Hydrogen Embrittlement

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Hydrogen Embrittlement

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## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tables</td>
<td>iii</td>
</tr>
<tr>
<td>Figures</td>
<td>iv</td>
</tr>
<tr>
<td>Definitions</td>
<td>v</td>
</tr>
<tr>
<td>Acronyms</td>
<td>vi</td>
</tr>
<tr>
<td>Foreword</td>
<td>vii</td>
</tr>
<tr>
<td>1.0 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2.0 Classification of Hydrogen Embrittlement</td>
<td>1</td>
</tr>
<tr>
<td>2.1 Hydrogen Environmental Embrittlement</td>
<td>2</td>
</tr>
<tr>
<td>2.2 Internal Hydrogen Embrittlement</td>
<td>3</td>
</tr>
<tr>
<td>2.3 Hydrogen Reaction Embrittlement</td>
<td>3</td>
</tr>
<tr>
<td>2.4 Hydrogen Embrittlement versus Stress Corrosion Cracking</td>
<td>4</td>
</tr>
<tr>
<td>3.0 Hydrogen Embrittlement Characterization</td>
<td>5</td>
</tr>
<tr>
<td>3.1 Material Screening Methods</td>
<td>5</td>
</tr>
<tr>
<td>3.2 Qualitative Ratings</td>
<td>6</td>
</tr>
<tr>
<td>3.3 Material Database for Hydrogen Environment Embrittlement</td>
<td>7</td>
</tr>
<tr>
<td>3.4 General Observation for Metallic Materials</td>
<td>13</td>
</tr>
<tr>
<td>Aluminum and Aluminum Alloys</td>
<td>13</td>
</tr>
<tr>
<td>Copper and Copper Alloys</td>
<td>13</td>
</tr>
<tr>
<td>Nickel and Nickel based Alloys</td>
<td>13</td>
</tr>
<tr>
<td>Titanium and Titanium Alloys</td>
<td>14</td>
</tr>
<tr>
<td>Iron-based Alloys and Steels</td>
<td>14</td>
</tr>
<tr>
<td>Superalloys</td>
<td>15</td>
</tr>
<tr>
<td>4.0 Hydrogen Effects on Mechanical Properties</td>
<td>15</td>
</tr>
<tr>
<td>4.1 Tensile Properties</td>
<td>15</td>
</tr>
<tr>
<td>4.2 Fracture Properties</td>
<td>15</td>
</tr>
<tr>
<td>4.3 Low Cycle Fatigue</td>
<td>19</td>
</tr>
<tr>
<td>4.4 High Cycle Fatigue</td>
<td>21</td>
</tr>
<tr>
<td>4.5 Crack Growth Rate</td>
<td>22</td>
</tr>
<tr>
<td>4.6 Creep Rupture</td>
<td>23</td>
</tr>
<tr>
<td>5.0 Important Factors in Hydrogen Embrittlement</td>
<td>25</td>
</tr>
<tr>
<td>5.1 Hydrogen Pressure</td>
<td>25</td>
</tr>
<tr>
<td>5.2 Temperature</td>
<td>26</td>
</tr>
<tr>
<td>5.3 Heat Treatment and Product Forms</td>
<td>28</td>
</tr>
<tr>
<td>5.4 Alloy Compositions</td>
<td>31</td>
</tr>
<tr>
<td>5.5 Surface Finish</td>
<td>34</td>
</tr>
<tr>
<td>5.6 Grain Directions and Crystal Orientations</td>
<td>34</td>
</tr>
</tbody>
</table>
## Contents (continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0 Prevention and Control Methods for Hydrogen Damage</td>
<td>35</td>
</tr>
<tr>
<td>6.1 General Guidelines</td>
<td>35</td>
</tr>
<tr>
<td>6.2 Controlling the Material Factors</td>
<td>36</td>
</tr>
<tr>
<td>Select Proper Materials</td>
<td>36</td>
</tr>
<tr>
<td>Select Steels Using Nelson Curve for Corrosive Environment</td>
<td>37</td>
</tr>
<tr>
<td>Select Proper Thermo-mechanical Treatment</td>
<td>38</td>
</tr>
<tr>
<td>Surface Barriers and Coatings for Limited and Short-term Applications</td>
<td>38</td>
</tr>
<tr>
<td>6.3 Controlling the Hydrogen Factors</td>
<td>38</td>
</tr>
<tr>
<td>Reduce Hydrogen Gas Pressure</td>
<td>38</td>
</tr>
<tr>
<td>Reduce Hydrogen Gas Purity</td>
<td>39</td>
</tr>
<tr>
<td>Select Proper Operating Temperature</td>
<td>39</td>
</tr>
<tr>
<td>Hydrogen Relief by Bake Out</td>
<td>40</td>
</tr>
<tr>
<td>Reduce Material Cooling Rate in Gaseous Hydrogen Environment</td>
<td>41</td>
</tr>
<tr>
<td>Use Proper Welding Procedures</td>
<td>41</td>
</tr>
<tr>
<td>Controlling Cathodic Protection System</td>
<td>41</td>
</tr>
<tr>
<td>Application of Inhibitors in Liquid Environment</td>
<td>41</td>
</tr>
<tr>
<td>6.4 Controlling the Stress Factors</td>
<td>42</td>
</tr>
<tr>
<td>Reduce External Applied Stress</td>
<td>42</td>
</tr>
<tr>
<td>Reduce Internal Residual Stress</td>
<td>42</td>
</tr>
<tr>
<td>Application of Fracture Mechanics</td>
<td>42</td>
</tr>
<tr>
<td>7.0 Hydrogen Codes and Standards in the U.S.</td>
<td>43</td>
</tr>
<tr>
<td>8.0 References</td>
<td>44</td>
</tr>
</tbody>
</table>
# Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Material screening for hydrogen embrittlement based on HEE Index from NTS ratio</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>HEE Indexes for selected metals tested at 24 °C under high hydrogen pressure</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>HEE Indexes for selected steels tested at 24 °C under high hydrogen pressure</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>HEE Indexes for selected superalloys tested at 24 °C under high hydrogen pressure</td>
<td>11</td>
</tr>
<tr>
<td>5</td>
<td>Threshold stress intensity ($K_{TH}$) for A-286, JBK-75 and Incoloy 903 in hydrogen</td>
<td>16</td>
</tr>
<tr>
<td>6</td>
<td>Hydrogen effects on life reduction factor under LCF loading at various temperatures</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>Effects of heat treatment &amp; product forms on HEE index for superalloys</td>
<td>29</td>
</tr>
<tr>
<td>8</td>
<td>Effects of solution treatment and aging time on superalloys</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>Effects of heat treatment and product forms for Inconel® 718 superalloy</td>
<td>31</td>
</tr>
<tr>
<td>10</td>
<td>HEE Index for Fe-Ni-Cr superalloys and stainless steels as a function of Ni content (wt.%)</td>
<td>32</td>
</tr>
<tr>
<td>11</td>
<td>HEE Effects on grain direction of selected wrought superalloys</td>
<td>34</td>
</tr>
<tr>
<td>12</td>
<td>HEE Effects on crystal orientation for PWA 1480E superalloy</td>
<td>35</td>
</tr>
</tbody>
</table>
# Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Classification of HEE, IHE and HRE type based hydrogen, stress and material factors</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Distinction between HE and SCC based on the behavior of strain rates during test</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Trend line for HEE effects on NTS and RA for electro-deposited nickel</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>Effects of hydrogen pressure on threshold stress intensity ($K_{TH}$) for superalloys</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>Trend lines for Inconel 718 based on HEE index from $K_{IH}/K_{IC}$ and RA ratio</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>Effects of hydrogen on strain Controlled Low Cycle Fatigue (LCF) of superalloys</td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>Effects on HCF of Inconel 718 in 34.5 MPa hydrogen pressure at room temperature</td>
<td>21</td>
</tr>
<tr>
<td>8</td>
<td>HEE effects for cyclic crack growth rates (da/dN) for several superalloys</td>
<td>22</td>
</tr>
<tr>
<td>9</td>
<td>Larson-Miller Parameter for creep-rupture of Inconel 718 tested in hydrogen</td>
<td>23</td>
</tr>
<tr>
<td>10</td>
<td>Creep stress-rupture of directionally solidified MAR-M246 in hydrogen at 758 MPa stress level</td>
<td>24</td>
</tr>
<tr>
<td>11</td>
<td>Effects of hydrogen pressure on HEE index for superalloys at 22 °C</td>
<td>25</td>
</tr>
<tr>
<td>12</td>
<td>Effects of temperature on HEE index for selected steels</td>
<td>26</td>
</tr>
<tr>
<td>13</td>
<td>Effects of temperature on HEE index for selected nickel-based superalloys</td>
<td>27</td>
</tr>
<tr>
<td>14</td>
<td>Effects of temperature on HEE index for selected PM superalloys</td>
<td>28</td>
</tr>
<tr>
<td>15</td>
<td>HEE index for Fe-Ni-Cr superalloys and stainless steels as a function of Ni content (wt.%) (Data are from references in Table 10)</td>
<td>33</td>
</tr>
<tr>
<td>16</td>
<td>General guidelines for prevention and control of hydrogen damage</td>
<td>36</td>
</tr>
<tr>
<td>17</td>
<td>The Nelson curve defining safe upper limits for steels in hydrogen service</td>
<td>37</td>
</tr>
<tr>
<td>18</td>
<td>Effects of hydrogen gas purity on fracture toughness of carbon steels</td>
<td>39</td>
</tr>
<tr>
<td>19</td>
<td>Effects of hydrogen baking time and applied stress for Type 4340 steel</td>
<td>40</td>
</tr>
</tbody>
</table>
Definitions

*Hydrogen Embrittlement* — A process resulting in a decrease in the fracture toughness or ductility of a metal due to the presence of atomic hydrogen.

*Hydrogen Environmental Embrittlement (HEE)* — The degradation of certain mechanical properties that occur while a material is under the influence of an applied stress and intentionally exposed to gaseous hydrogen environment.

*HEE Index* — An initial material screening tool to evaluate the severity of hydrogen embrittlement effects on certain materials.

*Internal Hydrogen Embrittlement (IHE)* — The degradation of certain mechanical properties that occur as the result of the unintentional introduction of hydrogen into susceptible metals during forming or finishing operations.

*Hydrogen Reaction Embrittlement (HRE)* — The degradation of certain mechanical properties that occur when hydrogen reacts with the metal matrix itself to form metallic compounds such as metal hydride at relatively low temperatures. This form of hydrogen damage can occur in materials such as titanium, zirconium, and even some types of iron or steel-based alloys.
### Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIAA</td>
<td>American Institute of Aeronautics and Astronautics</td>
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<tr>
<td>ASME</td>
<td>American Society of Mechanical Engineers</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BPVC</td>
<td>Boiler &amp; Pressure Vessel Code</td>
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<tr>
<td>CC</td>
<td>Conventionally Cast</td>
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<tr>
<td>CTF</td>
<td>Cycles-to-Failure</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy</td>
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<tr>
<td>DS</td>
<td>Directional Solidification</td>
</tr>
<tr>
<td>E</td>
<td>Elasticity</td>
</tr>
<tr>
<td>EL</td>
<td>Plastic Elongation</td>
</tr>
<tr>
<td>FCC</td>
<td>Face Centered Cubic</td>
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<tr>
<td>HAZ</td>
<td>Heat Affected Zone</td>
</tr>
<tr>
<td>HCF</td>
<td>High Cycle Fatigue</td>
</tr>
<tr>
<td>HE</td>
<td>Hydrogen Embrittlement</td>
</tr>
<tr>
<td>HEE</td>
<td>Hydrogen Environmental Embrittlement</td>
</tr>
<tr>
<td>HRE</td>
<td>Hydrogen Reaction Embrittlement</td>
</tr>
<tr>
<td>IHE</td>
<td>Internal Hydrogen Embrittlement</td>
</tr>
<tr>
<td>$K_{TH}$</td>
<td>Threshold Stress Intensity Factor</td>
</tr>
<tr>
<td>LCF</td>
<td>Low Cycle Fatigue</td>
</tr>
<tr>
<td>NTS</td>
<td>Notched Tensile Strength</td>
</tr>
<tr>
<td>ODS</td>
<td>Oxide-dispersed Strengthening</td>
</tr>
<tr>
<td>PM</td>
<td>Powder Metallurgy</td>
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<tr>
<td>RA</td>
<td>Reduction of Area</td>
</tr>
<tr>
<td>SCC</td>
<td>Stress Corrosion Cracking</td>
</tr>
<tr>
<td>SSR</td>
<td>Slow Strain Rates</td>
</tr>
<tr>
<td>ST</td>
<td>Solution Treated</td>
</tr>
<tr>
<td>ST+A</td>
<td>Solution Treated and Aged</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate Tensile Strength</td>
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<tr>
<td>ppm</td>
<td>Parts per Million by Volume</td>
</tr>
<tr>
<td>YS</td>
<td>Yield Strength</td>
</tr>
</tbody>
</table>
Foreword

This Technical Memorandum was originally prepared as an Annex on the topic of Hydrogen Embrittlement for the AIAA Guide to Safety of Hydrogen and Hydrogen Systems (G-095-2004), then in revision [1]. The Guide establishes a uniform NASA process for hydrogen system design, materials selection operation, storage and transportation, and represents a broad collection of aerospace acumen. In the years since the Guide's initial publication the understanding of fracture growth, an important mechanism involved with hydrogen embrittlement, increased greatly, bringing a need for the addition of substantial new material. This revision proved too long for an annex to the Guide, and was deemed better suited as a separate publication. While this Technical Memorandum does stand as a separate document, its purpose can be enhanced if used as a companion to the Guide.
1.0 Introduction

Hydrogen embrittlement (HE) is a process resulting in a decrease in the fracture toughness or ductility of a metal due to the presence of atomic hydrogen. In addition to pure hydrogen gas as a direct source for the absorption of atomic hydrogen, the damaging effect can manifest itself from other hydrogen-containing gas species such as hydrogen sulfide (H₂S), hydrogen chloride (HCl), and hydrogen bromide (HBr) environments. It has been known that H₂S environment may result in a much more severe condition of embrittlement than pure hydrogen gas (H₂) for certain types of alloys at similar conditions of stress and gas pressure. The reduction of fracture loads can occur at levels well below the yield strength of the material. Hydrogen embrittlement is usually manifest in terms of singular sharp cracks, in contrast to the extensive branching observed for stress corrosion cracking. The initial crack openings and the local deformation associated with crack propagation may be so small that they are difficult to detect except in special nondestructive examinations. Cracks due to HE can grow rapidly with little macroscopic evidence of mechanical deformation in materials that are normally quite ductile.

