Hydrogen Embrittlement of High-Strength Fasteners in Atmospheric Service

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The effects of dissolved hydrogen in the failure of plain and low-alloy steels has been studied extensively. Hydrogen embrittlement (HE), in the manifestation of sulfide stress cracking, is a continuing concern in the oil, gas, and petroleum industries, despite years of research into cracking mechanisms, parameters, and control methods. Also well documented is HE cracking of electroplated fasteners. Less appreciated is the long-term effect of hydrogen on cracking of high-strength steels and ferrous alloys under atmospheric exposure conditions. This article discusses failures of high-strength fasteners caused by HE in atmospheric environments and the danger this cracking presents. Recommendations are provided for reducing fastener failures by HE.

Hydrogen embrittlement (HE) is a much studied and documented phenomenon. It is the Achilles heel of high-strength ferrous steels and alloys. HE, in the manifestation of sulfide stress cracking (SSC), is a continuing concern in the oil, gas, and petroleum industries, despite years of research into cracking mechanisms, parameters, and control methods. The definitive materials selection documents for sour oilfield applications is NACE MR0175.1 HE, during manufacture of electroplated fasteners, is also well documented. Less appreciated is the long-term effect of hydrogen with cracking of high-strength steels and ferrous alloys under atmospheric exposure conditions.

HE is not completely understood; however, it is generally agreed that only atomic hydrogen will enter and diffuse through a steel, in this case during corrosion.2 Whether absorbed hydrogen causes cracking or not is a complex interaction of material strength, external stresses, and temperature. At high-strength levels (180 ksi [1,240 MPa]), only a few ppm of dissolved hydrogen can cause cracking.

We recently analyzed fasteners where failure was attributed to HE cracking. A common denominator was that the fasteners had been in service many years before failure. Macroscopic evidence of HE normally includes a rough, brittle-appearing fracture surface, usually with a single origin, although multiple fracture origins can be present (Figure 1). Fractures typically occurred in corroded thread roots. Another characteristic of HE cracking was that fractures do not necessarily occur in the last engaged thread as do fatigue fractures. In fact, fractures sometimes occur inside the nut.

Scanning electron microscopy (SEM) examination of fracture surfaces typically showed intergranular crack origins, with the final fracture areas exhibiting any combination of intergranular, cleavage, or ductile overload features. Metallographic examination of failed fasteners will normally not show any secondary hydrogen cracks, although subsurface cracking at inclusions has been observed (Figure 2).

The fasteners at most risk of HE cracking are high-strength studs and bolts, such as those manufactured to ASTM A 354 Gr. BD,3 A 490,4 and socket head capscrews manufactured to ASME/ANSI 18.3 and ASTM A 574.5 These standards specify greater maximum allowable hardnesses than other common fastener specifications (i.e., A 325,7 A 193,8 A 307,9 and A 44910). A 193 Gr. B7, a common fastener alloy, has no maximum hardness requirement; however, a minimum 1,100°F (593°C) tempering temperature is specified.
which should result in nominal hardnesses of 25 HRC to 30 HRC (Rockwell Hardness, C scale). Socket head capscrews have a specified hardness range of approximately 39-45 HRC and are typically heat-treated to hardness levels >40 HRC.

Fastener hardness is important; atmospheric service fasteners that failed because of HE were heat-treated to 35 HRC or greater (Table 1). This hardness is compared with the maximum allowable hardness of 22 HRC specified in MR0175 for fasteners in sour service. HRC 22 is considered a conservative maximum hardness for fasteners exposed to nonsour atmospheric service, as the exposure conditions are normally less severe than that of the MR0175 standard test solution. Insufficient field data points are available to recommend a maximum hardness for fasteners exposed to nonsour atmospheric service. However, based on the incidences of documented failures, fasteners manufactured to the specifications in references 7 through 10 should be resistant to HE cracking in most atmospheric applications. A factor that could increase the potential for HE cracking at lower hardnesses is accelerated hydrogen charging of a fastener acting as the cathode in a galvanic couple.

Fortunately, the number of documented fastener failures in atmospheric service caused by HE cracking is not many, considering the number of fasteners in service. A literature review of HE cracking of fasteners in Materials Performance and CORROSION revealed only a few articles, and those were laboratory studies concerned with the effects of cathodic charging and electroplating on HE cracking. 

