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Technical guide for materials of containment system for hydrogen fuels for ships

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Abstract: The International Maritime Organization (IMO) is adopting various regulations, goals, and measures for decarbonizing ships within the present century. The most environmentally friendly fuels for replacing conventional fuels in ships are low-flashpoint fuels, which are corrosive or cause embrittlement. Therefore, it is necessary to identify the requirements for storing individual fuels and choose the most realistic and economically feasible methods. Among the many alternative fuels, sufficient information is available regarding materials applicable to methanol—liquefied petroleum gas (LPG) and liquefied natural gas (LNG). Considering these fuels have long been handled by ships as fuel or cargo, sufficient regulations exist regarding the materials applicable to them. In the absence of conditions that lower the mechanical performance of materials, such as a hydrogen exposure environment or corrosion, materials applicable to cryogenic environments are generally applicable to higher temperatures without a problem. Liquid hydrogen is the fuel that presents the most difficult technical challenge for large-scale storage in ships. Hydrogen should be liquefied and stored in a containment facility designed to maintain a temperature below 20 K. Empirical studies on liquid hydrogen storage and fuel propulsion ships conducted in advanced countries have focused on 316 L stainless steel.

Keywords: Alternative Fuels, Hydrogen, Containment System, Safety, Technical guide

1. Introduction

The International Maritime Organization (IMO) adopted the Initial IMO GHG Strategy for reducing greenhouse gas (GHG) emissions from ships at the 72nd Marine Environment Protection Committee (MEPC) held in April 2018. The initial strategy includes reduction goals and measures for decarbonizing ships in the present century and is aimed at reducing the carbon intensity of international shipping by 40% by 2030 and 70% by 2050 and reducing the total GHG emissions by 50% by 2050, compared with the levels in 2008.

In achieving the goals of reducing the total GHG emissions specified in the Initial IMO GHG Strategy, using liquefied natural gas (LNG) fuel has limitations because LNG can reduce GHG emissions by only about 20% compared with conventional fuels. Ultimately, it is necessary to use alternative fuels, such as low-carbon or carbon-free fuels, to drastically reduce GHG emissions. Currently, studies are being conducted to apply various alternative fuels, including ammonia, biogas, and hydrogen, to ships.

2. Characteristics of alternative fuels

2.1 Alternative fuels for ocean-going vessel

The commonality of environment-friendly alternative fuels is that they are low-flashpoint fuels. Their flashpoints are lower than those of fuel oils and they are stored in a liquid state under atmospheric pressure at a low temperature. LNG, one of the representative environment-friendly fuels, is stored in a cryogenic environment below −163 ℃ under atmospheric pressure. Therefore, strict standards were applied to select the materials applied to the fuel containment system and to design and evaluate the structure. Using hydrogen as a fuel for ships requires liquefaction and storage at a temperature below −253 ℃, close to absolute zero; thus, hydrogen is rarely used as a fuel for large transport vehicles such as ships or is rarely transported as cargo. Therefore, many technical obstacles exist to the use of hydrogen. In addition to the technical difficulties involved in cryogenic liquefaction and storage and hydrogen embrittlement, the infiltration of hydrogen into metallic materials to cause damage is another major obstacle.

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Table 1: Overview of alternative fuels for ocean-going vessel

Category	LNG	LPG (Propane0	Methanol	Hydrogen		Ammonia
				Compressed	Liquefied	
Storage condition	– 163℃	– 42℃	Room Temp.	200 bar	– 253℃	– 34℃
Density (kg/m^3)	430~470	503	786	17.5	71	603 (liquefied at 25℃)
Toxicity	Not Toxic	Not Toxic	Low acute toxicity	Not Toxic		Toxic
Gravimetric energy density (MJ/kg)	50	46.3	19.9	120	120	18.6
Volumetric energy density (GJ/m^3)	23.4	24.7	15.8	4.5	8.5	12.7
Flammability limits (%)	4~15	1.8~10.1	6.7~36	4~74.2		15~28

This paper briefly introduces alternative fuels and their characteristics for ships currently being discussed in academic and industrial communities. **Table 1** summarizes the physical properties and availability of alternative fuels.

2.2 Hydrogen

Hydrogen, the lightest element on Earth, does not emit any pollutants, except for a minimal amount of NOx generated by combustion. However, because the hydrogen on Earth is mostly included in water or organic compounds, hydrogen can be obtained through electrolysis of water, reforming of natural gas, or from a petroleum refining process.

