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MECHANISM OF CORROSION OF PURE NICKEL IN SULPHURIC ACID SOLUTIONS

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ABSTRACT

The anodic behaviour of nickel in acid baths in plating, electrowinning and pickling processes is of industrial concern. Potentiostatic measurements were carried out to find corrosion rates in different concentrations of sulphuric acid solutions. To understand the dependence of E_{corr} and I_{corr} on solution parameters, a detailed investigation on nickel dissolution and hydrogen evolution has been carried out. In the mechanism of nickel dissolution, the number of electrons transferred has been identified from the equilibrium potential *vs* concentration of Ni^{2+} plots. The anodic and cathodic Tafel slopes, anodic and cathodic reaction orders with respect to Ni^{2+} ions, sulphate ions and pH revealed that the rate-determining step for dissolution is

$NiOH_{(ads)} \rightarrow NiOH^{+} + e.$

The variation of cathodic current densities with the concentration of H^{+} ions, or sulphate ions, and the value of 135 ± 15 mV/ decade for Tafel slope suggest the rate determining step as

$H^{+} + e \rightarrow H.$

The rate of sulphate ions on enhancing the exchange current density of the hydrogen evolution reaction has been pointed out.

INTRODUCTION

The dissolution of nickel in acid media is of theoretical and practical interest. The anodic behaviour of nickel in acid baths in plating, electrowinning and pickling processes is of industrial concern. Some work [1-3] has been done which would help towards a fundamental understanding of mechanism of corrosion of nickel in sulphuric acid solutions. Most of the earlier studies were towards understanding the nature of the passsive films. A detailed investigation was therefore undertaken on Tafel slopes, reaction orders and stoichiometric numbers for the metal dissolution and hydrogen evolution reactions by steady state method.

EXPERIMENTAL

The nickel electrodes were prepared from high purity rod (99.9999%) made into a cylindrical rod having an area of cross section of 0.196 cm^2. The rod was embedded in teflon gaskets and electrical connections were provided by screw and thread arrangement. For removing corrosion products, if any, formed on the surface, a dip in 1 M sulphuric acid for five minutes was made before polishing it successively in 1/0, 2/0, 3/0 and 4/0 emery papers. The specimens were degreased by trichloroethylene and immersed in the solution under study. A three electrode cell assembly was used. A platinum foil, 25.4 x 25.4 mm, was used as an auxiliary electrode, with saturated calomel electrode as reference electrode. The potential of the test electrode was kept at desired values using potentiostat. The current flowing between the test and the auxiliary electrodes was measured and the steady values obtained were noted. Purified hydrogen was used for deoxygenation and duplicated experiments were carried out at 32 ± 0.01°C.

RESULTS AND DISCUSSION

The corrosion potential was followed with time for 0.1 M to 1 M sulpuric acid solutions under deoxygenated condition. For all solutions the potentials became more positive and reached the steady values after about 20 minutes. The steady corrosion potentials were followed as a function of sulphuric acid concentration at constant pH or as a function of pH at constant sulphate ion concentration. The corrosion currents were obtained by extrapolation of the anodic and cathodic Tafel lines to the steady potential (Fig. 1). In order to understand the dependence on solution parameters, the anodic and cathodic reactions were studied in detail.

Anodic reaction

A plot of the equilibrium potential with log (Ni^{2+}) ion concentration (Fig. 2) gave a slope of 31 mV/decade suggesting the number of electrons involved is two, and the overall corrosion of nickel is $Ni \rightarrow Ni^{2+} + 2e$.

