Corrosion of Mild Steel in Alkaline Solutions

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Cyclic voltammetry and Tafel extrapolation methods have been used to study the corrosion behaviour of mild steel in concentrated alkaline solutions. Addition of lithium hydroxide and sodium sulfide to KOH solution is found to accelarate the corrosion significantly.

Nickel plated mild steel substrate is extensively used for making positive and negative electrode in alkaline batteries, because it gives mechanical strength to electrode materials and also acts as a current collector.

Generally a solution of 5.35 M KOH is used as the electrolyte in alkaline batteries. Usually 1.19 M LiOH is added to KOH solution to improve the performance of the battery system. In the case of nickel-iron batteries, 0.21 M Na_2S is also added to KOH solution containing LiOH. Sometimes the plating may be imperfect. In such a case, uncoated parts may easily be subjected to corrosion, which is turn leads to less electrical conductivity, loss of mechanical strength and finally cell failure.

During charging and discharging processes, the temperature of the electrolyte rises. The presence of additives in KOH and high temperature may induce corrosion in the uncoated mild steel substrate. In the present study, the corrosion behaviour of two different grades of mild steel in 5.35 M KOH containing LiOH and Na_2S at 60 $\pm$ 1°C has been examined using Tafel extrapolation and cyclic voltammetry methods.

EXPERIMENTAL

Two different grades of mild steel (given in Table 1) are used in the present study, both in annealed and unannealed condition. Annealed specimens were prepared by annealing at a temperature of 875 $\pm$ 1°C in hydrogen atmosphere for 45 minutes and cooling at room temperature. All chemicals used in this study (KOH, LiOH and Na_2S) were of AR grade and of Loba chemie make. Double distilled water was used for preparing all solutions.

Table 1

Composition of mild steel. Wt%

Grade	C	S	P	Si	Cu	Specimen designation	
						Unannealed	Annealed
IS/1786	.025	.056	0.55	-	.3	1	2
IS/432 66	.2	.55	.055	.1	-	3	4

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Mild steel specimens of surface area 1 cm^2 were connected to a copper rod (for better electrical conductivity), cloth buffed in presence of pumice, then degreased with trichloroethylene and were used in cyclic voltammetry and Tafel studies.

Cyclic voltammetry studies were carried out using a three electrode cell assembly having mild steel specimen as the working electrode, Hg/HgO reference electrode and platinum sheet of large surface area as the counter electrode. The cell was maintained at 60°C with the help of a thermostat. Potentioscan wenking POS-73 with Rikadenki X-Y recorder was used for potential scan and recording. Different sweep rates were used. The scan range used was -1200 mV to -200 mV.

Tafel extrapolation method was carried out at 60 ± 1 C using same cell set up as used for cyclic voltammetry studies and BAS - electrochemical analyser. In this case, experiments were carried out at a very low sweep rate of 2 mV sec^{-1}.

RESULTS AND DISCUSSION

Mild steel passivates readily in caustic alkaline solutions over a wide range of concentrations and temperatures. The surface film that is usually formed at potentials low in the passive range is magnetite; hematite is formed at higher potentials [1-3]. Electrochemical studies on mild steel in alkaline environments indicate that the anodic oxidation of mild steel occurs in two stages [4].

$$Fe + 2\ OH^- \longrightarrow Fe(OH)_2 + 2\ e^- \quad -(1)$$

$$3\ Fe(OH)_2 + 2\ OH^- \longrightarrow Fe_3O_4 + 4\ H_2O + 2e^- \quad -(2)$$

In KOH solution, the corrosion reaction is

$$3\ Fe + 4\ H_2O \longrightarrow Fe_3O_4 + 4\ H_2 \quad -(3)$$

When LiOH is added to KOH, the following reaction is taking place:

$$Fe + LiOH + H_2O \longrightarrow LiFeO_2 + 3/2\ H_2 \quad -(4)$$

Table 2

Anodic and Cathodic Peak Potentials of Mild Steel in alkaline solutions containing different additives.

Specimen Number	<- anodic I	II	(mV) -> III	IV	<- Cathodic V	(mV) -> VI
Medium: 5.35 M KOH (Fig 1)						
1	-968	-886	-719	-	-991	-1135
2	-974	-874	-720	-	-990	-1075
3	-953	-894	-722	-	-995	-1080
4	-981	-885	-724	431	-720	-1006
Medium: 5.35 M KOH + 1.19 M LiOH (Fig 2)						
1	-878	-720	-	-	-972	-1142
2	-880	-722	-	-	-975	-1130
3	-1082	-879	-718	-	-982	-1141
4	-879	-706	-432	-	-724	-0976
Medium 5.35 M KOH + 1.19 M LiOH + 0.21 M Na_2S (Fig 3)						
1	-954	-720	-515	-	-1006	
2	-988	-957	-	-	-1002	-
3	-965	-728	-	-	-1072	-
4	-978	-720	-310	-	-0997	-

Solutions prepared with Na_2S additions to the 5.35 M KOH + 1.19 M LiOH electrolyte gave more complex polarisation curves and finally sulfide was converted to sulphate.

