Pitting Corrosion Behaviour of Type SUS904L and SUS316L Stainless Steels in Chloride Solutions

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Pitting Corrosion behaviour of commercial stainless steels (SS) types 904L and 316L has been investigated in pure sodium chloride solutions of different pH values and at different temperatures.

Potentiodynamic polarization technique and scanning electron microscopy were utilized. The results indicated that pitting corrosion of 316L SS occurred readily at 30°C and in all chloride solutions of concentrations $\geq 10^{-3} \text{ mol} \cdot \text{m}^{-3}$ while 904L SS did not pit at temperatures and concentrations lower than 40°C and $0.6 \text{ mol} \cdot \text{m}^{-3}$ NaCl, respectively. Pitting potential (E_{pit}) for 904L SS was much more noble than that obtained for 316L SS while the protection potential (E_{prot}) values were almost the same for both alloys.

The pitting corrosion inhibition by OH ions was more pronounced for 316L SS and E_{pit} approached that obtained for 904L SS in alkaline solutions.

The alloy with the higher Cr, Ni and Mo content (904L SS) was more sensitive to the temperature effect as compared to 316L SS. It was concluded that E_{pit} was dependent on the alloy composition while E_{prot} was not affected by the alloy composition.

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I. Introduction

Pitting corrosion is a serious problem for metals that owe their corrosion resistance to passive film. The localized breakdown of passivity by aggressive anions such as chloride ions can lead to high rates of penetration. The effect of the different alloying elements on the pitting resistance of steels has been extensively studied (e.g. Refs. (1)–(4)). Thus concentrations of Ni up to 40%, Mn up to 7%, nitrogen up to 0.45% and silicon up to 3.6% have no significant effect⁽²⁾. On the other hand, additions of Cr and Mo increase considerably the resistance of steels towards pitting corrosion. Consequently the resistance of the alloy to pitting is dictated almost entirely by the content of Cr+Mo in the alloy⁽³⁾. It has been reported that in the absence of Cr, the addition of molybdenum to the alloy has no beneficial effect⁽⁴⁾ towards pitting corrosion resistance. High molybdenum-containing stainless steels, such as 904L SS, have been developed to resist severe aggressive environments such as sea water. Detailed studies on the electrochemical behaviour of 904L SS in sea water as well as under various environmental conditions simulating heat exchangers have been reported elsewhere⁽⁵⁾⁽⁶⁾.

The aim of the present study is to compare the pitting corrosion behaviour of two commercial stainless steel alloys having different compositions of important alloying elements, namely, Cr, Ni and Mo. These are stainless steels types 904L and 316L alloys which are of importance as they are being used extensively in different industrial applications.

II. Experimental

The materials used were types 904L and 316L commercial stainless steels. The chemical compositions of the alloys are given in Table 1.

Specimens were cut from 2 mm and 0.5 mm thick sheets of 904L SS and 316L SS, respectively. The electrodes used for electrochemical tests were mechanically polished with emery paper down to 600 grit, while specimens to be examined metallographically were fine polished with $0.3 \mu\text{m}$ alumina paste, ultrasonically cleaned and finally rinsed with acetone and double distilled water. The back and edges of the specimens were coated with epoxy resin, allowing 1 cm^2 to be exposed to the test solution.

All salt solutions were prepared from analytical reagents and double distilled water. The pH of the solutions

Table 1 Chemical compositions of the alloys (mass %).

UNS \ Element	Cr	Ni	Mo	Cu	Mn	C	P	S	Si	Fe
904L	20	23.5	4–5	1–5	1.55	0.015	0.028	0.035	0.58	balance
316L	17.5	9–8	2–3	—	1.6	0.05	0.02	0.02	0.7	balance

was adjusted to give values between 3 and 12.5 by adding HCl or NaOH. Depending on the need of the test, the experiments were conducted at the desired thermostated temperature.

Potentiodynamic anodic polarization experiments were conducted using a scan rate of 600 mV/h, commencing at the open circuit potential after the sample has been immersed for 30 min in the solution. The potential of the working electrode was referred to as a saturated calomel electrode (SCE). The counter electrode was a platinum wire.