Hydrogen is usually stored by compression at high pressure or by liquefaction. Liquefaction of hydrogen allows storing hydrogen in an amount approximately 800 times more than the hydrogen gas at room temperature under atmospheric pressure. Considering storage capacity, the storage density of liquid hydrogen is approximately four times higher than that of high-pressure hydrogen (200 bar), and the difference may be more than 10 times in terms of transport efficiency and installation site because manufacturing large high-pressure hydrogen vessels is difficult and requires numerous small-sized high-pressure hydrogen vessels. High-pressure hydrogen is normally stored at a pressure of 700 bar or lower; new technologies are now being developed in Korea to pressurize and store hydrogen at 900 bar.

Despite the disadvantages of hydrogen in terms of volume energy density, it is best in terms of mass-energy density **[1]**. As mentioned above, storing the largest amount of hydrogen in a limited volume involves liquefying and storing it as liquid hydrogen. This method allows for storing the largest amount of energy per fuel mass.

Considering hydrogen molecules are extremely small, they can penetrate a storage vessel or permeate into a material to cause damage. Therefore, hydrogen storage requires an analysis of its resistance to hydrogen damage, hydrogen permeability, and leakage. Liquid hydrogen storage requires maintaining a temperature of −253 ℃ or lower, and a storage vessel with a dual vacuum structure is necessary to suppress or minimize the three modes of heat transfer.

3. Evaluation of cryogenic environment applicability for hydrogen fuels

3.1 Key factors to mechanical performance for hydrogen fuels

Various factors affect the mechanical behavior of a material, ranging from the composition ratio to the manufacturing method of the material; however, temperature and strain rate are considered the major factors. Additional factors that affect the mechanical performance of a metal exposed to a hydrogen environment are described below.

Hydrogen atoms have an atomic radius of less than 1 Å, much smaller than that of other atoms; thus, they can easily penetrate the lattices of metals. Hydrogen embrittlement refers to the decrease in the mechanical properties of hydrogen-containing metals under an external force, including the yield strength, fracture strength, and elongation, caused by the internal pressure or dislocation slip due to the interactions between the grain boundary and hydrogen atoms. Generally, the average hydrogen concentration inside a material is not so high that embrittlement may occur, but the propagation of hydrogen atoms under the application of stress may result in the formation of hydrogen molecules in a local region of the material. When the threshold is reached, a sudden brittle fracture is likely to occur. The three major factors in hydrogen embrittlement fracture include the external environment to which the material is exposed, inherent properties of the material, and stress applied to the material.

Hydrogen embrittlement is viewed from different angles: 1) the process in which hydrogen permeates into a metallic material, and 2) the process in which the deterioration of the mechanical properties of a metallic material and fracture occurs due to hydrogen **[2]**. When a metallic material is exposed to a high-temperature and high-pressure hydrogen atmosphere for a long time, hydrogen invades and diffuses into the material, reacts with the solid-soluble carbon or carbines in the metal, and eventually generates methane gas. The irreversible internal cracking or swelling caused by the accumulation of methane gas is explained by a hydrogen attack. In contrast, hydrogen embrittlement is known as the direct action of hydrogen that penetrates a metal as part of the deformation mechanism of the metal, resulting in a decrease in mechanical properties such as strength and ductility. While hydrogen attack is considered a direct cause of cracking, hydrogen embrittlement is related more to the enhancement of crack growth. Different theories exist regarding the mechanism of hydrogen embrittlement. Representative hydrogen embrittlement theories are listed below, with their details described in Appendix C.

Hydrogen-Enhanced Decohesion Mechanism (HEDE)

Hydrogen-enhanced localized plasticity mechanism (HELP)

- Hydrogen Blistering

In a hydrogen environment, metallic materials undergo a decrease in mechanical performance; for example, tensile strength and elongation. The effect is significantly different on the material characteristics, including the chemical composition, manufacturing process, and hydrogen atmosphere. A previous study showed that in 316 L stainless steel, despite having a high hydrogen concentration, the degree of hydrogen damage was almost constant at different hydrogen concentrations, similar to the conditions without hydrogen charging. In contrast, Inconel 625 showed a considerable decrease in elongation and tensile strength as hydrogen charging was increased **[3]**. **Figures 1** and **2** show the results of the tensile test with 316 L stainless steel and Inconel 625, depending on the hydrogen concentration.