The cyclic voltammetry studies were made at scan rates of 2,5,10 and 15 mV sec^{-1}. The voltammograms (Fig.1-3) are all similar. The anodic and cathodic peak potentials were measured and are given in Table 2. Only a noble shift of the peak potential and an increase in the peak current was observed with an increase in the scan rate.

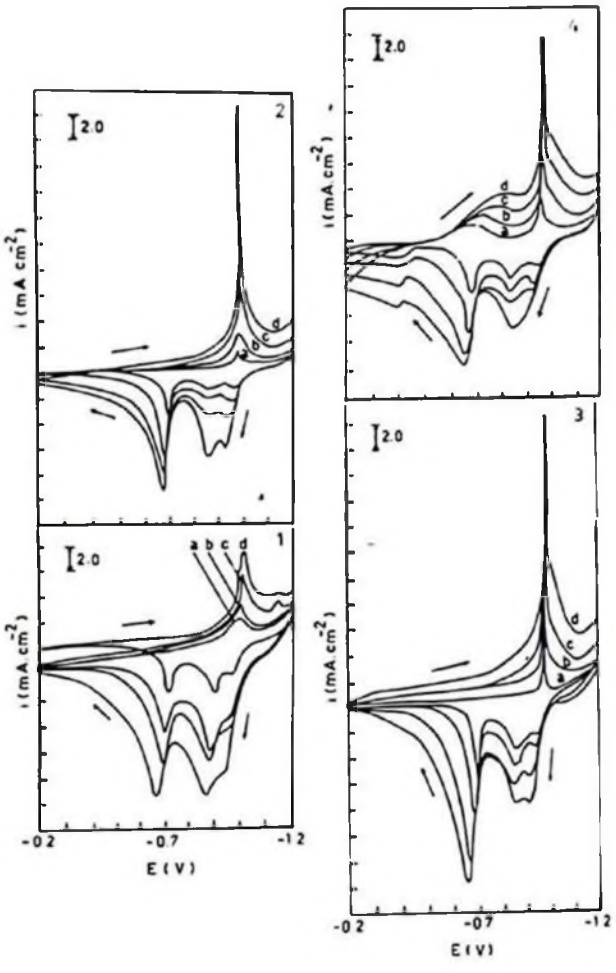


Fig1 Cyclic Voltammograms of mild steel in 5.35M KOH

Specimens 1- 4 as marked ; Temp. 60°

a 2mV Sec^{-1} b 5mV Sec^{-1}

c 10mV Sec^{-1} d. 15mV Sec^{-1}

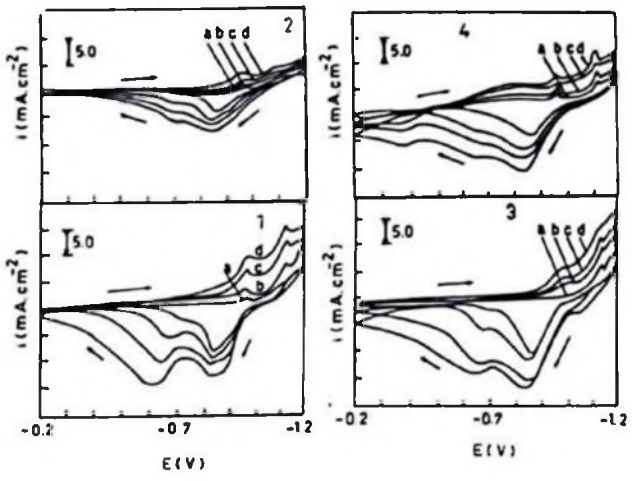


Fig2. Cyclic Voltammograms of mild steel in 5.35M KOH + 1.19 M LiCl.

Specimens 1-4 as marked ; T=60°C

a 2mV Sec^{-1} b 5mV Sec^{-1}

c 10mV Sec^{-1} d. 15mV Sec^{-1}

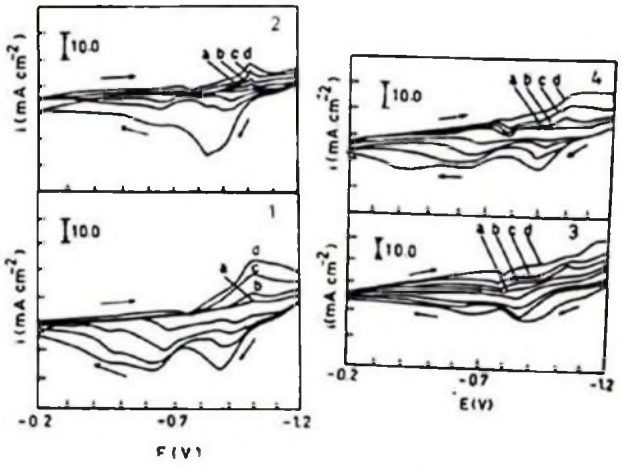


Fig3. Cyclic Voltammograms of mild steel in 5.35M KOH + 1.19 M LiCl + 0.21 M Na_2S.

