

# Development of material testing equipment in high pressure gaseous hydrogen and international collaborative work of a testing method for a hydrogen society

— Toward contribution to international standardization —

Takashi IJIMA<sup>1\*</sup>, Takayuki ABE<sup>1</sup> and Hisatake ITOGA<sup>2</sup>

[Translation from *Synthesiology*, Vol.8, No.2, p.62-69 (2015)]

To commercialize fuel cell vehicles and hydrogen filling stations, and to achieve a reliable and economical “hydrogen society,” international accordance of the material usage standard for high pressure gaseous hydrogen equipment is regarded as an important issue. Therefore, a precise method to evaluate the effect of gaseous hydrogen on structural metallic materials is required to qualify the materials compatibility for high pressure gaseous hydrogen equipment. For this purpose, our research group developed testing equipment capable of such examinations as slow strain rate tensile tests, fracture toughness tests, and delayed fracture tests up to 120 MPa of gaseous hydrogen. We acquired operation expertise of the equipment and testing data of commercialized metallic materials. In particular, fracture testing methods of Cr-Mo standard steel in Japan and USA were compared in an international collaborative study between Sandia National Laboratories, Livermore and our research group. We concluded that estimating fracture toughness with a rising displacement is essential for testing methods in a high pressure gaseous hydrogen environment.

**Keywords :** hydrogen embrittlement, fracture toughness, material testing, fuel cell vehicle, hydrogen filling station

## 1 Introduction

There is a plan to commercialize fuel cell vehicles (FCV) by FY 2015 with the goals of diffusion of about 2 million FCVs that use 70 MPa high-pressure gaseous hydrogen by FY 2025 and installment of about 1,000 hydrogen filling stations.<sup>[1]</sup> In June 2014, Toyota Motor Corporation showcased an FCV scheduled for commercial sales.<sup>[2]</sup> To realize these goals, the pricing of FCV and the reduced construction cost of hydrogen filling stations are important, and the “Strategic Road Map for Hydrogen and Fuel Cell” was released to achieve a hydrogen society.<sup>[3]</sup> The high-pressure hydrogen vessel is the most expensive part of the high-pressure gaseous hydrogen equipment used in 70 MPa FCV and hydrogen filling stations. With FCV, it is called the on-board container with assumed hydrogen gas pressure of 70 MPa. It is called the pressure vessel for hydrogen stations, and the hydrogen gas pressure of 82 MPa is assumed.<sup>[4]</sup> The accumulation of material database and the establishment of evaluation technology for the effect of hydrogen on materials including pipes, valves in high-pressure gaseous hydrogen condition over 100 MPa, particularly for hydrogen embrittlement of metallic materials, are important topics in achieving a safe and economic hydrogen society. Also, harmonization of the domestic and overseas standards for materials that are used for high-pressure gaseous hydrogen equipment is expected to promote the development of low-cost equipment and parts, as well as strengthen international competitiveness of

automotive and infrastructure industries.

Due to such a background, we believe the development of an experimental equipment that allows material testing in hydrogen gas surpassing 100 MPa, the establishment of a material testing method that allows accurate evaluation of hydrogen embrittlement and accumulation of test data using such equipment, and the diffusion to and sharing of knowledge of such material test data with related industries will greatly contribute to the international standardization of the evaluation method and qualification of materials compatibility for high-pressure gaseous hydrogen equipment. In this paper, we overview the properties of metallic materials that are demanded for use in high-pressure gaseous hydrogen equipment, including the situations in Japan and overseas. Next, we discuss the material testing equipment in high-pressure gaseous hydrogen at AIST, review the material testing methods using such equipment, and describe the international comparison of the material testing methods. Then we discuss our contribution that we may make toward the international standardization of the material testing method.

## 2 Properties demanded for the metallic materials used in high-pressure gaseous hydrogen equipment

### 2.1 What is hydrogen embrittlement?

When a metallic material is exposed to hydrogen atmosphere,

1. Energy Technology Research Institute, AIST Tsukuba West, 16-1 Onogawa, Tsukuba 305-8569, Japan \* E-mail :ijima-t@aist.go.jp, 2. Research Center for Hydrogen Industrial Use and Storage, Kyushu University 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

Original manuscript received August 29, 2014, Revisions received December 2, 2014, Accepted December 4, 2014

the hydrogen atoms diffuse in the metal lattice, and the material property of the metal declines. This is called hydrogen embrittlement. Specifically, when tensile tests for metallic materials are conducted in high-pressure gaseous hydrogen environment, or when tensile tests for metallic materials that are hydrogen-charged by exposure in testing chambers of hydrogen environment are conducted in atmosphere (in inert gas), the strength properties such as yield stress and tensile strength or the ductilities such as breaking elongation and reduction of area are reduced. Due to the word “embrittlement,” it may present the impression that “hydrogen embrittlement” is a breakage within the elastic range of metallic materials where no elongation takes place. Of course, some materials may break within the elastic range in the hydrogen atmosphere, but most materials show plastic deformation. Therefore, Murakami *et al.* described hydrogen embrittlement as “ductile fracture that is accompanied by microscopic plastic deformation.”<sup>[5]</sup>

Up to the present, so many research works have been performed for the effect of hydrogen on the strengths and ductilities of various materials. As a result, it became clear that while there is no metallic material that does not show some degree of hydrogen embrittlement, the materials can be roughly categorized as follows: (1) materials that cannot be used due to large effects of hydrogen embrittlement such as fractures occurring in the elastic range, (2) materials that may be used in certain conditions although ductility such as elongation and reduction of area may decrease due to the effect of hydrogen embrittlement, and (3) materials that receive little effect of hydrogen embrittlement under limited conditions. The materials categorized in (3) include austenitic stainless steel with high nickel content and aluminum alloys. One of the materials categorized in (2) is low-alloy steel. Low-alloy steel is a material used widely as structural material in various fields such as chemical plants, and it is characterized by having higher material strength and being less expensive than austenitic stainless steel.