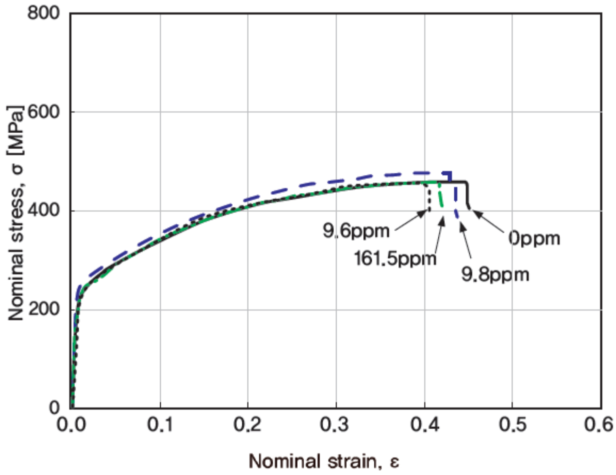

Figure 1: Tensile test result of hydrogen charged 316L stainless steel [3]

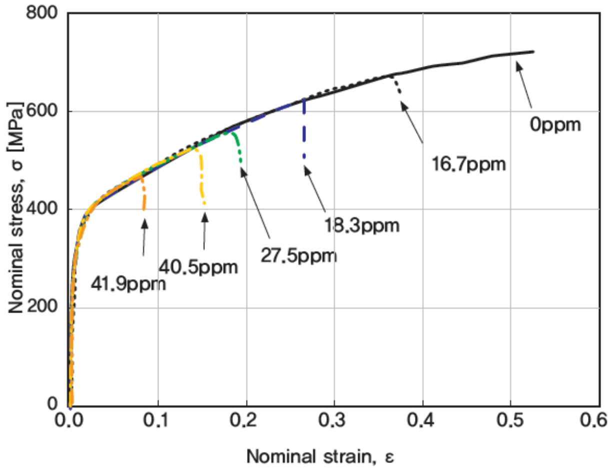

Figure 2: Tensile test result of hydrogen charged Inconel 625 **[3]**

3.2 Required performance test with materials for hydrogen fuel

Metallic materials for low-flashpoint fuel containment systems must satisfy the requirements of the IGC/IGF code and the Korean Register Rules for the classification of steel ships. Article 16 (Manufacturing and Testing) of the Low-Flashpoint Fuel Ship Rules, published by the Korean Register, stipulates that tensile tests, impact tests, flexural tests, and cross-sectional observations are necessary. In addition to the necessary testing methods and requirements, an evaluation of the thermal expansion coefficient and thermal conductivity (k) is required to determine the physical properties of the design.

The guidelines for ships carrying liquefied hydrogen in bulk published by the Korean Register require selecting appropriate materials to prevent damage caused by hydrogen embrittlement.

Hydrogen ions can easily diffuse into steel or other materials, caused by the exposure of the material to not only pure hydrogen gas but also the environment of other hydrogen-containing gases, including hydrogen sulfide, hydrogen chloride (HCl), and hydrogen bromide (HBr). Hydrogen ions that diffuse into the material affect its mechanical properties. In the case of steel, hydrogen ions decrease toughness and ductility, thereby embrittling the material. Considering embrittlement may cause a material to be quickly destroyed by a small impact load or deformation, a careful preliminary review of embrittlement is necessary considering its structural integrity.

Typical factors that cause embrittlement are the cryogenic and hydrogen environments. For cryogenic containment systems for low-flashpoint fuels in ships, embrittlement at a target temperature is the most important criterion in material selection. Therefore, to store and utilize liquid hydrogen as a fuel in a ship, it is necessary to determine the temperature and the embrittlement caused by hydrogen as one of the material selection criteria. ISO 16573 is a standard test method for evaluating the hydrogen embrittlement resistance of high-strength steels and presents electrochemical hydrogen charging **[4]**. Compared with high-pressure hydrogen charging, this method is less expensive and safer. Considering that the amount of hydrogen charging is very small in a cryogenic environment, where the hydrogen mobility is low, electrochemical hydrogen charging is an appropriate testing method.

The international standard provides a method for evaluating hydrogen embrittlement resistance (hydrogen delayed fracture) through a constant load test using a hydrogen-charging specimen. In the case of continuous hydrogen absorption, such as hydrogen charging in an aqueous solution at corrosion potential, hydrogen charging in atmospheric corrosion environments, and hydrogen charging in high-pressure hydrogen gas, the evaluation method is briefly described.

