KOREAN REGISTER

Research Report of Material Compatibility for Liquid Hydrogen Storage on Marine Application

2023


Hydrogen
H2

Preface

This technical document is intended to guide the selection of metallic materials that suit the conditions required for the operation of cargo and fuel containment and piping systems for liquid hydrogen for marine applications. Extensive R&D efforts have been made to enable the storage and utilization of liquid hydrogen in various types of transportation vehicles for the achievement of carbon neutrality. In order for hydrogen to be stored as cargo and treated as fuel in ships, one must be able to store a large amount of it in a limited space. Among the most widely used approaches to this end is the method of storing hydrogen in a liquid state. Implementing this method then requires developing a system that can be reliably maintained at a temperature of −253℃. Such a system must be made of a material that endures extremely low temperatures with a considerable level of resistance against hydrogen.

Chapter 1 provides a brief overview of this document. Chapter 2 and Chapter 3 identify materials that can be used in a liquid hydrogen atmosphere and the conditions required for them based on the results of recent studies while clarifying the difference between the above conditions and the requirements for materials used in LNG systems, for which a significant level of technical expertise has been achieved on the domestic front. LNG does not react with metals, while hydrogen tends to penetrate metallic materials, causing hydrogen embrittlement, in which their crack resistance is reduced. Given that hydrogen is a very small element, it can easily infiltrate and penetrate metals while diffusing through them. However, in order for hydrogen embrittlement to occur, three conditions must coincide: hydrogen atmosphere, specific material characteristics, and stress generation. This means that hydrogen embrittlement may be prevented or reduced by implementing measures focused on design and structural aspects, as well as material properties. This will be discussed in more detail below and in the Appendix.

Chapter 4 analyzes the safety standards and material compatibility test methods currently applied in a wide range of hydrogen storage applications and further proposes a test procedure for evaluating the compatibility of materials for liquid hydrogen storage for marine use. Most hydrogen safety regulations are intended for high-pressure hydrogen in a gas state, and thus there is a lack of safety regulations that properly reflect any risks arising from low temperatures and the unique characteristics of ship operations. In this document, a series of procedural evaluation steps to that end are proposed in consideration of the unique properties of liquid hydrogen based on the IGC and IGF codes.

In order for a procedure for evaluating the material compatibility of cargo and fuel containment and piping systems for liquid hydrogen for marine applications to be firmly established, academic consensus must be reached based on extensive research results. Given that in many aspects, it is very difficult to develop and build a test system that considers both extremely low temperature and hydrogen atmosphere conditions, even in advanced countries, only a few research institutions have been able to engage in this type of research. As a result, there is not enough research data available, making it more difficult to conduct further relevant research and analysis.

Chapter 5 provides an introduction to the test facility for cryogenic (20K) liquid hydrogen environments used in the present study. This facility was developed and built as part of the "Development of Safety Standards for Hydrogen Storage Containers and Fuel Feeding Systems for Marine Applications" project (Ministry of Oceans and Fisheries) led by the Korean Register of Shipping and jointly implemented by the Korea Institute of Machinery and Materials and Pusan National University. A future study will focus on using this facility to generate quality data that can be used in the ASME code-based design of pressure vessels while extending its applicability to more material types, thereby contributing to developing and commercializing novel liquified hydrogen storage systems for ships and achieving the carbon neutrality goal of the maritime industry.

Term Definition

1. Design Temperature refers to the minimum temperature at which cargoes can be loaded into cargo tanks and transported.

2. Independent Tank refers to a self-supporting tank that does not comprise a part of the ship's structure, which, therefore, does not necessarily affect the strength of the hull structure.

3. Primary Barrier refers to the internal component designed to provide containment to fuel or cargo in a fuel or cargo containment system equipped with two surrounding walls.

4. Secondary Barrier refers to the external liquid-tight component of a fuel containment system designed to temporarily store any liquid fuel that may leak through the primary barrier, thereby preventing the temperature of the hull structure from going below a critical level.

5. Insulation space refers to any space partially or fully filled with thermal insulation regardless of whether or not it is an inter-barrier zone.

6. Interbarrier space refers to the space between the primary barrier and the secondary barrier that is fully or partially filled with materials, including thermal insulation, or that remains empty.

7. Maximum Allowable Working Pressure (MAWP) refers to the maximum working pressure that is allowed for any device components or tanks.

8. Lower Explosive Limit (LEL) refers to the lowest gas concentration below which an explosion cannot occur.

9. Hydrogen Embrittlement refers to the phenomenon in which hydrogen, when absorbed into metallic materials, especially steel products, tends to reduce their ductility and toughness, making it more likely for them to fail without any plastic deformation.

10. Hydrogen Atmosphere refers to the state or condition in which the system of interest is exposed to hydrogen, which is defined by the phase and partial pressure of hydrogen. In this document, this term is considered to have the same meaning as Hydrogen Environment.


Hydrogen-powered
LH2
HYDROGEN POWER

1. Overview

Regulations on greenhouse gas emissions from ships have continuously been strengthened in an effort to address global warming and greenhouse gas issues faced by the shipping industry. In line with the greenhouse gas reduction initiative proposed by the International Maritime Organization, different methods of using various eco-friendly fuels for ship propulsion have been proposed. Extensive research has also been performed to use liquid hydrogen with high energy density as a fuel source to propel large merchant ships. In countries such as Korea and Japan, the introduction of liquid hydrogen carriers is currently under consideration to import large amounts of hydrogen from overseas sources for the achievement of carbon neutrality. Therefore, increasing attention has been paid to cargo containment systems for liquid hydrogen. It was not until the introduction of Suiso Frontier, a liquid hydrogen carrier produced by Kawasaki Heavy Industries, Japan, and Hydra, a liquid hydrogen-fueled ship produced by Norled, Norway (2021), that ships equipped with liquid hydrogen storage containers started to operate in practice. This was because it was difficult to fabricate a dual-vacuum container with excellent insulation performance, allowing large amounts of hydrogen to be transported and utilized for a long period of time. In addition, back then, there was less demand for the maritime transport of liquid hydrogen. Up until recently, hydrogen was stored and transported while being in a gaseous state, and most facilities were designed as a ground fixing or portable type. Various attempts have been consistently made to find ways to store liquid hydrogen since the 1960th, but the demand was so low that rather less attention was paid to this sector compared to research fields related to gaseous hydrogen.

The Sub-committee on Carriage of Cargoes and Containers (CCC) of the IMO started to establish safety standards for hydrogen fuels to achieve its greenhouse gas reduction goal. Not only the Interim Recommendations for Carriage of Liquefied Hydrogen in Bulk published by the Maritime Safety Committee (MSC) in 2016 but also the Interim Guidelines for the Safety of Ships Using Hydrogen as Fuel proposed by Norway in 2022 were basically drafted with reference to ISO/TR 15916 "Basic Considerations for the Safety of Hydrogen Systems" ISO/TR 15916 defines basic safety considerations and risks and provides specific descriptions of them so that they can be applied to a wide range of industrial fields. With that said, it does not cover specific safety requirements for the application of hydrogen, and thus one needs to refer to other standards to access such information. Specific requirements for materials allowed to be used for hydrogen storage, depending on how they are stored, are available in ANSI/AIAA G-095A-2017 "Guide to Safety of Hydrogen"

In selecting materials for hydrogen storage and transport, compatibility assessment, considering the environmental characteristics of the system, is considered the top priority. The load requirements and state conditions (purity, partial pressure, temperature, etc.) of storage systems may vary depending on the application and operation purposes of hydrogen, and so do the categories of materials that comply with such requirements. For example, at the 8th Technical Conference for the Phase 2 revision of the Global Technical Regulation on Hydrogen and Fuel Cell Vehicles (October 2020), it was discussed that the list of materials recommended for each hydrogen environment system provided in the Safety Standards (NSS1740.16) of the National Aeronautics and Space Administration (NASA) might not be used as a basis for material selection because this list was a sort of screening data, solely based on temperature and hydrogen embrittlement, without any considerations on fatigue assessments. Given that the longer the load cycle is, the faster the crack propagation rate becomes due to the intrinsic characteristics of hydrogen, thereby leading to reduced fatigue life, the load condition should be considered an important evaluation parameter. For the hydrogen storage and piping system of ships as well, the characteristics of the hydrogen atmosphere are considered to hold great significance in the compatibility assessment of materials.

Hydrogen embrittlement of a metal refers to a phenomenon in which hydrogen penetrates the metal, degrading its ductility and toughness and thus making it more prone to cracking. The occurrence of hydrogen embrittlement is mainly dependent on the following three factors: hydrogen atmosphere, material characteristics, and stress (load) conditions. Hydrogen embrittlement may result in different consequences depending on which part of the system is being considered, and thus the applicability of each material must be thoroughly examined. On that note, this technical document aims to propose a procedure for selecting suitable metallic materials based on the operational requirements for liquid hydrogen storage containers and piping systems for ships.

The main body of the document describes the requirements for LNG and liquid hydrogen storage systems, as well as the minimum requirements for their materials, to compare specific materials used for each system. In addition, the requirements for material selection provided in domestic and international safety regulations, along with the effect of hydrogen on the mechanical performance of metallic materials, are provided in the appendixes of this document for the convenience of system design and development. In an attempt to extend the material selection criteria for containment facilities for storing low-temperature cargoes and fuels in ships beyond the existing low flash-point fuels to include hydrogen, slow strain rate testing (SSRT), fatigue life, and fracture toughness were identified as evaluation items in consideration of the hydrogen atmosphere. With that said, the causes of cryogenic and hydrogen embrittlement damage have not been sufficiently identified, and there is also a lack of suitable databases, and thus, as it stands now, it is difficult to derive quantitative acceptance criteria for each evaluation item. Against this backdrop, the Korea Institute of Machinery and Materials (KIMM) has continued joint research with the Korean Register of Shipping and Pusan National University's Hydrogen Ship Technology Center by establishing hydrogen precharging facilities and physical property testers equipped with cryogenic (20K) chambers to simulate a liquid hydrogen atmosphere. Going forward, it will be possible to examine the applicability of various materials for hydrogen-storage systems based on the material compatibility criteria to be established, thereby enhancing their economic feasibility, although it will rather take a considerable amount of time to achieve such a goal.

1. Analysis of LNG Systems for Ships

1.1 System Configuration

This section describes in detail the conditions (temperature, pressure, etc.) of the major components of LNG-fueled ships, including fuel containment facilities, piping systems, and fuel consumers, while deriving design requirements for each system. Figure 2.1 presents a schematic representation of the LNG-based low-pressure fuel supply system. In general, this system is composed of a fuel containment facility, a fuel supply system, and fuel consumption sources (e.g., internal combustion engines). LNG is stored at a temperature of -163℃ or below, and the design pressure may vary depending on the type of tank used. LNG is kept at a temperature of about -130℃ and a pressure of 6.5 bar while being fed to the vaporizer among the key components of the fuel supply system. Engines and boilers for propulsion and power generation are generally used as fuel consumers. The fuel supply system allows a gaseous fuel at 0-50℃ to be supplied at a pressure of 5.6-9 bar in a gaseous state to the fuel consumer in which it is consumed.

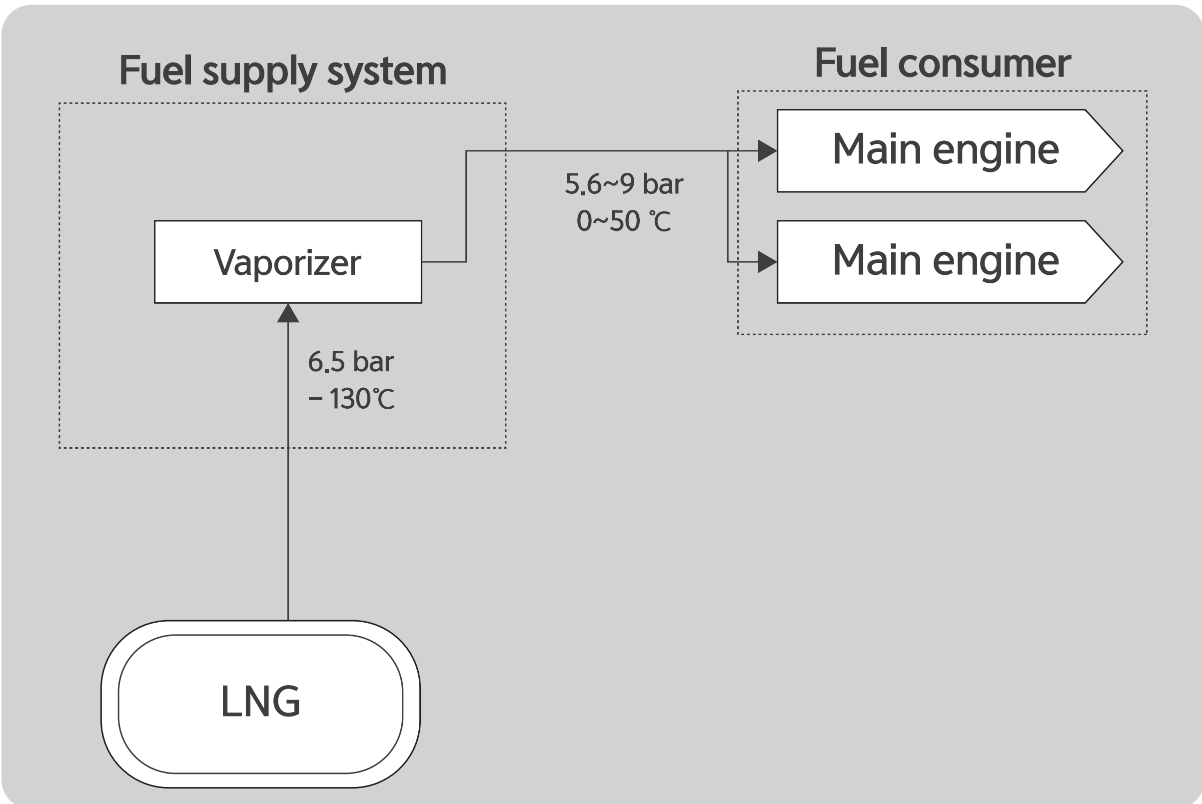


Figure 2.1 Schematic diagram of the natural gas storage and usage process of an LNG-fueled vessel

1.2 System Requirements and Minimum Allowable Conditions

Natural gas in a gaseous or liquid state is colorless, odorless, non-toxic, and non-corrosive. It is stored in a liquid state at a pressure of up to 10 bar in cargo or fuel containment systems. Risk factors related to LNG that affect the selection of system materials, as well as measures to reduce such risk factors, are as follows.

1) Risk factors related to LNG

- Cryogenic burns
- Low-temperature embrittlement
- Risk of suffocation
- Expansion and pressure
- Fire
- Rapid phase separation (evaporation)

2) Measures to reduce risk factors

- Protection from external environments (cofferdams, airlocks, etc.)
- Pressure relief and ventilation
- Secondary sealing (e.g., dual tubes and secondary barriers)
- Application of welded connections rather than flange connections
- Drip tray capacity and liquid detection
- Protection of the hull structure from released cryogenic, high-pressure steam and gas

The cargo and fuel containment systems specified in the IGC/IGF codes are required to be equipped with secondary full-liquid-tight barriers to safety contain any released fluid and must also be able to prevent the temperature of the hull structure, along with insulation facilities, from going below a critical level. If the possibility of structural damage and fluid leakage through the primary barrier[1] is extremely slight or virtually zero, as in Independent Tank Type C, no secondary barriers[2] are required for containment facilities for liquefied gas fuels. However, for independent tanks that require the installation of full or partial secondary barriers, additional measures to safely handle any possible leakage from tanks are required. In addition to the process facilities, as illustrated in Figure 2.1, drip trays may be additionally required depending on the type of tank used. Drip trays must be properly installed in places where any possible leakages that may damage the overall hull structure may occur. Suitable materials must be used to bear the low temperature of leaked liquified gas, and thus, aluminum alloys or austenitic stainless steel alloys are generally used.

[1] Primary Barrier refers to the internal component designed to provide containment to fuel or cargo in a contain-ment system equipped with two surrounding walls.

[2] Secondary Barrier refers to the external liquid-tight component of a cargo containment system designed to tem-porarily contain and store any liquid fuel that may leak through the primary barrier, thereby preventing the tem-perature of the hull structure from going below a critical level.

The piping system requires the design pressure to be equivalent to or higher than the atmospheric pressure so that liquified gas cargoes and fuels can be properly transported and supplied. Accordingly, it is important to use materials with sufficiently high strength and ductility even in a low-temperature environment. It is also necessary to determine whether the diameter and thickness of pipes are suitable for a given design pressure.

The inside wall of a tank (primary barrier) that is in direct contact with LNG must be made of a material that can maintain its strength and ductility at room temperature or in a cryogenic environment, along with sufficiently high impact resistance. This material must also not cause any excessive stress, considering the risk of thermal expansion or shrinkage due to extreme temperature differences. The IGC/IGF codes and the Rules for the Classification of Steel Ships of the Korean Register of Shipping prescribe the minimum requirements for the mechanical properties of metallic materials used to produce plates, section members, and forged parts that comprise tanks, secondary barriers, and pressure vessels for processes. Part 2 (Materials and Welding) of the Rules for the Classification of Steel Ships of the Korean Register of Shipping describes the criteria for the fabrication, chemical composition, testing, and inspection of materials that comprise the hull structure, vessel equipment, and engine components. The IGF/IGC codes and Part 2 (Materials and Welding) of the Rules for the Classification of Steel Ships of the Korean Register of Shipping specify that the execution of tensile tests and Charpy impact tests should be an essential requirement for metallic materials. Tensile tests are performed at the design temperature, i.e., -165℃, but Charpy impact tests are performed at -196℃, which is lower than the design temperature. Here, the impact absorption energy must be at least 27 J for parent materials. As such, low-temperature Charpy impact tests are performed at a temperature about 30℃ lower than the design temperature because a temperature increase may occur while taking out specimens that have been soaked in a cryogen to be exposed to the air or due to rapid deformation while allowing them to be hit by the hammer.

For piping systems and pressure vessels, all failure modes arising from any load scenarios that may possibly occur under given design conditions must be considered. Design conditions may be subdivided into final, fatigue, and accident conditions. The following requirements must be considered when defining the design load.

- Classification (permanence, function, environment, and accidents) and details of loads
- Load range according to the tank type
- Tank design, including its support structure and the design of other attachments

Functional requirements and safety principles for tank design and secondary barrier design according to the tank type are described in detail in the Korean Register of Shipping's regulations on ships using low flash-point fuels.

1.3 Applicable Materials

According to the IGF/IGC codes and Part 2 (Materials and Welding) of the Rules for the Classification of Steel Ships of the Korean Register of Shipping, applicable metallic materials for LNG containment systems are as below. At temperatures lower than the design temperature of LNG storage and supply systems, these metallic materials are considerably ductile and do not exhibit a ductile-brittle transition temperature (DBTT), demonstrating that they are highly stable.

- 9% nickel steel
- Austenitic stainless steel: AISI 304 ,304L, 316, 316L, 321, 347
- Aluminum alloys: Al 5083
- Austenitic Fe-Ni alloy steel: 36% nickel steel
- Cryogenic high-manganese steel

According to the IGC/IGF codes, the maximum thickness of each material is limited to 25 mm, but 50 mm is allowed for austenitic stainless steel and aluminum alloys. If this limit is exceeded, approval from the Korean Register of Shipping must be obtained. According to the Rules for the Classification of Steel Ships of the Korean Register of Shipping, the maximum thickness is set to 40 mm for nickel alloy steel for low-temperature rolled structural steel parts and 25 mm for 9% nickel alloy steel (RLP 9) for low-temperature steel tubes. If this limit is exceeded, separate guidelines must apply.

Regarding heat treatments, the IGC/IGF codes specify that 9% nickel steel may be subjected to two cycles of normalizing[1] followed by tempering[2] or quenching[3] followed by tempering. The code also specifies that solid solution treatment[4] is required for austenitic stainless steel alloys, and annealing[5] is required for aluminum alloys. Any heat treatment for 36% nickel steel requires separate approval from the Korean Register of Shipping. In addition, 5% nickel steel may be used at a temperature range up to -165℃ after specific heat treatments, e.g., three cycles of sequential heat treatments, followed by an impact test at -196℃. The heat treatments for nickel alloy steel (RL 9N490) provided in Part 2 (Materials and Welding) of the Rules for the Classification of Steel Ships of the Korean Register of Shipping are the same as those specified in the IGC/IGF codes, except that upon approval from the Korean Register of Shipping, thermo-mechanical control processes (TMCP) may also be allowed, and chemical compositions for TMCP may be set differently from the specifications provided in the Rules for the Classification of Steel Ships.

Regarding the mechanical properties of 9% nickel steel, the IGC/IGF codes specify that Charpy impact tests should be performed at -196℃, and the minimum absorbed energy must be at least 27 J on average. According to Part 2

[1] A treatment aimed at increasing the overall quality of grains to achieve a finer and more homogeneous standard microstructure by improving poorly developed ones, thereby enhancing the mechanical properties of materials, e.g., strength and toughness

[2] A treatment aimed at removing residual stress

[3] A heat treatment process performed to improve the hardness and strength of a material by hardening its micro-structure

[4] A treatment performed to improve the strength, machinability, corrosion resistance, and service life of austenitic stainless steel

[5] A treatment in which a given material is heated to a suitable temperature and then kept at the temperature for homogenization before being gradually cooled down to room temperature so that its microstructure becomes close to equilibrium

(Materials and Welding) of the Rules for the Classification of Steel Ships of the Korean Register of Shipping, tensile tests and impact tests must be performed for 9% nickel alloy steel, and when deemed necessary by the Korean Register of Shipping, notch toughness tests may be performed. Given that RL 9N490 is a rolled structural steel material for low-temperature purposes, its mechanical properties must be examined by tensile tests and impact tests, while RLP 9 requires bending tests because it is used for seamless steel tubes and ERW steel tubes. RLF 9 is used to produce forged steel parts, which are general applied to valves and attachments of the piping system for low-temperature purposes. Its cross-sectional reduction during tensile tests must be at least 45%, and other specific requirements for its mechanical properties are summarized in Table 2.1. The elongation is determined while the length direction of the specimen is placed in parallel with the rolling direction. The gauge length[1] and yield strength are defined differently according to the specimen thickness.

◦ Table 2.1 Mechanical properties of 9% Nickel alloy steel for low temperature

Grades	Tensile test			CVN test	
	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Test Temp. (℃)	Average absorbed energy(J)
RL 9N490	Min. 480	640-840	Min. 18	-196	Min. 27
RLP 9	Min. 520	Min. 690	Min. 15		Min. 41
RLF 9	Min. 520	Min. 680	Min. 19		Min. 41

According to Part 2 (Materials and Welding) of the Rules for the Classification, austenitic stainless steel alloys are classified into rolled structural steel (RSTS) and steel tubes (RSTS TP). The minimum yield strength of austenitic stainless steel alloys may be set higher than the designated value upon approval from the Korean Register of Shipping; hardness tests (Brinell, Rockwell, and Vickers tests) must also be performed. When necessary, corrosion resistance tests and impact tests may be required by the Korean Register of Shipping, depending on the purpose of use of the structural steel of interest, but given that LNG is a non-corrosive fuel, corrosion resistance tests are not required. According to Chapter 7 (Materials and Tube Design) of the Korean Register of Shipping's regulations on ships using low flash-point fuels (Table 7), impact tests may be omitted for austenitic stainless steel alloys upon approval from the Korean Register of Shipping. This is because it has been verified to exhibit sufficiently high impact toughness at the test temperature of -253℃, a condition achieved by cooling it using liquid helium [1]. The mechanical properties of austenitic stainless steel alloys are as follows

[1] The gauge length L is determined based on the following relationship: L= 5.65 ′ √(A). Here, A refers to the cross-sectional area of the specimen. The estimated gauge length may be defined as an integer value in units of 5 mm.

