The Susceptibility of Three Stainless Steel Alloys to Pitting Corrosion in Some Chloride Solutions

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Abstract. The corrosion and passivation behaviour of three stainless steels was examinated in chloride-containing solutions using cyclic polarisation techniques.

The duplex stainless steels showed a pitting corrosion resistance higher than the conventional 13 % Cr and modified 13 % Cr stainless steels.

The resistance of pitting of alloys depends on chemical composition such as molybdenum and Nickel.

0.07 % Molybdenum in the alloy is insufficient to avoid the pitting corrosion.

The presence of sodium chloride (NaCl) enhanced metal electrodissolution at higher chloride concentrations.

Introduction

Stainless steels are a family of special grade of iron-based alloys that contain at least 11Wt% chromium in their composition.

Stainless steels have found application in almost every industrial sector, such as petrochemical, oil and gaz, pharmaceutical, and marine.

Duplex stainless steels are a relatively new class in the stainless steels family. They are caracterised by a two-phase comprising a mixture of ferrite (α) and austenite grains (γ) (George F. Vander Fort. 2004).

Duplex stainless steels have superior corrosion resistance and better mechanical properties.

In particular, their pitting corrosion resistance is considerably high, as can be inferred from the value of their pitting potentials (Eb).

The work aims to find a correlation among The susceptibility of three stainless steel alloys to pitting corrosion in some chloride solutions and the chemical composition of the alloys.

Experimental

The three working electrodes used in the present work were a duplex (Steel **A**: 22 % Cr – 6 % Ni – 3 % Mo), a modified 13 % Cr (Steel **B** : 13 % Cr - 5 % Ni – 0.7 % Mo) and conventional cheap 13 % Cr (Steel **C**: 13 % Cr - 0.08 % Ni).

Cyclic polarisation scans were used to evaluate the alloys pitting corrosion susceptibility. It is well established that the majority of alloys present potentiodynamic polarization curves I = f(E), whose form depends on many parameters: proportions, composition, structure of the present phases ... (Qiu, J.H., 2002; Syrett, B.C. 1976; Ben Salah-Rousset, N. et al, 1996).

A PC driven EG&G PAR model 273A potentiostat was used to perform these electrochemical tests .A software EGG M 352 are used for the acquisition and the processing of data. In the testing cell, saturated calomel (SCE) and graphite electrodes were used as a reference and counter electrodes, respectively. The samples (working electrodes) were abraded using silicon carbide (SiC) papers to a 1200 grit finish.

The electrolyte was a NaCl solution (100 ppm and 20 g/l), pH 3, at 60°C. The pH value was controlled by HCl. After various tests, we chose a scan rate of 1 mV/per second (Souto, R.M., et. al., 2001; Cristofaro, N. 1998).

Before starting the test, the electrode was immersed in the deaerated solution with pure nitrogen for 45 minutes so that the open circuit potential was stabilised.

After the electrochemical test, the sample surface was examined by optical microscope at 100X magnifications.

Results and discussion

Cyclic polarisation curves were obtained in sodium chloride solution (100 ppm and 20 g/l) at 60° C for three stainless steels (Fig. 2).

Fig. 1. Cyclic curves of polarization with variable NaCl concentrations for the three stainless steels at 60°C.
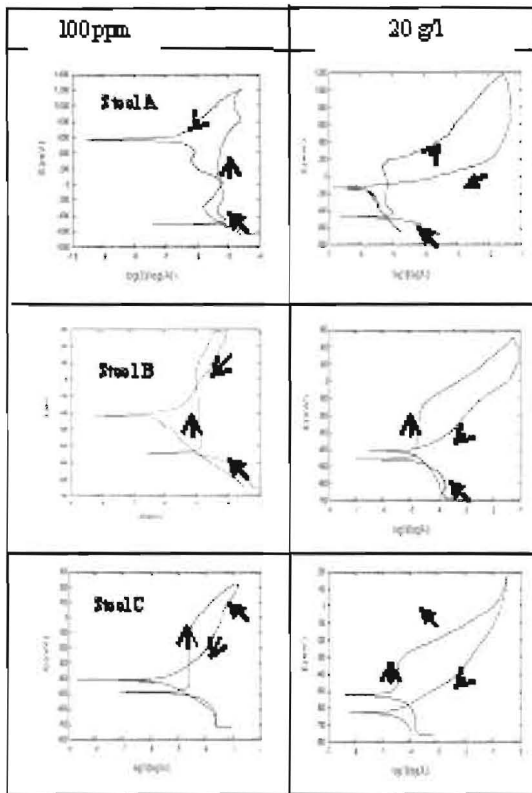
Data obtained from these plots are summarized in (Table 1).

The breakdown potential (pitting potential), Eb, is defined in terms of the potential at which the current density has shown an increase.

The protection potential, Erep, is the potential at which the descending curve intercepts the ascending curve. It was assumed that at this potential, the growing pits or pits formed at Eb become passive.

Table 1. The pitting potential values (Eb) and repassivation potential values (Erep) of three steels in medium NaCl (100 ppm and 20g/l) pH=3 at 60°C.

Potential mV/ECS	Steel C		Steel B		Steel A	
	100 ppm	20g/l	100 ppm	20g/l	100 ppm	20g/l
Eb	-84.0	-299.0	58	-96.01	·...	203.0
E rep	-313	-630.0	-47	-392.0	569	-134.0

The polarisation curves obtained for steel A in 100 ppm NaCl shows the presence of negative hysteresis compared with that of B and C steel.

Negative hysteresis occurs when reverse scan current density is less that for the forward scan. A damaged passive film repairs itself and pits do not initiate.

