Article

Metallic Material Evaluation of Liquid Hydrogen Storage Tank for Marine Application Using a Tensile Cryostat for 20 K and Electrochemical Cell

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Abstract: A series of material tests were performed on cryogenic metallic materials meant for liquid hydrogen storage tanks using a 20 K tensile cryostat and an electrochemical hydrogen-charging apparatus. Mechanical evaluation of the electrochemically hydrogen-charged specimen was performed in a tensile cryostat using helium gas at ambient temperature and cryogenic temperature (20 K). The tensile cryostat was equipped with a vacuum jacket and a G-M cryocooler with gaseous helium. Furthermore, the cathodic electrolysis cell used for charging the specimen was adopted for internal hydrogen conditions with a reflux condenser and heating mantle to increase hydrogen diffusivity. The target materials were austenite stainless steel and aluminum alloy, which are suitable for liquefied natural gas and gaseous hydrogen environments. No significant change in the yield strength and flow stress of the hydrogen-charged specimen up to 20% strain was observed. However, changes in tensile strength and elongation were observed thereafter. Electrochemical hydrogen charging of stainless steel leads to a high concentration of hydrogen on the surface of the specimen. The resulting surface cracks reduced the flow stress. The 20 K tensile test showed discontinuous yielding in the austenitic stainless steel with an abrupt increase in temperature. The mechanical performance of the aluminum alloys improved in terms of strength and elongation. Changes in the mechanical performance and relative area reduction were observed for all the metallic materials at 300 K and 20 K.

Keywords: liquid hydrogen; hydrogen embrittlement; tensile cryostat; cathodic hydrogen charging; austenite stainless steel; aluminum alloy

1. Introduction

Plans to use various eco-friendly fuels for ship propulsion have been proposed to keep pace with the International Maritime Organization’s (IMO) strategy to limit greenhouse gas emissions. Several studies applied liquid hydrogen as propulsion fuel for large vessels because of its high energy density [1–4].

The liquid hydrogen carrier, Suiso Frontier, of Kawasaki Heavy Industries and the liquid hydrogen propulsion ship, Hydra, of Norled were the first examples of liquid hydrogen storage containers being installed and operated on ships. Such containers are rare because manufacturing a double vacuum container with a high capacity for long-term utilization and transportation of a large amount of hydrogen in the sea is difficult; moreover, the evaporation of liquid hydrogen causes considerable economic losses. Hence, hydrogen is usually compressed and transported in a gaseous state through pipelines and mobile applications because of the boil-off problem [5–7]. Several attempts have been made to store hydrogen in a liquid state since the 1960s. However, liquid hydrogen has very limited
applications [8]. Hence, the safety standards for liquid hydrogen storage materials are insufficient compared to those for gaseous hydrogen storage.

In 2016, the IMO adopted interim guidelines for the carriage of liquefied hydrogen in bulk, which were prepared with reference to ISO TR 15916 (basic considerations for the safety of hydrogen systems). ISO TR 15916 provides basic safety measures and hazards related to the use of hydrogen and recommends applicable materials for hydrogen storage based on the state. However, it does not incorporate detailed safety requirements associated with specific hydrogen applications.

Safety standards, such as GTR No. 13 and SAE J2579, have been established for the commercialization of hydrogen-fueled vehicles. These regulations present various test items and acceptable criteria for high-pressure hydrogen storage containers and their applied materials because the high-pressure hydrogen environment can easily damage the material, resulting in hydrogen embrittlement. Hydrogen is adsorbed onto the metal surface in the form of H2 molecules or H3O+ ions, dissociates to atoms, and diffuses into the materials [9]. Hydrogen is trapped at specific locations, reducing the critical stress required for cracking [10–13]. Materials that can be used under high-pressure gaseous hydrogen conditions include 316L austenitic stainless steel and 6061-T6 aluminum alloy [14,15]. ASME STP/PT-003 presents various materials that can be applied to hydrogen storage tanks.

A lower probability of damage due to high-pressure hydrogen is the biggest obstacle in establishing safety standards for the storage and transportation of liquid hydrogen. Liquid hydrogen can be stored at \(-253^\circ\text{C}\) (20 K) at atmospheric pressure. The hydrogen embrittlement phenomenon is difficult to observe because the activity of hydrogen is very slow under these conditions. Hence, many safety standards recommend materials that can withstand the low-temperature embrittlement of the base metal of liquid hydrogen storage containers [16]. However, hydrogen affects material behavior at 20 K. Merket et al. (2021) performed a tensile test at 20 K by cooling gaseous helium after thermal hydrogen charging of 304L stainless steel [17]. The pre-charged specimen had 60% reduced ductility in terms of reduction in area. Tensile tests were performed at Stuttgart University, Germany, on 304LN and 316LN stainless steel in liquid hydrogen and gaseous helium at the same temperature. In the liquid hydrogen environment, the elongation decreased by 2–4%, and the relative reductions in the area were 61% and 77% for 304LN and 316LN, respectively, compared to that of gaseous helium [18].