◦ Table 2.2 Mechanical properties of austenitic stainless steel alloys for low temperature

Grades	Tensile Test		
	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation (%)
RSTS 304	205min.	520min.	Min. 40
RSTS 304L	175min.	480min.	
RSTS 316	205min.	520min.	
RSTS 316L	175min.	480min.	
RSTS 321	205min.	520min.	
RSTS 347			
RSTS 304 TP	205min.	520min.	Min. 22
RSTS 304L TP	175min.	480min.	
RSTS 316 TP	205min.	520min.	
RSTS 316L TP	175min.	480min.	
RSTS 321 TP	205min.	520min.	
RSTS 347 TP			

The IGC/IGF codes do not require impact tests for aluminum alloys and INVAR, and this is because the effect of temperature on the strength and ductility of aluminum alloys is generally very small, and its DBTT does not exist even though its impact absorption energy does not reach the standard threshold. In Part 2 (Materials and Welding) of the Rules for the Classification of Steel Ships, an aluminum alloy is indicated as P (plate) if it is a rolled product and S (shape) if it is an extruded product. The IGC/IGF codes define INVAR as one that can be used for liquified natural gas (LNG). This material is known to be able to maintain its performance without being embrittled even at low temperatures due to its very low thermal expansion coefficient, combined with excellent strength and elongation. The mechanical properties of aluminum alloys are as follows.

◦ Table 2.3 Mechanical properties of aluminum alloys for LNG services

Product	Grades	Tempering	Tensile test		
			Yield Strength (MPa)	Tensile Strength (MPa)	Elongation (%)
Rolled	5083 P	O(Annealing)	125 min.	275-350	14min.
Extruded Shapes	5083 S		110 min.	270-350	12min.

As it currently stands, the materials that can be used for systems whose minimum design temperature is -163℃ according to the interim guidelines of the IGC/IGF codes include high-manganese steel [2]. When compared to other cryogenic materials, high-manganese steel exhibits comparable toughness and tensile strength. It is also highly cost-effective when compared to nickel, among high-cost materials. According to Part 2 (Materials and Welding) of the Rules for the Classification of Steel Ships, high-manganese steel, once hot-rolled, may be control-cooled if necessary. After the final rolling process, further heat treatments must not be performed. The mechanical properties required for high-manganese steel are as follows.

◦ Table 2.4 Mechanical properties of high-Mn steel for low temperature

Grades	Tensile test			CVN test	
	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Test Temp. (℃)	Average absorbed energy(J)
HMN 40	400min.	800-970	22 min.	-196	27min.

The cryogenic materials mentioned above have a face-centered cubic (FCC) structure. Accordingly, these materials do not exhibit brittle behavior and thus are highly suitable for use in cryogenic environments. As an exception, nickel alloys have a body-centered cubic (BCC) structure, but it is still possible to use them at a temperature range up to 77 K because their low-temperature toughness can be improved by increasing the nickel content to the level of 9% [3,4].

2. Analysis of liquid hydrogen Systems for Ships

2.1 System Configuration

This section analyzes the state of hydrogen in liquid hydrogen–fueled ships, from fuel containment facilities to piping systems and fuel consumers, in an effort to derive environmental design requirements for each system. Figure 3.1 presents a schematic representation of the fuel supply system that is generally applied to hydrogen fuel cell–fueled ships based on liquid hydrogen. This system is composed of a liquid hydrogen tank, fuel supply system, and fuel consumer (e.g., fuel cells). Within each part of this system, hydrogen exists in various forms. Liquid hydrogen is stored in a tank at a temperature of −253 ℃ and fed to the fuel consumer via the fuel supply system. In general, the fuel supply system is composed of two heat exchangers, a compressor, and an LP heater. It is supplied to the heat exchangers in the state of either liquid or gas. From the liquid hydrogen tank, gaseous hydrogen is transported to one heat exchanger at −240℃ and 2 bar, while liquid hydrogen is transported to another heat exchanger at −245℃ and 4 bar. Afterward, the liquid hydrogen is converted into a gaseous form at the heat exchanger and then supplied to the LP heater while being kept at 4 bar and −10℃. Finally, the liquid hydrogen is supplied by the LP heater to the fuel cell in a gaseous state at 1–2 bar and −20–50℃. The fuel cell generates power by consuming the gaseous hydrogen to power the ship via the ECU, converter, and main propulsion motor.

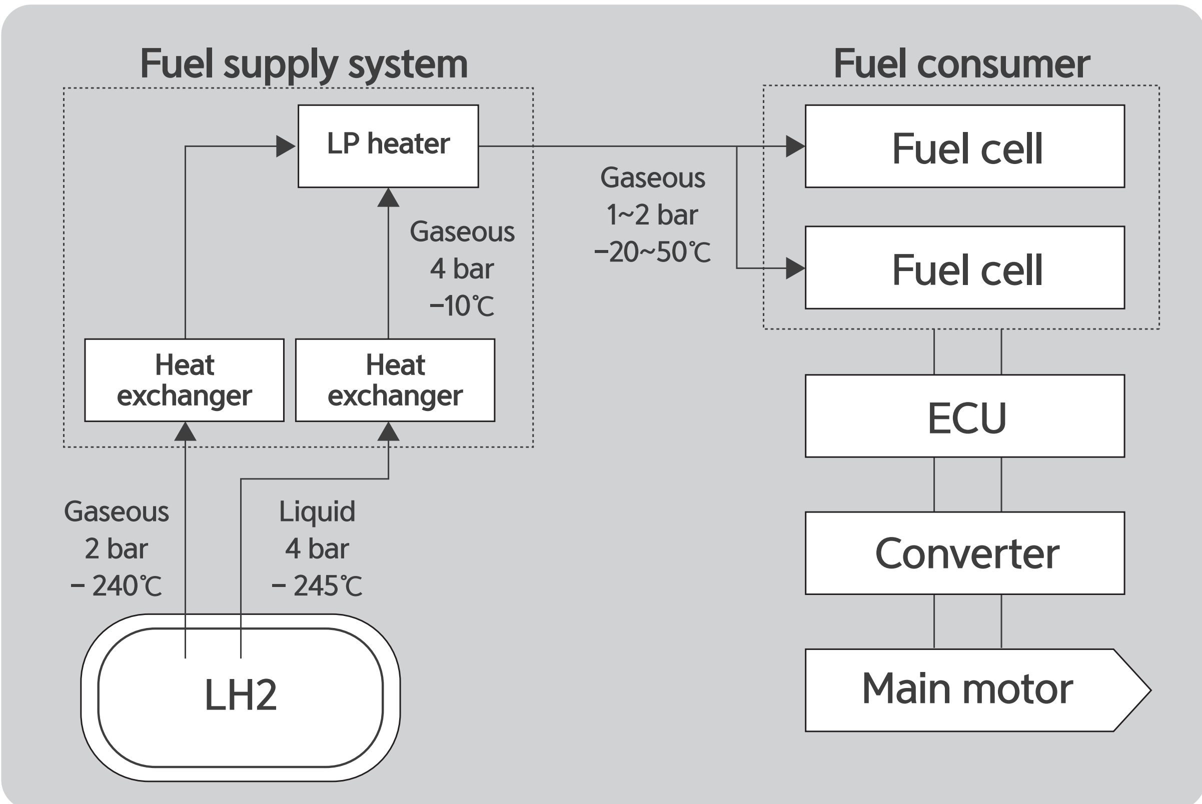


Figure 3.1 Schematic diagram of the hydrogen storage and usage process of a liquid hydrogen-fueled vessel

Currently, there are no standards available for the design pressure and maximum allowable working pressure of the hydrogen storage and transport system equipped in liquid hydrogen carriers and liquid hydrogen-fueled ships. Safety regulations on land-use liquid hydrogen systems, which are operated under hydrogen conditions similar to those illustrated in the schematic diagram of Figure 3.1, are summarized, along with relevant R&D activities, in Table 3.1.

Liquid hydrogen containers are known to be designed to have a pressure level of 1-10 bar. The CGA H-3 (Standard for Cryogenic Hydrogen Storage) of the Compressed Gas Association (CGA) limits the maximum allowable pressure to the level of 150 psi (≒10.3 bar), and the Sandia National Laboratory also applied the same maximum allowable pressure to liquid hydrogen-fueled ships in its feasibility study [5,6]. Kim et al.(2021) attempted to propose a methodology for determining the design pressure of liquid hydrogen storage tanks that can be applied to liquid hydrogen terminals. To that end, the researchers developed specific operation scenarios and performed a series of thermal and structural analyses based on them. The maximum pressure reached during the import of liquid hydrogen to the storage tank was 197.9 kPa, and the design pressure was defined to be 220 kPa, considering the hydrostatic pressure [7]. In practice, in GODU-LH_2 (Ground Operations Demonstration Unit), a project executed to verify the liquid hydrogen zero boil-off technology of NASA, the design pressure of a container with an internal capacity of 125,000 liters ($125m^3$) was found to be 95 psig (≒ 6.55 bar) [8].

Before the normal operation starts, liquified gas is imported into liquified gas cargo or fuel tanks via the sequential process of drying, inerting, gassing-up, and cooling down. In the gassing-up process, the inert gas contained in the tank is replaced by a gas of room temperature, and this process is followed by cooling down to prevent any damage due to a sudden temperature change. Here, the inside of the liquid hydrogen storage container may have different temperature distributions, ranging from 20K, the evaporation temperature of liquid hydrogen, to 300K, room temperature, depending on the position, and the pressure is expected to be 10 bar or lower.

The temperature range of the piping system may be wide, from 20K to 300K, because it should be able to properly transport liquid hydrogen and gaseous hydrogen from the fuel tank to the fuel consumer. The maximum pressure was assumed to be 10 bar, which was the same as that of the storage container. At the CCC's 8th conference, Norway proposed a requirement that the design pressure of liquid hydrogen supply and bunkering pipes be at least 20 bar, but further discussion is still needed on this issue. Accordingly, in this document, a review was performed while assuming that the design pressure was 10 bar or lower.

◦ Table 3.2 Operating condition of hydrogen system

Target	Category	Pressure (bar)	Temp. Range (K)	Reference
Ground Operation Demonstration Unit for Liquid Hydro-gen (GODU-LH2) project	Design pressure of inner tank	6.55	Abt.20	[8]
LH_2 terminal	Design pressure of inner tank	2.2	Abt.20	[7]
CGA Standard	MAWP[1] of inner tank	10.3	Abt.20	[6]
LH_2 tank	MAWP of inner tank	9.0	Abt.20	[10]
PEMFC	MAWP of inlet	≤3.5	Ambient	[10]
CGH tank	Maximum fueling pressure	≤875	233 to 358	[SAE]

[1] Maximum allowable working pressure

2.2 System Requirements and Minimum Allowable Conditions

Gaseous hydrogen is colorless, odorless, and highly penetrating because its molecules are very light and small, and thus it is able to easily pass through leakage paths while rapidly diffusing out into the surrounding environment. Hydrogen, once penetrating into a metal, diffusing, and accumulating in specific parts, reduces the critical stress level, above which cracking occurs, thereby degrading its mechanical properties, including strength and elongation. Liquid hydrogen has a light blue hue. When exposed to the atmospheric environment, it will rapidly start to evaporate. In case of other gases being directly exposed to liquid hydrogen, they may be solidified, damaging the overall system. Risk factors related to hydrogen that affect the selection of materials, as well as measures to reduce such risk factors, are as follows.

1) Risk factors related to hydrogen

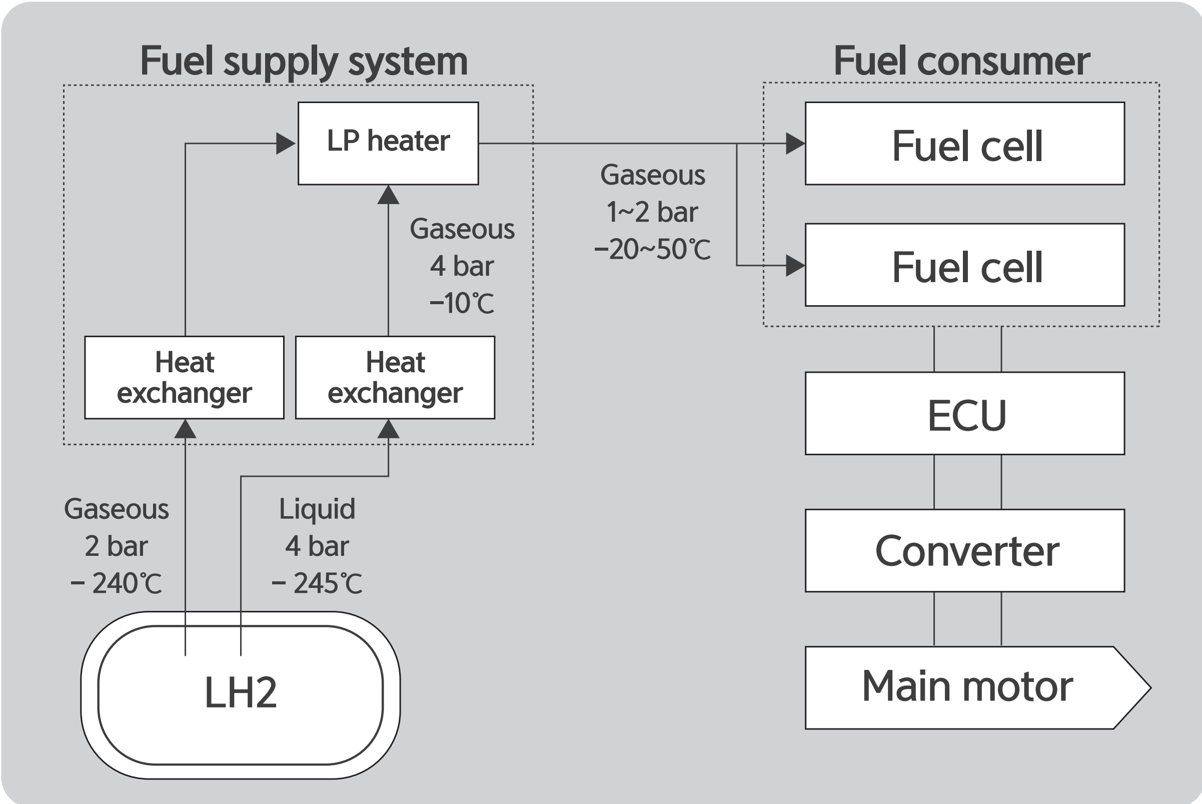
- Combustion-related factors: Low ignition energy, a wide range of combustion conditions, less visible flame, and fast flame propagation
- Low temperature-related factors: Low-temperature burns, oxygen enrichment by liquefaction/condensation, solidification of other fluids
- High permeability
- Low viscosity
- Hydrogen embrittlement in parent materials and weld metals

2) Measures to reduce risk factors (focused on hydrogen embrittlement)

- Reduction of working stress (to the level of 30-50% of yield strength) [11]
- Minimization of low-temperature plastic deformation during cold working (estimated while considering all generated stress)
- Solution heat treatment recommended for stainless steel
- Carbon steel pipes heat-treated by normalizing
- Alloy steel with a tensile strength of 950 MPa or less treated by quenching and tempering
- Seamless steel pipes used in a high-pressure hydrogen environment with a pressure level of 200 bar or more
- Flange connection methods avoided when connecting pipes if weld joints can be applied
- Full penetration butt weld

The risk reduction measures described above were prepared by summarizing the details of domestic and international safety standards on the use of hydrogen. More details regarding major safety standards are provided in the Appendix of this document. When it comes to the operation of the liquid hydrogen storage and supply system, its cryogenic properties, along with hydrogen permeability and embrittlement, must be thoroughly reviewed. For example, carbon steel may be used to a limited extent in a certain hydrogen environment, but it cannot be used in a temperature range below its ductile-brittle transition temperature.

The IMO's independent tank types are preferred as liquid hydrogen cargo and fuel containment systems because they are effective in minimizing heat transfer from the external environment. The liquid hydrogen storage and transport system using independent tanks equipped in ships requires the following facilities in addition to the ones described in Figure 3.1.



igure 3.1 Schematic diagram of the hydrogen storage and usage process of a liquid hydrogen-fueled vessel

- Cargo/fuel tanks and pressure vessels for processes
- Piping system for cargo/fuel and processes
- Drip trays
- Outer shells

The IMO’s Independent Tank Type C for LNG storage does not require the installation of drip trays and secondary barriers, but in places where leakage may possibly occur, drip trays are required to prevent damage to the hull structure. Any fuel supply pipes that pass through enclosed spaces or gas safety zones in the ship must be mechanically ventilated or composed of dual tubes pressurized with inert gas. These requirements aim at preventing the risk of gas leakage.

Dual vacuum insulation must be applied to liquid hydrogen storage containers and piping systems in accordance with numerous international safety standards, unlike in the cases of LNG applications. In the case of adopting mechanical ventilation or applying inert gas, the air or inert gas may be liquified or solidified due to the very low temperature of liquid hydrogen. Furthermore, achieving reliable insulation performance requires a dual vacuum insulation structure.

The inner walls and surface of liquid hydrogen storage containers and piping systems remain constantly exposed to low-temperature liquid hydrogen or a low-temperature hydrogen atmosphere at all times, and thus these parts must be sufficiently resistant to low temperatures and hydrogen penetration. The outer shells of liquid hydrogen storage containers and piping systems are separated by a vacuum layer and thus not exposed to a hydrogen atmosphere during normal operations. Even in case of leakage, they are exposed to hydrogen for a relatively short period of time due to the rapid evaporation of liquid hydrogen and forced ventilation. Therefore, a significantly high resistance to hydrogen embrittlement is not required. Similarly, drip trays are exposed to hydrogen only during abnormal operations, e.g., in case of leakage of liquid hydrogen, and thus do not have to be highly resistant to hydrogen embrittlement.

2.3 Applicable Materials

Low-temperature applicability is among the most important requirements for materials used for the LNG storage and transport system, but materials for liquid hydrogen facilities are additionally required to be suitable for the hydrogen atmosphere. Accordingly, according to historical safety regulations, including ISO/TR 15916, among materials that are applicable at the target temperature, those with excellent resistance to hydrogen are selected. These materials can be classified according to their sensitivity to hydrogen as follows [12].

1) Materials that are almost not affected by hydrogen embrittlement under limited conditions
2) Materials that undergo hydrogen embrittlement and thus can only be used under limited conditions
3) Materials that are significantly affected by hydrogen embrittlement, for example, ending up failing or breaking, in an elastic range in which the stress is lower than the yield strength of the material

Those that fall into Category 1) include aluminum alloys (Al 6061-T6) and austenitic stainless steel alloys (300 Series Stainless Steel). Not all austenitic stainless steel grades fall into this category. It has been found that if the Ni content is 12.5% or more, their mechanical properties are not affected even in an environment highly prone to hydrogen embrittlement [15,16]. ASME BPVC[1] specifies that materials applicable to a high-pressure gaseous hydrogen environment with a pressure level of 1030 bar or less include alloy steels, including SA-372 and SA-723; stainless steel, including SA-336 Gr. F316; and aluminum alloys, including Al 6061-T6 (refer to Code Case 2938).

Those that fall into Category 2) include stainless steel and carbon steel in addition to stable austenitic stainless steel grades. Different safety standards (KGS FU671: 2021, CGA G-5.6 (2005), and CGA H-5 (2020)) specify that some carbon steel grades may be used if the partial pressure of hydrogen is 10 bar or less. It is also recommended that metastable stainless steel that may undergo transformations, ferritic stainless steel, martensitic stainless steel, duplex stainless steel, and precipitation-hardened stainless steel be only used in parts with low operating stress. As such, the operating stress is limited to a certain level because hydrogen embrittlement occurs when the three conditions regarding material, environment, and stress are all satisfied at the same time.

Among austenitic stainless steel grades, 316L with the highest Ni content could be the safest choice for hydrogen-atmosphere applications, but applying 316L to all components of the system that are exposed to gaseous hydrogen is considered a very conservative approach to material selection. As summarized in 3.1, the liquid hydrogen containment and piping systems of ships are exposed to hydrogen at low temperatures (20-300 K) and relatively low pressures (1-10 bar); this condition is considered to be moderate from a hydrogen embrittlement perspective compared to a high-pressure gaseous hydrogen atmosphere. More cost-effective materials, such as metastable austenitic stainless steel grades, may be selected and applied through material compatibility assessments considering various conditions, including temperature and the partial pressure of gaseous hydrogen.

[1] It is an abbreviation of the ASME Boiler and Pressure Vessel Code. Section VIII describes the requirements for the design, fabrication, inspection, testing, and verification of pressure vessels that are used under an internal or external pressure of 10,000 psi or more.

2.4 Limitations of Existing Material Compatibility Test Procedure for Hydrogen Atmosphere

Carbon steel used for gaseous hydrogen transport pipes, when exposed to hydrogen, undergoes significant performance degradation, including ductility reduction, enhanced fatigue crack growth, and reduced fracture toughness. However, carbon steel is still widely used in various industrial applications thanks to efforts to ensure that only a limited level of stress is exerted through appropriate design, and that the maximum allowable limits of different defects, including cracks, can be thoroughly managed. As it currently stands, there are no material compatibility test methods that can be universally applied to all types of hydrogen atmospheres. Rather, it is necessary to establish individual evaluation items and acceptance criteria that suit each system's environmental conditions. Given that the degree of material damage caused by hydrogen may be affected by the surrounding environment and operating stress, evaluation standards should be established while properly considering all possible failure modes. For example, SAE J2579[1] determines the fatigue life of hydrogen-fueled vehicles by estimating the maximum number of fuel injection times over their durability life and adjusting it by considering a margin of error.

At the eighth conference of the Sub-committee on Carriage of Cargoes and Containers (CCC) of the IMO, the revision of the IGF Code was discussed, especially regarding the use of hydrogen as a fuel. In the process, Norway proposed a material compatibility test method based on CSA/ANSI CHMC-1[2]. CSA/ANSI CHMC-1 is considered one of the most acceptable protocols in material compatibility assessments dedicated to the hydrogen atmosphere. However, this assessment procedure was developed with a focus on providing guidance to material selection for high-pressure gaseous hydrogen-fueled systems, and the methodology involves the following limitations.

1) Possibility of rather optimistic estimates made by SSRT[3] in low-pressure gaseous atmospheres

- The design pressure of liquid hydrogen cargo and fuel containment and piping systems for ships is typically set to 4 bar or less. Thus, stainless steel, with high Ni content, easily satisfies the acceptance criteria for SSRT.

- Austenitic stainless steel alloys, aluminum alloys, and welding materials are verified to be compatible without conducting fracture toughness, fatigue life, and fatigue crack growth tests as long as they satisfy the acceptance criteria for SSRT.

2) Test temperature issues

- Tests are conducted only at a temperature within the operating temperature range where the effect of hydrogen embrittlement is the most pronounced.
- It is not possible to determine material compatibility in cryogenic conditions.

