Determination of Diffusible Hydrogen in Weldments by the RPI Silicone-Oil Extraction Method

A reliable, rapid, safe and inexpensive technique for determining diffusible $\text{H}_2$ contents in weldments is developed and qualified

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ABSTRACT. The control of the hydrogen content in weldments is necessary to prevent hydrogen-induced cracking in high-yield-strength steels. Because a critical amount of diffusible hydrogen must be present for hydrogen-induced cracking, it is essential to determine the amount of hydrogen introduced by various welding procedures.

In this investigation, the RPI silicone-oil-extraction method for the determination of diffusible hydrogen content in weldments was developed and qualified. This method is a reliable, rapid, safe and inexpensive technique for the determination of diffusible-hydrogen content in weldments.

The use of the composite-zone weight, rather than the deposited weld-metal weight, yielded a better consistency of results and a better correlation between these results and those obtained by the BWRA/IIW mercury extraction technique.

Introduction

The development of high-yield-strength, structural steels has led to an increase in the problems associated with hydrogen-induced cracking (cold cracking). This cracking, which occurs in either the heat-affected zone or the weld metal, may appear immediately, or after prolonged periods of time, extending up to several weeks.

Four conditions are required, simultaneously, for hydrogen-induced cracking:
1. A critical concentration of diffusible hydrogen,
2. A critical level of local tensile stress,
3. A crack-susceptible microstructure, and
4. A sufficient amount of time in the crack susceptible temperature range (~$-100$ to $200^\circ\text{C}$, i.e. $-148$ to $392^\circ\text{F}$).

Critical stress levels and crack-susceptible microstructures are usually present in high-strength-steel weldments. Therefore, when the steels are used at ambient temperatures, control of the hydrogen content is mandatory to prevent hydrogen-induced cracking.

Hydrogen is introduced into weldments as a result of the dissociation of hydrogen gas, water vapor, and hydrogen-bearing compounds to produce atomic hydrogen in the welding arc. The major sources of hydrogen are moisture in the coating of SMAW electrodes, moisture and/or contaminants in GMAW shielding gas, contamination on the filler metal, and surface contaminants on the base metal.

Because a critical concentration of diffusible hydrogen must be present for hydrogen-induced cracking, it is essential to determine the amount of hydrogen introduced by various welding procedures. Several different techniques have been employed to determine the hydrogen concentration in steel weldments:

1. The British Welding Institute (BWRA) technique, which was adopted by the IIW, involves placing a sample in a vacuum over mercury at room temperature for 72 hours (h) and collecting the hydrogen in calibrated glass tubing.

2. A carrier-gas technique developed at BWRA involves heating a sample at $650^\circ\text{C}$ ($1202^\circ\text{F}$) in a stream of argon carrier gas and monitoring the change in thermal conductivity of the gas stream produced by the evolution of hydrogen from the sample.

3. In a chromatographic method developed at the E. O. Paton Electric
Welding Institute,² 3 specimens are placed in a 150°C (302°F) reaction chamber. Argon, as a carrier gas, is passed through the chamber carrying the evolved gases to a chromatograph.

4. In an electrochemical technique, the Barnacle cell,¹ a sample is made the anode and the current required to convert the emerging atomic hydrogen to hydrogen ions is measured. Utilizing Fick's laws, the current is related to hydrogen content.

5. The Japanese glycerin replacement method (JIS)³ involves the immersion of a sample in a glycerin bath at 45°C (113°F) for two days and the collection of the extracted hydrogen in a buret.

These systems have one or more of the following disadvantages:

1. Large equipment expenditure.
2. Long test time.
3. Restricted specimen size and shape.
4. Reproducibility.
5. Accuracy.
7. Complexity.

Object

This investigation involved the development and qualification of the RPI silicone-oil extraction method for the determination of diffusible hydrogen content in weldments.

