EFFECT OF HEAT TREATMENT ON FRACTURE OF TYPE 304L STAINLESS STEEL IN A HYDROGEN ENVIRONMENT

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ABSTRACT

Thermal treatments have a significant effect on the mechanical behavior of Type 304L stainless steel tested in a high-pressure (69 MPa) hydrogen environment. A grain size increase from 10 to 350 μm increased susceptibility to hydrogen damage and accentuated changes in fracture morphology. The Hall-Petch relation for yield strength was the same for tests in both hydrogen and helium environments. Sensitization increased ductility loss in hydrogen but did not change the fracture mode of smooth bar tensile specimens. Variation in quench rate from 0.25 to 50 K/sec had only a minor influence on susceptibility to hydrogen embrittlement. The absence of an abrupt load drop at fracture and change in fracture morphology for tests in high-pressure hydrogen indicate that fracture initiated at or near the surface and rapidly propagated inward.

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INTRODUCTION

The mechanical behavior of austenitic stainless steels is progressively degraded in a hydrogen environment with increasing exposure time and hydrogen pressure up to pressures of about 12 MPa. Hydrogen-assisted fractures occur following deformation in a hydrogen environment or during testing in air after a prior exposure to hydrogen. In both cases, significant plastic deformation precedes failure and appears to be a necessary precursor to hydrogen-assisted fracture in austenitic steels. Changes in fracture appearance exist in those austenitic steels most severely degraded by hydrogen. These observations suggest that initial microstructure, deformation modes, and their various interactions are key factors in the mechanism of hydrogen-assisted fracture of austenitic steels. The effect of composition, mechanical working, and heat treatment on the susceptibility of austenitic steels to hydrogen damage is a continuing study because these processes develop and control the microstructure. The effects of heat treatment, temperature, quench rate, and surface finish on hydrogen embrittlement of Type 304L stainless steel alloy are reported in this paper.

MECHANICAL PROPERTIES

The mechanical properties and fracture of Type 304L stainless steel were investigated as a function of heat treatment for deformation in high pressure hydrogen and helium environments. Tensile specimens, 0.48-cm diameter by 2.5-cm long, were machined
from fine-grained (~10 μm average grain size) bar stock. Larger grain sizes of 30 to 40, 60 to 100, and 350 μm were obtained by vacuum annealing specimens for 24 hr at 1170, 1270, and 1470 K, respectively, followed by rapidly cooling to avoid sensitization. Typical microstructures are shown in Figure 1. A pair of specimens with grain diameters of ~10 μm were sensitized at 920 K to establish the influence of this condition on behavior in hydrogen. All of the specimens were pulled to failure either in 69 MPa hydrogen or 69 MPa helium at room temperature with the results shown in Table I.

The grain-size dependence of the yield strength, stressed at a plastic strain of 0.05, followed the Hall-Petch relation

\[ \sigma_{0.05} = \sigma_i + k_d^{-1/2}. \]

There was no significant effect of test atmosphere on the Hall-Petch parameters (\( \sigma_i \) and \( k_d \); Figure 2). Furthermore, the sensitization anneal did not alter grain size or affect yield strength.

Ductility loss, \([\text{RA(He)} - \text{RA(H}_2\text{)}]/\text{RA(He)}\), increased from 10% (for grain sizes of 10 and 40 μm) to 20 to 30% for the larger grain sizes (>60 to 90 μm), (Figure 3). Neither uniform nor total elongation was reduced by testing in a hydrogen environment. Vacuum annealing at high temperature increased uniform elongation from 55% to about 85%; but there was no direct correlation with grain size. Therefore, an external hydrogen environment does not affect either plastic deformation or formation of strain-induced α'-martensite — processes which
control uniform elongation. Hydrogen does, however, affect the nature and microstructural details of fracture, thus reducing necking strain and reduction-in-area.

Factors other than grain size had a significant effect on ductility. The sensitization anneal resulted in a decrease in alloy ductility in hydrogen with no change in the grain size. Cooling rate had a minor effect on the ductility of specimens annealed at 1170 K and tested in hydrogen (Table II). The more rapid cooling achieved by immersing in UCON-C® coolant (50 K/sec) appeared to have produced slightly higher ductility. The data in Table II are not directly comparable to those in Table I for 1170 K annealing temperature, as the time at temperature was only 5 minutes rather than 24 hours.