This Technical Memorandum presents a comprehensive review of experimental data for the effects of gaseous Hydrogen Environment Embrittlement (HEE) for several types of metallic materials. Common material screening methods are used to rate the hydrogen degradation of mechanical properties that occur while the material is under an applied stress and exposed to gaseous hydrogen as compared to air or helium, under slow strain rates (SSR) testing. Due to the simplicity and accelerated nature of these tests, the results expressed in terms of HEE index are not intended to necessarily represent true hydrogen service environment for long-term exposure, but rather to provide a practical approach for material screening, which is a useful concept to qualitatively evaluate the severity of hydrogen embrittlement. The effects of hydrogen gas on mechanical properties such as tensile strength, ductility, fracture, low and high cycle fatigue, crack growth rate, and creep rupture are analyzed with respect to the general trends established from the HEE index values. It is observed that the severity of HE effects is also influenced by environmental factors such as pressure, temperature, and hydrogen gas purity. The severity of HE effects is also influenced by material factors such as surface finish, heat treatment, and product forms, compositions, grain direction, and crystal orientations.

2.0 Classification of Hydrogen Embrittlement

The interaction between hydrogen and metals can result in the formation of solid solutions of hydrogen in metals, solid compounds as hydride, and gaseous compounds with other elements in the metal. The atomic hydrogen itself can also react to form molecular hydrogen. Because of these complex interactions, much confusion exists in the published literature over the definition of HE. Regardless, the hydrogen embrittlement effects do not require the entire component to become embrittled. The damaging effects usually manifest themselves as localized crack growths with little macroscopic evidence of mechanical deformation in susceptible materials. Hydrogen embrittlement through these hydrogen-metals interactions can be classified into three broad categories: Hydrogen Environmental Embrittlement (HEE), Internal Hydrogen Embrittlement (IHE), and Hydrogen Reaction Embrittlement (HRE). In general, HEE represents the condition when the materials are being exposed to a high-pressure gaseous hydrogen environment. The definition of IHE often implies that the source of hydrogen is usually not from a high-pressure gaseous system as in HEE, but the hydrogen for IHE is from an electrochemical process such as electroplating, corrosion, cathodic charging, and even from thermal charging. Furthermore, the source of hydrogen for IHE can also come from moisture and enter the metals during welding, casting, and solidification processes from the foundry. However, the HEE and IHE effects are similar in many instances and they both require an external applied stress in order for the hydrogen embrittlement effects to occur. In contrast with HEE and IHE, the
definition for HRE is usually irreversible hydrogen damage due to a chemical reaction with hydrogen, and that such damage can occur without an external applied stress.

Figure 1 is a diagram showing an overlapped region that forms the HEE, IHE, and HRE; and the size of this region graphically represents the severity for HE. The size of the overlapped region can increase or decrease, depending on how significant the intersections are from the three main circles that represent the influence of material type, hydrogen embrittlement, and the applied stress. By definition, the intersections of the hydrogen, material, and stress circles produce the HEE and IHE effects within the same overlapped region positioned at the center of this graph. The difference between HEE and IHE is that the source of hydrogen for IHE is not usually from a high-pressure system, but the hydrogen is unintentionally produced and the internally absorbed hydrogen can result in a time-delayed embrittlement effect under an applied stress. Because the HRE type is formed by the intersection between hydrogen and material, HRE type can exist without the influence of the applied stress circle. Additional information on these three broad categories of HEE, IHE, and HRE is given in the following sections.

2.1 Hydrogen Environmental Embrittlement

Hydrogen Environmental Embrittlement is commonly known as the degradation of certain mechanical properties that occur while the material is under the influence of an applied stress and intentionally exposed to a gaseous hydrogen environment. The crack initiation is usually at the surface near the root of a notch or surface defect. It is noted that the applied stress values required to cause failure are in tension mode and can stay well below the yield strength for highly susceptible materials. In most cases, the constant static loading is usually considered to be more sensitive to HE than cyclic or dynamic loading, particularly at high cycle. The residual stress is also important and must be considered in combination with the applied external stress. Material screening tests using SSR (pseudo-static) or static loading on specially designed notched coupons are commonly used to determine a threshold stress value. In a well-characterized condition, such threshold stress values may be used to indicate the maximum allowable stress that can be applied to avoid the HEE under an applied external load. In this Technical Memorandum, a comprehensive review of experimental data for the effects of HEE is presented for several types of metallic materials.
2.2 Internal Hydrogen Embrittlement

Internal Hydrogen Embrittlement is commonly recognized as the result of the unintentional introduction of hydrogen into susceptible metals during forming or finishing operations. For example, the IHE effect is the result of the absorption of atomic hydrogen from common chemical processes such as acid pickling, electroplating, corrosive and cathodic charging. All of these are considered as electrochemical processes involving the discharge of hydrogen ions. However, IHE can also be derived from exposing the susceptible material to certain aqueous environments, which is also an electrochemical process involving the discharge of hydrogen ions.

The cracks for IHE usually occur internally near the root of an internal defect, where the localized stress values are high. However, the distinction between IHE and HEE is not always clearly defined for the thermal charging of hydrogen at relatively high temperatures. For example, the IHE effects are often associated with the absorption of hydrogen at ambient atmosphere by molten metal during the welding or casting process. In this case, the sources of hydrogen include moisture in the high-humidity, organic contaminants on the surface of the prepared weld joint. Upon rapid cooling of the weld or casting, entrapped hydrogen can produce internal fissuring or other damaging effects that often attribute to IHE. Because of the higher solubility of hydrogen at high temperature, rapid cooling of heavy sections of certain materials operating in high pressure and temperature conditions can result in IHE without having to experience a high level of applied external stress. This is because the solubility and diffusivity of hydrogen in metals are sharply decreased with lowering of temperatures, making the materials become supersaturated by hydrogen under rapid cooling conditions.

Some differences are recognized between the hydrogen absorption process from a high-pressure gaseous environment for HEE versus the diffusion and absorption process from an electrochemical environment for IHE. However, once atomic hydrogen has been absorbed by a material, whether from a gaseous or electrochemical source, the HE effects for HEE and IHE are similar, which have been shown for a number of materials.

2.3 Hydrogen Reaction Embrittlement

At certain elevated temperatures and pressures, atomic hydrogen can easily diffuse through metal surfaces and react internally with certain elements and compounds. However, hydrogen can also react with the metal matrix itself to form metallic compounds such as metal hydride at relatively low temperatures. This form of hydrogen damage is known as Hydrogen Reaction Embrittlement (HRE), which can occur in materials such as titanium, zirconium, and even for some types of iron or steel-based alloys. For example, the common reaction is between hydrogen and iron-carbides to form methane (CH₄), according to the following chemical reaction (Eq. 1):

\[
4H + Fe₃C = CH₄ + 3Fe \quad \text{Eq. (1)}
\]

Beneath the surface layer and deep within the bulk of the material, the formation and migration of CH₄ gas molecules usually concentrate at grain boundaries, and metallurgical features such as inclusions, impurity, and defects can lead to brittle rupture through the formation of voids, blisters and a network of discontinuous microcracks. Moreover, because the carbide phase is a reactant in the mechanism, its depletion in the vicinity of generated defects serves as direct evidence of the HRE mechanism itself. The HRE sensitivity depends on the amount of carbon or carbide in the alloy, the hydrogen concentration, gas pressure, and temperature usually in the range of 200 to 600 °C (392 to 1110 °F). Alloy steels with stable carbides (e.g., chromium-carbides) are less susceptible to this form of hydrogen attack due to the greater stability of Cr₃C versus Fe₃C found in carbon steels. However, as the pressure and
temperature of hydrogen environment increases, a greater amount of these alloying additions are required to stabilize such attack.

For steel-based alloys, the susceptibility of steels to HRE can be judged from the Nelson curves, which indicate the regions of temperature and pressure in which a variety of steels will be sensitive to hydrogen. The Nelson curve is discussed in further detail in Section 6.3 for prevention and control of HE.

2.4 Hydrogen Embrittlement versus Stress Corrosion Cracking

When a metal is exposed to an aqueous environment that involves hydrogen, it is important to recognize the difference between HE and Stress Corrosion Cracking (SCC). In general, HE is considered as a cathodic mechanism and SCC as an anodic mechanism. The SCC is a dissolution mechanism of removing materials at the crack tip through a corrosion process, and the environments that cause SCC are usually aqueous in nature, such as by contact with condensed layers of moisture or by immersion in a bulk liquid solution. However, during a corrosion process, both anodic and cathodic reactions can occur near the crack tip for some materials, such that the cathodic mechanism is the hydrogen evolution at the surface, which would lead to the diffusion of hydrogen into the bulk of the material. For some materials, the synergistic mechanism of crack growth is thought to be a combination of local anodic dissolution and cathodic hydrogen embrittlement. Whether crack extension is by anodic dissolution or by HE remains an open question for some materials subjected to an aqueous environment.

In an aqueous medium, the distinction between HE and SCC sometimes can be made by noting the effect of small impressed currents on the time-to-failure in a constant load test. If cracking has occurred by an SCC mechanism, application of a small anodic current shortens the time to failure. When HE is the main mechanism, application of a cathodic current will accelerate the time to failure. The distinction between HE and SCC can also be made based on strain rates under HE testing. For SCC, if the strain rate is too high, ductile fracture will occur before the necessary corrosion reactions can take place; therefore, relatively slow strain rates must be used. However, if the strain rate is too low, corrosion may be prevented because of repassivation or film repair so that the necessary reactions of bare metal cannot be sustained and SCC reaction may not occur. Therefore, a unique range of strain rate must be determined in each SCC case [2]. For some materials, this mechanistic difference can be used to distinguish between anodic SCC and cathodic SCC mechanisms, as shown in Figure 2.
3.0 Hydrogen Embrittlement Characterization

3.1 Material Screening Methods

Material screening methods are used to rate the gaseous HEE of certain mechanical properties that occur while the material is under stress and exposed to gaseous hydrogen, as compared to air or an inert environment such as helium. Experimentally, it has been found that the general trend for HEE effects on Notched Tensile Strength (NTS), measured from a notched specimen, is well correlated with the Reduction of Area (RA) measured from a smooth specimen under SSR testing. For example, the trend line for HEE effects on NTS and RA as a function of temperature, at hydrogen pressure of 8.3 MPa (1.2 ksi), is shown in Figure 3 for electro-deposited nickel [3]. There are several proposed test standards for the HEE effects; however, the test procedures and specimen preparations as baselined in G129 and G142 [2, 4] from the American Society for Testing and Materials (ASTM) are commonly used as material screening methods for the HE susceptibility under SSR testing. These test methods can also be used to evaluate the effects of material composition, processing, and heat treatment when the materials are exposed to specific hydrogen pressure and temperature conditions.

According to the ASTM G129 standard [2], as a minimum the HEE effects can be evaluated in terms of the reduction ratio of NTS from a notched specimen, and the reduction ratio of RA from a smooth specimen. Due to the simplicity and accelerated nature of these tests, the results are not intended to necessarily represent true hydrogen service environment for long-term exposure, but rather to provide a basis for material screening for HEE.
3.2 Qualitative Ratings

The property ratio for NTS, RA, and EL (plastic elongation), tested in gaseous hydrogen environment as compared to helium or air, is commonly used as the HEE index. It should be noted that the RA and the EL values are obtained from smooth tensile specimens and not from notched tensile specimens. By using a compact tension, fatigue pre-cracked specimen, an important HEE index based on the threshold stress intensity factor ratio, is discussed in further detail for hydrogen effects on fracture properties (Section 4.2). In general, HEE index is a simple concept to evaluate the severity of HE as an initial material screening tool. In all cases, the material screening for the HEE effects is based on the decrease in the values of the HEE indexes from values of 1 to 0. Therefore, to maximize the HE resistance, it is desirable to obtain values for the HEE index as close to unity of 1 as possible. According to ASTM-G129, these commonly used HEE indexes are defined as follows (Eq. 2, 3, and 4):

\[
\text{NTS Ratio} = \frac{\text{NTS in Hydrogen}}{\text{NTS in Air or Helium}} \quad \text{Eq. (2)}
\]

\[
\text{RA Ratio} = \frac{\text{RA in Hydrogen}}{\text{RA in Air or Helium}} \quad \text{Eq. (3)}
\]

\[
\text{EL Ratio} = \frac{\text{(EL) in Hydrogen}}{\text{(EL) in Air or Helium}} \quad \text{Eq. (4)}
\]

Under the SSR testing procedures, typical strain rates for smooth specimens are \( \leq 0.0005 \text{ in/in/min (8.3 x 10^{-6} mm/mm/s)} \) and stroke rate of \( \leq 0.0005 \text{ in/min (2.1 x 10^{-4} mm/s)} \) for notched specimens, respectively. For notched specimens, the typical values for stress concentration factor (\( K_I \)) are 6 to 8. The HEE indexes based on the NTS and RA ratio are the most preferred and commonly available for material screening evaluation.
Historically, hydrogen embrittlement evaluation for a large number of metallic materials has been investigated by Walter and Chandler, who first suggested classifying the susceptibility of HEE index measuring at room temperature, in 10 ksi (69 MPa) hydrogen pressure, into four categories: negligible, slight, severe and extreme [5]. Their classification was based mostly on NTS ratio taken from notched tensile specimens, and the RA ratio taken from smooth specimens. Similar hydrogen embrittlement classifications for material screening were also suggested by J. Harris and M. VanWanderham [6]. Because of its usefulness for qualitative material screening method, a simplified suggestion format for hydrogen embrittlement categorization, based on these early works, is shown in Table 1. In this table, the HEE index is based on the NTS ratio taken from notched specimens. It must be noted that the proposed HEE index classification is only a qualitative material screening method based on an accelerated test in laboratory environment. It should not be used for component design without detailed fracture mechanics and design analysis for safety usage in hydrogen environment, particularly for materials that are qualitatively rated in the embrittlement category of High, Severe or Extreme.