The design pressure for liquid hydrogen storage tanks is typically 2–6 bar, and the maximum allowable pressure is limited to 10 bar or less [19–22]. This is a very low pressure compared with that of the high-pressure hydrogen environment. However, the mechanical performance degradation of steel by hydrogen is more pronounced at low temperatures than at room temperature [23–25] despite the hydrogen pressure being at atmospheric level [26,27]. Ogata (2018) observed a decrease in the elongation and reduction in the area of 304L stainless steel exposed to 10 bar gaseous hydrogen at various temperatures, which was not as dramatic as the effect of high-pressure hydrogen [28]. Considering that the pipe/tube/cylinder connected to the storage tank is exposed to low-pressure gaseous hydrogen below 10 bar from 20 to 300 K, further studies on the effect of material behavior on liquid hydrogen storage and transport systems are needed.

Therefore, this study performed mechanical performance tests at room temperature and cryogenic temperature (20 K) on various metallic materials in a tensile cryostat using helium gas on electrochemical hydrogen-charged specimens. The target materials were austenitic stainless steel and aluminum alloy, which are suitable for LNG and gaseous hydrogen environments. In the liquid hydrogen storage and piping system, the relationship between metal and hydrogen was assumed as follows: low-pressure gaseous hydrogen from 20 K to 300 K in liquid hydrogen storage and piping systems allows only small amounts of hydrogen to slowly diffuse into metallic materials, resulting in a high hydrogen concentration on the surface of cryogenic metallic materials, even with long-term exposure to hydrogen. A cathodic electrolysis cell was adopted for the internal hydrogen condition, assuming localized hydrogen concentration in the liquid hydrogen system.
mantle and reflux condenser were added to increase the temperature of the aqueous solution to maximize the effect of hydrogen by increasing the hydrogen concentration. A tensile cryostat was developed to simulate a liquid-hydrogen environment (20 K) with a vacuum jacket. The effects of hydrogen at 300 K and 20 K were evaluated using hydrogen-charged specimens in terms of their mechanical behavior and fracture morphology.

2. Experimental Preparation
2.1. Materials and Specimen

This study adopted austenite stainless steel and aluminum alloy, which are typically used in LNG storage containers and hydrogen storage containers. Two types of stainless steel were sampled from 304L and 316L hot-rolled stainless steel plates with a 20 mm thickness based on ASME SEC II SA240M/480M and ASTM A240M/480M, respectively. Two types of stainless steel plates were heat-treated with solution annealing at a minimum temperature of 1040 °C and then water cooled. For aluminum alloys (5083-H112 and 6061-T6), tensile specimens were extracted from 20 mm and 10 mm thick aluminum alloy plates manufactured according to ASTM B209 and KS D 6701 (Korean standard), respectively. The chemical compositions of the four metallic materials are listed in Table 1.

Table 1. Chemical composition of tensile specimen.

<table>
<thead>
<tr>
<th>Type</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
<th>Others</th>
<th>Al</th>
<th>-</th>
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<tr>
<td>Al alloy</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5083-H112</td>
<td>0.108</td>
<td>0.262</td>
<td>0.026</td>
<td>0.501</td>
<td>4.372</td>
<td>0.138</td>
<td>0.032</td>
<td>0.02</td>
<td>0.15</td>
<td>94.39</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6061-T6</td>
<td>0.692</td>
<td>0.456</td>
<td>0.275</td>
<td>0.069</td>
<td>1.108</td>
<td>0.187</td>
<td>0.011</td>
<td>0.03</td>
<td>0.052</td>
<td>97.12</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
<th>Co</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>0.025</td>
<td>0.4</td>
<td>1.64</td>
<td>0.033</td>
<td>0.002</td>
<td>18.14</td>
<td>8.07</td>
<td>0.11</td>
<td>0.073</td>
<td>0.22</td>
<td>0.22</td>
<td>bal.</td>
</tr>
<tr>
<td>304L</td>
<td>0.019</td>
<td>0.47</td>
<td>1.25</td>
<td>0.03</td>
<td>0.002</td>
<td>16.64</td>
<td>10.1</td>
<td>2.1</td>
<td>0.07</td>
<td>0.2</td>
<td>0.26</td>
<td>bal.</td>
</tr>
<tr>
<td>316L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tensile specimens were prepared according to the subsize of the round tension test specimens in ASTM E8/E8M. The aluminum alloy 5083-H112 tensile specimen had a diameter of 4 mm due to the thinness of the base plate, whereas all other materials had a diameter of 6 mm. The longitudinal direction of the tensile specimen was parallel to the rolling direction of the base material. The gauge length was 10 mm; it was measured using an axial extensometer (Epsilon 3442 model, Epsilon Technology Corp., Jackson, WY, USA).

