Stress Corrosion Characteristics of Maraging Steel Weldments in Air and Pentaborane

Hydrogen embrittlement plays a major role in failure associated with stress corrosion cracking, and delayed weldment failure in air is associated with a cathodic hydrogen reaction as the source for hydrogen embrittlement.

**BY S. M. TOY AND A. PHILLIPS**

**ABSTRACT.** The characteristics of the stress corrosion cracking of 18 Ni maraging steel weldments in air and pentaborane were identified by electron microscopy, electron microprobe, scanning electron microscopy, and by the use of the neodymium hydrogen detector system.

Electron fractographs of partial-through-thickness fracture toughness samples revealed the weld fracture to be primarily a quasi-cleavage type. The quasi-cleavage facets contained a herringbone with an included angle of approximately 100 to 110 deg depending on the line of sight position. These orientation lines were associated with thin martensite platelets in the massive martensite subgrains. Hydrogen was found to emanate from similar type martensite orientation locations. The austenite islands in the cored grain boundary encircling the martensite phase was observed to be cleaved.

A mechanism is postulated that hydrogen builds up in the retained austenite in the weld. The combination of local stress and hydrogen is necessary to transformation of the retained austenite into an H₂-embrittled martensite. Fracture then occurs along the preferred martensite or orientation directions observed.

Electron microprobe analysis indicated Ti and Fe segregated in the weld area; Ni, Co, and Mo concentration remained uniform. Methods recommended for reducing the stress corrosion susceptibility of these materials were based on our present knowledge of these phenomena.

**Introduction**

The high strength 18 Ni maraging steels used in the aircraft and missile industry are susceptible to delayed failure in air and pantaborane (B₅H₉) in the welded condition. Both 250 grade and 300 grade 18 Ni maraging steel weldments failed when tested in air and pentaborane, but not in a vacuum. The base metals did not fail under the fracture toughness test matrix condition reported by Taketani. He did find a homogenizing heat treatment of the retained austenite into an H₂-embrittled martensite. Fracture toughness specimens were fabricated from “as received” VASCO-MAX commercially annealed 250 grade maraging steels, but also for its effect on other high strength aircraft steels.

Delayed failure of the 18 Ni maraging steel weldments in air is believed to be associated with an electrochemical mechanism. It is not known whether the maraging steel failures in pentaborane are associated with a chemical or electrochemical hydrogen embrittlement mechanism.

The characteristics of the specimens showing delayed failure of 18 Ni maraging steel weldments in air and pentaborane were identified by electron microscopy, electron microprobe, scanning electron microscopy, and by the use of the neodymium hydrogen detector system.

The neodymium hydrogen detector system was used to determine the emanation and distribution of hydrogen in the weld. It was based on the reaction of hydrogen with neodymium to form a metal hydride. The neodymium film is optically transparent so that the microstructure can be related to the neodymium hydride reaction site.

**Experimental Procedure**

**Material Preparation**

Fracture toughness specimens were fabricated from “as received” VASCO-MAX commercially annealed 250 grade...
Fig. 1—Fracture toughness specimen

18 Ni and 300 grade 18 Ni maraging steel beveled sheet strips (24 x 4 x 1/4 in.) welded in the longitudinal direction by gas tungsten-arc welding with a modified 300 W grade filler metal high in titanium (see Table 1 for chemical compositions). The welded coupons 1.75 x 8 x 0.10 in. were machine welded into pin-loaded tensile specimens according to ASTM Standard E8-61T—Fig. 1.

Specimens were identified by two numbers:
1. A sequence number corresponding to slices from the test panel from right to left.
2. Test panel number.

An Elox notch 0.021 x 0.010 in. was formed 0.005 in. deep in the center of the weld area. The fracture toughness specimen was then aged 3 hr at 900°F (482°C in air) and then notch fatigued to form an 0.074 in. long starter crack (deflections of 0.300-0.25 in. were used). A Krouse flexural machine for flat sheets (3,500 cmp) was used to produce the crack length of 0.074 inch (approximately 6,000 to 13,000 cycles were required). These partial—through-thickness crack (PTC) tensile specimens were then loaded in a creep tensile tester to a $K_t/K_f$ ratio equal to 90% where $K_f$ is the initial stress intensity or point determined by mechanical tensile tests at which catastrophic failure occurs.

