SUMMARY AND CONCLUSION

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(1) The introduction included a literature survey of the different theories of corrosion and corrosion inhibition. The electrochemical behaviour of steel and nickel alloys in aqueous solutions (acidic, alkaline and neutral) was given with particular emphasis on the effect of aggressive as well as inhibitive anions.

(2) The anodic and cathodic Tafel lines were constructed for Ni, Inconel 600, Incoloy 800 and 316 stainless steel in deaerated HNO_3 solutions. This was made to elucidate the effect of acid concentration on the kinetic parameters of the dissolution of the different electrode samples studied.

a- Increase of acid concentration (decrease of pH) was accompanied by :

1 - A shift of the corrosion potential towards more negative values and increase of the corrosion rates, i_{corr}.

2 - An increase of the exchange current density i_o (A/Cm^2) of h.e.r.

3 - Change of cathodic Tafel slope, bc, (mV. S.C.E.).

4 - An increase of the anodic dissolution current

density (i_a, A/Cm^2) according to :

$$i_a = K_a [OH^-]^n \exp [\frac{\alpha zFE}{RT}] \qquad (9)$$

4 - An increase of the cathodic current density (of the h.e.r.) (i_c, A/Cm^2) according to :

$$i_c = K_c [H^+] \exp [\frac{-\beta FE}{RT}] \qquad (11)$$

5 - At one and the same acid concentration, the negative shift of $E_{corr.}$ and the increase of $i_{corr.}$ followed the sequence :

Sample I > Ni > Sample III > Sample II

That sample II was the more resistant one to attack by HNO_3 under natural corrosion conditions was attributed to its higher Cr content, which leads to enrichment of the passive film with the more resistant Cr_2O_3. The lower resistivity of sample I than sample III (of the same Cr content) was ascribed to the presence of Mo in the chemical composition of the latter. Molybdenum causes thickening and strengthening of the passive film of steel.

(3) Addition of some inorganic anions, namely, chloride, chromate, tungestate, molybdate, phosphate dibasic and carbonate affected the kinetic parameters of

the dissolution reaction for nickel and the alloy samples in 0.1M HNO_3. The various anions were found to fall into two main categories.

a- The first involved the chloride ions. Increase of Cl^- ion concentration leadsto :

1 - A linear shift of the change in corrosion potential ($\Delta E_{corr.}$) to more negative values.

2 - A linear shift of the change in corrosion current density ($\Delta i_{corr.}$) to higher values. This indicated that, Cl^- ions promote the corrosion process of all the electrode samples through destruction of the passive film formed on the electrode surface.

3 - At one and the same Cl^- ion concentration the shift in $\Delta E_{corr.}$ to more negative values and the increase of $\Delta i_{corr.}$ followed the sequence :

Ni > Sample I > Sample II > Sample III

This sequence reflects the high resistivity of sample III than the other electrode samples. Presence of Mo in the chemical composition of sample III impeds the adsorption of Cl^- ions on its surface by increasing the oxygen affinity of the surface.

b- The second category included the remainder anions, namely, CrO_4^{2-}, WO_4^{2-}, MoO_4^{2-}, HPO_4^{2-} and CO_3^{2-}. Increase of the concentration of these anions leads to :

1- Shift of the corrosion potential ($E_{corr.}$) toward positive direction.

2- Decrease of the anodic current density, cathodic current density of h.e.r. and the corrosion rate. Inhibition of these anion was attributed to either, precipitation of the corrosion products on the metal surface, thus blocking the active sites, or oxidation of corrosion products to higher states that, also, precipitate causing inhibition.

3- The percentage of the relative decrease of the corrosion rate ($Pi_{corr.}$) and the percentage of the relative decrease of the exchange current density (Pi_o) was calculated. The ratio $\frac{Pi_o}{Pi_{corr.}}$ was found to be less than one. This indicated that these anions affect the anodic dissolution reaction than the cathodic one.

(4) Cyclic voltammograms, were constructed for nickel and the alloy samples in HNO_3 solution as a function

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(4) Cyclic voltammograms, were constructed for nickel and the alloy samples in HNO_3 solution as a function

of electrolyte concentration.

a- The voltammograms were characterized by :

1 - All the curves were characterized by a dissolution peak (A) followed by a passive region (B), before oxygen evolution. Samples II and III showed an additional dissolution peak (C) and transpassive region followed by oxygen evolution.

2 - Passivation of Ni was suggested to be due to the formation of NiO.

3 - The passive film formed on the alloy samples was mainly composed of Ni^{2+}, Fe^{3+} and Cr^{3+} oxides in case of samples I and II, in addition to Mo^{6+} in case of sample III. Among these ions Cr^{3+} and Mo^{+6} should play a very important role in improving the corrosion resistance of the film.

