystal growth rate at the supersaturation which are implied by C^*. Around a freshly formed nucleus, there is obviously a complex mass-transfer situation which is superimposed upon the one dimensional concentration-distance profile. This should be taken into account when trying to arrive at values for the rate constants. These values and the C^* values must be independent of the potential or the current.

Solid-State Reaction in Parallel with Metal Dissolution :

In this situation, when a certain anodic potential (E^*) is exceeded, a film starts to be formed on the metal surface through the direct attack of the anions on the metal. The E^* values will generally be more positive than the thermodynamic reversible-potential values for the formation of the film, because of the existence of a nucleation or crystallization overvoltage. For a short time, this film is non dimensional or three dimensional in nature. For a longer time, these coalesce and form a continuous film varying in thickness from one monolayer to several monolayers. The "i-t" and "η-t" transients which occur for the different geometries of solid-state reactions in the absence of metal dissolution have been summarized elsewhere(7,8). Metal dissolution occurs at a reate greater at $E < E^*$ than that at $E > E^*$.

In many aqueous solutions, nickel has the ability to become passive over a wide range of pH values. The mechanism of passivation as well as the properties of the passive metal have been studied extensively. Early studies on the passivation of nickel were stimulated by the use of nickel anodes in alkaline batteries and in consequence the studies were conducted mainly in alkaline media. More recently, however, attention has been directed to the passivation of the nickel in acidic solutions.

Nowadays, it is generally accepted that passivity of nickel, as of most other metal, is due to the formation of a protective, self-repairing film of oxide or hydrated oxide a few nanometres thick. Another quite different, view regards the essential cause of passivation is due to formation of a monolayer of adsorbed oxygen(9). Ellipsometric measurements, both in alkaline solutions(10) and in acidic solution,(11), support the existance of surface oxide-film on passive nickel several nanometres thick. However, impedance measurements(12) seem to indicate that, in acidic solutions at least, the passive layer is electrically complex and is not an ideal dielectric. In alkaline solutions, cyclic-voltammetric and optical techniques(13) appear to support that the passivation of nickel could be due to the growth of $Ni(OH)_2$ film via oxidation of Ni to α-$Ni(OH)_2$ and then the conversion to B-$Ni(OH)_2$. A monolayer of $Ni(OH)_2$ would be sufficient to cause passivation.(14,15).

Many views of the mechanism of passivation of nickel in acid solutions were advanced. **Bockris et al.**(11) suggested that not the presence of an oxide film but rather the increase in its electronic conductance induced by a change of its stoichiometry, (i.e. its further oxidation) which led to passivity. The increase in the film electronic conductance reduced the electric field across it and consequently, the rate of metal ion transport through the film, (i.e. the rate of metal dissolution), decreased. Starting from a prepassive film of $Ni(OH)_2$, **Muller**(16) attributed passivation of nickel to the conversion of $Ni(OH)_2$ to a nonstoichiometric higher oxide $NiO_{1.5-1.7}$. Similar composition was suggested on the basis of x-ray diffraction studies in conjunction with electrochemical experiments.(17) On the other hand, the passive film on nickel could be stratified and consisting of layers of stoichiometric oxide separated by intermediate layers of non-stichiometric NiO species(18). A different view(19,20) regarded that the oxidation of nickel could take place through well-defined stages corresponding to the formation of oxides of stoichiometric composition viz-Ni-NiO-Ni_3O_4-Ni_2O_3. At potentials close to that predicted from thermodynamic considerations, Passivation(19) was considered to accompany the NiO-Ni_3O_4 transition.