## **2.2 Standards for qualifying the materials compatibility of high-pressure gaseous hydrogen equipment**

Determination and review of the standards for FCV on-board containers and hydrogen station vessels are being conducted around the world. Characteristically, since the hydrogen filling stations are installed domestically compared to FCVs that will be distributed widely around the world, the domestic considerations are reflected strongly in hydrogen filling stations.

For on-board containers, it is designated by the “Exemplified Standard for Container Inspections, etc.” (2013), which is the technical standard set by the Safety Regulations for Containers of the High-Pressure Gas Safety Law in Japan, that the maximum fill pressure of the compressed hydrogen FCV on-board container shall be 70 MPa, and the materials

that can be used for such containers are austenitic stainless steel (SUS316L) containing specific nickel content (nickel equivalent) and aluminum alloys (6061-T6).<sup>[6]</sup> In the USA, the 6061 aluminum alloys and high nickel SUS316 are designated as materials that can be used for on-board containers for 70 MPa compressed hydrogen FCV in the annex of SAE J2579 (2009) of the Society of Automotive Engineers (SAE). If any other materials are to be used, they must be subject to designated material tests: (1) slow strain rate tensile tests in hydrogen or of hydrogen-charged material, (2) fatigue tests in gaseous hydrogen, and (3) crack growth tests in gaseous hydrogen condition.<sup>[7]</sup> The standard for 70 MPa on-board containers in Europe used to follow the ISO/TS 15869 (2009) “Gaseous Hydrogen Blends & Hydrogen Fuels: Land Vehicle Fuel Tanks.” However, as the review of the global standard was started by the United Nations, as will be explained later, the review by the ISO Technical Committee (TC197/WG18) has started from 2013.<sup>[8]</sup> In the World Forum for Harmonization of Vehicle Regulations (WP29) of the United Nations Economic Commission for Europe (UNECE), the need to promote international mutual recognition of global standards with international harmonization was recognized to diffuse automobiles with excellent safety and environmental performance. Therefore, the creation of the “Global Technical Regulation for Hydrogen and Fuel Cell Vehicles (HFCV global technical regulations)” was started from 2007, and gtr Phase 1 was adopted in 2013. In accordance to this, the items of the Safety Regulations for Containers were revised in June 2014 in Japan.<sup>[9]</sup> However, the deliberation for the materials compatibility of on-board containers will be continued in gtr Phase 2.

For the vessels, Japan designates stainless steel (SUS316, SUS316L) as the compatible material for the compressed hydrogen vessels and the pipes through which compressed hydrogen passes, and designates the chemical composition (nickel equivalent) at normal operation pressure (82 MPa) and normal operation temperature (−40~250 °C), in the Exemplified Standard for Security Regulation for General High-Pressure Gas Safety Regulations (2014) of the High-Pressure Gas Safety Laws. It also allows the steel for machine structural use (SCM435) to be used for vessels at normal operation pressure of 40 MPa or less.<sup>[10]</sup> In the USA, alloy steels such as SA-372 and SA-723, stainless steels such as SA-336 and Gr.F316, and aluminum alloys such as 6061-T6 are indicated as compatible materials in high-pressure gaseous hydrogen up to 103 MPa, according to Article KD-10 in Division 3: Special Requirement for Vessels in Hydrogen Service (2010) of the American Society of Mechanical Engineers (ASME). For actual use, it requires evaluations of the following: (1) plane strain fracture toughness value  $K_{IC}$  by rising load and rising displacement in atmosphere (crack-initiation threshold test in accordance to ASTM E399 or E1820), (2) fracture toughness value  $K_{IH}$  by constant load or constant displacement in gaseous hydrogen (crack-arrest

threshold test in accordance to ASTM E1681), and (3) crack growth rate  $da/dN$  in gaseous hydrogen.<sup>[11]-[15]</sup> In Europe, high-pressure gas vessels are designated in the European Norm EN13445 (1999, Unfired Pressure Vessels) under PED97/23/EU (1997, Pressure Equipment Directive) that is equivalent to the High-Pressure Gas Safety Laws of Japan, but the evaluation of hydrogen embrittlement of materials follow ISO 11114-4.<sup>[16][17]</sup> The ISO 11114-4 (2005) requires the hydrogen embrittlement evaluation testing method when Cr-Mo alloy steel with tensile strength up to 950 MPa is used as the material for the gaseous hydrogen pressure vessel with normal operation pressure of 30 MPa or less as follows: (1) a rupture test where a crack is produced by increasing the pressure of gaseous hydrogen applied to one side of a discoid sample, (2) a crack-initiation threshold test where the load is increased in steps in gaseous hydrogen of 15 MPa, and (3) a crack-arrest threshold test at constant displacement or constant load in gaseous hydrogen of 15 MPa. However, since this test pressure in gaseous hydrogen is insufficient for the material testing method of hydrogen station vessels for which the normal operation pressure is 82 MPa, review is being continued for the standard of hydrogen station vessels at the ISO Technical Committee (TC197/WG15).

As it can be seen, the material compatibility standards for high-pressure gaseous hydrogen equipment such as FCV on-board containers and hydrogen station vessels are in the process of being established worldwide. Since SUS316L stainless steel and A6061aluminum alloys are expensive, it is necessary to increase the choice of materials that can be used for the vessels and pipes of high-pressure gaseous hydrogen equipment to achieve cost reduction that allows the diffusion of FCVs and hydrogen filling stations. Therefore, for low-alloy steel that has potential to be used in certain conditions although it may be affected by hydrogen embrittlement, it is necessary to consider the material evaluation technologies for fatigue property and fracture toughness in high-pressure gaseous hydrogen condition from the perspective of finite life design, and to establish a method for accurately evaluating the material behavior in high-pressure gaseous hydrogen. We aim to contribute to the international standardization of the testing method of materials compatibility in high-pressure gaseous hydrogen equipment, by developing material testing equipment for high-pressure gaseous hydrogen of 100 MPa or more, obtaining material test data using such equipment, investigating the efficacy of the testing method through accurate evaluation of hydrogen embrittlement phenomena and understanding the embrittlement mechanism, providing and diffusing this knowledge to the industry through creation of a database of the material evaluation results, and approaching the related organizations involved in standard formulation (Fig. 1).

