Sensitivity of Electroslag Weld Metal to Hydrogen

Hydrogen-charged tensile specimens of weld metal show that maximum embrittlement is caused by grain boundary separation mode

BY L. N. PUSSEGO DA AND W. R. TYSON

ABSTRACT. The susceptibility of electroslag weld metal to hydrogen has been studied by slow tensile testing and metallographic examination of fractured specimens from a weldment of ASTM A36 steel plate. With constant hydrogen concentration, three distinct hydrogen-assisted fracture modes were observed. The first at low temperatures was “quasi-cleavage.” As the temperature was increased, the second consisted of prior-austenite grain-boundary separations, and then microvoid—the third mode—coalescence occurred.

The embrittlement index is largest for the grain-boundary separation mode. Both the temperature of maximum embrittlement and the upper limit of the temperature range depend on hydrogen content, increasing from -10 and 55°C (14 and 131°F) respectively at 1 ppm to 30 and 145°C (86 and 293°F) at 3 ppm. The presence of internal hydrogen increases both the yield and flow stresses at temperatures where hydrogen embrittlement occurs.

Grain boundary separations which occur in electroslag weldments are discussed. It is concluded that these are a result of hydrogen-induced cracks in a microstructure which provides a crack path prone to low-energy fracture.

Introduction

Internal hydrogen embrittlement of weldments appears in the form of “cold cracks” (a form of delayed failure due to hydrogen) either in the weld metal or heat-affected zone (HAZ). The following factors play a major role in the formation of cold cracks:

1. A residual tensile stress on the weldment.
2. Sufficient hydrogen introduced during welding.
3. A susceptible microstructure.

The susceptibility of steels to hydrogen embrittlement generally increases with strength level, and cold cracking is usually associated with hard microstructures in welds. For example, it is well known that martensitic cracks, and this tendency increases with carbon content and hardness (Ref. 1). However, the microstructure also has an effect on hydrogen susceptibility in steels of the same hardness (Ref. 2). Therefore, it is not always possible to use steels with a low strength and softer microstructure, because some are susceptible to hydrogen-induced failure in spite of their low hardness (Ref. 3).

Small cracks in electroslag welds (ESW) which were observed recently both in the field and laboratory may be a result of a soft and susceptible microstructure (Ref. 4-7). In general, the hydrogen level at temperatures when cold cracks form is expected to be very low in these high heat input welds. The cracks in ESW metal have been observed almost entirely in the proeutectoid ferrite network which outlines the prior-austenite grain-boundaries, and hence are referred to as grain-boundary separations. It has been shown that these grain-boundary separations are hydrogen-induced cracks and that the critical hydrogen content for the occurrence of such separations is a function of both restraint and cooling rate of the weldment (Ref. 4-7). Similar cracks along the prior-austenite grain-boundaries, have been frequently observed in weld metal microstructures which simulate those found in arc welds (Ref. 1).

The discovery of hydrogen-induced cracks in ESW metal caused concern about the use of electroslag welding for critical applications such as tension members in bridges (Ref. 4). To make this economical welding process sufficiently reliable for such critical applications, the effect of variables such as hydrogen concentration, microstructure, and residual stress in the grain-boundary separation mechanism should be measured.

The purpose of the present study of the sensitivity to hydrogen of ESW metal was:

1. To determine hydrogen levels required to cause ductility loss in weld metal as a function of temperature, and
2. To study fracture paths and failure modes in an attempt to identify embrittlement mechanisms.

Experimental Procedures

Materials

The ESW metal used in this study was cut from a weldment made in the laboratory of the Dominion Bridge Co., Canada. The weld joined ASTM A36 steel plates 64 mm (2.5 in.) thick with a weld gap of 25 mm (1 in.) using an AWS EH14-EW electroslag electrode and Linde 125 flux (dry) in a dry atmosphere. Welding current and voltage were 600 amperes (A) and 40 volts (V), respectively. The chemical composition and mechanical properties of the weld metal are given in Table 1.

Specimen Preparation

Miniature Hounsfield tensile specimens of gauge diameter 3 mm (0.126 in.) were machined from the weld metal at locations shown in Fig. 1. The tensile axis of each specimen was in the welding direction.

