Topics

Development of a method for testing materials in high-pressure hydrogen using hollow specimens and acquisition of external funding and ISO Standardization History and Status

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In 2004, after the age of 50, I developed a method for testing materials in high-pressure hydrogen using hollow specimens, NEDO expected it to be a simple and convenient method, and it had been conducting tests requested by private companies, as the number of organizations implementing the standard increased and the demand for standardization grew, a proposal was submitted to ISO in 2020, and deliberations began in the working group. Standardization research is difficult to obtain budgets, especially for material testing of structural materials, which is often considered to have no research element, but this test method which enables the evaluation of material properties that were previously impossible, has received approximately 200 million yen in external funding over the past 10 years. An overview of this material test method and the history of its standardization will be presented.

1. Introduction (background)

In October 2002, at a liaison conference of related ministries and agencies concerning the commercialization of fuel cell vehicles, the target was set at a driving range of 500 km per fill, and the pressure of the on-board hydrogen tank was raised to 70 MPa (700 atmospheres). In order to develop example criteria for usable materials, it is necessary to fully understand the material properties of the candidate materials, but conventional material testing methods for high-pressure hydrogen environments are expensive and not easy to implement because the specimens are tested in a high-pressure hydrogen container. Furthermore, methods of cooling high-pressure hydrogen during filling or rapidly vaporizing liquefied hydrogen and filling with high-pressure hydrogen were considered. However, it is difficult to obtain material properties at low temperatures and in high-pressure hydrogen environments with conventional methods, so a new evaluation method was required.

However, NIMS had neither a testing machine with a high-pressure hydrogen container nor a building for high-pressure hydrogen testing, and had neither the experience nor the budget for hydrogen compatibility evaluation.

I soon came up with the idea of putting high-pressure hydrogen inside a hollow specimen instead of a high-pressure container, but I had a hard time deciding how to put the high-pressure hydrogen inside the specimen. Recalling that around 1985, a thermocouple was inserted from the end of a hollow specimen through a jig at the bottom to measure the temperature inside the specimen during fatigue testing in liquid helium[1)], I simply assembled a pressure gauge, valve, and piping, and tried it out fearfully at a pressure of 1 MPa at first, using existing testing equipment and fixtures. The results were confirmed to be almost equivalent to those obtained in a high-pressure vessel with a solid specimen, and the hydrogen pressure was increased.[2)] (Figure 1)

The budget doubled on the story of the invention of this test method (Table 1), and the research acceleration budget for the expansion of the testing machine was obtained after equivalent results were obtained. Also, a Grant-in-Aid for Scientific Research(GASR) was adopted, and requests for testing began to come in.

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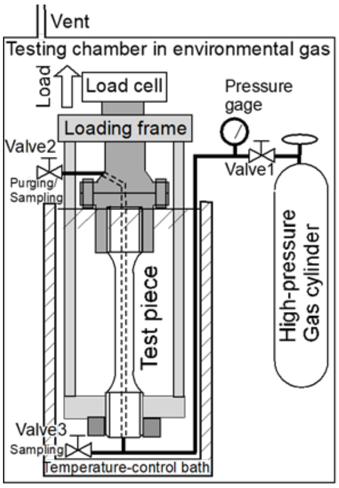

・A pressure booster is not required up to cylinder pressure (15 MPa), and a pressure gauge, valve, piping, fittings, and test space are all that is needed.
・If it is less than 1 MPa, you don't have to worry about the High Pressure Gas Safety Act.
・Effective for screening even at less than 1 Mpa.
・If the volume in the test piece and in the sealed piping is 1 ㎤ or less, the amount of gas used is only one liter at atmospheric pressure even at 100 MPa.

Figure 1. Principle of high-pressure hydrogen environment test method using hollow specimen

FY		Million yen	FY		Million yen
2004	NEDO	5	2014	NEDO	4
2005	NEDO	10	2015	NEDO	4
2006	NEDO	57		NEDO	9.2
2007	NEDO	20		Contract tests1	2.8
2008	NEDO	4.3		Contract tests2	1.4
	GASR-A	9.6	2016	NEDO	4
2009	NEDO	4.3		NEDO	1
	GASR-A	4.2		Contract tests3	3
	GASR-B	0.9		Contract tests4	3.2
2010	NEDO	20	2017	NEDO	4
	GASR-A	3.5		Contract tests5	2.2
	GASR-B	0.4	2019	Contract tests6	3.6
2011	NEDO	10.7	2005～2017	Subtotal	Approx.200
	GASR-B	0.3			
2012	NEDO	10.8	2018～2022	NEDO standardization	Approx.200
2013	NEDO	4		Total	Approx.400

Table 1. external funds obtained by the hollow specimen method

2. Utilization and standardization of hollow test methods

2.1 Obtaining Tensile and Fatigue Properties in High-Pressure Hydrogen Environments

The advantages of this test method are not only that a high-pressure container is not required and the cost is low, but also that a seal between the high-pressure container and the pull-rod is not required, so that a high-pressure hydrogen environment test from low temperature to high temperature is easy. By 2008, we conducted hollow tensile tests and fatigue tests (stress ratio: 0.01) in hydrogen on various candidate materials[3)] and found that "there is no effect of hydrogen if there is some bcc phase or if no new bcc phase is generated, but there is a possibility of fatigue property degradation at cyclic tensile stresses above 300 MPa and a higher possibility at stresses above 500 MPa. Therefore, when using high-strength materials in high-pressure hydrogen environments, it is necessary to confirm fatigue test data under actual conditions that take into account the gas environment, design stresses, and surface properties.[4)] Hydrogen is similar in some respects to the behavior of water and hydrolysis.

