Corrosion studies of Ni-free austenitic stainless steel in methanol containing H\textsubscript{2}SO\textsubscript{4}, HCl and LiCl

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The corrosion behaviour of an austenitic stainless steel containing nitrogen with negligible amount of nickel has been investigated in methanol-H\textsubscript{2}SO\textsubscript{4}, methanol-HCl, and methanol-LiCl solutions using potentiostatic polarization technique. The cathodic reaction was the hydrogen evolution reaction. Active, passive and transpassive behaviours were observed only at high concentrations of H\textsubscript{2}SO\textsubscript{4} (0.01-1.0 M) in methanol, and passivity was due to the high inherent water content in sulphuric acid. Pitting was also observed on the steel surface. The pitting potential became nobler as the concentration of H\textsubscript{2}SO\textsubscript{4} increased. In 0.1 and 1.0 M H\textsubscript{2}SO\textsubscript{4}, a cathodic loop, characterized by measured negative current in the anodic region, was also observed. In methanol-HCl and methanol-LiCl solutions, the steel dissolved actively and no active-passive transition was observed. The corrosion rate was significantly higher in methanol-HCl solution as compared to methanol-LiCl due to the synergistic effects of acid and chloride ion.

Keywords: Austenitic stainless steel, Potentiostatic polarization, Corrosion, Passivity, Pitting
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The austenitic stainless steels are regarded as promising materials for a wide range of applications because of their enhanced mechanical and corrosion resistant properties. It is well established that the stainless steels derive their corrosion resistance by forming the passive film which is primarily dependent on the chromium content. The minor alloying additions such as Mo, N, and Cu enhance the corrosion resistance by increasing the passivating ability\textsuperscript{1-3}. As an alloying element, nitrogen dissolves in the steel matrix and greatly improves the resistance of the austenitic stainless steel to pitting, stress corrosion cracking and intergranular corrosion\textsuperscript{4,5}, and is a stable austenitic former. Similarly, copper also stabilizes austenite, making it possible to reduce the expensive nickel content in the alloy\textsuperscript{6}. Moreover, being a good stabilizer against martensitic transformation in stainless steels, it gives rise to more stable austenite\textsuperscript{7}. It also improves the steel passivation in several non-oxidizing acid medium due to its low hydrogen overvoltage and shows beneficial effect on the pitting potential and crevice potential\textsuperscript{8-10}. Copper significantly increases the general corrosion resistance of stainless steels in acid solutions\textsuperscript{11}, and the mechanism of beneficial effect of copper is based on the suppression of anodic dissolution by elemental copper deposition on the steel surface immersed in the corrosive medium\textsuperscript{12}. Therefore, it is worthwhile to study the corrosion behaviour of the nitrogen and copper alloyed austenitic stainless steel having negligible amount of nickel in common aggressive media containing chloride, sulphate, and acid.

A review of literature shows some studies on the nitrogen and copper bearing stainless steels in aqueous chloride and sulphuric acid media\textsuperscript{13-15}. However, scarcely the work is available in organic solutions, particularly methanolic solution. Methanol is of utmost industrial importance because of its increasing use as an alternative fuel for oil in fuel cell electric vehicles due to low environmental pollution. The fuel cells use sulphuric acid as electrolyte for electrochemical oxidation of methanol. Moreover, methanol-sulphuric acid (0.5-1.0 M H\textsubscript{2}SO\textsubscript{4}) serves as a potent reaction mixture in biodiesel production where the tank material of the reaction vessel is made of stainless steel\textsuperscript{16}. Therefore, the present work is planned to investigate the corrosion behaviour of nitrogen and copper alloyed austenitic stainless steel bearing negligible amount of nickel in methanolic solutions of sulphuric acid, hydrochloric acid, and lithium chloride.

Experimental Procedure
The chemical composition (wt.\%) of the stainless steel used is as follows: 11.4% Cr, 17.0% Mn, 0.3% Ni, 0.65% Cu, 0.47% Si, 0.052% C, 0.197% N,
0.004% S and balance Fe. The working electrode sample was procured from Alloy Steel Plant, Durgapur, India. The specimen was polished to a mirror finish using successive grades of emery papers followed by polishing with alumina powder. It was then washed thoroughly with double distilled water, degreased with acetone and transferred quickly into the electrochemical cell.