Results and Discussion

Stress Corrosion Susceptibility in Air

Sustained Load Tests. Several sustained load tests on 250 grade Ni maraging steel weldments were run in air independently of those reported by Taketani (see Table 2). Specimen 1-5 failed in 210 hr and specimen 2-5 did not fail in 415 hr. Specimen 2-5 was unloaded and broken in a tensile machine at 243,000 psi. Fractographic examinations were conducted on these test specimens and compared to representative samples selected from the Taketani test group.

Fractography Studies. The fractured surfaces of representative PTC specimens that failed in air were replicated by the plastic-carbon technique and examined by electron microscopy. Electron fractographs revealed the 250 grade Ni specimen 1-5 surface morphology was more than one-half quasi-cleavage with the remainder dimple rupture. Specimen 2-5 showed a small flaw growth region which was quasi-cleavage; the remainder of the specimen fractured mechanically—Fig. 2.

The stretched zone in the overload region observed by Taketani in the base metal (specimen 2-4) was different from the fracture found in the welded samples. In the overload region of specimen 2-5, the fracture was observed to be a fixed mode of quasi-cleavage and dimple rupture (micro-void coalescence). These brittle fractures have quasi-cleavage facets containing a her-ringbone pattern with an included angle of approximately 100-110 deg, de-
Table 2—18 Ni Maraging Steel Sustained Load Test Matrix

<table>
<thead>
<tr>
<th>Test media</th>
<th>Welded 250 grade maraging steel</th>
<th>Welded 300 grade maraging steel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-welded and aged</td>
<td>1,800°F for 16 hr</td>
</tr>
<tr>
<td>Vacuum</td>
<td>NF—672 hr (No growth)</td>
<td>—</td>
</tr>
<tr>
<td>Air</td>
<td>F—48 hr (Flaw growth)</td>
<td>NF—405 hr (Flaw growth)</td>
</tr>
<tr>
<td>Pentaborane</td>
<td>F—sec</td>
<td>NF—672 hr (No growth)</td>
</tr>
</tbody>
</table>

a Aged—900°F for 3 hr.  
b NF—no failures, F—failed.

Extraction replica of specimen 31

<table>
<thead>
<tr>
<th>I/lo</th>
<th>d(Å)</th>
<th>I/lo</th>
<th>d(Å)</th>
<th>I/lo</th>
<th>d(Å)</th>
<th>I/lo</th>
<th>d(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>2.90</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.20</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>S</td>
<td>2.19</td>
<td>100</td>
<td>2.18</td>
<td>100</td>
<td>2.12</td>
<td>60</td>
<td>2.08</td>
</tr>
<tr>
<td>M</td>
<td>1.48</td>
<td>60</td>
<td>1.54</td>
<td>60</td>
<td>1.43</td>
<td>10</td>
<td>1.44</td>
</tr>
<tr>
<td>U</td>
<td>1.12</td>
<td>—</td>
<td>—</td>
<td>60</td>
<td>1.11</td>
<td>60</td>
<td>1.10</td>
</tr>
<tr>
<td>W</td>
<td>1.05</td>
<td>100</td>
<td>1.09</td>
<td>100</td>
<td>1.07</td>
<td>70</td>
<td>1.02</td>
</tr>
<tr>
<td>W</td>
<td>0.96</td>
<td>30</td>
<td>0.97</td>
<td>—</td>
<td>60</td>
<td>0.97</td>
<td></td>
</tr>
</tbody>
</table>

a ASTM X-ray powder data file card 6-9616.  
b ASTM X-ray powder data file card 3-9680.  
c ASTM X-ray powder data file card 3-290.

The 18 Ni maraging steel weldments failed rapidly in pentaborane. The 300 grade 18 Ni weldments appeared to be more susceptible than the 250 grade 18 Ni weldments. The homogenization heat treatment of the weldments increased the 250 grade weldment resistance to failure more effectively than the 300 grade (see Table 1).

