Proposal from Japan (6th GTR No.13 IWG, June, 2019)

- Rationale for high-pressure hydrogen material compatibility testing

  The compressed hydrogen storage and containment systems must be compatible with gaseous hydrogen over the entire applicable pressure and temperature ranges. The slow strain rate test (SSRT) and fatigue life test are intended to demonstrate that the materials of construction show adequate compatibility for the anticipated service conditions. The SSRT evaluates whether the structural metals maintain their strength and ductility properties in gaseous hydrogen at low temperature. The fatigue life test determines that the metals display sufficient fatigue life characteristics in gaseous hydrogen at relevant applied stresses (1.25 NWP) and worst-case temperature. The test evaluation metrics are specified to assure the materials of construction are appropriate for the limited life of the vehicle fuel system for service with gaseous hydrogen. These tests are not intended to provide design data.

- Rationale for Section 1

  This section defines the material and the environmental test conditions for the testing.

  Materials definition (sections 1.1-1.3). In general, materials should be defined by a materials specification, which specifies compositional ranges and specifies minimum tensile properties (yield strength (Sy), tensile strength (Su) and tensile elongation (El)). Allowable design stresses are often determined from the specified minimum strength properties of the material, while the elongation provides a qualitative assessment of damage tolerance. Verification that the material meets the materials definition can be based on the mill certification or based on testing by (or contracted for) the user. Verification tests are performed in laboratory air.

  Welds and metallurgically-bonded materials (section 1.4). Joining practice must be controlled through a welding procedure specification (WPS), which includes specifying the same requirements as the materials definition (although the values may be different; Sy(w), Su(w) and El(w)). This requirement ensures that the properties of the joined material are known and the minimum requirements are specified. The joined structure should be evaluated in gaseous hydrogen in the same way as the base materials with test specimens extracted from the joined structure whenever possible (or a representative test piece, also defined by the WPS) to ensure that joint meets the specified requirements. The mechanical properties of a metallurgical joint depend on the welding procedure and the configuration of the test specimens extracted from the joint. The effects of hydrogen on the joint also depend on the materials, welding procedure and welding conditions.

- Rationale for Section 2

  This section defines the environmental conditions for the testing.

  Gas purity (section 2.1). Small amounts of gas impurities (especially oxygen and water) can have significant effects on properties measured in gaseous hydrogen. Oxygen (and other species) can adsorb on the specimen surfaces and prevent hydrogen from penetrating the test specimen on the time scale of the test. While the effects of impurities have not been widely studied for tensile and fatigue life tests, fatigue crack growth testing shows clear effects of oxygen content on measured fatigue crack growth rates [B.P. Somerday, P. Sofronis, K.A. Nibur, C. San Marchi, and R. Kirchheim, “Elucidating the variables affecting accelerated fatigue crack growth of steels in hydrogen gas with low oxygen concentrations”, Acta Mater 61 (2013) 6153–6170]. The test volume must be effectively purged to ensure that air is removed from the test environment, but it is generally observed that the test environment and the sampled gas are not as “clean” as the source gas. Therefore, the test gas must be measured periodically to ensure that the adequate purging processes are maintained. Verification of the quality of the test gas hall be measured at least once every 12 months, consistent with standard practice for verification of transducers in test systems. Allowance for additional impurities (relative to the source gas) are made in table 2.1, since purging can never remove all of the oxygen and water. The requirements in table 2.1 are consistent with the requirements in CSA CHMC1.