Apparatus

Figure 1 is a schematic illustration of the apparatus used in the RPI method. The apparatus consists of two Pyrex beakers set up in a “double-boiler” bath configuration, heated by a standard temperature-controlled laboratory hot plate. Both the inner and outer baths are a standard high-grade, high-temperature silicone oil which is stabilized with hydrogen by bubbling hydrogen through the meniscus. The apparatus is a Pyrex collection funnel, evolves hydrogen which rises to the top of the silicone-oil column and is trapped in the buret.

An advantage of the RPI system is its adaptability. Variable specimen size and shape can be accommodated by scaling up the entire apparatus.

Method of Determination of Diffusible Hydrogen Contents

After the equipment has been assembled, the temperature has equilibrated to 100°C (212°F), and the silicone oil has become saturated with hydrogen, the initial hydrogen volume must be established. This is achieved by a two-step process:

1. Drawing the silicone oil up the entire length of the calibrated buret.
2. Placing the fritted disc bubbler under the funnel and bubbling enough hydrogen into the buret to lower the meniscus to the calibrated portion of the buret.

The position of the hydrogen meniscus before and after a test determines the change in volume, ΔV, of evolved hydrogen in cc. By use of the following equation, ΔV is converted into ppm of hydrogen in weld metal at STP:

\[
\text{PPM} = \Delta V \cdot \frac{273}{T} \cdot \frac{P}{760} \cdot \frac{90}{\text{metal (grams)}}
\]

where T is the temperature of the buret at the collection point °K, P is atmospheric pressure (mm. of Hg), W is the weight of the deposited weld metal (grams), and 90 is a conversion factor.
factor to convert the results from cc/gm to ppm of deposited weld metal.

Atmospheric pressure \( P \) does not include a correction factor to compensate for the column of silicone oil. However, a 6 in. (15 cm) column of silicone oil results in only a 1.3% error in the diffusible hydrogen content calculated from the equation above.

Even though the cover plate acts as a thermal barrier, the heated baths can influence the temperature \( T \) of the hydrogen collected in the column. Therefore, the initial hydrogen level should be re-established when the meniscus is within 3 in. (7.5 cm) of the bath.

The data for both the BWRA/IIW and the RPI silicone oil extraction methods are presented in units of ppm of hydrogen in the deposited weld metal, ppm\(_{d}\), and ppm of hydrogen in the fusion zone metal, ppm\(_{c}\). The use of these units requires the determination of the weight of the deposited weld metal, \( W_{d} \), and that of the fusion zone (the solidified weld pool) which can be approximated by the weight of the composite zone, \( W_{c} \). The weight of the deposited weld metal, \( \Delta W_{d} \), is determined by subtracting the initial (before welding) weight of the specimen from the final (after welding) weight of the specimen. On the other hand, the total weight of the composite zone of the weld is determined from planimeter measurements on a photomacrograph of:

1. The total area of the specimen, including the weld, \( A_{t} \).
2. The area of the composite zone, \( A_{c} \).

Calculations for the BWRA/IIW and the RPI silicone oil extraction techniques were performed utilizing both \( \Delta W_{d} \) and \( W_{c} \) to express the diffusible hydrogen contents in terms of ppm\(_{d}\) and ppm\(_{c}\), respectively.

### Materials and Procedures

Initially, specimens were produced by welding HY-130, a high-strength low alloy steel, with E14018 SMAW coated electrodes. Later investigations utilized a Russian pipeline steel 15F2Ag (referred to as steel 15 hereafter) as the base metal which was welded with either E7018 or E6010 SMAW coated electrodes. The chemical composition and mechanical properties of the materials used in this investigation are presented in Tables 1 and 2, respectively.