There are four hydrogen charging methods: hydrogen absorption in an aqueous solution at free corrosion potential, cathodic charging, hydrogen absorption in atmospheric corrosion environments, and hydrogen absorption in high-pressure hydrogen gas. The amount of hydrogen absorbed in the specimens can be quantitatively analyzed by thermal desorption analysis, such as gas chromatography and mass spectrometry. The conditions for each method are as follows.

① Hydrogen charging by cathode charging: Hydrogen was forced to diffuse into the specimens by the cathodic method to estimate the effect of hydrogen on the mechanical properties of steels. **Table 2** shows the chemical compositions of the solutions for hydrogen charging. Solution 1 can be used to introduce a relatively large amount of hydrogen, while Solution 2 can be used to introduce a small amount of hydrogen. The anode of the electrochemical cell for hydrogen charging is made of spiral platinum wire (0.5 mm diameter and 2 m length), and the specimen serves as the cathode. After the platinum wire and specimen were placed in the cell, a constant current with a current density of 0–20 A/m^2 was applied using a potentio/galvanostat for 48 h. After hydrogen charging, cadmium (Cd) plating was performed to prevent hydrogen leakage. A charging time of 48 h is recommended; however, a total charging time of 72 h may be applied to compensate for the amount of hydrogen discharged by room temperature exposure during hydrogen charging and cadmium plating. The hydrogen charging time can be increased for materials with low hydrogen diffusion coefficients. The surface area of the specimen should be calculated for proper current supply, and the charged hydrogen content may be changed by varying the current density or charging time. However, a fixed charging time and current density are recommended to obtain reproducible test results.

Table 2: Chemical composition of the solutions for electrochemical hydrogen charging

Charging solution	Element	Content (g/L)	Mark
Solution 1	NaCl	30	Large amount of hydrogen
	NH4SCN	3	
Solution 2	NaOH	4	Small amount of hydrogen

② Hydrogen absorption in aqueous solution at free corrosion potential: For hydrogen charging by corrosion in acid, HCl solutions with CH3COOH/CH3COONa buffer solution were used. The specimen was immersed in a 5% HCl solution to perform hydrogen charging, and the charging time was determined according to the specimen size and hydrogen diffusion coefficient of the material.

③ Hydrogen absorption in corrosion environments: For hydrogen charging in corrosion environments, the salt spray test (SST) or cyclic corrosion test (CCT), including salt spraying, drying, and humidifying, is performed.

④ Hydrogen absorption in high-pressure corrosion environments: For hydrogen charging in high-pressure corrosion, the specimen is exposed to a high-temperature, high-pressure hydrogen environment to induce hydrogen invasion. The charging time was determined according to the specimen size and hydrogen diffusion coefficient of the material.

⑤ Hydrogen thermal desorption analysis: Thermal desorption analysis was used to quantitatively calculate the amount of hydrogen diffusion to a material using the four hydrogen charging methods. The equipment for the thermal desorption analysis comprised heating, gas sampling, and detecting parts. When the specimen was heated, the hydrogen inside the specimen diffused and flowed into the gas chromatography column with carrier gas (high-purity Ar or He gas). The heating rate was fixed at 100 ℃/h and the specimen was heated to 400 ℃. The gases were then separated using an adsorption column. To accurately measure the hydrogen content, it is recommended to measure the background. Generally, diffused hydrogen is calculated by integrating the first peak of the thermal desorption curve. However, when several peaks are observed at low temperatures (i.e., below 400 ℃), the diffused hydrogen can be calculated by integrating the peaks of the thermal desorption analysis curve below 400 ℃. Considering the heating rate did not significantly affect the test results, a high heating rate, such as 100 ℃/h, was recommended. In mass spectrometry, when a radio-frequency voltage is applied, only a selected gas or ion is detected because of the characteristic mass-to-charge ratio. Hydrogen was continuously detected during heating. The heating rate was fixed at 100 ℃/h and the specimen was heated up to 400 ℃.

4. Materials for hydrogen fuels cryogenic environments

4.1 Metallic materials for cryogenic environments

This study introduces materials suitable for low-flashpoint fuel-containment systems. The materials mentioned herein are based on the materials applicable to a design temperature of −165 ℃ according to Volume 2 (Materials and Welding) of the Korean Register Rules for the classification of steel ships. The rolled steel materials for the cryogenic environment include nickel alloys, rolled stainless steels, aluminum alloys, and high-manganese steels.

4.2 Liquid hydrogen containment systems

Guidelines from the world’s major research institutes and ISO standards provide the following considerations for selecting materials for liquid hydrogen storage: (1) Resistance to hydrogen embrittlement: materials insensitive to hydrogen; (2) Securing ductility at low temperatures: materials with a DBTT lower than the operational temperature; (3) Materials that simultaneously satisfy the two aforementioned conditions.