Test pressure (section 2.2). The minimum test pressure shall be 1.25xNWP to ensure that pressure effects are captured. Testing at higher pressure (>1.25NWP) can be used – for example, data from tests at 100 MPa can be used to qualify materials in a system with NWP at 70 MPa, since the test pressure must be ≥87.5 MPa. While burst testing may be performed at pressure up to 1.5xNWP and off-normal conditions could also expose materials to pressure up to 1.5xNWP, the difference in hydrogen effects between 1.25xNWP and 1.5xNWP will generally be insignificant at least with the austenitic stainless data shown in Fig. 1[H. Kobayashi, T. Yamada, H. Kobayashi, S. Matsuoka, "Criteria for selecting materials to be used for hydrogen refueling station equipment", (PVP2016-64033), Proceedings of the ASME 2016 Pressure Vessels and Piping Division Conference, Vancouver, British Columbia, Canada, 17-21 July 2016] Therefore, for consistency with the fatigue testing, the test pressure for SSRT testing is specified at 1.25xNWP.

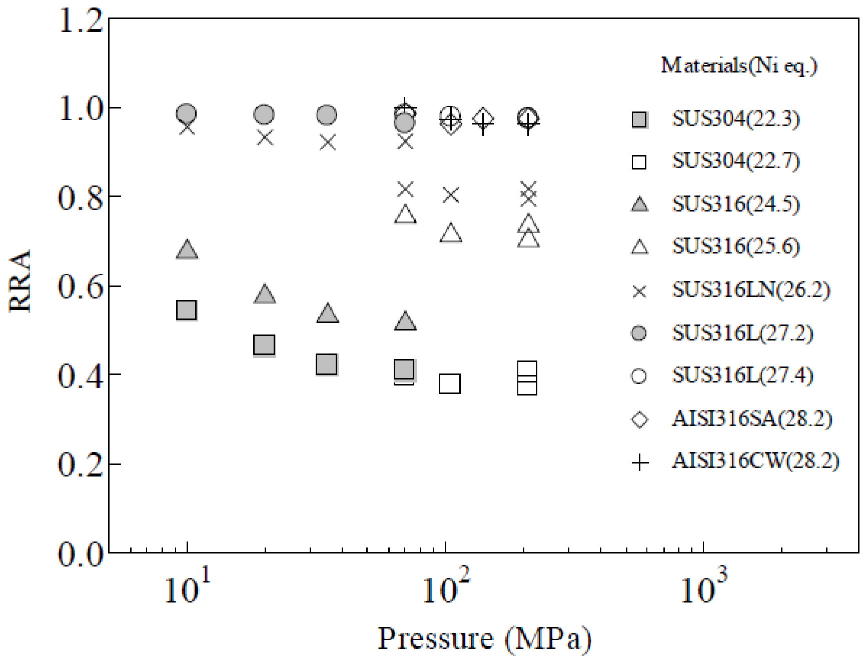

Figure 1. Effect of hydrogen pressure on RRA in SSRT

Test temperature (section 2.3). The environmental test range for the vehicle is generally considered to be 233K to 358K (-40˚C to +85˚C). While the effects of hydrogen are not sensitive to temperature for many materials, relevant experimental data shows degradation of tensile ductility at cold temperature in some steel alloys. The enhanced ductility loss of austenitic stainless steel alloys in hydrogen at low temperature (≤233K) is shown in Figure R1 and refs. [(i) S. Fukuyama, D. Sun, L. Zhang, M. Wen and K. Yokogawa, "Effect of temperature on hydrogen environment embrittlement of type 316 series austenitic stainless steels at low temperature", J. Japan Inst. Met. 67 (2003) 456-459; and (ii) L. Zhang, M. Wen, M. Imade, S. Fukuyama, K. Yokogawa, "Effect if nickel equivalent on hydrogen gas embrittlement of austenitic stainless steels based on type 316 at low temperatures", Acta Metall. 56 (2008) 3414-3421]. For austenitic stainless steels and nickel-based alloys, the SSRT temperature of 228K is recommended to capture these effects. For non-ferrous metals, room temperature is sufficient to capture ductility loss in hydrogen, while for other metals, testing at both room temperature and low temperature is recommended until the performance limiting temperature can be established. The effect of temperature on fatigue is generally improved at low temperature for austenitic stainless steels (related to increase of strength) shown in Figure 2 [NIMS, "Data sheet on fracture toughness and high-cycle fatigue properties of forged 304L", NIMS space use materials strength data sheet, No. 7 (2006)].

