Technical Reference on Hydrogen Compatibility of Materials

Introduction

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Introduction

The Technical Reference on Hydrogen Compatibility of Materials summarizes materials data originating from scientific articles and institutional reports with the aim of assisting materials selection for service in hydrogen gas, with emphasis on structural materials. It is compromised of a collection of electronic documents (or sections) that are updated periodically; the latest revisions are available at http://www.ca.sandia.gov/matlsTechRef/ In addition, these documents have been assembled into a report [1] that will be revised occasionally based on substantial overall content change.

The data included in the Technical Reference reflect two primary phenomena associated with materials in hydrogen gas service: 1) permeation of hydrogen through materials, resulting in an effective leak through a structure, and 2) degradation of the mechanical properties of materials, which compromises structural integrity. The well-documented degradation phenomena consist of a number of possible mechanisms that we refer to collectively as hydrogen-assisted fracture (in the literature these are often called hydrogen embrittlement). The Technical Reference does not provide specific recommendations for materials selection as the suitability of a given material depends on service conditions, in particular the mechanical, environmental, and material conditions associated with a particular component. Examples of important mechanical, environmental, and material variables that generally contribute to hydrogen-assisted fracture include loading mode (e.g., static *vs* cyclic stress), hydrogen gas pressure, temperature, and material strength level. It is recommended that safety factors for hydrogen gas systems be established based on materials tests performed under relevant mechanical, environmental, and material conditions without significant extrapolation. For example, mechanical properties measured for a low-strength steel in low-pressure hydrogen gas should not be applied for exposure to high-pressure hydrogen gas or to the same steel in a high-strength condition. It is important to emphasize that engineering systems have been successfully designed for high-pressure hydrogen service, much of this experience is summarized in an ASME report [2].

The Technical Reference is organized by specific alloy (e.g., type 304 austenitic stainless steel) or alloy system (e.g., Cr-Mo steels) according to common and relevant nomenclature. Materials are primarily grouped by base element, such as steels or aluminum alloys, which are further distinguished by characteristics such as microstructure, composition, and heat treatment. A four-digit number (code) is assigned to each section to assist organization and revision: the first digit corresponds to the base element; steels constitute the majority of structural materials, and two distinct broad categories are used: ferritic steels (1xxx code series) and austenitic steels (2xxx code series). The second digit refers to the alloy class, and the final two digits specify the alloy or alloy system. For example, within the ferritic steels (1xxx code series), the low-alloy steels are distinguished by code numbers 12xx. At the alloy system level, the low-alloy steels include the tempered Cr-Mo steels (code 1211) and the tempered Ni-Cr-Mo steels (code 1212). When a section provides information at a level higher than the alloy family, zeros are used, such as code 1500 to designate the broad class of ferritic stainless steels.

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For the purposes of this Technical Reference, the susceptibility of structural materials to hydrogen-assisted fracture in hydrogen gas is evaluated by mechanical testing in two broad categories of environmental conditions: (1) testing in high-pressure hydrogen gas (applying stress concurrent with hydrogen gas exposure) or (2) testing in air subsequent to precharging with hydrogen (applying stress following hydrogen gas exposure). In the Technical Reference sections, these environmental conditions are referred to as *external* hydrogen and *internal* hydrogen respectively. In general, hydrogen precharging is not appropriate for ferritic steels, since the diffusion of hydrogen is relatively rapid on the time scale of typical tests (thus significant hydrogen egress can occur between hydrogen precharging and completion of testing). For some materials, such as austenitic stainless steels, testing in external hydrogen may not produce relevant data because of the slow rate of hydrogen transport in these materials. Specific guidelines for testing in external hydrogen versus testing with internal hydrogen have not been established; however, we believe that materials with hydrogen diffusivity $>10^{-10}$ m^2/s (e.g., carbon and low-alloy steels) should not be tested in air with internal hydrogen. In addition, tests in external hydrogen on materials with hydrogen diffusivity $<10^{-15}$ m^2/s (e.g., austenitic steels) may not provide lower bound properties with the possible exception of long-time tests such as sustained-load cracking. One notable exception to these recommendations is that austenitic stainless steels that form strain-induced martensite may, in some cases, be effectively tested in external hydrogen since the martensite substantially enhances hydrogen diffusion. More discussion of hydrogen transport in austenitic stainless steel can be found in Refs. [3, 4].

