The Role of Aging Reactions in the Hydrogen Embrittlement Susceptibility of an HSLA Steel

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Hydrogen embrittlement susceptibility, as measured from room temperature precharged tensile specimens, indicates that the type, extent, and morphology of carbide precipitation are all important in determining the degree and mode of degradation. At equivalent charging conditions, embrittlement is virtually eliminated by aging to produce fine scale clustering of Ti(C, N), even when concurrent with cementite precipitation. High temperature aging (> 500 °C) results in exclusive precipitation of the alloy carbide, but also in a total loss of ductility due to a fracture mode transition to intergranular. This is shown to be associated with metalloid (P, S) segregation to grain boundaries accompanying depletion of Ti in solution. Intermediate behavior is observed in microstructures produced by high temperature quenching or aging at temperatures (~ 400 °C) where only cementite precipitation is observed.

I. INTRODUCTION

RECENTLY, much of the research on the hydrogen embrittlement susceptibility of metals and alloys has centered on the role of metallurgical variables. This emphasis is an outgrowth of the better emerging picture of the basic physical parameters which govern the manifestation of hydrogen embrittlement in many systems. Although some mechanistic models have been suggested, no single mechanism is yet satisfactory in explaining the range of hydrogen effects, particularly in ferrous alloys.

As stated above, there have been several recurring phenomenological features of hydrogen embrittlement identified, such as temperature dependent ductility minima, an inverse strain rate effect on ductility, and three stage ln(ν) vs $K_I$ hydrogen induced crack growth dependence. These and other observations have led to the general premise that the embrittlement step is preceded by localized transport of hydrogen to incipient failure initiation sites such as re-entrant crack tips, inclusions, and grain boundaries. This step may be particularly detrimental in bcc metals such as iron, due to the relatively high diffusivity (approximately $10^{-6}$ cm$^2$ per second at 25 °C) and low equilibrium solubility (0.01 ppm at 25 °C) in the lattice. Previous measurements of these parameters have been complicated by the effects of hydrogen “trapping” at microstructural features such as grain boundaries, dislocations, second phase particles, voids, and interstitial solute atoms. Attempts have been made to correlate the susceptibility of alloys to hydrogen embrittlement with independent determinations of such trapping parameters. Although certain of the above-mentioned traps will act as failure initiation sites (e.g., grain boundaries), it has also been suggested that the detrimental effects of internal hydrogen may be ameliorated by the proper control of a benign trapping population. Such a trapping density would either preclude the accumulation of critical hydrogen concentrations at incipient failure initiation sites by maintaining a distributed hydrogen profile, or it could delay the onset of hydrogen embrittlement to higher bulk concentrations at longer times.

Specifically, Pressouyre and Bernstein have studied the hydrogen trapping and embrittlement susceptibility of a number of Fe-Ti-C alloys with varying Ti:C ratios. Through the use of electrochemical permeation techniques and analyses, these authors characterized Ti substitutional atoms as low occupancy reversible trap sites with an interaction energy of 0.27 eV (~ 30 kJ/mol). Incoherent TiC particles, on the other hand, were found to be larger occupancy, irreversible trap sites with an interaction energy of 0.98 eV (~ 100 kJ/mol). Embrittlement susceptibility determinations led to the conclusions that an alloy consisting of fine, homogeneously distributed, irreversible traps (TiC) possessed the greatest resistance under dynamic and static testing conditions whereas reversible traps (Ti substitutional atoms) were found to give detrimental effects under dynamic conditions by acting as an additional internal hydrogen source and beneficial effects under static conditions, by acting as an additional hydrogen trap.

In a previous paper, the authors reported on the correlation of embrittlement susceptibility with trapping in an HSLA steel of nominally identical composition to that of the present paper. It was indeed found that deep trapping of hydrogen was associated with the precipitation of fine (20 to 40 Å) TiC particles. Combined with the strong, ductile properties of the highly dislocated, fine ferrite lath structure, microstructures containing these precipitates displayed enhanced ductility under conditions where internal hydrogen was present during uniaxial loading. Furthermore, these traps were found to be saturable under the given charging conditions, returning the microstructure to a highly susceptible condition after overcharging.

The highly reactive nature of Ti has concurrently prompted studies to evaluate its use to offset the temper embrittlement of steels due to segregation of phosphorus to grain boundaries. Since titanium is known to have a highly attractive interaction energy with P and forms stable phosphides, a beneficial scavenging effect is predicted. However, extended period exposure to temperatures ≥ 500 °C may lead to formation of the more stable carbide phase, release of the phosphorus, and perhaps subsequent embrittlement. In such a case and if the precipitation of the
alloy carbide phase results in segregation of P, then the presence of temper embrittlement could offset or even cancel any beneficial effects of deep hydrogen trapping at the carbide interfaces.

However, it has been suggested that if phosphorus can be effectively trapped at TiC particle interfaces in analogy with the hydrogen trapping case, then controlled precipitation of this phase should result in enhanced hydrogen and temper embrittlement resistance simultaneously.

In a recent study, part of which is the subject of the present paper, a titanium bearing HSLA steel was chosen in order to study the effect of aging condition on hydrogen trapping and embrittlement susceptibility. In this case, since the stoichiometry was fixed, the type and extent of carbide precipitation was varied by using different aging temperatures. It will be seen that the mechanical and trapping response of the steel to moderate hydrogen charging was markedly dependent on the extent of TiC precipitation for a variety of reasons.

II. MICROSTRUCTURES AND AGING REACTIONS

All materials for this study were taken from a single heat of experimental HSLA steel prepared as a 45 kg ingot, hot-rolled from a temperature of 1260 °C to a thickness of 25 mm. The chemical composition of this heat is given in Table I. Standard tensile specimens from the as-received plate were subsequently reheated to 1200 °C for 1 hour, water quenched, and aged for 1 hour at temperatures between 400 °C and 900 °C.

The microstructure produced as a result of the quench from 1200 °C is shown in Figure 1. This acicular ferrite matrix was characterized by a high dislocation density and a mean ferrite lath width of 0.5 μm. These two factors are commonly associated with the high ductility, smooth yielding, and moderately high strength common in these steels.

No evidence for cementite or alloy carbide phases was found in these as-quenched microstructures as a result of auto-tempering.

Aging at 400 °C led to the nucleation of cementite at lath boundaries, as shown in Figure 2. The associated loss of carbon from the matrix resulted in a decrease in hardness, as is common during the precipitation of carbide in iron-carbon martensites. The progress of this precipitation can be seen in Figure 3 which summarizes the time dependence of the isothermal aging response at 400 °C, 500 °C, and 550 °C. A slight increase in hardness can be observed after aging at 400 °C for aging times greater than 10,000 seconds. This most likely is associated with Ti(C, N) clustering, although no direct evidence for this was obtained.

Table I. Chemical Composition of HSLA Steel (Wt Pct)

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Al</th>
<th>V</th>
<th>Ti</th>
<th>N</th>
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<td>0.050</td>
<td>1.30</td>
<td>0.005</td>
<td>0.028</td>
<td>0.31</td>
<td>0.003</td>
<td>&lt;0.002</td>
<td>0.22</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Fig. 1 — TEM micrograph of as-quenched microstructure of HSLA steel. Note fine lath size and heavily dislocated substructure.

Fig. 2 — Grain boundary precipitation of cementite after aging 1 h at 400 °C: (a) bright field and (b) centered dark field.