Surface condition also influenced the ductility of specimens tested in hydrogen (Table II), an effect that has been noted before. Ductility (true strain-to-fracture) of a specimen with an as-machined surface was only about 80%, in contrast to about 90% for an electropolished specimen and for a specimen tested in helium. The ductility of electropolished specimens tested in hydrogen was reduced to 85% by coating the specimen surface with palladium. The lower ductilities of the as-machined and palladium-coated surfaces have been attributed to the presence of α'-martensite and a more rapid absorption of hydrogen, respectively.
FRACTOGRAPHY

Ductile failure by normal and shear rupture was observed on specimens tested in helium (Figure 4). Void coalescence proceeded across the central portions of all these specimens and was terminated by catastrophic shear-lip formation corresponding to the vertical drop in load at failure (Figure 5). In contrast, fractures occurring in hydrogen environments formed irregular surfaces with a pronounced crystalline appearance (Figure 6). The load drop at failure, while rapid, was not instantaneous as observed in the tests in helium environments. Void coalescence was observed in a few limited regions of the fine-grained specimens (10 and 40 μm) (Figure 5a), but was absent in the large-grained specimens (90 and 350 μm) (Figure 6b).

The alloy fractures occurring in hydrogen environments featured cracks and fracture surfaces nearly parallel to the tensile axis (Figure 6c). These surfaces had either a series of features suggesting the underlying microstructures of deformation and martensite bands or were smooth shear surfaces (Figure 6d). Faces of the cracks were not visible; but in many cases, they appeared to be forming along boundaries in the microstructure, such as twin boundaries or deformation bands, which were nearly parallel to the specimen axis (Figure 6b).

High-temperature annealing (1270 and 1470 K) also changed nucleation and growth of microvoids. The average dimple size was larger in the specimens heated to 1270 and 1470 K than that
in the specimens heated to 1170 K. Photomicrographs (Figure 7) show typical dimples on surfaces of specimens fractured in high-pressure helium environments.

Fractures of specimens sensitized by annealing were similar in overall appearance to the other failures (Figure 6a and 8a), except that these fractures were mostly by void coalescence. The dimples were shallow and elongated (Figure 8b), rather than deep and equiaxed as in the non-sensitized specimens. Intergranular fracture in these specimens was not evident, although intergranular fracture has been reported for notched Type 304 stainless steel after sensitizing 24 hours at 920 K and testing in low-pressure hydrogen environments (1). The difference in behaviors between the Type 304 specimens reported in the literature and the Type 304L specimens of this investigation may be attributed to the presence of the notch on the Type 304 specimens and their higher carbon contents which aggravates the effect of the sensitization treatment.

DISCUSSION

The load drop at failure and the absence of a central region of microvoid coalescence on the fracture surfaces of the specimens suggest that fracture in hydrogen propagates continuously from one or more nucleation sites at or near the surface. Cup formation at the center of a specimen in the necked region depends upon a state of triaxial tension. In these tests, there was a superimposed hydrostatic pressure of 69 MPa that would counterbalance
in part any triaxial tension in the specimen. This effect is not large enough to have a significant effect on fracture in 69 MPa helium environments and should not have had a significant effect in the case of hydrogen environments either. The reduction in void coalescence in fine-grained specimens and its absence in large-grained specimens must have been due to effects of hydrogen on fracture nucleation as well as on fracture path and mechanism.

Multiple fracture initiation at the external surfaces of the specimens tested in hydrogen environments is likely, as there were numerous surface cracks in the vicinity of the fractures. These surface initiation sites do not require the prior existence of martensite, as the fractures were similar for as-machined specimens (where martensite was present at the surface) as well as for electropolished or annealed specimens where no martensite was present. However, surface initiation sites were not numerous on as-machined surfaces.

Cracks propagate into the specimen simultaneously from several sites and finally link by shear fracture of the intervening ligaments, thus generating an irregular surface with nearly axial orientation to some faces. The inward propagation of these cracks apparently reduces the probability for void nucleation and growth in the interior of the specimen. The reason for a grain-size effect in this process is not clear. The inward propagation may be a direct effect of grain size or an effect of the high temperature anneal on the submicroscopic inclusions (or solute distribution) which, in turn, alters the fracture path.
These tests and related investigations conducted earlier emphasize the importance of processing history on resistance to hydrogen damage in austenitic stainless steels. Further investigation of heat treatment effects in Type 304L stainless steel will include notched as well as smooth bar tensile specimens and specimens saturated with hydrogen.

