Hydrogen Sulfide Corrosion of Weld Regions in API X52 Steel

Corrosión por ácido sulfhídrico de las regiones de soldadura en acero API X52

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Abstract

The corrosion behavior of gas metal arc welding (GMAW) regions has been studied using potentiodynamic polarization and polarization resistance (LPR) techniques. Experiments were conducted in hydrogen sulfide (H_2S)-containing brine and in H_2S-free brine. Welds were made on API 5L X52 steel. Due to differences in their microstructure, chemical composition and residual stress level, weld regions exhibited different responses under H_2S corrosion. Base metal exhibited the highest corrosion rate (CR) and the most cathodic corrosion potential.

Keywords:

- Weld regions
- X52 steel
- hydrogen sulfide
- GMAW
- corrosion

Resumen

Se estudió el comportamiento ante la corrosión de las regiones de soldadura de un cordón realizado por arco metálico con gas (GMAW) sobre un acero grado API X52 mediante las técnicas de polarización potenciodinámica y resistencia a la polarización (LPR). Los experimentos se realizaron utilizando salmuera con 300 ppm deácido sulfhídrico (H_2S) y salmuera libre de H_2S como electrolitos. Debido a las diferencias en su microestructura, composición química y el nivel de esfuerzos residuales, las regiones de soldadura mostraron diferentes respuestas a la corrosión por H_2S. El metal base exhibió la velocidad de corrosión (CR) más alta y el potencial de corrosión más catódico.

Descriptores:

- regiones de soldadura,
- acero X52,
- ácido sulfhídrico,
- GMAW,
- corrosión

Introduction

Hydrogen sulfide corrosion is one of the most important sources of concern in the gas and oil transport industry. Over several decades, a considerable amount of literature has been published on this topic (Smith and Pakalapati, 2004). Pipelines used for oil and gas transport are manufactured by welding segments of carbon steel pipe. Welding seams can be divided into three regions: the weld metal (WM), the heat affected zone (HAZ) and the base metal (BM). These regions differ in their microstructure, chemical composition and residual stress level. A variety of corrosion types, like sulfide stress cracking (SCC) and hydrogen-induced cracking (HIC), affect the steel weldment used in sour environments (Makarenko and Khalin, 2005; Tsay *et al.*, 2001).

However, SSC and HIC are not the only types of corrosion to which welds are exposed. Electrochemical corrosion by H_2S also occurs on the welds and clearly plays an important role in the deterioration of pipeline joints. The following redox reaction describes this process

$$Fe + H_2S \rightarrow FeS + H_2$$
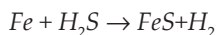
In most of the cases, H_2S presence increases the CR but, at low concentrations and prolonged immersion times, H_2S has an inhibition effect due to the formation of a ferrous sulfide (FeS) protective film (Ma *et al.*, 2000). Other studies (Fragiel *et al.*, 2005; Pound *et al.*, 1989; Brown *et al.*, 2003; Genescá and Arzola, 2003), have considered the electrochemical H_2S corrosion of carbon steel and the susceptibility of welds to SSC (Kobayashi *et al.*, 1986; Zhao *et al.*, 2003; Radkevych, 1999) but, to our knowledge, no corrosion analysis of the weld regions has been performed on X52 steel in sour environment for electrochemical corrosion. The aim of this work is to determine the specific response of each weld region to H_2S corrosion.

Experimental procedure

The welds were made by gas metal arc welding (GMAW) with E71T-1 flux-cored wire of 0.114 cm (0.045'') caliber at a speed of 0.254cm/s. The electrode was fed at 14.816cm/s. The welding was performed at 25 V and 190 A with a calculated heat input of 18.75 KJ/cm.

Metal samples were obtained from the weld regions and used as working electrodes. The samples were cut from a piece of welded tube with disk cutter at a speed of 0.15 mm/s and 3400 rpm. The specimens were grounded with SiC 240-600 grit paper in a polishing wheel and mounted in thermoplastic resin. A stainless steel screw was connected from the working electrodes to the electrochemical circuit. The exposed surface of the working electrodes was prepared by polishing with SiC grit paper, cleaned with deionized water and acetone, and dried with hot air. Surface areas were calculated using the dimensions obtained with a calibrated vernier caliper. A calibrated pycnometer was used to determine sample's densities.

The metallographic specimens were prepared in a similar way. Transverse segments of the studied welds were cut in order to observe all weld regions. Once the specimens were polished with SiC240-600 grit paper, the specimens were polished with diamond paste of 1 μm until a mirror-like surface was obtained. Just before the microscopic observation, the specimens were attacked with Nital (10% HNO_3 in absolute ethanol), rinsed with ethanol and acetone, and dried with hot air. Microstructure images were obtained with a metallographic optical microscope.