Fatigue life data in gaseous hydrogen at moderate pressure (10 MPa) suggest that fatigue life is limited by performance at room temperature [see data in Ref. C. San Marchi, P. Gibbs, J. Foulk, K.A. Nibur, “Fatigue life of austenitic stainless steels in hydrogen environments”, 43rd MPA Seminar, 11-12 October 2017, Stuttgart, Germany] and this trend is supported by tests at high pressure (~100 MPa).

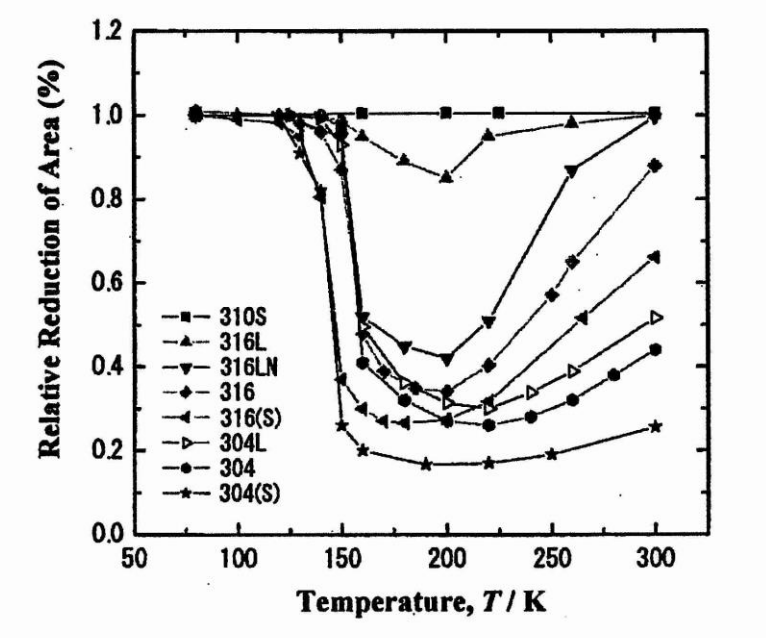

Figure R1. Slow strain rate test (SSRT) results; from: Fukuyama et al, J. Japan Inst. Met. 67 (2003) 456-459

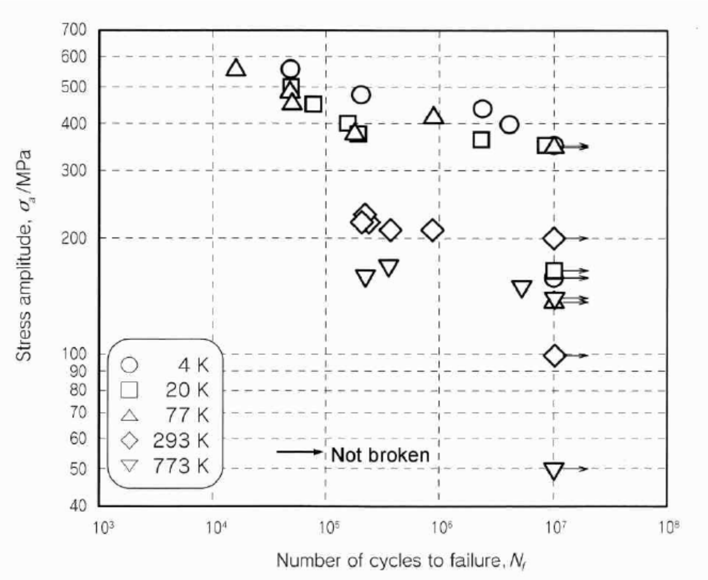

Figure R2. Fatigue life data for type 304L stainless steel tested at liquid helium (4 K). liquid hydrogen (20 K), liquid nitrogen (77 K), ambient temperature (293 K), and elevated temperature (773 K); from: NIMS spaced use materials strength data sheet no. 7 (2006).