With regard to internal hydrogen, there are several methods of precharging materials with hydrogen, the two most common being electrolytic precharging and thermal precharging. For the purposes of the Technical Reference sections, data from electrolytic precharging are largely precluded in favor of thermal precharging because the conditions under which electrolytic precharging occurs are generally not relevant to service in high-pressure hydrogen gas. For example, the hydrogen fugacity associated with electrolytic precharging can be many orders of magnitude greater than can be obtained in hydrogen gas. In addition, since electrolytic charging is typically conducted near ambient temperature, hydrogen penetration into low-diffusivity materials is limited, often leading to large hydrogen concentration gradients near the surface of the test specimen.

1. General

Each Technical Reference *section* consists of a series of *subsections*, which have a consistent numbering system, titles, and content. Each subsection focuses on a particular characteristic or property of the alloy or alloy system represented in the section. The numbering system, title, objective and general content of the subsections are described below.

This subsection summarizes the results that follow. In particular, we emphasize the key characteristics and concepts that are important for interpreting data related to hydrogen-assisted fracture in the material that is the topic of this section.

1.1 Composition and microstructure

This subsection summarizes the characteristics of the material(s) that are referenced in the particular section of the Technical Reference. Typical compositional ranges are given using designations from the unified numbering system (UNS). The specific compositions of the materials that are cited throughout the section are also provided. In this context, we refer to microstructure in a general sense from the perspective of product forms, processing conditions, and strength, which are also summarized when relevant. Specific microstructural details (such as phase distributions, precipitate structure, etc) are generally not provided except when essential to the following subsections.

Alloy composition is an important variable for understanding the performance of structural metals in hydrogen gas, particularly since compositional specifications tend to allow a wide range for each alloying element. It is noted, however, that alloy specifications with wide compositional ranges may be inadequate for specifying materials for hydrogen service. Indeed, this is true for applications other than hydrogen service and explains the plethora of materials specifications, such as those provided by various standards development organizations (ASME, SAE-AMS, ASTM, etc.) for specific applications. Manufacturers also typically have their own compositional specifications relevant for specific products and materials performance, which can specify tighter limits than the public domain specifications. The strength level of the alloy is also an important characteristic for pressure-bearing materials in hydrogen service as high-strength microstructures tend to be significantly more susceptible to hydrogen-assisted fracture than low-strength microstructures.

1.2 Common designations

In this subsection, we associate common names and trade names with the compositional specifications that apply to the materials from that section. The reader is referred to the UNS guide [5] and other standard references, such as the Aerospace Structural Metals Handbooks [6], for comprehensive summaries of various materials specifications that are related to common materials. In general, we have tried to avoid using trade names in favor of general common names, however, for some materials classes this is not practical.

2. Permeability, Diffusivity and Solubility

This subsection summarizes hydrogen permeability, diffusivity, and solubility data. Permeability, diffusivity and solubility collectively describe the dissolution and transport of hydrogen atoms in the lattice of a given material. The solubility (S) is a measure of hydrogen dissolved in a material at equilibrium and can be related to the concentration of hydrogen in a metal lattice (c_L) using Sievert's Law:

$$S = \frac{c_L}{f^{1/2}} \tag{1}$$

where f is the fugacity of hydrogen gas in equilibrium with the lattice (the fugacity of an ideal gas is equivalent to the pressure). Hydrogen dissociates on metal surfaces and diffuses as atomic hydrogen in metals, which accounts for the square root dependence on hydrogen fugacity. In most non-metals, hydrogen diffuses as the molecular species, thus $S \propto 1/f$. Hydrogen can be trapped by microstructural features [7], thus increasing the concentration of hydrogen dissolved in the material; this is particularly true of ferritic and martensitic steels and depends on the density and strength of trapping sites.

