Original Article

Corrosion behavior of API 5L X65 steel subject to plastic deformation

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ARTICLE INFO

Article history:
Received 20 November 2017
Accepted 23 February 2018
Available online 16 April 2018

Keywords:
API 5L X65
Plastic deformation
Corrosion
Electrochemical

ABSTRACT

The API 5L X65 steel is widely used as one of the most economical and safe ways of transporting oil and gas. The significant number of accidents caused by failures of pipelines is due to corrosion. Plastic deformation can modify the mechanical properties of these pipelines, so study the steel's corrosive behavior when deformed plastically is important to avoid failures. In this research, samples were taken from a region free of solder and plastically deformed from 0 to 2.5% in a tensile machine. The samples were analyzed by chemical and electrochemical tests in NACE 177-A solution. It was concluded that the corrosion resistance was not affected by the different conditions of plastic deformation.

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1. Introduction

The API 5L X65 steel is classified as a high resistance and low alloy steel, which presents low carbon content, less than 0.30%, good tenacity and weldability. Pipelines for petroleum industry applications are constructed according to the American Petroleum Institute technical specifications [1–3]. This steel is used in construction of long-distance, high-pressure transportation pipelines that need to show the best combination of strength and hardness to support high internal pressures [4].

The water used in this process contains many corrosive agents like carbon dioxide and hydrogen sulfide that represent an important factor in the internal corrosion of steel pipelines [5]. Besides that, transmission pipelines have residual stresses due to manufactured and welding process, which can alter the structure's load capacity when subjected to external stresses. This is a big problem, because pipelines are subject to plastic deformation by outside forces as ground liquefaction, mechanical damages and buckling [6,7]. The corrosion is responsible for half of pipelines failures, which can cause catastrophic and environmental damages [8]. In this research, samples of API 5L X65 were plastic deformed in...
different percentages and corrosive tests were performed to understand how the plastic deformation can influence the corrosive behavior of the steel in an acid solution.

2. Methods

Samples were cut of a weld-free region of a tube and machined in a lathe. A traction machine was used to plastically deform them in 0.5%, 1.0%, 1.5%, 2.0% and 2.5%. The immersion tests were carried out according to ASTM standards G31-72 and G1-90 [9,10] for the deformation conditions of 0.0% and 2.5%. All faces of the samples were polished with emery paper. The NACE 177-A solution [11] was composed of 236.25 g of deionized H₂O, 1.25 g of CH₂COOH and 12.5 g of NaCl and pH 2.68. The tests were carried out in duplicate, at room temperature for 96 h. After the tests the samples were washed with distilled water, dried and weighed. The pickling process was done with the Clark solution, which contains 50.0 g of SnCl₂ and 20.0 g of Sb₂O₃ in 1.0 L of HCl 50% (v/v) at room temperature.

Each immersion cycle was 1 min and the pickling finished when the difference between two successive weights differed by 0.0001 g [12]. The preparation of the working electrodes for the electrochemical tests consisted of the mechanical polishing of samples (25 mm × 25 mm × 5 mm) with emery paper (120–2500). Then, the samples were rinsed in an ultrasonic bath containing propan-2-ol and then for each deformation condition 5 replicates were made. It was used an electrochemical cell (Princeton Applied Research – PAR), an Ag/AgCl reference electrode, a Pt wire as a counter electrode, and a solution containing 236.25 g deionized H₂O, 12.5 g NaCl and 1.25 g of CH₂COOH (NACE 177-A) as electrolyte. The medium was depleted of oxygen, bubbling N₂ for 30 min before starting the experiment and also during the experiment. An Autolab potentiostat/galvanostat, model PGSTAT 302N and Nova 1.8 software was used to obtain and analyze the data. The open circuit potential (OCP) was measured for 3 h in order to verify the stability of the potential in open circuit. In order to obtain Tafel curves, the scanning was started of −250 mV to +250 mV from OCP, at 0.166 mV s⁻¹. The impedance measurements (EIS) were performed at the OCP, applying a sinusoidal signal of 0.01 V rms, in the frequency range of 100 kHz to 10 mHz.