SUMMARY

Heat treatment had a significant effect on the mechanical properties of 304L stainless steel tested in a high pressure (69 MPa) hydrogen environment through changes in grain size and solute segregation. Observed effects were as follows:

- Ductility loss increased as the grain size increased.
- Fracture mode changes in hydrogen environments were more pronounced for larger grain sizes.
- Yield strength followed the Hall-Petch relation for grain size and was not affected by testing in hydrogen environments.
- Sensitization reduced the steel's ductility and caused an increased ductility loss in hydrogen environments that was not related to grain size.
- Sensitization did not change the fracture mode of smooth bar tensile specimens tested in hydrogen environments.
- Quench rate in the range of 50 to 0.25 K/sec had only a minor effect on susceptibility to hydrogen embrittlement.
- Surface treatment affected ductility in hydrogen environments.
TABLE I

Effect of Heat Treatment on Mechanical Properties of Type 304L Stainless Steel

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Test Atmosphere</th>
<th>Strength, MPa</th>
<th>Elong., %</th>
<th>Plastic Strain To Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Yield</td>
<td>Ultimate</td>
<td>Uniform</td>
</tr>
<tr>
<td>As-received</td>
<td>69 MPa He</td>
<td>390</td>
<td>930</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>69 MPa H₂</td>
<td>390</td>
<td>910</td>
<td>56</td>
</tr>
<tr>
<td>1170K-24 hrs.</td>
<td>69 MPa He</td>
<td>260</td>
<td>970</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>69 MPa H₂</td>
<td>240</td>
<td>970</td>
<td>88</td>
</tr>
<tr>
<td>1270K-24 hrs.</td>
<td>69 MPa He</td>
<td>250</td>
<td>970</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>69 MPa H₂</td>
<td>240</td>
<td>930</td>
<td>86</td>
</tr>
<tr>
<td>1470K-24 hrs.</td>
<td>69 MPa He</td>
<td>190</td>
<td>830</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>69 MPa H₂</td>
<td>180</td>
<td>830</td>
<td>84</td>
</tr>
<tr>
<td>920K-24 hrs.</td>
<td>69 MPa He</td>
<td>380</td>
<td>930</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>69 MPa H₂</td>
<td>380</td>
<td>940</td>
<td>57</td>
</tr>
</tbody>
</table>
### TABLE II

**Effect of Heat Treatment and Surface Condition on Hydrogen Environment Embrittlement of Type 304L Stainless Steel**

<table>
<thead>
<tr>
<th>Specimen Treatment</th>
<th>Test Environment</th>
<th>Strength, MPa</th>
<th>Elongation, %</th>
<th>Plastic Strain to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-machined</td>
<td>69 MPa H₂</td>
<td>370 910</td>
<td>60 66</td>
<td>1.52</td>
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<tr>
<td>Electropolished</td>
<td>69 MPa He</td>
<td>376 990</td>
<td>68 76</td>
<td>2.41</td>
</tr>
<tr>
<td>Electropolished</td>
<td>69 MPa H₂</td>
<td>370 960</td>
<td>62 73</td>
<td>2.30</td>
</tr>
<tr>
<td>Electropolished &amp; Pd Plated</td>
<td>69 MPa H₂</td>
<td>390 970</td>
<td>64 73</td>
<td>1.91</td>
</tr>
<tr>
<td>Annealed 1170 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 min. in Argon</td>
<td>69 MPa H₂</td>
<td>270 950</td>
<td>83 93</td>
<td>2.04</td>
</tr>
<tr>
<td>Quench in 8% UCONC® Coolant</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealed 1170 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 min. in Vacuum</td>
<td>69 MPa H₂</td>
<td>260 990</td>
<td>86 92</td>
<td>1.77</td>
</tr>
<tr>
<td>Slow Cool</td>
<td></td>
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<td></td>
<td></td>
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</tbody>
</table>

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FIGURE 1. Grain Size of As-Received and Annealed Type 304L Stainless Steel
FIGURE 2. Hall-Petch Plot of Yield Strength for Type 304L Stainless Steel Listed in High-Pressure Helium or Hydrogen Environments
FIGURE 3. Grain-Size Dependence of Ductility Loss for Type 304L Stainless Steel
FIGURE 4. Fracture Surfaces of Fine-Grained Type 304L Stainless Steel in Helium and Hydrogen Environments
FIGURE 5. Load-Extension Curves at Fracture (specimens annealed at 1237 K for 24 hr)
a. Grain Size = 40 μm

b. Grain Size = 340 μm

c. Grain Size = 10 μm

d. Grain Size < 10 μm

FIGURE 6. Fracture Surfaces of Type 304L Stainless Steel Tested in High-Pressure Hydrogen Environments
FIGURE 7. Variation of Dimple Size with Annealing Temperature for Type 304L Stainless Steel Tested in High-Pressure Helium Environments
FIGURE 8. Fracture of Sensitized Specimen Tested in 69 MPa Hydrogen Environment