DEVELOPMENT OF STANDARDS FOR EVALUATING MATERIALS COMPATIBILITY WITH HIGH-PRESSURE GASEOUS HYDROGEN

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ABSTRACT

The Hydrogen Safety, Codes and Standards program element of the US Department of Energy's Fuel Cell Technologies Office provides coordination and technical data for the development of domestic and international codes and standards related to hydrogen technologies. The materials compatibility program task at Sandia National Laboratories (Livermore CA) is focused on developing the technical basis for qualifying materials for hydrogen service, i.e., accommodating hydrogen embrittlement. This presentation summarizes code development activities for qualifying materials for hydrogen service with emphasis on the scientific basis for the testing methodologies, including fracture mechanics based measurements (fracture threshold and fatigue crack growth), total fatigue life measurements and full-scale pressure vessel testing.

1.0 INTRODUCTION

Hydrogen embrittlement is an important phenomenon that can strongly impact the performance of systems for the storage and delivery of gaseous hydrogen [1], including fuel cell vehicles and their refueling systems. As markets for other fuel cell systems grow, such as hydrogen-powered forklifts and stationary backup power modules, there is a need for both specific and general standards for materials selection to accommodate hydrogen embrittlement in the performance of these systems. Materials selection and qualification for gaseous hydrogen service must recognize that hydrogen embrittlement susceptibility is not an intrinsic characteristic; rather, it depends on numerous variables such as hydrogen gas pressure, temperature and applied stress. Furthermore, material qualification is not necessarily an exercise in demonstrating immunity to hydrogen embrittlement. The objective of materials qualification is to quantify hydrogen embrittlement susceptibility using an accepted design-relevant metric (e.g., material tensile strength), and then to employ this metric in engineering designs to define limits on allowable operating conditions (e.g., gas pressure, temperature, stress).

Existing documents related to material and component qualification for gaseous hydrogen service can be categorized as (1) general guidance documents; (2) component standards; and (3) materials testing standards. In some cases, documents specific to gaseous hydrogen incorporate elements of more than one of these categories. After introducing the most commonly referenced documents in these categories, several of the component standards that incorporate evaluation of hydrogen compatibility of materials are described. Finally, a new standard is introduced that combines elements of all three categories (described above) to provide a standard for qualifying materials for hydrogen service that can be applied generally to any application.

1.1 General guidance

There are a number of documents that provide qualitative guidance on materials selection and best practices for designing hydrogen systems. One of the most commonly referenced documents stems from a substantial effort in the 1960s and 1970s funded by the National Aerospace and Aeronautics Association (NASA) in the United States to establish methods and data for selecting materials for hydrogen systems. There are many seminal works from that period on characterizing the performance of materials in high-pressure gaseous hydrogen (e.g., refs. [2-4]). These early studies and the engineering experience garnered from designing and building hydrogen systems at NASA were consolidated in a single, public report entitled "Guide to Safety of Hydrogen and Hydrogen Systems"

[5]. This report has been issued by the American Institute of Aeronautics and Astronautics (AIAA), as document number G-095.

Engineering societies and industrial associations have also developed guidance for hydrogen systems, usually specific to particular engineering technology. The European Industrial Gases Association (EIGA) has issued several reports on hydrogen [6, 7]. Two related to pressure vessels and pipelines are entitled "Hydrogen Cylinders and Transport Vessels" and "Hydrogen Transportation Pipelines" respectively. These documents make specific suggestions to limit the effects of hydrogen embrittlement on materials, such as appropriate materials classes, compositional limits and strength limits. The American Society of Mechanical Engineers (ASME) issued a report summarizing engineering experience and providing some limited guidance on materials selection; this report is entitled "Hydrogen Standardization Interim Report for Tanks, Piping and Pipelines" [8]. A report entitled "Design Guide for Hydrogen Piping and Pipelines" was issued by ASME a few years later.

As part of current activities funded by US Department of Energy's Fuel Cell Technologies Office, the hydrogen codes and standards program at Sandia National Laboratories (Livermore CA) is focused on developing the technical basis for qualifying materials for hydrogen service. One portion of this activity is the creation and maintenance of the "Technical Reference for Hydrogen Compatibility of Materials". The Technical Reference (TR) is structured by material class, including specific materials that are commonly used in hydrogen service, and summarizes materials properties that meet two criteria: (1) measured in gaseous hydrogen and (2) reported in the open literature. While it does not provide direct guidance on materials selection, the TR provides a summary of materials data measured in gaseous hydrogen, thus serving to provide the basis for materials selection decisions. The TR is available online, where its contents are periodically updated; it has also been released in its entirety as a formal report in 2008 [9] and updated in 2012 [10].