---

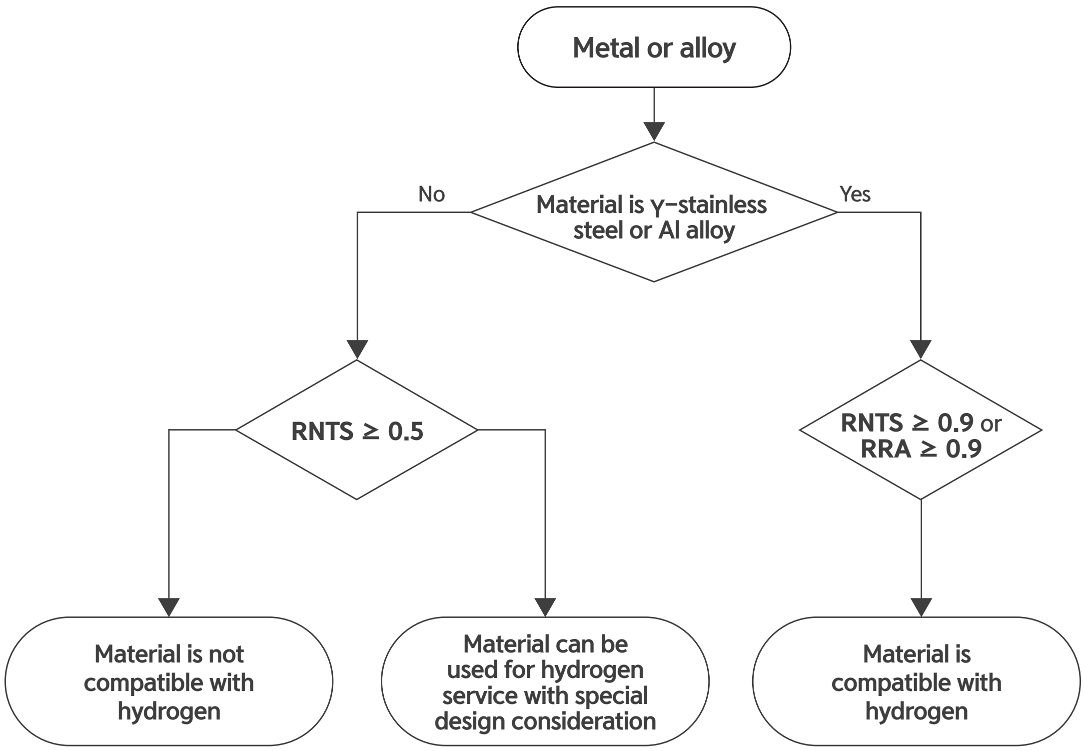
[1] Standard for Fuel Systems in Fuel Cell and Other Hydrogen Vehicles enacted by the Society of Automotive Engineers (SAE International)

[2] ANSI/CSA CHMC1-2014 (R2018) Test Methods for Evaluating Material Compatibility in Compressed Hydro-gen Applications - Metals

[3] Slow strain rate test (SSRT)

- DBTT tests are not performed.

The material compatibility test procedure provided in CSA/ANSI CHMC-1 is briefly illustrated in Figure 3.2. Austenitic stainless steel alloys and aluminum alloys are deemed to be resistant to hydrogen embrittlement when they satisfy the requirements for the ratio of notch-tensile strength (RNTS) and relative reduction area (RRA). Recent studies, however, have reported that their fracture toughness and fatigue crack growth may be significantly affected when they are subjected to environmental conditions in which hydrogen embrittlement is particularly pronounced [17,18]. Indeed, the fracture toughness of 316L stainless steel was significantly reduced when the tests were performed at 4 K, the evaporation temperature of liquid helium, while varying welding conditions [19]. As such, CSA/ANSI CHMC-1 is suitably applicable to typical high-pressure hydrogen storage containers and hydrogen stations; however, given that the possibility of hydrogen embrittlement and any risks arising from cryogenic conditions in low-pressure gaseous hydrogen atmospheres are not thoroughly considered reflected, it is rather inappropriate to apply this material compatibility test procedure, as it is, to the IGF and IGC codes, which is intended for liquid hydrogen. On that note, the IGF and IGC codes need to be revised while considering the unique characteristics of the marine environment, as well as the liquid hydrogen atmosphere.



RNTS: Notch tensile strength ratio (=NTS_H/NTS_R)
NTS_H: Notch tensile strength under hydrogen environment
NTS_R: Notch tensile strength under reference environment

RRA: Reduction of area ratio (RA_H/RA_R)
RA_H: Reduction area under hydrogen environment
RA_R: Reduction area under reference environment

Figure 3.2 Flowchart of material qualification in the CHMC 1 standard

3. Proposal of Material Compatibility Test Method for Liquid Hydrogen Atmosphere in Ships

3.1 Basic Concepts and Procedures

The proposed material compatibility test procedure for liquid hydrogen storage and utilization in ships is briefly illustrated in Figure 4.1. The major details of the procedure are outlined below.

1) Identify a hydrogen atmosphere.

- Determine whether being exposed to hydrogen.
- Check the design temperature and hydrogen pressure.

2) Check the material specifications.

- Chemical compositions, microstructure, mechanical performance, heat treatment, certification, etc.

3) Check to see whether the target material is registered on the lists that are reported to have allowed the use of the material.

- Check to see whether the material of interest has been allowed for the target environment (including temperature and hydrogen pressure).
- Perform material compatibility assessments if the target material is not available in the reported lists.

4) Execute material compatibility assessments.

- Introduce a simplified version of the hydrogen sensitivity test procedure (refer to SAE J2579)
- Design the procedure for fracture toughness tests to consider the combined effects of embrittlement by liquid hydrogen and gaseous hydrogen.

The existing codes intended for low-temperature liquified substances, such as LNG, only consider pressure in the design of pressure vessels and pipes, but when hydrogen is treated not only as cargo but also as fuel, material compatibility assessments should be designed to consider both temperature and gaseous hydrogen pressure at the same time[1]. If the metallic material of interest is verified to be compatible with the target environment by the reported list, any specific assessments are not required. For example, austenitic stainless steel alloys may be applied to a high-pressure gaseous hydrogen atmosphere as long as they have been subjected to solution heat treatment, and their nickel equivalent exceeds a certain level. Any materials that are found to be not registered on the reported lists must be subjected to specific material assessments to verify their environmental compatibility. Mechanical performance tests

[1] The major factors that affect hydrogen embrittlement are described in Appendix B.

(SSRT, fatigue life tests, fracture toughness tests, etc.) should be performed under test conditions that are equivalent to or harsher than the target environment to make a quantitative estimate of hydrogen sensitivity and thereby verify material compatibility.

The IGC and IGF codes and ASME BPVC allow the application of V-notch Charpy impact tests, which qualitatively measure the fracture toughness of materials based on their impact absorption energy, instead of conventional fracture toughness tests methods, in an attempt to quickly measure the degree of embrittlement at different temperatures. These Charpy impact tests, however, may underestimate hydrogen sensitivity due to high strain rates and often fail to maintain the intended temperature conditions because of the loss of control over the thermal energy generated during the deformation or fracture of specimens. It is recommended that the test procedure provided in ASTM E1820 be applied to fracture toughness assessments intended for hydrogen-sensitive or cryogenic environments. The detailed methods of and acceptance criteria for this assessment procedure are described later in 4.2.

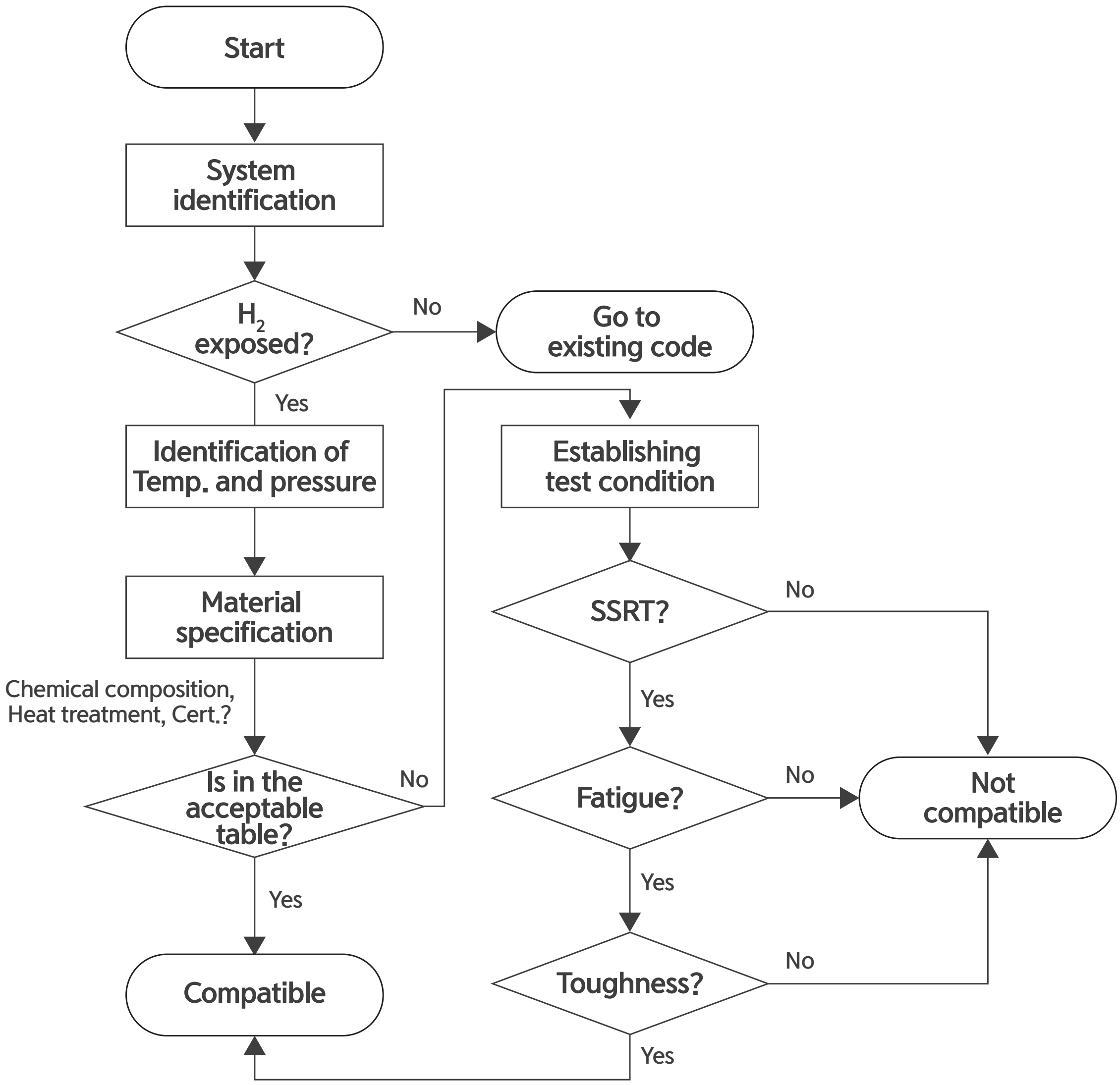


Figure 4.1 Flow chart of material selection for liquid/gas hydrogen containment, piping, and related systems

3.2 Detailed Assessment Methods

Three types of tests should be combined to evaluate the hydrogen sensitivity and low-temperature embrittlement of metallic materials at the same time. SSRT and fatigue life test procedures were prepared with reference to the material screening method for hydrogen atmosphere compatibility provided in SAE J2579 and ANSI/CSA CHMC 1:2004. Fracture toughness tests were designed to identify ductile-brittle transition criteria with respect to hydrogen atmosphere and temperature conditions.

Hydrogen atmosphere and temperature conditions are applied differently by test item, and this approach aims to achieve the desired results that suit the test purpose. First, it is necessary to identify the temperature range within the operating conditions of the target system in which the effect of embrittlement by hydrogen penetration is the most pronounced. Hydrogen embrittlement occurs at different temperatures for each material type. In general, it occurs near 200 K in austenitic stainless steel and at room temperature in most other metallic materials[1]. If the material of interest is not to be exposed to the hydrogen atmosphere, tests must be performed in the temperature range in which low-temperature embrittlement is highly likely to occur.

Hydrogen sensitivity tests are performed in two ways: first, mechanical performance is measured while the specimens are exposed to gaseous hydrogen, and second, mechanical properties are measured after injecting hydrogen into the specimens in advance. It is generally recommended that hydrogen sensitivity tests be performed under the same test conditions as the target environment; however, the mentioned hydrogen precharging method is widely adopted as an alternative because the method is capable of achieving comparable results. When performing tests for simulating the gaseous hydrogen atmosphere, the purity of hydrogen must be considered, and it is also recommended to set the pressure to 1.25 times the maximum allowable working pressure. Given that most liquid hydrogen cargo and fuel containment and piping systems are designed to have a working pressure of 5 bar or less, it is expected that the pressure of gaseous hydrogen will not exceed 10 bar. The detailed procedural steps and acceptance criteria for each test item considering test environments are as follows (please note that any details proposed in this research report should not be construed as absolute statements and thus will be edited and improved later through further discussion).

1) Slow strain rate tensile (SSRT) test

- Test temperature: Design temperature or the temperature where hydrogen embrittlement is most pronounced (or the temperature close to the range)
- Hydrogen exposure conditions: Exposed to high-purity gaseous hydrogen at the maximum allowable working pressure (or tests performed after injecting an equivalent amount of hydrogen into the specimen)

[1] The effect of hydrogen on materials will be discussed in detail in Appendix B.

- Test specimen: Typical round-bar tensile specimen (ASTM E8/E8M)
- Strain rate control: 5.0×10^{-5} s^{-1} or less (with the initial strain rate as the reference)
- Acceptance criteria: A relative reduction of area (RRA)[1] of 0.5 or more after being exposed to hydrogen
- If notched specimens are used in fatigue life tests, SSRT may be omitted.

2) Fatigue life

- Test temperature: Room temperature (fatigue life increased when exposed to low-temperature hydrogen)
- Hydrogen exposure conditions: Same as in SSRT
- Test specimen: Either of notched specimen (ASTM G142) or typical round-bar tensile specimen (ASTM E8/E8M)
- Load control: Maximum stress set to 1/3 or more of the tensile strength with a frequency of 1Hz
- Stress ratio: 0.1 for notched specimens and -1.0 for round-bar specimens
- Evaluation criteria: Further discussion needed for the criteria for fatigue life (10^5 or more for notched specimens and 2.0×10^5 or more for round-bar tensile specimens according to the reference standards)

3) Fracture toughness

- Test temperature: Design temperature or the temperature where hydrogen embrittlement is most pronounced (should be conducted at a specific temperature interval to be able to identify DBTT, considering all possible temperature ranges, including room temperature, design temperature, and the temperature with the most pronounced hydrogen embrittlement)
- Hydrogen exposure conditions: Same as in SSRT
- Test specimen and procedure: ASTM E1820 (J_{IC} threshold fracture toughness measurement)
- Acceptance criteria: Further discussion needed for fracture toughness indexes to replace impact absorption energy
- Remarks: Charpy impact tests not allowed for hydrogen sensitivity tests

[1] This parameter is defined as the relative ratio of cross-sectional area reduction rates between a specimen exposed to hydrogen and a specimen for comparison.

4. Mechanical Performance Tests for Simulating Liquid Hydrogen Atmosphere

4.1 Overview

Existing conventional material assessment methods have many limitations in examining both low-temperature embrittlement and hydrogen sensitivity of materials at the same time, as previously discussed in 3.4. It is never an easy task to design and build test facilities that can suit both liquid and gaseous hydrogen atmospheres at the same time. Even in advanced countries, such facilities have been implemented by only a handful of research institutes. Against this backdrop, it is no surprise that there is only a limited amount of research data available on this issue. In order for a procedure for evaluating the material compatibility of cargo and fuel containment and piping systems for liquid hydrogen to be firmly established, academic consensus must be reached based on extensive research results. The implementation of test facilities capable of simulating liquid hydrogen atmospheres in ships, combined with sufficient research data, will accelerate the establishment of a test procedure for material compatibility assessments intended for liquid and gaseous hydrogen atmospheres.

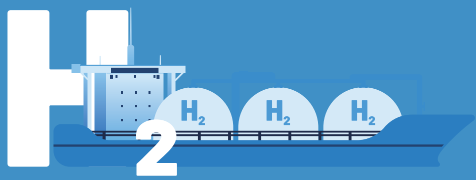
To this end, the Korean Register of Shipping, jointly with the Korea Institute of Machinery and Materials (KIMM) and Pusan National University's Hydrogen Ship Technology Center, established a set of test facilities capable of simulating the storage of liquid hydrogen in ships (refer to Figure 5.1). In this study, the method of hydrogen precharging was adopted to allow hydrogen sensitivity to be measured over a broad temperature range, including room temperature and ultra-low temperatures. This approach was intended for the following two purposes. First, cooling is performed using gaseous helium instead of liquid or gaseous hydrogen, and thus this test facility is exempt from the requirements for explosion-proof equipment. Second, the diffusivity of hydrogen[1] is significantly reduced in cryogenic conditions, and therefore it is possible to interpret the effect of hydrogen at ultra-low temperatures in a more conservative manner by injecting hydrogen into specimens in advance of testing.

Chapter 5 describes details of this hydrogen precharging method and cryogenic mechanical performance test equipment while also providing the hydrogen sensitivity test results of applicable materials for cryogenic conditions and their mechanical property measurements.

[1] Hydrogen diffusivity refers to the degree of diffusion of hydrogen in the matrix of a metallic material. It varies depending on temperature, hydrogen concentration, and the characteristics of the target material. In general, hy-drogen is less likely to exhibit sufficient mobility to penetrate and diffuse into a metallic material and end up being concentrated on defects in liquid hydrogen atmospheres.

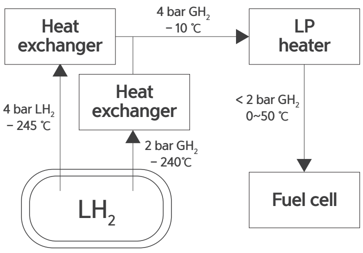
Evaluation of Material Compatibility for Liquid Hydrogen Environment

Infrastructure Establishment of Cryogenic and Hydrogen Embrittlement Resistance Evaluation



1. Establish Material Evaluation Scenarios

Enviornment Identification



Setting Up Test Condition

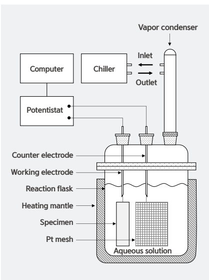
Temperature	SSRT
H_2 Pressure	Fatigue Test
H_2 Charging	Fracture Toughness
Chemical Compos.	FCGR

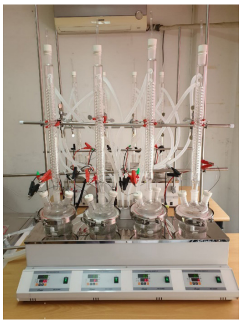
Tensile test specimen

CT specimen

2. Test Infra. for Cryogenic Environment and Hydrogen Embrittlement

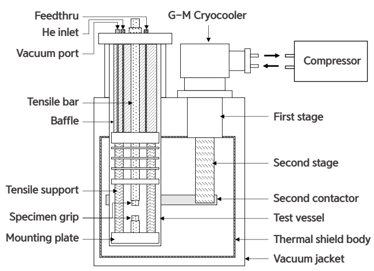
Hydrogen Charging Equipment





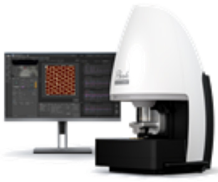
- Equipped with heating mantle & reflux condenser
- ISO 16773-2

Material Testing Machine

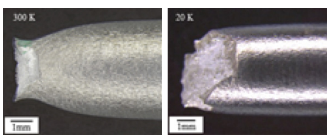


- Load Capacity: 80kN
- Design Temperature: 20 K
- Cryocooler with GHe

3. Hydrogen Sensitibity Analysis

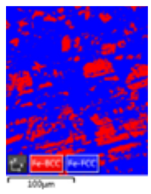


Atomic Force Microscopy
- High accuracy 3D measurement
- Hydrogen trapped site



Fractography
- Reduction of area
- Grain and etc.

Gas Chromatography
- Hydrogen concentration
- Material characteristics



EBSD
- Phase transformation
- Residual stress

Figure 5.1 Test procedure and infrastructure for metallic material compatibility for liquid hydrogen environment

4.2 Hydrogen Precharging

Liquid hydrogen cargo and fuel containment and piping systems may undergo temperatures higher than the design temperature for many reasons, for example, during the suspension of operation for facility maintenance. If this happens, hydrogen fails to be uniformly distributed throughout the metal matrix, ending up being concentrated on the metal surface. The method of hydrogen precharging using electrochemical cells allows extremely high hydrogen fugacity[1] to be generated near the specimen surface via cathodic electrolysis, therefore making it possible to effectively simulate hydrogen penetration or diffusion behavior. On that note, in this study, electrochemical hydrogen charging was adopted in an attempt to simulate the situation in which hydrogen is assumed to have already penetrated into a material for the liquid hydrogen storage and transport system. This section describes equipment and existing & improved test procedures for hydrogen precharging. The method for creating various hydrogen atmospheres for hydrogen sensitivity tests is described in detail in Appendix B.

1) Configuration of Test Facility

The method for maintaining high-temperature conditions while recondensing the steam generated in the process was introduced in this study with reference to the test equipment for maintaining constant temperatures proposed in ASTM G31 [20]. A reaction flask is covered by a heating mantle to keep the electrolyte solution at high temperatures, and the volume of the aqueous solution was also kept within a variation of ±1% after a long period of hydrogen charging using a vapor condenser and a chiller (refer to Figure 5.2). This electrolyte solution was prepared using 3% of sodium chloride (NaCl) and 0.3% of ammonium thiocyanate (NH_4SCN). The prepared metal specimens were pre-treated and post-treated in accordance with ISO 16573-2:2022. In this study, a constant current of 300 A/m^2 was applied for 72 hours, which was higher than the typical current density proposed in ISO 16573-2:2022, and the temperature of the electrolyte solution was kept at 80℃.

2) Preliminary Test for Validity Verification

The current density for hydrogen precharging was determined by preliminary tests using sheet-type tensile specimens. 304L stainless steel, which comprises the primary barrier of the LNG membrane panel, was used to fabricate specimens with a gauge length of 25 mm, width of 6.25 mm, and thickness of 1.2 mm in accordance with ASTM E8/E8M. The composition and temperature of the electrolyte aqueous solution were set in the same way as the conditions mentioned above. The current density was set to 200, 300, and 500 A/m^2 for optimization, and the current was applied to each specimen for 72 hours to ensure the uniform distribution of hydrogen.

Preliminary tensile tests were performed at an initial strain rate of 10^{-3} s^{-1} at room temperature. The obtained test results,

[1] Fugacity: Effective partial pressure of individual gases

along with images of fractured specimens, are presented in Figure 5.3. A decrease in the overall flow stress[1] during hydrogen charging led to reduced tensile strength compared to pristine specimens with no hydrogen injected. The elongation was found to decrease significantly with increasing current density. This suggests that an increase in the amount of hydrogen charging caused both tensile strength and elongation to decrease sharply.

