Preliminary Evaluation of Localized Corrosion Using Potentiodynamic and Potentiostatic Techniques

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ABSTRACT

Introduction

Conventional 13% Cr martensitic stainless steel has been employed as OCTG (Oil Country Tubular Goods) tubing material due to its strength and corrosion resistance. The growing demand of energy has resulted in an industry desire for an improvement in an alloy corrosion resistance. Due to this fact it was developed a modified 13% Cr, also called Super 13% Cr, which is a combination of low carbon content and additions of Ni and Mo in order to achieve superior mechanical and corrosion properties over the conventional one [1,2].

The major parameters that affect the performance of conventional and Super 13%Cr (S13Cr) in oil and gas production are pH, chloride (Cl^-), temperature and the partial pressures of H_2S and CO_2. The relationship between chlorides and S13Cr corrosion performance relates to the breakdown of the passive film which leads to a localized corrosion – pitting or crevice attack. Sulfide Stress Corrosion (SSC) is almost always preceded by some form of localized attack. Cracking is due to a combination of increased hydrogen charging and stress concentration associated with the presence of pitting or crevice corrosion [3].

The aim of this work is to evaluate of localized corrosion of Super13Cr in 1g/l NaCl solution in several heat treatment routes using both, potentiodynamic and potentiostatic polarization and also develop the Step Potential technique to be used in the industry.

Experimental

The steel used in all tests was a Super 13% Cr supermartensitic stainless steel in four different heat treatment routes. The chemical composition is given in Table 1. All samples presented mechanical properties in accordance to ISO 13680 standard [4].

Table 1 – Chemical Composition (%wt) – Super 13Cr martensitic stainless steel.

%	C	Si	Mn	P	S	Cr	Mo	Ni
Min.		0.10	0.30			11.50	1.50	5.50
Max.	0.03	0.50	0.70	0.025	0.010	13.50	2.50	6.50

Potentiostatic and Potentiodynamic measurements were conducted using an Autolab PGSTAT 128N potentiostat with Nova 1.8 software. The tests were carried out in a deaerated solution with 1g/l NaCl and 4 g/l of sodium bicarbonate at a pH of 4, adjusted with HCl, in a conventional three electrode cell. The electrochemical cell consisted of the working electrode, an Ag/AgCl (1.0 $mol.L^{-1}$) reference electrode and a platinum counter electrode. Thus, all potentials cited in this study will be in reference to Ag/AgCl. The experimental temperature was 24ºC.

The samples for pitting corrosion evaluation with dimensions of 10 mm x 10 mm were taken from the pipe and prepared with epoxy resin. For the crevice analysis, the samples were cut with dimensions of 25 mm x 25 mm x 2 mm with a hole of Ø 8 mm for the crevice formers, which were mounted on both sides of the sample with the disc spring set up and a 5 N/mm^2 clapping force was applied. For both tests the surfaces exposed to the electrolyte, were sequentially grinded with silicon carbide paper up to 600 mesh. The tests were carried out in triplicate for each condition and comparing the results of all experiments.

The cyclic polarization tests were performed according to ASTM G61-86 [5]. Before each cyclic polarization scan, the sample was allowed to stabilize in the electrolyte for 50 min. The scan was started at the corrosion potential and continued in the anodic direction until a potential of 1,500 V was reached. At this point, the scan direction was reversed and the potential was decreased.

In the potentiostatic test – Step Potential – after measured the open circuit potential during two hours, the potential was increased in steps of 50 mV every one hour and at each step the current variation was recorded as a function of time until the current of 10 mA was attained. The potential level at which the current density is equivalent to 0.1 mA/ cm^2 was defined as the crevice initiation potential [6]. After the electrochemical crevice corrosion test the sample surface was examined to confirm the presence of crevice attack.

Results and Discussion

In Figure 2 is shown the cyclic polarization curves obtained for Super 13 Cr submitted at different heat treatment routes. The purpose of these experiments was to measure pitting potential (E_{pit}) and the repassivation potential (E_{rep}). As can be seen the curves presented hysteresis indicating possibility of localized corrosion occurs. Hysteresis happens when the forward and reverse scan do not overlay each other, due to current density difference between the forward and reverse portions of the scan at the same potential. It is a result of the disruption of the steady state surface structure by the increase in potential. The hysteresis reflects the ease or difficulty with which that initial structure is restored as the potential is decreased back toward the corrosion potential at constant scan rate. When larger hysteresis is observed greater is the difficulty of repassivation and usually greater is the risk of localized corrosion [7]. All studied routs showed similar tendency to the occurrence of localized corrosion due the difference between E_{pit} and E_{rep}.

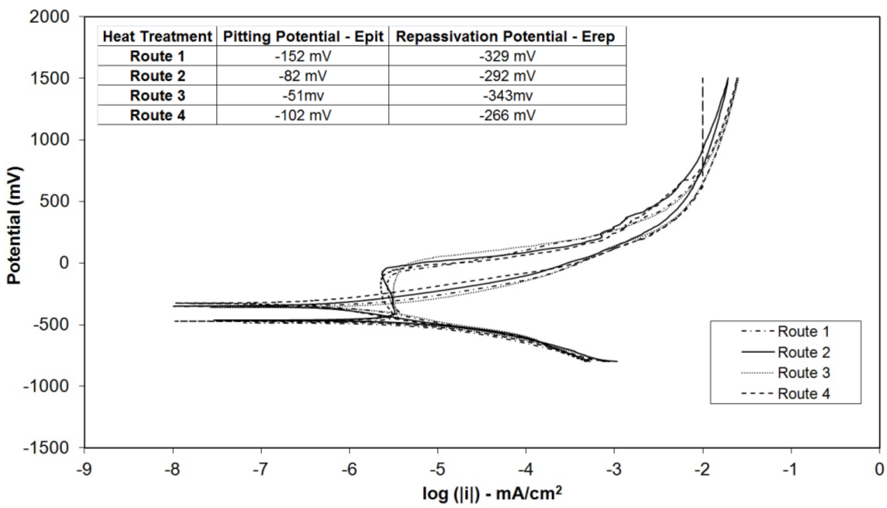

Figure 2 – Cyclic polarization test results for 13Cr martensitic stainless steel in 1g/l NaCl.

Some parameters obtained from the Step Potential tests for pitting and crevice corrosion are presented in Table 2. It can be observed that the route 3 present the less corrosion resistance to pitting corrosion in accordance of the test results obtained from the cyclic polarization curves. For the crevice potential was not observed significant difference for the results obtained in different heat treatments routes.

Table 2 – Step Potential results for 13Cr martensitic stainless steel in 1g/l NaCl.

Heat Treatment	Crevice		Pitting	
	OCP	Potential at 0,1 mA/cm²	OCP	Potencial at 0,1 mA/cm²
Route 1	-359	192	-358	-207
Route 2	-386	192	-420	-158
Route 3	-408	188	-407	-269
Route 4	-421	217	-437	-137

Conclusions

The trend values for the occurrence of localized corrosion obtained from the cyclic polarization curves were similar for the four routes. In the Step Load technique it was possible to better distinguish the pitting potential although the crevice potential values were similar.

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