- Rationale for Slow Strain Rate Tensile (SSRT) test (section 3.1)

The objective of the SSRT is to verify the strength and ductility properties of the material satisfy specified minimum requirements in the worst-case hydrogen environment. For austenitic stainless steels, strength properties at low temperature are generally greater than at room temperature, however, when tested in gaseous hydrogen at low temperature, the tensile strength (Su) of austenitic stainless steel can be significantly decreased relative to testing in air.

Specimen size (section 3.1.1). To ensure hydrogen penetration into the interior of the specimen, it is recommended that the diameter of the test specimen be limited to ≤8 mm. ASTM G142 recommends diameter of 6 mm, while a diameter ≤4mm is recommended in Ref. [H. Kobayashi, T. Yamada, H. Kobayashi, S. Matsuoka, "Criteria for selecting materials to be used for hydrogen refueling station equipment" (PVP2016-64033), Proceedings of the ASME 2016 Pressure Vessels and Piping Division Conference, Vancouver, British Columbia, Canada, 17-21 July 2016].

Strain Rate for SSRT (section 3.1.2). Experimental references suggest a worst-case strain rate of $<1x10^{-4}$ s^{-1} [T. Omura, K. Kobayashi, M. Miyahara, and T. Kudo, "Hydrogen embrittlement properties of stainless steels in high pressure gaseous hydrogen environment" (in Japanese), Zairyo to Kankyo/Corros. Eng. 55 (2006) 139–145]. The recommended strain rate from CSA CHMC1 is $1x10^{-5}$ s^{-1}, while a strain rate of $\leq 5x10^{-5}$ s^{-1} is recommended in Ref. [H. Kobayashi, T. Yamada, H. Kobayashi, S. Matsuoka, "Criteria for selecting materials to be used for hydrogen refueling station equipment" (PVP2016-64033), Proceedings of the ASME 2016 Pressure Vessels and Piping Division Conference, Vancouver, British Columbia, Canada, 17-21 July 2016].

Acceptance Criterion (section 3.1.3). Consistent with the intent of the SSRT, the criteria for SSRT ensure that the strength properties meet the requirements of the materials specification; generally, allowable design stresses are derived from the minimum strength properties defined by the materials specification (fatigue and other considerations may also refine allowable design stresses). Additionally, the strain hardening capacity requirement of 1.07 (Sy/Su > 0.935) establishes a minimum residual ductility for high-strength materials consistent with requirements in KHK S 0220 (standard for "Ultra-high pressure gas equipment", as well as other standards for pressurized components, such as API 5L). The material specification such as Sy and Su was decided from the tensile properties at the room temperature. However, SSRT testing temperature for some kinds of material is 228K. The yield and tensile strength measured at low temperature are higher than those measured at room temperature. Therefore, if yield and tensile strength measured at 228K were higher than Sy and Su, it does not mean that yield and tensile strength measured at room temperature meet the material specification of Sy and Su. Materials should be extended to some extent beyond the yield point. The requirement for elongation should be decided from the test data. For example, the elongation of austenitic stainless steels should be higher than 12% which is based on materials acceptance for high-pressure components in the KHKS 0220 (and consistent with other standards for the cold worked austenitic stainless steel data from ASTM A276 standard.).

- Rationale for Fatigue Life Test (section 3.2).

The objective of the fatigue life test is to verify that materials show sufficient fatigue life at high stress. The test method does not attempt to generate design data, but identifies simple fatigue life metrics based on number of cycles to failure that are conservative relative to the design life of vehicles.

Fatigue test configuration (section 3.2.1). Two fatigue test options are allowed: (i) smooth specimens cycled at load ratio of -1 (equal to the ratio of the minimum to maximum applied load and referred to as R); or (ii) notched specimens cycled at R = 0.1. The objective of the fatigue life test using smooth specimens is to show that the fatigue life in gaseous hydrogen is significantly greater than the design life requirements for the fuel system. The objective of the fatigue life test using the notched specimens is to show that the durability of the material near the fatigue limit is significantly greater than the design life requirements for the fuel system.