The micrographs obtained (Fig. 2), confirm the results revealed by the curves of polarisation. The B and C steels in 100 ppm NaCl present the same behaviour- positive hysteresis. The reverse scan depicts a large hysteresis loop, indicating that the material had great difficulties in passivating after discruption of the film. This loop was associated with pitting corrosion. The micrographs confirm the results.
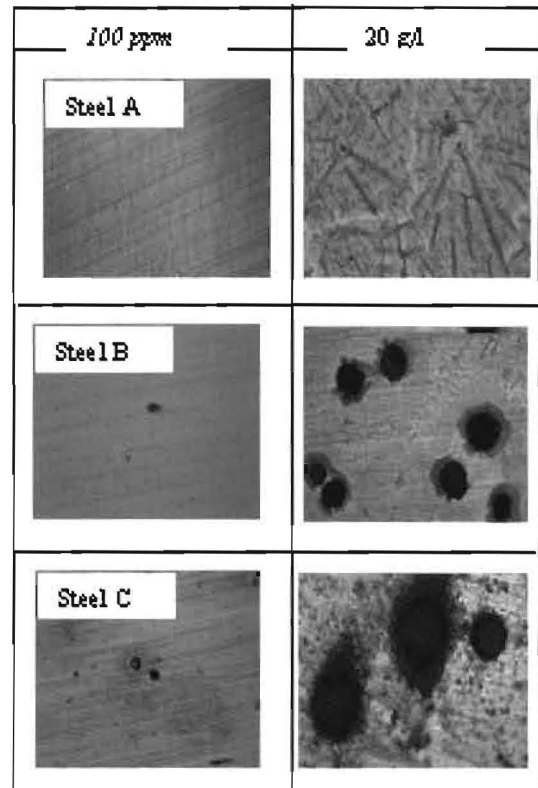

Fig. 2. Optical micrographs after potentiocyclic test at 60°C.

On increasing the chloride concentration (20 g/l NaCl), the three stainless steels present the same behaviour- positive hysteresis. The potential range for passivity was subsequently reduced compared with the lesser concentration of chloride.

We observe that for C steel there is a considerable reduction of the potential rang for passivity compared with that of A and B steels and that the loop is more significant, the micrographs shows large pits.

A first conclusion that can be drawn from the results included in (Table 3) is related with the pitting corrosion of steel A compared with that of the B and C steels. It can be observed in this table, that the higher the value of Eb, the more resistant is the steel to pitting corrosion (Syrett, B.C.1976; Frankel, G.S.1998; Merello, R., et al., 2003; Alonso-Falleiros, N., et. al., 1999; Lacombe, P., et. al., 1990). The same observation was made for the value of repassivation potential Erep.

It was reported that the pitting potential for type 304 stainless steel is directly proportional to the concentration of chloride ion on the semi-log scale (Lacombe, P., et. al., 1990).

$$Eb = A + Blog [Cl^-]$$

The sign (*) indicates the absence of a pitting potential according to experimental measurements. The results show that alloys A would resist low concentration of solutions of chloride of at 60°C.

Increasing the chloride concentration reduces the value of potential of pitting.

It has been well established that passivity is caused by the formation of a compact ultrathin surface oxide film - the passif film (Qiu, J.H. 2002). The corrosion resistance of stainless steels under service conditions is essentially determined by the stability of such a passif film, which is further determined by composition, thickness and structure (Qiu, J.H., 2002).

In addition to environmental considerations, the pitting and crevice corrosion resistance of stainless steels are also determined by alloying elements such as chromium, molybdenum, nitrogen and tungsten (Qiu, J.H., 2002).The synergistic effects alloying elements help to stabilize the passive film, and in case of breakdown, rapid repassivation can take place heal the damaged area.

Merello, R., et al., 2003 (Merello, R., et al., 2003) had studied the influence of chemical composition in the pitting corrosion resistance of duplex stainless steels characterised by low Ni content and high N and Mo contents. They suggested that pitting corrosion depends basically on the content of Cr, Mo and N.

Nickel in the alloy is also able to reduse the passive current density within the passive potential range (Qiu, J.H. 2002; Souto, R.M., et al., 2001)

The presence of Molybdenum and Chromium in stainless steels promotes the passivation process and improves the pitting corrosion behaviour (Qiu, J.H. 2002; Merello, R., et al., 2003; Kaneko, M. and Isaacs, H.S. 2002).

The addition of Ni in alloy is insufficient to avoid the pitting corrosion .Therefore it is necessary to add Molybdenum element to improve resistance to pitting corrosion of these alloys. In the steel B we observed the small amelioration of resistance confirmed by the cyclic curve (Table 2).

In order to achieve improved pitting corrosion resistance, Mo content should be higher than 1 %. The best results are obtained for alloys with Mo content between 3% and 4% (Merello, R., et. al., 2003).

Conclusions

❖ With the cyclic polarisation technique, it was possible to measure Eb and Erep, this technique provide information about pitting corrosion and passivation.

❖ Breakdown of passivity due to chemical attack often leads to pitting corrosion.

❖ The higher the value of Eb, the more resistant is the alloy to pit initiation and the lower the value of Eb- Erep.

❖ The corrosion resistance of stainless steels depends on the stability of ultrathin passive film on their surfaces.

❖ Chromium and molybdenum enhance the stability of passive films.

❖ The potential of pitting decreases with the increase in the chloride concentration.

❖ Increasing the chloride concentration causes the surface film to become less stable.

❖ 0.07 % on Molybdenum in the alloy is insufficient to avoid the pitting corrosion.

❖ Duplex stainless steels showed pitting corrosion resistance higher than, the conventional 13 % Cr and modified 13% Cr stainless steels.

The Duplex stainless steels with 22 % Cr-5% Ni-3% Mo remains the most resistant alloy since it contains alloy elements like molybdenum and the Nickel which ensure the passivity and resist to chloride

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