1.2 Component standards

Component standards are often distinguished as being either a prescriptive or performance standards. For the purposes of this discussion on materials qualification for hydrogen service, the term design standard is used to distinguish as a standard that prescribes the design methodology based on measured (or tabulated) materials properties. The ASME Boiler and Pressure Vessel Code (BPVC) and the Code for Pressure Piping are examples of design standards. In contrast, a performance standard does not prescribe the details of the design, but requires a minimum threshold be achieved in a design metric or materials response. In other words, performance standards often use pass-fail criteria to establish the acceptability of a component or material. In some cases, elements of both design and performance requirements are included in a standard.

The ASME Code for Pressure Piping has a recent addition specific to hydrogen: B31.12 Hydrogen Piping and Pipelines. This code is a design standard with specific requirements for hydrogen piping and pipelines, but it also provides general guidance similar to the NASA/AIAA report. In particular, this report distills the problem of materials selection for hydrogen into this relatively concise statement: "Because no structural metal can be labeled as "immune" to hydrogen embrittlement, designing structures for hydrogen service does not involve simply selecting a material from a list of "hydrogen-compatible" alloys" [11]. B31.12 references the ASME Boiler and Pressure Vessel Code (BPVC) and a relatively new article in Section VIII, Division 3 for hydrogen tanks. This article (KD-10) provides design requirements for high-pressure hydrogen systems and incorporates elements of a testing standard to evaluate fatigue performance of materials in gaseous hydrogen to inform the design; details of this article will be discussed below in Section 2.1.

Another document specific to pressure vessels is ISO 11114-4, which was developed to qualify high strength steels (ultimate strength > 950 MPa) for construction of seamless hydrogen pressure vessels. This document is often referenced informally as a general test method for evaluating materials for hydrogen embrittlement susceptibility, however, the requirements are specific to seamless hydrogen pressure vessels and will be discussed in more detail in Section 2.2.

A number of documents are currently being developed or updated to include design or performance requirements specific to gaseous hydrogen service. In particular, the CSA HPIT1 document, entitled "Compressed Hydrogen Powered Industrial Truck On-Board Fuel Storage and Handling Components", is an example of a standard that incorporates both design and performance requirements for a specific application: in this case, gaseous hydrogen fuel systems onboard industrial trucks, such as forklifts. This document is still in the final stages of being released, but it is discussed in Section 2.3 because of its novel approach to requirements for type 1 (all metal) pressure vessels. Like the ASME BPVC, HPIT1 allows materials that are strongly affected by hydrogen, but in contrast to the ASME BPVC, this allowance is accommodated by constraining the design space.

The Society of Automotive Engineers (SAE) has been discussing materials compatibility for some time as part of developing the J2579 standard [12]; the J2579 document is currently a Technical Information Report (TIR) for "Fuel Systems in Fuel Cell and Other Hydrogen Vehicles". The appendices specify certain classes of austenitic stainless steels and aluminum alloys for use in onboard hydrogen storage systems, while other alloys must be qualified either through materials testing or performance testing on prototype components.

To complement standards for transportable pressure vessels (such as ISO 11114), ISO is developing a document for the design of pressure vessels for stationary storage of hydrogen: ISO-DIS 15399 Gaseous hydrogen – Cylinders and tubes for stationary storage. ISO-DIS 15399 will likely account for fatigue behavior of pressure vessel steels in gaseous hydrogen from a materials perspective. In general, ISO documents are arguably performance standards, thus it seems likely that ISO-DIS 15399 will also be a component-level performance standard. The authors do not participate on technical committee for hydrogen technologies at ISO (TC 197), thus an informed description of the current state of the 15399 cannot be provided here.

1.3 Materials testing standards

In contrast to the above (incomplete) list of documents that address the hydrogen embrittlement problem with some guidance or requirements for a specific application, there are a few documents describing best practices for materials testing. Two documents from the ASTM International provide details of testing in gaseous hydrogen (G129 [13] and G142 [14]). The latter document is the more specific and describes best practices for slow strain rate testing in gaseous hydrogen.

There remains a need for general materials qualification for materials of construction for components in hydrogen service, such as valves, pressure relief devices, regulators and metering devices. In 2012, the Canadian Standards Association, America (CSA) released a document entitled "Test methods for evaluating material compatibility in compressed hydrogen applications", which describes best practices for tensile, fracture and fatigue testing of metals in high-pressure gaseous hydrogen. This document, referred to as CHMC1, has recently been revised to provide specific requirements for qualifying materials for service in gaseous hydrogen; it is currently following the internal review and comment process within CSA. This may be the first document to provide general requirements for materials qualification for hydrogen service and will be discussed in more detail in Section 4.

2.0 REQUIREMENTS FOR HYDROGEN PRESSURE VESSELS

2.1 ASME BPVC VIII.3. KD-10

Article KD-10 is a design standard for pressure vessels for hydrogen service that was developed by the ASME Project Team on Hydrogen Tanks to provide fracture-mechanics-based design rules for metal pressure vessels [15]. It also incorporates a description of required test methods since fracture-mechanics-based test methods specific to high-pressure gaseous hydrogen were not available for reference. High pressure is defined in this document as greater than 42 MPa for seamless pressure vessels and greater than 17 MPa for welded pressure vessels. Additional requirements are related to the strength of the steel.