The pitting potentials were determined from the anodic polarization curves where a stable increase in the current density occurs. The protection potential was determined from the reverse cyclic polarization at the intersection point with the forward polarization curve. All potentials quoted in the text are with respect to SCE.

Scanning electron microscopic examinations were conducted on the specimens after anodic polarization experiments to confirm the occurrence of pitting corrosion.

III. Results and Discussions

1. Effect of temperature on the pitting corrosion of 904L SS and 316L SS in $0.6 \text{ mol} \cdot \text{m}^{-3}$ sodium chloride solutions

The potentiodynamic anodic reverse scans were determined in $0.6 \text{ mol} \cdot \text{m}^{-3}$ NaCl solutions at 30, 35, 40, 50, 60 and 70°C. Examples of the curves obtained for 904L SS and 316L SS are given in Figs. 1 and 2, respectively. In case of 316L SS breakdown of passivity occurred at all temperatures tested. On the other hand, in case of 904L SS breakdown of passivity occurred at temperatures 40°C. For both alloys, E_{pit} as well as E_{prot} decreased with

Fig. 1 Potentiodynamic cyclic anodic polarization of 904L SS in $0.6 \text{ mol} \cdot \text{m}^{-3}$ NaCl pH 5.8 at different temperatures.

Fig. 2 Potentiodynamic cyclic anodic polarization of 316L SS in $0.6 \text{ mol} \cdot \text{m}^{-3}$ NaCl pH 5.8 at different temperatures.

the increase of temperature.

The relationship between E_{pit} or E_{prot} with temperature is given in Fig. 3. It is evident that values of E_{pit} for 904L SS are more noble than that obtained for 316L SS. The difference in the values amounted to 420 mV at 40°C that decreases with the increase of temperature and the difference reaches only 230 mV at 70°C. It is interesting that a linear relationship holds between E_{prot} and the temperature and that the values for both alloys are almost the same. Thus for both alloys E_{prot} decreases by about 35 mV/10 degree rise in temperature. From these results it can be concluded that E_{pit} is greatly influenced by the type of the stainless steel while E_{prot} is not.

In general the pitting potential decreases with the increase in temperature for all types of stainless steels, not only those containing molybdenum, although the particular dependence on temperature depends on the grade of steel. The results of the present study agree with that reported by Rujinini *et al.*⁽⁷⁾ that the protective efficiency of molybdenum containing stainless steels decreases with the increase in temperature. In other words, the pitting behaviour of molybdenum containing steels is dependent on temperature, and that the higher molybdenum content, the greater is the effect.

Although the tendency for pit initiation of 904L SS is considerably lower than that for 316L SS, yet the tendency towards pitting propagation for both alloys are equal as judged from E_{prot} values. Consequently it can be concluded that E_{prot} is not dependent on the composition of the stainless steel. This point will be discussed later.

2. Effect of pH on pitting corrosion

The effect of pH on pitting corrosion has been investigated in $0.6 \text{ mol} \cdot \text{m}^{-3}$ NaCl solutions. The relationship between E_{pit} and pH is shown in Fig. 4. It is clear that for both alloys E_{pit} is not significantly changed in the range of pH 3–7.5. However, at higher pH values than 7.5, a sharp rise in E_{pit} values is noticed which is more pronounced with 316L SS. It is interesting to observe that the difference in E_{pit} values for both alloys in the acidic range is ~ 230 mV while at pH 10.5 the difference

Fig. 3 Temperature dependence of E_{pit} and E_{prot} of 316L and 904L SS in $0.6 \text{ mol} \cdot \text{m}^{-3}$ NaCl pH 5.8 solution.

Fig. 4 Effect of pH on E_{pit} of 316L and 904L SS in $0.6 \text{ mol} \cdot \text{m}^{-3}$ NaCl pH 5.8 solution at 60°C .

becomes 30 mV. This indicates that pitting of 316L SS is much more dependent on the pH value of the solution than is 904L alloy.