Electrochemical experiments were performed in a three-electrode cell with a graphite rod as auxiliary electrode and an Ag/AgCl electrode as reference. A Solartron SI 1287 potentiostat was used for the potentiodynamic polarization and LPR tests. CorrWare and CorrView version 2.9 were used to process and visualize data. The potential sweeps were performed over a range of -0.1 to 0.1 V (vs Ag/AgCl) from open cell potential at a constant rate of 0.1 mV/s. Working electrodes were immersed in the electrolyte for 5 minutes before the potential sweeps. All the experiments were carried out at room temperature (25°C).The corrosion current I_{corr} was calculated from the linear polarization resistance R_p in the Stern-Geary equation

$$I_{corr} = \frac{b_a b_c}{2.23 (b_a + b_c) R_p} \qquad (1)$$

where b_a and b_c are the Tafel slopes. I_{corr} can be related directly to the corrosion rate CR (in millimeters per year) through the following equation

$$CR = \frac{0.13 \, l_{corr} (E.W.)}{d} \qquad (2)$$

where *E.W.* is the equivalent weight of the corroding species and *d* is the density of the corroding species in g/cm^3.

The electrolyte solutions were prepared by the addition of 10.700 g of NaCl, 0.339 g of $CaCl_2$ and 0.207 g of $MgCl_2 \cdot 6H_2O$ in 1 liter of deionized water, according to

the procedure detailed in NACE standard 1D182 (2005) (NACE Technical Publication 1D182, 2005). Dissolved oxygen was removed by bubbling nitrogen (99.9% pure) through the cell for 30 minutes before the tests. For experiments in sour environment, H_2S was synthesized in the above solution by the addition of 0.170 g of acetic acid and 0.353 g of Na_2S to 1 liter of brine. This technique yielded approximately 300 ppm of H_2S, according to the results of an indirect iodometric titration. This method is described in NACE Standard TM0284-2003 (NACE Standard TM0284, 2003).

Results and discussion

Metallographic analysis

As shown in Figure 1, the welding metal shows the acicular ferrite columnar grains found in common carbon steel welds. HAZ is composed of refined grains of ferrite-pearlite (Figure 2), product of the transformation of base metal with the heat provided by the welding process. The base metal consists of equiaxed grains of ferrite-pearlite, typical in all carbon steels (Figure 3).

Potentiodynamic polarization and LPR in Brine

Polarization curves of each weld region are shown in Figure 4. Each material exhibited a characteristic corrosion behavior (Table 1). Weld metal presents the most anodic E_{corr} value; therefore, it is the least thermodynamically favored region for corrosion attack. HAZ and base metal exhibited more cathodic values, being more susceptible to corrosion. Interestingly, HAZ and base metal have similar E_{corr} values. However, there is a significant difference between the responses of these regions. The base metal exhibits uniform E_{corr} values, while HAZ E_{corr} values are scattered. This could be interpreted as evidence of the corrosion mechanism occurring on the electrodes. Scattered E_{corr} values are an indication of localized corrosion pitting (Videm and Kvarekval, 1995). Table 2 shows that CR values exhibited by the base metal are larger than those corresponding to the weld metal and the HAZ.
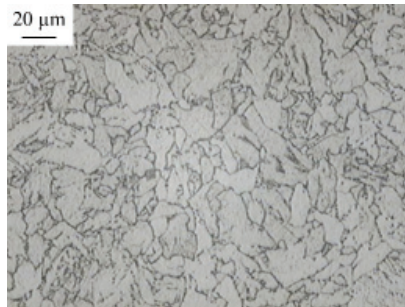

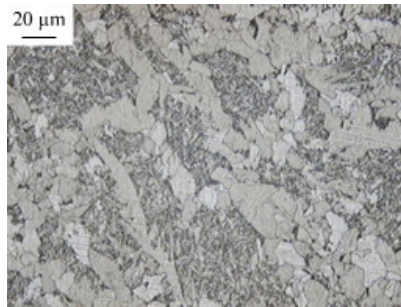Figure 1. Base metal microstructure of a GMAW weld on API X52 steel. Magnification 500x

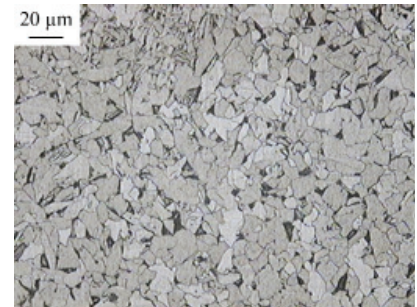Figure 2. Weld metal microstructure of a GMAW weld on API X52 steel. Magnification 500x

Figure 3. HAZ microstructure of a GMAW weld on API X52 steel. Magnification 500x

Electrolyte	WM	HAZ	BM
	-0.432	-0.504	-0.526
Brine	-0.435	-0.518	-0.524
	-0.453	-0.549	-0.525
	-0.775	-0.790	-0.800
Brine with 300 ppm of H_2S	-0.775	-0.791	-0.799
	-0.777	-0.783	-0.795