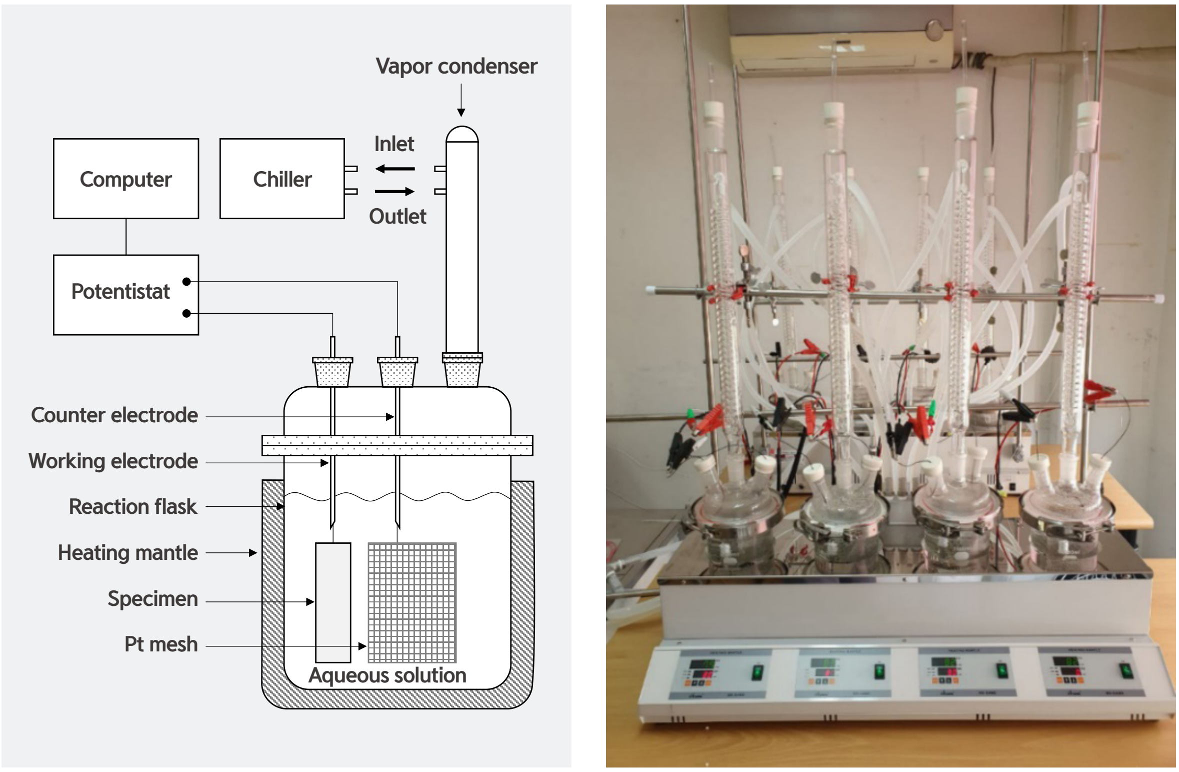
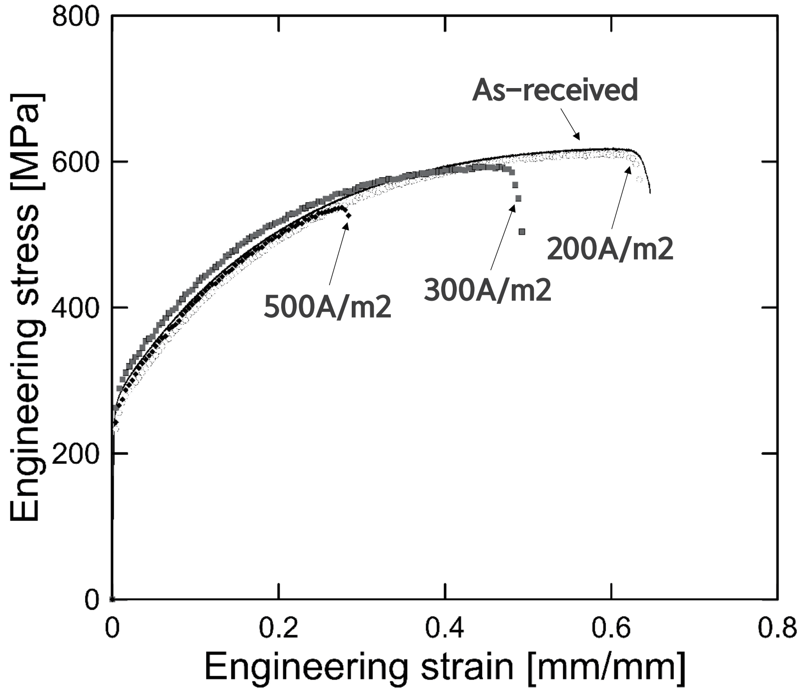
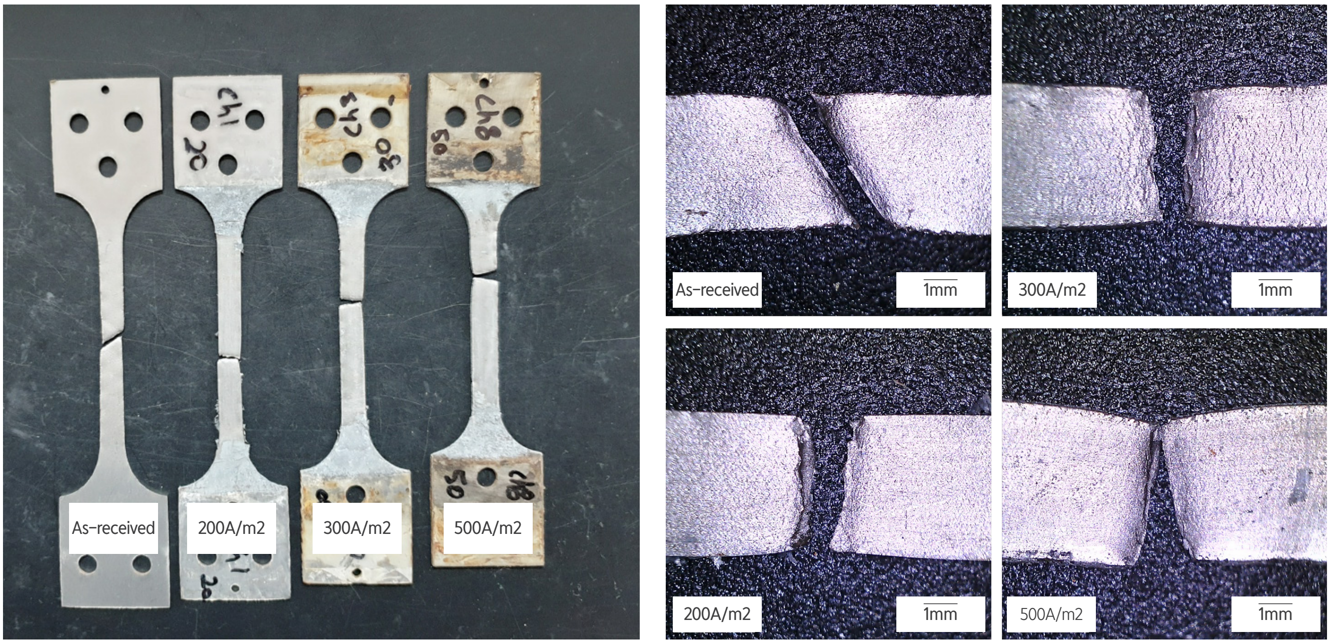


Figure 5.2 (a) Schematic diagram and (b) Experimental set-up of the electrochemical hydrogen charging system for high temperatures

[1] Flow stress refers to the stress level that is required to initiate the plastic deformation of a metallic material.



(a)



(b)

Figure 5.3 Preliminary test results: (a) Stress-strain curves and (b) Fractured specimens with respect to the current density

◦ Table 5.1 Comparison of hydrogen charging conditions

	Preliminary study	Hatano et al. (2014)	Zhou et al. (2019)
Material	304L stainless steel	304 stainless steel	304 stainless steel
Specimen	Sheet type specimen (Gauge length: 25mm, width: 6.25mm, thickness: 1.2mm)	Sheet type specimen (Gauge length: 60mm, width: 12.5mm, thickness: 0.8mm)	Sheet type specimen (Gauge length: 30mm, width: 10mm, thickness: 2mm)
H_2 charging	Electrochemical precharging (80℃, 72h)	Thermal precharging (100 bar, 400℃, 200h)	Tested at gaseous hydrogen (50 bar)
Elongation(Air)	64.68%	68.2%	66.8%
Elongation(H_2)	28.6%(500A/m^2) 49.5%(300A/m^2)	22.4%	52.2%
Ratio of Elong. (H_2/Air)	44.2~76.5%	32.8%	78.1%

The obtained preliminary test results were compared with the results reported in similar previous studies to verify the validity of the proposed test method and determine the optimal current density range. Zhou et al.(2019) performed tensile tests at a gaseous hydrogen pressure of 50 bar, while Hatano et al.(2014) attempted thermal hydrogen charging at 100 bar [21,22]. The researchers examined the amount of elongation reduction for each hydrogen atmosphere, and the results are summarized in Table 5.1. The liquid hydrogen storage system was expected to be exposed to a gaseous hydrogen pressure of 10 bar or less. In the present study, the current density for electrochemical hydrogen charging was set to 300 A/m^2, which corresponded to a degree of hydrogen embrittlement similar to that observed when exposed to a gaseous hydrogen pressure of 50 bar.

4.3 Mechanical Property Test Equipment for Cryogenic Environments

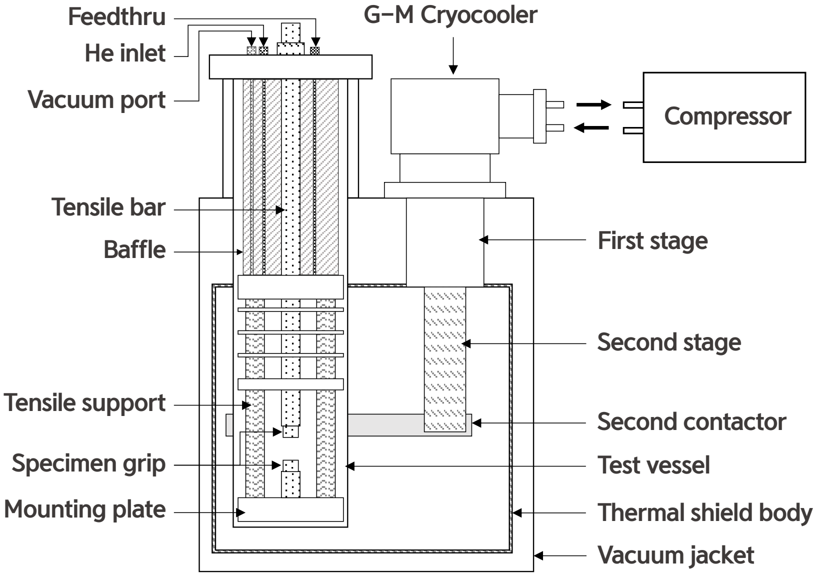
A low-temperature environment can be achieved by the following two methods: one that uses a cryogen and the other that uses a mechanical cooler. Liquid nitrogen (77K), liquid hydrogen (20K), and liquid helium (4K) are among the most widely used cryogens. Cooling using a cryogen makes it possible to reach the evaporation of the corresponding fluid or higher. For example, by using liquid nitrogen as a cryogen, the temperature can be cooled down to its evaporation temperature (77K), and if necessary, the temperature can be adjusted to the range above 77 K using a heater. A temperature range over 77K is achieved using liquid nitrogen in most cases from a cost-effectiveness perspective. A temperature range of 20K or higher could be achieved using liquid hydrogen and liquid helium, but helium, an inert gas, is preferred since gaseous hydrogen is combustible and explosible.

A mechanical cooler-based approach is often implemented by employing a cryostat combined with a G-M refrigerator. T. Ogata(2010) employed a cryostat and cooled its interior walls using a G-M refrigerator. The helium gas contained in the cryostat was cooled down to 20K by heat transfer via convection, and this cooling process took ten hours [23]. This mechanical cooler-based method uses a small amount of gaseous helium, and thus the target temperature can be reached at a relatively low cost.

The cryogenic mechanical property test equipment established at KIMM was designed to reach 20K, the target temperature, by allowing gaseous helium to be injected into its insulation chamber attached with a G-M refrigerator. Reaching a certain low temperature, e.g., 20K, requires a fluid that can remain in a gaseous or liquid form at the corresponding temperature. Most substances exist in a solid form at ultra-low temperatures, and thus the following three methods are widely used to that end: liquid hydrogen soakage, evaporation of liquid helium, and temperature reduction of gaseous helium. The present study adopted a gaseous helium-based cooling method using a refrigerator, which requires a long process time but is the safest and most cost-effective in terms of equipment installation.

As shown in Figure 5.4, the cryostat has a double-vacuum structure made of 304L stainless steel with a vacuum level of 1.0×10^{-5} Torr. UHE15, produced by ULVAC, was used as a refrigerator. Metal specimens are supposed to be mounted on the specimen grip placed inside a test vessel. A tensile load is applied to a metal specimen as follows. Changes in the resistance of silicon diodes attached to three tensile supports, caused by temperature variations, are measured using Lakeshore Model 335. The temperature of the specimen is then indirectly estimated based on the temperatures measured at nearby locations. This approach is feasible because even a small amount of thermal energy generated leads to a noticeable increase in temperature and internal pressure because the temperature of the test vessel is very low. Simply put, this system is very sensitive to temperature changes.

Cooling specimens using a refrigerator requires the entire set of internal jigs, including a test vessel, to have a low thermal capacity. Thus, the tensile supports were designed to be very thin. This constraint, in turn, limits the dimensions of test specimens. For that reason, most test equipment with an operating temperature of 4K or 20K has a capacity of 100 kN or less. Walter+bai's dynamic fatigue tester, capable of precise dynamic displacement and load control, was adopted as a material property tester. The basic specifications of each tester, along with the various performance indexes of the vacuum chamber, are summarized in Table 5.2.



(a)

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Figure 5.4 (a) Schematic diagram of a cryostat attached to the tensile testing machine for cryogenic environments and (b) Overall experimental set-up and tensile specimen mounting

◦ Table 5.2 Specifications of the material performance evaluation apparatus equipped with a cryostat and the fatigue testing machine for cryogenic environments

Volume of test vessel	10L
Material	304 stainless steel
Design pressure	2 barg
Design temperature	4-300K
Refrigerator capacity	1.5W @4.2K (ULVAC社, UHE15)
Loading capacity	10kN (static), 80kN (dynamic)

Figure 5.5 presents the temperature-time history measured by silicon diodes during the cooling of a 316L stainless steel tensile specimen to 20K, followed by tensile testing. As can be seen in Fig 5.4(a), it takes about 13 hours for the specimen temperature to reach the target. At the target temperature, tensile testing starts, causing the energy intended to deform the specimen to turn into heat. This leads to an increase in the specimen temperature. This tendency becomes more pronounced when the strain rate is higher [24]. Accordingly, when tests are performed in cryogenic conditions, the strain rate needs to be limited to a certain level to ensure that the temperature of the test specimen can be stably maintained. T. Ogata(2014) concluded, based on long-term research results, that these tests must be performed at a strain rate of 3×10^{-3} s^{-1} or less. However, ASTM E1450 recommends that the strain rate be lower than that, i.e., 10^{-3} s^{-1} [25,26]. The test equipment used in the present study will keep decreasing the temperature using a G-M cryocooler, and thus the temperature near the test specimen is maintained within a variation of ±0.3K.

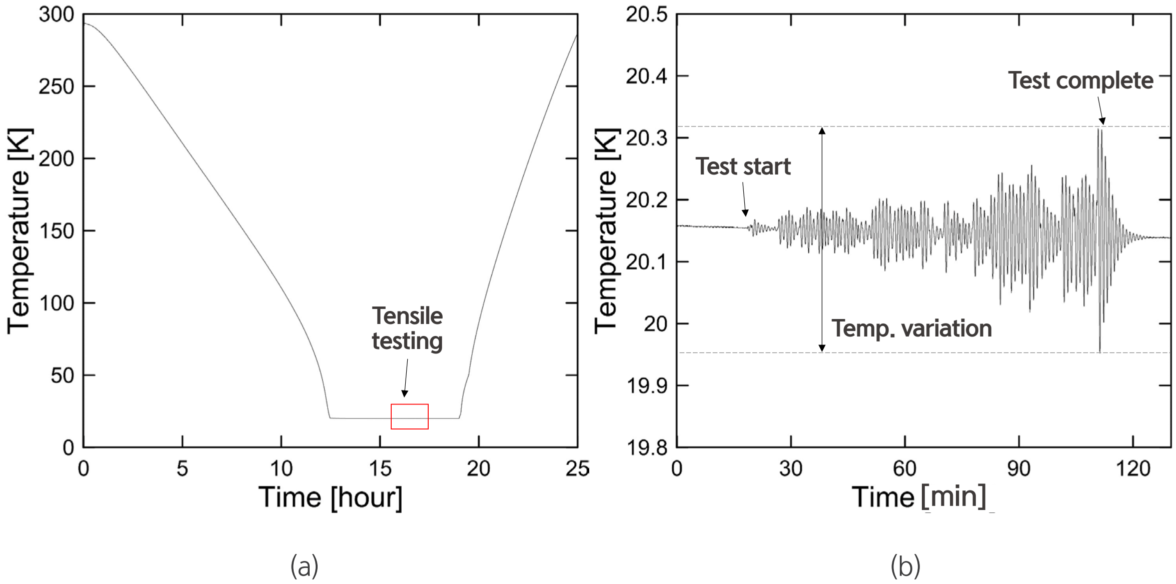


Figure 5.5 Temperature-time history of a 316L stainless steel specimen in a cryostat while cooling from room temperature to 20 K: (a) Entire temperature range and (b) Tensile testing range

4.4 Test Materials and Procedures

Among austenitic stainless steel and aluminum alloy grades, which have been widely used for low-temperature and hydrogen atmosphere applications, those deemed applicable to liquid hydrogen atmospheres were selected. More specifically, 304L (stainless steel) and 5083-H112 (aluminum alloy), widely used for LNG storage (with an evaporation temperature of -163℃), were selected, and 316L (stainless steel) and 6061-T6 (aluminum alloy), mainly used for high-pressure hydrogen storage, were also selected. The selected materials were processed into compact round-bar tensile specimens according to ASTM E8. Since the parent material thickness of 5083-H112 was different from that of the others, its tensile specimens were prepared to have a diameter of 4 mm and a parallel length of 16 mm, different from the specimens of the others with a diameter of 6 mm and a parallel length of 28.6 mm. When specimens were prepared by processing each parent material, it was ensured that the longitudinal direction of each specimen was aligned with the rolling direction. The shape and chemical composition of each material's specimens are presented in Figure 5.6 and Table 5.3.

The strain of each specimen was measured using Epsilon's Model 3442, which can be used in cryogenic conditions, and its gauge length was 10 mm. Once the strain within the gauge length exceeded 25%, the strain value was estimated by calibrating the displacement of the stroke. The tensile tests were displacement-controlled with an initial strain rate of 2.5 ´ 10^{-4} s^{-1}.

Figure 5.6 Tensile specimens of target materials

◦ Table 5.3 Chemical composition of each tensile specimen

Material	Type	Chemical composition (%)											
		Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Others	Al	-	-
Al alloy	5083-H112	0.108	0.262	0.026	0.501	4.372	0.138	0.032	0.02	0.15	94.391	-	-
	6061-T6	0.692	0.456	0.275	0.069	1.108	0.187	0.011	0.03	0.052	97.12	-	-
Material	Type	C	Si	Mn	P	S	Cr	Ni	Mo	N	Co	Cu	Fe
Stainless steel	304L	0.025	0.4	1.64	0.033	0.002	18.14	8.07	0.11	0.073	0.22	0.22	bal.
	316L	0.019	0.47	1.25	0.03	0.002	16.64	10.1	2.1	0.07	0.2	0.26	bal.

4.5 Experimental Results

1) Mechanical Property Test Results in Cryogenic Environments

All tensile tests were performed twice to verify reproducibility. In the case of cryogenic test results, due to reduced visibility caused by the occurrence of discontinuous yielding, only a single curve was plotted for each material. The tensile test results of the four target materials at room temperature (300K) and at an ultra-low temperature (20K) are summarized in Figure 5.7. At room temperature (300K), there was no significant difference in yield strength (with an offset of 1%) between the stainless steel grades. The flow stress[1] of 304L (stainless steel) was found to steadily increase until it reached the tensile strength. In the cryogenic environment (20K), the two material types exhibited significantly different test results. The difference in yield strength between the two steel types was more pronounced at the ultra-low temperature than at room temperature. In the austenitic stainless steel alloys, deformation-induced transformation and strain hardening were observed at 20K, exhibiting a significant change within the range from yield strength to ultimate tensile strength. The elongation and strength of the aluminum alloys were greater at 20K than at room temperature. The mechanical performance of each material type at room-temperature and cryogenic conditions is summarized in Table 5.4.

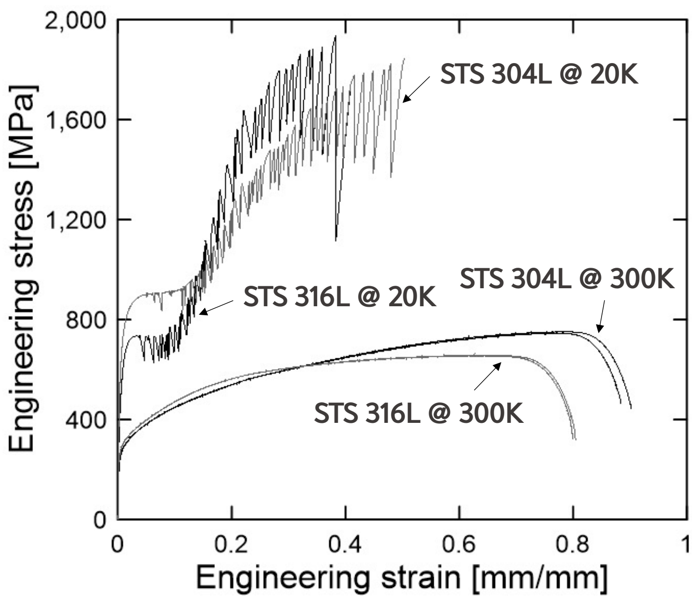
The most distinctive difference in mechanical behavior between the stainless steel and aluminum alloy grades was discontinuous yielding. In the present study, a temporary strength reduction was observed in the aluminum alloy grades, but the degree of reduction was insignificant. In the stainless steel grades, the degree of discontinuous yielding continued to increase as plastic deformation accumulated. Discontinuous yielding is also known as discontinuous plastic flow. As a metallic material deforms, this phenomenon occurs, causing a sudden stress drop coupled with an increase in temperature. Each material undergoes discontinuous yielding at different temperatures and strain rates [27,28]. At ultra-low temperatures, discontinuous yielding is known to be caused by adiabatic heating occurring inside the specimen due to significantly reduced heat conduction. This leads to localized deformation, giving rise to cross-sectional area reductions across the specimen in a non-uniform manner. This phenomenon is generally observed in FCC metals. As the strain rate increases, the degree of localized temperature elevation also becomes larger; as a result, this phenomenon temporarily disappears [29].