### 3 Development of the material testing equipment for high-pressure gaseous hydrogen

Globally, there are not many research institutes that possess material testing equipment for gaseous hydrogen pressure of over 100 MPa. In Japan, as of October 2014, Kyushu University (120MPa), Energy Technology Research Institute, AIST (120 MPa), and a few private companies have materials testing equipment for 100~120 MPa. In USA, the Sandia National Laboratories (140 MPa); in Europe, The Welding Institute of Britain (100 MPa); and in Asia, China and Korea each has material testing equipment for 120 MPa.

In our research group, we accumulated the operational know-how by gradually increasing the pressure of the gaseous hydrogen used from 1 MPa, 40 MPa, 70 MPa, and then to 120 MPa. Based on the know-how, we further improved the safety for experiments using high-pressure gaseous hydrogen in 2011, through simplification of the system by integration of high-pressure gaseous hydrogen gas supply systems, remote control using PCs, introduction of monitoring cameras and an emergency shut-down system, and automation of the testing area by mutual isolation of individual testing devices using protective shields. The fatigue testing device, slow strain rate tensile testing device, and exposure chambers are connected in line to the 120 MPa compressor. The operations of the compressor and each valve are done by remote control using the PC mouse from the control room shown in Fig. 2, and hydrogen gas cannot be supplied all at once to the devices. As shown in Fig. 3, a protective shield is installed in the explosion-proof area surrounded by fireproof walls to isolate the individual testing devices. Moreover, high-pressure gaseous hydrogen is sealed in the test vessel, and after the gaseous hydrogen is introduced into the test vessel, the gas inside the pipes and the compressor is released and decompressed to atmospheric pressure. It is designed so that even if the gaseous hydrogen leaks from the test vessel during the material test, the hydrogen concentration in the

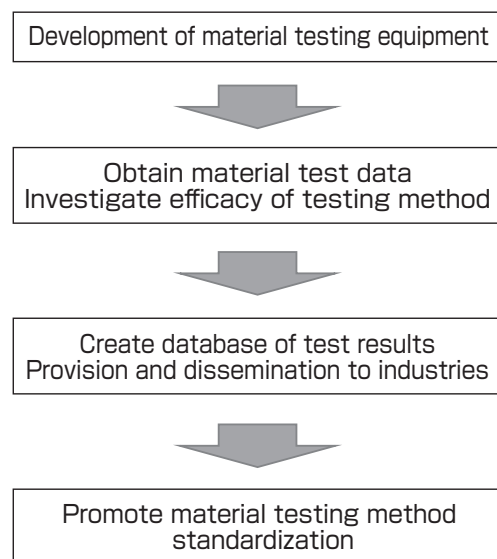


Fig. 1 Work toward contribution to international standardization

laboratory space will be much lower than the explosion limit.

The shapes of the main testing devices are shown in Fig. 4. The fatigue testing device of Fig. 4(a) has the signal output port and internal load cell using strain gauge that functions stably in hydrogen. It is capable of conducting fatigue tests at load cycle 1 Hz, crack growth tests, and fracture toughness tests by a rising displacement method, in gaseous hydrogen atmosphere at normal operation pressure of 115 MPa and room temperature. The slow strain rate tensile testing device shown in Fig. 4(b) is capable of tensile tests at a rate of  $1 \times 10^{-5} \text{S}^{-1}$  in gaseous hydrogen atmosphere at normal operation pressure of 70 MPa and room temperature. The exposure chamber of Fig. 4(c) has a signal output port, and is capable of hydrogen charging materials at operation pressure of 115 MPa and temperatures from room to 350 °C, as well as fracture toughness tests (delayed fracture tests) by a constant displacement method.

#### 4 International comparison of fracture toughness



Fig. 2 PC control system installed in the control room

#### testing methods

##### 4.1 Consideration of fracture toughness evaluation method for finite life design

In the vessels and pipes to which stress is repeatedly applied due to the cycle of filling and releasing of gaseous hydrogen, in order to attempt finite life design based on the leak-before-break (LBB) thinking and supposition of fracture critical crack length, it is important to calculate the fracture toughness value of the materials in high-pressure gaseous hydrogen environment. As mentioned earlier, in the ASME Article KD-10 in Division 3, which is one of the testing standards for high-pressure gas vessel materials, the execution of fracture toughness tests by the constant displacement method or constant load method in gaseous hydrogen are required.<sup>[11]</sup>

However, the Sandia National Laboratories recently conducted research on ferrite steel with relatively low

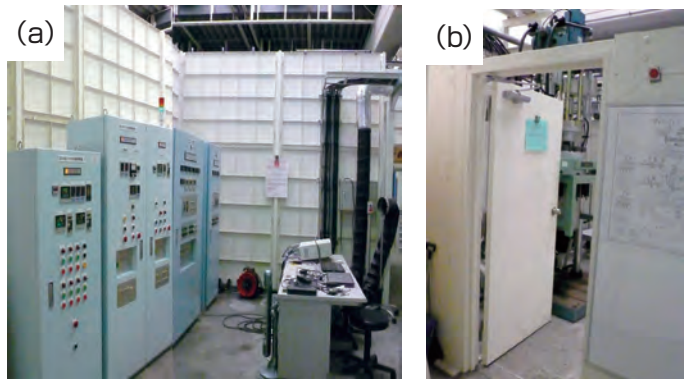


Fig. 3 (a) Fireproof wall and control panel installed in non-explosion-proof area and (b) protective wall isolating the individual testing devices