The design analysis in Article KD-10 requires the fracture threshold and fatigue crack growth rate be measured in gaseous hydrogen. The minimum life of a pressure vessel can be predicted using these data and the minimum detectable flaw size, following standardized and robust design procedures already incorporated in the ASME BPVC VIII.3.KD-4. The basic design strategy of Article KD-4 is a proven and conservative methodology and well suited to pressure vessels that can be inspected regularly and that can tolerate a small, growing crack.

The total fatigue life of a component is comprised of a regime of fatigue crack initiation and a regime of long-crack growth (the growth of "short cracks" is included in the initiation regime, while "long cracks" refers to the regime in which fracture mechanics can be applied [16]). The first of these processes is statistical in nature and is difficult to quantify accurately, however the growth of long cracks may be measured with reasonable accuracy in the laboratory. KD-4 design methods neglect the life associated with crack initiation and define component life by considering only the growth of long cracks. Hydrogen is known to accelerate the growth rate of long cracks, while it may have little effect on crack initiation. The result is that this design method becomes more conservative for hydrogen tanks as compared to tanks containing non-embrittling gasses. Consequently, design using Article KD-10 may be unnecessarily conservative for some applications, as was demonstrated for transportable hydrogen pressure vessels in Refs. [17, 18]. The ASME BPVC VIII.3 allows for stress-based fatigue life design (Article KD-3), which implicitly accounts for both crack initiation *and* crack growth; however, this methodology has not been adopted for hydrogen service in the ASME code.

While the efficacy of the design strategy in Article KD-10 is without question, recent results suggest the materials testing methods described in Article KD-10 are not as robust as originally believed. In particular, Article KD-10 requires the measurement of crack-arrest fracture thresholds following procedures in ASTM E1681. As described in Ref. [19, 20] and shown in Figure 1, crack-arrest fracture thresholds can be greater than the rising-displacement fracture thresholds for the same steel (both measured in high-pressure gaseous hydrogen). Based on fracture mechanics theory, these two test methods are expected to give similar results when the plasticity that accompanies fracture is small. However, if the amount of plasticity that accompanies fracture is large, the constant displacement test method produces non-conservative results relative to the fracture threshold measured by the rising displacement test method [19, 20]. Large amounts of plasticity accompanying fracture is desirable as this translates to higher fracture resistance; e.g. these materials are desirable for hydrogen pressure vessel applications and are the most likely materials for construction of pressure vessels designed according to the rules of KD-10. Therefore, methods currently described in Article KD-10 are unlikely to provide conservative measurement of the critical stress intensity factor for fracture of hydrogen pressure vessels.

Article KD-10 requires fatigue crack growth measurements be conducted at a frequency of 0.1 Hz, however the time required to complete the required testing at this frequency can present a substantial burden on the user. The low frequency is meant to capture the effects of loading rate on fatigue crack growth, as reported in the literature, but simple constant load amplitude tests over a large range of driving force (ΔK) can require thousands of hours to perform, as shown in Figure 2. Revision of the fatigue crack growth rate procedures to improve testing efficiency would add significant value to this standard. One way to accomplish this, as has been suggested in the literature, is to vary the frequency over different portions of the test such that the crack growth rate always remains slower than the limiting hydrogen transport kinetics [21]. The testing community has made other suggestions as well, such as producing the fatigue crack growth data at high frequency (1 to 10 Hz) to establish the shape of the curve, then performing limited testing at fixed driving force (constant ΔK) and low frequency to establish the amplification of fatigue crack growth due to frequency at strategic points along the fatigue crack growth curve. The fatigue crack growth curve at high frequency can then be adjusted for the effects of frequency.

Article KD-10 provides one robust methodology for design of hydrogen pressure vessels; however, there is opportunity to improve the materials testing methodologies in this Article. The critical stress intensity factor determined by constant displacement (crack arrest) fracture tests is non-conservative relative to other measures of the critical stress intensity factor. One possible improvement would be replacing constant displacement fracture test methods with methods that concurrently load fracture specimens in gaseous hydrogen, such as those used to report elastic-plastic fracture toughness measured in gaseous hydrogen [19, 20, 22, 23]. Another improvement would be allowing greater flexibility for frequency during fatigue crack growth testing. In any case, the design strategy embraced in Article KD-10 is conservative especially for hydrogen pressure vessels. Thus, the development of a complementary design method using stress-life predictions (similar to Article KD-3) is also encouraged for pressure vessels in high-pressure gaseous hydrogen service.