◦ Table 5.4 Mechanical performance of target materials at 300K and 20K

Material	Temp. (K)	Yield strength (MPa)		Tensile strength (MPa)		Elongation	
		Avg.	Std.	Avg.	Std.	Avg.	Std.
STS 304L	300	299.0	2.6	765.3	11.8	86.2	3.8
	20	682.0	7.1	1943	9.9	39.0	1.1
STS 316L	300	313.5	2.1	660.5	7.8	80.0	0.3
	20	777.0	18.4	1824	9.5	50.4	0.0

[1] Flow stress refers to the stress level that is required to initiate the plastic deformation of a metallic material.

Al 5083-H112	300	294.0	2.8	313.5	2.1	22.6	0.3
	20	353.5	0.7	470.5	0.7	26.7	2.3
Al 6061-T6	300	269.5	3.5	291.0	1.4	27.1	0.0
	20	331.0	1.4	461.0	1.4	36.6	0.3



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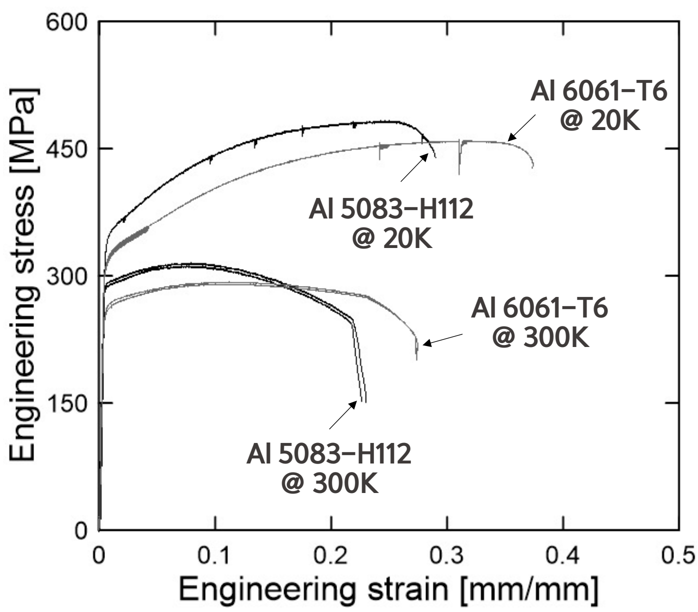
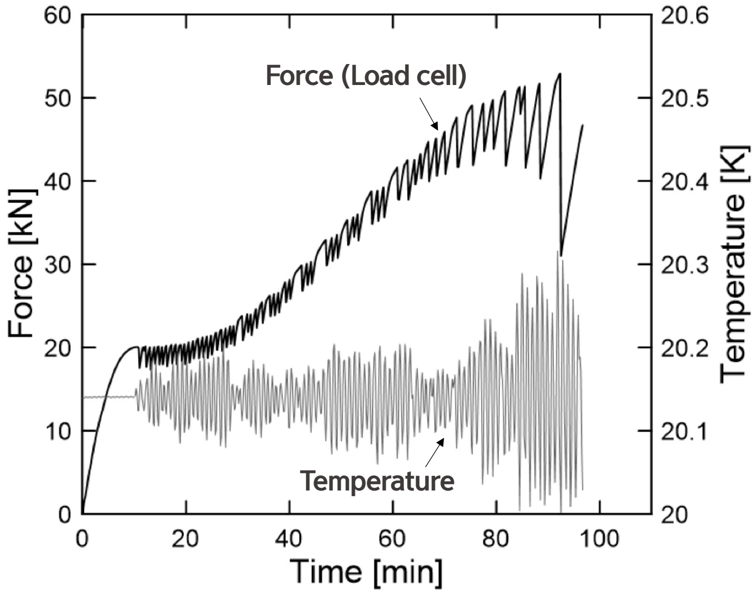


(b)

Figure 5.7 Effect of temperature on the mechanical behavior of (a) Austenitic stainless steel grades and (b) Aluminum alloys

In the present study, a temperature increase due to discontinuous yielding was similarly observed, as presented in the load cell force and temperature curves plotted as a function of time Figure 5.8. In the 304L stainless steel specimen, after the yield point was exceeded, discontinuous yielding continued. In contrast, the 316L stainless steel specimen intermittently exhibited discontinuous yielding in the plateau range. In both grades, discontinuous yielding, coupled with a significant temperature change, was commonly observed, and as plastic deformation accumulated, the amplitude of the force–time curves increased, and so did that of the temperature–time curves. The aluminum alloy specimens did not exhibit noticeable discontinuous yielding, and thus no significant temperature variations were observed, unlike in the stainless steel specimens. In both stainless steel and aluminum alloy specimens, a large temperature variation was observed right before a fracture occurred. This behavior ended right after the completion of the test.



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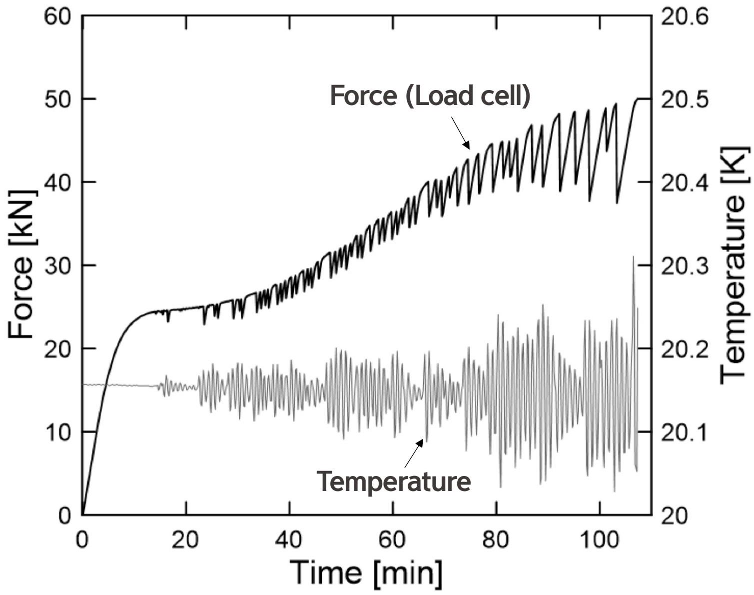

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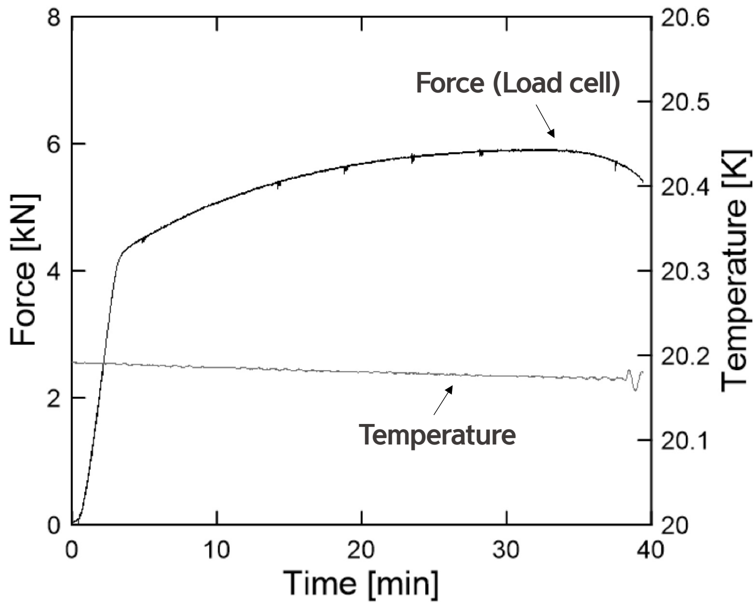

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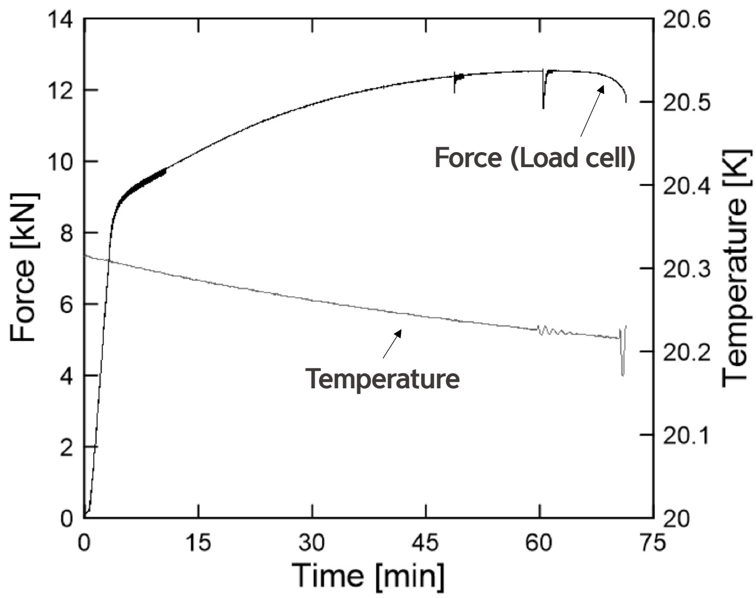


(b)

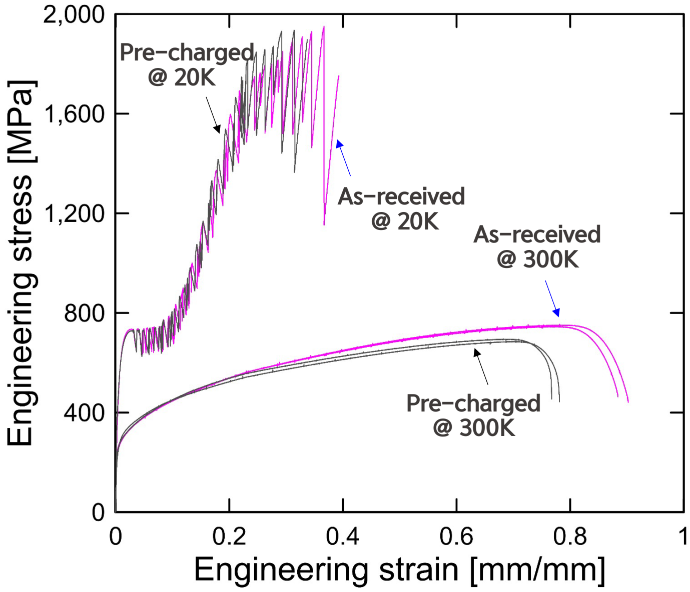
Figure 5.8 Force-time and temperature-time curves at 20 K of (a) 304L and (b) 316L (stainless steel) and (c) 5083-H112 and (d) 6061-T6 (aluminum alloy)

In the present study, even though discontinuous yielding occurred in the stainless steel grades, the temperature was stably maintained at 20 K within an error of ±0.2 K. The temperature variations observed in this study were considered to be very small compared to the results reported in previous studies. Indeed, when a tensile test was performed on 304 stainless steel at 4.2K, discontinuous yielding occurred, and the temperature suddenly soared to over 20 K, according to a previous study [30]. A literature survey was performed to find previous studies that conducted tensile tests at 20K, the same temperature as applied in the present study, for fair comparison; however, these researchers did not measure the temperature during tensile testing. Thus, a direct comparison with the literature was not possible. The main cause of this difference was that a relatively low strain rate was applied in the present study (displacement-controlled at a rate of 0.0025 mm/s with an initial strain rate of $2.5 \times 10^{-4}\ s^{-1}$). It can also be attributed to the following two reasons. First, there was a possibility that the G-M refrigerator was so efficient that it was able to effectively keep the temperature low. The second possible reason is that the temperature was indirectly measured using the silicon diodes attached to the tensile supports near the specimen. These silicon diodes are placed very close to the specimen. As a matter of fact, however, these devices are used not for the purpose of specimen temperature measurement but to measure the ambient temperature so that the cryogenic refrigerator and heaters can be properly controlled. In a cryogenic environment, heat transfer occurs by the convection of the gaseous helium contained in a cryostat [28]. Given that at ultra-low temperatures, the internal temperature of a cryostat is sensitively affected by even a very small amount of heat generated, this system was assumed to be suitable for specimen temperature measurement. In a future study, silicon diodes that can be attached directly to the specimen will be adopted to monitor the specimen temperature during fatigue and fracture toughness tests. This effort will improve precision in temperature measurements.

2) Effect of Hydrogen Embrittlement on Mechanical Properties

The effect of hydrogen precharging in 304L and 316L stainless steel grades was examined based on their strain-stress curves measured in room-temperature and cryogenic environments, as presented in Figure 5.9. At room temperature, in both 304L and 316L grades, the effect of hydrogen precharging on yield strength was observed, but the difference was insignificant. In the 304L specimen, as the strain exceeded 20%, the strain hardening became weaker compared to the as-received specimen, and the tensile strength and elongation were also reduced after hydrogen charging. It has been reported that when the occurrence of hydrogen-induced cracking leads to a decrease in tensile strength [13]. While a sudden fracture occurred in the preliminary tests, the effect of hydrogen charging on the elongation of the 304L and 316L specimens was rather limited, with a reduction rate of 9.1% and 3.6%, respectively. It was initially expected that there would be no significant effect of hydrogen charging in cryogenic conditions regardless of the material type, but, in reality, there was a difference, for example, accelerated strain hardening. To be more specific, there was no significant difference in yield and tensile strengths between the precharged and as-received specimens, but it was found that strain hardening was accelerated after hydrogen charging. A recent study reported that hydrogen charging induced a phase transformation [31], to which the observed acceleration may be attributed. The elongation was also reduced, but not to a significant extent.

The effect of hydrogen charging on strength and elongation is summarized for quantitative analysis in Table 5.5. Here, the term “ratio” refers to the relative proportion of each mechanical performance index between the hydrogen-charged and as-received specimens. This parameter is used to indicate how large the effect of hydrogen is.



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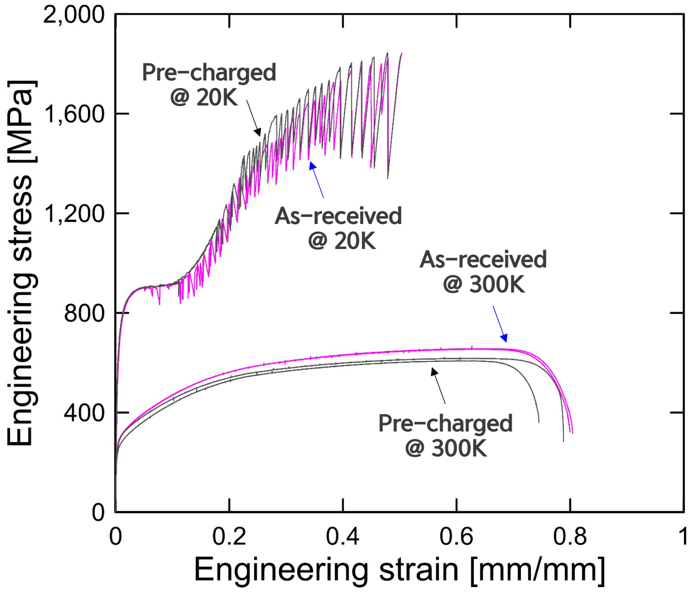


(b)

Figure 5.9 Comparison of stress-strain relationships between the as-received and hydrogen-precharged specimens: (a) 304L stainless steel at 300K and 20K and (b) 316L stainless steel at 300K and 20K

◦ Table 5.5 Mechanical performance with respect to the testing temperature and hydrogen charging conditions

Material	H_2 charging	Testing Temp.	Yield strength (MPa)			Tensile strength (MPa)			Elongation (%)		
			Avg.	Std.	Ratio (%)	Avg.	Std.	Ratio (%)	Avg.	Std.	Ratio (%)
STS 304L	AR	300	299	2.6	99.7	765	11.8	89.1	86.2	3.8	89.5
	PC	300	298	11.3		682	3.5		77.1	0.9	
	AR	20	682	7.1	97.4	1943	9.9	97.4	39.0	1.1	89.6
	PC	20	664	26.9		1893	31.1		34.9	2.8	
STS 316L	AR	300	313	2.1	95.8	661	7.8	93.3	80.0	0.3	95.5
	PC	300	300	19.8		616	8.5		76.4	3.1	
	AR	20	777	18.4	98.8	1824	9.5	97.6	50.4	0.0	103
	PC	20	768	8.5		1780	68.6		51.9	2.6	

* AR: As-recived
* PC: Pre-charged
* Ratio: Relative ratio of each mechanical performance index (including yield strength, tensile strength, and elongation) between the as-received and precharged specimens

3) Morphological Analysis of Fractured Surface

Much research attention has been dedicated to fracture morphology and microstructure analysis to examine the effect of hydrogen embrittlement on the mechanical properties of materials and further identify its root causes. In the present study, the reduction of area, among the most widely used indexes for evaluating the effect of hydrogen on ductility, was measured to determine the effect of hydrogen at different test temperatures, and fracture morphology was analyzed. In doing so, the effect of hydrogen charging was examined. All length measurements and fractography were conducted using Leica's M165C, a stereomicroscope).

The fractured surface of the as-received aluminum alloy specimens before hydrogen charging was observed. The fractured surfaces of each aluminum alloy specimen are presented with respect to the test temperature in Figure 5.10. The images on the left column were photographed from the direction perpendicular to the fractured surface, while those on the right column are side-view images. In both aluminum alloy specimens, wrinkles aligned with the loading direction were observed near the fractured surface. At 300K, wrinkles were localized near the fractured surface, but at 20K, wrinkles were rather distributed along the specimen length due to increased elongation. A sudden cross-sectional area reduction was observed near the fractured surface in both aluminum alloy tensile specimens tested at room temperature. This was consistent with the results discussed above that at room temperature, the ultimate tensile strength was reached earlier, followed by a longer necking region. At 20K, there was no significant cross-sectional area change near the fractured surface. This was attributed to the fact that plastic deformation occurred along the entire specimen length until the tensile strength was reached, and the subsequent necking region was short, within which the cross-sectional area may be reduced.

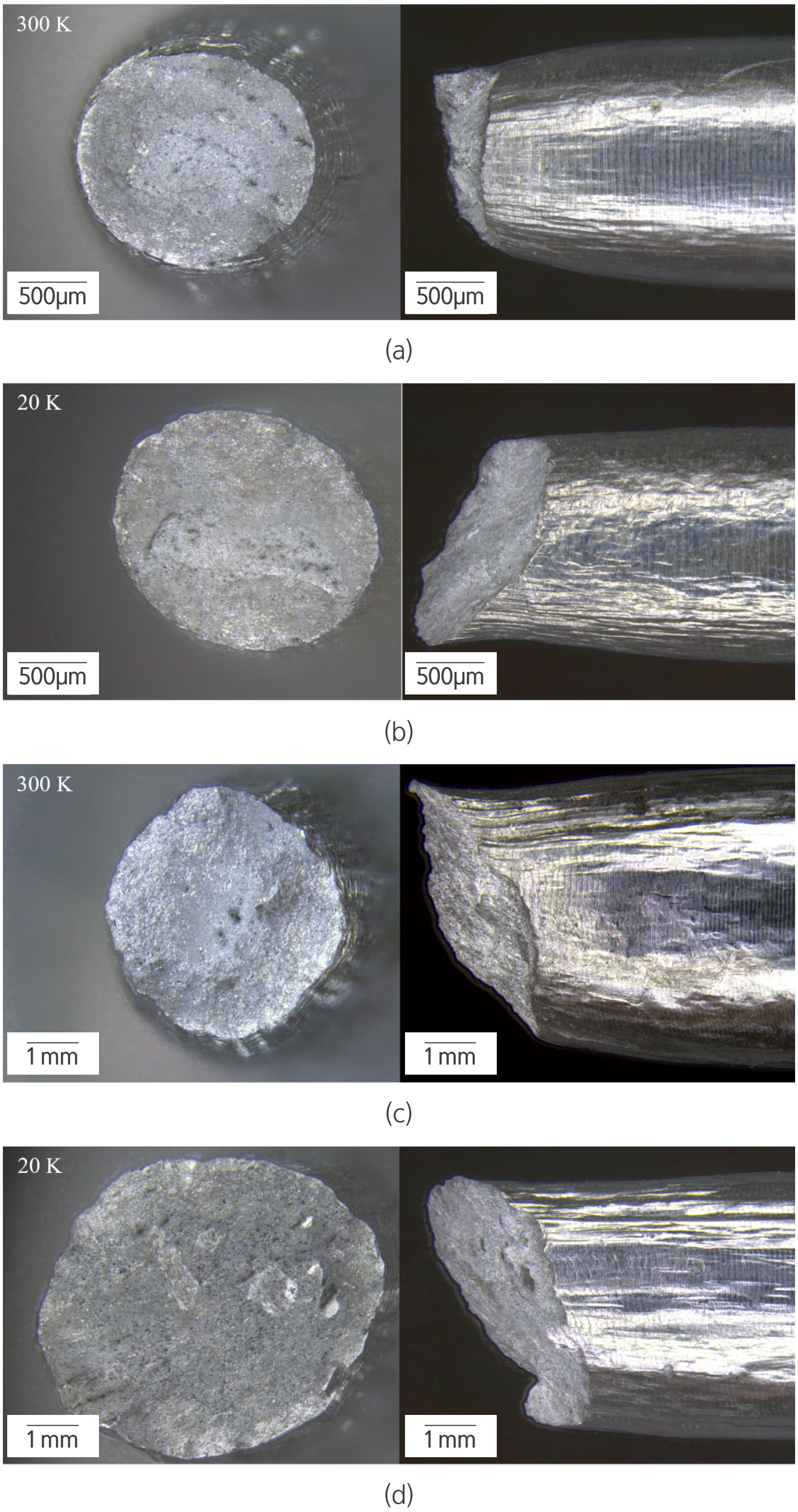


Figure 5.10 Fractured morphologies of the aluminum alloy tensile specimens:
Al 5083-H112 (a) 300K and (b) 20K and Al 6061-T6 (c) 300K and (d) 20K

The reduction of area (RA) was defined as follows to quantitatively evaluate the degree of cross-sectional area reduction after the fracture of each specimen.

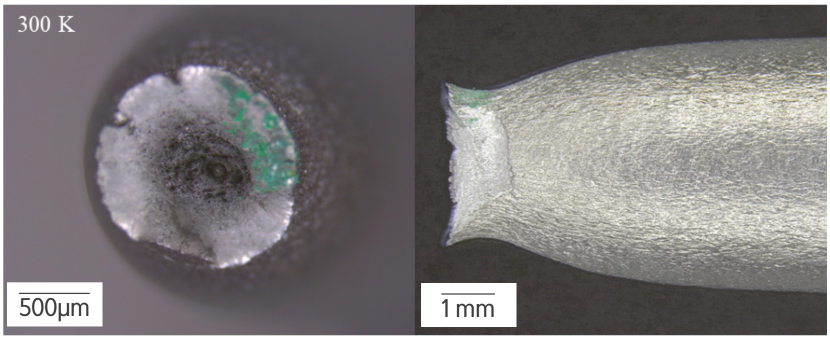
$$RA = \frac{A_0 - A_f}{A_0} \times 100(\%)$$

Here, A_0 and A_f are the cross-sectional area of the specimen before and after tensile testing, respectively. The RA of 5083-H112 and 6061-T6, aluminum alloys, was 53.6% and 43.0% at 300K and 34.6% and 23.5% at 20K, respectively. The RA values of the two aluminum alloy grades measured at 20K accounted for 64.6% and 54.6% of those measured at 300K, respectively.