Cathodic Charging and Hydrogen Analysis

The gauge length of the electropolished tensile specimen of the weld metal was cathodically charged with hydrogen in a solution of 0.1 N H2SO4 with 0.2 mg/L of As2O3 as poison. The solution was heated to 80°C (176°F) to promote

<table>
<thead>
<tr>
<th>Table 1—Composition and Mechanical Properties of Weld Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical analysis, wt-%:</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>P</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Mechanical properties:</td>
</tr>
<tr>
<td>0.2% P.S., MPa</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
</tr>
<tr>
<td>Elongation, %</td>
</tr>
</tbody>
</table>
hydrogen diffusion and homogenization, and was continuously stirred.

In a previous study on HSLA steel it was found that for this specimen size and charging conditions, homogenization occurred in 2 hours (h) (Ref. 8). Specimens were charged for this time at current densities of 5, 25 and 50 mA/cm² to obtain a range of hydrogen levels (≈1, ≈3, and ≈8 ppm respectively). Hydrogen content was measured by cutting out the gauge section with an abrasive wheel and extracting the hydrogen by heating under vacuum; care was taken not to lose any hydrogen during handling. Three sets of test specimens were charged, and immediately stored in liquid nitrogen until tested.

Tensile testing

Tensile tests of both charged and uncharged specimens were performed at a nominal strain rate of $3.7 \times 10^{-4}$ sec⁻¹ on an Instron testing machine, at temperatures between -100 and 135°C (−148 and 275°F). The test temperatures were obtained by immersing specimens in heated baths of nitrogen-agitated heavy oil for testing above ambient temperature, and nitrogen-agitated methylbutane immersed in a bath of boiling liquid nitrogen for tests between 0 and -100°C (32 and -148°F). Charged specimens tested above ambient temperature were electroplated with a thin layer of cadmium to prevent hydrogen loss during testing.

The reduction in area of the fracture surface was calculated from measurements on the specimens, using a binocular microscope. Hydrogen determination by vacuum extraction was made for each condition of charging, using half of each broken tensile specimen. The average values are given in Table 2. Some uncharged specimens were analyzed to check for residual hydrogen in the as-welded metal; the result was zero ±0.5 ppm.

Table 2—Hydrogen Analyses of Broken Tensile Specimens

<table>
<thead>
<tr>
<th>Current density, mA/cm²</th>
<th>Hydrogen level, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.9 ± 0.5</td>
</tr>
<tr>
<td>25</td>
<td>2.7 ± 0.5</td>
</tr>
<tr>
<td>50</td>
<td>6.8 ± 1.0</td>
</tr>
</tbody>
</table>

Metallography

The microstructure of the ESW metal was examined both by optical microscopy and SEM. Selected fractures were examined by SEM. Longitudinal sections of some broken tensile specimens were also examined by optical microscopy and SEM.

Experimental Results

Tensile tests

The effect of hydrogen on the stress-strain curve of the ESW metal is shown in Fig. 2. The effect of hydrogen content and test temperature on reduction in ductility as measured by the true fracture strain ($\varepsilon_u$) is shown in Fig. 3. It is evident that with increasing hydrogen content ($C_H$) there is an increase in ductility loss and a widening of the temperature range where hydrogen embrittlement occurs in the ESW metal.

The effect of 3 ppm hydrogen on yield and flow stresses is shown in Fig. 4. Hydrogen increases both stress levels, at least over the temperature range shown. Other hydrogen contents give similar results, although the scatter is greater at $C_H$ ≈ 1 ppm.

Metallography

The microstructure of the ESW metal consists of pro-eutectoid ferrite; this outlines the prior austenite ($\gamma$) grain-boundaries, and acicular ferrite/pearlite within the massive (columnar) prior $\gamma$ grains—Fig. 5. Cross sections of tensile specimens were found to contain a minimum of three prior $\gamma$ grains.