In many previous studies, sulphuric acid was employed as electrolyte because the influence of the weak adsorption of its anion on the anodic process could be neglected. Several studies were advanced to show the behaviour of Ni in acidic solutions. **Petit et al.**(21) and **Skaya**(22) as well as **Novosel**(23) studied the anodic dissolution and passivation of Ni in sulphuric acid solutions under different experimental conditions. The results seemed indicat the participation of the anions in the disturbance of the Ni passive-state. However, **Muralidharan et al.**(24) proposed a mechanism for the dissolution of nickel in sulphuric acid solutions. Corrosion rate, dependence of corrosion-potential and corrosion-current on the solution parameters as well as hydrogen evolution were the important factors examined. The Ni dissolution took place and the metal entered into the passive state. Certainly the reported informations obtained with sulphuric acid solution were not completely co-incident. This could be due to various concurrent facts. For example, the surface-state of the metal and the composition of the solution change during the electrochemical measurements and the preturbation conditions of the metal/solution interface are, therefore, different.

It is of interest, therefore, to discuss the effect of sweep rate on active-passive transitions of the Ni/H_2SO_4 system in an attempt to obtain further information on the thermodynamic and kinetic factors that influence the onset of passivation. The anodic dissolution process, could be considered as follow :

(A) $Ni + OH^- \longrightarrow NiOH(ads) + e^-$... (2)

(B) $NiOH(ads) \longrightarrow NiOH^+ + e^-$.... (3)

(C) $NiOH^+ \longrightarrow Ni^{2+} + OH^-$..... (4)

The rate-determining step changes from step (A) to step (C) as $NiOH^+$ ion concentration increases in the vicinity of the surface. The rate of anodic dissolution is controlled also by the amount of OH^- ion involved in a reaction cycle consisting of steps (A), (B) and (C).

The anodic and cathodic Tafel slopes and their reaction orders with respect to Ni^{2+}, SO_4^{2-} and the pH of solution reveales that the rate determining step for the dissolution of Ni in H_2SO_4 solution could be :-

$$NiOH_{ads} \longrightarrow NiOH^+ + e^- \quad .... \qquad (3)$$

The corrosion and passivity of Ni in nitric acid solutions are also of interest. As one of the iron group metals, Ni is known to be passivated chemically in concentrated solutions of HNO_3. However, few work was preformed to elucidate the passivation process using various modern electrochemical techniques. The polarization studies techniques(25-27) were not able to control completely the electrode interface. **Abd-El Haleem et al.**(28) studied the polarization of nickel electrodes in sulphuric acid solution behaviour systematically using the Milys thermometer technique. A chain mechanism involved the formation of HNO_2 was suggested. On the other hand, **Shams El-Din et al.**(29) followed the variation of the open-circuit potential of a Ni rod electrode in solution of different concentrations as a function of time. They claimed that the passivation of Ni could be due to Ni_3O_4.

The passive film formation on Ni was studied by measuring both the reflectometry and impedance.(30) The complex refractive index and the dielectric constant of the film increased with anodic potential of film formation, indicating that the nonstoichiometric composition of the film was potential-dependent.

The anodic oxidation of nickel in neutral sulphate solutions was studied by **Cohen et al.**(31) using different physicochemical techniques and found it to be highly dependent on the extent of coverage with prior surface-oxide. Electropolishing of nickel in sulphuric acid gave a thin (6-8 A^o) film of NiO which could be removed by cathodic reduction in sulphate solution. However, anodization of nickel in the same solution gave a thicker NiO film (9-12 A^o) which could not be removed by cathodic reduction. The latter film, which was formed directly by the electropolished and anodized nickel exhibited nickel dissolution. They differ with regard to their thickness, lattice parameters and cathodic reproductibility. The film on anodized nickel being the passive oxide.

Weininger and Breiter(32) show the electrochemical behaviour and passivation of Ni in alkaline medium have been studied extensively, specially in connection with the alkaline-Ni battaries. Most of these studies were carried out on passive electrodes. To study the oxidation process cyclic voltammetry on nickel-metal electrodes showed that the anodic behaviour of nickel in strongly influenced by the previous polarisations. (i.e.) the first cyclic voltammogram of nickel electrode differs from the successive voltammograms etc.