The cell used was a conventional three electrode electrochemical cell consisting of a working electrode, a platinum counter electrode of large surface area and a saturated calomel reference electrode (SCE). The details of experimental set-up and working procedures were described elsewhere\textsuperscript{17,18}.

The electrochemical potentiostatic polarization experiments were carried out using a potentiostat (Wenking POS 73). The working electrode specimen of 2 cm\textsuperscript{2} exposed area was immersed in the experimental solution for 30 min to stabilize the open-circuit potential (OCP). Then, the polarization was performed potentiostatically by starting at a negative potential and then moving towards positive potential in steps of 20 mV/min. All measured potentials were referred to saturated calomel electrode (SCE). All experiments were carried out in aerated solution at 35 ± 1°C under unstirred condition. The solutions were prepared using distilled purified methanol and analytical grades of chemicals (H\textsubscript{2}SO\textsubscript{4}, HCl and LiCl).

After the experiment was completed, the specimens were rinsed in deionised water in an ultrasonic bath and were subsequently examined using a scanning electron microscope (Philips XL-20).

**Results and Discussion**

**Methanol-H\textsubscript{2}SO\textsubscript{4}**

Figure 1 shows the cathodic and anodic polarization curves of the steel in methanol containing different concentrations of H\textsubscript{2}SO\textsubscript{4} (0.001-1.0 M). The cathodic polarization curves were almost linear over a large range of potentials and the cathodic Tafel slopes ($b_c$) ranged between 80 and 175 mV/dec. Evolution of a gas was observed on the surface of the electrode during cathodic polarization which was considered to be hydrogen, indicating the cathodic reaction to be hydrogen evolution reaction in the acidic medium.

The anodic polarization curves revealed active dissolution in methanol containing 0.001 M H\textsubscript{2}SO\textsubscript{4}. From the corrosion potential ($E_{corr}$), the anodic current increased largely with small applied potential and at potential > -40 mV, the increase in current became steady indicating limiting nature. This is most likely due to the diffusion controlled anodic reaction probably due to the formation of a sulphate salt film on the surface of the steel.

![Polarization curves](image)

*Fig. 1 — Polarization curves of Ni-free austenitic stainless steel in different concentrations of H\textsubscript{2}SO\textsubscript{4} in methanol, at 35°C.*

(i) ▼ — ▼ 0.001 M H\textsubscript{2}SO\textsubscript{4}; (ii) ▼ — ▼ 0.01 M H\textsubscript{2}SO\textsubscript{4}; (iii) O — O 0.10 M H\textsubscript{2}SO\textsubscript{4} and (iv) ● — ● 1.0 M H\textsubscript{2}SO\textsubscript{4}
Active, passive, and transpassive regions were observed for 0.01 to 1.0 M H2SO4 solutions, though the active to passive transition region was not observed for 0.01 M H2SO4. The corrosion current density ($i_{corr}$) and the critical current density for passivation ($i_{crit}$) increased as the concentration of H2SO4 in methanol increased from 0.01 to 1.0 M. Moreover, the stainless steel showed negative current loop in the potential range from -120 to 20 mV and from -160 to 140 mV for 0.1 and 1.0 M H2SO4, respectively (dashed lines in Fig. 1). Such negative loop for different metals in different aqueous environments has been observed earlier also. The negative loop has been termed as ‘cathodic loop’ which appears when the net cathodic current exceeds the net anodic current. Several explanations have been given for the appearance of such loop. According to Greene and Pickering et al., it is due to oxygen reduction even in the helium-saturated solution while for Fe-Cr alloy in 1 N H2SO4, it was due to the reduction of protons. Similarly, in the case of copper-containing austenitic stainless steels in 1 N H2SO4, it is because of the proton reduction reaction on the copper layer formed on the steel surface during the anodic polarization. Further, Hiromoto et al. suggested that the reduction of protons on the passive oxide surface of the chromium-containing amorphous alloys as one of the causes.