The independence of E_{pit} on pH in acid solutions is in agreement with that reported by Fokin, *et al.*⁽⁸⁾ and Leckie and Uhlig⁽⁹⁾. This behaviour may be explained on the premise that the hydrolysis reaction in the pits generates its own characteristic acidity which is most probably slightly influenced by the pH of the bulk solution. The

fact that in alkaline solutions E_{pit} is significantly displaced in the noble direction is in line with the well established pitting inhibition effect of high concentrations of OH ions on different iron base alloys⁽¹⁾⁽⁹⁾.

3. Effect of chloride ion concentration on pitting corrosion

Figure 5 shows the effect of chloride ion concentration on E_{pit} and E_{prot} for both alloys at 60°C . It is worth mentioning that below $0.6 \text{ mol} \cdot \text{m}^{-3}$ NaCl and $10^{-3} \text{ mol} \cdot \text{m}^{-3}$ NaCl at 60°C no pitting corrosion took place for 904L SS and 316L SS, respectively. It is clear from Fig. 5 that a linear relationship holds between E_{pit} and log chloride ion concentration as follows:

$$E_{\text{pit}} = A - B \log C_{\text{Cl}^-}$$

where A and B are constants dependent on the alloy and the environment, and C_{Cl^-} is the NaCl concentration.

This kind of relationship has been verified experimentally and theoretically for various alloys (*e.g.* Refs. (1) and (8)). It is interesting that the lines are parallel but displaced from each other by about 240 mV and the slope of the lines are 140 mV/decade. Thus E_{pit} for both alloys is displaced in the negative direction by 140 mV/decade for a tenfold increase of Cl^- ion concentration.

An earlier work on 904L SS⁽⁶⁾ indicated that B value is dependent on the presence or absence of air in the test solution. Thus B value for 904L SS in aerated salt solutions amounted to $\sim 135 \text{ mV}$ while in N_2 saturated salt solution it amounted to 320 mV but the critical chloride concentration for pitting was the same whether the salt solution was aerated or deaerated.

Figure 5 also indicates a linear relationship between E_{prot} and $\log C_{\text{Cl}^-}$. However, E_{prot} values for both alloys are lying on one line and the slope is 90 mV/decade. This confirms the results reported earlier on the effect of temperature on pitting corrosion for both alloys in $0.6 \text{ mol} \cdot \text{m}^{-3}$ NaCl where the values of E_{prot} for both alloys at the different temperatures tested were similar⁽⁶⁾. Thus, it

Fig. 5 Effect of chloride ion concentration on E_{pit} and E_{prot} of 316L and 904L at 60°C and pH 5.8.

is evident that the superiority of 904L SS over 316L SS can be judged only from the values of E_{pit} .

It is worth emphasizing that the pitting performance of a given material does not only depend on E_{pit} but also on E_{prot} . The latter value corresponds to the potential below which the already initiated pits become passivated. According to Smialowska⁽¹⁰⁾ the difference value of ($E_{\text{pit}} - E_{\text{prot}}$) as well as pit morphology can be used as a measure for pit repassivation ability. Thus this difference is higher for 904L SS as compared to that of 316L SS and hence it has lower pit repassivation ability inspite of its high resistance to pit initiation (exhibited high E_{prot}). Such a behaviour was explained for high Cr and Mo alloys on the basis that the oxide film covering the pits has a shielding effect and thus closes the pits that impedes repassivation. On the other hand, the pits formed on 316L SS are open hence more prone to repassivation.

IV. Conclusions

(1) At 60°C the critical sodium chloride concentrations for pitting occurrence are $0.6 \text{ mol} \cdot \text{m}^{-3}$ and $10^{-3} \text{ mol} \cdot \text{m}^{-3}$ for 904L SS and 316L SS, respectively.

(2) In $0.6 \text{ mol} \cdot \text{m}^{-3}$ NaCl pitting takes place readily at 30°C for 316L SS while a minimum temperature of 40°C

is necessary for pitting of 904L SS.

(3) In spite of the high resistivity of 904L SS towards pitting initiation (as judged from noble E_{pit} values), yet pitting propagation can take place at considerably low potential values that coincides with that obtained for 316L SS. Consequently, pits formed on 316L SS are more prone to repassivation as compared to that obtained on 904L SS.

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