Hydrogen Attack Behavior of the Heat Affected Zone of a 2.25Cr-1Mo Steel Weldment

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The kinetics of hydrogen attack (HA) has been studied in the heat affected zone (HAZ) in a 2.25Cr-1Mo steel weld to determine the relative rates of attack of bubble nucleation in the HAZ, base metal, and weld metal. The HAZ was found to suffer hydrogen attack at nearly twice the rate of the base metal, but not as rapidly as the weld metal. Nucleation of bubbles does not occur during HA of the HAZ of a 2.25Cr-1Mo steel, on exposure to hydrogen pressure of 20.5 MPa or less, but does occur at higher pressures up to 31.5 MPa (4500 psi) at 550 °C, or up to 27.5 MPa (4000 psi) at 580 °C. Such nucleation results in enhancement of the HA rate by a factor of six. The weak dependence of nucleation effects on hydrogen pressure and the saturation of the nucleation effects in a short time suggest some thermally activated nucleation of fresh bubbles.

I. INTRODUCTION

HYDROGEN Attack (HA) is a form of material degradation that occurs in steels exposed to high temperature (over 250 °C), high pressure (over 2 MPa) hydrogen. Reaction between hydrogen and the carbon in the steel results in the formation of methane bubbles, which nucleate and grow preferentially along grain boundaries. After a long incubation time the steel loses its room temperature mechanical properties (in carbon steels) or its creep ductility (in 2.25Cr-1Mo steels). Additions of stable carbide formers such as Cr and Mo result in a substantial increase in HA resistance. Of the steels developed 2.25Cr-1Mo is the leanest alloy with good HA resistance. It has been widely used in the industry and is a potential structural material for future applications.

Dilatometric measurements on the kinetics of HA of carbon and 2.25Cr-1Mo steels have been made by several investigators. Analysis of these dilatometric data suggests that the high HA resistance of 2.25Cr-1Mo steels compared to carbon steels is chiefly due to the lower bubble density that it develops. The analysis shows that HA kinetics depend sensitively on the bubble density. Transmission electron microscope replica work by Lopez and Shewmon has shown that the bubble density in 2.25Cr-1Mo steels is determined directly by the density of pre-existing microvoids. This work also indicated that no new bubbles nucleated during HA at 550 °C and 20.5 MPa. However, Thygeson and Molstad reported that exposure of this steel to much higher hydrogen pressures of 100 MPa (15 ksi) at 500 °C (for 1700 hours) leads to a high density of bubbles on the grain boundaries. In carbon steels where the carbon activity is 10 times higher, such active nucleation of new bubbles takes place at 3 MPa of hydrogen at 450 °C, which translates to an equilibrium methane pressure of 380 MPa. If the methane pressure for active bubble nucleation in 2.25Cr-1Mo steel was the same as that found in carbon steel, one would expect an increase in bubble density on exposure to 25 to 30 MPa of hydrogen at 550 to 580 °C.

It has been shown by many workers that in carbon steels plastic strain prior to HA greatly increases the density of bubbles, especially along grain boundaries. There has been less study of this effect in 2.25Cr-1Mo steel, but our understanding of the mechanism in carbon steel, and the enhanced nucleation of voids in creep samples as a result of prior strain, strongly suggest that prior strain would also increase the rate of HA in 2.25Cr-1Mo steel.

Limited work on the HA of the 2.25Cr-1Mo weld metal shows that it is hydrogen attacked faster than the wrought base metal, primarily as a result of the higher density of bubbles that develop in the weld metal due to higher density of pre-existing voids. This higher density could stem from plastic strain in the weld metal or an inherently higher density of inclusions; the cause is unclear.

Reports of the nature of hydrogen attack in the heat affected zone (HAZ) are varied and contradictory. Stress relief cracking by 'intergranular microvoid coalescence' has been reported in the HAZ of 2.25Cr-1Mo steel, suggesting incipient microvoids on the boundaries in this region. One paper on HA in the HAZ reports a bubble density more than 16 times higher than in the base metal, while another reports no effect at all. Masaoka et al. coarsened the austenite grain size of 2.25Cr-1Mo steel, called it a 'simulated HAZ' and reported essentially no change in HA kinetics. We are uncertain of the merits of using such a simulated HAZ since it would contain neither the strains that occur in a real weld HAZ due to temperature gradients, nor the high residual stresses.

The present study attempts to answer the following questions:

1. How do the kinetics of HA of the HAZ compare with that of the base metal and the weld metal of a 2.25Cr-1Mo weldment?
2. Can nucleation during HA be induced in the HAZ of a 2.25Cr-1Mo weldment by higher hydrogen pressures, i.e., above 21 MPa?

II. EXPERIMENTAL

PROCEDURE AND RESULTS

The material studied was a commercial multi-pass Shielded Metal Arc Welding (SMAW) weldment of a
Table I. Chemical Composition (Wt Pct)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cu</th>
<th>As</th>
<th>Sb</th>
<th>Sn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>0.13</td>
<td>2.32</td>
<td>0.98</td>
<td>0.51</td>
<td>0.006</td>
<td>0.008</td>
<td>0.25</td>
<td>0.13</td>
<td>0.031</td>
<td>0.002</td>
<td>0.012</td>
<td>0.019</td>
</tr>
<tr>
<td>Weld</td>
<td>0.055</td>
<td>2.42</td>
<td>1.01</td>
<td>0.69</td>
<td>0.010</td>
<td>0.012</td>
<td>0.30</td>
<td>0.14</td>
<td>0.022</td>
<td>0.002</td>
<td>0.012</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Accordingly, nucleation in the HAZ was studied by following the kinetics of growth of the sample as a function of increasing hydrogen pressure at 550 °C. The HA rates were studied at hydrogen pressures of 20.5, 24.5, 28, and 31 MPa (3000, 3550, 4050, and 4500 psi). On returning to a pressure of 24.5 MPa (3550 psi) of hydrogen it was found that the HA strain rate had doubled, from 20 to 39 × 10⁻⁸/hr. This is clear indication of nucleation during the preceding high pressure treatment. The HAZ sample was then studied at a higher temperature of 580 °C at different hydrogen pressures and a similar effect was observed. On returning to 550 °C and 20.5 MPa (3000 psi) of hydrogen the HA rate was found to be 71 × 10⁻⁸/hr, more than six times the original value (11 × 10⁻⁸/hr). The dilatometric strain rates measured at various temperatures and hydrogen pressures are tabulated in Table II, in the sequence of exposure.

B. Metallography

The sample was prepared for metallography after the dilatometric study and a scanning electron micrograph of the hydrogen attacked sample is shown in Figure 2. The bubbles were nearly spherical and distributed preferentially (10:1) along the grain boundaries, suggesting grain boundary diffusional growth. However, a few bubbles were also found to form along interfaces of inclusions, as shown in Figure 3. The elongated inclusions were identified as MnS particles using Energy Dispersive Analysis system. Montage micrographs were used to count manually the number of bubbles for an area of nearly 191,000 square microns. The bubble density thus obtained was 6 × 10⁻³ per square micron. As seen from Figure 2, roughly one out of four grain boundaries was cavitated, and the bubbles are spaced nearly 10 microns apart.

![Diagram](image)

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Fig. 1 — Outline of specimen preparation for capacitance study of HAZ of 2.25Cr-1Mo steel weldment.