2.2 ISO 11114-4

The ISO 11114-4 document, entitled “Transportable gas cylinders: Part 4, compatibility of cylinder and valve materials with gas contents”, is a materials performance standard specific for hydrogen pressure vessels constructed with steel having tensile strength greater than 950 MPa. Three materials evaluation options are provided in this standard with essentially pass-fail criteria for this specific application: (1) disc rupture test (Method A); (2) rising-displacement fracture mechanics test (Method B); and (3) sustained load cracking test (Method C). Since transportable gas cylinders are filled infrequently, this standard does not consider fatigue. Despite the narrow scope of the 11114 documents, the compatibility tests (part 4) are often referred to as general test methods for evaluating hydrogen embrittlement. It should be emphasized that these test methods and performance criteria are limited to the specific requirements of all steel transportable gas cylinders that are pressurized infrequently.

The three materials evaluation methods are vastly different and are not equivalent. The disc rupture test (Method A) is an empirical test based on engineering experience for transportable gas cylinders. The rising-displacement fracture mechanics test (Method B) is similar to conventional fracture toughness determinations (such as ASTM E1820); however, the test method is employed to establish that cracks do not propagate prior to reaching a minimum applied stress intensity factor during step loading. The step-loading method seems unnecessary, as the effects of hydrogen have been successfully evaluated using monotonic loading methods [19, 20, 22-24]. This method could be broadened in scope to evaluate fracture resistance of materials in gaseous hydrogen for design purposes, which would require a more rigorous fracture analysis and in situ measurement of the crack mouth opening displacement (and/or angle). The sustained-load cracking test (Method C) is subject to similar non-conservative tendencies as the methods in ASME BPVC VIII.3.KD-10, as discussed in the previous section. The lower-bound critical stress intensity factor (rising-displacement fracture toughness measured in gaseous hydrogen) is more representative of the loading condition of a vessel during pressurization; thus the sustained load cracking test is non-conservative, at least for strain-controlled fracture of low-strength steels [19, 20]. In summary, the three test methods in ISO 11114-4 measure different characteristics of materials and are not equivalent [25]. The methods and criteria in ISO 11114-4 appear adequate as materials performance tests for transportable gas cylinders, but these methods and criteria should not be extrapolated to other applications without careful understanding of the application and requirements.

2.3 CSA HPIT1

The CSA HPIT1 document, entitled “Compressed Hydrogen Powered Industrial Truck On-Board Fuel Storage and Handling Components”, describes the requirements for the hydrogen fuel system onboard hydrogen-powered industrial trucks, such as forklifts. While the HPIT1 document provides requirements for the fuel system, in this context, the hydrogen pressure vessels are the primary interest. HPIT1 provides two options for qualifying pressure vessels, representing performance and design methodologies respectively : (i) fatigue life verification by performance testing of the full-scale pressure vessel, or (ii) fatigue life qualification by design analysis. The performance methodology allows for the qualification of pressure vessels (in particular composite pressure vessels) while avoiding the standardization of a specific design philosophy. The design-analysis methodology allows for qualification without the burden of accelerated full-scale testing to the end of life and beyond. The design-analysis methodology, however, is limited to relatively simple designs that can easily be standardized, namely all steel (type 1) pressure vessels. While the HPIT1 document does not provide any language for qualifying materials for hydrogen service, the concepts employed in the design requirements are instructive and may be a useful template for the development of design standards for other applications.

The design-analysis method in HPIT1 employs stress-life fatigue assessment from ASME BPVC VIII.3.KD-3. There is no *a priori* reason that Article KD-3 can or should be invoked for hydrogen service, since it does not account for the effects of hydrogen on fatigue behavior. An empirical approach was employed in the development of HPIT1, using engineering experience and testing results to show that within a conservatively defined design space for this application the design curves in Article KD-3 are conservative for gaseous hydrogen service [18]. HPIT1 defines the allowable design space by way of requirements on the materials that can be used with the design-analysis method option. A more flexible approach would be to measure the total fatigue life properties of pressure vessel steels in gaseous hydrogen and develop conservative design curves for hydrogen service. Such testing was beyond the scope of HPIT1.

Stress-life fatigue assessment represents an opportunity to complement the fatigue crack growth methods embraced in Article KD-10 (ASME BPVC VIII.3). It is hoped that the community will consider developing stress-life methods analogous to Article KD-3, but for hydrogen service, as well as generalize the methods for a range of applications beyond pressure vessels. Indeed, the stress-life concept is employed in CHCM1, as described in Section 4.

3.0 REQUIREMENTS FOR PIPING AND PIPELINES

The ASME code B31.12 Hydrogen Piping and Pipelines provides general guidance for selecting materials for hydrogen service and some specific language for pipeline materials (i.e., carbon steels). The B31.12 code refers to article KD-10 for determining fracture resistance of pipeline steels in gaseous hydrogen. As described previously, for low-strength steels, such as pipeline steels, the critical stress intensity factor for fracture is generally quite large [22, 24] and cannot be measured by the constant displacement (crack arrest) method described in article KD-10. As mentioned previously, the EIGA report on hydrogen pipelines [7] provides guidance on materials selection for hydrogen service and the ASME Interim Report [8] summarizes industrial experience with hydrogen pipelines.