Sato and Okomoto(33) suggested that the overall dissolution reaction to Ni^{2+} proceeded in three steps involving the species (NiOH(ads) and $NiOH^+$). **Bockris et al.**(34) favoured a dissolution-precipitation mechanism for the formation of $Ni(OH)_2$ from $NiOH^+$. They suggested that the cause of passivity was neither a monolayer nor a multilayer of oxide but was the conversion of the multilayer from an ionic to an electric conductor at the passivation potential. The work of **Ebersach et al.**(35) with a rotating nickel electrode suggested that passive films were formed by a solid state mechanism rather than by a dissolution-precipitation mechanism. **Okamoto et al.**(36) suggested that passive nickel was covered by a compact pseudomorphic film. They showed that increasing the electrolyte temperature above $60^{o}C$ resulted in crystallization of the film and the formation of "active patches" upon which the dissolution was concentrated. Metallographic studies by **Myers et al.**(37), supported the belief that the "active patches" were generated in the transpassive dissolution region.

With regard to oxides electrochemically, the literature contains a large(38,14,11,39) number of publications on the electrochemistry of nickel and much remains uncertain of the chemical composition and thermodynamic properties of the oxide.

The following oxides were reported to be formed on nickel depending on experimental conditions NiO or ($Ni(OH)_2$). Ni_3O_4 or ($Ni_3O_2(OH)_4$), Ni_2O_3 or B. NiOOH and NiO_2(14). However, it is generally believed that mixed oxides are produced in strong alkaline solutions and, therefore, their anodic behaviour of the metal in the transpassive potential region. Under transpassive dissolution condition, the passive films present on a metal surface may break-down locally or may undergo chemical changes favouring uniform dissolution. Localized film-breakdown leading to pitting has attracted the attention of many workers in the field of corrosion.(46-50)

Pitting corrosion is observed most frequently in chloride containing solutions although other ions are also known to act as pitting agent. For a given metal, the value of the critical potential, above which pitting is observed, depends on the ratio of "aggressive" to "nonaggressive" ions(49).

Once a pit is initiated, local dissolution within the pit is believed to proceed in the active dissolution mode.(46) In electropolishing, on the other hand, anodic dissolution in the transpassive potential region occurs uniformaly over the entire surface.(51) Here, the rate of metal dissolution is thought to be governed by the rate of chemical dissolution of the anodic film.(52) At steady state, film-formation and film-dissolution proceed at the same rate. It is well known that during electropolishing, local pitting may occur also, but the reason for this is not well understood(53). Recently pitting and brightening were found to occur under electrochemical machining conditions.(54-57)

Many authors examined the potential range in which passive metals show pitting caused by different aggressive anions. For most metals, a pitting potential, (E_p) was found, below which pitting corrosion did not occur. Further more, inhibition potentials (E_I) was found in the presence of inhibitors above which no pitting could be observed. The pitting potential, (E_p) and the inhibition potential, (E_I) values depended on the concentration of the aggressive anions (A) and the inhibitor (I) according to the following equations,

$$E_p = a-b \log [A] \quad (b < o) \ldots\ldots \qquad (5)$$

$$E_I = a+b \log [A][I] \ldots (b > o) \ldots \qquad (6)$$

For the inhibition potential large values of (b) were observed.(58) The critical potentials were determined by galvanostatic and potentiostatic measurements and were explained by the adsorption of aggressive anions on the metal surface and their competition with the inhibitor which represented the beginning stable pit growth in the passive potential range. These critical potentials depended on the logarithmic concentration of aggressive anions and inhibitors and were mostly independent on the pH values.

Some authors(59-61) detected a decisive difference between the potential of pit nucleation and repassivation of corroding pits. The pit-nucleation rate diminished appreciably when the potential was set in the vicinity of the critical potential and it appeared that in many cases this difference could be explained by the kinetic factors. Measurements of rate of pit development in width (2 r) and depth (h) on Ni in solutions containing various Cl^-/SO_4^{2-} ratios were performed at constant potentials.(62) The amount of Ni dissolved during corrosion was determined analytically and the amount of Ni derived from the pit was calculated. It was found that during corrosion the (h/2r) ratio gradually increased. At higher Cl^-/SO_4^{2-} ratios the development of pits was considerably slower. In the presence of a high Cl^- ion concentration, besides pitting, there also occured a general corrosion of the remaining part of the metal surface. The exponent (b) in eq. $i = 1\ (t^b)$ depended upon the change in radius, depth, and number of pits, and upon the change with time of the ratio of general corrosion to pitting.