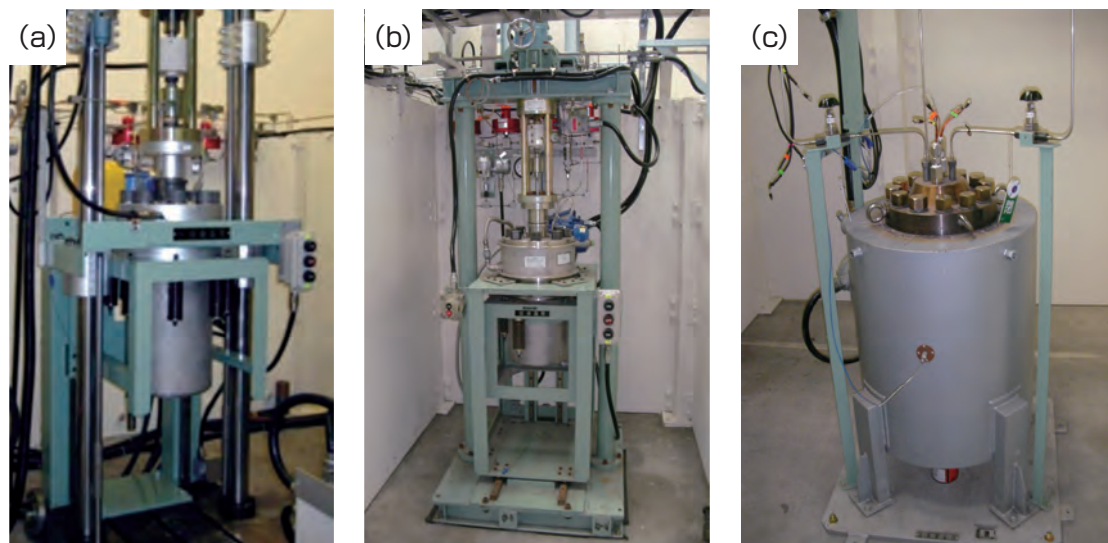
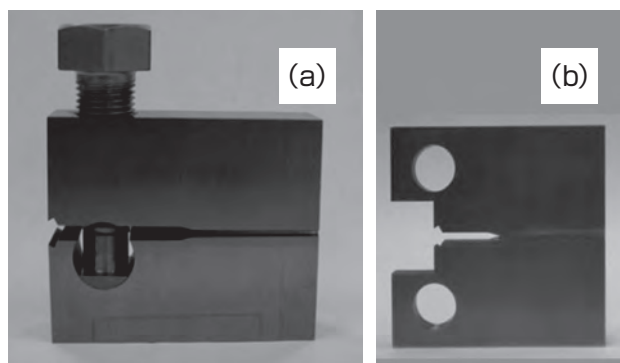


Fig. 4 (a) Fatigue testing device: normal operation pressure of 115 MPa, room temperature. (b) Slow strain rate tensile testing device: normal operation pressure of 70 MPa, room temperature. (c) Exposure testing chamber: normal operation pressure of 115 MPa, room temperature ~ 350 °C

**Table 1. Material properties and compositions of SCM 435 and SA-372 Grade J**

	Yield stress	Tensile strength (MPa)	C	Cr	Mo	Mn	Si	P	S	Fe (mass%)
SCM 435	700	828	0.38	1.1	0.23	0.79	0.22	0.006	0.004	Bal
SA-372 Grade J	762	889	0.49	0.99	0.18	0.93	0.28	0.008	0.004	Bal

strength and high toughness with tensile strength of 950 MPa or less that is expected to be used in high-pressure gaseous hydrogen equipment. As a result of comparing the fracture toughness value calculated by the constant displacement method ( $K_{THa}$ , crack-arrest threshold) and the fracture toughness value calculated by the rising displacement method ( $K_{JH}$ , crack-initiation threshold) in 103 MPa high-pressure gaseous hydrogen atmosphere, the  $K_{JH}$  value was lower than the  $K_{THa}$  value, and as a fracture resistance value,  $K_{JH}$  was shown to be a conservative value.<sup>[18][19]</sup> The constant displacement method is a testing method in accordance with ASTM E1681, where the bolt-load compact specimen (Fig. 5(a)), which is pre-cracked in advance, is used, the crack opening displacement is held constant by tightening the bolt, the load is applied to the tip of the crack, and the load is maintained until the crack grows and stops under certain conditions.<sup>[15]</sup> This is also called the delayed fracture test. At the Sandia National Laboratories, the fracture toughness value was calculated from the length of the crack that finally stopped after tightening the bolt in inert gas conditions and then maintaining the specimen to a maximum of 3,800 hours in high-pressure gaseous hydrogen. Since the fracture toughness value of the crack arrest is calculated, it can be considered as a crack growth stop test. The rising displacement method is a material test where the load is applied continuously to the pre-cracked compact specimen (Fig. 5(b)) in the high-pressure gaseous hydrogen atmosphere, so the crack opening displacement will increase, and this method is in accordance with ASTM E1820.<sup>[13]</sup> At the Sandia National Laboratories, the crack opening displacement was measured with the linear variable differential transformer (LVDT) and the crack length was measured by the direct-current potential difference (DCPD) method, and the



**Fig. 5 (a) Bolt-loaded compact specimen and (b) compact specimen**

fracture toughness value of the crack initiation under the continuously rising displacement is calculated from the load, opening displacement, and crack length. Therefore, this can be considered the crack growth starting test.