The base metals did not fail under the test conditions tried. 

Stress Corrosion Susceptibility in Pentaborane 

Fractography Studies. Fractography examination of 250 grade 18 Ni weldment (specimen 12) which failed in pentaborane, revealed practically a complete quasi-cleavage surface morphology—Fig. 5. This mode of cracking was typical of other PTC specimens which failed in pentaborane. The flat cleavage facies have similar herringbone morphology found for the specimens which failed in air.

The 18 Ni maraging steel weldments was also evident. Stress Corrosion Susceptibility is by an electrochemical reaction. The stress corrosion cracking mechanism is supported by the sustained load test evidence that the weldments do not fail in vacuum but do in air. It can be assumed that the air provides moisture for the electrolyte necessary for an electrochemical reaction to proceed and supply the hydrogen. The 18 Ni maraging steel weldment becomes susceptible by a thermal sensitization process. If the thermal embrittlement was inherent in the material, it would have failed in vacuum.

The nonsusceptibility of the base metal to stress corrosion cracking may be a function of the protective film that forms on the fracture surface prior to the exposure of the test environment. The improvement of the resistance to failure of the weldments by a homogenization heat treatment further emphasizes the need to identify the microstructural features that sensitize the steel weldments.

The introduction of hydrogen into...
these local microstructural features of the Ni maraging steels, when exposed to pentaborane has not been directly established. It is assumed that the hydrogen could be supplied by either a chemical reaction or by an electrochemical reaction. The fracture surface of 300 grade 18 Ni (specimen 31) was etched with Fry's etchant for 8 sec to accentuate the local microstructural phase. Figure 6 shows the fine precipitate in the martensite phase lines in a herringbone fashion similar to the pattern in the martensite flat cleavage facets and where hydrogen emanation was observed.

Figure 7 is an electron fractograph of a typical austenite island revealing the large angular precipitates and other finer particles. The large angular particles are probably titanium compounds. Particles with similar morphology have been identified as Ti (C, N).3

Electron diffraction of one of the fine particles extracted from another austenite island indicated it to be either Fe3Mo3C or α-FeMo compound (see Table 3 and Fig. 8). The presence of a complex metal carbide in the austenite is generally associated with stress corrosion cracking of austenitic stainless steels.4

Figure 9 shows an electron diffraction pattern taken from extractive replica of the martensite fractured surface region of the 300 grade 18 Ni weldment specimen 31. The electron diffraction data give indirect evidence of Ti (C, N) and 𝜏-TiS in the region (see Table 4). This is a reasonable interpretation based on examined electron diffraction data reported by other investigators.3,5

Microstructural Investigation. The fracture profile of the 250 grade 18 Ni weldment (specimen 12) which failed in pentaborane was examined. Fracture failure mode is quasi-cleavage through the martensite laths with cleavage across the austenite islands—Fig. 10.

Electron microprobe analysis of this fracture profile section was made. The back scattering electron micrograph shown in Fig. 11 indicates heavy elements in the light region and light elements in the dark regions of the fracture profile. X-ray scanning (Fig. 12) indicates specific weld areas have higher concentrations of titanium associated with them. The opposite effect was found for iron—Fig. 13. The percentage of iron varied from 49 to 66%. Ni, Co, and Mo concentrations remained uniform.

Figure 14 is an electron micrograph of 300 grade 18 Ni weldment (specimen 52B) which failed in air and 250 grade 18 Ni base metal next to the weldment (specimen 12).

The absence of austenite islands and the cored cast structure of the original weld are observed. The local precipitation appears to be general.

Electron micrographs of the 250 grade...

