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Electrochemical investigations of pitting corrosion behaviour of type UNS S31603 stainless steel in thiosulfate-chloride environment

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Abstract

The pitting corrosion behaviour of type UNS S31603 stainless steel (316L SS) in 0.01, 0.05 and 0.1 M thiosulfate ion ($S_2O_3^{2-}$) in the absence and presence of various concentrations of chloride ion (Cl^-) was studied using the cyclic potentiodynamic polarization method. The influence of major factors which affect pitting corrosion such as pH and temperature, were also investigated. It was found that both the pitting potential (E_{pit}) and the repassivation potential (E_{rp}) decreased with increase in Cl^- concentration and solution temperature and a more pronounced difference in E_{pit} values for various concentrations of $S_2O_3^{2-}$ in 1.0 M Cl^- was obtained at lower temperatures. The effect of pH on E_{pit}, E_{corr} and E_{rp} values for different concentrations of $S_2O_3^{2-}$ in the presence of 1.0 M Cl^- was also determined.

1. Introduction

Stainless steel (SS) is frequently used as a construction material in various aggressive environments such as chemical plants, desalination plants, wastewater treatment plants and the petroleum industry. Stainless steel is resistant to corrosion due to the formation of a passive film; however, localized corrosion can occur in the presence of aggressive anionic species. Chloride ions (Cl^-) are usually, although not always, the main cause. The aggressiveness of the Cl^- is due to its small size, high diffusivity and strong acidic anionic nature [1]. Thiosulfate ions ($S_2O_3^{2-}$) have also been reported as potentially detrimental to the stability of the passive film [2, 3]. It has been found that $S_2O_3^{2-}$ alone are not enough to cause pitting of stainless steel. In conjugation with chloride or sulfate ions localized corrosion has been reported [2]. The stability of the passive film formed on stainless steel and its susceptibility to breakdown depends on certain parameters such as applied potential, pH, temperature and solution composition [4]. Studies of UNS S30400 and UNS S31603 in chloride/thiosulfate solution have revealed that ratio of these ions concentration controls pitting behavior because of the variation in overall ionic strength [5, 6]. UNS S31603 is one of the most common and widely used construction material for desalination plants and for storage and transportation of chemical reagents such as thiosulfate in paper and pulp industries. However many authors have reported poor performance in environments with low pH, high temperature, and high Cl^- concentrations [7, 8].

Systematic work on the effect of thiosulfate ion together with chloride ion for UNS S31603 is limited. In previous work the authors have studied the pitting corrosion behaviour of UNS S31603 in artificial seawater in absence and presence of SO_4^{2-}, HCO_3^-, Mg^{2+} and Ca^{2+} [9]. In the present work, the authors have investigated the effect of Cl^-, pH and temperature on the thiosulfate pitting of UNS S31603.

2. Experimental details

Test specimens were produced from austenitic stainless steel UNS S31603 with the chemical composition (wt %): 0.025% C, 1.85% Mn, 0.75% Si, 0.37% P, 0.017% S, 17% Cr, 12% Ni, 2.5% Mo and balance Fe. The working electrode was machined in the shape of cylinder and polished with different grades of emery papers down to 600 grit, washed with methanol and double distilled water immediately before testing. The whole area of the electrode was coated with an epoxy resin leaving an exposed area of 0.64 cm^2 (0.251 in^2).

Cyclic potentiodynamic polarization study was conducted using EG&G Princeton Applied Research (PAR) model 263A potentiostat/galvanostat controlled using a computer equipped with PAR M352 SoftCorr II software. The working electrode was immersed in the naturally aerated test solution for 1 h at the open circuit potential and the scan rate was fixed at mV s^{-1}. Platinum wire and a saturated calomel electrode (SCE) were used as auxiliary and reference electrode, respectively.

The solutions were prepared using analytical reagent grade chemicals and double distilled water. The pH of the solution was adjusted using hydrochloric acid and sodium hydroxide. The volume of the test solution was 650 ml. The temperature of the test solution was maintained thermostatically with an accuracy of ±1 °C.