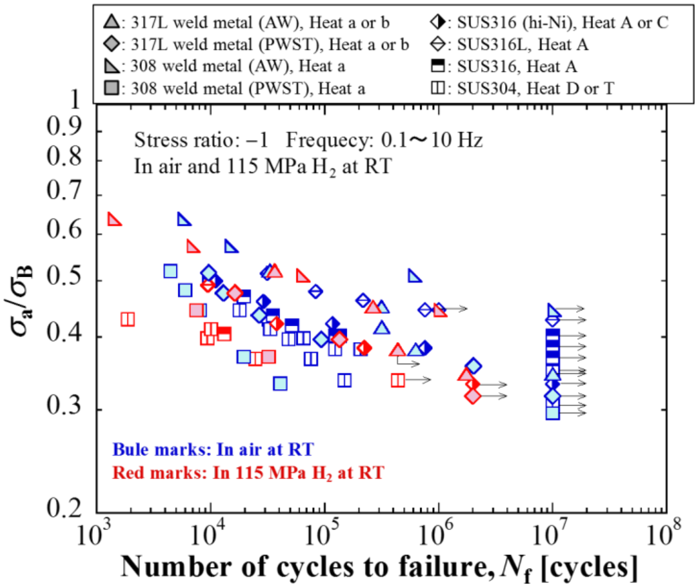

Figure R3. Example fatigue life data from smooth specimens with normalization by the tensile strength; from: M. Nakamura et al, M&M2017 Conference, 7-9 October 2017, Hokkaido, Japan.

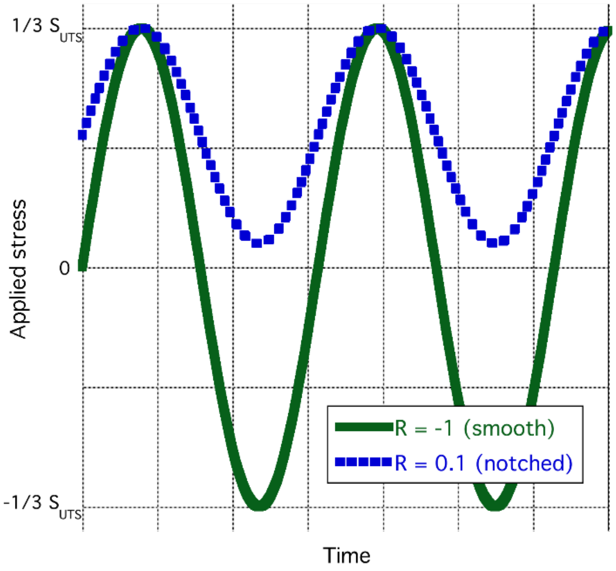

Figure R4. Schematic of stress cycles for fatigue life testing.

Definition of stress of fatigue life tests (section 3.2.2.). In both fatigue life options (smooth and notched specimen configuration), the fatigue test is conducted with maximum applied stress of 1/3 of the tensile strength of the material measured at room temperature in air (S*). For the smooth specimen configuration, the stress amplitude is equivalent to 1/3 S* and the stress range (difference between the maximum and minimum stresses) is twice this value, representing a very conservative bound on nominal stresses in a component. For the notched specimen configuration, the maximum nominal stress is also 1/3 S* and the applied stresses are tension-tension, which is consistent with nominal stresses in pressure systems. Additionally, the presence of the notch evaluates the sensitivity of the material to stress concentrations in the presence of hydrogen. Figure R3 shows the required stress cycle for both the smooth and notched configurations.

Fatigue test frequency (section 3.2.3.). Measurements in gaseous hydrogen can be sensitive to rate of testing. While testing rate effects can depend on the material being tested, frequency of 1Hz is generally accepted as an appropriate rate for materials testing.