### Table 1

<table>
<thead>
<tr>
<th>H Embrittlement Category</th>
<th>HEE Index (NTS Ratio)</th>
<th>Material Screening Notes *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negligible</td>
<td>1.0 - 0.97</td>
<td>Materials can be used in the specified hydrogen pressure &amp; temperature range with fracture mechanics &amp; crack growth analysis in hydrogen.</td>
</tr>
<tr>
<td>Small</td>
<td>0.96 - 0.90</td>
<td></td>
</tr>
<tr>
<td>High</td>
<td>0.89 - 0.70</td>
<td>Cautiously use only for limited applications with detailed fracture mechanics &amp; crack growth analysis in hydrogen.</td>
</tr>
<tr>
<td>Severe</td>
<td>0.69 - 0.50</td>
<td>Not recommended for usage at specific pressure and temperature where the HEE Index is measured.</td>
</tr>
<tr>
<td>Extreme</td>
<td>0.49 - 0.0</td>
<td></td>
</tr>
</tbody>
</table>

*Based on application at specific hydrogen pressure and temperature, where HEE Index is measured. In all categories, additional testing and fracture analysis must be performed beyond the material screening phase.

### 3.3 Material Database for Hydrogen Environment Embrittlement

A comprehensive worldwide database compilation over the past 50 years has shown that the HEE index for metallic materials is mostly collected at two high hydrogen pressure points of 5 ksi (34.5 MPa) to 10 ksi (69 MPa), near room temperature. This invaluable database is commonly used as a qualitative material screening process for HE severity based on the decrease in the value of the HEE index from unity. Tables 2, 3 and 4 represent a critical review of the available HEE indexes for several metallic materials, based on the property ratios for NTS, RA, and EL testing at room temperature for hydrogen pressure range mostly between 5 ksi (34.5 MPa) to 10 ksi (69 MPa). The HEE index for selected nickel, titanium, copper, and aluminum based alloys are given in Table 2. The HEE index for several different types of austenitic, ferritic, and martensitic steels is given in Table 3. The HEE index for Nickel, Iron and Cobalt based superalloys is given in Table 4.

It must be noted that the material database, using the HEE index classification shown here in Table 2, is only a qualitative material screening method based on an accelerated test in laboratory environment testing at near room temperature 22 °C (75 °F) for hydrogen pressure range mostly between 5 ksi (34.5 MPa) to 10 ksi (69 MPa). This material database should not be used to estimate the HEE effects at high temperature, nor for components design without the detail fracture analysis for safety usage in hydrogen gas environment, particularly, for materials that are qualitatively rated in the HE category of High, Severe and Extreme.
### Table 2

**HEE Indexes for selected metals tested at 24 °C under high hydrogen pressure**

<table>
<thead>
<tr>
<th>Alloy System</th>
<th>MATERIAL</th>
<th>H Pressure (MPa)</th>
<th>Qualitative Rating for HEE</th>
<th>HEE Index, (Ratio H/He)</th>
<th>Smooth Ductility, (%), in Helium or Air</th>
<th>Tensile Strengths, in Helium or Air (MPa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Based</td>
<td>Nickel (electroformed)</td>
<td>68.9</td>
<td>extreme</td>
<td>0.31</td>
<td>827</td>
<td>a, b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nickel 270</td>
<td>68.9</td>
<td>high</td>
<td>0.70</td>
<td>531</td>
<td>34</td>
<td>331</td>
</tr>
<tr>
<td></td>
<td>Nickel 301</td>
<td>68.9</td>
<td>extreme</td>
<td>0.35</td>
<td>482</td>
<td>792</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>K-Monel (precipitated)</td>
<td>68.9</td>
<td>extreme</td>
<td>0.45</td>
<td>1729</td>
<td>958</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>K-Monel (annealed)</td>
<td>68.9</td>
<td>high</td>
<td>0.73</td>
<td>992</td>
<td>689</td>
<td>a</td>
</tr>
<tr>
<td>Titanium Based</td>
<td>Titanium (pure)</td>
<td>68.9</td>
<td>small</td>
<td>0.95</td>
<td>686</td>
<td>365</td>
<td>434</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4V (annealed)</td>
<td>34.5</td>
<td>high</td>
<td>0.89</td>
<td>1426</td>
<td>1006</td>
<td>1040</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4V (annealed)</td>
<td>68.9</td>
<td>low</td>
<td>0.08</td>
<td>1674</td>
<td>909</td>
<td>1075</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4V (STA)</td>
<td>48.2</td>
<td>severe</td>
<td>0.58</td>
<td>1571</td>
<td>1082</td>
<td>1130</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-4V (STA)</td>
<td>68.9</td>
<td>severe</td>
<td>0.85</td>
<td>1385</td>
<td>730</td>
<td>779</td>
</tr>
<tr>
<td></td>
<td>Ti-5Al-2.5Sn (ELI)</td>
<td>68.9</td>
<td>high</td>
<td>0.91</td>
<td>551</td>
<td>785</td>
<td>f</td>
</tr>
<tr>
<td></td>
<td>Ti-11.5Mo-6Zr-4.5Sn (STA)</td>
<td>34.5</td>
<td>extreme</td>
<td>0.18</td>
<td>978</td>
<td>1068</td>
<td>g</td>
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<tr>
<td></td>
<td>Alpha-Ti alloy</td>
<td>13.8</td>
<td>extreme</td>
<td>0.54</td>
<td>537</td>
<td>537</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>Gamma-TiAl alloy</td>
<td>13.8</td>
<td>extreme</td>
<td>0.39</td>
<td>0.95</td>
<td>4.1</td>
<td>4</td>
</tr>
<tr>
<td>Copper Based</td>
<td>Copper (OFHC)</td>
<td>68.9</td>
<td>negligible</td>
<td>1.00</td>
<td>599</td>
<td>269</td>
<td>289</td>
</tr>
<tr>
<td></td>
<td>Aluminum Bronze</td>
<td>68.9</td>
<td>negligible</td>
<td>1.02</td>
<td>220</td>
<td>599</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td>Be-Cu alloy 25</td>
<td>68.9</td>
<td>small</td>
<td>0.93</td>
<td>1344</td>
<td>544</td>
<td>648</td>
</tr>
<tr>
<td></td>
<td>GRCoP-84 (Cu-8Cr-4Nb)</td>
<td>34.5</td>
<td>negligible</td>
<td>1.03</td>
<td>241</td>
<td>413</td>
<td>i</td>
</tr>
<tr>
<td></td>
<td>NARloy-Z (Cu-3Ag-0.5Zr)</td>
<td>40.0</td>
<td>negligible</td>
<td>1.10</td>
<td>138</td>
<td>269</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>70-30 Brass</td>
<td>68.9</td>
<td>negligible</td>
<td>0.98</td>
<td>124</td>
<td>365</td>
<td>h</td>
</tr>
<tr>
<td>Aluminum Based</td>
<td>1100-T0</td>
<td>68.9</td>
<td>negligible</td>
<td>1.38</td>
<td>124</td>
<td>34</td>
<td>110</td>
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<tr>
<td></td>
<td>2011</td>
<td>68.9</td>
<td>negligible</td>
<td>1.01</td>
<td>227</td>
<td>296</td>
<td>h</td>
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<tr>
<td></td>
<td>2024</td>
<td>68.9</td>
<td>negligible</td>
<td>0.95</td>
<td>324</td>
<td>441</td>
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<tr>
<td></td>
<td>5086</td>
<td>68.9</td>
<td>negligible</td>
<td>1.05</td>
<td>193</td>
<td>303</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td>6061-T6</td>
<td>68.9</td>
<td>negligible</td>
<td>1.07</td>
<td>496</td>
<td>227</td>
<td>269</td>
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<tr>
<td></td>
<td>6069</td>
<td>68.9</td>
<td>negligible</td>
<td>1.00</td>
<td>158</td>
<td>193</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td>7039</td>
<td>68.9</td>
<td>negligible</td>
<td>1.00</td>
<td>152</td>
<td>179</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td>7075-T73</td>
<td>68.9</td>
<td>negligible</td>
<td>0.98</td>
<td>799</td>
<td>372</td>
<td>455</td>
</tr>
</tbody>
</table>

NTS = Notched Tensile Strength; EL = Plastic Elongation; RA = Reduction of Area; YS = Yield Strength; UTS = Ultimate Tensile Strength

e. NASA Marshall Space Flight Center unpublished data [10].
### Table 3

HEE Indexes for selected steels tested at 24 °C under high hydrogen pressure

<table>
<thead>
<tr>
<th>Alloy System</th>
<th>MATERIAL</th>
<th>H Pressure (MPa)</th>
<th>Qualitative Rating for HEE</th>
<th>HEE Index, (Ratio H/He)</th>
<th>Smooth Ductility (%), in Helium or Air</th>
<th>Tensile Strengths, in Helium or Air (MPa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Austenitic Steels</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CG-27 (precip. hardened)</td>
<td>68.9</td>
<td>extreme</td>
<td>0.34</td>
<td>29</td>
<td>806</td>
<td>1164</td>
<td>a</td>
</tr>
<tr>
<td>Tenelon</td>
<td>68.9</td>
<td>high</td>
<td>0.85</td>
<td>65</td>
<td>496</td>
<td>875</td>
<td>a</td>
</tr>
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<td>A302B</td>
<td>68.9</td>
<td>high</td>
<td>0.79</td>
<td>0.85</td>
<td>0.50</td>
<td>26</td>
<td>44</td>
</tr>
<tr>
<td>A286 (Sol Treat @1640°F)</td>
<td>68.9</td>
<td>negligible</td>
<td>0.97</td>
<td>1.10</td>
<td>0.98</td>
<td>45</td>
<td>586</td>
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<tr>
<td>216</td>
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<td>high</td>
<td>0.87</td>
<td>0.92</td>
<td>0.91</td>
<td>86</td>
<td>78</td>
</tr>
<tr>
<td>304L</td>
<td>68.9</td>
<td>high</td>
<td>0.93</td>
<td>0.84</td>
<td>43</td>
<td>627</td>
<td>847</td>
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<tr>
<td>304N</td>
<td>68.9</td>
<td>high</td>
<td>1.00</td>
<td>0.75</td>
<td>62</td>
<td>72</td>
<td>379</td>
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<tr>
<td>304LN</td>
<td>68.9</td>
<td>high</td>
<td>0.89</td>
<td>1.03</td>
<td>0.96</td>
<td>63</td>
<td>78</td>
</tr>
<tr>
<td>305</td>
<td>68.9</td>
<td>high</td>
<td>0.86</td>
<td>0.83</td>
<td>0.60</td>
<td>53</td>
<td>71</td>
</tr>
<tr>
<td>3095</td>
<td>68.9</td>
<td>small</td>
<td>0.96</td>
<td>0.97</td>
<td>85</td>
<td>76</td>
<td>241</td>
</tr>
<tr>
<td>310</td>
<td>68.9</td>
<td>small</td>
<td>0.93</td>
<td>1.00</td>
<td>0.96</td>
<td>56</td>
<td>64</td>
</tr>
<tr>
<td>316</td>
<td>68.9</td>
<td>negligible</td>
<td>1.00</td>
<td>0.95</td>
<td>1.04</td>
<td>59</td>
<td>72</td>
</tr>
<tr>
<td>321</td>
<td>34.5</td>
<td>high</td>
<td>0.88</td>
<td>0.83</td>
<td>0.90</td>
<td>77</td>
<td>66</td>
</tr>
<tr>
<td>347</td>
<td>34.5</td>
<td>small</td>
<td>0.92</td>
<td>1.00</td>
<td>1.00</td>
<td>38</td>
<td>70</td>
</tr>
<tr>
<td>18-2-12 (Nitronic 32)</td>
<td>68.9</td>
<td>severe</td>
<td>0.64</td>
<td>0.47</td>
<td>75</td>
<td>78</td>
<td>482</td>
</tr>
<tr>
<td>21-6-9 + 0.1N (Nitronic 40)</td>
<td>68.9</td>
<td>high</td>
<td>0.89</td>
<td>0.80</td>
<td>65</td>
<td>74</td>
<td>434</td>
</tr>
<tr>
<td>21-6-9 + 0.3N (Nitronic 40)</td>
<td>68.9</td>
<td>high</td>
<td>0.85</td>
<td>56</td>
<td>78</td>
<td>462</td>
<td>799</td>
</tr>
<tr>
<td>22-13-S (Nitronic 50)</td>
<td>68.9</td>
<td>negligible</td>
<td>1.00</td>
<td>1.00</td>
<td>51</td>
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<td>586</td>
</tr>
<tr>
<td>18-18 Plus</td>
<td>68.9</td>
<td>severe</td>
<td>0.67</td>
<td>63</td>
<td>517</td>
<td>909</td>
<td>a</td>
</tr>
<tr>
<td>18-2-Mn</td>
<td>68.9</td>
<td>severe</td>
<td>0.64</td>
<td>51</td>
<td>730</td>
<td>1006</td>
<td>a</td>
</tr>
<tr>
<td>18-3-Mn</td>
<td>68.9</td>
<td>small</td>
<td>0.92</td>
<td>50</td>
<td>531</td>
<td>785</td>
<td>a</td>
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<tr>
<td>Ferritic Steels</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A106-Gr. B</td>
<td>6.9</td>
<td>high</td>
<td>0.78</td>
<td>0.86</td>
<td>14</td>
<td>58</td>
<td>462</td>
</tr>
<tr>
<td>A212-61T (normalized)</td>
<td>68.9</td>
<td>severe</td>
<td>0.68</td>
<td>0.60</td>
<td>57</td>
<td>765</td>
<td>l</td>
</tr>
<tr>
<td>A372 (class 4)</td>
<td>68.9</td>
<td>high</td>
<td>0.74</td>
<td>0.50</td>
<td>0.34</td>
<td>20</td>
<td>53</td>
</tr>
<tr>
<td>A372 (grade J)</td>
<td>24.1</td>
<td>severe</td>
<td>0.45</td>
<td>0.34</td>
<td>37</td>
<td>68</td>
<td>296</td>
</tr>
<tr>
<td>A515-Gr. 70</td>
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**Table Notes:***