Performance tests in a high-pressure hydrogen environment have been suggested for evaluating the hydrogen embrittlement resistance of metallic materials. ANSI/CSA CHMC 1-2014(Test Methods for Evaluating Material Compatibility in Compressed Hydrogen Applications – Metals), which is the standard for evaluating compatibility with compressed hydrogen applications, recommends that the specimen should be exposed to a gaseous hydrogen environment at 300 ℃ and 100 bar for eight days to ensure that hydrogen can sufficiently reach the inside of the specimen. However, in liquid hydrogen environments below 20 K, hydrogen mobility is extremely low; thus, hydrogen penetration into the material is extremely limited. Therefore, high-temperature and high-pressure hydrogen environments may cause excessive hydrogen charging, in contrast to cryogenic environments. This study considers that electrochemical hydrogen charging, provided in ISO 16573, may be appropriate for evaluating compatibility with liquid-hydrogen environments.

Candidate materials for application to liquid hydrogen containment systems include a wider range of materials compared to materials applicable to LNG containment systems. Based on the evaluation results, candidates were classified into three groups.

Group A includes materials already extensively applied to liquid hydrogen vessels, with their performance and safety already validated. Group A included 316 L stainless steel and 6061-T6 aluminum alloys. Aluminum alloys have a considerably high resistance to hydrogen and are widely used in cryogenic environments; for instance, Al 6061-T6 is applied to Type 3 high-pressure hydrogen storage vessels.

Group B includes materials expected to be sufficiently applicable to liquid-hydrogen environments, but have not been used for liquid-hydrogen vessels. These are austenitic stainless steels and aluminum alloys that do not exhibit brittle behavior in cryogenic environments. Austenitic stainless steels may be inappropriate for high-pressure hydrogen environments but are highly appropriate for cryogenic environments where hydrogen mobility is decreased, and hydrogen permeation into the materials is low.

Group C includes materials not applicable to cryogenic environments below 20 K or hydrogen environments. Nickel steels with a low nickel content may not be used in cryogenic environments. Special alloy steels, which contain a large amount of nickel, can be used in cryogenic environments; however, they are highly vulnerable to hydrogen environments and are therefore, inapplicable. Nickel steel (9%) is not suitable for liquid hydrogen because it exhibits brittle behavior in cryogenic environments below the LNG storage temperature.

5. Conclusion

The most environmentally friendly fuels for replacing conventional fuels for ships are low-flashpoint fuels, which are corrosive or cause embrittlement. Therefore, it is necessary to identify the requirements for storing individual fuels and choose the most realistic and economically feasible methods.

Among the many alternative fuels, sufficient information is available regarding materials applicable to methanol, ethanol, ammonia, LPG, and LNG. As these fuels have long been handled by ships as fuel or cargo, sufficient regulations exist regarding the materials applicable to them. In the absence of conditions that lower the mechanical performance of materials, such as a hydrogen exposure environment or corrosion, materials applicable to cryogenic environments are generally applicable to higher temperatures without a problem.

Liquid hydrogen is the fuel that presents the most difficult technical challenge for large-scale storage in ships. Hydrogen should be liquefied and stored in a containment facility designed to maintain a temperature below 20 K. The IGC/IGF Code and the Korean Register Rules for the classification of steel ships require an impact test to be performed at temperatures lower than the operational temperature; however, realistically, it is difficult to carry out an impact test in a cryogenic environment below 20 K.

The design and manufacturing of low-flashpoint fuel containment systems should consider their effects on the base metal and welding. Hence, studies on applying liquid hydrogen to ships require the results of performance tests conducted under conditions equivalent to or harsher than the operational environments. Empirical studies on liquid hydrogen storage and fuel propulsion ships, carried out in advanced countries, have focused on 316 L stainless steel, which has traditionally been known to have excellent hydrogen resistance and applicability to cryogenic environments. However, using only one material is a substantial design constraint and may cause problems in terms of securing economic feasibility.

Therefore, we need to obtain mechanical performance data for tensile, fatigue, and fracture toughness at 20k through follow-up studies, which will provide the performance data of various materials, in addition to 316 L stainless steel, in liquid-hydrogen environments.

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Author Contributions

Investigation, K. W. Chun; Resources, K. W. Chun; Writing-Original Draft Preparation, K. W. Chun; Writing-Review & Editing, K. W. Chun.

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