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The permeability (Φ) is used to calculate the steady-state flux of hydrogen permeating through a structure using Fick's first law of diffusion ($J = -D(dc/dx)$), where the permeability is defined as the product of the hydrogen diffusivity (D) and solubility:

$$\Phi \equiv DS \tag{2}$$

For example, the hydrogen flux permeating through a semi-infinite metal plate with a finite hydrogen gas pressure on one side and approximately zero pressure on the other side can be expressed as

$$J_\infty = D\frac{Sf^{1/2}}{t} = \frac{\Phi}{t}f^{1/2} \tag{3}$$

where J_∞ is the steady-state diffusional flux of hydrogen, t is the structure thickness, and f is the fugacity of hydrogen gas on the high-pressure side of the plate.

Typically, permeability and diffusivity are determined from direct measurements of the flux of hydrogen through a membrane that is pressurized with hydrogen gas on one side. This experiment must be set up such that lattice diffusion is the rate-limiting step of hydrogen transport and the equilibrium hydrogen concentrations have the correct dependence on hydrogen fugacity (generally, $\propto f^{1/2}$ for metals or $\propto f$ for non-metals). In many cases, hydrogen transport properties are measured at elevated temperature to determine the temperature dependence and to facilitate the measurements. The temperature dependence generally follows the classic exponential form:

$$A = A_0 \exp\left(\frac{-E_A}{RT}\right) \tag{4}$$

where A is the transport property of interest (permeability, diffusivity, or solubility), A_0 is a constant, E_A is an activation energy, R is the universal gas constant, and T is temperature in Kelvin. Many of the principles of permeation are reviewed in Ref. [8] in the context of metals, and an assessment of data can be found in the companion reference [9]. For polymers the reader is referred to Refs. [10, 11].

In general, permeation data are consistent in the literature, and experimental measurements are facilitate by the steady-state definition of Φ. Reported diffusivities, however, have significantly more scatter because diffusivity is determined from transient data, which are inherently more difficult to analyze than steady-state data. Since hydrogen solubility is generally determined from the ratio of the permeability and diffusivity, reported values for hydrogen solubility are dependent on the quality of the diffusivity measurement.

Electrochemical permeation measurements (ASTM G148) are not recommended for determining hydrogen transport properties in materials exposed to high-pressure hydrogen gas. However, in the absence of gas permeation data, we report effective hydrogen diffusivity (D_{eff}) from electrochemical measurements.

3. Mechanical Properties: Effects of Gaseous Hydrogen

These subsections summarize the mechanical properties that are commonly used to quantify the susceptibility of structural metals to hydrogen-assisted fracture. Results from scientific articles and institutional reports that were generated from non-standard techniques or are qualitative in nature have been precluded from these subsections

3.1 Tensile properties

Tensile properties are important for characterizing deformation and fracture in hydrogen environments. Strain rate is a particularly important test parameter as susceptibility to hydrogen-assisted fracture can be sensitive to strain rate, even in the rather narrow range from 10^{-6} to 10^{-2} 1/s [12].

3.1.1 Smooth tensile properties

Properties are reported according to definitions in ASTM E6. Except when noted yield strength refers to the 0.2% offset yield strength. If the method of determination is not given in the source article or report, it is assumed that yield strength is determined by the 0.2% offset method. The geometry of tensile specimens is assumed to follow the basic guidelines in ASTM E8.