### Table 4

**HEE Indexes for selected superalloys tested at 24 °C under high hydrogen pressure**

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<th>Alloy System</th>
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<th>HEE Index, (Ratio H/He)</th>
<th>Smooth Ductility (%), in Helium or Air</th>
<th>Tensile Strengths, in Helium or Air (MPa)</th>
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<td>severe</td>
<td>0.60</td>
<td>0.40</td>
<td>28</td>
<td>1688</td>
<td>c</td>
</tr>
<tr>
<td>Incoloy 903 (ST only)</td>
<td>34.5</td>
<td>negligible</td>
<td>0.98</td>
<td>1.00</td>
<td>0.96</td>
<td>42</td>
<td>2122</td>
</tr>
<tr>
<td>Incoloy 903 (ST + Aged)</td>
<td>24</td>
<td>(T.C.)*</td>
<td>severe</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Incoloy 907</td>
<td>68.9</td>
<td>small</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Incoloy 909 (ST + Aged)</td>
<td>34.5</td>
<td>extreme</td>
<td>0.36</td>
<td>0.39</td>
<td>12</td>
<td>22.4</td>
<td>1054</td>
</tr>
<tr>
<td>JBK-7S (ST only)</td>
<td>34.5</td>
<td>negligible</td>
<td>0.98</td>
<td>0.92</td>
<td>28</td>
<td>51</td>
<td>1585</td>
</tr>
<tr>
<td>JBK-7S (ST + Aged)</td>
<td>172</td>
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<td>0.75</td>
<td>0.45</td>
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<tr>
<td>MA 956 (Longitudine)</td>
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<td>severe</td>
<td>0.58</td>
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<td></td>
</tr>
<tr>
<td>MA 956 (Transverse)</td>
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<td>extreme</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-SPAN-C (alloy 902)</td>
<td>68.9</td>
<td>small</td>
<td>0.93</td>
<td>16</td>
<td>751</td>
<td>1158</td>
<td>s</td>
</tr>
<tr>
<td>Haynes 188</td>
<td>48.2</td>
<td>high</td>
<td>0.92</td>
<td>0.63</td>
<td>63</td>
<td>1130</td>
<td></td>
</tr>
<tr>
<td>MP3SN</td>
<td>24</td>
<td>high</td>
<td>0.73</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MP3SN</td>
<td>24</td>
<td>high</td>
<td>0.70</td>
<td>0.85</td>
<td>23</td>
<td>58</td>
<td>2425</td>
</tr>
<tr>
<td>MP159</td>
<td>24</td>
<td>high</td>
<td>0.66</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MP98T</td>
<td>34.5</td>
<td>severe</td>
<td>0.63</td>
<td>7</td>
<td>31</td>
<td>2253</td>
<td>1895</td>
</tr>
<tr>
<td>X-45 (superalloy)</td>
<td>34.5</td>
<td>high</td>
<td>0.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*T.C. = H$_2$ thermally charged at 200°F at indicated pressure for 200 hrs (A286) and 500 hrs (Incoloy 903). HEE tested at 24°C.

b NASA Marshall Space Flight Center unpublished data [10].
3.4 General Observation for Metallic Materials

Aluminum and Aluminum Alloys

Dry hydrogen gas environment has negligible effects on aluminum and its alloys. The major issue with hydrogen arises mostly from the exposure to moisture and the formation of gas-filled voids during molten, casting, and solidification processes from the foundry. These voids are material defects, which affect both cast and wrought product’s mechanical properties such as ductility and fracture toughness. During cooling from the melt, hydrogen diffuses to and precipitates in casting defects, producing cracks from the decreased solubility of hydrogen in solid metal at lower temperature. Dry hydrogen gas near room temperature, at pressure up to 10 ksi (69 MPa), does not cause a significant hydrogen embrittlement effect in aluminum alloys. However, when high-strength aluminum alloy is electrochemically charged by hydrogen in an aqueous solution, its ductility is reduced. The main mechanism of embrittlement for aluminum alloys in an aqueous medium could be the SCC rather than the pure HE effect. The combined mechanism of anodic material dissolution SCC or cathodic hydrogen embrittlement remains an open question for aluminum alloys when subjected to an aqueous environment.

Copper and Copper Alloys

Copper and the copper-rich alloys are usually not susceptible to hydrogen embrittlement unless they contain oxygen or copper-oxide. When oxygen-bearing copper and copper alloys are annealed or heated in hydrogen environment, the atomic hydrogen diffuses into the metals and reacts with the copper-oxide or the oxygen to form water, which is converted to high-pressure steam if the temperature is above 375 °C (705 °F). This is a classic example of HRE, as the steam will induce hydrogen damage in the forms of fissures and blisters, decreasing the fracture toughness and ductility of the metals even without the application of external pressure. Tough pitch coppers usually contain small quantities of Cu₂O; therefore, they should not be exposed to hydrogen gas at any temperature if they will subsequently be exposed to temperature above 370 °C (700 °F). The equation for reaction with cuprous oxide particles is (Eq. 5):

\[ \text{Cu}_2\text{O} + 2\text{H} = 2\text{Cu} + \text{H}_2\text{O (g)} \]  

Eq. (5)

Nickel and Nickel based Alloys

Nickel and nickel-based alloys have good properties for high-temperature strength, oxidation, and hot corrosion resistance. However, a nickel-based alloy that has good ratings for dry-oxidation and chemical corrosive environment does not automatically mean that it is also immune to HE. As an element, pure nickel is severely embrittled by hydrogen; therefore, most binary alloys with nickel-rich composition such as nickel-copper, nickel-iron, nickel-cobalt, and nickel-tungsten are also found to be highly embrittled by hydrogen in the nickel-rich regions [40]. In some nickel-rich alloy systems, the same observation is held. For example, the nickel-rich alloys known as K-Monel® have been known to be embrittled by hydrogen at high pressure. However, the influence of nickel on complex compositions for steels and superalloys is more complex to analyze due to factors such as heat treatment and product forms. The measurement of HEE indexes for several materials that contain nickel and the nickel-based superalloys are shown in Table 3 and Table 4, respectively.

\[ ^1 \text{ Monel® is a registered trademark of Inco Alloys International, Inc., Huntington, West Virginia.} \]
Titanium and Titanium Alloys

In general, titanium and its alloys usually have excellent corrosion resistance properties in aqueous environment. This superior corrosion resistance property is due to a thin, stable, and tenacious titanium-oxide (TiO$_2$) film that naturally forms in air and water under the oxidizing conditions. However, under excessive cathodic charging from an impressed current, hydrogen embrittlement has been observed for some of these titanium alloys in aqueous media. The naturally formed TiO$_2$ film on titanium appears to inhibit hydrogen uptake effectively under low-to-moderate cathodic charging conditions. However, under high cathodic charging current densities this protective film can break down and become non-protective for titanium alloys and will allow atomic hydrogen to penetrate into the bulk of the materials. In near-neutral electrolytes such as seawater, galvanic coupling to metals such as zinc, aluminum, and magnesium can induce enhanced hydrogen uptake and hydride formation when coupled with titanium at temperature above 80 °C (175 °F). On the other hand, in dry-hydrogen gas environment, titanium and its alloys will absorb hydrogen readily as the temperatures and pressures increase. Relatively small amounts of titanium-hydride precipitates are not detrimental for most applications, particularly in the hydrogen concentrations range of 40 to 80 ppm (part per million). However, excessive formation of titanium-hydride can form rapidly when the temperature is above 250 °C (480 °F). This type of hydrogen embrittlement is the HRE type; however, it is also considered as the IHE type by some industries during high-temperature processes such as welding or heat treatment in the presence of hydrogen. The distinction between IHE and HRE is not always well recognized for metals that form unstable hydrides, as they are positioned closely in the overlapping region, as shown in Figure 1.

Iron-based Alloys and Steels

The HEE susceptibility of steels can generally be viewed in four categories: austenitic, ferritic, martensitic, and precipitation hardening. In general, most low-strength austenitic steels are not very susceptible to hydrogen embrittlement, relative to the ferritic steels. However, the martensitic and precipitation-hardening steels are known to be extremely susceptible to the HEE and IHE effects. There is some commonality between the austenitic stainless steels and the Fe-Ni-Cr superalloys in terms of compositions versus the HEE effects, which is discussed in more detail in Section 5.4 (Alloy Compositions). Concerning the HRE effects, at certain elevated temperatures and pressures, atomic hydrogen can diffuse through metal and react internally with certain types of elements and compounds in the steel-based alloys. The most common reaction is between hydrogen and iron-carbides to form methane gas (CH$_4$). Because CH$_4$ cannot diffuse out of steel, an accumulation occurs, and this causes fissuring and blistering that leads to hydrogen embrittlement in loss of strength and ductility.

For steel-based alloys, the susceptibility of steels to HRE can be judged from the Nelson curves, which indicate the regions of temperature and pressure in which a variety of steels will be sensitive to hydrogen. The Nelson curve is discussed in further detail in Section 6.2 for prevention and control of hydrogen embrittlement. The addition of chromium and molybdenum to many carbon and low-alloy steels act as beneficial alloying elements, preventing HRE, whose effects are also termed the hydrogen attack phenomenon from decarburizing and fissuring.
**Superalloys**

Nickel-based superalloys have the most complex microstructure, which can be either solid solution or precipitation strengthened. More HEE index data are available for nickel-based alloys than any other types of superalloys. Iron-based superalloys have their origin of development from austenitic stainless steels and they are evolved on the principle of combining the (face centered cubic (FCC) matrix with both solid-solution hardening and precipitate-forming elements. The key feature for Iron-based superalloys is that the austenitic matrix is made from nickel and iron, with at least 25% Ni to stabilize the FCC phase. For this reason, iron-based superalloys are also called the nickel-iron based superalloys. The microstructure for cobalt-based superalloys is less complex than nickel-based alloys. Most cobalt alloys do not form gamma-prime strengthening phase, and they depend on the combination of solid-solution austenitic matrix FCC, and most importantly form the hard-carbide particles as strengthening mechanisms. The product forms for these three types of superalloys are commonly classified into cast or wrought. The differences in superalloy heat treatment and product form can have an effect on the degree of HE, as shown in Section 5.3. In general, conventional wrought and powder metallurgy (PM) processed superalloys have been found to be slightly less influenced by high-pressure hydrogen environments than cast polycrystalline superalloys with similar compositions.

### 4.0 Hydrogen Effects on Mechanical Properties

#### 4.1 Tensile Properties

It is experimentally found that the values for modulus of elasticity (E) and the yield strength (YS) of most materials are not affected by hydrogen. However, the ultimate tensile strength (UTS), taken from smooth tensile specimens, can be slightly or at best moderately reduced if the materials are deemed to be very susceptible to hydrogen embrittlement. Therefore, the ratio of E, UTS, and YS taken from smooth tensile specimens are not to be used as good indicators for HEE index.

The basic tensile properties that are strongly affected by hydrogen can be listed as the NTS from a sharp notched tensile specimen, or RA and EL from a smooth tensile specimen. Tables 2, 3, and 4 represent a critical review of the available HEE indexes for several metallic materials, based on the property ratios for NTS, RA, and EL, tested at room temperature for hydrogen pressure range mostly between 5 ksi (34.5 MPa) to 10 ksi (69 MPa). Experimentally, it has been found that the general trend for hydrogen effects on NTS ratio, measured from a notched specimen, is well correlated with the RA ratio and EL ratio, measured from a smooth specimen under SSR testing.

#### 4.2 Fracture Properties

Hydrogen has a significant influence on the crack initiation and growth behavior, particularly when reasonably large surface flaws exist on a susceptible material exposed in high-pressure hydrogen environment. Therefore, fracture mechanics is usually required to assess the maximum allowable stress and service life of a component, based on the surface flaw sizes and crack growth rates, in hydrogen environment. The published information for crack growth behaviors and particularly the fracture properties in hydrogen environment are significantly less extensive than for notched tensile strength (NTS) and smooth ductility (RA, EL). Two common types of fracture properties have been studied in hydrogen for several superalloys: the threshold stress intensity factor \( K_{TH} \), and the associated crack growth rates.

Using the ASTM E1681 test standard [41], the threshold stress intensity factor \( K_{TH} \) in hydrogen environment determined from a pre-cracked specimen, under static loading, can be a
very time-consuming task. For instance, according to work performed by M. Perra [42], his hydrogen test duration was typically 5000 hours (7 months) so that an average crack velocity as small as $10^{-11}$ m/s could be resolved. According to W. Chandler [7], for some materials the $K_{TH}$ values are difficult to measure because of the basic problem in determination of actual crack growth versus crack branching in gaseous hydrogen environment on a fracture sample. Because of the intrinsic nature from the experimental setup to determine the $K_{TH}$ by using a monitoring system for the “onset” of crack initiation, theoretically it appears that the $K_{TH}$ measurement may be more sensitive as an HE indicator than the simple HEE index based on NTS or RA ratio. In reality, the $K_{TH}$ proves to be difficult to measure accurately for certain gaseous hydrogen temperature and pressure set-up conditions. According to M. Perra [42], his reported $K_{TH}$ values, as shown in Table 5, for superalloys such as A-286, JBK 75, and Incoloy 903\textsuperscript{1} must be interpreted, in his own view, as “on a relative rather than an absolute basis, and the apparent $K_{TH}$ values within each sample group can vary as much as ±15%.” Figure 4 shows the trend behavior of $K_{TH}$ values as a function of hydrogen pressure for Inconel\textsuperscript{1} 718 and Incoloy 903 tested at room temperature [43]).

<table>
<thead>
<tr>
<th>Superalloys</th>
<th>Heat Treatment</th>
<th>Yield Strength (MPa)</th>
<th>Threshold (Kth) Stress Intensity, MPa.m$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M. Perra, ref. a)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Incoloy\textsuperscript{®} 903</td>
<td>Solutionize: 940°C/1hr/WQ. Age: 720°C/16hr.</td>
<td>917</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
<td>Solutionize: 940°C/1hr/WQ. Age: 720°C/16hr. + 620°C/8hr.</td>
<td>1055</td>
<td>33</td>
</tr>
<tr>
<td>JBK-75</td>
<td>High Energy Forging 970°C/WQ. Age: 675°C/8hr + 600°C/8hr</td>
<td>855</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>High Energy Forging 970°C/WQ. Age: 675°C/32hr.</td>
<td>923</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>Solutionize: 980°C/1hr/WQ. Age: 720°C/16hr.</td>
<td>717</td>
<td>44</td>
</tr>
<tr>
<td>A-286</td>
<td>Solutionize: 980°C/1hr/WQ. Age: 720°C/16hr.</td>
<td>779</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

n.a. = not applicable

\textsuperscript{1} Inconel\textsuperscript{®} and Incoloy\textsuperscript{®} are registered trademarks of Inco Alloys International, Inc., Huntington, West Virginia.

\[1\]

\[\text{Inconel® and Incoloy® are registered trademarks of Inco Alloys International, Inc., Huntington, West Virginia.}\]
For material screening purposes, the $K_{TH}$ values can also be used as the HEE indexes according to the ASTM-G129 test standard [2]. There are two types of HEE indexes based on the $K_{TH}$ ratios relative to the fracture toughness $K_{IC}$ and $K_C$ (Eq. 6 and 7):

1. **Plane Strain Threshold Stress Intensity Factor Ratio**, HEE index = $K_{I(TH)}/K_{IC}$ Eq. (6)

2. **Threshold Stress Intensity Factor Ratio**, HEE index = $K_{TH}/K_{C}$ Eq. (7)

Notice that the denominators or the “normalizing factors” for the first index is $K_{IC}$ and for the second index is $K_C$, both measuring in air or inert environment. The values for $K_{I(TH)}$ and $K_{TH}$ are stress intensity factors measured in hydrogen for plane strain and non-plane strain specimens, respectively. Accelerated test procedures for $K_{TH}$ measurement have also been proposed in recent years to estimate the $K_{TH}$ values from a pre-cracked specimen, without spending a considerable amount of time for the specimen to be under a constant static loading as baseline in ASTM-E1681 [41]. These relatively rapid test procedures are proposed in terms of using a minute incrementally rising load or displacement based on relatively slow strain rates (SSRs) on the pre-cracked specimens. According to ASTM-G129 [2] and more importantly ASTM F1624-06 [44], ISO 7539-9 [45], and W. Dietzel [46, 47], the proposed incremental step loading technique and/or SSR for the estimation of $K_{TH}$ are usually in the order of 1 to 10 μm/h. Notice that these SSR values for the pre-cracked specimens (the determination for $K_{TH}$) are much slower than the typical SSR values for notched and smooth tensile specimens (the determinations for NTS and ductility, respectively).