4.0 GENERAL MATERIALS QUALIFICATION: CSA CHMC1

4.1 Overview

A new document from CSA provides guidance on evaluating tensile, fracture and fatigue properties of structural metals in gaseous hydrogen. This document is entitled “Test methods for evaluating material compatibility in compressed hydrogen applications”; the document identification is CHMC1 (Compressed Hydrogen Materials Compatibility). The 2012 version of this document (CHMC1-2012) provides comprehensive rules for measuring standard material properties for use in engineering design. CHMC1-2012, however, does not provide quantitative metrics to qualify a material for service in gaseous hydrogen, nor to qualify a specific component.

After completion of CHMC1-2012, the technical advisory group (TAG) quickly began work on the next release of the document, which provides general rules for qualifying materials for gaseous environments containing hydrogen. As of April 2013, the revised version of CHMC1 has been completed and is being reviewed internally at CSA; for the purposes of this discussion, CHMC1-TBD (”to be determined”) is used to designation this revised version of CHMC1 and distinguish from the version previously published (CHMC1-2012). CHMC1-TBD will represent the first document to provide a general framework for qualifying materials for hydrogen service. Due to the importance of its unique role in qualifying metals for hydrogen service, the basic features of the qualification requirements are summarized.

CHMC1-TBD is consistent with the 2012 release. It provides requirements for the equipment and for the environment in which the testing is executed. Specific procedures for tensile, fracture and fatigue testing are provided, referencing primarily ASTM documents and specifying testing rates and fatigue frequency. CHMC1-TBD provides several additional sections specifying requirements for materials qualification, which includes qualification of a specific batch of metal as well as the qualification of a materials specification. Since different components can have substantially different design requirements, the CHMC1 TAG has proposed a stress-based safety factor approach that can be broadly applied; the document, however, allows other approaches to design, such as fatigue crack growth approaches provided that the data needed in design is measured in an environment that is consistent with the application. The TAG also recognized the extensive engineering experience available for hydrogen systems and tried to limit the testing burden for materials that are generally accepted for hydrogen service, such as the materials deemed acceptable by other standards and guidance (e.g., SAE J2579).

4.2 Requirements

CHMC1-TBD provides three routes by which a material may be deemed compatible with gaseous hydrogen, as depicted by the logic flow chart in Figure 5. Austenitic stainless steel and aluminum alloys, owing to the depth of knowledge regarding the performance of these alloys in gaseous hydrogen, may be deemed compatible based only on a stringent notched-tensile test requirement. Two additional methods are provided for all other materials (including austenitic stainless steels and aluminum alloys that do not satisfy the simpler, but very stringent notched tensile test requirements). The first is a safety factor method in which fatigue life tests are used to determine a safety factor to account for the effect of hydrogen on strength and fatigue. The second is a design method in which specific mechanical properties are measured from specimens exposed to gaseous hydrogen and are used to as component design inputs. All materials that show 50% or more reduction of NTS are not to be used in gaseous hydrogen according to the method in CHMC1-TBD

Austenitic stainless steels and aluminum alloys are known to be among the most compatible alloys with gaseous hydrogen and are also among the best characterized alloys in the same regard. These two alloys classes may, therefore, be deemed compatible hydrogen based only on the notched tensile test results if those results demonstrate a negligible effect of hydrogen. Specifically the notched tensile strength (NTS) in hydrogen must be greater than 90% of the NTS measured in a reference environment (e.g., air). Alternatively, aluminum and stainless steel alloys may also be qualified if the reduction in area (RA) in hydrogen is greater than 90% of the RA in a reference environment.

The safety factor multiplier method requires generating a fatigue stress-life curve (S-N or Wohler curve) using the notched specimen in both gaseous hydrogen and the reference environment. With appropriate statistical treatment of the data, the ratio of stress in these environments (reference environment to hydrogen environment, such that the ratio is generally greater than or equal to one) is determined at several cycle numbers: 10^3, 10^4 and 10^5, as well as at 10^0 (i.e., the ratio of the NTS). This is shown schematically in Figure 6. The safety factor multiplier is the largest of these ratios and must be multiplied by other safety factors used in the design. For example, consider a particular component/standard that requires a stress-based safety factor of 2, while testing of the materials of construction according to CHMC1-TBD found the stress ratios to be 1.2, 1.15, 1.0 and 1.0 for the NTS and at 10^3, 10^4 and 10^5 cycles respectively. The safety factor multiplier is the largest of these stress ratios: 1.2, thus the required stress-based safety factor for hydrogen service is 2.4 (or 2 times 1.2). Implementation of the safety factor multiplier method implicitly requires the component standard to state a minimum safety factor or otherwise allow a means to de-rate the maximum allowable stress in the component.