### Table 2—Mechanical Properties\(^{(a)}\) of Materials Used

<table>
<thead>
<tr>
<th>Material</th>
<th>YS ksi(^{(a)})</th>
<th>TS ksi(^{(b)})</th>
<th>Elongation (2 in. gage length), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HY-130</td>
<td>136</td>
<td>147</td>
<td>19</td>
</tr>
<tr>
<td>15F2Ag</td>
<td>60</td>
<td>78</td>
<td>19</td>
</tr>
<tr>
<td>E14018</td>
<td>141</td>
<td>147</td>
<td>18</td>
</tr>
<tr>
<td>E7018</td>
<td>73</td>
<td>84</td>
<td>30</td>
</tr>
<tr>
<td>E6010</td>
<td>55</td>
<td>65</td>
<td>25</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Weld metal properties for 43kJ/in. heat input.
\(^{(b)}\) Typical values for this material taken from producer's literature.

**YS**—yield strength; **TS**—tensile strength.

By using the final weight, \( W_{f} \), and a simple ratio of areas, the weight of the composite zone, \( W_{c} \), is determined:

\[
W_{c} = \frac{A_{c}}{A_{t}} W_{f}
\]

### Table 3—Welding Conditions Employed

<table>
<thead>
<tr>
<th>Heat Input</th>
<th>Welding Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 kJ/in.</td>
<td>80% of the time</td>
</tr>
<tr>
<td>90 kJ/mm</td>
<td>20% of the time</td>
</tr>
</tbody>
</table>

**Run-on and run-off tabs were machined and ground flat to dimensions 1/2 X 1/2 X 1/2 in. (15.9 X 15.9 X 6.3 mm).**

Several polished specimens were positioned between the run-on and run-off tabs and loaded into the welding fixture, as illustrated in Fig. 3. The entire assembly was degreased with acetone and demagnetized. Figure 4 shows the semiautomatic electrode feeder which was used to deposit the SMAW beads at ~30 kJ/in. (1180 J/mm) heat input.

Table 3 summarizes the welding conditions employed. Within 15 seconds(s) after extinguishing the arc, the welded specimens were quenched in an agitated dry ice and alcohol bath at \(-70°C (-94°F)\). Then, the specimens were mechanically separated and stored individually in liquid nitrogen at \(-196°C (-320°F)\). At no time during the mechanical separation procedure were the specimens re-
moved from the dry ice and alcohol bath for more than 10 s, as specified by the BWRA/IIW procedure.

Prior to testing, the specimens were washed and dried according to the following three-step procedure established by the BWRA:
1. Rinse in pure ethyl alcohol for 3-5 s.
2. Rinse in anhydrous ethyl ether for 3-5 s.
3. Dry with a blast of low-dew-point argon gas for 20-30 s.

The total time of the wash is specified not to exceed 60 s. This washing procedure removes surface contaminants which could lead to inaccurate analysis of hydrogen content. After completion of a hydrogen analysis, the specimen was reweighed and a photomacrograph of its cross section was taken.

Results and Discussion

Diffusible hydrogen content of HY-130 and Soviet steel 15Ст2А weldments, as determined utilizing both the BWRA/IIW and RPI silicone oil methodologies.

Fig. 5—Photomacrograph of a high-hydrogen weld which exhibits porosity (ppm = 18.6). ×3
extraction methods, are presented and discussed in the following paragraphs.

**Diffusible-Hydrogen Content in HY-130 Weldments**

Table 4 shows typical data for low- and high-hydrogen welds in HY-130. These welds were deposited utilizing E14018 SMAW electrodes. The two levels of hydrogen content were achieved by using the electrodes in the as-received condition (low-range, approximately 2 ppm) or by soaking the electrodes in water for a minimum of 24 h prior to welding (high-range, approximately 30 ppm). The welding conditions were previously noted in Table 3.

Note in Table 4 that only one determination of hydrogen content in each weld was made using the BWRA/IIW technique. This resulted from problems which were encountered in maintaining the BWRA/IIW apparatus in working condition, results in this section were limited to a comparison of four RPI diffusible-hydrogen determinations with only one BWRA/IIW determination for each weld.