During the process of determining the $K_{TH}$ values for A-286 superalloy using a monitoring system for the “onset” of crack initiation under slow rising displacement, W. Chandler [7] reported that evidence of slow crack growth did occur in hydrogen environment for A-286, which has been qualitatively classified as negligibly embrittled by hydrogen based on the NTS index ratio of 0.97, shown in Table 4. However, this crack growth observation occurred only with loads large enough to cause yielding, and the crack growth for A-286 was considered to be very slow by Chandler. If the material was tested under such large loads as to cause yielding, one may expect that the resulting $K_{TH}$ value could be high and possibly approaching the $K_C$ value for
A-286 as tested in air. For A-286, JBK-75 and Incoloy 903, under various Solution Treated and Aged (ST+A) conditions as shown in Table 4, their $K_{TH}$ values are shown to be heavily affected by hydrogen. Therefore, the HEE index based on smooth RA ratio for these materials in Table 4, for heat treatment in ST+A conditions, are in qualitative agreement with the trend behavior for $K_{TH}$ values in hydrogen.

As an illustration for the similar behaviors between the HEE index derived from $K_{(TH)/KIC}$ and RA ratio, Figure 5 shows two HEE index trend lines for Inconel 718 tested in 34.5 MPa hydrogen pressure for a wide range of temperatures from -195 °C (-320 °F) to 540 °C (1000 °F). Surprisingly, the trend line for HEE index from RA ratio appears to be a better indicator or more sensitive than the HEE index from $K_{(TH)/KIC}$ ratio, with an exception for a single data point at -195 °C where the $K_{(TH)/KIC}$ ratio appears to be more sensitive to HE detection [48]. Both of these trend lines show that the maximum HEE effect occurs near room temperature, and this effect diminishes when the temperature is below -200 °C and above 550 °C.

![Figure 5](image_url)

**Figure 5**
Trend lines for Inconel 718 based on HEE index from $K_{TH}/K_{IC}$ and RA ratio [48]
4.3 Low Cycle Fatigue

It is usually found that gaseous hydrogen has a considerable effect on Low Cycle Fatigue (LCF) properties for susceptible materials tested in strain-cycling controlled mode. The hydrogen degradation for LCF is also a function of strain range, as shown in Figure 6, for several PM superalloys tested at 24 °C (75 °F) in 34.5 MPa (5 ksi) hydrogen pressure. By selecting a typical strain range from 1% - 2%, the values for Cycles-to-Failure (CTF) obtained in hydrogen and in air can be qualitatively compared to indicate the severity of HEE. For example, at a typical strain range of 1.2%, the typical CTF ratios for the PM superalloys, as shown in Figure 6, are reduced nearly by a factor of 10 at room temperature [28]. Because the CTF values for fatigue testing are plotted on a log scale instead of using a linear scale similar to measuring the NTS or RA, the ratio of CTF will not be used as the typical HEE index as specified in the ASTM-G129 test standard. The typical HEE index is based on a linear scale, with a ratio ranking from 1 to 0.

![Figure 6](image_url)

Effects of hydrogen on strain controlled LCF of superalloys [28]

Although not commonly used as the HEE index based on the ratio of CTF for LCF life testing, the trend behavior for hydrogen embrittlement based on LCF correlates qualitatively well with the HEE index values, as shown in Table 4 for superalloys. In general, the greatest reduction in LCF life ratio is also found near room temperature for most superalloys, while at cryogenic and at relatively high temperature the LCF properties are not as severely reduced, similar to the HEE index trend lines for Inconel 718 as shown in Figure 5. When dealing with an HEE index for LCF, a comparative value of strain range should be specified since the LCF degradation is also controlled by the strain range. The LCF data under the influence of hydrogen environment for a number of superalloys are summarized in Table 6. Comparing the LCF data against the data in Table 4, superalloys such as Inconel 100, 718, 625, or Hastelloy-X®,¹ which exhibit severe HEE in high hydrogen pressure at room temperature, are similarly affected in LCF tested in strain-controlled mode at room temperature. It has been found that the strain-control test mode is more sensitive to HEE than LCF testing based on the load-controlled mode.

¹ Hastelloy® is a registered trademark of Union Carbide and Carbon Corporation, New York, New York.
Table 6
Hydrogen effects on life reduction factor under LCF loading at various temperatures

<table>
<thead>
<tr>
<th>Superalloys</th>
<th>Hydrogen Environment</th>
<th>Low Cycle Fatigue (LCF)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure (MPa)</td>
<td>Temperature (°C)</td>
<td>Strain Range (%)</td>
</tr>
<tr>
<td>Inconel® 718 (STD HT)</td>
<td>34.5</td>
<td>677</td>
<td>1</td>
</tr>
<tr>
<td>Inconel® 718</td>
<td>34.5</td>
<td>25</td>
<td>2</td>
</tr>
<tr>
<td>(940 °C Sol. + Aging)</td>
<td>34.5</td>
<td>677</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>34.5</td>
<td>162</td>
<td>2</td>
</tr>
<tr>
<td>Inconel® 625</td>
<td>34.5</td>
<td>25</td>
<td>2</td>
</tr>
<tr>
<td>Hastelloy® X</td>
<td>34.5</td>
<td>25</td>
<td>2</td>
</tr>
<tr>
<td></td>
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<td>1</td>
</tr>
<tr>
<td>IN 100</td>
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<td>538</td>
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<tr>
<td></td>
<td>34.5</td>
<td>677</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>34.5</td>
<td>760</td>
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</tr>
<tr>
<td>Astroloy</td>
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<td>649</td>
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</tr>
<tr>
<td></td>
<td>34.5</td>
<td>760</td>
<td>2</td>
</tr>
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<td></td>
<td>34.5</td>
<td>538</td>
<td>2</td>
</tr>
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<td>Incoloy® 903 (ST+ no aging)</td>
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<td>25</td>
<td>2</td>
</tr>
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<tr>
<td>CC MAR-M246</td>
<td>34.5</td>
<td>750</td>
<td>0.5</td>
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</table>

c NASA Marshall Space Flight Center unpublished data [10].
4.4 High Cycle Fatigue

As a general trend, it has been observed that HEE has little effect on High Cycle Fatigue (HCF) properties for many superalloys. Historically, the data for HEE effects on HCF properties were reported by J. Harris [6]. However, these tests were not typical HCF tests since the maximum cycles-to-failure were in most cases well below $10^4$ cycles, and the maximum stresses were high, usually above the yield strengths. Typical HCF regimes are usually defined when the CTFs are at or above the $10^6$ cycles. When the maximum stress amplitude stays significantly below YS, it is possible that no significant HCF life degradation would be observed because the majority of the test time involved in HCF testing is for crack initiation mode and not for crack propagation mode under high cyclic loading at low stress level. According to L. Fritzemeier [29], his estimation is that the HCF life can often be considered to be around 90% crack initiation and 10% crack propagation. In addition, when testing HEE using tensile smooth specimens, it is often observed that the most severe property degradation usually occurs when the tensile specimens are entering their high plastic strain regions. At the low plastic range region, the HEE effects are usually not well detected for smooth specimens. This condition may translate to the axially loaded, smooth HCF test specimens when they are subjected to the high CTF region near $10^6$ cycles, in which region the strain range is usually very low [49]. Figure 7 shows the typical effects of HEE on both the LCF and HCF regimes for Inconel 718 superalloy, tested in 5 ksi (34.5 MPa) hydrogen pressure at room temperature. In this figure, it should be noted that the HCF regime is considered when the CTF is greater than $10^6$ cycles.

![Figure 7](image-url)

**Figure 7**
Effects on HCF of Inconel 718 in 34.5 MPa hydrogen pressure at room temperature
4.5 Crack Growth Rate

The hydrogen data for sustained-load crack growth rates (da/dt) are not as common as the cyclic-load crack growth rates (da/dN) for several superalloys. The HEE effects for cyclic crack growth rates (da/dN) as a function of stress intensity factor range (ΔK) of several superalloys at 5 ksi (34.5 MPa) to 7 ksi (48.2 MPa) are shown in Figure 8 [50]. With the exception for Mar-M-246 from conventional cast, which was tested at 538 °C (1000 °F), the most rapid crack growth at room temperature was observed for Inconel 718 that was solution treated at 940 °C (1725 °F) and then aged (STA 2 condition). Following Mar-M-246, the third fastest cyclic crack growth rate is Inconel 718, labeled as STA 1 heat treatment, which was solutionized at 1038 °C (1900 °F) and aged. The least HE effect is with cast Inconel 718 in annealed conditions. Therefore, heat treatment can change the HE behaviors significantly for certain superalloys, such as Inconel 718, with complex and precipitation hardening phases. These crack growth rates are non-linear curves and also plotted on a log scale as a function of either K or ΔK values; therefore, these data are not commonly used as the typical HEE index as specified in the ASTM-G129 test standard. The typical HEE index is based on a linear scale, with a property ratio ranking from 1 to 0.

Figure 8
HEE effects for cyclic crack growth rates (da/dN) for several superalloys [50]
4.6 Creep Rupture

For high-temperature applications, creep resistance over extended periods of time is a very important design property for superalloys. Since plastic strain is accumulated over time by the process of creep, this effect is pertinent to the design of complex shaped turbine blades, which are machined to tight tolerances with respect to the inside dimensions of the turbine housings. Historic data for creep resistance of superalloys in hydrogen environment for aerospace applications are somewhat limited because most rocket engine applications have a relatively short design life at high temperature. Even though the available data for creep is not extensive, it reveals a similar trend that, if the common HEE indexes are degraded by hydrogen near the vicinity of room temperature, then it is likely that the creep properties will be affected by hydrogen at high temperature. Some significant but limited studies of creep properties for superalloys in hydrogen were performed by Harris for aerospace [51, 9, 52], and by Bhattacharyya for automotive applications [53, 54]. For creep rupture, a common time-temperature parameter used to present the rupture-stress is the Larson-Miller (L.M.) Parameter, which is expressed in the following form (Eq. 8):

\[ P \text{ (L.M.)} = T [C + \log (t)] \]  

Eq. (8)

Where: \( T \) = test temperature (in K or R), \( t \) = stress-rupture time (in hour), \( C \) = constant usually in the order of 20. According to the L.M. parameter, at a given stress level the log time to stress rupture plus a constant of the order of 20, multiplied by the test temperature remains a constant for a given material. Several \( P \text{ (L.M.)} \) values for creep-rupture behaviors of superalloys, tested in high-pressure and high-temperature hydrogen, were documented by L. Fritzemeier [29]. One example for the \( P \text{ (L.M.)} \) for creep rupture of Inconel 718, solutionizing at 1920°F (1050°C), is given in Figure 9.

\[ P \text{ (L.M.)} = 1.8 \times T \text{ (K deg)(20} + \log t) \times 10^{-3} \]

Figure 9
Larson-Miller Parameter for creep-rupture of Inconel 718 tested in hydrogen [29]
Since creep testing is a long-term test involving inelastic strain, considerable reductions of creep stress-rupture strengths are expected for highly susceptible materials. Additionally, the reduction in time-to-failure without significant creep ductility loss is also possible. In the initial stage, or primary creep, the creep strain rate is relatively high; therefore, no significant effect of hydrogen-enhanced deformation is observed. However, during the secondary stage or the stage of slow but steady-state creep rate, the primary observation for creep in hydrogen environment is an increase in creep strain rate, leading to the reduction in time-to-rupture. This action, causing hydrogen-enhanced deformation in a later stage of creep deformation, thus reduces the rupture life under creep strain testing. An example of this effect is shown in Figure 10 for the Directional Solidification (DS) of MAR-M246 superalloy tested at 760 °C (1400 °F) in 5 ksi (34.5 MPa) hydrogen pressures. The creep test was conducted with 110 ksi (758 MPa) stress level [55]. However, it has been found that the total creep ductility for superalloys is not affected very much by hydrogen.

The reduction in time-to-rupture, or the total rupture life, without significant creep ductility loss is possible because the dissolved hydrogen in the metals can increase the mobility of glide dislocations at elevated temperatures. This dislocation climb mechanism does not tend to create localized strain; therefore, it would not be susceptible to a condition for high hydrogen concentrations near the crack tips. The net effect is that an increased creep strain rate would lead to a reduction of rupture life, without the loss of total rupture ductility in hydrogen environment at high temperature.