SEM examination revealed that the constituents unresolved optically, primarily near prior $\gamma$ grain-boundaries (Fig. 5B), are mainly pearlite colonies containing fine lamellae—Fig. 6A. This indicates that the pearlite has formed at low temperatures in spite of the low cooling rate of the ESW weld. Pearlite nucleation has likely been inhibited by the large grain size of the parent austenite. SEM examination also showed that the acicular ferrite in the prior $\gamma$ grains were interspaced with carbide lamellae—Fig. 6B. The MnS inclusions were of globular shape, randomly distributed in the weld metal.

All uncharged specimens had ductile fractures. SEM fractography showed non-metallic inclusions at the bottom of some microvoids, which is a common feature of fracture by microvoid coalescence. SEM fractography of hydrogen-charged specimens ($C_H$ ≈ 1 ppm) showed the following as test temperature is increased:

1. At -50°C (-58°F), hydrogen-assisted “quasi-cleavage” facets originate at inclusions (Fig. 7A), and the final fracture occurs by shear failure at an angle to the tensile axis.
2. At 0°C (32°F), the fracture was...
Fig. 3 — Effect of test temperature \( T \) and hydrogen content \( C_H \) on true fracture strain \( \varepsilon_f = \ln (A_0/A_f); A_0 \) and \( A_f \) are initial and final cross-section areas, respectively.

Fig. 4 (right) — Effect of test temperature \( T \) and hydrogen (\( C_H \sim 3 \) ppm) on: \( A - 0.2\% \) proof stress (P.S.); \( B - 1\% \) flow stress (F.S.)

3. At 25°C (77°F), hydrogen-assisted microvoid coalescence — Fig. 7C.

Similar fracture modes were observed at larger \( C_H \) values, although the effect of hydrogen was more severe; the grain-boundary separation mode which gives maximum embrittlement was extended over a wider temperature range. Figure 8 shows a fracture where grain interior (region B) and grain-boundaries (region A) of the prior \( \gamma \) grains are clearly distinguished. SEM fractographs of the prior \( \gamma \) grain-boundaries (A) and the prior \( \gamma \) grains (B) of Fig. 8 are shown in Fig. 9. The fracture may be classified as of the "quasi-cleavage" type, i.e., predominantly cleavage accompanied by substantial plastic deformation evidenced by tear ridges.

Examination of longitudinal sections of broken tensile specimens confirmed that those with grain-boundary fractures predominate, had regions where the fracture path was along grain-boundary proeutectoid ferrite — Fig. 10A. Subsidiary crack formation is also evident, and shows preferential plastic deformation in these regions — Fig. 10B. SEM examination showed that the subsidiary crack paths in general appear to follow ferrite-pearlite or ferrite grain-boundaries — Fig. 11.

**Discussion**

**Reduction in Ductility**

The results given in Fig. 3 are shown in the form of an "embrittlement index" \( E_I \) in Fig. 12 — that is, \( E_I = (\varepsilon_0 - \varepsilon_f)/\varepsilon_0 \), where \( \varepsilon_f \) is true fracture strain, and subscripts u and c designate uncharged and charged conditions respectively. The limited temperature range of hydrogen embrittlement has been observed in mild (Ref 9), medium (Ref. 8, 10), and high strength (Ref. 11) steels. It has been ascribed by the present authors to the upper limit of the temperature range has been found to be independent of the strain rate, and hence hydrogen would not be expected to cause embrittlement above that at the corresponding \( C_H \) levels (Ref. 10, 12).

It may be deduced from these results that a hydrogen content of 1 ppm in the weld metal at ambient temperature can result in a form of delayed failure if sufficient restraint is present. The work of Boniszewski, et al. shows that hydrogen embrittlement as measured by the reduction in ductility in a slow tensile test at ambient temperature also causes delayed failure in a constant load rupture (CLR) test (Ref. 13). The CLR test is better than a slow tensile test at ambient temperature for comparing the susceptibility of similar microstructures, but it takes more time.
It has often been suggested in the past that in the presence of nonmetallic particles or films on boundaries, cracking can occur in weld metal during solidification, commonly known as "hot cracking" or "burning" (Ref: 1). Where the impurities are not at a sufficiently high level for this to occur, hydrogen cracks can occur along these boundaries. However, a recent study of electroslag welds has shown that prior γ grain-boundary separations are not related to solidification boundaries (Ref: 7). Microprobe analysis performed in the present work gave no evidence of impurity (sulphur or phosphorus) being present in sufficient quantities to cause cracking.

