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Corrosion and Passivation Behaviour of Three Stainless Steels in Differents Chloride Concentrations

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The corrosion and passivation behaviour of three stainless steels were examined in chloride-containing solutions using cyclic polarization 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. The presence of sodium chloride enhanced metal electrodissolution at higher chloride concentrations. In addition to chromium and nickel, other alloying element like molybdenum, may be added to control structural balance and to improve corrosion resistance characteristics.

Key Words: Stainless steels, Pitting corrosion resistance, Passivation, Potentiocyclic curve, Sodium chloride.

INTRODUCTION

Stainless steels are a family of special grade of iron-based alloys that contain at least 11 % (by weight) chromium in their composition. They 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)[1]. 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 breakdown potentials (Eb).

The aim of this work is the study of the passivation and passivity breakdown of three stainless steels and the deleterious effects of the chloride ion on passivation characteristics. The work has been focused, towards of effects of alloying element on passivity.

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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 13 % Cr (Steel C: 13 % Cr-0.08 % Ni). Table-1 shows the chemical composition range of these alloys.

TABLE-1
CHEMICAL COMPOSITION OF STAINLESS STEELS

Element (%)	Fe	Cr	Ni	Mn	Si	Cu	Mo	C
A	66.9338	21.3330	6.2328	1.3775	0.6521	0.0737	3.1550	0.0399
B	79.4400	13.5567	5.2284	0.6060	0.2059	0.0130	0.7490	0.0853
C	84.6780	12.9000	0.0800	0.7900	0.7200	0.0100	0.0150	0.2000

With reference to the identification system of the American Iron and Steel Institute (AISI), the conventional 13 % Cr is close to that of the conventional martensitic stainless steel of type 420[1].

The electrochemical study, based on the layout of the diagrams of cyclic polarization, was retained to evaluate the alloys pitting corrosion susceptibility through the measurement of the pitting potential as well as the tendency to reproduce its surface quality through the repassivation potential. It is well established that the majority of alloys present potentiodynamic polarization curves I = f (E), depend on many parameter *i.e.*, proportions, composition, structure of the present phases[2-4].

Measurements of cyclic polarization are carried out using equipment made up of the following elements: a cell of the type EGG with five openings and the counter electrodes with two graphite bars. A saturated calomel electrode (SCE) is used as a reference. The work electrode (sample to be tested) is abraded using silicon carbide papers to a 1200 grit finish. The last opening receives the wash-bottle of gases. A potentiostate galvanostate EGG PAR model 273 A, an electrometer EGG which will ensure the bond between the electrochemical cell and the potentiostate and a microcomputer provided with a software EGG M 352 are used for the acquisition and the processing of data.

An optical microscope with reflected light model Metallux 3 mark Leitz with a camera N/B of Sony mark and a video acquisition chart were used. The unit is connected to a microphone-computer of the type PII provided with software "ANALYSIS" for the image processing. This software allows us to take photographs of pitting surfaces. The selected electrolytic medium is: deaerated solutions of sodium chloride (100 ppm and 20 g/L), pH 3, at 60 °C.

Before the test, the electrode was immersed in the deaerated solution for 45 min so that the open circuit potential was stabilized. After various tests, a scan rate of 1 mV/s were chosen[5,6]. After the electrochemical test, the sample surface was examined by optical microscope at 100X magnifications.

RESULTS AND DISCUSSION

Cyclic polarization curves were obtained in sodium chloride solution (100 ppm and 20 g/L) at 60 °C for three stainless steels (Table-2). Data obtained from these plots are summarized in (Table-3).

TABLE-2
CYCLIC CURVES OF POLARIZATION WITH VARIABLE NaCl CONCENTRATIONS FOR THE THREE STAINLESS STEELS AT 60 ºC

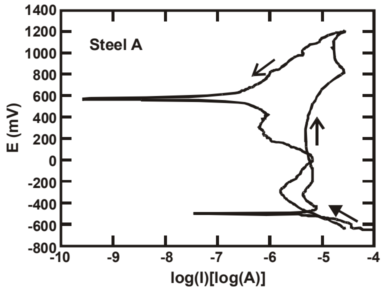
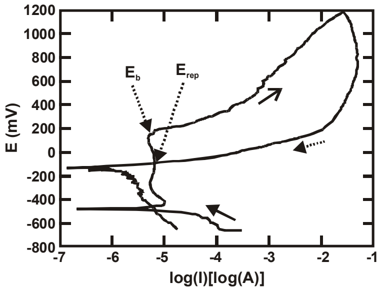
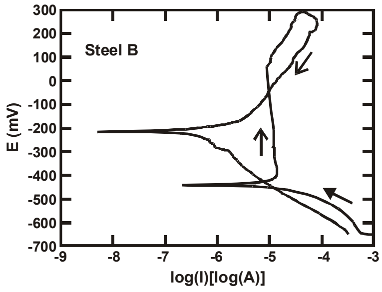
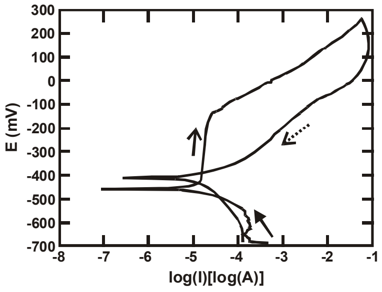
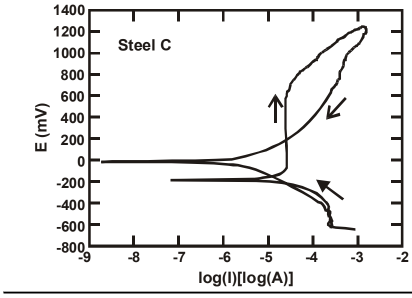
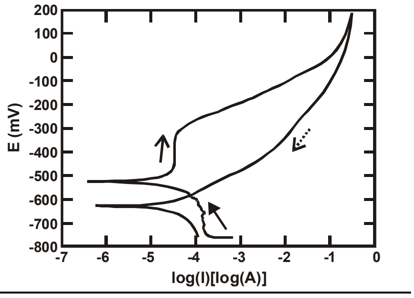
100 ppm	20 g/L
	