The following nomenclature is used to summarize the deformation and fracture results from tensile tests with smooth specimens:

S_y (MPa)	0.2% offset yield strength: determined by drawing a line that has the slope of the elastic modulus and intersects the strain axis at 0.2% on a plot of the stress-strain curve; the intersection of this construction line with the flow stress is the yield strength, see ASTM E6
S_u (MPa)	tensile strength: maximum load divided by the original cross-sectional area
El_u (%)	uniform elongation: engineering strain at maximum load
El_t (%)	total elongation: engineering strain at fracture (depends on gauge length)
RA (%)	reduction of area: difference of original cross-sectional area and the minimum cross-sectional area after fracture normalized by the original cross-sectional area
RRA	relative reduction in area: ratio of RA measured for a specific test condition (external or internal hydrogen) to RA measured in air or inert environment, see ASTM G129

3.1.2 Notched tensile properties

Notched tensile specimens generate high hydrostatic tensile stresses, which can amplify the effects of hydrogen-assisted fracture. Common specimen designs are based on cylindrical tensile specimens but are modified by including a circumferential notch. ASTM G142 provides a standard notched tensile geometry for testing in high-pressure hydrogen gas; however, few studies have used this geometry. We report the notch geometry and dimensions of specimens described in the source articles and reports, including the elastic stress concentration factor. In addition, yield strength from smooth tensile tests is also reported since notch sensitivity in the absence of hydrogen will generally be a function of the material's microstructure and strength. Data measured from other notched-specimen designs, such as single-edge notched tensile specimens, are generally not included in this subsection; although when such tests demonstrate important trends, those trends are summarized.

The following nomenclature is used for notched tensile specimens:

σ_s (MPa)	notched tensile strength: maximum load divided by the original cross-sectional area at the notch, see ASTM E602
RA (%)	reduction of area: difference of original notch cross-sectional area and the minimum notch cross-sectional area after fracture normalized by the original notch cross-sectional area
K_t	elastic stress concentration factor

3.2 Fracture mechanics

We emphasize that fracture mechanics testing is imperative for the design of pressure-bearing structures with large section sizes. Fracture mechanics design methods allow safety margins against hydrogen-assisted crack propagation to be quantified. These design methods require material property inputs that are measured using fracture mechanics techniques. Proper interpretation of fracture mechanics data is critical for the design of safe structures. For example, fracture mechanics data should represent lower-bound values for a given material, environment, and testing protocol.

3.2.1 Fracture toughness

The fracture toughness of materials is measured using precracked specimens that are subjected to a constant displacement rate. Fracture toughness testing generally yields measures of both the fracture initiation and crack propagation resistances. Similar to tensile testing, the displacement rate during fracture toughness testing in hydrogen gas can affect the results. Standardized specimen geometry and testing procedures for determine of fracture toughness are outlined in ASTM E1820.

The following nomenclature is used for summarizing results from fracture toughness testing:

K_{Ic} (MPa $m^{1/2}$)	stress-intensity factor for fracture initiation under small-scale yielding, plane strain conditions
K_Q (MPa $m^{1/2}$)	value of stress-intensity factor for fracture initiation measured from specimen that does not meet dimensional requirements according to ASTM E1820
K_{JIc} (MPa $m^{1/2}$)	equivalent stress-intensity factor calculated from the J-integral value of fracture initiation toughness (J_{Ic})
J_{Ic} (kJ m^{-2})	J-integral for fracture initiation under large-scale yielding, plane strain conditions
J_Q (kJ m^{-2})	value of J-integral for fracture initiation measured from specimen that does not meet dimensional requirements according to ASTM E1820
dJ/da (MPa)	slope of the J-integral *vs* crack extension curve; a measure of the crack propagation resistance
K_{IH} (MPa $m^{1/2}$)	stress-intensity factor for fracture initiation measured in hydrogen gas; may be determined from values of the J-integral and may not meet the dimensional requirements according to ASTM E1820

3.2.2 Threshold stress-intensity factor

The threshold stress-intensity factor for sustained-load cracking (K_{TH}) is a measure of a material's resistance to hydrogen-assisted crack propagation under static loading. In general, the value of K_{TH} is not a material property, since the value of K_{TH} may depend on the geometry of the test specimen (i.e., may not be a value that is independent of specimen geometry such as K_{Ic}). One of the common test configurations is the modified bolt load compact specimen (ASTM E1681), where a constant displacement is applied with the aid of a bolt. This configuration is also referred to as the wedge-opening load (WOL) specimen. In these tests, an initial stress-intensity factor less than K_{Ic} is applied before placing the precracked specimen in the environment of interest, in this case high-pressure hydrogen gas. If susceptible to environment-assisted fracture, the precrack will extend under decreasing stress-intensity factor until the crack arrests at the threshold value.