#### **4.2 Fracture toughness evaluation using the unloading elastic compliance method**

In our research group, the rising displacement test was conducted using the unloading elastic compliance method that is another crack length measurement in accordance with ASTM E1820, and we attempted direct comparison with the measurement data obtained at the Sandia National Laboratories.<sup>[20]</sup> The rising displacement test using the unloading elastic compliance method is a method of calculating the fracture toughness value of the crack initiation, as the crack opening displacement of the pre-cracked compact specimen (Fig. 5(b)) is increased at a certain rate, part of the load is removed at arbitrary crack opening displacement, and then the crack length from the relationship of the crack opening displacement and load at that moment is calculated. For the experiment, SCM435 (Japan standard) and SA-372 Grade J (American standard; supplied by Sandia National Laboratories) were used. These are standard materials of the Cr-Mo alloy steel and are expected to reduce the cost of high-pressure gaseous hydrogen equipment in the future. Table 1 shows the material properties and composition of SCM435 and SA372 Grade J. The outline of the testing conditions by the unloading elastic compliance method is presented in Reference [20].

#### **4.3 Direct comparison of Japanese and American data for fracture toughness evaluation**

Figure 6 shows the load vs. crack opening displacement ( $P$ - $COD$ ) curve calculated using the unloading compliance method in 115 MPa gaseous hydrogen for SCM435. The relationship between the  $J$  integral value and crack growth length ( $R$  curve) was calculated, and the fracture toughness value ( $J_{Ic}$ ) of crack-initiation was determined. Using the relation equation between  $J$  and  $K$  described in ASTM E1820 shown below, the stress intensity factor ( $K_{JIC,H}$ ) of the minimum limit of crack-initiation was derived. Here, Young's modulus was  $E = 206$  GPa and Poisson ratio was  $\nu = 0.3$ .

$$K_F = \sqrt{\frac{EJ_F}{1 - \nu^2}}$$

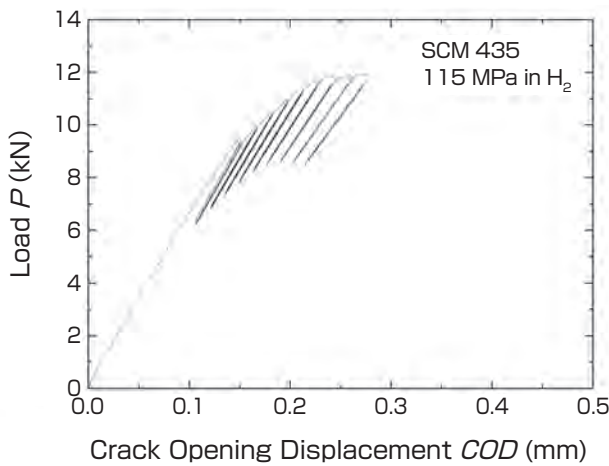
The fracture toughness value of SCM435 obtained by this

**Table 2. Fracture toughness of SCM435 and SA-372 Grade J<sup>[20]</sup>**

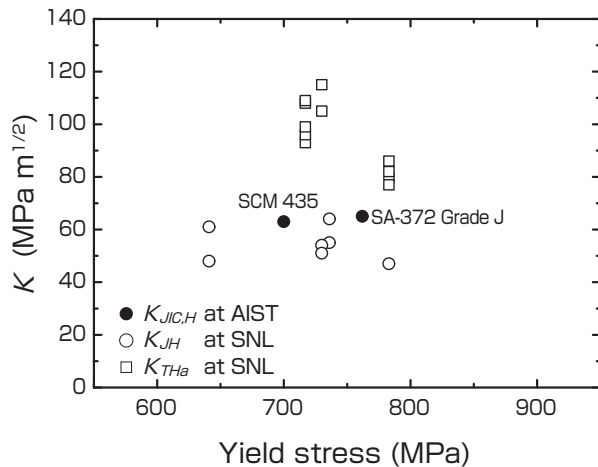
	Yield stress $\sigma_{ys}$ (MPa)	115 MPa in H <sub>2</sub> $K_{JIC,H}$ (MPa m <sup>1/2</sup> )
SCM 435	700	63
SA-372 Grade J	762	66 ( $K_{Q,H}$ )

experiment was  $K_{JIC,H} = 63 \text{ MPa m}^{1/2}$  in 115 MPa gaseous hydrogen. The fracture toughness value of SA-372 Grade J was  $K_{Q,H} = 66 \text{ MPa m}^{1/2}$  in 115 MPa gaseous hydrogen.<sup>[20]</sup> The fracture toughness values of SCM435 and SA-372 Grade J in 115 MPa gaseous hydrogen are shown in Table 2.

Figure 7 shows the relationship between the material strength and fracture toughness values in high-pressure gaseous hydrogen (103 MPa) obtained by the constant displacement method ( $K_{THa}$ ) and the continuously rising displacement



**Fig. 6 P-COD curve of SCM435 by the unloading elastic compliance method**



**Fig. 7 Relationship between yield stress and fracture toughness of Cr-Mo low-alloy steel<sup>[18][20]</sup>**

method ( $K_{JH}$ ) at the Sandia National Laboratories,<sup>[18]</sup> and the fracture toughness value ( $K_{JIC,H}$ ) in high-pressure gaseous hydrogen (115 MPa) obtained by the rising displacement method using the unloading elastic compliance method. It can be seen that the fracture toughness value  $K_{JIC,H}$  obtained by the unloading elastic compliance method, one of the rising displacement methods, showed almost equivalent values as  $K_{JH}$  obtained by the continuously rising displacement method at the Sandia National Laboratories, and was lower than  $K_{THa}$  obtained by the constant displacement method.