Acceptance criteria (section 3.2.4). The acceptance criteria for fatigue life are intended to demonstrate that the fatigue life of the material at a relatively high stress significantly exceeds the design life for the vehicle application. For both specimen-loading options, three specimens must show 200,000 cycles prior to failure for the prescribed maximum applied stress of 1/3S*. No failure of all the three specimens means that a failure probability is zero and 200,000 cycles correspond to the number of cycles at the knee point for the smooth specimen of common annealed austenitic stainless steels. Tests can be terminated after 200,001 cycles if the specimen has not failed. The fatigue life test of the smooth specimen intends to identify no degradation in the fatigue limit in high-pressure hydrogen gas. To facilitate testing and reduce testing time of the notched specimens, a lesser requirement of 100,000 cycles prior to failure is acceptable; however, to ensure materials performance additional specimens are required: total of 5 specimens must be tested and all specimens must demonstrate a minimum of 100,000 cycles prior to failure. Materials that are tested in the notched configuration, but show cycles to failure between 100,000 and 200,000 cycles are acceptable, provided that all tested specimens (minimum of 5) show cycles to failure greater than 100,000 cycles. Fatigue life testing results show that a variety of stainless steels display fatigue life curves with greater cycles to failure in gaseous hydrogen than annealed type 316L austenitic stainless steels at the same stress [C. San Marchi, P. Gibbs, J. Foulk, K.A. Nibur, “Fatigue life of austenitic stainless steels in hydrogen environments”, 43rd MPA Seminar, 11-12 October 2017, Stuttgart, Germany]. When normalized by S*, these austenitic stainless steels display similar performance (~100,000 cycles to failure) for stress greater than 1/3S*, Figure R5.

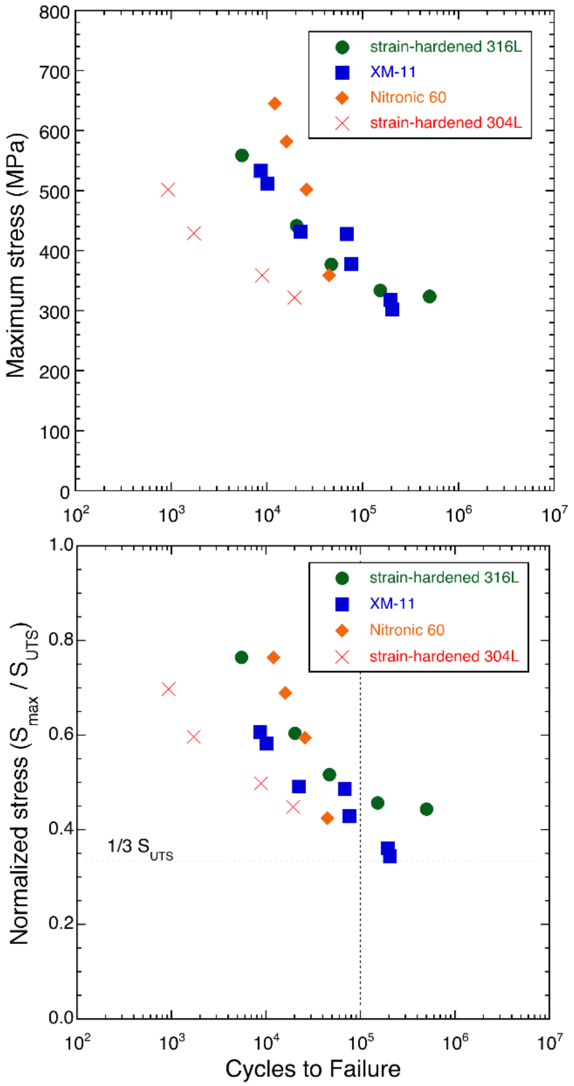

Figure R5. Example fatigue life data from notched specimens test in gaseous hydrogen at pressure of 100 MPa and room temperature without and with normalization by the tensile strength; from: C. San Marchi et al, 43rd MPA Seminary, 11-12 October 2017, Stuttgart, Germany.