![Figure 10](image.png)

**Figure 10**
Creep stress-rupture of directionally solidified MAR-M246 in hydrogen at 758 MPa stress level [55]
5.0 Important Factors in Hydrogen Embrittlement

5.1 Hydrogen Pressure

As hydrogen gas pressure increases, the susceptibility for hydrogen embrittlement is also increased, resulting in the reduction of HEE index values from unity. However, the HEE index seems to decrease exponentially when a saturation pressure is reached. The decaying exponent in this relationship may reflect the kinetic effects or rate limitations in the hydrogen embrittlement process as a function of pressure. At a constant temperature, the influence of hydrogen gas pressure is qualitatively understood based on the fact that high-pressure hydrogen will increase the amount of atomic hydrogen available per unit volume, therefore enhancing the localized HEE effects at the tip of a propagating crack. Figure 11 shows the effect of hydrogen pressure on HEE index based on NTS ratio for several different superalloy systems that include nickel, Astroloy, Hastelloy X, Haynes 188, Rene 41 and Inconel 718. Historically, based on Sievert’s pressure-gas law for hydrogen concentration as a function of pressure, the degree of HE was often assumed to be proportional to the square root of the hydrogen pressure [5, 56, 57]. However, recent studies [58, 59] have indicated that HE may indeed follow a more general power-law relationship, based on the exponential function of hydrogen pressure instead of the square root of hydrogen pressure, as shown in Eq. 9:

\[
\text{HEE index} = \alpha \cdot (P)^{-n}
\]

Eq. (9)

Where: \(\alpha\) is a proportional constant, \(P\) is the hydrogen pressure at constant temperature, and \(n\) is the material dependent and decaying exponential that indicates the embrittlement severity for that particular material. It can be seen that when \(n = 0.50\), this is just a special case for the “square root” of hydrogen pressure \(P\) as it was often assumed by early researchers based on Sievert’s pressure-gas law.

Figure 11

Effects of hydrogen pressure on HEE index for superalloys at 22 °C [29, 31, 3, 7, 60]
5.2 Temperature

It has been observed that HEE can occur over a wide range of temperatures; however, it is most severe in the vicinity of room temperature for many materials. Based on the so-called hydrogen trapping model, a hydrogen trapping may be considered as the binding of hydrogen atoms to impurities, structure defects, or microstructure constituents in the alloy. Qualitatively, the binding energy and the diffusivity of hydrogen in the trapping models have been proposed to explain why hydrogen embrittlement is most severe near room temperature and becomes less severe or negligible at higher or lower temperature range [61]. At lower temperatures, the diffusivity of hydrogen is too sluggish to fill sufficient hydrogen traps; but at high temperatures, hydrogen mobility is enhanced, and trapping is diminished. At high strain rates, fracture may proceed without assistance of hydrogen, because the slow mobility of hydrogen is not sufficient to maintain a hydrogen-trapped atmosphere slightly ahead of the fast advancing crack tip. Figure 12 shows the hydrogen embrittlement effect of several steel alloys as a function of temperature. It is found that many austenitic stainless steels (Fe-Ni-Cr) are mostly sensitive to hydrogen embrittlement at a temperature range from -150 °C to +150 °C.

![Figure 12](image-url)

**Figure 12**
Effects of temperature on HEE index for selected steels [62]

The HEE of some superalloys can occur over a wide range of temperatures from cryogenic to at least 800 °C (1500 °F), but it is most severe in the vicinity of room temperature. This is an important factor to consider for safe design, since superalloys are often used for high-temperature applications. This temperature effect for superalloys is unlike some austenitic stainless steels (Fe-Ni-Cr), which are mostly sensitive to HE at lower temperature range. It is possible that some iron-based superalloys, because their compositions are evolved from...
common stainless steel, would tend to have a lower temperature range for hydrogen embrittlement. However, this assumption may not be applied to some nickel and cobalt-based alloys. For instance, Figure 13 shows the HEE index, based on area reduction ratio, for three nickel-based superalloys: Inconel 718, EP99, and EP741. The HEE index for Inconel 718 is most severe near the vicinity of room temperature [29]. However, significant hydrogen embrittlement (e.g., HEE index = 0.60) is still evident for Inconel 718 even at temperature as high as 425 °C (800 °F). As for EP99 and EP741, it is apparent that the hydrogen embrittlement effects are more severe near 485 °C (905 °F) rather than near room temperature [63]. Similarly, the most severe temperature for HEE index, based on NTS ratio, occurs at 538 °C (1000 °F) rather than near the vicinity of room temperature for Astroloy, Merl 76, IN100 and Waspaloy, as shown in Figure 14 [28]. Experimental data for nickel-based Udimet 700® superalloy has shown that its extent of hydrogen embrittlement, as a function of temperature, is far greater at high temperature than for any other superalloy [64].

At high temperature, with sufficient thermal activation energy, there is a potential for HRE, in which hydrogen atoms are chemically reacted with certain material’s constituents or impurities at the grain boundaries. The HRE type of embrittlement can additionally enhance the appearance of HEE at high temperature, which one would not anticipate near ambient temperature.

![Figure 13](image_url)

**Figure 13**
Effects of temperature on HEE index for selected nickel-based superalloys [29, 63]

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1 Udimet® is a registered trademark of Special Metals, Inc., New Hartford, New York.
Heat treatment and product forms can have a profound effect on the degree of HE for certain types of materials with complex microstructures. In general, wrought and PM processes have been found to have a slightly less influence by high-pressure hydrogen environment than cast superalloys with similar compositions and heat treatment \[29\). Table 7 shows the influence of heat treatment and product forms on the HEE index, based on NTS ratio, for five different types of superalloys tested at room temperature with pressure at 5 ksi (34.5 MPa). For Astroloy in standard heat treatment, a moderate improvement for the HEE index can be achieved when this material is in wrought (PM) product form instead of cast. For IN100 and Waspaloy, both in PM product form, different heat treatment conditions give rise to a small change in HEE index. However, the effect of heat treatment becomes very profound for Inconel 718 in wrought form. Choosing between 1750°F (955°C) or 1900°F (1037°C) as solution annealing temperature, Inconel 718 can become extremely embrittled (HEE index = 0.53) or slightly embrittled (HEE index =0.92) by high-pressure hydrogen gas, respectively. This phenomenon may be related to the precipitation of the delta (δ) phase at the grain boundaries when treating at a lower solution temperature \[65\]. It is obvious that HEE susceptibility of materials within a given alloy system can vary significantly, and the majority of these superalloys have been found to be very susceptible to HEE. For superalloys A-286, JBK-75, and Incoloy 903, the data trend reveals an important factor that heat treatment can drastically affect the HEE behaviors for some materials. In this case, the ST+A conditions for these materials would enhance the HEE effects much more than Solution Treated (ST) without Aging. Typical ST+ A conditions are given in Table 8 for JBK-75, A-286, and Incoloy 903.

Because Inconel 718 has been used extensively, detailed heat treatment studies were conducted by Walter and Chandler \[3, 19\] for applications in high-pressure hydrogen environment. Table 9 presents the results of HEE index for Inconel 718 in combinations of five different heat treatments and product forms, which also include weld and Heat Affected Zone.
(HAZ) materials. In all heat treatment cases, Inconel 718 in plate form appears to be less influenced by hydrogen than in rolled-bar and forging forms. Microstructure analysis shows that heat treatment A produced a fine-grained structure with discontinuous Ni3Nb intermetallic delta (δ) phase for the plate product, which was the least embrittled by hydrogen. However, this same heat treatment A in rolled-bar and forged products resulted in larger grains and continuous intergranular Ni3Nb precipitates that formed a preferential fracture path, resulting in a structure that was the most embrittled in hydrogen environment.

Similar to A286, JBK-75 superalloy, when solution annealed with no aging, is negligibly embrittled by hydrogen at 5 ksi (34.5 MPa) pressure. Heat treatment study has shown that aging conditions would dramatically increase the yield strength and ultimate tensile strength for JBK-75. However, such aging conditions would make JBK-75, A-286 and Incoloy 903 become very susceptible to HE, as shown in Table 8.

<table>
<thead>
<tr>
<th>Superalloys</th>
<th>Heat Treatment</th>
<th>Product Form</th>
<th>HEE Index, (NTS)</th>
<th>H Pressure MPa (ksi)</th>
<th>Temp. °C (°F)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Astroloy®</td>
<td>Standard</td>
<td>cast</td>
<td>0.90</td>
<td>34.5 (5)</td>
<td>22 (72)</td>
<td>a</td>
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<tr>
<td></td>
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<td></td>
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<td></td>
<td>MATE (proprietary HT)</td>
<td>PM</td>
<td>0.98</td>
<td></td>
<td></td>
<td>b</td>
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<tr>
<td>IN 100</td>
<td>Standard</td>
<td>PM</td>
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<td>34.5 (5)</td>
<td>22 (72)</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>DTP (proprietary HT)</td>
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<td></td>
<td></td>
<td>b</td>
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<tr>
<td>Inconel® 718</td>
<td>Solutionized + Aging</td>
<td>wrought</td>
<td>0.54</td>
<td>34.5 (5)</td>
<td>22 (72)</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>Solutionized + No aging</td>
<td>wrought</td>
<td>0.83</td>
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<td></td>
<td>c</td>
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<td>MERL 76</td>
<td>Standard</td>
<td>wrought</td>
<td>0.85</td>
<td>34.5 (5)</td>
<td>22 (72)</td>
<td>d</td>
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<td></td>
<td>Standard</td>
<td>PM</td>
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<td></td>
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<td>Waspaloy®</td>
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<tr>
<td></td>
<td>Forged at Sub-Solvus temp.</td>
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### Table 8
Effects of solution treatment and aging time on superalloys

<table>
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<tr>
<th>Superalloys</th>
<th>Heat Treatment</th>
<th>Aged Time (hr)</th>
<th>HEE Index</th>
<th>H pressure, (MPa)</th>
<th>Test Temp. °C</th>
<th>Strengths in Air, (MPa)</th>
<th>Ref.</th>
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<td>JBK-75</td>
<td>Solution Treated @ 980°C/1 hr./WQ. Aged @ 720°C as a function of aging time</td>
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<td>172</td>
<td>22</td>
<td>241 620</td>
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<td></td>
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<td>985 1220</td>
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<th>Solution Treatment and Aging Schedule for Inconel 718</th>
<th>Product Form</th>
<th>HEE Index, (NTS)</th>
<th>H Pressure (MPa)</th>
<th>Temp (°C)</th>
<th>Strengths in Helium (MPa)</th>
<th>Ref.</th>
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<td>HEAT TREATMENT A: 940°C/1hr (solutionized) + 720°C/8hr (1st aging) + 620°C/8hr (2nd aging).</td>
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<td>Rolled Bar</td>
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<td>22</td>
<td>1124</td>
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<tr>
<td></td>
<td>HEAT TREATMENT E: 1025°C/10 min. (solutionized) + 760°C/9.5hr (1st aging) + 650°C/9hr (2nd aging).</td>
<td>Rolled Bar</td>
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<td>Plate (Weld Metal)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.4 Alloy Compositions

The effects of alloy compositions on hydrogen embrittlement for certain groups of superalloys and austenitic stainless steels, which are in the simple form of the Fe-Ni-Cr ternary alloy system, are examined together in this section. Obviously, the hydrogen effect based on alloy composition alone is difficult to isolate separately from the influence of other factors such as microstructure, phases and thermal processes. It is important to recognize that HE effects based on compositions of many high-strength engineering alloys and superalloys have been studied extensively because these materials are useful for the industry; however, these engineering alloys are sometimes the least suitable for the purpose of discovering the general scientific principles because of their inherit complexity in the compositions and microstructures [68]. However, a comparative study based on composition may be possible, providing that these alloys are produced or selected intentionally to share relatively common features among each other such as being a solid solution, having similar alloying phase, heat treatment, product forms, etc.

For austenitic stainless steels, experimental tests conducted at -50 °C (-58 °F) by T. Michler [69] for a large number of test samples shows that nickel content is the main factor that controls...
the HE effect. Specifically, when Ni contents are above 12.5 wt%, the HE becomes negligible. In another study, Michler [70] conducted HEE testing for several Fe-Ni-Cr austenitic steels at different temperature and pressure combinations, which again showed that HE becomes negligible when Ni contents is above 11.5 wt%. Similarly, the work of Fe-Ni-Cr stainless steel from Caskey [62] reveals a wider range of Ni, but provides similar conclusion about Ni contents when it is above 12.5 wt%. From these studies, it can be shown that HE becomes negligible when Ni contents are from 12.5wt% to 35wt% for most austenitic stainless steels in the Fe-Ni-Cr system, where Cr remains in the range of 16 to 20 wt%.

The alloy compositional works from Caskey and Michler for Fe-Ni-Cr stainless steels could logically extend into higher ranges of Ni to examine the compositional effects for some selected superalloys. However, for a comparative study these selected superalloys were intentionally heat treated under solution-annealed conditions so that the effects of the precipitate phases are significantly reduced or eliminated. For several Fe-Ni-Cr based superalloys, with their Ni contents varying from 25% to 80 wt%, Table 10 and Figure 15 show the HE effects with the HEE index based on NTS and tensile ductility ratios. Interestingly, the trend for hydrogen embrittlement of these superalloys, as a function of Ni contents, is matched very closely with the trend line for Fe-Ni-Cr austenitic stainless steels. That is, HE becomes negligible when Ni contents are from 12.5% to 35%. Moreover, the influence of minor elements seem to have only a minor effect on hydrogen embrittlement, and Ni content is the main factor that controls the HE effect for Fe-Ni-Cr superalloys under solution-annealed condition.