It was previously stated that the RA was adopted in the present study because it was considered one of the most widely used indexes for evaluating ductility. That said, however, this approach may mislead if it is applied to all material types. Based only on the fact that the RA of the aluminum alloy tensile specimens fractured in a cryogenic environment was found to be significantly reduced, these aluminum alloys might be deemed unsuitable because they were susceptible to embrittlement at low temperatures. In reality, however, plastic deformation occurred along the entire length of the specimen, and thus the elongation was even greater than that measured at room temperature (refer to Table 5.4).

Changes in the morphology of the fractured surface of the 304L and 316L stainless steel specimens after hydrogen charging at 300K and 20K are presented in Figure 5.11 and Figure 5.12, respectively. In both stainless steel specimens before hydrogen charging, the RA sharply increased as it moved toward the fractured surface at 300K; a typical cup-cone shape was observed. The RA was found to be 78.3% for 304L and 84.5% for 316L. At the center of the fracture surface, dimples were observed.

Distinctive differences were found in both stainless steel specimens after hydrogen charging. First of all, cracks perpendicular to the tensile loading direction were observed along the entire length of the specimen. Such cracks are typically found in hydrogen-charged specimens [13,21]. This type of cracking is initiated as plastic deformation starts, followed by crack growth as the elongation increases. The reduction in the effective cross-sectional area caused by cracking was considered to lead to a decrease in the flow stress after yielding. After hydrogen charging, the RA near the fractured surface also decreased. In the 304L and 316L stainless steel specimens, the RA after hydrogen charging was 66.4% and 71.4%, which accounted for 84.8% and 89.0% of that measured before hydrogen charging, respectively. On the fractured surface, a brittle fracture morphology was found. In the 304L stainless steel specimen, there were clear traces of brittle fracture around the edge of the fractured surface. The 316L stainless steel specimen exhibited a relatively smaller brittle fracture area. Brittle fracture regions are typically observed in hydrogen-precharged specimens. Koide et al. (2015) performed tensile tests on austenitic stainless-steel alloys in a gaseous hydrogen atmosphere at a pressure level of 1 bar, reporting that a ductile–brittle fracture surface was observed, similar to that observed in the present study [32]. Michler et al. (2015) conducted tensile tests in a 10-bar hydrogen atmosphere at 223 K and reported that a residual fracture area was observed [14]. On the fractured surface, some traces of brittle fracture were found.



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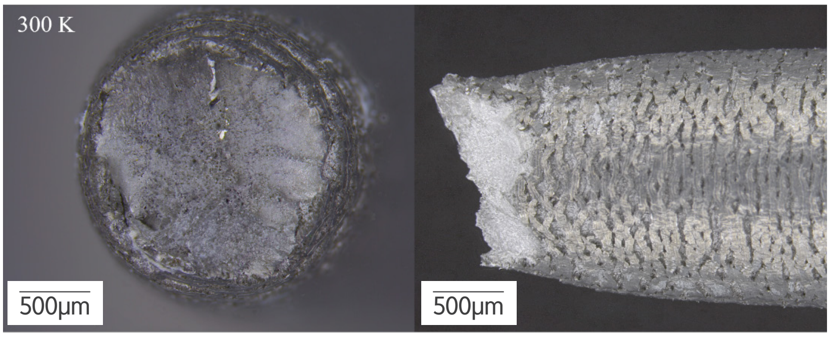

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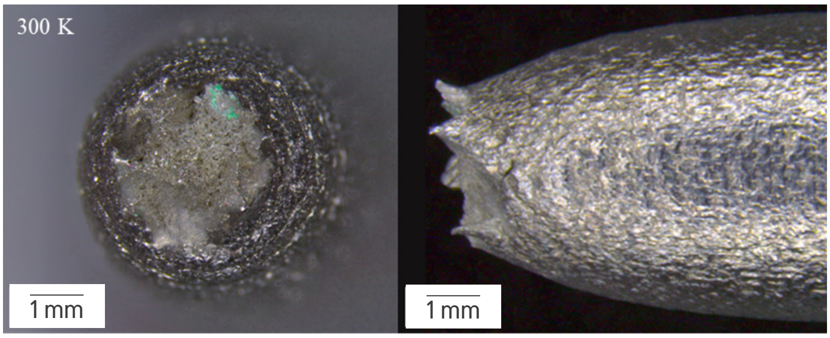

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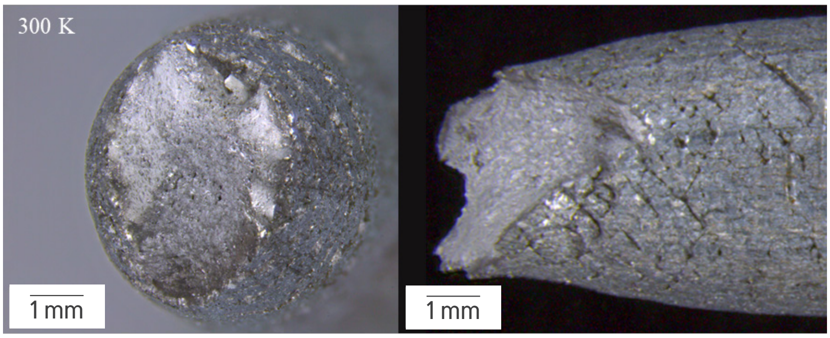
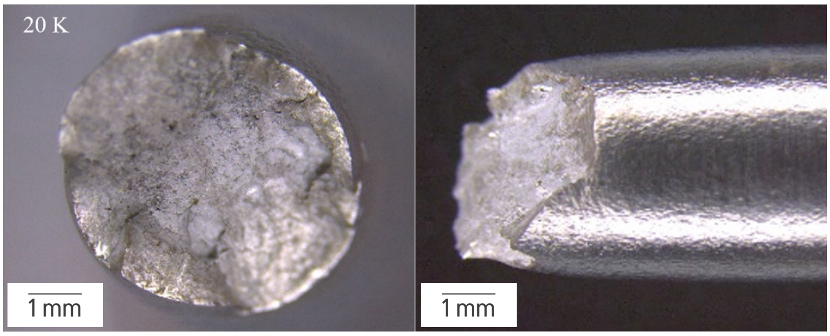


(d)

Figure 5.11 Fracture morphology of stainless steel specimens at 300K: (a) As-received 304L, (b) Hydrogen-precharged 304L, (c) As-received 316L, and (d) Hydrogen-precharged 316L



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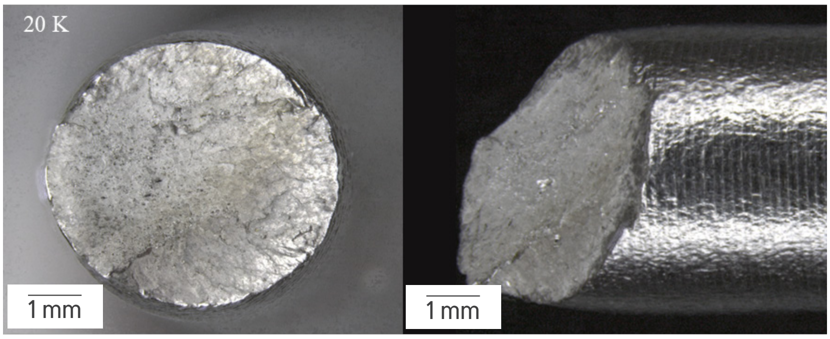

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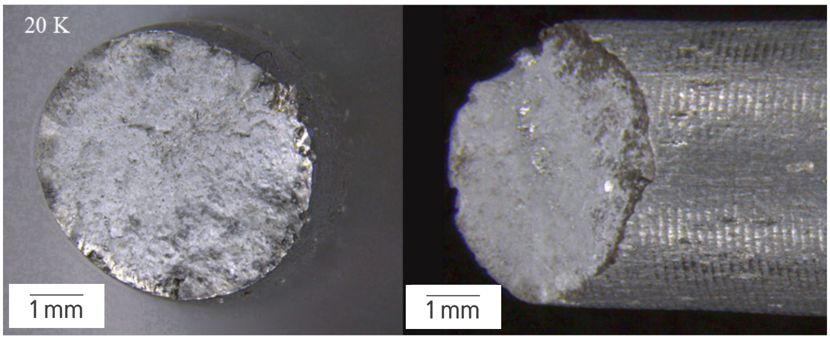

(d)

Figure 5.12 Fracture morphology of stainless-steel specimens at 20K: (a) As-received 304L, (b) Hydrogen-precharged 304L, (c) As-received 316L, and (d) Hydrogen-precharged 316L

At 20K, no significant difference was found before and after hydrogen charging or between the material types. There was no sharp cross-sectional area reduction near the fractured surface, and an oblique fracture plane was formed. In addition, secondary cracks occurred in all specimens. Cross-sectional shrinkage in the form of localized necking was observed throughout the entire specimen, i.e., typical discontinuous yielding observed at ultra-low temperatures. In a cryogenic environment, the reduction of area (RA) is used as a parameter to quantitively evaluate changes in the cross-sectional area caused by hydrogen. The effect of a cross-sectional area reduction by hydrogen is then evaluated using the relative reduction of area (RRA). The RRA is defined below.

$$RRA = \frac{RA_{H2}}{RA_{air}} \times 100(\%)$$

RA_{H2} refers to the reduction of area in a hydrogen atmosphere, and RA_{air} refers to that measured in the air as a comparison group. Here, the comparison group refers to tensile test measurements that were conducted in a helium or atmospheric environment at the same temperature as the control group. This means that the smaller the RRA of a material is, the more its mechanical properties are degraded by hydrogen embrittlement. The RRA values of the aluminum alloys and austenitic stainless steel alloys for each test condition are summarized in Table 5.6. If it is assumed that hydrogen has no effect in a cryogenic environment, the RA of each specimen is likely to remain the same before and after hydrogen charging. This means that the RRA would be below 100% at room temperature and close to 100% in a cryogenic environment. In the present study, however, the RRA values measured in a cryogenic environment were comparable to those measured at room temperature, indicating that even at ultra-low temperatures, the mechanical properties of the hydrogen-charged specimens were affected by hydrogen.

◦ Table 5.6 Macroscopic analysis with respect to the testing temperature and hydrogen charging conditions

Material	Testing Temp. (K)	Hydrogen charging	Reduction of area (%)		RRA (%)
			Avg.	Std.	Avg.
STS 304L	300	As-received	78.3	0.3	84.8
		Pre-charged	66.4	1.8	
	20	As-received	47.2	1.2	89.0
		Pre-charged	42.0	4.6	
STS 316L	300	As-received	84.5	1.7	84.6
		Pre-charged	71.4	0.9	
	20	As-received	38.6	0.5	83.8
		Pre-charged	32.4	2.3	
Al 5083-H112	300	As-received	53.6	1.7	N.A.
	20		34.6	0.0	
Al 6061-T6	300	As-received	43.0	1.7	N.A.
	20		23.7	1.3	

5. Conclusions and Discussion

This research report analyzed the safety standards and material compatibility test methods currently applied in a wide range of hydrogen storage applications and further proposed a test procedure for evaluating the compatibility of materials for liquid hydrogen storage for marine use. Numerous domestic and international safety standards were analyzed to identity risk factors that may arise from hydrogen embrittlement and cryogenic conditions and further review measures to reduce them. Further analysis was also performed on some of the material compatibility test methods that were currently widely used. Based on this analysis, the IGC/IGF codes were reviewed for the need for revision to implement the effective storage and utilization of liquid hydrogen as cargo or fuel.

Austenitic stainless steel is highly susceptible to hydrogen embrittlement at a gaseous hydrogen pressure of 1 bar or more. Despite that, the relationship between the pressure of gaseous hydrogen and the resultant ductility reduction by hydrogen embrittlement is not linear, and thus metallic materials intended for use in low-pressure gaseous hydrogen atmospheres (10 bar or less) or liquid hydrogen environments do not necessarily have to be as resistant to hydrogen as those used for high-pressure gaseous hydrogen storage. This also implies that a broader range of materials may be used for environmental conditions where liquid hydrogen is stored and utilized. However, more clarification needs to be provided regarding this issue. The major prerequisites for the establishment of the material compatibility test procedure for liquid hydrogen atmospheres are as follows.

1) Hydrogen precharging to simulate a low-pressure gaseous hydrogen atmosphere

Many material compatibility assessments require performing tests in a high-purity, high-pressure gaseous hydrogen environment. This is because these test methods concern the performance of high-pressure hydrogen storage containers and other related facilities. The establishment of infrastructure for simulating a gaseous hydrogen atmosphere is conducted only by a handful of research institutions for safety purposes.

Thus, various test methods have been continuously proposed to replace the existing assessment procedures for such infrastructure, which have proved difficult to apply to a wide range of applications. Ogata (2010) attempted to establish a gaseous hydrogen atmosphere with a pressure level of 10 MPa by charging a small amount of gaseous hydrogen (100 cc or less) into the internal pores of hollow specimens for tensile testing. In general, an autoclave[1] is widely used to create a high-pressure gaseous hydrogen environment, but this system requires large amounts of hydrogen and high-cost systems for sealing purposes because this process involves tensile specimens and various test jigs. Disk tests or small punch tests are specified in ISO 11114-4. These test methods are not effective in evaluating

[1] It refers to a heat-resistant, pressure-resistant container in which synthesis, decomposition, sublimation, extrac-tion, and other chemical treatments can be performed under high-temperature, high-pressure conditions.

fracture toughness and crack propagation. Small punch tests, in particular, require very thin test specimens, and preparing this type of specimen is likely to affect the properties of the target material.

The limitations of the alternative test methods may be compensated for by the application of hydrogen precharging for test specimens. Most austenitic stainless steel alloys and carbon steel grades are susceptible to embrittlement in a gaseous hydrogen atmosphere. Similar results or trends may be achieved using hydrogen precharging. The application of electrochemical precharging under certain conditions is considered sufficient if one intends to simulate a gaseous hydrogen atmosphere with a pressure level of 10 bar or less. In fact, thermal hydrogen charging is capable of simulating an environment in which hydrogen is uniformly distributed throughout the material matrix; however, hydrogen infiltration may be limited only to the surface layer of the specimen in materials with low hydrogen diffusivity, such as austenitic stainless steel alloys unless specific constraints are imposed with regard to the potential difference, the temperature of electrolyte solutions, and the dimensions of specimens. On that note, the hydrogen precharging test methods provided in ISO 16573-2:2022, which were mutatis mutandis applied in this study, need to be further improved to make them more universal and usable.

2) Establishment of Acceptance Criteria for Each Test Item

The material compatibility test method for liquid hydrogen atmospheres proposed in this research report was designed to evaluate the degree of embrittlement while considering the effect of both hydrogen and cryogenic conditions. If acceptance criteria are set to allow only insignificant levels of material degradation, only certain alloy grades with high Ni content or those that do not undergo a phase transformation into martensite, which is a phase susceptible to hydrogen embrittlement, such as austenitic stainless steel alloys, will be considered applicable. 304 stainless steel is known to be affected by hydrogen embrittlement even at a hydrogen partial pressure of 1 bar or less at room temperature. A previous study reported that a more conservative approach was required to eliminate the effect of hydrogen embrittlement, i.e., by setting the hydrogen partial pressure to 0.5 bar or less [32].

Slow strain rate testing (SSRT) is used for evaluating hydrogen sensitivity, with the relative reduction of area (RRA) in air and hydrogen atmospheres set as the reference index. The acceptance criteria proposed in this report require the RRA to be at least 0.5. This requirement was made based on the observations that in low-pressure gaseous hydrogen atmospheres, the cross-sectional area reduction of even 304L stainless steel easily reached 0.5, but as a matter of fact, it was not accompanied by a significant reduction in ductility. When stainless steel grades with high Ni content were exposed to a high-pressure gaseous hydrogen atmosphere, the RRA was found to be around 0.5, as long as their tensile strength was equivalent or similar to that of the comparison group [13]. When 304 stainless steel with relatively low Ni content (Ni content: 8.1%, Nieq: 21.6%, and solution heat treatment performed) was exposed to a hydrogen partial pressure of 1–3 bar, the RRA was also found to be close to 0.5. The figure gradually decreased as the partial pressure of hydrogen increased. Ogata (2018) attempted to charge gaseous hydrogen with a pressure of 10 bar into 304L stainless steel tensile specimens (Ni content: 9.42% and solution heat treatment performed) and perform tensile tests on them at 190K. The study reported that the maximum load reduction was about 14%, and the corresponding RRA was 0.5 [33].

As it currently stands, the best approach to establishing acceptance criteria for fracture toughness evaluation would be to identify temperature ranges where embrittlement occurs while considering the effect of both hydrogen and cryogenic conditions and further determine the condition under which the reduction of fracture toughness would not be significant compared to when tested in a non-hydrogen atmosphere. Going forward, it will be possible to provide further quantitative evidence as research data accumulate.

From a design perspective, further research needs to be focused on fatigue cracking and fracture toughness to properly evaluate the fatigue life of the system. Given that crack development and growth are directly related to the service life of pressure vessels equipped in ships, sufficient research data must be available to ensure flexibility in pressure vessel design. Unfortunately, however, the currently available data is limited to just a few material types.

The Korean Register of Shipping, the Korea Institute of Machinery and Materials (KIMM), and Pusan National University's Hydrogen Ship Technology Center jointly executed a project titled the "Development of Safety Standards for Hydrogen Storage Containers and Fuel Feeding Systems for Marine Applications" project (organized by the Ministry of Oceans and Fisheries) to establish a test facility for cryogenic (20K) liquid hydrogen environments. The researchers have been working to employ electrochemical hydrogen charging to simulate a cryogenic low-pressure gaseous hydrogen atmosphere, thereby establishing a more reasonable and safer material compatibility test procedure for that purpose. A future study will focus on using this facility to generate quality data that can be used in the ASME code-based design of pressure vessels while extending its applicability to more material types, thereby contributing to commercializing liquified hydrogen storage systems for ships and achieving the carbon neutrality goal of the maritime industry.

Appendix A. Analysis of Domestic and International Safety Regulations on Hydrogen

A.1 Safety Standard Type 1: General Requirements for System Safety

ISO/TR 15916 (Basic considerations for the safety of hydrogen systems) is one of the most fundamental safety standards for systems that handle hydrogen in a liquid or gaseous form [34]. The standard defines basic safety considerations and risks. The interim guidelines on hydrogen carriers and hydrogen-fueled ships currently under discussion by the Sub-committee on Carriage of Cargoes and Containers (CCC) of the International Maritime Organization (IMO) have also been developed and reviewed with reference to this standard. This section analyzes other safety standards for pressure vessels, cylinders, and piping systems for liquid and gaseous hydrogen storage, similar to ISO/TR 15916, especially with regard to 1) Material restrictions and 2) Material recommendations for different temperatures and hydrogen atmospheres.

A.1.1 ISO/TR 15916

ISO/TR 15916 defines different risk factors related to the hydrogen system. The standard specifies that among various risk factors, low temperature and hydrogen embrittlement may pose significant damage, but these risk factors can also be addressed by proper design and material selection. Hydrogen attack mainly occurs at temperatures higher than 200℃, and thus this phenomenon is not considered in the design of liquid hydrogen storage systems. The standard states that the following factors must be considered for the selection of materials suitable for a given hydrogen application and exposure condition.

- Temperature, hydrogen embrittlement, permeability, porosity, and compatibility between different metals

Here, the term "temperature" mainly refers to low-temperature conditions. Given that most materials tend to shrink, and their ductility and specific heat are reduced when cooled down to the temperature of liquid hydrogen, sufficient toughness must be ensured at low temperatures. Charpy impact tests are among the simplest test methods for low-temperature toughness. This test aims to confirm that the ductile-to-brittle transition temperature (DBTT) of the tested material is lower than the target temperature. Here, the temperature difference between the air and liquid hydrogen is as large as 280K, and thus any heat stress that may arise from thermal expansion and contraction must also be considered. Thermal shrinkage resulting from the temperature difference between atmospheric and cryogenic conditions is known to be 0.3% for steel alloys and 0.4% or more for aluminum.

Measures to address hydrogen embrittlement may be divided into 1) Those focused on design and structural aspects and 2) Others focused on material characteristics, as follows.

1) Design and structural aspects

- Reduction of operating stress levels
- Minimization of low-temperature plastic deformation during cold working
- Avoidance of repetitive loading to prevent fatigue cracks

2) Material aspects

- Constraints on the hardiness and strength of metallic materials
- Minimization of residual stress
- Application of materials with excellent resistance to hydrogen, e.g., austenitic stainless steel
- Assessments based on ISO 11114-4 in material selection

Appendix C of the safety standard provides a table that categorizes materials according to their sensitivity to hydrogen embrittlement. The major details are summarized in Table A.1 and Table A.2, which are also consistent with the content described in ASME B31.12 and ANSI/AIAA G-095A-2017.

◦ Table A.1 Susceptibility of hydrogen embrittlement of metal (ISO/TR 15916)

Category	Material	Sensitivity of Hydrogen embrittlement		
		Extreme	Moderate/small	Negligible
Al alloy	Al 6061-T6			√
Fe	Steel	√		
	Carbon steel		√	
Stainless steel	A286			√
	304ELC		√	
	310			√
	316			√
	410	√		
Ti	Ti		√	

◦ Table A.2 Material selection in accordance with hydrogen environment

Material	GH_2	LH_2	Mark
Aluminum and Al alloy	○	○	
Copper and Cu alloy	○	○	
Gray, ductile, or cast iron	ʹ	ʹ	Not permitted for hydrogen service
Ni and its alloy (such as Inconel™, Monel™ or the equivalent)	△	△	Susceptible to hydrogen embrittlement
Austenitic stainless (Ni > 7%, 304(L), 308, 316, 321, 347 STS)	○	○	Some make martensitic conversion if stressed above yield point at low temperature
Carbon steel	△	ʹ	Too brittle for cryogenic service
Low-alloy steel	△	ʹ	Too brittle for cryogenic service
Martensitic stainless (such as 410, 440C)	△	△	Susceptible to hydrogen embrittlement
Nickel steels (such as 2.25, 3.5, 5, 9% Ni)	△	ʹ	Ductility lost at LH2 temperature
Ti and its alloy	△	△	Susceptible to hydrogen embrittlement

○: suitable for use, △: material compatibility evaluation should be performed,

ʹ : Not suitable for use

A.1.2 KGS Code (Korea Gas Safety Code)

The Korea Gas Safety Code (KGS Code) presents a systematic, detailed description of the technical matters specified in gas-related laws and regulations based on specific criteria, especially with respect to facility, technology, and inspection aspects. This technical standard was approved by the Ministry of Trade, Industry and Energy upon deliberation and resolution by the Gas Technical Standard Committee. This standard was enacted to streamline the existing complex procedure for legislative enactment and revision, thereby ensuring the safety of the general public in the use of gas. This code is applied based on the three acts on gas (High-Pressure Gas Safety Control Act, Safety Control and Business of Liquefied Petroleum Gas Act, and Urban Gas Business Act), along with the Hydrogen Economy Promotion and Hydrogen Safety Management Act. This code defines specific restrictions and technical/facility standards that must be applied in the manufacturing of vessels (containers, refrigerators, and other specific facilities), gas consumers, and other gas-related equipment or in the operation of facilities that treat gases (charging, producing, selling, supplying, storage, and utilization). Liquid hydrogen is related to the part of the KGS Code regarding the use of hydrogen and high-pressure gases. The following three specific codes were found to provide detailed standards for materials considering cryogenic conditions (with a liquefaction temperature of -253℃) and fuel characteristics (hydrogen and high-pressure gases).