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**Table 4—Electron Diffraction Pattern from Extraction Replica Surface of 300 Grade 18 Ni Weld Fracture**

<table>
<thead>
<tr>
<th>Extraction replica of specimen 31 (Unknown)</th>
<th>TiC*</th>
<th>TiN*</th>
<th>TiS†</th>
</tr>
</thead>
<tbody>
<tr>
<td>l/10</td>
<td>d(A)</td>
<td>l/10</td>
<td>d(A)</td>
</tr>
<tr>
<td>2.92</td>
<td>2(1.54)</td>
<td>56</td>
<td>2(1.50)</td>
</tr>
<tr>
<td>2.68, 2.70</td>
<td>—</td>
<td>—</td>
<td>20</td>
</tr>
<tr>
<td>2.19</td>
<td>—</td>
<td>100</td>
<td>2.12</td>
</tr>
<tr>
<td>2.14</td>
<td>100</td>
<td>2.18</td>
<td>100</td>
</tr>
<tr>
<td>1.37</td>
<td>—</td>
<td>—</td>
<td>60</td>
</tr>
<tr>
<td>1.33, 1.34</td>
<td>30</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>1.27</td>
<td>10</td>
<td>1.76</td>
<td>26</td>
</tr>
<tr>
<td>1.20, 1.21</td>
<td>16</td>
<td>1.22</td>
<td>50</td>
</tr>
<tr>
<td>0.99</td>
<td>5</td>
<td>1.09</td>
<td>7</td>
</tr>
<tr>
<td>0.90</td>
<td>30</td>
<td>0.97</td>
<td>22</td>
</tr>
</tbody>
</table>

* ASTM X-ray powder data file card 6-0614,
† ASTM X-ray powder data file card 0642,
‡ ASTM X-ray powder data file card 11-664.

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18 Ni grade weldments revealed a rod-like and angular precipitate. These precipitates are indirectly identified to be Ti compounds by their color and by similar shape precipitates being reported as Ti (C, N). The segregation of this precipitate at the austenite/martensite interface can reduce the mechanical strength and does affect the mode of cracking—Figs. 15-17.

The Role of Hydrogen in Stress Corrosion Cracking of 18 Ni Maraging Steel Weldments

An optical method for detecting the emanation and distribution of hydrogen in maraging steels was developed based on the reaction of hydrogen with a rare earth metal to form a metal hydride. Neodymium film is evaporated on a polished and etched cross-section of a 250 grade 18 Ni weldment. The sample is heated to evolve the hydrogen from the steel surface and to speed up the reaction of the emitted hydrogen with the neodymium metal overlay. The neodymium film is optically transparent so that the microstructure can be related to the black neodymium hydride reaction sites.

An 18 Ni maraging steel weldment was charged with 1 Hg. Examination of the maraging steel microstructure, in relation to the hydrogen, revealed hydrogen emanating from the martensite islands and along the martensite subgrain boundaries—Fig. 18.

This sample was previously evaporated with a Nd film and heated before being artificially charged with hydrogen. Hydrogen was observed to emanate from the austenite island (Fig. 19) with only a few large H2 reaction sites. Another hydrogen test was performed on the same specimen after repolishing and cathodically charging with H2 to reveal additional emittance characteristics. Hydrogen was observed to emanate in a preferred mode associated with unidentified martensite crystallographic directions—Fig. 20. Similar martensite laths were also observed forming in the H2 cathodically charged austenite islands—Fig. 21. These strain induced martensite transformations could be produced by a combination of hydrogen and stress interaction.

The hydrogen reaction sites were further resolved by examination with a scanning electron microscope (SEM). An SEM micrograph revealed the cluster...
Table 5—Theoretical Ca etched by the two-step etching process.

Neodymium was deposited on half of the specimen, and the specimen was then heated at 300°F (149°C) for 1½ hr in vacuum and then removed; the optical resolution was excellent—Fig. 18.

A Zeiss surface interferometer was used to measure the Nd film thickness which was 2,825 ± 125Å.