This indicates that although the detailed measurement conditions such as the displacement rate, load-unloading process, hydrogen purity, and pre-crack formations, as well as the form of the testing device and the measurement know-how such as hydrogen replacement procedures may be different, there is no major difference in the fracture toughness evaluation results by the rising displacement method, and that this method possesses universality as an evaluation method. Also, since the  $K_{JH}$  and  $K_{JIC,H}$  calculated by the rising displacement method were lower than the  $K_{THa}$  calculated by the constant displacement method, the fracture toughness value obtained by the rising displacement method is a conservative value, and it can be considered an effective method for quantitative evaluation of the metallic materials in high-pressure gaseous hydrogen conditions.

## 5 Summary

To establish a testing method of the hydrogen effect on the metallic materials used in high-pressure gaseous hydrogen, our research group developed a set of material testing devices that allows tensile tests, fracture toughness tests, and delayed fracture tests in high-pressure gaseous hydrogen up to normal operation pressure of 115 MPa. Using such testing devices we gathered data for materials in high-pressure gaseous hydrogen for general-use metallic materials to increase the choice of materials that can be used for the vessels and pipes of high-pressure gaseous hydrogen equipment. Particularly, with the cooperation of the Sandia National Laboratories, we conducted international comparison of the fracture toughness testing method for the standard material of Japan and USA for Cr-Mo low alloy steel that is expected to contribute to reducing the cost of high-pressure gaseous hydrogen equipment. As a result, it became clear that the fracture toughness test using the rising displacement method in high-pressure gaseous hydrogen was effective as a material testing method that allows quantitative evaluation of hydrogen embrittlement of general-use metallic materials. In the future, by accumulating data of the effects of various testing conditions, particularly of hydrogen gas pressure and displacement rate, we can review the effectiveness of the fracture toughness test by the rising displacement method in high-pressure gaseous hydrogen. We also plan to consider whether we can contribute to the international

standardization of the testing method for materials to be used in high-pressure gas equipment, through collaboration with related research institutes including the Sandia National Laboratories.

## Acknowledgement

This work was partially conducted as the “Japan-US cooperation project for research and standardization of clean energy technologies” of the Ministry of Economy, Trade and Industry. I express my gratitude to Dr. Bai An, Dr. Zheng Ming Sun, and Shuhei Nakamichi of the Hydrogen Industrial Use and Storage Group, Energy Technology Research Institute, AIST, for their support of this work. I also express my gratitude to Prof. Saburo Matsuoka and Prof. Nobuhiro Kuriyama of the Kyushu University for their advice for the high-pressure gaseous hydrogen equipment and the effect of hydrogen on material strength properties.