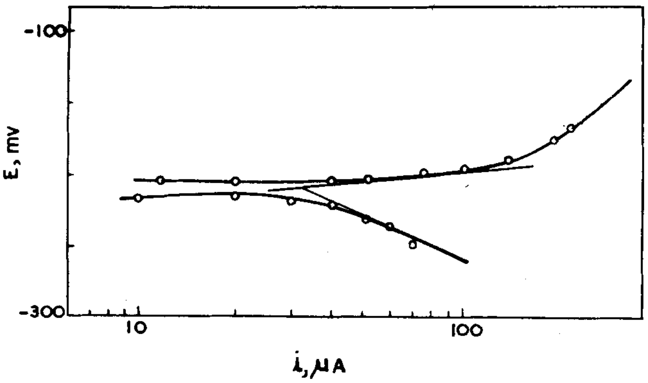

Fig. 1 : Potentiostatic polarisation curves in 0.1 M H_2SO_4

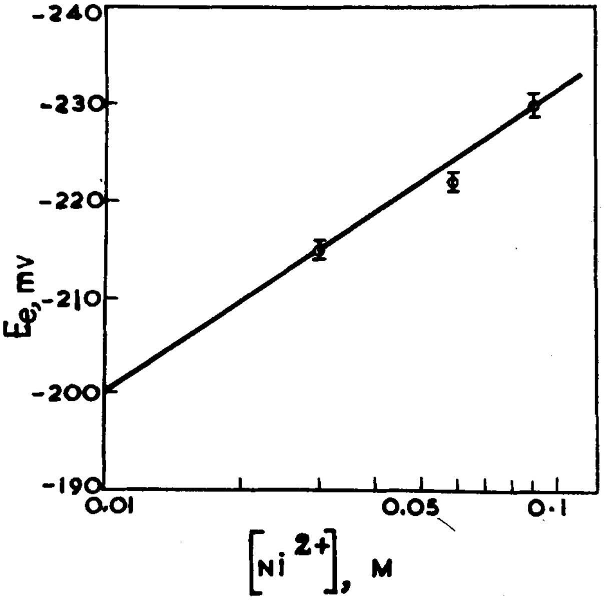

Fig. 2 : Variation of equilibrium potential with nickel concentration in 1.0M H_2SO_4

Different schemes are proposed for the dissolution and deposition of nickel from acid solutions and theoretical mechanistic parameters are given in Table I. A typical experimental anodic reaction order plot with respect to pH is given in Figure 3. Table I also presents experimental values (2b) along with theoretical mechanistic parameters (2a) for the second scheme proposed. It may be seen that except ($d \log i_o / d \log Ni^{2+}$) and cathodic reaction order with reference to Ni^{2+} ions all parameters agree closely with the theoretical values. In the nickel deposition reaction there may be interference by H^+ ions which may also co-deposit, giving lower values of cathodic reaction orders.

Cathodic reaction

In solutions free of oxygen, the possible cathodic reaction is the evolution of hydrogen on nickel surface. Different schemes for hydrogen evolution reaction have been discussed by earlier workers. Figure 4 presents the dependence of cathodic current on pH.