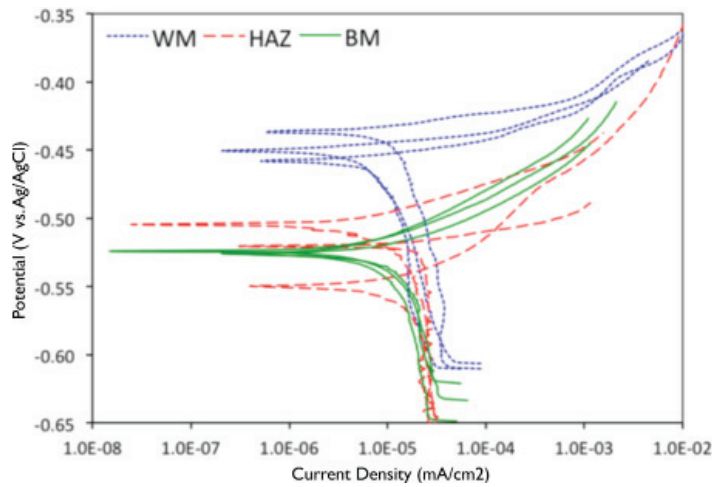Table 1. Corrosion potentials (V) of weld regions in a GMAW weld on API X52 steel

Figure 4. Potentiodynamic curves of weld regions in a GMAW weld on API X52 steel. Results obtained in H$_2$S-free brine

Electrolyte	WM	HAZ	BM
	0.108	0.138	0.217
Brine	0.078	0.213	0.172
	0.062	0.102	0.132
	0.067	0.026	0.083
Brine with 300 ppm of H$_2$S	0.085	0.054	0.106
	0.064	0.028	0.186

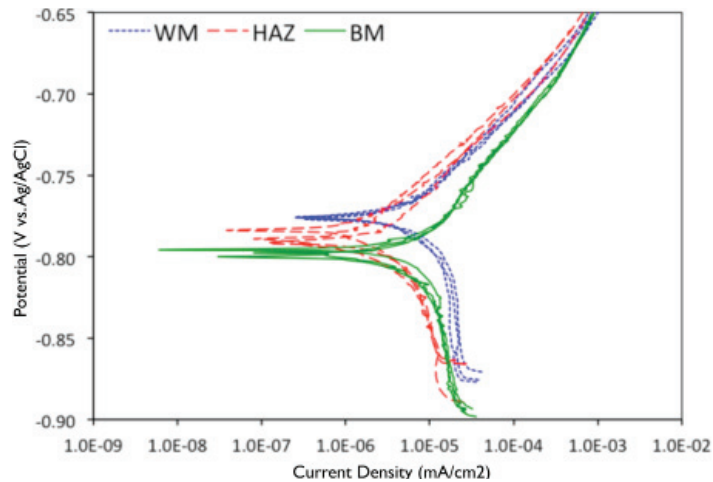Table 2. Corrosion rates (mm/year) of weld regions in a GMAW weld on API X52 steel

Figure 5. Potentiodynamic curves of weld regions in a GMAW weld on API X52 steel. Results obtained in brine with 300 ppm of H$_2$S

Potentiodynamic polarization and LPR in Brine with 300 ppm H$_2$S

Figure 5 shows the polarization curves of the different weld regions in presence of 300 ppm of H$_2$S. E$_{corr}$ values show very little dispersion and the order of susceptibility is quite clear (Table 1). The small dispersion of the E$_{corr}$ values of the HAZ can be attributed to a process moderate pitting. As in the H$_2$S-free brine

tests, the weld metal has the most anodic E$_{corr}$ value. HAZ has an intermediate E$_{corr}$ value while the base metal E$_{corr}$ is the most cathodic.

Table 2 shows the results of LPR for the weld regions in the presence of 300 ppm of H$_2$S. The HAZ presents the lowest CR. All the weld regions presented lower CRs in H$_2$S-containing solution than in the brine. These results are consistent with the findings of Galvan *et al.*, 2003).

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Conclusions

When a GMAW weld on X52 steel is subjected to electrochemical corrosion attack by H_2S, the base metal shows the higher corrosion rate and the most cathodic corrosion potential of weld regions. The weld metal and HAZ are more resistant to electrochemical corrosion by H_2S than the rest of the steel pipe. The HAZ presents no special susceptibility to electrochemical corrosion by H_2S, the latter having an intermediate value between the base metal and weld metal. Weld regions showed higher corrosion rates in the presence of H_2S. However, their E_{corr} values were more anodic in the H_2S-free brine, which means they are more susceptible to corrosion in this environment.

Acknowledgments

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