The CHMC1-TBD document also allows other design strategies to be used, as long as the appropriate material properties are measured according to the rules in CHMC1. For instance, fatigue crack growth methods of life prediction as specified in ASME BPVC VIII.3.KD-4 can also be used in conjunction with CHMC1-TBD, but require measuring fatigue crack growth in gaseous hydrogen. In summary, CHMC1-TBD requirements allow essentially three options for qualifying a material for a component: (1) use stainless steels or aluminum alloys that are not affected by the environmental conditions for the application; (2) determine the safety factor multiplier and increase the required safety factor for the component (or de-rate the maximum allowable pressure of a designed component); (3) measure the properties of the material of construction in gaseous hydrogen and apply these measurements in the design process.

4.3 Qualification of a materials specification

The qualification methods described in CHMC1-TBD apply to a given batch or heat of material. However, conducting the suite of materials testing required to determine the safety factor multiplier for every batch of material used during the life of a product line is impractical. Therefore, CHMC1-TBD provides provisions for qualifying a materials specification, such that testing does not need to be repeated. This is achieved by testing three batches of material that satisfy a material specification. Each material in the bill of materials that is continuously exposed to hydrogen during normal operation most be controlled by a materials specification and that specification must be qualified for hydrogen service; if a material specification changes, additional testing may be required as specified in CHMC1-TBD to re-qualify the revised material specification. The materials specification can be an internal specification, which allows industry to use materials that might generally be unacceptable for a given application; for example, this can be accomplished by specifying a narrower composition range or particular processing method to achieve improved performance in gaseous hydrogen.

4.4 Discussion

The three routes to qualification of an alloy with gaseous hydrogen represent attempts to provide the most efficient methods for qualification that also remain consistent with the data available. Because of the amount of data available for stainless steel and aluminum alloys, the most efficient test procedures could be developed for these alloys. The safety factor multiplier concept is relatively simple and this method gives an engineering-based approach to account for the effects of hydrogen: essentially a stress correction, such that conservative safety factors are maintained and which are consistent with the design requirements of the component.

Pressure systems are usually designed with large safety factors, meaning that the stresses in the component are well below the yield strength of the material. The relatively limited fatigue data for structural materials in gaseous hydrogen suggest that for fatigue nominally in the elastic range (high-cycle fatigue) there is relatively little effect of hydrogen on S-N fatigue performance. Therefore, in general, pressure components with large safety factors are likely to perform similarly in gaseous hydrogen and in an inert environment. In these cases, the safety factor multiplier method will likely be dominated by the ratio of NTS; the NTS is known to show significant degradation in gaseous hydrogen for a large number of structural metals [4]. The safety factor multiplier ensures that the environmental impact of hydrogen on the structural integrity of component (i.e., fatigue life) is maintained at values deemed appropriate for the specific application. In other words, the stress-based safety factor in hydrogen is the same or greater than the safety factor in an inert environment.

The spirit of the safety factor multiplier method is similar to the rules incorporated in CSA HPIT1 for steel pressure vessels and described in Section 2.3 above. Comprehensive fatigue data (i.e., S-N curves) measured in gaseous hydrogen are not available for the Cr-Mo steels, thus the safety factor multiplier method cannot be applied based on existing data. Additionally, engineering experience suggests that the generation of extensive data required by CHMC1-TBD is not needed for this application, provided that the pressure-vessel design stresses are relatively low. In this case, of the HPIT1 document, the design of Cr-Mo steel pressure vessels is limited to safety factors of 2.5 or greater (ratio ultimate tensile stress to wall stress) and maximum tensile strength of 890 MPa. Moreover, the fatigue-life predictions from the ASME code using data from tests in air were found to be conservative relative to full-scale testing in gaseous hydrogen, primarily due to the large safety factor. The large safety factor is consistent with existing design rules, such as those for transportable gas cylinders, suggesting that a broad range of existing components are acceptable for the service environment associated with gaseous hydrogen. CHMC1-TBD provides a framework to test these designs.

Gaseous hydrogen enhances fatigue crack growth by a factor of 10 or more at higher stresses. It seems unlikely that stress-life fatigue will capture the magnitude of this degradation, since it quantifies the sum of initiation and crack growth. However, for low-strength steels from which high-pressure components are typically manufactured, acceleration of fatigue cracks is primarily observed for large cracks with large driving force for extension. In general, defects are small, under which conditions gaseous hydrogen has comparatively little effect on fatigue crack growth. Thus, for the majority of the lifetime of a defect, hydrogen does not significantly accelerate fracture. High-strength steels that show large hydrogen effects are essentially precluded from use in hydrogen by the requirement that the materials have NTS in hydrogen greater than 50% of the NTS in an inert environment.