<table>
<thead>
<tr>
<th>Table 1 – Percentage of relative weight loss for the deformation conditions 0% and 2.5%.</th>
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<tr>
<td>Deformation condition – sample</td>
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<tr>
<td>0% – 1</td>
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<tr>
<td>0% – 2</td>
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<tr>
<td>2.5% – 1</td>
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<tr>
<td>2.5% – 2</td>
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</tbody>
</table>

![Weight loss per area for each immersion cycle of the pickling process, plastic deformation and samples: (a) 0% – 1; (b) 0% – 2; (c) 2.5% – 1; (d) 2.5% – 2.](image-url)
3. Results

The pickling process was done as described in section 2 and the mass loss per area for each sample in a function of time are shown in Fig. 1.

Table 1 shows the relative weight loss for each deformation condition, which was calculated using the following equation.

\[
\text{Relative weight loss} = \frac{M_i - M_f}{M_i \times A} \times 100
\]  

where \(M_i\) is the mass before starting the immersion test (g); \(M_f\) is the mass at the end of the pickling process (g); \(A\) is the exposed area of c-d-p (cm²).

Fig. 2 shows one of the five replicates obtained from the OCP, Fig. 2(a), and Tafel curves, Fig. 2(b), for each plastic deformation condition, where it is found that the different deformation conditions apparently do not affect the corrosion potential and the current density.

From the impedance measurements, the spectra were obtained in Nyquist format, Fig. 3(a), showing a capacitive arc at high frequencies and inductive at low frequencies. And in the Bode format, Fig. 3(b), with only one maximum for the variation of the phase angle with the frequency suggesting an active dissolution behavior of the electrode.

The circuit proposed by Poorqasemi and collaborators [13], Fig. 4, was used to analyze the impedance curves, which fitted very well to the experimental EIS spectra obtained, Fig. 5.

4. Discussion

The weight loss during the pickling process presented in Table 1 show small variation, <0.3 g. Fig. 1 shows the graph of weight loss as a function of area, from which it can be observed that for all conditions, mass loss is minimal, which was already expected, since the material does not form a passivation film.

The graphs show the behavior required by the G1-90 standard. The resulting percentages of weight loss per unit area are equal for the two deformation conditions tested, Table 1, indicating that the percentage of plastic deformation was not sufficient to cause differences in the corrosion rate of the material when exposed to long periods. The open circuit potential, Fig. 2(a), minimally varies over time and
stabilizes at very close values on all deformation conditions. This behavior indicates that it is not a significant change in anode and cathode regions during corrosion. Fig. 2(b) presents the polarization curves, from which it can be observed that all the deformation conditions show similar profiles and corrosion rates. It is found that the polarization is controlled by activation process because there is a continuous increase of the anodic and cathodic current as the potential increases.

In this way, there is no formation of a passivation film due to the dissolution of the corrosion products, maintaining an exposed area always active, according to Veloz and González [15]. The EIS spectra in Nyquist format, Fig. 3(a), show a capacitive behavior at high frequencies and inductive semicircle at low frequencies, which can be explained by a process of adsorption and desorption of species at the electrode surface, such as Cl⁻, H⁺ [13,15]. It can be observed in Fig. 3(b) the Bode formats showing only one maximum significantly lower than 90° for the phase angle stating that it is an active corrosion process.

It was used the equivalent electric circuit, Fig. 4, was used to analyze the EIS spectra, where the resistance Rs refers to the resistance of the solution, the capacitor (CPE) in parallel with the charge transfer resistance (Rct) represent the capacitive arc that can be attributed to the charge transfer reaction. The inductor (L) and its resistance (RL) represent the inductive arc that appears at low frequencies, and can be justified by the adsorption of electroactive species. It was obtained good agreement between calculated and experimental results, Fig. 5. In addition, comparing the values of impedance modules, at the frequency limit that tends to zero, |Zjω| ≈. Rp (Tafel) and Rct (equivalent circuit modeling) are found to be all of the same magnitude, approximately 10² Ω cm, a very low value that describes a corrosive metal surface.

5. Conclusions

In this work the effect of the plastic deformation on the corrosive behavior of API 5L X65 steel in acidic medium containing chloride was investigated. The tests of chemical and electrochemical corrosion indicated that the plastic deformation did not significantly affect the corrosion resistance of the steel and that the corrosion process is represented by dissolution active. A good fitting was obtained to the EIS spectra by the proposition of an equivalent electric circuit.
Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

Thanks to the FAPESP (process n. 2017/11361-5) and to the Capes by financial support.

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[9] ASTM G31 72.[s.d.].