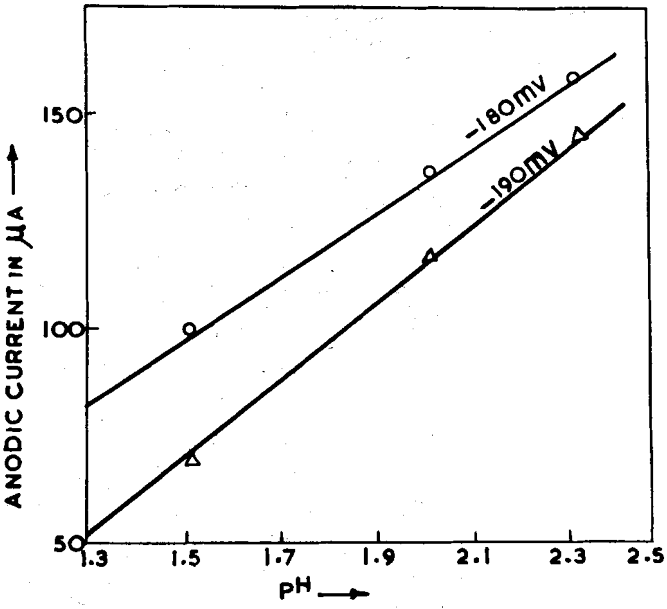

Fig. 3: Anodic reaction order w.r.t. pH

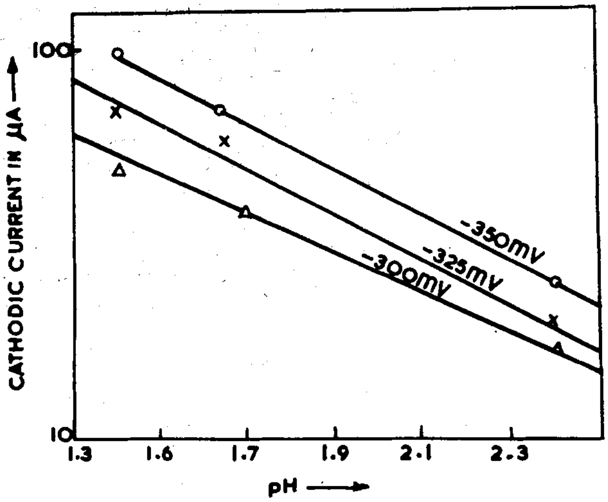

Fig. 4 : Dependence of cathodic current on pH for hydrogen evolution

Table II gives the diagnostic criteria for the mechanism of hydrogen evolution reaction on nickel from acid solutions compared with the experimental results. It may be seen that the proton discharge is the rate-determining step. The hydrogen evolution may take place either coupled with chemical desorption or electrochemical desorption.

Table I: Different schemes proposed for the dissolution/deposition of nickel

Scheme	Tafel slope		Reaction order w.r.t. pH		Reaction order w.r.t Ni^{2+}		Reaction order w.r.t SO_4^{2-}		$\left(\frac{d \log i_o}{d \log Ni^{2+}}\right)$	$\left(\frac{d \log i_o}{d\, pH}\right)$
	Anodic (mV/decade)	Cathodic	Anodic	Cathodic	Anodic	Cathodic	Anodic	Cathodic		
1	120	40	1.0	1.0	0	1.0	–	–	0.25	1.0
2a	40	120	1.0	1.0	0	1.0	0	0	0.75	1.0
2b	50 ± 10	120 ± 15	0.9 ± 0.1	0.67	0	0.33	0	0	0.30	1.0
3	30	–	1.0	1.0	0	1.0	–	–	1.0	1.0

Scheme 1. $Ni + OH^- \rightarrow NiOH_{ads} + e;\ NiOH_{ads} \rightleftarrows NiOH^+ + e;\ NiOH^+ \rightleftarrows Ni^{2+} + OH^-$

Scheme 2. $Ni + OH^- \rightleftarrows NiOH_{ads} + e;\ NiOH_{ads} \rightarrow NiOH^+ + e;\ NiOH^+ \rightleftarrows Ni^{2+} + OH^-$

2a gives theoretical values for scheme 2 and 2b presents experimental results of the present investigation at 32°C in the above table

Scheme 3. $Ni + OH^- \rightleftarrows NiOH_{ads} + e;\ NiOH_{ads} \rightleftarrows NiOH^+ + e;\ NiOH^+ \rightarrow Ni^{2+} + OH^-$

Table II: Diagnostic criteria for the mechanism of hydrogen evolution reaction on nickel from acid solutions and comparison with experimental results

Schemes	Theoretical (25°C) Tafel slope mV/decade	Cathodic reaction order w.r.t. (H^+) ion
1. $H^+ + e \rightarrow H$ $2H \rightleftarrows H_2$	120	1
2. $H^+ + e \rightleftarrows H$ $H + H \rightarrow H_2$	30	2
3. $H^+ + e \rightarrow H$ $H^+ + He \rightleftarrows H_2$	120	1
4. $H^+ + e \rightleftarrows H$ $H^+ + H + e \rightarrow H_2$	40	2