## References

- [1] Fuel Cell Commercialization Conference of Japan (Eng. v. 2010-07): Commercialization Scenario 2010 for FCVs and H<sub>2</sub> Stations) (March 2010), [http://fccj.jp/pdf/22\\_cse.pdf](http://fccj.jp/pdf/22_cse.pdf), 2014-07-09.
- [2] Toyota Motor Corporation (2014-06-25): Toyota Jidosha, sedan taipu no nenryo denchi jidosha o, Nihon de 2014 nendonai ni 700 man yen teido no kakaku de hanbai kaishi (Toyota will start sales of a sedan type fuel cell vehicle at a price of about 7 million yen during FY 2014 in Japan), News release, <http://newsroom.toyota.co.jp/jp/detail/3274916/>, 2014-07-09 (in Japanese).
- [3] Ministry of Economy, Trade and Industry (2014-06-24): METI has compiled a Strategic Road Map for Hydrogen and Fuel Cells, News release, [http://www.meti.go.jp/english/press/2014/0624\\_04.html](http://www.meti.go.jp/english/press/2014/0624_04.html), 2014-07-06.
- [4] Ministry of Economy, Trade and Industry: Article 7.3of the General High Pressure Gas Safety Ordinance and Article 7.3 of the Industrial Complex Safety Ordinance (in Japanese).
- [5] Y. Murakami, S. Matsuoka, Y. Kondo and S. Nishimura: *Suiso Zeika Mekanizumu To Suiso Kiki Kyodo Sekkei No Kangaekata* (The Mechanism of Hydrogen Embrittlement and Approach to Strength Design of Hydrogen Equipment), Yokendo, Tokyo (2012) (in Japanese).
- [6] The High Pressure Gas Safety Institute of Japan: “Yoki hoan kisoku no seino kijun no unyo ni tsuite (Operation of performance standards of Safety Regulations for Containers)” and “70 MPa asshuku suisu jidosha nenryo sochiyo yoki no gijutsu kijun KHK S0128 (2010) (Technological standard for compressed hydrogen containers for vehicle fuel device with maximum fuelling pressure of 70MPa KHK S0128 (2010))”, *Yoki Hoan Kisoku Kankei Reiji Kijunshu Kaiteiban* (Exemplified Standards Container Safety Ordinance, Revised Edition), The High Pressure Gas Safety Institute of Japan (2013) (in Japanese).
- [7] SAE International (2013-03-28): SAE J2579, Standard for Fuel Systems in Fuel Cell and Other Hydrogen Vehicles, [http://standards.sae.org/j2579\\_201303/](http://standards.sae.org/j2579_201303/), 2014-10-14.
- [8] The High Pressure Gas Safety Institute of Japan: *Heisei 22 Nendo Keizai Sangyosho Itaku Nenryo Denchi Shisutemu Fukuyuo Gijutsu Kijun Chosa Hokokusho* (Survey Report of the Technological Standard for the Diffusion of Fuel Cell Systems Commissioned by METI in FY 2010), The High Pressure Gas Safety Institute of Japan (2011) (in Japanese).
- [9] Ministry of Economy, Trade and Industry (2014-05-30): New Measure for Promoting Dissemination of Fuel Cell Vehicles – METI to revise the technical standards for compressed hydrogen storage containers for vehicle fuel systems to harmonize with gtr on Hydrogen and Fuel Cell Vehicles established by the UNECE – , [http://www.meti.go.jp/english/press/2014/0530\\_02.html](http://www.meti.go.jp/english/press/2014/0530_02.html), 2014-06-17.
- [10] The High Pressure Gas Safety Institute of Japan (2014-05): Koatsu gasu hoan horei kankei reiji kijun shiryosho dai 6 ji kaiteiban (Heisei 25 nen 3 gatsu 22 nichi hakko) shinkyu taishohyo [Comparison table of old and new exemplified standards, Reference material for exemplified standards for High Pressure Gas Safety Act, 6th revised edition (issued March 22, 2013)], [https://www.khk.or.jp/publications\\_library/publications/dl/kouatsu\\_reiji\\_sinkyuu.pdf](https://www.khk.or.jp/publications_library/publications/dl/kouatsu_reiji_sinkyuu.pdf), 2014-10-16 (in Japanese).
- [11] 2010 ASME BPVC Section VIII - Division 3, Article KD-10, Special Requirements for Vessels in High-Pressure Gaseous Hydrogen Transport and Storage Service, ASME, New York, (2010).
- [12] ASTM E 399-09, Standard Test Method for Linear-Elastic Plane-Strain Fracture Toughness  $K_{IC}$  of Metallic Material, ASTM International, West Conshohocken, PA (2009).
- [13] ASTM E 1820-09, Standard Test method for Measurement of Fracture Toughness, ASTM International, West Conshohocken, PA (2009).
- [14] M. D. Rana, G. B. Rawls, J. R. Sims and E. Uptis: Technical basis and application of new rules on fracture control of high pressure hydrogen vessel in ASME Section VIII, Division 3 code, *Proc. ASME 2007 PVP Conference*, PVP2007-26023 (2008).
- [15] ASTM E 1681-03, Standard Test Method for Determining Threshold Stress Intensity Factor for Environment-Assisted Cracking of Metallic Materials, ASTM International, West Conshohocken, PA (2013).
- [16] The High Pressure Gas Safety Institute of Japan: *Heisei 23 Nendo Keizaisangyosho Itaku Sekiyuseiseigyo Hoan Taisaku Jigyō (Kaigai Ni Okeru Gijutsu Kijun Ni Kansuru Chosa (Koatsu Gasu Setsubi Ni Kansuru Obei No Sekkei Kijun No Chosa)) Hokokusho* [Report of Safety Measure Project for Oil Refining Industry Commissioned by METI in FY 2011 (Survey on Overseas Technological Standards (Survey on European and American Design Standards and Maintenance Standards of High Pressure Gas Facilities))], The High Pressure Gas Safety Institute of Japan (2012) (in Japanese).
- [17] ISO 11114-4, Transportable gas cylinders - Compatibility of cylinder and valve materials with gas contents - Part 4: Test methods for selecting metallic materials resistant to hydrogen embrittlement, (2005).
- [18] K. A. Nibur, B. P. Somerday, C. San Marchi, J. W. Foulk, III, M. Dadfarnia, P. Sofronis and G. A. Hayden: Measurement and interpretation of threshold stress intensity factors for steels in high-pressure hydrogen gas, *Sandia Report*, SAND2010-4633, Sandia National Laboratories, Livermore, CA. (2010).
- [19] K. A. Nibur, B. P. Somerday, C. San Marchi, J. W. Foulk, III, M. Dadfarnia and P. Sofronis: The relationship between crack-tip strain and subcritical cracking threshold for steels in high-pressure hydrogen gas, *Metall. Mat. Trans., A*, 44A, 248-269 (2013).
- [20] T. Iijima, H. Itoga, B. An, C. San Marchi and B. P. Somerday: Measurement of fracture properties for ferritic steel in high-pressure hydrogen gas, *Proc. ASME 2014 PVP Conference*, PVP2014-28815 (2014).

---

## Authors

### Takashi IJIMA

Completed the doctorate courses at the Department of Metallurgy, Materials Science and Materials Processing, Graduate School of Engineering, Tohoku University in 1988. Doctor of Engineering. Joined the Tohoku National Industrial Research Institute, Agency of Industrial Science and Technology in 1993. Visiting researcher at the Max Plank Institut für Metallforschung in 1997-1998. After reorganization to AIST in 2001, worked at the Smart Structure Research Center, Research Institute of Instrumental Frontier, and Research Center for Hydrogen Industrial Use and Storage. Group Leader, Hydrogen Industrial Use and Storage Group, Energy Technology Research Institute, AIST from 2013. Visiting Professor, Tokyo University of Science (Collaborative Graduate School) and Visiting Professor, Kyushu University. In this paper, was in charge of organizing the data and writing up the paper.



### Takayuki ABE

Engaged in the research of metal fatigue fracture at the National Research Institute for Metals (NRIM) (currently National Institute for Materials Science (NIMS)) from 1970 to 2009. Obtained Doctor of Engineering at the Shibaura Institute of Technology in 2004. Joined the Hydrogen Industrial Use and Storage Group, Energy Technology Research Institute, AIST in 2011. Engaged in fracture toughness tests in high-pressure gaseous hydrogen environment at the Hydrogen Industrial Use and Storage Group, Energy Technology Research Institute, AIST from 2013. In this paper, was in charge of the consideration of conditions for fracture toughness tests and the execution of the tests.



### Hisatake ITOGA

Completed the doctorate courses at the Mechanical and Civil Engineering Division, Graduate School of Engineering, Gifu University in 2005. Doctor of Engineering. Faculty member, Nakanihon Automotive College from 1995 to 2007. Research Fellow, Research Center for Hydrogen Industrial Use and Storage, AIST from 2007 to 2013. Associate Professor, Research Center for Hydrogen Industrial Use and Storage, Kyushu University from 2013. Engaged in the research for strength property of metallic materials, and particularly after 2007, engages in the research on effect of hydrogen on the material strength property. In this paper, was in charge of the analysis of fracture toughness test results.