**Table 10**

<table>
<thead>
<tr>
<th>Superalloys</th>
<th>Heat Treatment</th>
<th>Product Form</th>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>HEE Index</th>
<th>HEE Type</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A286</td>
<td>annealed</td>
<td>wrought</td>
<td>26.0</td>
<td>54.0</td>
<td>15.0</td>
<td>0.98</td>
<td>NTS</td>
<td>a</td>
</tr>
<tr>
<td>JBK-75</td>
<td>annealed</td>
<td>wrought</td>
<td>30.0</td>
<td>50.0</td>
<td>15.0</td>
<td>0.98</td>
<td>NTS</td>
<td>b</td>
</tr>
<tr>
<td>Incoloy 801</td>
<td>annealed</td>
<td>wrought</td>
<td>32.0</td>
<td>44.5</td>
<td>20.5</td>
<td>0.87</td>
<td>NTS</td>
<td>c</td>
</tr>
<tr>
<td>Incoloy 800</td>
<td>annealed</td>
<td>wrought</td>
<td>32.5</td>
<td>46.0</td>
<td>21.0</td>
<td>0.94</td>
<td>NTS</td>
<td>d,c</td>
</tr>
<tr>
<td>Incoloy 802</td>
<td>annealed</td>
<td>wrought</td>
<td>32.5</td>
<td>46.0</td>
<td>21.5</td>
<td>0.99</td>
<td>NTS</td>
<td>b</td>
</tr>
<tr>
<td>Carpenter 20-Cb3</td>
<td>annealed</td>
<td>wrought</td>
<td>34.0</td>
<td>42.5</td>
<td>20.0</td>
<td>0.98</td>
<td>elong (IHE)</td>
<td>d</td>
</tr>
<tr>
<td>Inconel 706</td>
<td>annealed</td>
<td>wrought</td>
<td>41.5</td>
<td>40.0</td>
<td>16.0</td>
<td>0.82</td>
<td>elong (IHE)</td>
<td>e</td>
</tr>
<tr>
<td>Incoloy 825</td>
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<td>wrought</td>
<td>42.0</td>
<td>21.5</td>
<td>22.0</td>
<td>0.75</td>
<td>NTS</td>
<td>c</td>
</tr>
<tr>
<td>Inconel X750</td>
<td>annealed</td>
<td>wrought</td>
<td>73.0</td>
<td>7.0</td>
<td>16.0</td>
<td>0.26</td>
<td>NTS</td>
<td>b</td>
</tr>
<tr>
<td>Inconel 600</td>
<td>annealed</td>
<td>wrought</td>
<td>76.0</td>
<td>8.0</td>
<td>15.5</td>
<td>0.23</td>
<td>RA (IHE)</td>
<td>f</td>
</tr>
<tr>
<td>Inconel MA 754</td>
<td>annealed</td>
<td>wrought</td>
<td>78.6</td>
<td>0.0</td>
<td>20.0</td>
<td>0.19</td>
<td>RA</td>
<td>e</td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
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<td>wrought</td>
<td>8.1</td>
<td></td>
<td></td>
<td>0.23</td>
<td>RA</td>
<td>T. Michler (g,h)</td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
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<td>wrought</td>
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<td></td>
<td></td>
<td>0.26</td>
<td>RA</td>
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</tr>
<tr>
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<td>wrought</td>
<td>8.6</td>
<td></td>
<td></td>
<td>0.34</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
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<td>wrought</td>
<td>8.8</td>
<td></td>
<td></td>
<td>0.28</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
<td>annealed</td>
<td>wrought</td>
<td>9.9</td>
<td></td>
<td></td>
<td>0.66</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
<td>annealed</td>
<td>wrought</td>
<td>10.1</td>
<td></td>
<td></td>
<td>0.55</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
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<td>wrought</td>
<td>10.2</td>
<td></td>
<td></td>
<td>0.48</td>
<td>RA</td>
<td></td>
</tr>
<tr>
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<td>annealed</td>
<td>wrought</td>
<td>10.5</td>
<td></td>
<td></td>
<td>0.48</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
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<td>wrought</td>
<td>11.2</td>
<td></td>
<td></td>
<td>0.64</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
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<td>wrought</td>
<td>11.2</td>
<td></td>
<td></td>
<td>0.85</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
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<td>wrought</td>
<td>12.5</td>
<td></td>
<td></td>
<td>0.96</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
<td>annealed</td>
<td>wrought</td>
<td>12.8</td>
<td></td>
<td></td>
<td>0.98</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
<td>annealed</td>
<td>wrought</td>
<td>13.0</td>
<td></td>
<td></td>
<td>0.98</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
<td>annealed</td>
<td>wrought</td>
<td>14.0</td>
<td></td>
<td></td>
<td>0.98</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
<td>annealed</td>
<td>wrought</td>
<td>18.0</td>
<td></td>
<td></td>
<td>0.98</td>
<td>RA</td>
<td></td>
</tr>
</tbody>
</table>

G. Caskey (i)
### Table 1

<table>
<thead>
<tr>
<th>Superalloys</th>
<th>Heat Treatment</th>
<th>Product Form</th>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>HEE Index</th>
<th>HEE Type</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austen. Stainless Steel</td>
<td>annealed</td>
<td>wrought</td>
<td>19.0</td>
<td></td>
<td></td>
<td>0.98</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
<td>annealed</td>
<td>wrought</td>
<td>25.0</td>
<td></td>
<td></td>
<td>0.97</td>
<td>RA</td>
<td></td>
</tr>
<tr>
<td>Austen. Stainless Steel</td>
<td>annealed</td>
<td>wrought</td>
<td>32.0</td>
<td></td>
<td></td>
<td>0.96</td>
<td>RA</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 15**

**HEE Index for Fe-Ni-Cr superalloys and stainless steels as a function of Ni content (wt.%)**

(Data are from references in Table 10)
5.5 Surface Finish

The sensitivity of the HEE index for susceptible materials can also be slightly affected by the surface finish on HE test coupons. This is because gaseous hydrogen has a significant influence on the surface’s microcrack initiation and growth behavior, particularly when relatively large surface flaws exist on a susceptible material exposed in high-pressure hydrogen environment.

Therefore, some care must be taken in specimen preparation and component fabrication for surface machining and finishing. Internal cracks by HE can initiate and propagate with little macroscopic evidence of corrosion or damaging features and no warning as catastrophic failure approaches. These internal cracks initiate frequently at surface flaws that are either preexisting or formed during service in hydrogen environment. The flaw features may include sharp corners, grooves, laps, or burrs resulting from fabrication processes.

5.6 Grain Directions and Crystal Orientations

Limited numbers of studies were taken to determine the influence of HE on the grain directions of wrought superalloys. Table 11 shows the HEE index, based on NTS ratio, for transverse and longitudinal grain direction of wrought Oxide-Dispersed Strengthening (ODS) superalloys in 5 ksi (34.5 MPa) hydrogen pressures at 72°F (22°C). The results show that grain directions have a small effect on HEE, with longitudinal being slightly less influenced by hydrogen than the transverse direction. In another study of grain orientations from cast superalloys, using directionally solidified and Conventionally Cast (CC) processes, the MAR-M246 superalloy shows that with the higher microstructure-uniformity process obtained from the DS, it tends to be slightly less influenced by hydrogen than the CC process [55]. HEE effects on grain directions have not been extensively studied for wrought superalloys; however, the general trends indicate that the difference in HE effect is relatively small for polycrystalline wrought alloys due to the grain directions.

<table>
<thead>
<tr>
<th>SUPERALLOYS</th>
<th>Grain Direction</th>
<th>HEE Index (NTS)</th>
<th>H Pressure MPa (ksi)</th>
<th>Temp. °C (°F)</th>
<th>Alloy Based</th>
<th>Process</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA 754</td>
<td>Transverse</td>
<td>0.94</td>
<td>34.5 (5)</td>
<td>22 (72)</td>
<td>Nickel</td>
<td>ODS</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>Longitudinal</td>
<td>0.96</td>
<td>34.5 (5)</td>
<td>22 (72)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA 956</td>
<td>Transverse</td>
<td>0.34</td>
<td>34.5 (5)</td>
<td>22 (72)</td>
<td>Iron</td>
<td>ODS</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Longitudinal</td>
<td>0.58</td>
<td>34.5 (5)</td>
<td>22 (72)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA 6000</td>
<td>Transverse</td>
<td>0.92</td>
<td>34.5 (5)</td>
<td>22 (72)</td>
<td>Nickel</td>
<td>ODS</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Longitudinal</td>
<td>0.86</td>
<td>34.5 (5)</td>
<td>22 (72)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Historic data for the influence of hydrogen embrittlement on the crystallographic orientation of single crystal superalloys are somewhat limited. A preliminary study of single crystal PWA 1480E was conducted by K. Bowen [34], based on the HEE index for NTS ratio, in hydrogen 5 ksi (34.5 MPa) at 72°F (22°C) and 1600°F (875°C). At very high temperature, the hydrogen effect is diminished as expected, without showing a definite trend for HE based on crystal directions. However, Table 12 shows that the <111> crystal direction retains the best and the <001> direction gives the worst HEE index when tested at room temperature. Evidently, crystal orientations from single crystal materials do have a strong effect on HE in comparison to polycrystalline materials with similar composition.
### Table 12

<table>
<thead>
<tr>
<th>Superalloys (Single Crystal)</th>
<th>Crystal Orientation</th>
<th>HEE Index (NTS)</th>
<th>NTS in Helium, MPa (ksi)</th>
<th>H Pressure MPa (ksi)</th>
<th>Temp. °C (°F)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PWA 1480E</td>
<td>&lt;001&gt;</td>
<td>0.57</td>
<td>1531.0 (222.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt;111&gt;</td>
<td>0.88</td>
<td>1566.5 (227.2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt;112&gt;</td>
<td>0.73</td>
<td>1633.4 (236.9)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt;110&gt;</td>
<td>0.79</td>
<td>1692.1 (245.4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt;223&gt;</td>
<td>0.76</td>
<td>1618.2 (234.7)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>&lt;123&gt;</td>
<td>0.74</td>
<td>1672.7 (242.6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt;013&gt;</td>
<td>0.65</td>
<td>1583.0 (229.6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PWA 1480E</td>
<td>&lt;111&gt;</td>
<td>0.99</td>
<td>1308.6 (189.8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt;112&gt;</td>
<td>0.94</td>
<td>1297.6 (188.2)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>&lt;100&gt;</td>
<td>0.90</td>
<td>1442.4 (209.2)</td>
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<tr>
<td></td>
<td>&lt;110&gt;</td>
<td>1.07</td>
<td>1168.7 (169.5)</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>&lt;223&gt;</td>
<td>1.01</td>
<td>1225.2 (177.7)</td>
<td></td>
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<tr>
<td></td>
<td>&lt;123&gt;</td>
<td>0.97</td>
<td>1291.4 (187.3)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>&lt;013&gt;</td>
<td>0.97</td>
<td>1319.6 (191.4)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


### 6.0 Prevention and Control Methods for Hydrogen Damage

#### 6.1 General Guidelines

Figure 16A depicts the overlapped regions for HEE, IHE and HRE that are created by the intersections of three circles representing the influence factors from the material type, hydrogen environment, and the applied stress. By reducing or removing only one of these three factors, it is possible to alter the hydrogen damaging effects for many susceptible materials, as shown in Figure 16B. This concept is the general guideline for prevention and control methods for hydrogen damage as listed in this section.

For the HEE and IHE type, the influence of the applied stress is an important factor and the stress should be reduced or removed when possible to control the embrittlement effects. In contrast, the HRE type is formed by the intersection between hydrogen and material, and it can be an irreversible damage resulting without the influence of an applied stress. In theory, the hydrogen damaging effects can be altered by reducing or removing only one of these three main factors. In practice, it is often difficult to be able to completely eliminate or remove only one of these three influential factors; therefore, it is advisable to find a combination of methods that would work best for reducing the influence of all three factors. Several practical techniques for controlling the material type, hydrogen environment, and applied stress are briefly suggested in the following sections.
6.2 Controlling the Material Factors

Select Proper Materials

At relatively low hydrogen pressures, the degradation of fracture properties for many susceptible materials is not as severe as at high pressure. In addition, at a certain cryogenic temperature range, most materials are negligibly embrittled by hydrogen even when they are exposed to a relative high pressure of greater than 5 ksi (34.5 MPa). Therefore, depending on the hydrogen pressure and temperature range, it is possible to select certain materials for hydrogen applications based on the qualitative rating method as shown in Table 1. Historically, notable service failures associated with susceptible materials in hydrogen gas environment have been linked to a combination of highly stressed components that were operated outside of the allowable ranges of hydrogen pressure and temperature. It must be noted that the material database, using the HEE index classification, is only a qualitative material screening method based on an accelerated test in laboratory environment at near room temperature (22 °C (75 °F)) for a hydrogen pressure range mostly between 5 ksi (34.5 MPa) to 10 ksi (69 MPa). This material database should not be used for component design without detailed fracture analysis, particularly for materials that are qualitatively rated in the HE category of High, Severe or Extreme. Selecting proper materials should be done with design using sufficiently high safety factors, coupled with vigorous material characterization based on fracture mechanics, non-destructive evaluations (e.g., flaw size inspections), and material testing in specific relevant hydrogen pressures and temperature ranges. It should be noted that material test data taken from thermal pre-charging in hydrogen gas or any electrochemical method may not be treated as identical to the data taken from actual testing in high-pressure gaseous hydrogen.
Select Steels Using Nelson Curve for Corrosive Environment

At certain elevated temperatures, atomic hydrogen can react internally with certain types of elements and compounds in the material. This form of Hydrogen Reaction Embrittlement (HRE) can occur in carbon steels. The common reaction is between hydrogen and iron-carbides to form methane gas (CH₄). Deep within the bulk of the material, the formation and migration of CH₄ molecules, usually concentrated at grain boundaries and metallurgical features such as inclusions, impurities, trap elements, and defects, can lead to brittle rupture through the formation of voids, blisters and a network of discontinuous microcracks. Moreover, because the carbide phase is a reactant in the mechanism, its depletion in the vicinity of generated defects serves as direct evidence of the HRE mechanism itself. The HRE sensitivity depends on the amount of carbon or carbide in the alloy, the hydrogen concentration, gas pressure, and temperature usually in the range of 200 to 600 °C (400 to 1110 °F). Alloy steels with stable carbides such as chromium-carbides are less susceptible to this form of hydrogen attack due to the greater stability of Cr₃C versus Fe₃C found in carbon steels. However, as the pressure and temperature of hydrogen environment increases, a greater amount of these alloying additions are required to minimize such attack.

The addition of chromium and molybdenum are beneficial alloying elements for many carbon and low-alloy steels to prevent the HRE from decarburizing. For example, 2.25Cr-1Mo steel undergoes some decarburization in high pressure and temperature hydrogen, but it is less likely to fissure than carbon steels. However, as the conditions increase in severity, higher-alloy steels such as 5Cr-0.5Mo or 9Cr-1Mo may be required. Figure 17 shows the Nelson curve as a selection guide for the operating limits of certain types of steels in hydrogen service from the influence of HRE effects [73].

![Nelson curve defining safe upper limits for steels in hydrogen service](image-url)

**Figure 17**

The Nelson curve defining safe upper limits for steels in hydrogen service [73]
Select Proper Thermo-mechanical Treatment

Heat treatment can have a profound effect on the degree of HE, particularly for materials with complex microstructures. However, these general trends can often be influenced by the particular grain sizes and phases resulting from solution and aging heat treatments. As previously described, such combinations of microstructure, precipitates, and morphology can either enhance or degrade hydrogen resistance properties. For example, Table 8 presents the results of HEE index for Inconel 718 in combinations of five different heat treatments and product forms. In general, superalloys and steel-based alloys that have low tensile strengths and, when heat treated in annealed conditions, will tend to have better HE resistance than higher strength alloys. Therefore, it is advisable that studies be conducted to determine the HE effects when selecting proper thermo-mechanical treatment of susceptible materials. For example, the data trend for A-286, JBK-75, and Incoloy 903 reveals an important factor that aging treatment can drastically affect their HEE behaviors. In this case, the ST+A conditions for these materials would enhance the HEE effects much more than ST without aging. Typical ST conditions without aging are given in Table 8 for A-286, JBK-75, and Incoloy 903. In general, aging conditions would dramatically increase the YS and UTS for many materials. However, these aging conditions would make most of these high-strength materials have lower ductility and also become very susceptible to HE.