4 - Peak (C) which appears in case of samples II and III was ascribed to the electrooxidation of $Cr_{(III)}$ which present in the passive film to $Cr_{(VI)}$ according to :

$$Cr_2O_3 + 5H_2O = 2\,CrO_4^{2-} + 10H^+ + 6e^- \qquad (18)$$

b- Increasing the concentration of HNO_3 leads to :

1 - Shift of the peak potential (i_{peak}) for peaks

(A and C) towards more positive values according to the equation :

$$\log i_{peak} = a_1 + b_1 \log C_{HNO_3} \qquad (19)$$

2 - The peak potential for peaks (A and C) was independent on the concentration of HNO_3.

3 - Reversing the scan to the cathodic direction was accompanied by current drop to Zero value along the passive region.A variety of cathodic peaks were appeared :

Peak G : was suggested to correspond to hydrogen evolution on Ni surface and not the reduction of products formed under anodic peak (A).

Peak E : was suggested to be associated with the $Cr_{(VI)}$ to $Cr_{(III)}$ transition.

Peak D : appeared in the anodic branch of the CV's, was attributed to a reductive dissolution of iron.

(5) Potentiodynamic anodic polarization curves of Ni and the three alloys were reported in 0.1M HNO_3 devoid of and containing increasing concentrations of Cl^- ions. It was found that the Cl^- ions cause the destruction of the passivating oxide film and

initiate pitting corrosion. The pitting corrosion potential varies with the logarithm of molarity of Cl^- ion according to :

$$E_{pitt.} = a_2 - b_2 \log C_{Cl^-} \qquad (20)$$

At one and the same Cl^- ion concentration, the shift of pitting corrosion potentials to less noble values increased in the order :

Sample III < Sample II < Sample I < Ni

This order is the same as that obtained for the shift in $\Delta E_{corr.}$ to negative values with the increase of Cl^- ions, obtained in part I.

(6) Inhibition of pitting corrosion of Ni and the alloy samples was tried using :

a- The sodium salts of chromate, tungestate, molybdate, phosphate dibasic and carbonate. Chromate ions showed the highest inhibitive effect followed by HPO_4^{2-} for samples of high Ni content. For samples of higher iron content HPO_4^{2-} had a poor inhibitive efficiency. This was ascribed to the lower solubility product of nickel phosphate than that of iron phosphate. Molybdate anions play a direct role in the inhibition process through the formation of a protective layer of molybdenum oxid of low valency.The low inhibiting efficiency of carbonate anion was attributed to partial passivation of the electrode surface because CO_3^{2-} does not manifest oxidizing properties.

b- Pyrazole and some of its derivatives. Inhibition by these compounds was discussed in terms of hard and soft acids and bases (HSAB) principle. Pyrazoles were classified as hard bases due to the high electronegativity of nitrogen atom and its low polarizability. Cations of the transition elements were classified as hard acids and those of higher charges are the harder ones. Inhibition occurred through the interaction between the hard acid and the hard base to form an insoluble salt, complex or chelate.

(7) Cyclic voltammograms were constructed for nickel and the alloy samples in NaOH solution as a function of alkali concentration.

a- The voltammograms were characterized by :

1- An anodic peak (A) which was attributed to the electrooxidation of Ni to Ni $(OH)_2$ in case of Ni and sample I (of high Ni content). For samples II and III (of high Fe content) this peak was ascribed to the formation of $Fe(OH)_2$.

2- A passive region (B); the current flowing along it was identified as the corrosion current which used to counteract the chemical dissolution of the passive film. The alkali concentration had no effect on the current following along this region.

3- At higher potentials, an additional anodic peak (C) was observed. This peak was ascribed to the oxidation of the hydroxides formed before to higher oxidation products.

b- Increase of alkali concentration caused a shift of the peak currents (i_p) for peaks (A) and (C) to higher values indicating the increase of the corrosion rate.

c- The cathodic branch of the CV's was characterized by two peaks (D) and (E). These peaks were corresponding to the reduction of the products formed during the anodic scan.

(8) Addition of increasing concentrations of Cl^- ions caused a marked increase of the integrated charge under the voltammograms, indicating the propogation of pitting corrosion. The difference between the integrated charge (Δq_a Coulomb cm^{2-}) in presence and absence of Cl^- ions was found to increase with

Cl^- ion concentration according to a straight line relationship.

(9) The effect of Cl^- ions was further examined by the potentiodynamic polarization technique. It was found that, Cl^- ions destruct the passive film and initiate pitting corrosion. The pitting corrosion potential varied with the logarithm of the molar concentration of Cl^- ions according to :

$$E_{pitt.} = a_2 - b_2 \log C_{Cl^-} \qquad (20)$$

(10) Trials were made to inhibit pitting corrosion using the previously mentioned inorganic anions. These anions shifted the pitting potential of all the electrode samples to more positive values. This was explained on the basis that, these compounds concentrate in the diffuse part of the double layer. Thus inhibit pitting corrosion through the reduction of the Zeta-potential at the oxide film/solution interface. This in turn reduces the potential field and retards the electrochemisorption of Cl^- ions from solutions on the oxide film.