2.2. Hydrogen Charging

Thermal pre-charging and electrochemical pre-charging were used to diffuse hydrogen into the metal. Thermal hydrogen charging is recommended for metallic materials with a low hydrogen diffusion coefficient [29]. Elevated temperatures increase the diffusion rate and solubility of hydrogen in austenitic stainless steel without significantly affecting the microstructure. A uniform hydrogen distribution was generated throughout the specimen, and the hydrogen concentration was predicted to a significant degree using thermodynamic relationships [30,31].

Electrochemical hydrogen charging is a convenient method for diffusing hydrogen into metallic materials using a potentiostat. The hydrogen concentration is affected by the hydrogen fugacity, which is affected by the electrochemical potential [9,10,32]. Cathodic electrolysis can be used to generate extremely high hydrogen fugacity near the surface of the specimen, which can lead to surface cracking and phase transformation [33]. According to Fick’s law, gaseous hydrogen charging produces a relatively low fugacity under the same temperature conditions [34].

Nevertheless, cathodic hydrogen charging yields metallic materials with a low hydrogen diffusion coefficient and low hydrogen content in an ambient environment. Duportal et al. (2020) performed cathodic hydrogen charging on AISI 316L stainless steel
(Ni wt%: 12.4%) in an electrolyte solution of sodium hydroxide and ammonium thiocyanate with a high current density of 100 mA/cm² at 50 °C [35]. A charging time of 72 h resulted in a hydrogen content of 80 ± 17 wppm. However, the measured sample was only a 1 mm thin plate. The hydrogen concentration within 15% of the thickness (76 µm) of the surface was 526 wppm, meaning that a high hydrogen fugacity was produced by the high current density; however, hydrogen did not diffuse sufficiently into the center of the specimen. A long duration of hydrogen charging results in a higher hydrogen concentration in the interior of the specimen [36]. The hydrogen diffusion coefficient of austenitic stainless steel increases by more than 30 times at 80 °C compared to room temperature according to Fick’s law [37]. In other words, the most dominant factor for hydrogen diffusion is the hydrogen-charging at high temperatures.

The hydrogen charging apparatus used in this study was composed of cathodic electrolysis cells with a heating mantle and vapor condenser, according to ASTM G31. The reaction flask (cell) was surrounded by a heating mantle to control the temperature of the aqueous electrolyte solution significantly above ambient temperature; the reflux condenser with a chiller reliquefied the evaporated gas (see Figure 1). This method can maintain the original volume for a long time. A tensile specimen as the working electrode and platinum mesh as the counter electrode were connected to a potentiostat (WonATech) by a platinum wire.

![Figure 1. (a) Schematic diagram and (b) set-up of electrochemical hydrogen charging system for a high-temperature environment.](image)

The aqueous electrolyte solution was composed of 3% sodium chloride (NaCl) and 0.3% ammonium thiocyanate (NH₄SCN). Ultrasonic cleaning with Citranox detergent was performed on the tensile specimens before hydrogen charging. A constant current of 30 mA/cm², which was higher than the general current density suggested by ISO 16573-2:2022, was applied for 72 h. Furthermore, the aqueous electrolyte solution was maintained at 80 °C. Zn plating was conducted to prevent hydrogen release after the hydrogen charging process, according to ISO 16573-2:2022.

Hydrogen charging was performed only on the 304L and 316L austenitic stainless steel. The hydrogen content charged by the cathodic electrolytic method was measured using an ELTRA ONH-2000, according to ASTM E1447 (see Table 2).
Table 2. Hydrogen charging condition and hydrogen contents of stainless steel.

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>Hydrogen Content (wppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L stainless steel</td>
<td></td>
</tr>
<tr>
<td>As-received</td>
<td>3</td>
</tr>
<tr>
<td>Pre-charged</td>
<td>12</td>
</tr>
<tr>
<td>316L stainless steel</td>
<td></td>
</tr>
<tr>
<td>As-received</td>
<td>4</td>
</tr>
<tr>
<td>Pre-charged</td>
<td>13</td>
</tr>
</tbody>
</table>

2.3. Apparatus for Cryogenic Tensile Test

The following are two methods for achieving a low-temperature environment: cryogens and mechanical coolers. The representative cryogens are liquid nitrogen (77 K), liquid hydrogen (20 K), and liquid helium (4 K). A heater can be used to vaporize the liquid cryogen to achieve the target temperature. For cost considerations, liquid nitrogen at a target temperature above 77 K is preferred. Liquid hydrogen, and liquid helium can be used to create a temperature environment above 20 K. However, helium, an inert gas, is preferred because gaseous hydrogen is a flammable and explosive gas. Typically, a mechanical cooler uses a Gifford-McMahon (G-M) cryocooler in a cryostat. Ogata (2010) reported that the inner wall of a cryostat was cooled using a G-M cryocooler. The helium gas inside the cryostat was cooled to 20 K within 10 h using the convection heat transfer principle [38]. Cryogenic temperature can be achieved at a relatively low cost via the mechanical cooling method because it requires a small amount of gaseous helium [39]. This study adopted the most cost-effective and safe cooling method of using helium gas with a G-M cryocooler at 20 K, despite it taking a long time.