Porosity was discovered in approximately 80-90% of the HY-130 welds. Figure 5 is a photomicrograph of a specimen with a 18.6 ppm hydrogen content which exhibits porosity. It has been demonstrated by Moreton, et al., and confirmed at RPI, that hydrogen diffuses into the porosity voids where it reassociates into molecular form. Therefore, in view of the extreme amount of porosity encountered in HY-130 welds, the accuracy of the measured values of hydrogen concentration should be questioned.

**Diffusible-Hydrogen Content in Soviet Steel 15T2A Weldments**

Correlation between the BWRA/IIW and RPI Methods. In order to decrease the failure rate of the hydrogen determinations utilizing the BWRA/IIW apparatus, a softer steel (steel 15) was used as the base metal; also, porosity was reduced by replacing the E14018 electrodes with two SMAW electrodes, E7018 and E6010, which produced low- and high-hydrogen levels, respectively. Utilizing this softer steel, two BWRA/IIW hydrogen determinations were obtained from each weld run. For both low- and high-hydrogen content welds, porosity was virtually eliminated.

Figures 8 and 9 show comparisons between the hydrogen contents determined by the RPI and BWRA/IIW methods based on ppm_d and ppm_c, respectively. Note that in both cases there is good correlation between the two methods. In contrast to most published findings, utilization of the com-
posite-zone weight results in significantly better correlation than that of the deposited-metal weight. This is evidenced by the correlation coefficients, $R^2 = 0.93$ and $R^2 = 0.74$, for the calculations utilizing $W_c$ and $\Delta W_c$, respectively.

Research by Tsunetomi, et al., has demonstrated that the entire molten weld pool, a mixture of base and deposited metal, acts as the sink for diffusible hydrogen. Therefore, it is appropriate to use the composite-zone weight (the solidified weld pool) for calculating the diffusible-hydrogen contents.

The liberation of gas from the entire fusion zone of the weld, which was observed during testing in the RPI method, confirmed that the entire weld pool is a sink for diffusible hydrogen during welding.

Table 5 shows typical diffusible-hydrogen content data for a low- and a high-hydrogen weld in steel 15. Calculations of hydrogen content expressed in ppm show much greater consistency than those expressed in $ppm_c$. This is exemplified by their standard deviations: 0.8 ppm vs. 5.6 ppm for the high-hydrogen weld and 0.3 ppm vs. 1.3 ppm for the low-hydrogen weld.

Data from an additional low-hydrogen weld are presented in Table 6. Note that sample 23 has a negative $\Delta W_c$ value, although weld metal was deposited, as shown in Fig. 10. The mechanical separation of sample 23 produced a specimen surface which was not planar, and a fracture surface which was not parallel to the original specimen surface. As a result, the thickness of the specimen in the fused region was less than the original thickness of the specimen.

This condition, in conjunction with the small amount of weld reinforcement, resulted in the negative value of $\Delta W_c$, shown in Table 6. However, the value of the hydrogen content of this specimen, obtained by utilizing the composite-zone weight, is comparable with those obtained from other specimens in this weld.