2.2 KHK's Special Recognition and Adoption to Exemplary Standards

Some test requests from private companies include data acquisition for internal use, but also for obtaining special approval from the High Pressure Gas Safety Institute of Japan (KHK) for materials used in manufactured equipment. Data obtained by the hollow test method is used because the conventional method cannot obtain data on the operating environment (temperature and hydrogen pressure), which is the criterion for approval.

In addition, the materials SUH660 and XM-19, which were recognized as hydrogen-compatible materials but not listed in the example standards, were listed in the example standards related to the General High Pressure Gas Safety Regulations in July 2019 as materials that can be used at -253 to 120 °C and 90 MPa, from the result of hollow tensile properties from room temperature to -240 °C in 90 MPa hydrogen, solid tensile properties at 120 °C and fracture toughness at -253 °C obtained in a NEDO recommissioning project.

2.3 Standardization of Hollow Test Methods

In Japan, the data obtained by the hollow test method is also used to certify hydrogen-compatible materials, and the fact that the method has been implemented by private testing organizations and overseas has led to requests for standardization from companies wishing to start the hollow test method.

NEDO project started in 2018 to prepare a draft domestic standard (Japan High Pressure Technology Association standard) with a budget of approximately 200 million yen over 5 years. The plan is to develop a draft standard for hollow specimen low-velocity tensile testing in FY2020 and a hollow fatigue testing bill by the end of FY2022. The price of a conventional material testing machine using a high-pressure vessel is about 100 million yen without including the building and related equipment, and about 150 million yen if equipment up to temperatures as low as around -80°C is included. The effect of being able to conduct hydrogen hollow tests at many institutions is significant.

Table 2 shows the history of the ISO proposal for the hollow tensile test method. ISO proposals and participation expenses are not included in this NEDO project but treated as just the overseas announcement.

Table 2. History of ISO Proposal for Hollow Specimen Tensile Test Method

Year/Month	event
2017/08	Proposed a hollow tensile specimen method in high-pressure hydrogen to the Japanese Standards Association, the secretariat of ISO/TC 164 (Mechanical testing of metallic materials).
2017/11	The proposal plan of TC 164 was approved by the International Standards Division of METI, 3 years later to confirm the verification of the hollow test method in the NEDO project.
2018/03	The ISO TC 164 Steering Committee of the Japanese Standards Association (JSA) approved this as a test method to be proposed in FY2020.
2020/09	Since more than 5 countries are required to support the ballot for a new ISO proposal at the expense of personnel costs for experts in the WG, an e-mail was sent to those involved in high-pressure hydrogen-compatible materials in the US, China, Korea, Germany, France, UK, and Italy requesting their cooperation. The U.S. was initially opposed. China asked a former acquaintance in the cryogenic materials field.
2020/10	Proposal explained at TC 164/SC 1 (uniaxial testing) meeting and new proposal document (Form 04 and reference draft) submitted to SC 1 secretariat (France)
2021/02	Voting opens for new proposal NP7039
2021/05	Adopted by a vote of 12 in favor, 9 against, 9 abstentions, and 5 experts elected (Japan, Germany, UK, Korea, and China).
2021/06	Notification of voting results and vote on resolution to establish new WG; due 2021/07
2021/09	Notification of approval of a resolution to create a new working group, ISO/TC 164/SC 1/WG 9, which will be formally established for a period of three years only.
2021/10	Final confirmation of WG 9 at SC 1 meeting (6 months late)
2021/12	ISO/TC 164/SC 1/WG 9 (Hollow Hollow Tension Tests in Hydrogen) was held on the web at Zoom (ISO) as convener and secretary of the WG, revised WD, and asked for comments again by the end of February 2022.

3. Summary (Prospects)

①If the hollow test method enables strain-controlled low-cycle fatigue tests in a high-pressure hydrogen environment, which is not possible with conventional methods, the ripple effect will be extremely large because the allowable stress of the material can be confirmed.

② The hollow specimen faithfully corresponds to the loading stress, which increases the stress at the interface with hydrogen, and the more accurate determination of the stress at which hydrogen acts has helped us understand that strength is not determined by "defects" but by the type and number of chemical bonds between atoms that change bonding partners depending on the loading energy, that "dislocations" are the shadows of rows of bonds with high energy that are difficult for electron beams to penetrate, and their relation to hydrogen excitation[5]. We hope that standardization of test methods will also expand this understanding.

③ The acquisition of the GI Fund for the evaluation of liquefied hydrogen-related materials has been attributed to the realization and standardization of cryogenic testing technologies since 1980, the standardization of the VAMAS /ISO tensile test method in liquid He, the publication of space-related materials data sheets and the hydrogen compatibility evaluation by the hollow test method.

References

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