HE failure of fasteners may be isolated because fastener corrosion in atmospheric service is usually caused by periodic exposure to water (i.e., rain water, cooling tower over-spray, or firefighting water). Water from these sources is normally neutral in pH and atomic hydrogen is not readily available at the cathodic sites of corrosion cells. However, if appreciable chlorides are present, as from cooling tower over-spray, or wet-dry conditions exist that can concentrate corrosive species in occluded areas of fasteners (i.e., in the thread contact area), low pH solutions can exist, providing a ready source of atomic hydrogen.

The presence of hydrogen at the cathode of a corrosion cell does not necessarily mean that it will automatically diffuse into the steel. Studies show that hydrogen diffusion into steel is accelerated by promoters present in some steels, including arsenic, selenium, tellurium, antimony, and phosphorus, and by cathodic poisons in the aqueous solution (i.e., cyanides). That many corroded high-strength fasteners do not fail is probably because the environments preventing cathodic hydrogen reduction are rare.

Even though reported incidents of fastener failure from HE are low, the consequences of failure can be great in equipment and piping in high-pressure, flammable, or toxic services. In one incident, two bolts holding the body of a ball valve together failed because of HE, separating the attached piping and releasing a propane cloud. In another instance, seven of 12 body studs in a pump containing high-pressure isobutane failed because of HE. Fortunately, no one was injured in either incident. The risk associated with bolt failures in critical services warrants prudent action to minimize this occurrence.

The following inspection and management practices associated with bolted connections are recommended:

- Locate and document all corroded bolted connections during external visual inspections of equipment and piping, especially inspections preceding a scheduled mainte-
TABLE 1
Fastener Hardness vs HE Cracking

<table>
<thead>
<tr>
<th>Material Specification</th>
<th>Hardness (HRC)</th>
<th>HE Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>17-4 PH</td>
<td>35.0</td>
<td>Yes</td>
</tr>
<tr>
<td>Unknown</td>
<td>44.0</td>
<td>Yes</td>
</tr>
<tr>
<td>Unknown</td>
<td>39.5</td>
<td>Yes</td>
</tr>
<tr>
<td>SAE J429 Gr. 5</td>
<td>27.0</td>
<td>No</td>
</tr>
</tbody>
</table>

nance shutdown. Corroded, high-strength fasteners should be replaced during the outage and protected with a barrier coating, anti-seize compound, or rust preventative.

- Incorporate inspection of bolted connections in risk-based inspection management programs.
- Include provisions in maintenance management procedures to protect newly installed fasteners from corrosion.

The role of counterfeit fasteners in fastener failures has received much publicity. A potentially greater haz-

ard in the sudden failure of fasteners from HE is less well-appreciated.

References

1. NACE Standard MR0175, "Standard Material Requirements—Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment" (Houston, TX: NACE).

David E. Hendrix is President of The Hendrix Group, Inc., a materials and corrosion engineering consulting company. Prior to founding the company, he held various positions in metallurgical engineering at Law Engineering, Texaco, Inc., and Arco Chemical Co. He is the author of "High Temperature Wrought Alloys" in NACE's Process Industries Corrosion.
Maximum hardness questioned for fasteners in atmospheric service

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EDITOR:

I have three comments regarding statements made on p. 55 of the article, “Hydrogen Embrittlement of High-Strength Fasteners in Atmospheric Service,” by David E. Hendrix (December 1997 MP, p. 54-56).

First, socket head capscrews do not only “have a minimum hardness requirement instead of a maximum.” Paragraph 7.1 of ASTM A 574-92a specifies a Rockwell hardness C (HRC) range of 39 to 45, or 37 to 45 HRC for 0.625-in, diameter and larger.

Second, the references apparently got scrambled in editing. It is stated that fasteners made to specifications in references 6 through 9 should be resistant to hydrogen embrittlement (HE). Fasteners made to references 7 through 10 should be resistant to HE cracking in most atmospheric applications; reference 6 is to ASTM A 574, which may crack.