Surface Barriers and Coatings for Limited and Short-term Applications

Surface barriers and coatings can retard hydrogen entry into the substrate metal by virtue of their low hydrogen solubility and diffusivity. Surface coatings can also potentially modify the surface properties involving the adsorption, metal surface catalytic reactions, or by combinations of these factors. For application in aqueous media, certain types of stable coatings can be formed or applied to the metal surface for corrosion protection and also to reduce the absorption rate of atomic hydrogen. For application in a gaseous environment, certain surface coatings may be applicable for short-term exposure to hydrogen gaseous environment at relatively low pressure and temperature. For long-term servicing of components in high-pressure gaseous hydrogen at high temperature, surface coatings may not work effectively and are not recommended in many cases. This is because the hydrogen diffusion rate is sufficiently high enough that the atomic hydrogen, being very small relative to the metal atoms, would eventually diffuse through most metals. This condition is similar to the thermal charging of hydrogen in the materials by using high pressure at high temperature. It is advisable that a surface coating study be conducted as a function of long-term exposure to the hydrogen environment, to determine coating effectiveness for susceptible materials before actual use in gaseous environment.

6.3 Controlling the Hydrogen Factors

Reduce Hydrogen Gas Pressure

High-pressure hydrogen gas has a direct influence on the HEE effects of materials. By reducing the hydrogen gas pressure to low levels, susceptible materials will become less embrittled as compared to the hydrogen environment at high pressure. At a constant temperature, the influence of hydrogen gas pressure is qualitatively understood based on the fact that high-pressure hydrogen will increase the amount of atomic hydrogen available per unit volume, thereby enhancing the localized HEE effects at the tip of a propagating crack. It has been shown that HE may indeed follow a general power-law relationship based on the exponential function of hydrogen pressure instead of the square root of hydrogen pressure, as described in Section 5.1.
Reduce Hydrogen Gas Purity

It has been shown experimentally that embrittlement by gaseous hydrogen can be effectively inhibited by the additional of certain gas species such as O\textsubscript{2}, CO, N\textsubscript{2}O, and SO\textsubscript{2}. As little as 100 vppm (parts per million by volume) of oxygen mixed with 7 MPa (1 ksi) hydrogen gas could effectively eliminate the HEE effects on fatigue crack growth of X42 pipeline steel [24]. Similar results have also been demonstrated for gaseous inhibitors such as CO and SO\textsubscript{2} in hydrogen gas. Figure 18 shows the effects of hydrogen gas purity on fracture toughness of X42 and X70 carbon steels [24]. However, caution should be given to hydrogen-sulfide (H\textsubscript{2}S) gas, which did not halt the HE effect from pure hydrogen gas. In fact, the H\textsubscript{2}S gas could accelerate the HE effects more than pure hydrogen gas environment alone. In practice, this method has not been widely used or popularly applied, perhaps because many gaseous hydrogen environments will not be able to tolerate a low hydrogen gas purity or being mixed with other gas impurities, particularly in aerospace propulsion applications. However, when it is possible to reduce the hydrogen gas purity, this method should work well to control the HEE effects for a hydrogen system at certain pressure and temperature conditions.

Select Proper Operating Temperature

Hydrogen damage can occur over a wide range of temperatures; however, it is most severe in the vicinity of room temperature for many materials. By selecting a proper operating temperature range, the hydrogen embrittlement can be reduced for many materials. In general, materials are less susceptible to HEE, IHE, and even HRE if the temperature is in the cryogenic range. At high temperature, the HEE and IHE effects will also become less susceptible for most materials due to hydrogen mobility enhancement and the reduction hydrogen trapping sites within the bulk of the materials. However, attention must be given for the HRE effects, which may occur for some materials at relatively high temperature. Therefore, the HEE index near room temperature should not be used to estimate the HE effects at high temperatures. For some superalloys, their HEE can occur over a wide range of temperatures from cryogenic to at least 800 °C (1500 °F), but it is most severe in the vicinity of room temperature. This is an
important factor to consider for safe design since superalloys are often chosen for use in high temperature applications. This temperature effect for superalloys is unlike some austenitic stainless steels (Fe-Ni-Cr), which are mostly sensitive to hydrogen embrittlement at a lower temperature range near -100 °C (-150 °F) (see Figure 12). It is advisable that testing for hydrogen damage must be conducted at the operating temperature to verify the exact HE effects.

**Hydrogen Relief by Bake Out**

For Internal Hydrogen Embrittlement (IHE), if the materials have not yet started to crack, the condition may be reversed by removing the absorbed hydrogen through a diffusion process at high temperature. To be fully reversible, the material must not have undergone any permanent chemical reaction between hydrogen and the metals through an HRE process. This method would work well if the original hydrogen charging conditions were not severe enough to cause internal hydrogen damage known as IHE by a supersaturated charging condition. Hydrogen charging conditions can come from electroplating, cathodic protection, molten metal casting or melting process, welding process and thermo-mechanical heat treatment with hydrogen gas, and operating equipment in hydrogen gas environment at high pressure and temperature. Furthermore, certain charging conditions that exceed the solubility limit for hydrogen will result in massive brittle formations of metal-hydride phases in some types of alloys made from titanium, zirconium, and magnesium. In this case, the hydrogen bake-out method may not be effective to completely drive out hydrogen. The specification for embrittlement relief (baking) of steel parts to remove hydrogen infused during plating and certain other chemical processing such as stripping, plating, chemical milling, acid pickling, and etching is given in AMS 2759-9D [74]. This procedure can be used for rapidly driving out trapped atomic hydrogen in the materials through the thermal diffusion process. For plating processes, the values for minimum baking time at 191 °C (375 °F) are also given in AMS 2759 for different types of steels. Figure 19 shows a typical result for the hydrogen relief process as a function of baking time, fracture time, and applied stress for high-strength 4340 steel [75].

![Figure 19](image-url)

Effects of hydrogen baking time and applied stress for Type 4340 steel [75]
**Reduce Material Cooling Rate in Gaseous Hydrogen Environment**

Because of the higher hydrogen solubility for metals at high temperature, rapid cooling of heavy sections of certain materials operating at high temperature can result in Internal Hydrogen Embrittlement (IHE) without having to experience a high level of applied external stress. This is because the solubility and diffusivity of hydrogen in metals are sharply decreased with lowering of temperatures, making the materials become supersaturated with hydrogen under rapid cooling conditions. This condition is particularly important for materials undergoing thermal cycling combined with loading at high temperatures, in that they are capable of being super-saturated with a large amount of hydrogen. Upon rapid cooling of the components to ambient conditions, this could result in IHE. Therefore, a slow cooling rate, which allows hydrogen to be slowly released from the alloys, is a general solution to this problem. Proper hydrogen out-gassing procedures should be followed when equipment is depressurized and rapidly cooled prior to being shut down.

**Use Proper Welding Procedures**

Solutions to the hydrogen damage problem associated with welding include the use of a proper inert shielding gas to minimize hydrogen pickup from the humidity and air, use of dry welding electrodes, and proper cleaning and degreasing procedures for prepared weld joints. The welding electrodes should be kept dry. If they are moistened or exposed in the ambient atmosphere for prolonged periods, low-hydrogen coated electrodes must be preheated at 370 °C (700 °F) to remove moisture prior to welding. For carbon-manganese steels, appropriate post-weld heat treatments can range from a hydrogen bake-out procedure at temperatures as low as 175 °C (350 °F) to a martensitic tempering treatment at temperatures as high as 705 °C (1300 °F) for certain materials.

**Controlling Cathodic Protection System**

In an aqueous environment, excessive usage of cathodic charging, from an impressed current in the corrosion protection system, will greatly enhance the production of atomic hydrogen and its absorption into the bulk metals submerged in aqueous solutions. Therefore, careful control of cathodic charging systems should help to reduce the production and absorption of atomic hydrogen. Because of the similarly between the HEE and the IHE effects, the usage of material screening data under the influence of gaseous hydrogen environment (HEE index), as given in Tables 2, 3, and 4, can be helpful for material screening. However, it is often difficult to compare the effect of pressurized gaseous hydrogen to some equivalent level of hydrogen in terms of the amount of impressed current in the cathodic charged systems. Therefore, it is advisable that material testing should be conducted under the actual influence of a cathodic impressed current, to determine the HE effects from a cathodic corrosion protection system.

**Application of Inhibitors in Liquid Environment**

In an aqueous environment, HE can be reduced by the application of inhibitors such as nitriles, organic nitrogen compounds, phosphates, chromates, and organic amines. These liquid inhibitors are used to prevent excessive corrosion of metals in certain acidic environments, and they are also known to prevent HE in some aqueous environment as well. Using the correct type and amount of inhibitors in the liquid environment is important; however, the chemical composition details for some inhibitor mixtures are unclear for many commercially available inhibitors. Therefore, it is advisable to test a selected inhibitor’s effectiveness to prevent HE before actual use.
6.4 Controlling the Stress Factors

Reduce External Applied Stress

Reducing the maximum applied stress is one of the best approaches to prevent or control HE effects for most materials. This could be achieved by increasing the load-bearing cross-section of parts, avoiding stress raisers in the design, or simply reducing the external load on the part, if possible. A constant (static) loading is usually considered to be more conducive to hydrogen damage than a cyclic (dynamic) loading, particularly at high frequencies. This method of reducing the external stress is applicable for HEE types of embrittlement. However, stress reduction techniques may be applicable in most IHE cases, but not necessarily for all cases because of possible combination effects of IHE and HRE. Reducing external applied stress may not be applicable for HRE because the HRE effects can occur even without applied stress. External stress reduction should be performed with detailed fracture analysis for safe usage, particularly for materials that are qualitatively rated in the hydrogen embrittlement categories of High, Severe or Extreme.

Reduce Internal Residual Stress

The internal residual stresses developed in the metal during processes such as heat treatment, fabrication, and welding can be high and must be reduced in some cases. For wrought products, fabricating methods such as forming, straightening, and stretching that involve localized plastic deformation can exceed the elastic limit of the material due to high residual stress. In cast products, because the hot or molten metal shrinks as it cools, cast components or welding parts that are joined into a more complex structure can have high internal residual stress. Reducing residual tension stress can be done through thermal treatments such as annealing and aging, including preheating or post-weld heat treatment. In addition, surface preparation techniques that would impact residual compressive stress to the surface in order to improve resistance to cracking due to tension stress can also be used. However, attention must be given to some of these surface preparation techniques that may not be helpful if an undesirable rough surface finish or a surface cracking is induced, which has been known to accelerate hydrogen embrittlement effects for highly susceptible material, as described previously in this section for material surface finishing effects.

Application of Fracture Mechanics

Fracture mechanics is a material design methodology to control the critical crack size and its propagation rates under the influence of an applied stress. This method can greatly reduce the HE effects for many susceptible materials. In its simplicity, it is possible to determine the maximum allowable stress for a given material’s flaw size in hydrogen environment when the pressure and the temperature factors cannot be reduced or altered. Because certain fracture mechanics properties are important to be measured in hydrogen under SSR conditions, reliable and conservative methods for measuring the plane strain fracture toughness and threshold stress in hydrogen are necessary for a safe design component. Therefore, it should be noted that material test data taken from thermal pre-charging in hydrogen gas or any electrochemical method should not be treated as identical to test data taken from actual testing in high-pressure gaseous hydrogen. In recent years, emerging fracture mechanics methods for preventing and controlling hydrogen embrittlement have been developed by several government agencies and industry organizations such as NASA, the U.S. Department of Energy (DOE), American Society of Mechanical Engineers (ASME), and ASTM.
7.0 Hydrogen Codes and Standards in the U.S.

In recent years, the DOE has initiated programs to develop a national template of hydrogen codes and standards with the focus on hydrogen delivery technologies that enable the usage and dispensing of hydrogen as an energy carrier for vehicle transportation, refueling stations, or stationary power sites. The program consists of codes and standards grouped into three levels: 1) Primary adoption of building and fire codes, 2) Hydrogen-specific codes and standards references in the primary adopted code, and 3) Hydrogen-specific component standards referenced in hydrogen-specific codes. The third level of documents set very detailed requirements for hydrogen system components or subsystems such as hydrogen venting systems, hoses, nozzles, and dispensers for refueling stations. This DOE activity for hydrogen delivery technologies is on-going with collaborations from different government agencies [76].

In conjunction with the hydrogen activity from the DOE, the ASME has also developed Codes and Standards that are applicable to hydrogen-material infrastructure such as hydrogen piping and pipelines, valves, flanges and fittings, storage tanks, and boiler vessels. An example is given in Part 12 of the ASME B31 document [77] for the design of hydrogen piping and pipelines. The intent of this particular piping and pipeline code is to set forth engineering requirements deemed necessary for safe design, construction, and installation of piping and pipeline systems in hydrogen service. The engineering requirements of this code, while considered necessary and safe design, generally employ a simplified approach to the subject. A designer capable of applying a more rigorous analysis is encouraged to do so; however, the approach must be documented in the engineering design and its validity accepted by the customers. In general, the ASME code requirements include specific provisions applicable to hydrogen service, which include the selection and application of materials, components, and joints for piping and pipelines.

Another example is given in the ASME Boiler & Pressure Vessel Code (BPVC), ASME Section VIII-Division 3 Rules for Construction of High Pressure for hydrogen. In particular, the ASME BPVC Article KD-10 governs the fracture mechanics and evaluation of materials for storage vessels in hydrogen service up to 103 MPa (15,000 psig) [78]. This article defines specific material testing in hydrogen environment in terms of measuring fracture mechanics properties such as the plane strain fracture toughness (K_{IC}), threshold stress intensity factor (K_{IT}), and the fatigue crack growth rate (da/dN). Reliable and conservative methods for measuring these basic fracture mechanics properties are important to ensure the effectiveness of the fracture mechanics approach for component safe design in hydrogen environment. As an example of how these fracture properties should be used to calculate critical crack propagation, maximum allowable stress, and even predicting the maximum service life, a sample calculation for fracture control is given in [79] for the design of a hydrogen pressure vessel service up to 103 MPa (15,000 psi).
8.0 References


10. NASA-MSFC unpublished data.


AMS 2759-9D. “Hydrogen Embrittlement Relief (Baking) for Steel Parts”, American Meteorological Society, Boston, Massachusetts. Revised 2009-05.


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