In the present study, an increase in the concentration of H2SO4 from 0.1 to 1.0 M shifted the potential corresponding to the initiation of the cathodic loop ($E_{init}$) in the negative direction and the terminal potential of the loop ($E_{term}$) in the positive direction, thus expanding the region of the cathodic loop. Also, the slope of the linear region at the lower potentials of $E_{init}$ increased from 0.035 to 0.040 V dec$^{-1}$. The slopes were very close to those reported earlier, for proton reduction reaction in the anodic region. Therefore, the reaction associated with the cathodic loop as observed in the present case is most likely the proton reduction reaction because the Tafel slope of the following reaction is 0.041 V dec$^{-1}$.

$$\text{MH} + \text{H}_2\text{O}^+ + e^- \rightarrow \text{M} + \text{H}_2 + \text{H}_2\text{O} \quad \text{…(1)}$$

where M and H2O$^+$ represent the metal and the hydronium ion generated by the hydration of proton, respectively.

In the present case it is considered that during the cathodic polarization, the hydrogen gets adsorbed on the metal surface which is significant for the concentration of H2SO4 ≥ 0.1 M, and due to the anodic dissolution the more active constituent of the steel (Fe, Cr, Mn) goes into the solution along with the release of the adsorbed hydrogen as proton (H$^+$ ion) leading to the enrichment of the surface with copper and simultaneous passive oxide film formation. This in turn reduces the hydrogen overpotential considerably and the reduction of the proton occurs on the oxide film. Thus the net cathodic reaction suppresses the net anodic reaction resulting in the initiation of the cathodic loop.

The passive region was characterized by the low and constant current density over a large range of the potential and the passive current density ($i_p$) marginally increased with the concentration of H2SO4, i.e., in the order 0.01 < 0.1 < 1.0 M, probably due to the increasing acidity of the solution. At the same time the range of passivity was widened and the breakdown (or pitting) potential ($E_{break}$ or $E_{pit}$) shifted in the noble direction. The behaviour of the stainless steel in H2SO4 is complex since it is neither strong oxidizing nor strong reducing solution. In the case of highly concentrated sulphuric acid solution, the passivation proceeds with the direct participation of undissociated sulphuric acid molecules via solid-state mechanism. However, in the dilute solutions (H2SO4 concentration up to 6 M), water molecules are the main passivating agents. In non-aqueous organic solutions, passivity is strongly dependent on the water content of the solution which is either added externally or provided by any of the species present in the solution. In the present case, the solutions are dilute (0.01-1.0 M H2SO4); therefore, the passivating species in this case is certainly water which is inherent in sulphuric acid and the concentration of the inherent water is likely to be higher than the critical concentration required to render stable passivity. It is obvious that the water concentration in the solution increases with sulphuric acid concentration which enhances the passivation of the steel and is marked by widening of the range of passivity and shifting of the pitting potential ($E_{pit}$) in the noble direction. At more positive potentials in the transpassive region, a current plateau was observed indicating mass-transfer controlled reactions.

The scanning electron micrograph of the steel in 0.1 M H2SO4 in methanol showed that the surface of the steel suffered from pitting attack (Fig. 2). Thus, the transpassive behaviour was due to the breakdown of the passive film in the form of pitting at local points. However, the pits were shallow and irregular in shape and overlapped on each other.
The anodic polarization curves revealed only active dissolution of the steel in all concentrations of HCl due to the presence of aggressive chloride ion (Cl\textsuperscript{−}). The polarization curves shifted to higher current densities as the concentration of HCl increased. Consequently, the corrosion current density ($i_{\text{corr}}$) increased largely. For 0.001 M HCl, $i_{\text{corr}}$ was 1.2 μA/cm\textsuperscript{2} whereas for 1.0 M HCl, it became 850 μA/cm\textsuperscript{2}. Thus the rate of corrosion, represented in terms of $i_{\text{corr}}$, increased largely due to an increase in the concentration of HCl to 1.0 M. This is due to the synergistic effect of increase in the concentration of Cl\textsuperscript{−} ion and the higher acidity of the solution. The results are in well accordance with earlier findings\textsuperscript{28,29} where the rate of corrosion depends directly on the concentration of the aggressive species (Cl\textsuperscript{−}) and the acidity of the solution.

