Hydrogen Sulfide Corrosion of Weld Regions in API X52 Steel

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

Arenas-Martínez L.F
Facultad de Ciencias Químicas
Universidad Autónoma de Coahuila
E-mail: fernando.arenas@uadec.edu.mx

García-Cerecero G.
Corporación Mexicana de Investigación en Materiales SA de CV
Saltillo, Coahuila
E-mail: ggarcia@comimsa.com

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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 (H₂S)-containing brine and in H₂S-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 H₂S 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 potenciodynamic y resistencia a la polarización (LPR). Los experimentos se realizaron utilizando salmuera con 300 ppm de ácido sulfhídrico (H₂S) y salmuera libre de H₂S 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 H₂S. 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, SCC and HIC are not the only types of corrosion to which welds are exposed. Electrochemical corrosion by H2S also occurs on the welds and clearly plays an important role in the deterioration of pipeline joints. The following redox reaction describes this process:

\[ \text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2 \]

In most of the cases, H2S presence increases the CR but, at low concentrations and prolonged immersion times, H2S 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 H2S 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 H2S 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 ground 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% HNO3 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

\[
I_{corr} = \frac{b_i b_p}{2.23(b_i + b_p) R_p}
\]

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

\[
CR = \frac{0.13 I_{corr}(E.W.)}{d}
\]

where E.W. is the equivalent weight of the corroding species and \( d \) is the density of the corroding species in g/cm³.

The electrolyte solutions were prepared by the addition of 10.700 g of NaCl, 0.339 g of CaCl₂, and 0.207 g of MgCl₂6H₂O 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, H₂S was synthesized in the above solution by the addition of 0.170 g of acetic acid and 0.353 g of Na₂S to 1 liter of brine. This technique yielded approximately 300 ppm of H₂S, 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 Ecorr 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 Ecorr values. However, there is a significant difference between the responses of these regions. The base metal exhibits uniform Ecorr values, while HAZ Ecorr values are scattered. This could be interpreted as evidence of the corrosion mechanism occurring on the electrodes. Scattered Ecorr 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.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>WM</th>
<th>HAZ</th>
<th>BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brine</td>
<td>-0.432</td>
<td>-0.504</td>
<td>-0.526</td>
</tr>
<tr>
<td></td>
<td>-0.435</td>
<td>-0.518</td>
<td>-0.524</td>
</tr>
<tr>
<td></td>
<td>-0.453</td>
<td>-0.549</td>
<td>-0.525</td>
</tr>
<tr>
<td></td>
<td>-0.775</td>
<td>-0.790</td>
<td>-0.800</td>
</tr>
<tr>
<td>Brine with 300 ppm</td>
<td>-0.775</td>
<td>-0.791</td>
<td>-0.799</td>
</tr>
<tr>
<td>of H₂S</td>
<td>-0.777</td>
<td>-0.783</td>
<td>-0.795</td>
</tr>
</tbody>
</table>

Table 1. Corrosion potentials (V) of weld regions in a GMAW weld on API X52 steel
Potentiodynamic polarization and LPR in Brine with 300 ppm H₂S

Figure 5 shows the polarization curves of the different weld regions in presence of 300 ppm of H₂S. Eₘₚ values show very little dispersion and the order of susceptibility is quite clear (Table 1). The small dispersion of the Eₘₚ values of the HAZ can be attributed to a process moderate pitting. As in the H₂S-free brine tests, the weld metal has the most anodic Eₘₚ value. HAZ has an intermediate Eₘₚ value while the base metal Eₘₚ is the most cathodic.

Table 2 shows the results of LPR for the weld regions in the presence of 300 ppm of H₂S. The HAZ presents the lowest CR. All the weld regions presented lower CRs in H₂S-containing solution than in the brine. These results are consistent with the findings of Galvan et al., 2003).
Conclusions

When a GMAW weld on X52 steel is subjected to electrochemical corrosion attack by H$_2$S, 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$_2$S than the rest of the steel pipe. The HAZ presents no special susceptibility to electrochemical corrosion by H$_2$S, the latter having an intermediate value between the base metal and weld metal. Weld regions showed higher corrosion rates in the presence of H$_2$S. However, their $E_{corr}$ values were more anodic in the H$_2$S-free brine, which means they are more susceptible to corrosion in this environment.

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About the authors

Luis Fernando Arenas-Martínez. Is a postgraduate student in Chemistry at the Autonomous University of Coahuila, pursuing a M.S. through a scholarship from the National Council on Science and Technology of Mexico (CONACYT). Research interests include inorganic chemistry, electrochemistry and corrosion science.

Gabriel García-Cerecero. Is a professor of metallurgy at the Postgraduate Studies Department in COMIMSA (Mexico), teaching students of the Master’s Program in Industrial Welding Technology. He is a Metallurgical Engineer graduated from Saltillo Technological Institute. He received his M.S. in nonferrous metallurgy from CINVESTAV Saltillo of the National Polytechnic Institute (IPN). Before joining COMIMSA, worked in several metallurgical companies, including SICARTSA and CIFUNSA. He was a Certified Associate Welding Inspector from July 2001 to July 2004. His research interests are in the corrosion and failure analysis of oil and gas pipelines.