Ni is one of the metal which is exposed to pitting corrosion if passivity breaks down locally. The pitting susceptibility of prepassivated Ni electrodes was determined by using the induction time, (T_{ind}), for pitting at constant Cl^- for constant pretreatment condition, (T_{ind}) varies exponentially with potential. The reproducibility of induction time was very good and permited a careful study of the influence of electrochemical pre-treatment on the pitting susceptibility of Ni. The resistance to pitting increased with increasing perfections of the passive oxide film. Pretreatment in the transpassive region led to an increase in pitting susceptibility in agreement with the increased deffectiveness of the prior oxide, the results indicated that potential-dependent modification of the oxide film occuring to pitting. This modification which is a measure of the pitting susceptibility is highly dependent on the prior state of the oxide film. A simple Cl^- in corporation into the oxide lattice does not appear to be the mechanism of oxide lattice modification because prior incorporation of Cl^- actually increases the pitting resistance. The anodic galvanostatic charging techniques was used to study the pitting of Ni in acid and neutral Na_2SO_4 solutions,(64) containing various concentrations of Cl^- ions. Pit initiation is indicated by a change in potential in the cathodic direction, this potential being substantially higher than that required to sustain pitting. The steady-state pitting potentials are in the passive, rather than the active potential region, which is due to the highly localized nature of pitting process. Increasing the Cl^- concentration lowers the potential for pit initiation as well as the steady-state pitting potential. The influence of anodic charging rate (iga) on pit initiation depends on the Cl^- concentration in solution. At high Cl^- concentration the charging curves are similar except for the potential shift with Iga, where as at low Cl^- concentration, pit initiation is more difficult. The minimum Cl^- concentration required for pit initiation increases with decreasing solution temperature. The potential for pit initiation is higher at lower solution. Temperature and/or at higher pH's. The Cl^- concentration, anodic charging rate, solution temperature and pH influence pit initiation by affecting the efficiency of oxide repair at local breakdown sites in the passive oxide film. Pitting was also observed when Ni was polarized in lower alcohol solutions(65) in absence of aggressive anions. In this case the acids produced from the oxidation of alcohols would react with NiO film. A part from the aggressive anions, water is also a necessary component for pitting of Ni to take place. In anhydrous organic medium pitting was detected only when water was added.(66) In Cl^- and Br^-(67) solutions the anodic current remains very low but increases abruptly with pit initiation. The breakdown results in F solution, are completely different, with the measured anodic current increasing gradually with time of polarization, the rate of current increase is at first very low, but then increases with time and eventually slows as passivity breakdown approaches completion. In other words(68) Cl^- and Br^- only temporarily delays the establishment of passivity, while F^- has little short term influence but a massive long term effect in the anodic current. Open-circuit experiments were designed to distinguish between the influence of a particular halide ion on either the establishment of passivity or its breakdown. Difference in the establishment and breakdown of passivity can be correlated with anticipated differences in the interaction of the halide ions with the surface. Galvanostatic charging experiments indicate that distinct pitting attack occurs with Cl^- and Br^- while general film breakdown in the form of attack in F^- solution.