3. Results and discussion

3.1. *Effect of Cl^- concentration*

The cyclic potentiodynamic polarization curves for 0.01 M $S_2O_3^{2-}$ in the absence and presence of various concentrations of Cl^- at 25 °C (pH 7) are shown in Figure 1. It is clear from the presence of a hysteresis loop in the curves that the UNS S31603 stainless steel suffers from pitting corrosion at high Cl^- ion concentrations. At a particular Cl^- concentration an E_{pit} develops which is sufficient to displace oxygen from the protective oxide layer. It was found that at 25 °C for less than 0.1 M Cl^-, no pitting corrosion occurs. It was found also that Cl^- concentration has a pronounced effect on E_{pit} values. The E_{pit} decreased with increase in Cl^- concentration. It was also found that corrosion potential (E_{corr}) values changed slightly towards active direction with increase in chloride ion concentration.

Figure 2 depicts E_{pit} and E_{rp} as a function of the logarithmic of Cl^- concentration in the presence of 0.01 M $S_2O_3^{2-}$ (pH 7) at 25 °C. The linear dependence of E_{pit} and E_{rp} on log [Cl^-] was expressed in the conventional form as

$$E_{pit} = a - b\log[Cl^-]$$

where *a* and *b* are constants and depend on the conditions and nature of the electrode [3, 10, 11]. The values of *a* and *b* were obtained from the data plotted in Figure 2 for the pitting potential, 400 mV vs SCE for *a* and 122 mV vs SCE per decade for *b* at 25 °C. The *b* value is close to (130 mV ± 10 mV) reported previously for UNS S31603 in pure chloride solution [13, 12]. This data indicates that the UNS S31603 would be appreciably more resistant to pitting corrosion at low Cl^- concentration. The slope obtained from the line E_{rp} vs log [Cl^-] was found to be 180 mV with displacement towards more active direction is about 0.5 V. This indicates the continuous growth of pit on UNS S31603 at more negative potential than E_{pit}. A similar result was reported earlier by Atrens [13] who used 12Cr steel for the dependency of E_{pit} and E_{rp} with logarithm of Cl^- concentration.

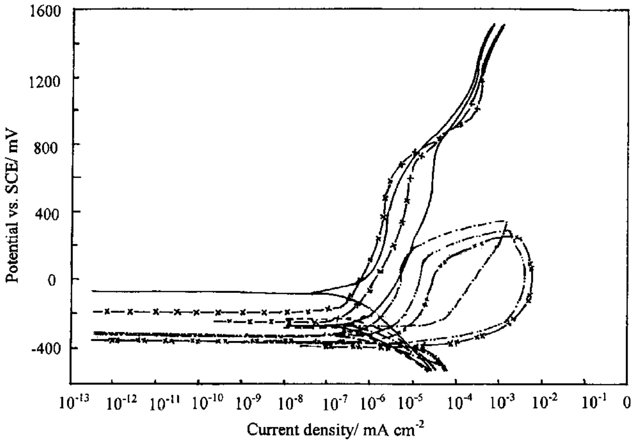

Fig. 1. Cyclic potentiodynamic polarization curves of type UNS S31603 with a scan rate of 1.0 mV s^{-1} at temperature 25 °C and pH 7 in aerated solution of 0.01 M $S_2O_3^{2-}$ containing different concentrations of Cl^-: (–) 0, (×) 0.01, (---) 0.5, (-·-·-) 1.0 and (××) 2.0 M.

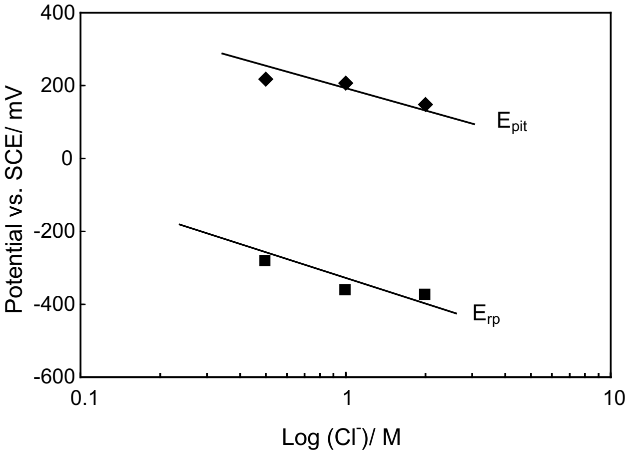

Fig. 2. E_{pit} and E_{rp} in 0.01 M $S_2O_3^{2-}$ as a function of Cl^- concentration at 25 °C for type UNS S31603.