5.0 SUMMARY

There are many sources of general guidance for materials selection for service with high-pressure gaseous hydrogen. Several documents provide quantitative requirements for qualifying materials for specific application in high-pressure gaseous hydrogen, in particular pressure vessels. The existing documents are not sufficiently general to be applied for components other that those for which the standard was specifically written.

There remains a need for general materials qualification for materials of construction for components in hydrogen service, such as valves, pressure relief devices, regulators and metering devices. The CSA CHMC1 document provides general guidance on materials testing, which is otherwise lacking from existing standards. Moreover, a revision of the CHMC1 document is currently being reviewed. This revision provides general methods for qualifying materials (and materials specifications) for hydrogen service. One of the proposed methods provides metrics for classifying materials as (i) compatible without special design consideration, (ii) compatible with additional safety factor, and (iii) not appropriate for hydrogen service. The CHMC1 document also provides a quantitative method to determine appropriate safety factors for hydrogen service using stress-based fatigue analysis.

ACKNOWLEDGEMENTS

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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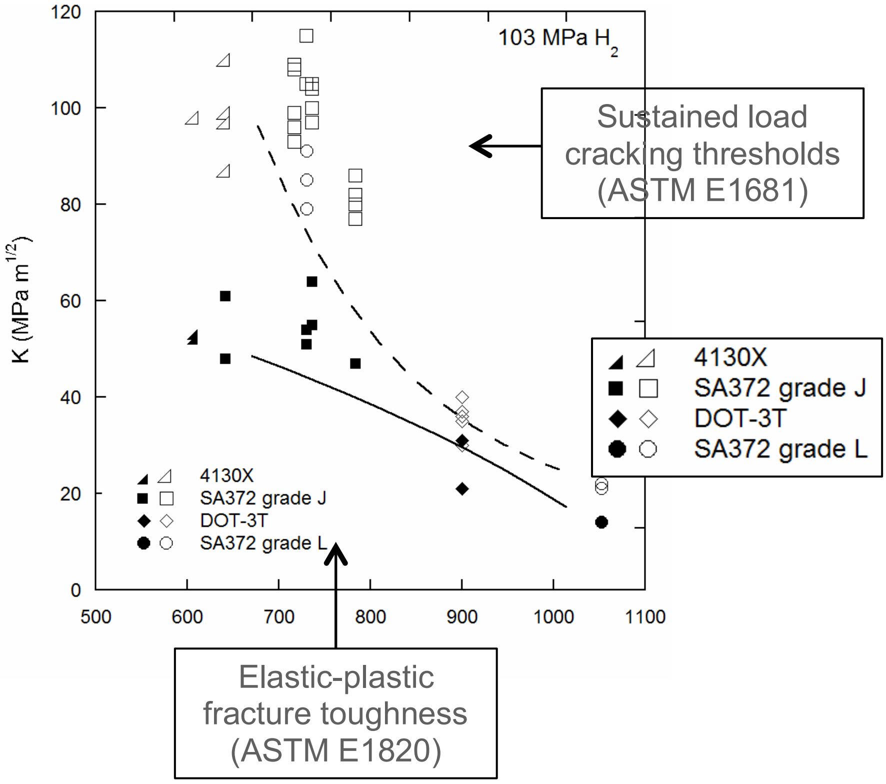

Figure 1. Comparison of fracture resistance measured by constant displacement tests (crack arrest methodology) and elastic-plastic fracture mechanics tests (crack initiation methodology).

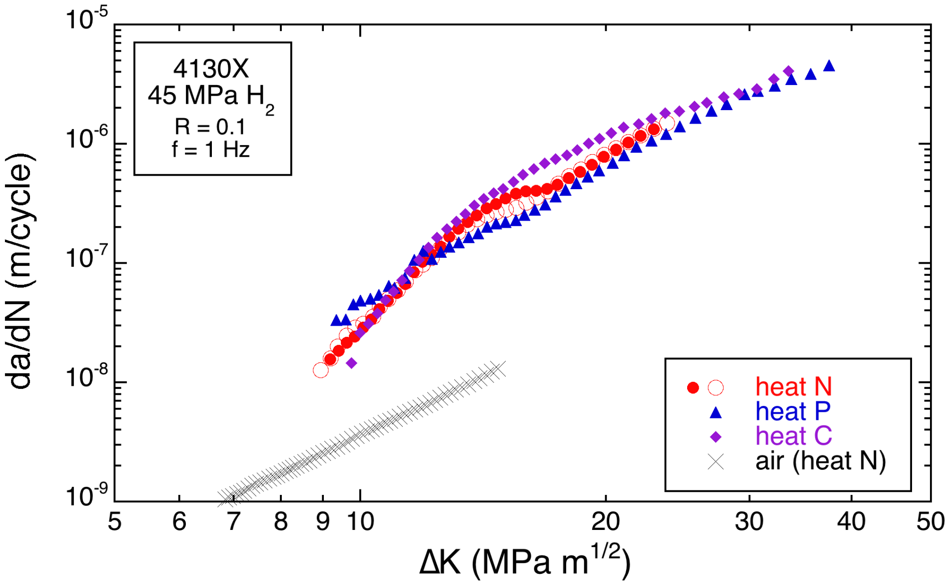

Figure 2. Fatigue crack growth curves for Cr-Mo pressure vessel steel (4130X).