---

## Discussions with Reviewers

### 1 Overall

#### Question & Comment (Mamoru Nakamura, AIST)

The establishment of a material evaluation system to

guarantee the reliability of metallic materials that can be used in high-pressure hydrogen conditions and the establishment of its international standard are essential for the construction of hydrogen storage and a supply system to enable practical use of FCVs. This paper is very interesting as it describes the results of joint research with an American national institute for an evaluation method of the material properties, particularly, fracture toughness.

#### Question & Comment (Hiroaki Hatori, AIST)

The history of development of the material evaluation method for high-pressure hydrogen storage vessels that are essential for realizing FCVs is interesting in terms of synthesesiology, and this is a technological development field that is clearly related to society. The international standardization strategy that is currently in progress will be a key to the further diffusion of FCVs, and I think there is great significance in conducting a synthesesiological consideration with an eye on future efforts.

### 2 Current situation of the research pertaining to standardization in Japan and overseas, and organization of the descriptions of international standardization strategies

#### Question & Comment (Mamoru Nakamura)

The international standardization of the evaluation method for fracture toughness of metallic materials that can be used under hydrogen pressure is still in the phase of comparing three methods, and there is no indication of the direction or strategy for standardization. It will be easier for readers of this paper to understand, if you first describe the overall picture and the current situation of property evaluation under hydrogen pressure in Japan and overseas, then explain the positioning of fracture toughness that is discussed here, and then describe the result of the international joint research.

Specifically, the relationships among some of the ASME standards described in “2.2 Use standard of the materials used in high-pressure gaseous hydrogen equipment” and “4.1 Consideration of the fracture toughness evaluation method for finite life design,” the Japanese standard (is it in a preparatory stage?), and the international standard are unclear. I think you should organize and describe them carefully.

#### Answer (Takashi Iijima)

For the standardization in Japan, USA, and Europe, I organized the situations of the FCV on-board vessel and the hydrogen filling station vessel in chapter 2, and described the strategy for contributing toward the international standardization of material testing methods. The situation of testing equipment for high-pressure gaseous hydrogen condition in the world was overviewed in chapter 3, and we explained our efforts in developing the equipment. Also, for fracture toughness value, as mentioned in chapter 2, various evaluation methods are being suggested and searched. We described the result of international joint research with the Sandia National Laboratories for the fracture toughness evaluation method by the constant displacement method and the rising displacement method in chapter 4.

#### Question & Comment (Hiroaki Hatori)

Comment 1: For chapter 3, I think it is necessary to strengthen the synthetic consideration of the process (scenario, hypothesis) to realize the research goal for the material evaluation method that you succeeded in developing, as well as the selection and integration of the elemental technologies. Along with the efforts toward future international standardization in chapter 4, I think the readers will understand better if you add a figure that summarizes the scenario and strategy of R&D as a model. For the details of technology in chapter 4, the explanation should be simplified and some parts should be left to the reference material,



and the discussion should focus on the scenario and strategy.

Comment 2: Pertaining to international standardization, while the technological comparison with USA is clearly presented in this paper, there is no description of the situation in Europe. Doesn't the trend in Europe have effect on the international standardization in this field? Including the perspective of social demand of this technological field, I think the international standardization strategy will become clearer by considering and comparing Japan, USA, and Europe.

**Answer (Takashi Iijima)**

As you indicated in Comment 2, there was no description of the trend in Europe including that of ISO. Therefore, we described the trend on the standardization in Japan, USA, and Europe for on-board vessels and hydrogen station vessels in chapter 2. Then we discussed the R&D scenario toward international standardization and added the schematic diagram (Fig. 1) of the development model. Since we are not in the position to directly promote standardization, we used the expressions "approach" or "contribute" to the international standardization of the material testing method. Also, in terms of capturing the efforts in Japan, USA, and Europe, we added the global situations of the testing equipment for high-pressure gaseous hydrogen in chapter 3.

Following Comment 1, we simplified the description on the technological details in chapter 4, and the data for SA-372 Grade J are referred to the paper published in July 2014.

### **3 Comparison of the fracture toughness value in gaseous hydrogen evaluated by different methods**

**Question & Comment (Mamoru Nakamura)**

In the "direct comparison of Japanese and USA fracture toughness evaluation data" in this paper, the crack growth

behaviors in gaseous hydrogen for SA-372 Grade J and SCM435 are quite different, and therefore, you describe that different evaluation methods were used for SA-372 Grade J, but the fracture toughness values obtained were almost the same. I felt it was rather unnatural that the fracture toughness values were almost the same, despite the greatly different crack growth behaviors. Do you mean to say that the obtained evaluation values of the fracture toughness were quite different by different evaluation methods, but in this case, you obtained the same values using different methods by "coincidence"?

**Answer (Takashi Iijima)**

As you can see from the experimental data, the fracture toughness values of SA-372 Grade J and SCM435 in 115 MPa gaseous hydrogen became very low, and although the detailed mechanisms are unknown, it is assumed that the behavior is somewhere between linear elastic fracture and elastic-plastic fracture. For this point, I think we have to do further, careful experiments. The ASTM E1820 describes the method for evaluating the fracture toughness of samples that show unstable crack extension and stable crack extension, where the fracture toughness values are derived using the J-R curve calculated from the unloading elastic compliance method. At the same time, in the case where the unstable crack extension is mainly seen, the method for calculating the fracture toughness value from the P-COD curve without unloading is mentioned in ASTM E1820 Annex A5. Therefore, the fracture toughness values of SA-372 Grade J and SCM435 turned out to be the same values not by "coincidence," but we determined that they are comparable values obtained in the material test based on ASTM E1820. The details of the evaluation of fracture toughness value of SA-372 Grade J are described in Reference [20].