Grain Boundary Separations

This feature was studied in depth, since it is the main form of cracking in electroslag weldments (Ref: 5, 7). In the present study, maximum embrittlement of the ESW metal was found when the fracture was primarily along prior γ grain-boundaries.

It has been generally accepted that internal hydrogen embrittlement results from hydrogen transport to susceptible sites such as inclusions, interfaces, grain boundaries, etc. However, it is now recognized that different mechanisms may operate depending on composition, microstructure, density and type of trap sites, and even test conditions, and that a unique "hydrogen fracture mode" does not exist (Ref: 2, 15).

In A36 steel, hydrogen increases both yield and flow stresses over the temperature range studied—Fig. 4. This effect is consistent with a hydrogen-dislocation interaction of the classic type with hydrogen atoms being dragged by mobile dislocations (Ref: 16). The possible transport of hydrogen by mobile dislocations to sites of fracture nucleation is discussed by Tien (Ref: 17); the other explanation for hydrogen transport is bulk diffusion.

The fractographic studies of this work showed three distinct forms of hydrogen-assisted fracture: quasi-cleavage facets nucleating at inclusions (Fig. 7A), prior γ grain-boundary separations (Fig. 7B), and hydrogen-assisted microvoid coalescence (Fig. 7C).

1. The quasi-cleavage facets observed around inclusions at test temperatures below maximum embrittlement may be caused by hydrogen transport to inclusions. Subsidiary cracks formed at inclusions were found to be normal to the tensile axis and do not appear to follow any microstructural features.

2. The prior γ boundary separations occurred at test temperatures which gave maximum embrittlement, (discussed in detail below under separate heading).

3. Hydrogen-assisted microvoid coalescence may occur by assisting either void nucleation which leads to a decreased dimple size or void growth which leads to increased dimple size (Ref: 18). No attempt was made in the present work to perform the extensive quantitative fractographic work to identify which mechanism operated in the present case.

The above fracture modes were found in specimens where cathodic charging caused no permanent damage (i.e., CH up to 3 ppm) as confirmed by full recovery in ductility of an outgassed specimen (see Fig. 3).
Table 3—Results of a Micro-Hardness Survey on ESW Metal

<table>
<thead>
<tr>
<th>Region</th>
<th>Prior γ grain (acicular ferrite)</th>
<th>Prior γ grain-boundary (pro-eutectoid ferrite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VHN</td>
<td>201</td>
<td>156</td>
</tr>
</tbody>
</table>

have a substantially higher fracture transition temperature than the relatively fine acicular ferrite/pearlite structure of the prior γ grain-interior. This could be a factor in causing embrittlement at higher temperatures than for the tougher HSLA steel at similar hydrogen concentrations (Fig. 13), because hydrogen-induced crack paths can control susceptibility (Ref. 3).

Of the factors that play a major role in forming cold cracks, it is clear that the microstructure of the ESW metal is responsible for cracks forming along prior γ grain-boundaries. Reduction of hydrogen sensitivity may be possible by refinement of the crack path microstructure, i.e., the grain-boundary pro-eutectoid ferrite region (Ref. 3), although this may not be sufficient to eliminate grain boundary separations.

Reducing the grain-boundary ferrite constituent of the weld metal microstructure may be achieved by lowering the γ → α transformation temperature by either increasing the cooling rate or alloying (Ref. 21-23). The former is not a feasible method in this case. Alloying with elements such as Mn, Mo, Ni and Cr suppresses grain-boundary pro-eutectoid ferrite formation in favour of fine-grained structures in the prior γ grain-interior, such as acicular ferrite, and may be achieved with the same welding conditions (Ref. 22,23). The commonly known low-hydrogen welding techniques or low external restraint can also be used. Low-hydrogen techniques have

![Figure 9](image1.png)

**Fig. 9**—SEM fractographs of (A) prior γ grain-boundary, A, and (B) prior γ grain, B, in Fig. 8.

![Figure 10](image2.png)

**Fig. 10**—Optical micrographs of longitudinal sections of fractured specimens, charged to CH = 8 ppm: A—tested at −40°C (−40°F), showing portion of the fracture profile, X200, B—tested at −90°C (−130°F), showing a subsidiary crack, X500 (A and B reduced 50% on reproduction).