**Table 5—Typical Data for a Low- and a High-Hydrogen Weld in Steel 15**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Hydrogen evolved, cc</th>
<th>$\Delta W_c$, g</th>
<th>ppm</th>
<th>$W_c$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>46</td>
<td>0.015</td>
<td>0.5465</td>
<td>2.3</td>
<td>1.4500</td>
</tr>
<tr>
<td>47</td>
<td>0.090</td>
<td>0.7336</td>
<td>3.7</td>
<td>1.3644</td>
</tr>
<tr>
<td>48</td>
<td>0.100</td>
<td>1.3045</td>
<td>2.3</td>
<td>2.3703</td>
</tr>
<tr>
<td>49</td>
<td>0.020</td>
<td>0.7515</td>
<td>2.2</td>
<td>1.7027</td>
</tr>
<tr>
<td>410</td>
<td>0.020</td>
<td>0.3221</td>
<td>5.1</td>
<td>1.5756</td>
</tr>
<tr>
<td>181</td>
<td>0.120</td>
<td>0.5139</td>
<td>19.6</td>
<td>1.6705</td>
</tr>
<tr>
<td>182</td>
<td>0.120</td>
<td>0.2739</td>
<td>35.2</td>
<td>1.2563</td>
</tr>
<tr>
<td>183</td>
<td>0.095</td>
<td>0.4105</td>
<td>19.4</td>
<td>1.3686</td>
</tr>
<tr>
<td>184</td>
<td>0.170</td>
<td>0.5459</td>
<td>16.9</td>
<td>1.3421</td>
</tr>
<tr>
<td>185</td>
<td>0.170</td>
<td>0.3183</td>
<td>21.8</td>
<td>1.2977</td>
</tr>
<tr>
<td>186</td>
<td>0.220</td>
<td>0.3796</td>
<td>25.1</td>
<td>1.2764</td>
</tr>
<tr>
<td>187</td>
<td>0.080</td>
<td>0.4041</td>
<td>16.6</td>
<td>1.2474</td>
</tr>
<tr>
<td>188</td>
<td>0.100</td>
<td>0.4738</td>
<td>17.6</td>
<td>1.2582</td>
</tr>
<tr>
<td>189</td>
<td>0.100</td>
<td>0.3614</td>
<td>23.2</td>
<td>1.3065</td>
</tr>
<tr>
<td>1810</td>
<td>0.145</td>
<td>0.6477</td>
<td>18.8</td>
<td>1.8672</td>
</tr>
</tbody>
</table>

**Table 6—Data for a Low-Hydrogen Weld in Steel 15**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Hydrogen evolved, cc</th>
<th>$\Delta W_c$, g</th>
<th>ppm</th>
<th>$W_c$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>0.020</td>
<td>0.3220</td>
<td>5.2</td>
<td>1.0502</td>
</tr>
<tr>
<td>22</td>
<td>0.020</td>
<td>0.5275</td>
<td>2.3</td>
<td>1.3066</td>
</tr>
<tr>
<td>23</td>
<td>0.015</td>
<td>-0.0033</td>
<td>-</td>
<td>1.3986</td>
</tr>
<tr>
<td>24</td>
<td>0.050</td>
<td>0.6183</td>
<td>4.1</td>
<td>2.0576</td>
</tr>
</tbody>
</table>

**Influence of Hydrogen Content on Extraction Time.** Figure 11 shows the extraction volume of diffusible hydrogen as a function of time for two specimens: sample 1810 with a high-hydrogen content (6.5 ppm) and sample 46 with a low-hydrogen content (0.3 ppm).

Note that for both specimens, there is an incubation time before evolution begins. This time delay, which is necessary for hydrogen diffusion to the sample surface, is a characteristic of hydrogen-extraction methods. Also, it is to be noted that the extraction curves for both samples level off well before the recommended test time of 90 min.

**Advantages of the RPI Silicone Oil Extraction Method.**

Hydrogen determinations utilizing the RPI method have shown a direct correlation with those utilizing the BWRA/IIW technique. In addition, the
RPI silicone oil extraction method exhibits several important advantages over the BWRA/IW technique:
1. Short test time of 90 min.
2. Vacuum is not necessary.
3. Hazardous mercury is not required.
4. Adaptable to large specimen sizes.
5. Non-magnetic specimens may be used.
6. Simple and inexpensive test equipment.
7. The location from which gas evolves from the specimen may be observed.

Conclusions
1. The RPI silicone oil extraction method is a reliable, rapid and inexpensive technique for the determination of diffusible-hydrogen content in weldments.
2. The use of the composite-zone weight, rather than the deposited weld metal weight, in determining the diffusible-hydrogen content yields a better correlation between the results of the RPI and the BWRA/IW extraction techniques.

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