Third, it is stated that “insufficient field data points are available to recommend a maximum hardness for fasteners in atmospheric service.” In fact, for low-alloy steels, the upper limit of 38 HRC for ASTM A 490 structural bolts (and very similar 39 HRC for automotive bolts in SAE J429 Grade 8 and J1199 Class 10.9) is about as well based on field data as the 22 HRC upper limit in NACE MR01 75 for sour service.

Blake points out that “Extensive research, coupled with highly unfortunate field experience, has shown that unless exceptional precautionary steps are taken during manufacture, products of hardness higher than C39 have an unacceptably high susceptibility to stress embrittlement.” However, he does not include literature references to support this statement. Two large studies were done on structural bolts after field failures were encountered. Boyd & Hyler conducted a combination of lab and field tests that led to the recommended 170 ksi (~1,200 kPa) tensile strength limit (equivalent to 38 HRC) for ASTM A 490 bolts. Kanao reported the results of another study involving more than 8 years of field tests. Hughel analyzed field failures of SAE J1199 Class 12.8 bolts (39 to 44 HRC), which led to a recall of more than 5 million vehicles. This grade did not reappear in the 1983 revision of the standard.

References


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REPLY:

First, I want to thank Richard Garber for taking the time to read the subject article and provide his welcome feedback. I originally wrote the article in an effort to increase the technical and end-user communities’ awareness of the dangers of HE failures of high-strength fasteners in
atmospheric service. It is my belief that the risk of equipment failure and human injury from long-term HE failures of atmospheric-service fasteners is less appreciated in the chemical/refining industry than in other industries, such as automotive.

Dr. Garber made three comments regarding perceived inaccuracies in the article, which I address as follows:

Comment 1: Regarding the hardness limits for ASTM A 574 capscrews, Dr. Garber is correct. A 574 capscrews have a minimum and a maximum hardness limit (39 to 45 HRC). The practical significance of the distinction, however, is minimal, as A 574 fasteners may crack at their specified minimum hardness range.

Comment 2: Again, Dr. Garber is correct and the reference inaccuracies are important to clear up. The numbered references were inadvertently offset by one when a reference was added during article revisions. The correct references to fastener specifications that should be resistant to HE are 7 through 9. References 3 through 6 refer to fastener specifications where HE might be anticipated.

Comment 3: This comment refers to an unfortunate choice of wording. The sentence was meant to refer to my personal experience data points. Also, there was a reluctance to recommend an absolute upper hardness limit based on the litigious society we are living in. Dr. Garber stated that, in his opinion, an upper limit of 38 HRC to prevent HE of ASTM 490 fasteners (and a similar hardness limit for other low-alloy fasteners) was as well based on field data as the 22 HRC limit in MROI 75 for sour service. I might argue whether published field data regarding upper hardness limits for low-alloy fasteners is as extensive as field and laboratory MRO175 data; however, I will not debate that point.

I do believe that, within a HRC unit or two, Dr. Garber’s stated upper limit of 38 HRC is a reasonable one for low-alloy steels. However, in the article I was not confining my comments to low-alloy steels. Table I referred to a data point for HE of a 17-4 pH stainless steel (SS) fastener at 35 HRC. Also, I think it inadvisable to place excessive emphasis on 38 HRC as an absolute upper limit, based on his cited references. His reference 3, where he appears to have obtained the 38 HRC limit, was based on laboratory and field testing where material strength was reported in kg/mm² units. The 38 HRC value was apparently converted from HE resistance vs. tensile strength data. As the tensile strength to hardness conversion is an approximate one (±2%), his 38 HRC could actually range from 37 to 39 HRC. My preference is to state that a reasonable safe upper hardness limit for low-alloy steel fasteners to prevent HE is 36 HRC ± 2. This limit also is intended to apply to properly manufactured fasteners that have uniform material properties and minimal nonmetallic inclusions. I cannot state an accurate limit for precipitation hardening SS fasteners. Perhaps other MP readers will write to share their experiences. The important point to be gained from the article is that fastener specifiers should be aware of the HE cracking phenomena and not specify fastener strength any higher than is needed.

I want to again thank Dr. Garber for taking the time to submit his comments about the article. They have acted not only to make the article more technically accurate, but I hope they also have stimulated interest in the subject and will generate comments from other readers. I suspect that many atmospheric-service fasteners have experienced HE and have gone undiagnosed or unreported.

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