	
	

TABLE-3

BREAKDOWN POTENTIAL VALUES (E_b) AND REPASSIVATION POTENTIAL VALUES (E_{rep}) OF THREE STEELS IN MEDIUM NaCl (100 ppm and 20 g/L) pH = 3 at 60 °C

Potential (mV/SCE)	Steel A		Steel B		Steel C	
	100 ppm	20 g/L	100 ppm	20 g/L	100 ppm	20 g/L
E_b	*	203.0	58	-96.01	-84.01	-299
E_{rep}	569	-134.0	-47	-382.00	-313.00	-630

The breakdown potential (E_b), is defined in terms of the potential at which the current density has shown an increase. The repassivation potential (E_{rep}), 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 breakdown potential became passive.

The polarization 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 (Table-4), confirm the results revealed by the curves of polarization. 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 disruption of the film. This loop was associated with pitting corrosion. The micrographs confirm the results.

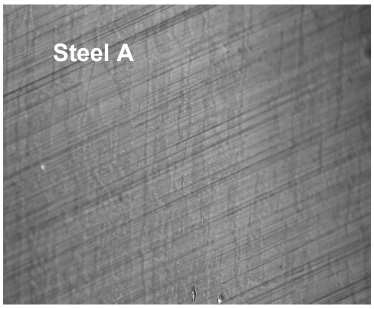
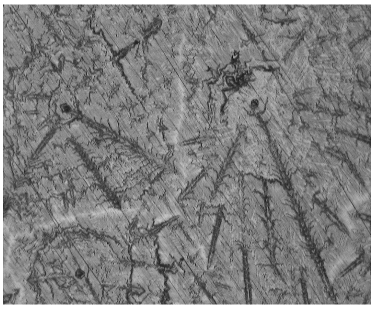
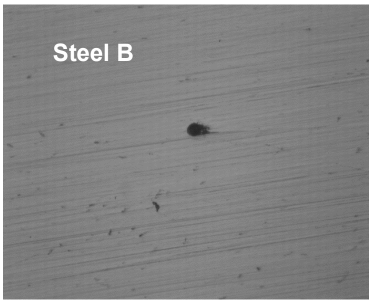
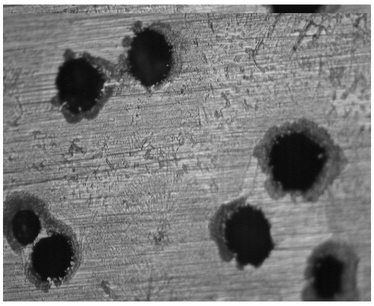
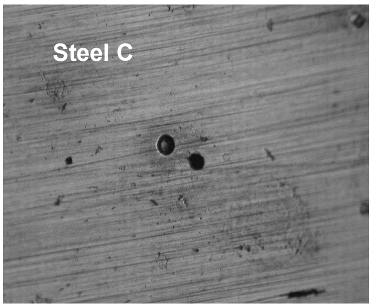
On increasing the chloride concentration (20 g/L NaCl), the three stainless steels present the same behaviour-positive hysteresis. The potential range for passivity was subsequently reduced compared with the lesser concentration of chloride.

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

The first conclusion 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 breakdown potential, the more resistant is the steel to pitting corrosion[3,7-10]. The same observation was made for the value of repassivation potential.

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

TABLE-4
OPTICAL MICROGRAPHS AFTER POTENTIOCYCLIC TEST AT 60 °C

100 ppm	20 g/L
	
	
	

It has been well established that passivity is caused by the formation of a compact ultra thin surface oxide film-the passive film[2]. The corrosion resistance of stainless steels under service conditions is essentially determined by the stability of such a passive film, which is further determined by composition, thickness and structure[2].

Merello and Botana[8] had studied the influence of chemical composition in the pitting corrosion resistance of duplex stainless steels characterised by low nickel content and high nitrogen and molybdenum contents. They suggested that pitting corrosion depends basically on the content of chromium, molybdenum and nitrogen. Nickel in the alloy is also able to reduce the passive current density within the passive potential range[2,5].

The presence of molybdenum and chromium promotes the passivation process and improves the pitting corrosion behaviour[2,8,11]. In order to achieve improved pitting corrosion resistance, molybdenum content should be higher than 1 %. The best results are obtained for alloys with molybdenum content between 3 and 4 %[8].

Conclusion

With the cyclic polarization technique, it was possible to measure breakdown potential and repassivation potential. This technique provide information about pitting corrosion and passivation. Passivity breakdown due to chemical attack often leads to pitting corrosion. More the value of breakdown potential, more the alloy resist to pitting corrosion. 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 breakdown potential decreases with the increase in the chloride concentration. Increasing the chloride concentration causes the surface film to become less stable. Duplex stainless steels showed pitting corrosion resistance higher than, the conventional 13 % chromium and modified 13% chromium 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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