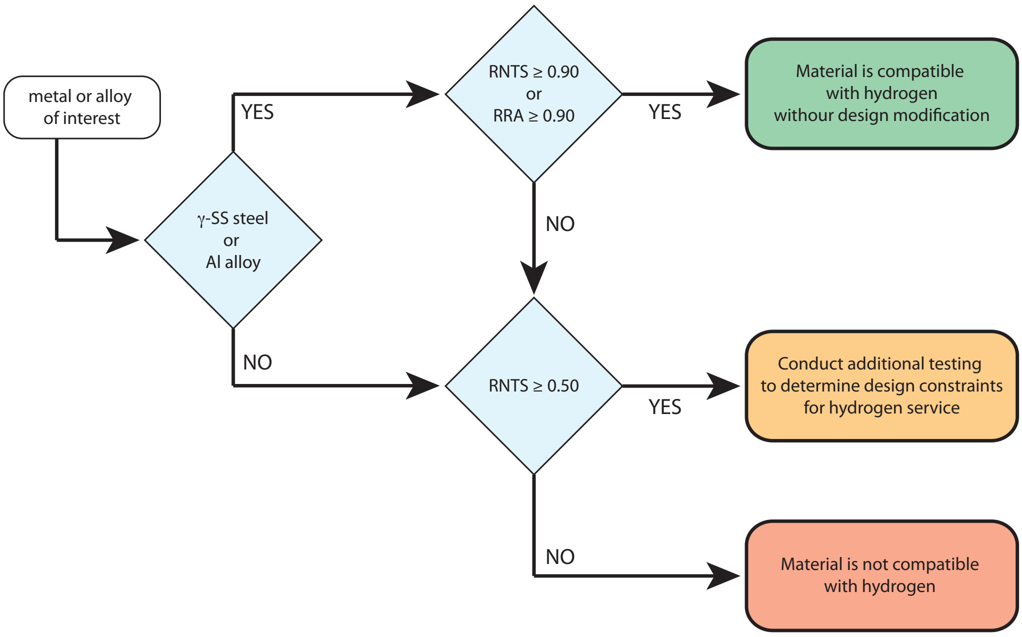

Figure 5. Logic flow diagram for safety-factor multiplier method from CSA CHMC1.

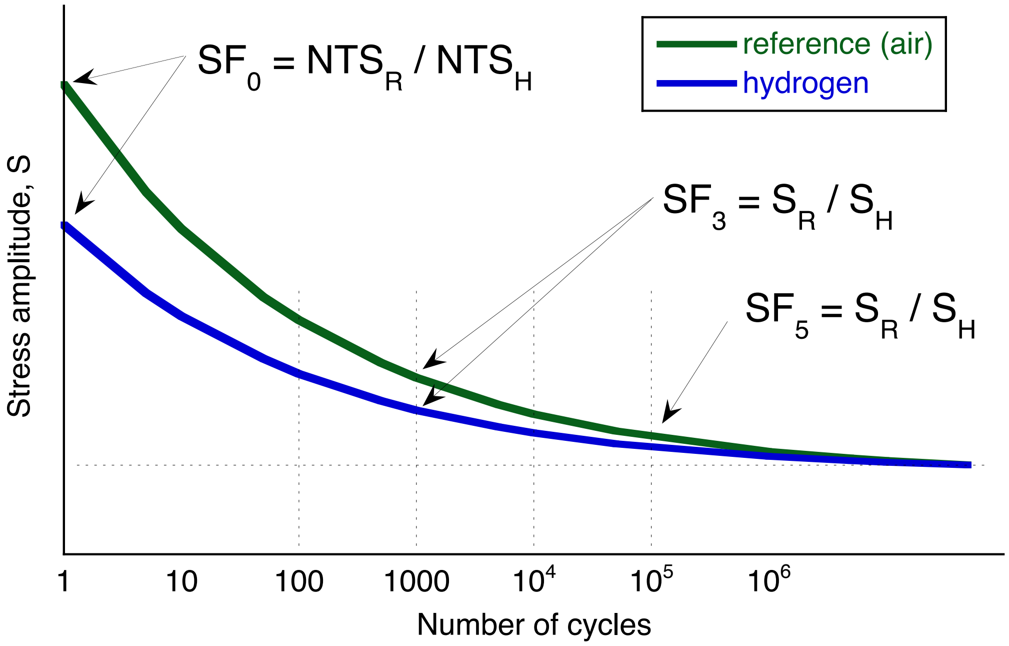

Figure 6. Schematic of safety-factor multiplier method.