The Inhibition of Corrosion :

Inhibitions means corrosion processes decade. The use of inhibitors to protect metals against corrosion is based on the ability of a certain individual chemical compound or a mixtures of them to reduce the rate of the corrosion process or to completely suppress it when they are added in small amounts to a corrosive medium. Addition of certain organic compound to corrosive solutions greatly diminishes their aggressiveness to metals. Corrosion is principally an electrochemical reaction, involving the release of ions. In fact the rate of any given electrochemical process depends on the rates of two conjugate reactions proceeding at the metal surface. An anodic reaction consisting in the transfer of metal atoms from the lattice to the solution with an attendant liberation of electrons and a cathodic reaction consisting in the assimilation by some depolarizer of the electrons liberated during the anodic reaction

$$M \longrightarrow M^{n+} + ne^{-} \;........ \qquad (7)$$

$$O_x + ne^{-} \longrightarrow Red.......... \qquad (8)$$

Inhibitors can change the rate of corrosion process only if they influence the kinetics of the electrochemical reactions responsible for this process. The actual inhibiting mechanism will be revealed most fully if the fundamental regularities of the electrochemical kinetics in the presence of the inhibitors are established, as well as, the molecular mechanism of their action. The mode of inhibitors action is controversial and it is not clear as to whether the anodic or cathodic partial reactions, or both are affected.

The result obtained by considering separately inorganic inhibitors and organic inhibitors, the action mechanisms of which are quite different. Inorganic inhibitors which are used mostly in neutral electrolytes, chiefly affect the anodic process and the passive state of the metal. The suppression of corrosion by just varying the kinetics of the cathodic reaction in neutral electrolytes rarely has any appreciable effect, unless a complete removal of the cathodic depolarizer (O_2) is realized.

The one essential is that the cathodic reduction of inhibitor shall accomplish the passivation by only electrochemical polarization. According to the "Electrostatic Polarization Hypothesis" proposed by **Gartledge,**(69-74), inhibition of corrosion by the XO_4^{n-} ions cannot be attributed to protective film formation, since the TcO_4^- ion, which exerts good inhibiting properties-does not possess either a buffering action or an adequate redox-potential. The XO_4^{n-} anions do not possess a certain behaviour. Thus, whereas MnO_4^- reacts rapidly to give a non-protective film, SO_4^{2-} does not. PO_4^{3-} is effective only in the presence of oxygen and CrO_4^{2-} causes passivity even in the absence of oxygen. On the other hand, although TeO_4^- and ReO_4^- ions have similar charge, size and geometrical configuration, yet TcO_4^- is a strong inhibitive anion while ReO_4^- fails to inhibit corrosion under aerated conditions(74). However, **Cartledge**(69-74) is of the opinion that the inhibition properties exhibited by the TcO_4^-

ions arises from the irreversible adsorption of the ions at the interface, whereby the surface undergoes an electrostatic polarization under the influence of the interionic polarity of the inhibitor particles.

Organic inhibitors, used mainly in acid electrolytes in which the stability of the phase- layer is lower, operate according to a different mechanism. The decrease in the corrosion rats is attributed to physical and/or chemical adsorption. In this case, adsorption as well as the effect which it has on the kinetics of the cathodic reaction are of great importance. In acid electrolytes, the rate of dissolution can be reduced considerably by lowering the rate of the cathodic reaction of hydrogen-ion discharge or discharge of some other decolarizing agent. Another way to reduce the dissolution rate is to remove the intermediate product of the reduction reaction from the reaction sphere.

The action of organic inhibitors on metal surfaces must normally be linked with the phenomenon of chemisorption, which varies from simple adsorption to the formation of true physical barriers. From the result of electrochemical measurements, the action of inhibitors is based on the increase in the overvoltage of the hydrogen discharge process, forming the partial cathodic reaction of the corrosion process(76-77) or on the increase in the ohmic resistance due to the presence of an inhibitor film at the metal solution interface(78).

Hackerman,(79) who investigated the inhibiting properties of pyridine and its derivatives, found that the inhibition increases when the electron density at the nitrogen is increased the sequences: pyridine < 3-picoline < 2-picoline=4 picoline. He developed a theory for inhibition in the presence of a series of secondary alphatic amines and cyclicimines as inhibitors in acid media,(80,81) and concluded that the greater the presence in percentage of π-orbitols of the free electrons 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.