3.2. *Effect of $S_2O_3^{2-}$ concentration*

The values of E_{pit}, E_{rp} and ΔE obtained from the cyclic potentiodynamic polarization curves for 1.0 M Cl^- in the presence of 0.01, 0.05 and 0.1 M $S_2O_3^{2-}$ concentration at pH 7 and temperature 25 °C are shown in Figure 3. The values of E_{pit} decreases, while E_{rp} increases with the increase in $S_2O_3^{2-}$ concentration. The difference between E_{pit} and E_{rp}, called ΔE ($E_{pit} - E_{rp}$), decreases with $S_2O_3^{2-}$ concentration showing its dependency on $S_2O_3^{2-}$ concentration. The magnitude of ΔE is often considered as an indicator of pitting resistance; that is, the higher the ΔE value the lower the pitting resistance [14]. This indicates that UNS S31603 is more susceptible to pitting corrosion at higher $S_2O_3^{2-}$ concentration upto 0.1 M $S_2O_3^{2-}$.

3.3. *Effect of temperature*

Cyclic potentiodynamic polarization curves for UNS S31603 in naturally aerated 0.01 M $S_2O_3^{2-}$ containing 1.0 M Cl^- solution at pH 7 for different solution

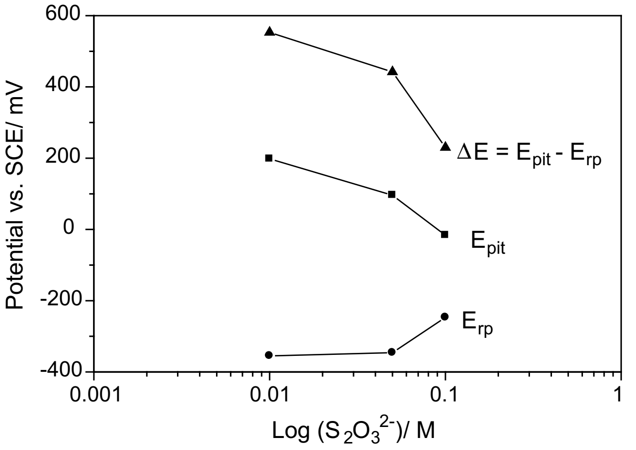

Fig. 3. E_{pit}, E_{rp} and ΔE ($E_{pit} - E_{rp}$) in 1.0 M Cl^- as a function of $S_2O_3^{2-}$ concentration at 25 °C for type UNS S31603.

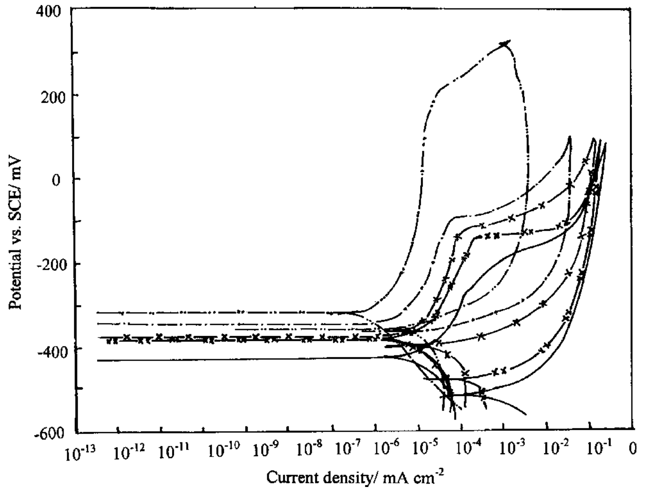

Fig. 4. Cyclic potentiodynamic polarization curves of type UNS S31603 with a scan rate of 1.0 mV s^{-1} at pH 7 in aerated solutions of 0.01 M $S_2O_3^{2-}$ containing 1.0 M Cl^- concentration at: (-···-) 25, (-·-) 35, (×) 45, (××) 55 and (—) 65 °C.