![Figure 11](image3.png)

**Fig. 11**—SEM micrograph of a grain-boundary separation in specimen with CH = 8 ppm tested at −90°C (−130°F).

![Figure 12](image4.png)

**Fig. 12**—Variation of embrittlement index EI with test temperature T at CH = 1, 3, and ~ 8 ppm.

![Table 3](image5.png)

**Table 3**—Results of a Micro-Hardness Survey on ESW Metal

- **Region**: Prior γ grain (acicular ferrite), Prior γ grain-boundary (pro-eutectoid ferrite)
- **VHN**: 201, 156

When strong traps are present, such as in martensitic/bainitic structures, there is only partial recovery in ductility after mild degassing treatments (Ref. 8, 19); in contrast the ESW metal recovered fully after this treatment—Fig. 3. The increase in yield and flow stresses is evidence of hydrogen-dislocation interaction—Fig. 4. This effect was not observed in martensitic/bainitic structures because of the large density of trap-sites where most of the hydrogen is immobilized (Ref. 8). This suggests that most of the hydrogen is available for transport either by dislocations or bulk diffusion to sites of fracture nucleation in the ESW microstructure.

Fractography of the grain-boundary separations shows cleavage accompanied by substantial plastic deformation. In the grain-boundary regions containing the softer pro-eutectoid ferrite (Table 3) (Ref. 1, 5), preferential plastic deformation can occur under application of stress. As discussed earlier, hydrogen is available to diffuse to these regions when cracks form. Hence, grain-boundary separations can occur more readily with a microstructure having an inherently susceptible crack path in the grain-boundary pro-eutectoid ferrite and the adjacent pearlite, than with the more refined acicular ferrite/pearlite structure of the prior γ grain-interior—Fig. 5A. This supports the view that the effect of hydrogen increases where there are pre-disposed fracture paths (Ref. 3, 15).

Crack paths of similar morphology following ferrite-pearlite boundaries were observed in banded line-pipe steels (Ref. 20). In this instance, however, the effect appears to be due to preferential hydrogen segregation. It should be noted that the coarse ferrite and pearlite grains outlining the prior γ grain-boundaries will

![Image 1](image1.png)

**Fig. 13**—SEM microwave of a grain-boundary separation in specimen with CH = 8 ppm tested at −90°C (−130°F).
been effective in eliminating grain-boundary separations in electroslag welds produced in the laboratory (Ref. 7).

Conclusions

The effect of internal hydrogen on the fracture behaviour of ESW metal obtained from a weldment of ASTM A36 steel plate, has shown the following:

1. At C_H of 1 and 3 ppm, the upper limits of the temperature range for hydrogen embrittlement are 55 and 145°C (131 and 293°F) respectively. Further increase in C_H only marginally increases this temperature. The temperature of maximum embrittlement is −10°C (14°F) at C_H ~ 1 ppm, and 30°C (86°F) at C_H ~ 3 ppm.

2. Three distinct modes of hydrogen-assisted fracture occur as test temperature is increased; these are: "quasi-cleavage" at inclusions, grain-boundary separation, and microvoid coalescence. The embrittlement index is largest for the grain-boundary separation mode.

3. At similar C_H values, the weld metal has a substantially higher temperature of maximum embrittlement than a HSLA direct-quenched steel (of low hydrogen susceptibility). Consequently, the upper limit of the temperature range for hydrogen embrittlement is higher than in the HSLA steel.

4. Slow strain-rate tensile tests confirm that hydrogen can cause prior γ grain-boundary separations, previously only observed in electroslag weldments.

5. Internal hydrogen increases both yield and flow stresses at temperatures where hydrogen embrittlement occurs.

Acknowledgments

The authors wish to thank NSERC and EMR of Canada for award of a Fellowship to L.N.P., and the staff at PMRL, EMR who have contributed to this work—in particular, Dr. J.D. Boyd for comments on the manuscript. We are also grateful to Dominion Bridge Co., Canada, for the material and information, and also for useful discussions.

References