Specimens 1-4 as marked ; T=60°C

a 2mV Sec^{-1} b 5mV Sec^{-1}

c 10mV Sec^{-1} d. 15mV Sec^{-1}

Fig. 1-3 showed clearly defined peaks on cyclic sweeping betwen hydrogen and oxygen evolutions. Three peaks (I, II and III) were seen on anodic sweeping (lower half) and upto three peaks on the reverse cathodic sweeping (upper half). The current/voltage traces showed that on repetitive sweeping, the charge consumed at peaks I and III decreased while that consumed at peaks II & IV increased. Annealed specimens (2 and 4) gave similar results, except that peak I was greatly reduced in size relative to peak II; peaks II & IV showed little variation on repetitive sweeping.

On the anodic side peaks refer to the formation of $Fe(OH)_2$ and $Fe(OH)_2$ —> Fe_2O_3 & Fe_3O_4. Sodium sulfide itself is electrochemically active and the increase in anodic current at potentials above $E_{crit.}$ can be attributed to the oxidation of sulfide (peak III) to higher forms [9]. Values of i_{corr} and E_{corr} were obtained from Fig.4 and given in Table 3.

Table 3.

Values of E_{corr} and i_{corr} for mild steel in alkaline solutions containing different additives

Specimen Number	E_{corr} (mV)	i_{corr} (mA.cm^{-2})
Medium 5.35 M KOH (Fig 4A)		
1	-947	0.199
2	-939	0.166
3	-950	0.447
4	-945	0.262
Medium 5.35 M KOH + 1.19 M LiOH (Fig 4B)		
1	-972	0.316
2	-962	0.224
3	-950	0.398
4	-948	0.355
Medium 5.35 M KOH + 1.19 M LiOH + 0.21 M Na_2S (Fig 4C)		
1	-1000	0.631
2	-992	0.355
3	-1007	0.708
4	-960	0.631

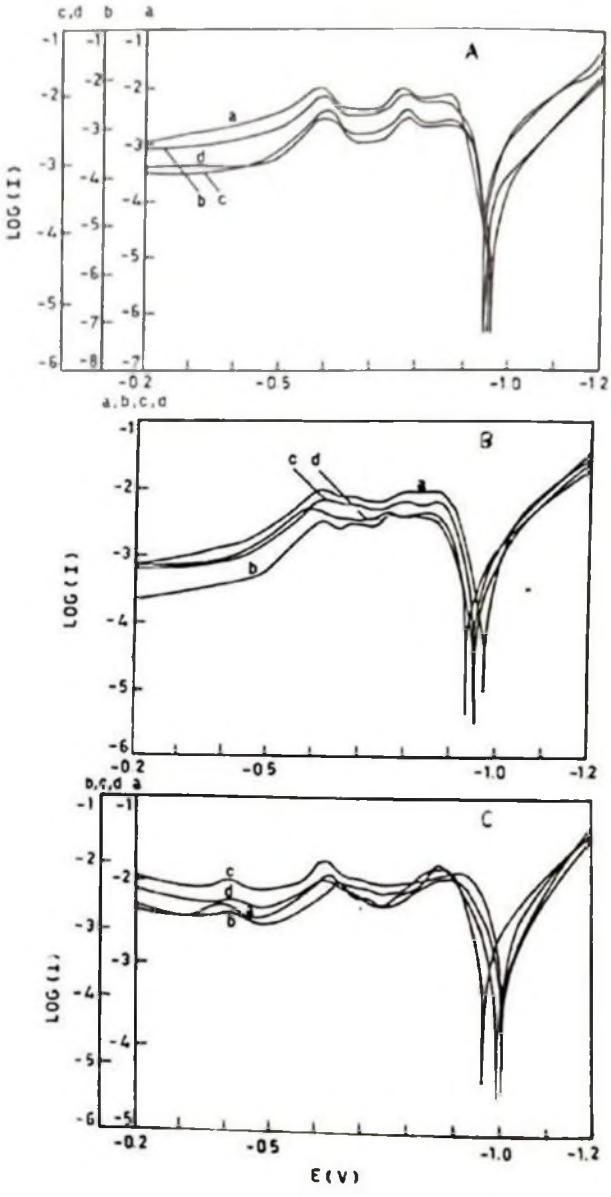


Fig. 4.E vs log C plot for mild steel.

A 5.35 M KOH B 5.35M KOH+1.19M LiCl

C 5.35M KOH+1.19M LiCl+0.21M Na_2S

a Speciman 1 b Speciman 2

c Speciman 3 d Speciman 4

CONCLUSION

1. From the E *vs* log I plots for mild steel in alkaline electrolytes, it can be seen that the anodic polarisation is more pronounced than the cathodic polarisation. Hence the corrosion of mild steel in these electrolytes is under anodic control.

2. The corrosion rate of mild steel in these solutions is found to be in the order KOH < KOH + LIOH < KOH + LIOH + Na_2S.

3. The presence of sulfide ion in alkaline solution enhances the corrosion rate by increasing the solubility of the $Fe(OH)_2$ film.

4. The performance of annealed specimens is found to be superior to that for other specimens.

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