- KGS AC111 2021 (Code for Facilities, Technology and Inspection for Manufacturing of High-Pressure Gas Storage Tanks and Pressure Vessels)
- KGS AC213 2021 (Code for Facilities, Technology and Inspection for Manufacturing of Cryogenic Cylinders)
- KGS FU671 2021 (Facility/Technical/Inspection Code for Use of Hydrogen Gases)

Most details of the KGS Code are referenced to the ASME Code. The major details and characteristics of each code, except for structure-related descriptions (structure thickness estimation, supports, etc.), are as follows.

① Major Details of KGS AC111: 2021

KGS AC111 applies to the facilities, technology, and inspection that are employed for the manufacturing of storage tanks and pressure vessels, except for LNG storage tanks. The term “pressure vessel” refers to a container with a design pressure of 2 bar or more for liquified gas and 10 bar or more for compressed gas at 35℃. Hydrogen embrittlement resistance tests[1] may be required for pressure vessels operated at a temperature of 95℃ or less if the partial pressure of hydrogen with respect to the design pressure is 52 bar or more[2]. This threshold may vary depending on the material type. This hydrogen embrittlement resistance assessment is performed by a series of tests, including SSRT, fracture tests, fatigue fracture tests, and fatigue tests, to determine the service life of materials.

The upper and lower limits of temperatures and tensile stress for materials are estimated (in the same manner as specified in ASME BPVC) based on the maximum allowable tensile stress levels for each temperature range specified in Appendix A (Maximum Allowable Tensile Stress for Steel Materials). Appendix B defines suitable impact test

[1] Interpreted as having the same meaning as material compatibility assessments for hydrogen atmospheres

[2] This figure is the lowest hydrogen partial pressure, and this threshold may vary depending on the material con-ditions and the presence of welded joints.

methods for each material type while also considering the test temperature and specimen thickness, but the test temperature range is defined to be up to -196℃.

② Major Details of KGS AC213: 2021

KGS AC213 applies to the facilities, technology, and inspection that are employed for the manufacturing of vessels intended for charging liquified gas with a temperature of -50℃; however, a hydrogen atmosphere is not considered. Here, allowed materials will be limited to austenitic stainless steel alloys or aluminum alloys (5052, 5083) for safety purposes.

The material acceptance criteria for austenitic stainless steel include elongation-tensile strength measurements and squeeze test results. Tensile tests are performed according to KS B 0802 (Method of Tensile Test for Metallic Materials), and the elongation of the tested material must be in the range of 15-30%. Squeeze tests are performed on vessels after specific heat treatments. At the onset of cracking, the distance between the two wedges must not be more than eight times the thickness of the vessel shell.

Among aluminum alloys, 5082 and 5083 grades must have a tensile strength of at least 176-265 N/mm^2 with an elongation of at least 15-18%. In squeeze tests on these alloys, at the onset of cracking, the distance between the two wedges must not be more than 8.7 times the thickness of the vessel shell, similar to the cases of austenitic stainless steel.

Appendix A also presents material characteristic curves that can be used to estimate the properties of a cylindrical or spherical shell under external force, especially with regard to various materials, including austenitic stainless steel and aluminum alloys.

Materials for welded joints must be verified for compatibility in terms of the following items.

- Tensile tests for welded seams: In terms of tensile strength/yield strength
- Bending tests for the inside of the welded joint: In terms of the amount of cracking
- Bending tests for the side of the welded joint: In terms of the amount of cracking
- Bending tests for the backside of the welded joint: In terms of the amount of cracking
- Tensile tests for the used weld metal: In terms of tensile strength/yield strength, with an elongation of 22% or more
- Impact tests for welded joints (applied only to stainless steel): In terms of impact absorption energy, measured by Charpy impact tests at -150℃ or less (with an impact absorption energy of at least 20 J/cm^2 and 30 J/cm^2 or more on average

③ Major Details of KGS FU671: 2021

KGS FU 671 applies to the facilities, technology, and inspection of systems that use hydrogen as fuel. These systems include hydrogen facilities, including those used for hydrogen production and storage, as well as other gases and supplies. Applicable materials include those with specific mechanical properties and chemical compositions that suit the nature, temperature, and pressure of hydrogen.

If the hydrogen pressure is 10 bar or more, any material used should be regarded as a material for high-pressure piping systems. Thus, any materials with mechanical properties and chemical compositions equivalent or superior to those required for such material may be selected and used. If the hydrogen pressure is 10 bar or less, any material used should be regarded as a material for low-pressure piping systems. Thus, any materials that fulfill the requirements specified in KS D 3631 (Carbon Steel Pipes for Fuel Gas Piping) may be selected and used. The chemical composition requirements are presented in Table A.3, and the requirements for mechanical properties are omitted here because they vary depending on the material thickness. The material specifications corresponding to materials for high-pressure and low-pressure piping systems are specified in the KGS Code.

◦ Table A.3 Chemical composition of carbon steel for low pressure piping under 10 bar according to KS D 3631

Code	Chemical composition (%)				
	C	Si	Mn	P	S
KS D 3631	< 0.30	< 0.35	< 0.95	< 0.040	< 0.035

Any material that meets its material specifications may not be used beyond the temperature range that corresponds to the allowable stress of the material, and Appendix A of KGS AC111 may be referenced. Other materials that are equivalent or superior must meet the requirements for Charpy impact tests at the design temperature. The minimum allowable absorption energy may vary depending on the tensile strength and thickness of the parent material. There are restrictions on the use of materials in certain pressure and temperature ranges, and some of the details are summarized in Table A.4.

- Carbon steel: Type 1 A, Type 2 A, and Type 3 A of KS D 3503 (Rolled Steel Materials for General Structures) and KS D 3515 (Rolled Steels for Welded Structures)
- Cast iron: Type 3, Type 4, and Type 5 of SPS-KFCA-D4302-5016 (Spheroidal Graphite Iron Castings) and GCMB 30-6, white malleable iron castings, and pearlite malleable iron castings of SPS-KOSA0179 -ISO5922-5244 (Malleable Iron Castings)

◦ Table A.4 Restriction of piping material depending on pressure and temperature

Material type	Design Pressure	Design Temp.	System part
Carbon steel	> 16 bar	-	Inner pressure
	> 10 bar	-	Pipe and Pipe joint
	-	-	Inner pressure & thickness > 16mm
Cast iron	> 2 bar	-	Pipe
	-	< 0℃ & > 250℃	Pipe

A.1.3 CGA standard

The Compressed Gas Association (CGA) works for the enactment and dissemination of technical safety standards for the manufacturing, storage, transport, an supply of compressed, liquefied, and cryogenic gases while engaging in R&D activities to improve the quality of compressed gases while developing relevant technologies. As it currently stands, researchers in private-sector businesses, such as the American Society of Mechanical Engineers (ASME) and the American Petroleum Institute (API), are in charge of gas safety management based on collaboration with universities and government agencies. The following parts of the CGA Standard provide important safety standards for liquid hydrogen storage systems.

- CGA H-3 (2019) Standard for Cryogenic Hydrogen Storage
- CGA H-5 (2020) Standard for Bulk Hydrogen Supply Systems
- CGA G-5.4 (2019) Standard for Hydrogen Piping System at User Locations
- CGA G-5.6 (2005) Hydrogen Pipeline Systems

① Major Details of CGA H-3 (2019)

CGA H-3 applies to liquid hydrogen storage vessels (with a design temperature range between -253 and 38℃) with a gross volume of 3.8-94.6m^3 and a maximum allowable working pressure (MAWP) of 12.1 bar or less. Aluminum alloys are not recommended as materials for the inner vessel because their thermal conductivity and coefficient of thermal expansion are significantly larger than those of stainless steel. Similarly, 9% nickel steel alloys are not considered suitable for the inner vessel due to their low ductility.

Only full penetration butt welding may be applied to the inner vessel, and any corrosion allowance is not considered; thus, 300-series austenitic stainless steel alloys are mainly used for the inner vessel according to the ASME Boiler and Pressure Vessel Code. Austenitic stainless steel alloys are required to be subjected to solution heat treatment to reduce the generation of residual stress during cold working.

Steel may be used as a material for the outer jacket. Material selection and design for any pipes connected to pressure vessels are conducted according to ASME B31.12(Hydrogen Piping and Pipelines). There are many measures available to minimize the occurrence of hydrogen embrittlement in piping systems.

- All annular-space pipelines must be composed of seamless tubes or pipes made of austenitic stainless steel. Welding on tube or pipe connections should be avoided as much as possible, and if unavoidable, butt welding should be used.
- For 304 stainless steel, it must be ensured that any stress that exceeds 20% of its tensile strength is not generated. Here, any stress generated during cold working should also be counted in the estimation process.
- 316 stainless steel is a material with excellent resistance to hydrogen embrittlement.

② Major Details of CGA H-5 (2020)

CGA H-5 applies to liquid and gaseous hydrogen fuel supply systems with a capacity of 141.6 m^3 or more for gaseous hydrogen and 150 L or more for liquid hydrogen. The maximum allowable working pressure is 1034 bar.

Liquid hydrogen is a cryogenic liquid, and high-strength steel is generally susceptible to hydrogen embrittlement, and thus low-strength carbon steel is more suitable. Hydrogen embrittlement causes vessels to be damaged even under a stress that is significantly lower than the yield stress of the material used. Accordingly, the risk of hydrogen embrittlement must be thoroughly reviewed, especially in welded areas. Low-strength carbon steel is hardly affected by hydrogen in a gaseous hydrogen atmosphere (with a pressure of 10 bar or less) at room temperature. However, when the hydrogen pressure is 25 bar or more, the effect of hydrogen embrittlement is pronounced, and thus the use of each material may be limited depending on the given pressure conditions.

Drip trays for liquid hydrogen storage vessels are supposed to collect the condensed air. Therefore, they must be installed under pipelines. Drip trays are mainly made of aluminum or stainless steel alloys.

③ Major Details of CGA G-5.4 (2019)

CGA G-5.4 applies to pipe systems for liquid or gaseous hydrogen, from the pipes of the hydrogen supply system (including hydrogen valves) to the pipes of other systems in which hydrogen is consumed. The pipe system must be made of materials that comply with ASME B31.12. If the design temperature is below -29℃, any materials that meet the minimum temperature requirements for each material specified in ASME B31.12 should be selected. If not applicable, the Charpy impact test requirements must be satisfied.

316 and 316L stainless steel alloys may be used in both high-pressure gaseous hydrogen and liquid hydrogen atmospheres. Here, the high-pressure hydrogen is defined as having a pressure of 20,680 kPa (abt. 200 bar). 316 and 316L stainless steel alloys are generally preferred over 304L and 321 alloys. It is recommended that stainless steel alloys be subjected to solution heat treatment. In a high-pressure hydrogen atmosphere, seamless pipes and tubes are preferred. Welded pipelines are very susceptible to hydrogen embrittlement unless they are properly annealed.

④ Major Details of CGA G-5.6 (2005)

CGA G-5.6 applies to metallic piping systems that deliver pure hydrogen and hydrogen mixtures with a working temperature range between -40 and 175℃ and a gaseous hydrogen pressure of 10-210 bar. If the partial pressure of gaseous hydrogen is 2 bar or more, stainless steel is recommended.

According to the guidelines for preventing hydrogen embrittlement, metallic materials may be used only to the extent that the upper limits for hardness and tensile strength are not exceeded, and those with a fine and uniform microstructure should be selected to ensure that the surface of all parts is free from defects. It is necessary to limit the stress to a certain level (whichever is lower between 30 % of the yield strength and 20% of the tensile strength) for any materials other than austenitic stainless steel or carbon steel grades that are likely to fail to meet the requirements specified above. Sufficient toughness is also required, especially when the gaseous hydrogen pressure is 50 bar or more.

Safety precautions when applying stainless steel to the hydrogen atmosphere (regarding deformation-induced transformation) are as follows.

- Ensure that the austenite stability factor has a positive value (typically 300-series stainless steel alloys with a Ni content of 10.5% or more).
- Metallic materials with a high austenite stability factor (or with a high nickel equivalent) should be selected as much as possible.
- The use of stainless steel grades with a metastable austenite phase, such as 201, 301, 302, 304, 304L, and 321, must be avoided in a high-pressure hydrogen atmosphere.
- Ferritic stainless steel, martensitic stainless steel, duplex stainless steel, and precipitation-hardened stainless steel may only be used for parts with low operating stress.

A.1.4 ISO 19881

ISO 19881:2018 (Gaseous hydrogen — Land vehicle fuel containers) specifies the material, design, and manufacturing of and test methods for gaseous hydrogen storage vessels for land-use transportation equipment. This standard applies to vessels with a nominal working pressure of 250, 350, 500, and 700 bar at 15℃, and the applicable gas temperature range within the vessel is -40℃ - 85℃, which is the same temperature condition as applied to hydrogen vehicles.

The material requirements are mainly evaluated based on hydrogen compatibility and mechanical performance assessments. Hydrogen compatibility assessments considering hydrogen embrittlement and hydrogen fatigue may be performed by referring to the documents regarding hydrogen compatibility provided in ISO 11114, Sandia National Lab., as well as the acceptance criteria provided in AIAA, ANSI/CSA CHMC 1, ASME B31.12, and SAE J2579. Material characteristics, along with the required performance tests, are presented below.

1) Material characteristics

- Steel: Vessels must be made of aluminum-killed steel with fine grains that is resistant to corrosion, deformation, and degradation when exposed to high-pressure hydrogen.
- The content of additives must be specified, such as carbon, manganese, aluminum, silicon, nickel, chromium, molybdenum, boron, and vanadium.

2) Impact tests

- Applicable to steel structures
- Tests are performed in accordance with ISO 148-1 (Metallic materials - Charpy pendulum impact test - Part 1: Test method) or ASTM E23 (Standard Test Methods for Notched Bar Impact Testing of Metallic Materials).
- The notch is made in the C-L direction (perpendicular to the circumference and along the length direction).
- All impact tests are performed at the lowest test temperature (-40℃).

3) Tensile tests

- Applicable to all metallic materials
- Subject to ASTM E8 (Standard Test Methods for Tension Testing of Metallic Materials), etc.

4) Sustained load cracking tests

- Applicable to aluminum alloys
- Tests are performed in accordance with Appendix B of ISO 7866:2012 (Gas Cylinders–Refillable Seamless Aluminum Alloy Gas Cylinders–Design, Construction and Testing).

5) Corrosion tests

- Applicable to aluminum alloys
- Tests are performed in accordance with Appendix A of ISO 7866:2012 (Gas Cylinders–Refillable Seamless Aluminum Alloy Gas Cylinders–Design, Construction and Testing).

A.1.5 ASME B31.12

In the petroleum refining industry, the design of hydrogen piping systems had been subject to ASME B31.3 (Process Piping) for more than a half-century. However, the ASME determined that it was inappropriate to apply this standard to the design of hydrogen infrastructure and thus issued B31.12 (Hydrogen Piping and Pipelines) of B31.3 (Process Piping), which specified the requirements for the design, manufacturing, operation, and maintenance of piping systems for hydrogen atmospheres, as a separate standard in 2008.

ASME B31.12 applies to pipe systems for gaseous/liquid hydrogen and specifies materials suitable for hydrogen atmospheres. The standard also proposed the material performance factor, an index designed to consider the reduction of mechanical properties in carbon steel and low-alloy steel grades operating under hydrogen embrittlement conditions.

In a hydrogen atmosphere, the bursting strength and toughness of piping materials are known to be reduced by 15% and 30%, respectively, making it difficult to supply hydrogen in a stable manner. B31.12 also attributes this reduction in fracture toughness mainly to hydrogen-induced fatigue crack growth and hydrogen embrittlement.

The requirements for hydrogen piping systems in terms of alloying elements, steel grades, pipe shapes, and working pressure vary due to restrictions resulting from hydrogen embrittlement. Given that alloying elements, such as Mn, S, P, and Cr, tend to improve the hydrogen embrittlement sensitivity of low-alloy steel, both hydrogen embrittlement and hydrogen-induced fatigue cracking become more pronounced as the hydrogen pressure and material strength increase. Accordingly, ASME B31.12 recommends the use of steel pipes while considering their material characteristics. It is also necessary to consider all relevant issues, including hydrogen embrittlement, low-temperature performance degradation, and cryogenic performance degradation.

A.2 Safety Standard Type 2: Material Compatibility Assessment

This section specifies materials that can be applied to specific hydrogen atmospheres, along with their required specifications. Any materials other than the standard materials need to be verified to have resistance to hydrogen embrittlement that is equivalent or superior to that of the standard ones. The next section identifies and analyzes safety standards for evaluating the compatibility of materials used for pressure vessels, cylinders, and piping systems for liquid and gaseous hydrogen storage. For some of the material compatibility test methods, detailed test procedures are proposed, but in most cases, the focus is placed on proposing material screening methods. Thus, it is guided that fatigue tests or fracture toughness tests be subject to established international test standards. Safety standards, material compatibility assessments, and detailed test procedures that are currently widely used are summarized in Table A.5.

◦ Table A.5 Classification of safety standards related to hydrogen storage systems

Classification		List of standards
Basic consideration		ISO/TR 15916 (2015) Basic considerations for the safety of hydrogen systems
		ISO 19881 (2018) Gaseous hydrogen — Land vehicle fuel containers
		ISO 11114-1 (2020) Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 1: Metallic materials
		CGA H-3 (2019) Standard for cryogenic hydrogen storage CGA H-5 (2020) Standard for bulk hydrogen supply systems CGA G-5.4 (2019) Standard for hydrogen piping system at user locations CGA G-5.6 (2005) Hydrogen Pipeline Systems
		KGS AC111 (2021) 고압가스용 저장탱크 및 압력용기 제조의 시설·기술·검사 기준 KGS AC213 (2021) 초저온가스용 용기 제조의 시설·기술·검사 기준 KGS FU671 (2021) 수소연료사용시설의 시설 기술 검사 기준
Material compatibility		ANSI/CSA CHMC1-2014 (R2018) Test Methods For Evaluating Material Compatibility In Compressed hydrogen Applications - Metals
		ASME BPVC Section VIII Division 3 KD-10 Special Requirements for Vessels in Hydrogen Service
		SAE J2579 (2018) Standard for Fuel Systems in Fuel Cell and Other Hydrogen Vehicles
		ISO 11114-4 (2017) Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 4: Test methods for selecting steels resistant to hydrogen embrittlement
Test method	H_2 charg-ing	ASTM G142-98(2022) Standard Test Method for Determination of Susceptibility of Metals to Embrittlement in Hydrogen Containing Environments at High Pres-sure, High Temperature, or Both

Test method	H_2 charg-ing	ISO 16573-1 (2020) Steel — Measurement method for the evaluation of hydrogen embrittlement resistance of high strength steels — Part 1: Constant load test ISO 16573-2 (2022) Steel — Measurement method for the evaluation of hydrogen embrittlement resistance of high-strength steels — Part 2: Slow strain rate test
	Fatigue crack growth	ASTM E647 (2015) Standard Test Method for Measurement of Fatigue Crack Growth Rates
	Fatigue life	ASTM E466 (2021) Standard Practice for Conducting Force Controlled Constant Amplitude Axial Fatigue Tests of Metallic Materials ASTM E606/E606M (2021) Standard Test Method for Strain-Controlled Fatigue Testing
	Fracture toughness	ASTM E1820 (2022) Standard Test Method for Measurement of Fracture Tough-ness
		ASTM E1681-03 (2020) Standard Test Method for Determining Threshold Stress Intensity Factor for Environment-Assisted Cracking of Metallic Materi-als (K_{IH})
		ASTM E399 (2022) Standard Test Method for Linear-Elastic Plane-Strain Fracture Toughness of Metallic Materials (K_{IH})

A.2.1 CSA/ANSI CHMC 1-2014

CSA/ANSI CHMC 1 (Test Methods for Evaluating Material Compatibility in Compressed Hydrogen Applications - Metals) specifies methods for evaluating the properties of metallic materials in gaseous hydrogen atmospheres. Any materials that fail to comply with the acceptance requirements for slow strain-rate tensile tests (SSRT) must be further verified for compatibility with the design conditions by fracture toughness and fatigue tests.

1) Hydrogen atmosphere: Tests are performed by designing a test chamber that complies with ASTM G142 or using hydrogen-precharged specimens.

2) Test temperature: At a temperature within the operating temperature range where the effect of hydrogen embrittlement is the most pronounced

- At 220K for 300-series stainless steel and at room temperature for other metallic materials

3) Test pressure: Set equivalent or superior to the MAWP

4) SSRT: Tests are performed on notched or smooth tensile specimens either in a hydrogen atmosphere or in a non-hydrogen atmosphere.

- Verified to be compatible if the notch-tensile strength ratio (under ASTM G129) or the relative reduction area (under ASTM E8) is 0.9 or more
- Notched specimens must comply with ASTM G142, or the notch stress concentration coefficient should be 3 or more.
- For smooth tensile specimens, the upper limit of the strain rate is twice the rate of 10^{-5} s^{-1}. For notched specimens, the gauge length is set to 25.4mm, and the effective strain rate is 10^{-6} s^{-1}.

5) Fracture toughness tests: JIC threshold fracture toughness measured according to ASTM E1820

6) Fatigue crack growth rate tests: ASTM E647

7) Fatigue life tests: Evaluated according to ASTM E466 and ASTM E606

- In load-controlled tests, the stress ratio is 0.1 for notched specimens and -1.0 or 0.1 for smooth specimens.

A.2.2 ASME BPVC Division III Article KD-10

In ASME BPVC as well, which specifies the requirements for the design of high-pressure gas vessels, Article KD-10 provides the detailed specific requirements for pressure vessels intended for hydrogen atmospheres. The standard describes the requirements for the evaluation of fatigue crack growth and fracture toughness in materials used in a gaseous hydrogen atmosphere. It applies to the same items as those subject to hydrogen compatibility assessments specified in KGS AC111. Material compatibility assessments require a fracture mechanics-based evaluation approach, unlike the method provided in CHMC-1. For some materials for which sufficient research data have been obtained from specific hydrogen atmospheres, additional tests are not required (refer to Code Case 2938).

1) Applicable materials (in a high-pressure hydrogen atmosphere with a pressure of 1030 bar or less)

- Alloy steel grades, including SA-372 and SA-723
- Stainless steel grades, including SA-336 Gr. F316
- Al 6061-T6

2) Required tests for high-pressure hydrogen atmospheres

- Crack growth initiation tests (KIC) according to ASTM E399 or E1820
- Crack growth stoppage tests (KIH) according to ASTM E1681
- Crack growth rate (da/dN) tests according to ASTM E647

A.2.3 SAE J2579

Appendix B of SAE J2579 (Standard for Fuel Systems in Fuel Cell and Other Hydrogen Vehicles), enacted by the Society of Automotive Engineers (SAE International), provides material recommendations, lists of allowed materials, and test procedures for material compatibility assessments. SAE J2579 specifies detailed test procedures based on fatigue life tests, including SSRT, and adopts part of the material compatibility criteria provided in CSA CHMC-1. It has been determined that SAE J2579, which is considered less demanding, will be adopted in the material compatibility test method of UN GTR No.13 Phase 2, which is currently under discussion. The decision may be attributed to the argument that CSA CHMC-1 and ASME are rather too demanding.