temperatures are shown in Figure 4. The effect of temperature on E_{pit}, E_{rp}, E_{corr} and passivation current (I_{pass}) derived from Figure 4 has been represented in Figure 5. It is clear that the values of E_{pit} and E_{rp} move in the active direction, whereas E_{corr} values changed slightly in the active direction with increase in temperature from 25 to 65 °C. The decrease in E_{pit} and E_{rp} with increase in temperature may be attributed to the increased ionic activity of $S_2O_3^{2-}$ and Cl^- or their collective synergistic effects. The most significant change was observed in the I_{pass} values. I_{pass} values were found to increase from 0.05×10^{-5} to 10.06×10^{-5} with increase in temperature from 25 to 65 °C. ΔE ($E_{pit} - E_{rp}$) and the difference between E_{corr} and E_{rp} values were found to increase with temperature, indicating that UNS S31603 is more prone to pitting corrosion at higher temperatures upto 65 °C. The Figure also indicates that the shift in E_{pit} values in the noble direction is more pronounced at lower temperatures. The present results are in agreement with those reported by Abd El Meguid et al. [3] for UNS S31603. The order $E_{pit} > E_{corr} > E_{rp}$ stood at any condition indicating that the steel suffers from pitting corrosion [15].

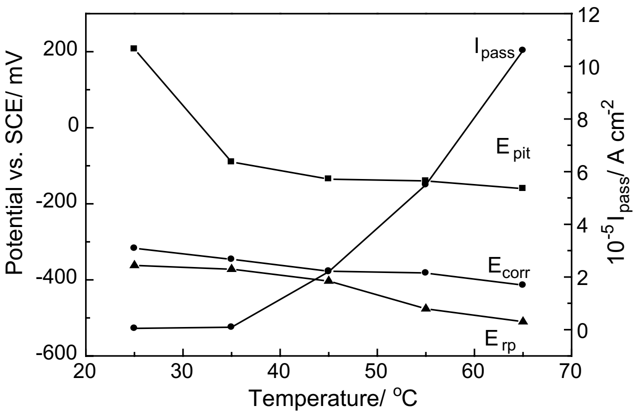

Fig. 5. Variation of E_{pit}, E_{corr}, E_{rp} and I_{pass} with temperature for 0.01 M $S_2O_3^{2-}$ solution containing 1.0 M Cl^-.

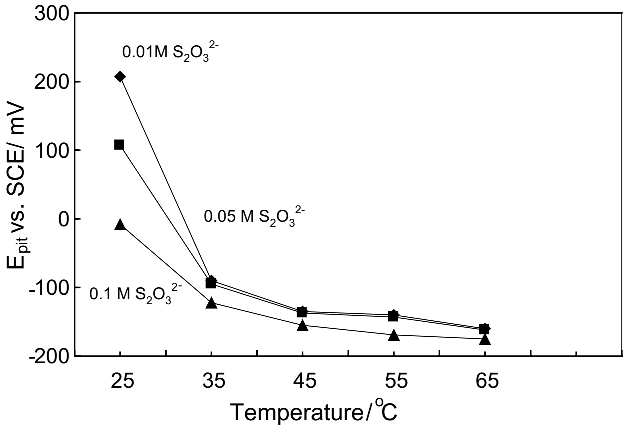

Fig. 6. Variation of E_{pit} with temperature in 1.0 M Cl^- as a function of $S_2O_3^{2-}$ concentration.

The effect of temperature on E_{pit} when the $S_2O_3^{2-}$ concentration was increased from 0.01 to 0.1 M Cl^- solutions at pH 7 is shown in Figure 6. Values of E_{pit} decrease with the increase in temperature. It was also found that more pronounced difference in E_{pit} values occurred at lower temperatures but higher concentrations of $S_2O_3^{2-}$.