The nature of the curves revealed that the anodic current increased rapidly from the corrosion potential ($E_{\text{corr}}$), but as the potential approached more positive value, the increase in the current became steady showing somewhat limiting nature (0.1 and 1.0 M). In the higher concentration of HCl, the rate of anodic dissolution is very high and as a result the electrolyte near the metal-electrolyte interface gets saturated with the corrosion products (metal chlorides), which may
then stick to the alloy surface and act as a barrier layer for metal ions entering into the solution indicating the limiting currents. Sometimes, the corrosion products form a salt film on the surface of the metal that are loosely bound and are not as protective as the passive film.

**Methanol-LiCl**

The cathodic and anodic polarization curves of the steel in methanol containing different concentrations of LiCl (0.001 to 0.25 M) are illustrated in Fig. 4. The cathodic polarization curves were almost linear and exhibited well-defined Tafel regions. An increase in the concentration of LiCl from 0.001 to 0.25 M shifted the cathodic polarization curves towards higher current density regions. However, the increase in current with respect to the concentration was not much as was observed in the case of methanol-HCl solutions. Moreover, for a particular chloride concentration, the cathodic current density was always higher in the acidic solutions of methanol than in the lithium chloride solutions. This is certainly due to the higher acidity of the methanol-HCl solution.

The anodic polarization curves showed only active dissolution and were associated with well-defined Tafel regions. The nature of the curves was similar in all the concentrations of LiCl (0.001-0.25 M) i.e. the initial active region where the current increased largely from the corrosion potential ($E_{corr}$) with small applied potential and then a limiting current region arising due to the steady increase in the current at more positive potentials. The limiting current region was likely due to the mass-transfer controlled reactions. The anodic current density increased as the concentration of LiCl increased from 0.001 to 0.25 M. Consequently, the corrosion current ($i_{corr}$) also increased. But this increase was much less compared to that in the case of methanol-HCl solutions. Moreover, the chloride ion concentration remaining the same, $i_{corr}$ was always higher in the methanol-HCl solution. For example, $i_{corr}$ for 0.1 M LiCl was 0.21 µA/cm² and that for the same concentration of HCl was 21 µA/cm². Similar was the case for 0.001 and 0.01 M concentrations i.e. $i_{corr}$ for 0.001 and 0.01 M LiCl were 0.08 and 0.25 µA/cm² and those for 0.001 and 0.01 M HCl were 1.2 and 3.8 µA/cm², respectively. Thus the rate of corrosion was significantly higher in methanol-HCl solution than in methanol-LiCl solutions. The large difference in corrosion rate is due to the high acidic conditions prevailing in methanol-HCl solution. In presence of the acid, methanol gets protonated as:

$$\text{CH}_3\text{OH} + \text{H}^+ \rightarrow \text{CH}_3\text{OH}_2^+$$ …(2)
The discharge of CH$_3$OH$_2^+$ may be associated with lower overvoltage as compared to H$_3$O$^+$ discharge on cathode and hence facilitates the cathodic reaction which results in an accelerating effect on the anodic dissolution showing high corrosion rates$^{31}$.

Conclusion

The Ni-free austenitic stainless steel shows active-passive-transpassive dissolution only at higher concentrations of H$_2$SO$_4$ (0.01-1.0 M) in methanol with the occurrence of pits on the surface. High concentration of H$_2$SO$_4$ showed enhanced pitting resistance by shifting the $E_{\text{pit}}$ to noble direction. Passivation process seems to be facilitated by the emergence of the ‘cathodic loop’ in 0.1 and 1.0 M H$_2$SO$_4$. No passive behaviour is observed in methanol-HCl and methanol-LiCl solutions; instead the steel dissolves actively. The corrosion current density increases as the concentration of chloride ion increases. For all concentration of chloride ions, the rate of corrosion is significantly higher in methanol-HCl solution in comparison with methanol-LiCl solution.

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References