The time for initiation of crack propagation can be unpredictable, possibly requiring many thousands of hours. Therefore, the lack of an environmental cracking response may not imply that the applied stress-intensity factor is less than the threshold. Thus, crack advance and arrest is the only unambiguous method of determining a threshold value.

More specifics of the method recommended for testing in gaseous hydrogen can be found in the ASME Boiler and Pressure Vessel Code, Section VIII, Division 3, Article KD-10.

3.3 Fatigue

Fatigue is a material failure mode particular to cyclic loading. The effects of hydrogen gas on fatigue properties have not been extensively investigated for most alloy classes. Fatigue is arguably the most important failure mechanism in structures subjected to cyclic stress, therefore this failure mechanism must be considered in the design of hydrogen gas components subjected to pressure cycling. Given the importance of this failure mode, more efforts are needed to measure fatigue properties of materials in hydrogen gas. Frequency of the load cycle and the ratio of minimum load to maximum load (R-ratio) are two important variables that have been shown to affect fatigue properties measured in hydrogen gas.

3.3.1 Low-cycle and high-cycle fatigue

Perhaps the most common fatigue testing method involves smooth cylindrical specimens, which are used to generate the so-called S-N curves. The S-N curves are plots of alternating stress amplitude (S) *vs* number of cycles to failure (N). The number of cycles to failure includes both crack initiation and propagation.

3.3.2 Fatigue crack propagation

Although results from fatigue testing of smooth specimens do not separate fatigue crack initiation and propagation, testing of fracture mechanics specimens can provide data solely on fatigue crack propagation. Precracked specimens are tested using fracture mechanics methods (ASTM E647) to generate plots of fatigue crack growth rate (crack extension per load cycle, da/dN) as a function of stress intensity factor range (ΔK). These data can be used to quantify design margins that accommodate the propagation of known defects in pressure-bearing structures or that eliminate the propagation of critical defects all together.

3.4 Creep

Creep is a high-temperature failure mode, where materials can deform and ultimately fracture under static loading. Although creep may not be a consideration for most hydrogen infrastructure components, effects of hydrogen could be strongly manifested in creep due to the low strain rates typically involved and the fact that hydrogen solubility increases with temperature.

3.5 Impact

Notched-bar impact tests, such as Charpy impact, are standard methods of estimating fracture toughness in steels (ASTM E23). Due to the nature of strain rate effects on hydrogen-assisted fracture, impact testing is not the most effective method for quantifying hydrogen-assisted fracture in materials. Consequently, correlations between impact properties and fracture toughness are not appropriate for assessing hydrogen-assisted fracture.

3.6 Disk rupture testing

The disk rupture test is a qualitative assessment of susceptibility to hydrogen-assisted fracture. This method involves pressurizing identical membranes of material with hydrogen gas and with inert gas (such as helium) until the membranes fail. The ratio of the burst pressure in inert gas to the burst pressure in hydrogen gas is an index of susceptibility to hydrogen-assisted fracture (ASTM F1459). These tests do not provide data that are used to quantify the safety margins of components in hydrogen gas systems; however, disk rupture tests can be used as a simple screening tool for evaluating the relative susceptibility of materials to hydrogen-assisted fracture.

4. Fabrication

In the 4.x subsections, we describe specific processing variables and metallurgical features that should be considered in assessing susceptibility to hydrogen-assisted fracture. Primary processing (forging, cold-working, etc.) as well as subsequent heat treatment are important variables. For example, aging of A-286 (precipitation-strengthened austenitic stainless steel) significantly impacts the ductility in this alloy, and appears to increase the susceptibility to hydrogen-assisted fracture. Welding is another important fabrication variable, particularly in ferritic steels where martensite can form during heating and cooling at the weld. Martensite is known to be vulnerable to hydrogen-assisted fracture.

5. References

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