3.4. *Effect of pH*

The pitting corrosion of UNS S31603 is influenced by variation in pH. Various parameters such as E_{pit}, E_{rp} and E_{corr} were calculated using cyclic potentiodynamic polarization curves of UNS S31603 immersed in naturally aerated 0.01 M $S_2O_3^{2-}$ containing 1.0 M Cl^- solutions at 25 °C as shown in Figure 7. The resistance of UNS S31603 to pitting corrosion is lower below pH 8.5. The pitting potential in very alkaline solutions is significantly displaced in the noble direction, in line

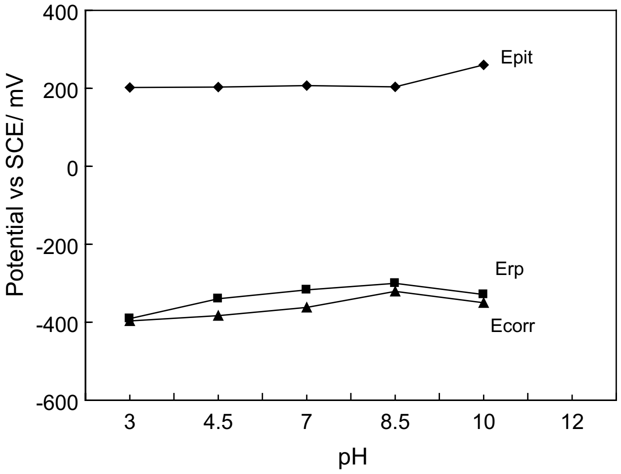

Fig. 7. Variation of E_{pit}, E_{corr} and E_{rp} with pH for 0.01 M $S_2O_3^{2-}$ solution containing 1.0 M Cl^-.

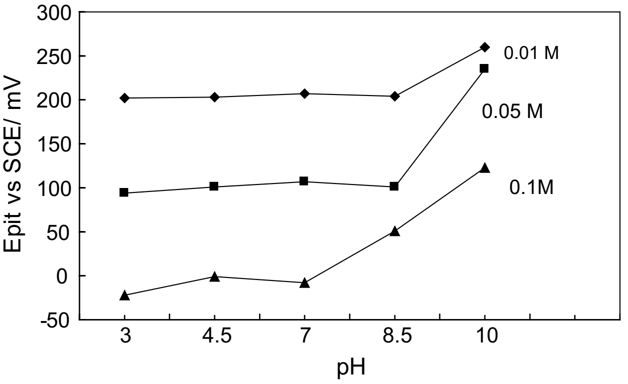

Fig. 8. Variation of E_{pit} with pH in 1.0 M Cl^- as a function of $S_2O_3^{2-}$ concentration.

with the known inhibiting effect of higher concentrations of OH^- ions. The relationship between E_{pit} and pH, with the increasing $S_2O_3^{2-}$ concentration in 1.0 M Cl^- at 25 °C is shown in Figure 8. It is notable that effect of pH on E_{pit} at level $\leqslant 7$ was generally of low order. An increase in pH above 7 indicated a more pronounced effect on the E_{pit} values, particularly at higher $S_2O_3^{2-}$ concentration (0.1 M $S_2O_3^{2-}$). At lower concentrations of 0.01 M $S_2O_3^{2-}$ and 0.05 M $S_2O_3^{2-}$ a similar effect is observed but at higher pH level (pH 8.5), which is the same pH level for chloride containing solutions without thiosulfate.

4. Conclusions

E_{pit} values of UNS S31603 were found to shift in the active direction with increase in Cl^- concentration in 0.01 M $S_2O_3^{2-}$ solution (pH 7) at 25 °C. It was found that the UNS S31603 is more susceptible to pitting corrosion at higher $S_2O_3^{2-}$ concentration. E_{pit} values decreased with increase in temperature and more pronounced difference in E_{pit} values was obtained at lower temperatures for various concentrations of $S_2O_3^{2-}$ in 1.0 M Cl^- (pH 7).

The effect of pH at $\leqslant 7$, particularly at lower concentrations of $S_2O_3^{2-}$, was found to be of lower order.

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