1) Applicable to: Compressed hydrogen vessels for automobiles with a pressure of 700 bar

2) Test conditions for SSRT

- Test temperature: 228±5K (room temperature only for aluminum alloys)
- Hydrogen pressure: 1.25 times the pressure level of 700 bar (under the same gas purity condition as specified in CSA CHMC-1)
- Test specimen: Only smooth tensile specimens allowed
- Strain rate control: 5.0 ´ 10^{-5} s^{-1} or less (2.0 ´ 10^{-5} s^{-1} or less under CSA CHMC-1)
- Evaluation criteria: The yield strength in a hydrogen atmosphere should be at least 0.8 times that measured in the air.

3) Test conditions for fatigue life tests

- Test environment: Only at room temperature At the same hydrogen pressure
- Test specimen: Either notched specimens or round-bar tensile specimens
- In load-controlled tests, the maximum stress should be at least 1/3 of the tensile strength, and the frequency is set to 1 Hz.
- Stress ratio: 0.1 for notched specimens and -1.0 for round-bar tensile specimens
- Evaluation criteria: 10^5 or more for notched specimens and 2.0 x 10^5 or more for round-bar tensile specimens

A.2.4 Other Regulations

ASTM G142(Standard Test Method for Determination of Susceptibility of Metals to Embrittlement in Hydrogen Containing Environments at High Pressure, High Temperature, or Both) presents methods for evaluating hydrogen embrittlement and hydrogen sensitivity in metallic materials used in high-pressure, high-temperature hydrogen atmospheres. The standard specifies the configuration of test chambers for high-temperature, high-pressure hydrogen atmospheres, and detailed test methods using notched and smooth specimens. Here, only tensile characteristics are considered, and therefore fracture toughness and fatigue life tests are beyond the scope of this standard.

ISO 11114-4(Transportable gas cylinders — Compatibility of Cylinder and Valve Materials with Gas Contents — Part 4: Test Methods for Selecting Steels Resistant to Hydrogen Embrittlement) describes methods for evaluating the hydrogen compatibility of metallic materials used for portable gas cylinders. This standard may apply to gas cylinders with a seamless steel structure whose gas partial pressure is 50 bar or more. However, this standard does not include methods for fatigue life evaluation, which has recently drawn significant research attention.

EC 79, enacted upon request from the European Parliament, regulates the type approval of hydrogen vehicles, which will be adopted for environmental purposes, issued in Europe. The standard provides the specific requirements for parts designed to use gaseous/liquid hydrogen. Any materials for parts that use gaseous hydrogen are subject to hydrogen compatibility tests. Among parts that use liquid hydrogen, valves, receptacles, fuel inlets, and regulators are the subject of hydrogen compatibility tests. However, flexible fuel lines do not have to be verified for hydrogen compatibility.

Appendix B. Effect of Hydrogen Atmospheres on Metallic Materials

Based on the details discussed above, Appendix B proposes methods for selecting suitable metallic materials for liquid hydrogen storage vessels and piping systems for ships, along with relevant considerations. Given that safety standards for pressure vessels for hydrogen storage are mainly focused on gaseous hydrogen, low-temperature material characteristics required for liquid hydrogen storage, along with the requirements provided in the IGC and IGF codes of the International Maritime Organization (IMO), are comprehensively considered.

B.1 Major Determining Factors of Hydrogen Embrittlement

This section analyzes the effect of hydrogen atmospheres on the mechanical properties of metallic materials before examining detailed procedures for material compatibility assessments. From a test environment perspective, the major determining factors of hydrogen atmospheres include the test temperature, hydrogen exposure conditions, hydrogen partial pressure, and deformation rates.

B.1.1 Hydrogen Charging Conditions

Hydrogen, once penetrating into a metal, diffuses through the metal matrix and ends up being trapped in certain areas, thereby decreasing the critical stress required to initiate cracking, and this mechanism is related to hydrogen sensitivity [35-38]. There are two methods for simulating a hydrogen atmosphere to determine the degree of possible damage caused by such hydrogen penetration: either applying a load to specimens in a gaseous hydrogen atmosphere or precharging hydrogen into specimens and applying a load to the precharged specimens. These test environments are called external hydrogen and internal hydrogen conditions, respectively.

1) Tests in Gaseous Hydrogen Atmospheres (External Hydrogen Condition)

The external hydrogen condition is generally considered desirable because they are quite similar to the target environment [39]. This type of test requires high-pressure hydrogen chambers that comply with the requirements provided in ASTM G142. The effect of hydrogen is more pronounced when the strain rate is lower, and the partial pressure of hydrogen is higher [40]. It is also significantly affected by the test temperature [41]. Take austenitic stainless steel, for example. During tensile tests in a gas atmosphere, austenite is transformed by deformation into martensite, in which hydrogen can diffuse more easily. Meanwhile, in metal specimens precharged with hydrogen, such deformation-induced transformation into martensite is less pronounced [42]. Indeed, the degree of reduction in ductility is generally larger in the external hydrogen condition. However, establishing facilities for this type of test requires high costs and involves safety issues as well.

In the internal hydrogen condition, metallic specimens are precharged with hydrogen first, and their mechanical performance is then evaluated. The effect of hydrogen on the deformation behavior of materials is fundamentally the same in external and internal hydrogen conditions [43-45]. Indeed, it is possible to find the same tendency in both conditions that the elongation decreases during a tensile test [13,46,47]. Thus, these internal hydrogen condition tests are currently widely employed because these methods are relatively safer and more cost-effective [48-50]. However, given that the achieved hydrogen content and distribution differ between the external and internal hydrogen conditions, the development of damage may vary depending on hydrogen charging conditions [13].

2) Hydrogen Precharging (Internal Hydrogen Condition)

The internal hydrogen condition is implemented mainly by thermal precharging and electrochemical recharging. Thermal hydrogen precharging is recommended for materials with low hydrogen diffusion coefficients [51].

Thermal hydrogen precharging is performed by exposing metallic specimens to high-pressure gaseous hydrogen at high temperatures of 200-350℃. The increased temperature enhances the diffusion rate and solubility of hydrogen in austenitic stainless steel while having no significant effect on its microstructure. This allows hydrogen to be uniformly distributed through the entire specimen, and the amount of hydrogen charged can be precisely estimated based on the thermodynamic relationships [52,53].

Electrochemical hydrogen charging is a cathodic electrolytic method in which the hydrogen generated via electrochemical reactions at the cathode of the polarization system is forced into specimens. The amount of hydrogen charged into the metal specimen is affected by the fugacity of hydrogen, which refers to the activity of hydrogen. More specifically, the hydrogen fugacity is affected by the electrochemical potential [35,54,55]. It is possible to achieve an extremely high hydrogen fugacity near the specimen surface using cathodic electrolysis, and this leads to surface cracking and phase transformation [56]. Extensive research is currently underway to find methods for estimating the hydrogen concentration achieved by electrochemical hydrogen charging. However, it is difficult to predict and control the amount of hydrogen charged into specimens because this process involves various factors. Furthermore, as far as austenitic stainless steel is concerned, it is difficult to charge large amounts of hydrogen. The amount of hydrogen charged is 10 ppm or less when electrochemical hydrogen charging is performed according to ISO 16573-2: 2022 [57]. This level of hydrogen content is known to hardly affect the mechanical performance of austenitic stainless steel [58].

This limitation may be overcome by either increasing the hydrogen fugacity or raising the temperature of electrolyte solutions for enhanced reaction rates. The first method can be implemented by controlling the applied current, but the second method often leads to the evaporation of electrolyte solutions due to high-temperature conditions. Thus, most studies are currently focused on electrochemical hydrogen charging at room temperature.

B.1.2 Test Temperature and Partial Pressure of Hydrogen

The test temperature is an index that is directly related to atomic-level particle motions, thereby not only affecting the mechanical behavior of metallic materials but also having a significant effect on hydrogen penetration into metals, as well as hydrogen embrittlement, which causes performance degradation. The effect of the test temperature on material compatibility tests for hydrogen atmospheres can be summarized below.

1) Maximum Hydrogen Embrittlement Temperature

The test temperature affects the diffusion rate of hydrogen while it is penetrating and diffusing into a metal, having a direct effect on metallic defects. Accordingly, hydrogen embrittlement observed in metallic materials exposed to a gaseous hydrogen atmosphere is more pronounced within a specific temperature range [51,59,60]. In typical steel grades, hydrogen embrittlement is more pronounced at room temperature, and this is attributed to the mobility of hydrogen atoms. The temperature range for each material type that can be applied to low-temperature hydrogen atmospheres, in which hydrogen embrittlement is pronounced, is summarized below.

- Nickel base alloys: Room temperature [61]
- Carbon steel and low-alloy steel: 250 – 300K [62,63]
- Aluminum alloys: Room temperature
- Austenitic stainless steel (300-series Cr-Ni stainless steel): 200 – 220K [59]

In carbon steel and low-alloy steel grades, hydrogen embrittlement occurs even at around 250K, but it is typically observed over the entire room-temperature range. Thus, tests may be performed at room temperature. For aluminum alloys, it is recommended that tests be conducted at room temperature because they are hardly affected by hydrogen.

However, austenitic stainless steel exhibits different behavior. In a previous study, in which tensile tests were performed in a gaseous hydrogen atmosphere at different temperatures [33], the degree of reduction in both elongation and the maximum load was significantly larger at 190K than at room temperature, even though the gaseous hydrogen pressure was 10 bar (refer to Figure B.1 (a)). When the gaseous hydrogen pressure was higher, the degree of performance degradation was larger when the temperature was the same. However, at 77K, the results did not vary between different gaseous hydrogen pressures. Various austenitic stainless steel grades were subjected to tensile tests at a gaseous hydrogen pressure of 11 bar in a temperature range of 80 – 300 K, and the relative reduction of area of the fractured specimens was calculated, as shown in Figure B.1 (b) [33,59,64,65].

Despite some variations depending on the applied conditions, the mobility of hydrogen atoms was significantly reduced at the temperature went below 200K [66]. Nonetheless, in austenitic stainless steel, the effect of hydrogen embrittlement is pronounced in the temperature range between 200 and 220K, and this is attributed to the acceleration of the deformation-induced transformation of austenite into martensite [16,67]. The maximum hydrogen embrittlement temperature range discussed above may be subject to change depending on various conditions. Therefore, it is necessary to set temperature ranges based on the results of previous studies and separately evaluate the effect of hydrogen embrittlement for each of the predefined temperature ranges.

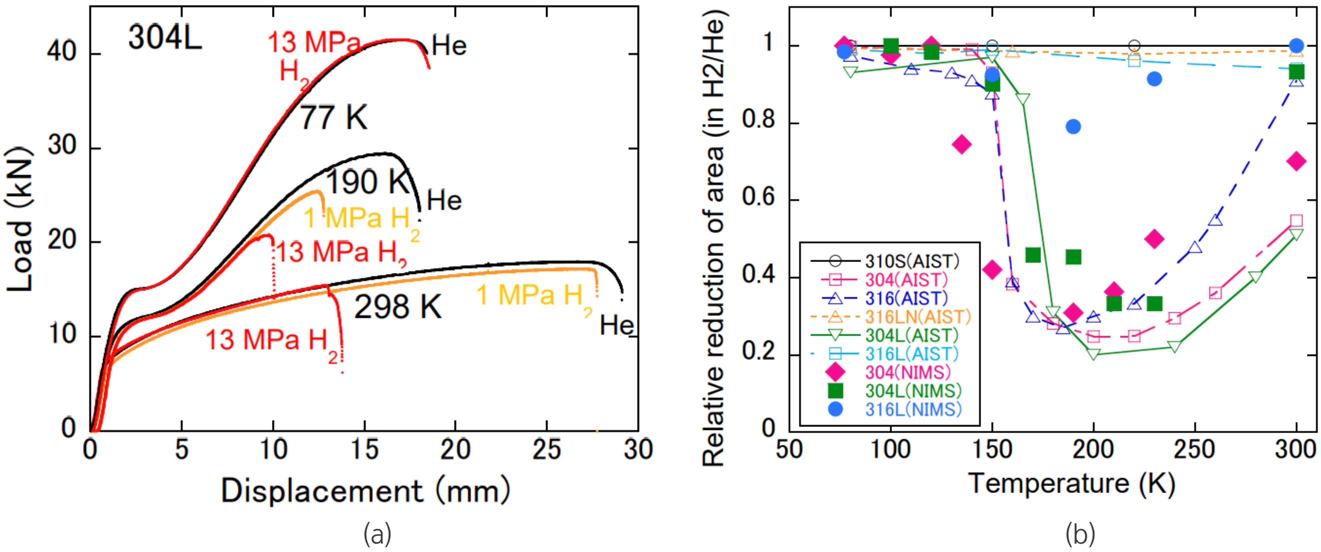

Figure B.1 Effect of hydrogen gas pressure and temperature on the mechanical performance of stainless steel alloys; (a) Load-displacement curves for 304L stainless steel under various hydrogen gas pressure and temperature conditions[33] and (b) Relative reduction of area in various stainless steel alloys under 11 bar H2 in the temperature range between 80 and 300K [33,59,68]

2) Partial Pressure of Hydrogen

Hydrogen embrittlement is generally known to depend on the hydrogen pressure. Technically speaking, however, it is dependent on the partial pressure of hydrogen. Given that there is no such thing as 100% pure gas composed solely of molecules of the desired substance, it is generally recommended that high-purity hydrogen be used as a test gas. Koide et al. (2015) examined the effect of the partial pressure of hydrogen on the relative reduction of area (RRA) in 304 stainless steel and concluded that the effect of hydrogen was significant even at a pressure of 1 bar [32]. As the pressure increased, the RRA decreased, but the figure remained around 0.4.

Estimations based on the partial pressure of hydrogen in a mixed gas are likely to result in valid results, but it has recently been reported that even more accurate relationships can be obtained if one determines the hydrogen fugacity by considering the compressibility factors of other gases in the mix [69].

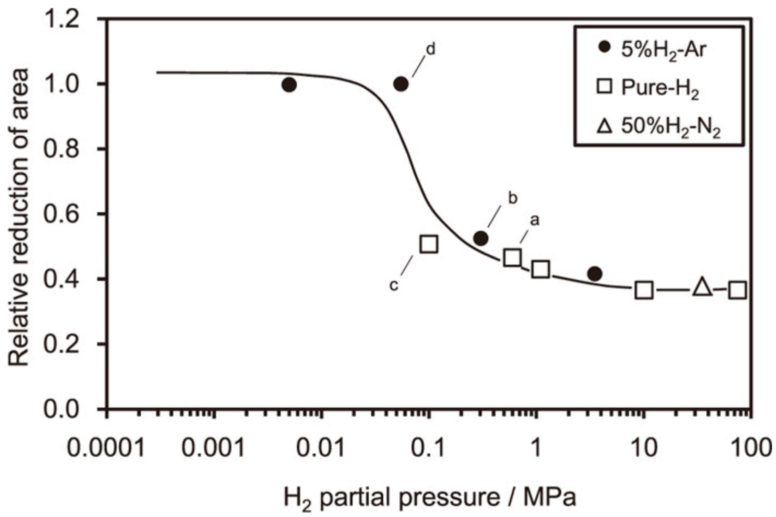

Figure B.2 Effect of the partial pressure of hydrogen on the relative reduction of area of 304 stainless steel (Ni equivalent: 21.6%) [32]

3) Effect of Test Items

The effect of the test temperature on the degree of hydrogen embrittlement may not be universally applied to all mechanical performance tests. Hydrogen sensitivity is mainly evaluated by the SSRT, and thus the specific explanations discussed above may apply better to tensile tests. Fatigue life tests at low temperatures genially exhibit improved results, and even if tests are performed in a hydrogen atmosphere, similar results are obtained [67,70]. In this regard, ANSI/CSA CHMC-1 and SAE J2579 require that fatigue performance tests be performed at room temperature [71].

In a hydrogen atmosphere, fatigue crack growth in stainless steel is accelerated, and this process is significantly affected by the frequency of the applied load. Once fatigue cracking is initiated in austenitic stainless steel, austenite-to-martensite transformation occurs at the tip of each crack. The diffusion rate of hydrogen is higher in martensite than in austenite, and thus martensite is less resistant to hydrogen-induced cracking [72]. Accordingly, the load frequency should be low enough to ensure the diffusion of hydrogen after the completion of phase transformation at the tip of each fatigue crack.

In a previous study, specimens welded to stainless steel plates (304L and 316L) were precharged with hydrogen, and their fracture toughness was evaluated based on the J-R curves obtained at low temperatures. The researchers confirmed that their resistance to crack growth was significantly reduced at a low temperature of −40℃ compared to when tested at room temperature [73].

In another study, Charpy impact tests were performed on hydrogen-precharged 304L stainless steel specimens, and it was found that the degree of reduction in the impact absorption energy increased as the temperature decreased within a temperature range below −80℃ [74]. This was inconsistent with the results of other previous studies in two aspects: first, this was much faster than when measured at the quasi-static strain rate, and second, the effect of hydrogen embrittlement became more pronounced in a low-temperature range below 200K. In other studies in which Charpy impact tests were performed at different temperatures after electrochemical hydrogen charging, the effect of hydrogen was not observed [75].

B.2 Characteristics of Cryogenic Environments

In a cryogenic environment below 20K, various physical phenomena that are different from those observed at room temperature are observed. Many previous studies have reported that the effect of hydrogen embrittlement is insignificant in the temperature range close to the evaporation temperature of hydrogen. This is attributed to the reduced mobility of hydrogen atoms in a cryogenic environment, leading to changes in the thermal characteristics of metallic materials. In some studies in which tensile tests were performed at 20K, however, the reduction of area (RA) was found to vary depending on the hydrogen conditions. Merket et al.(2021) charged hydrogen into 304L stainless steel specimens via thermal hydrogen precharging and created a cryogenic environment with a temperature of 20K by cooling gaseous helium. Under this condition, tensile tests were performed. At 20K, the relative reduction of area (RRA) of the hydrogen-precharged specimens was found to amount to about 60% of that of the pristine specimens as a comparison group [76]. A research team of Stuttgart University in Germany attempted to create a cryogenic environment for tensile tests by two methods, i.e., first, by directly exposing 304LN and 316LN stainless steel specimens to liquid hydrogen and, second, by cooling gaseous helium. The temperature was the same in both environments. The elongation of the specimens that were directly exposed to liquid hydrogen was 2-4% lower than that measured in the cryogenic environment achieved by using gaseous helium. The relative reduction of area (RRA) was 61% and 77%, respectively [77].

Given that tested materials and applied hydrogen exposure conditions were different from study to study, further research is needed to be sure; however, it was clearly confirmed that the evaluation of hydrogen sensitivity was affected by cryogenic conditions. However, it is not that these materials may not be used as materials for liquid hydrogen storage systems rather but that such an effect cannot be completely ruled out, as previously discussed in 3.2.2 presenting the results of the Charpy impact tests performed on hydrogen-precharged specimens in a cryogenic environment.

The National Institute of Standards and Technology (NIST) performed fracture toughness tests, instead of Charpy impact tests, at 4K on specimens welded to 316L stainless steel plates at the quasi-static strain rate, confirming that their fracture toughness was about seven times smaller when tested at 4 K than when tested at 77 K, the evaporation temperature of liquid nitrogen [19]. Charpy impact tests were not employed because it was difficult to maintain the temperature as desired due to the nature of the test material, combined with the effect of external factors. Maintaining the temperature at 4K, close to absolute zero, requires a test facility equipped with a cryostat with vacuum insulation, and any thermal radiation from the external atmosphere also needs to be controlled. Furthermore, it is also necessary to control not only the effect of the external environment but also any thermal energy generated from the test material so that the temperature can be maintained at the target value during tests.

If one intends to determine the effect of hydrogen on the fracture toughness of metallic materials in a cryogenic environment, their fracture toughness should be evaluated at slow strain rates. However, given that the diffusion of hydrogen is extremely limited at 20K, it is deemed more appropriate to apply cryogenic tests using hydrogen-precharged specimens. Unlike land structures under static loading conditions, offshore structures are subject to sustained complex loads, and thus, the impact toughness of materials at different temperatures is considered an important evaluation index. In this regard, the accurate evaluation of fracture toughness while considering the combined effect of cryogenic conditions and impact toughness is very important in the shipbuilding and marine industry. In recognition of the significance of these issues, the Korea Institute of Machinery and Materials (KIMM) has established test facilities for evaluating fracture toughness in cryogenic hydrogen environments, and various tests are currently underway.

Appendix C. Material Selection Based on Economic Feasibility

316L stainless steel, which is highly resistant to hydrogen, may be considered a safe choice in material selection, but it is far from cost-effective to apply the material universally to all hydrogen applications across the board. As of October 2022, cold-rolled 316 stainless steel cost the price of 304 stainless steel on a wholesale price basis. Given the volume of materials required to build liquid hydrogen storage vessels for ships, the cost will significantly vary depending on the type of material selected. In the case where there are multiple materials that satisfy the acceptance criteria for material compatibility under the same hydrogen atmosphere, design factors should be considered to be sure, but on top of that, it is also important to take an approach from an economic feasibility standpoint.

The annual average prices of some mineral resources since 2010 provided by the Korea Mineral Resource Information Service are summarized in Table C.1. Nickel, which accounts for the largest part of the price of austenitic stainless steel, has large price variations and is generally considered a high-cost material. The contents of some elements in austenitic stainless steel may vary from product to product, even if it is certified as a certain grade. For example, the required content of nickel for 304L and 316L under ASTM A240 is 8-12% and 10-14%, respectively. As previously discussed in 3.1, an increase in the nickel content may lead to significantly enhanced resistance to hydrogen embrittlement, but this is also accompanied by an increase in the unit cost of liquid hydrogen storage systems.

◦ Table C.1 Market price of metals for the last 20 years from KOMIS

Year	Price (USD/ton)		
	Aluminum[1]	Nickel[2]	Chrome[3]
2010	2,173	21,809	4,784
2011	2,395	22,831	5,027
2012	2,018	17,526	4,740
2013	1,845	15,004	4,431
2014	1,867	16,867	4,542
2015	1,661	11,807	4,564
2016	1,605	9,609	4,123
2017	1,969	10,411	4,497
2018	2,110	13,122	4,806
2019	1,791	13,936	4,057
2020	1,704	13,789	3,638
2021	2,479	18,487	5,490

[1]LME Cash
[2]LME Cash
[3]Ferro-chrome 0.10%C - 62% min Cr, US market price

Many safety regulations state that when the nickel content is 12.5% or more (corresponding to a nickel equivalent of 27.5), the effect of hydrogen is not significant. However, such a conclusion was drawn from experimental results obtained in a high-pressure hydrogen atmosphere. In a gaseous hydrogen atmosphere with a pressure of about 10 bar, if the relative reduction of area (RRA) is 0.5 or more, it may be deemed that there is no significant effect of hydrogen because the tensile strength measured in this condition amounts to about 90% of that measured in a non-hydrogen atmosphere. A gaseous hydrogen pressure of 10 bar in a cryogenic environment is considered a rather conservative threshold, but any materials with a nickel content that is rather lower than that required in a high-pressure gaseous hydrogen environment can sufficiently meet this requirement.

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