Experimentally obtained values:
Cathodic Tafel slope 135 ± 15 mV/decade
Cathodic reaction order w.r.t. pH = −1.0 ± 0.01

Mechanism of corrosion

At E_{corr}, corrosion potential,

and $i_{corr} = i_a = i_e$

Metal dissolution current = Hydrogen evolution current. It was found for anodic reaction the rate-determining step is

$$(NiOH)_{ads} \rightarrow NiOH^+ + e$$

$$i_a = K_a [Ni] [OH^-] \exp \{(2-\beta) F \Delta \phi_{corr}/Rt\}$$

and for the cathodic reaction, the rate-determining step is

$$H^+ E \rightarrow H$$

$$i_c = K_c [H^+] \exp \{-\beta F \Delta \phi_{corr}/RT\}$$

$$\therefore \phi_{corr} = \phi^o_{corr} + RT/2F \ln [H^+]^2$$

$$i_{corr} = K_a [Ni] [H^+]^{0.5}$$

$$= K_c [H^+]^{0.5}$$

Table III presents the comparison of theoretical and experimental results for the corrosion of nickel and dependence of E_{corr} and i_{corr} on solution parameters. It may be seen that anodic Tafel slope for metal dissolution, cathodic Tafel slope for hydrogen evolution, the dependence of E_{corr} on sulphuric acid concentrations, log sulphate ion concentration at constant pH and variation of pH at constant sulphate ion concentrations agree with the theoretical values. The dependence of i_{corr} on solution parameters does not agree with the theoretical values. Though sulphate ions are not participating in either of the electrode processes, a layer adjacent to the electrode surface is always covered by a layer of adsorbed sulphate ions. The adsorption of sulphate anion may have increased the $i_{O,H}$ and thereby corrosion current. The value obtained for

$\frac{d \log i_{corr}}{d\,pH}$ at constant sulphate concentration is in the same

Table III: Comparison of theoretical and experimental results for the corrosion of nickel – E_{corr} and i_{corr} dependence on solution parameter

No.	Parameter	Experimental value 32°C	Theoretical value at 25°C
1.	Anodic Tafel slope (metal dissolution)	50 ± 10 mV/decade	40 mV/decade
2.	Cathodic Tafel slope (Hydrogen evolution)	135 ± mV/decade	120 mV/decade
3.	$\frac{dE_{corr}}{d \log C_{H_2SO_4}}$	70 mV/decade	60 mV/decade
4.	$\frac{d \log i_{corr}}{d \log C_{H_2SO_4}}$	0.72	–
5.	$\frac{d \log i_{corr}}{d \log C_{SO_4^{2-}}}\ {}_{pH}$	0.39	–
6.	$\frac{d E_{corr}}{d \log C_{SO_4^{2-}}}\ {}_{pH}$	0.0	0.0
7.	$\frac{d E_{corr}}{d\,pH}\ C_{SO_4^{2-}}$	0.0	0.0
8.	$\frac{d\ lof\ i_{corr}}{d\,pH}\ C_{SO_4^{2-}}$	−2.55	−0.5

direction as predicted by the theoretical model, but the higher value obtained has to be investigated further.

CONCLUSIONS

The mechanism of corrosion of nickel in sulphuric acid is investigated by steady state method. The anodic reaction is the dissolution of nickel giving rise to Ni^{2+} and the cathodic reaction is the hydrogen evolution.

The diagnostic criteria for the nickel dissolution reaction revealed

$$\begin{array}{lcl} Ni + CH^{-} & \rightleftarrows & (NiOH)_{ads} + e \\ (NiOH)_{ads} & \rightarrow & NiOH^{+} + e \\ NiOH^{+} & \rightleftarrows & Ni^{2+} + OH^{-} \end{array}$$

and the cathodic reaction, namely, hydrogen evolution is having proton discharge as rate determining step which is followed by chemical desorption or electrochemical desorption.

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