Hydrogen embrittlement

Hydrogen Induced Cracks (HIC)

Hydrogen embrittlement is the process by which metals such as steel become brittle and fracture due to the introduction and subsequent diffusion of hydrogen into the metal. This is often a result of accidental introduction of hydrogen during forming and finishing operations. This phenomenon was first described in 1875.[1]

1 Process

During hydrogen embrittlement, hydrogen is introduced to the surface of a metal and individual hydrogen atoms diffuse through the metal. Because the solubility of hydrogen increases at higher temperatures, raising the temperature can increase the diffusion of hydrogen. When assisted by a concentration gradient where there is significantly more hydrogen outside the metal than inside, hydrogen diffusion can occur even at lower temperatures. These individual hydrogen atoms within the metal gradually recombine to form hydrogen molecules, creating pressure from within the metal. This pressure can increase to levels where the metal has reduced ductility, toughness, and tensile strength, up to the point where it cracks open (*hydrogen-induced cracking*, or HIC).[2] Though hydrogen atoms embrittle a variety of substances, including steel,[3][4][5] aluminium(at high temperatures only[6]), and titanium,[7] hydrogen embrittlement of high-strength steel is of the most importance. Austempered iron is also susceptible, though austempered steel (and possibly other austempered metals) display increased resistance to hydrogen embrittlement.[8] Steel with an ultimate tensile strength of less than 1000 MPa (~145,000 psi) or hardness of less than 30 HRC is not generally considered susceptible to hydrogen embrittlement. In tensile tests carried out on several structural metals under high-pressure molecular hydrogen environment, it has been shown that austenitic stainless steels, aluminium (including alloys), copper (including alloys, e.g. beryllium copper) are not susceptible to hydrogen embrittlement along with a few other metals.[9][10] As an example of severe hydrogen embrittlement, the elongation at failure of 17-4PH precipitation hardened stainless steel was measured to drop from 17% to only 1.7% when smooth specimens were exposed to high-pressure hydrogen.

Hydrogen embrittlement can occur during various manufacturing operations or operational use - anywhere that the metal comes into contact with atomic or molecular hydrogen. Processes that can lead to this include cathodic protection, phosphating, pickling, and electroplating. A special case is arc welding, in which the hydrogen is released from moisture, such as in the coating of welding electrodes.[7][11] To minimize this, special low-hydrogen electrodes are used for welding high-strength steels. Other mechanisms of introduction of hydrogen into metal are galvanic corrosion, as well as chemical reactions with acids or other chemicals. One of these chemical reactions involves hydrogen sulfide in sulfide stress cracking (SSC), an important process for the oil and gas industries.[12]

1.1 Counteractions

Hydrogen embrittlement can be prevented through several methods, all of which are centered on minimizing contact between the metal and hydrogen, particularly during fabrication. Embrittling procedures such as acid pickling should be avoided, as should increased contact with elements such as sulfur and phosphate. The use of proper electroplating solution and procedures can also help to prevent hydrogen embrittlement.[13] Furthermore, metal substrates (generally ferrous sulfide or other sulfides) can be applied to metal in order to prevent hydrogen embrittlement.[14][15]

If the metal has not yet started to crack, embrittlement can be reversed by removing the hydrogen source and causing the hydrogen within the metal to diffuse out through heat treatment.[16] This de-embrittlement process, known as “baking”, is used to overcome the weaknesses of methods such as electroplating which introduce hydrogen to the metal, but is not always entirely effective.[17]

In the case of welding, often pre- and post-heating the metal is applied to allow the hydrogen to diffuse out before it can cause any damage. This is specifically done with high-strength steels and low alloy steels such as the chrome/molybdenum/vanadium alloys. Due to the time needed to re-combine hydrogen atoms into the hydrogen molecules, hydrogen cracking due to welding can occur over 24 hours after the welding operation is completed.

2 Examples

- In 2013, six months prior to opening, the East Span of the Oakland Bay Bridge failed during testing. Catastrophic failures occurred in shear bolts in the span, after only two weeks of service, with the failure attributed to embrittlement, possibly from the environment.[18]

3 Related phenomena

If steel is exposed to hydrogen at high temperatures, hydrogen will diffuse into the alloy and combine with carbon to form tiny pockets of methane at internal surfaces like grain boundaries and voids. This methane does not diffuse out of the metal, and collects in the voids at high pressure and initiates cracks in the steel. This selective leaching process is known as hydrogen attack, or high temperature hydrogen attack and leads to decarburization of the steel and loss of strength and ductility.

Copper alloys which contain oxygen can be embrittled if exposed to hot hydrogen. The hydrogen diffuses through the copper and reacts with inclusions of Cu_2O, forming H_2O (water), which then forms pressurized bubbles at the grain boundaries. This process can cause the grains to literally be forced away from each other, and is known as *steam embrittlement* (because steam is produced, not because exposure to steam causes the problem).

A large number of alloys of vanadium, nickel, and titanium absorb significant amounts of hydrogen. This can lead to large volume expansion and damage to the crystal structure leading to the alloys becoming very brittle. This is a particular issue when looking for non-palladium based alloys for use in hydrogen separation membranes.[19]

4 Testing

There are two ASTM standards for testing embrittlement due to hydrogen gas. The Standard Test Method for Determination of the Susceptibility of Metallic Materials to Hydrogen Gas Embrittlement (HGE) Test,[20] uses a diaphragm loaded with a differential pressure. The Standard Test Method for Determination of Susceptibility of Metals to Embrittlement in Hydrogen Containing Environments at High Pressure, High Temperature, or Both[21] uses a cylindrical tensile specimen tested into an enclosure pressurized with hydrogen or helium.

Another ASTM standard exists for quantitatively testing for the Hydrogen Embrittlement threshold stress for the onset of Hydrogen-Induced Cracking due to platings and coatings from Internal Hydrogen Embrittlement (IHE) and Environmental Hydrogen Embrittlement (EHE) - F1624-06 Standard Test Method for Measurement of Hydrogen Embrittlement Threshold in Steel by the Incremental Step Loading Technique.[22][23] and ASTM STP 962, "Hydrogen Embrittlement: Prevention and Control."

- NACE TM0284-2003 (NACE International) Resistance to Hydrogen-Induced Cracking
- ISO 11114-4:2005 (ISO)Test methods for selecting metallic materials resistant to hydrogen embrittlement.
- Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement in Plated or Coated Fasteners[24]
- Standard Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating/Coating Processes and Service Environments[25]

5 See also

- Hydrogen analyzer
- Hydrogen damage
- Hydrogen piping
- Hydrogen safety
- Low hydrogen annealing
- Nascent hydrogen
- Oxygen-free copper

6 References

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[25] http://www.astm.org/Standards/F519.htm

7 Further reading

- ASM international, *ASM Handbook #13: Corrosion*, ASM International, 1998

8 External links

- Resources on hydrogen embrittlement, Cambridge University
- Zinc Plating and Hydrogen Embrittlement
- Hydrogen embrittlement
- Corrosion-Doctors.org Hydrogen embrittlement
- Hydrogen purity plays a critical role
- A Sandia National Lab technical reference manual.
- Hydrogen Embrittlement group
- The Network of Excellence (NoE) in Hydrogen Embrittlement

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