Theoretical Calculation of Hydrogen Emission

A theoretical calculation of hydrogen emanating from an austenite island and from martensite subgrains was estimated, based on a cylinder shape. The facets have the average diameter of the NdH$_2$ reaction sites observed in the photographs. The length of the cylinder for the steel specimen was based on diffusion length $x_t$ calculated by the familiar approximation that $x_t = Dr$ where $D$ is the diffusion coefficient and $t$ is the time.$^8$ The length of the NdH$_2$ cylinder was assumed to be an average measured thickness of 2,800 Å. An average hydrogen content of 6 ppm for the 250 grade 18 Ni maraging steel after H$_2$ charging was assumed to be reasonable.$^8$ H$_2$ diffusion time, $t$, was 1 hr at 300°F (149°C). Diffusion coefficient values were taken from published data.$^{10}$

The entry, movement, and diffusion of hydrogen in the 250 grade 18 Ni maraging steel weldments is not fully understood. Theoretical calculations on the amount of hydrogen expected to be emitted from the austenite and martensite sites by diffusion can be made and then compared to the theoretical calculated amount of hydrogen reacted with the neodymium film to form the compound NdH$_2$.

The H$_2$-Nd reaction site is assumed to be a cylinder of austenite with an overlay of an evaporated Nd film which converts completely to NdH$_2$—Fig. 23. The H$_2$ emits from the austenite assuming a concentration of 6 ppm. This concentration of hydrogen is reasonably expected for H$_2$ cathodically charged into martensite.

For these calculations the density values used were $\rho$(Fe) = 7.87 gm/cc and from martensite subgrains was estimated, based on a cylinder shape. The facets have the average diameter of the NdH$_2$ reaction sites observed in the photographs. The length of the cylinder for the steel specimen was based on diffusion length $x_t$ calculated by the familiar approximation that $x_t = Dr$ where $D$ is the diffusion coefficient and $t$ is the time.$^8$ The length of the NdH$_2$ cylinder was assumed to be an average measured thickness of 2,800 Å. An average hydrogen content of 6 ppm for the 250 grade 18 Ni maraging steel after H$_2$ charging was assumed to be reasonable.$^8$ H$_2$ diffusion time, $t$, was 1 hr at 300°F (149°C). Diffusion coefficient values were taken from published data.$^{10}$

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Assume 6 ppm H₂ in austenite, then the weight of hydrogen emitted can be calculated.

\[ W_{H_2} = (6 \times 10^{-6}) \cdot (W_{Pb}) \]
\[ = (6 \times 10^{-6}) \cdot (1.48 \times 10^{-11}) \]
\[ = 8.8 \times 10^{-12} \text{ gm} \ (H_2 \text{ emitted}) \]

Now the weight of neodymium, Nd, can be calculated where \( T \) is Nd film thickness.

\[ W_{Nd} = \rho V = \rho tA \]
\[ = (6.8) \cdot (2800 \times 10^{-6}) \cdot (3.14 \times 10^{-6}) \]
\[ = 5.45 \times 10^{-12} \text{ gm} \]

The weight of hydrogen reacted with Nd can be calculated by the following equation where molecular weight is \( m_w \):

\[ W_{H_2} = \frac{W_{Nd}}{m_w} \cdot m_w (H_2) \]
\[ = 5.45 \times 10^{-12} \left( \frac{2}{60} \right) \]
\[ = 1.82 \times 10^{-13} \text{ gm} \ (H_2 \text{ reacted with Nd}) \]

\[ W_{H_2} = 1.82 \times 10^{-13} \times 10^6 \]
\[ = 1.82 \times 10^{-7} \text{ gm} \]

The theoretical calculations of hydrogen emitted in 1 hr are given in Table 5. By comparing the amount of hydrogen that can be emitted by diffusion with that detected by the hydrogen reacted to form NdH₄, the following interpretations are made:

**Case No. 1a.** Hydrogen emission by bulk diffusion through austenite cannot account for the amount of hydrogen detected by the Nd hydrogen detector. Hydrogen diffusion from traps can give the right order of magnitude of \( H_2 \). Compare \( W_{H_2}, \ D_{H_2} \) values (columns 4 and 5, Table 5).

**Case No. 2b.** Grain boundary diffusion of hydrogen in austenite is sufficient to account for the \( H_2 \) detected. Compare \( W_{H_2}, \ D_{H_2} \) values (columns 4 and 5, Table 5).
of the maraging steel weldments. A stress is concentration at one of the observed preferred crystallographic interfaces (along subgrain boundaries) of the martensite. The martensite is strained and the movement of interstitial hydrogen by diffusion to this local area results in hydrogen embrittlement. When a stress concentration situation occurs, a high H-containing austenite island is strained and transforms to martensite. The movement of the hydrogen from the martensite to the remaining austenite embrittles the transforming martensite, particularly at the points of the feathery needle-like phase. This propagates into the martensite matrix where it initiates martensite cleavage along the similar crystallographic direction observed both in transformed martensite, in austenite, and martensite subgrain boundaries.

Obviously, the reverse situation can occur where movement of the hydrogen embrittles the strained matrix martensite. It cracks and propagates into the austenite causing the austenite to transform to martensite. The hydrogen solubility in martensite is lower than for austenite and the hydrogen must diffuse.

Three electrochemical electrodes which can provide favorable cathodic hydrogen reduction are: γ-metal carbide; α-Ti (C,N); and γ-α. These phases form electrochemical cells with austenite or the martensite matrix causing enough hydrogen to be generated at the cathode to embrittle the austenite or martensite. Iron is the principal oxidized element and hydrogen the reduced element.

A model of a proposed stress corrosion mechanism of 18 Ni maraging steel weldment is illustrated in Fig. 24. An electrochemical cell is formed on the surface of the maraging steel weldment. Iron goes into solution and hydrogen is introduced into the austenite.

A crack at the FeMoC or other precipitate is formed in the austenite when stress is applied. The stress intensity increases ahead of the crack in the austenite. When a critical stress is reached, transformation of the austenite to martensite is initiated along preferred orientations. The hydrogen originally in the untransformed austenite now embrittles the strained martensite which cleaves and the crack prefers to propagate into the martensite matrix along a matching martensite similarly oriented. The process is repeated until failure occurs.

The hydrogen embrittlement process is also applicable to delayed failure of the 18 Ni maraging steel in pentaborane. If pentaborane is decomposed by a catalytic or chemical reaction, hydrogen is released. The γ-Ti(S) could be a suitable catalytic poison. The atomic hydrogen prefers to enter the austenite. When sufficient strain is introduced into the austenite it transforms to hydrogen embrittled martensite.

Recommendations for Prevention of Stress Corrosion Cracking of 18 Ni Maraging Steel Weldments

It is recommended that the chemistry of the austenite be modified to raise the Ms temperature to provide complete transformation of the austenite to martensite during welding or to lower the Ms temperature to stabilize the austenite. This would require developing a welding rod with a suitable chemical composition.

It should also be noted that martensite reverting to austenite in the heat affected zone is another possible H2 sensitive phase. The reverted austenite could be transformed to martensite in a similar manner as the retained austenite.

Conclusions

The characteristics exhibited by stress corrosion cracking of 18 Ni maraging steel weldments identified by electron microscopy, scanning electron microscopy, electron diffraction, H2 emission and distribution, and electrochemical data are presented as evidence that hydrogen embrittlement plays a major role in the failure mechanism.

Delayed failure of the 18 Ni maraging steel weldment in air is associated with an electrochemical mechanism, wherein cathodic hydrogen reaction is the source for the hydrogen embrittlement to occur. Delayed failure of the weldments in pentaborane has not been identified as chemical or electrochemical at this time.

The retained austenite in the weldment is primarily responsible for the stress corrosion susceptibility. It is postulated that hydrogen is built up in the retained austenite. It has been shown that the combination of local stress and hydrogen is necessary to initiate transformation of the retained austenite into an H2 embrittled martensite along preferred orientations.

It is recommended that the chemistry of the austenite be modified to alter the Ms and Mf temperature resulting in either a stable austenite or a complete transformation of the austenite to martensite during welding. Theoretical calculations of Ms and Mf indicated that this could be accomplished by modifying the composition of the welding rod to attain the desired results.

Acknowledgment

This work was sponsored by Independent Research and Development Funding at McDonnell Douglas Astronautics Company.

References