Figure 2 illustrates a tensile cryostat. The vacuum state (10–5 Torr) was achieved between the test vessel and vacuum jacket, which were made of copper and 304 stainless steel, respectively. The thermal body shield was made of aluminum and covered by multi-layer insulation comprising 30 layers as a radiation barrier. The G-M cryocooler (ULVAC, UHE15) was directly connected to the thermal body shield and cooled through the first-stage cold head (45 W at 50 K). The second-stage cold head (1.5 W at 4.2 K) at the bottom of the G-M cryocooler was connected to the test vessel through a copper block.

The test jig inside the test vessel must have a low thermal capacity to cool down the tensile specimen using the G-M cryocooler; hence, the tensile support and bar were dimensioned to be very thin, contributing to limiting the dimensions of the tensile specimen. The test specimen was installed at the specimen grip of the testing jig. The tensile bar of the testing jig was connected to the servo-hydraulic load frames and pulled to apply a tensile load to the specimen. The servo-hydraulic load frames (Walter + bai) had 100 kN static loading capacity and 80 kN dynamic loading capacity.

The temperature of the test vessel was measured using a silicon diode, which was attached to a tensile support. Lakeshore Model 335 measures the resistance change according to the temperature of the silicon diode and controls the temperature using a heater when the temperature of the test vessel is lower than the target temperature. Before cooling down, the test vessel was purged three times with high-purity helium (99.999%).

Figure 3 shows the temperature–time history of the 316L stainless steel tensile specimen measured through a silicon diode. It took approximately 13 h to reach the target temperature (Figure 3a). The temperature variation range around the specimen was controlled within ±0.3 K during tensile testing, as illustrated in Figure 3b, because the energy required to deform the material was converted into heat, which increased the temperature of the material and the G-M cryocooler of the tensile cryostat decreased the temperature of the test vessel simultaneously. This heating phenomenon, known as adiabatic heating, becomes more pronounced at higher strain rates [40]. Therefore, limiting the strain rate is necessary to maintain the temperature of the target material for testing at extremely low temperatures. Ogata (2014) recommended testing at a strain rate lower than $3 \times 10^{-3}$ s$^{-1}$.
based on a previous study, whereas ASTM E1450 recommends tensile testing at a lower strain rate of $3 \times 10^{-3}$ s$^{-1}$ [41,42].

Figure 2. (a) Schematic diagram of the cryostat with the tensile testing machine for the cryogenic environment and (b) overall set-up and installation of tensile specimen.

2.4. Test Procedure

Hydrogen charging and low-temperature tensile tests were performed using the following two-step procedure. First, electrochemical hydrogen pre-charging was conducted on the target specimen. Aluminum alloys are considered insensitive to hydrogen [43], so that aluminum alloys did not carry out hydrogen pre-charging. Constant current of 30 mA/cm$^2$ was applied for 72 h. After hydrogen pre-charging, a tensile test was performed in a tensile cryostat at room temperature or after cooling it down to 20 K. All tensile tests were performed with stroke control (0.0025 mm s$^{-1}$), and the initial strain rate is $2.5 \times 10^{-4}$ s$^{-1}$. 
3. Results and Discussion

3.1. Effect of Low Temperature

This section discusses the investigation of the effect of low temperature on mechanical behavior. All tensile tests were performed twice for reproducibility, and the results are shown in Figures 4–6. Only one stress–strain curve is illustrated for the mechanical behavior at 20 K owing to poor visibility caused by discontinuous yielding. Figure 4 shows the tensile test results in an ambient environment (300 K) and liquid-hydrogen temperature (20 K) for the four types of tensile specimens. No significant difference in yield strength (1% offset) was observed for stainless steel at 300 K. The yield strength of 316L stainless steel was 4.9%, which is greater than that of 304L stainless steel. However, we found a remarkable difference between the stainless steels at 20 K. The gap in yield strength increased by 13.9%. After yielding, austenitic stainless steel exhibited a large change in tensile strength as the strain-induced phase transformation and hardening were promoted at low temperatures [44]. Simultaneously, the elongation of both stainless steels decreased. For the two aluminum alloys, the yield, tensile strength, and elongation increased at 20 K compared to those at 300 K. Improvements in the mechanical performance of 5083-H112 and 6061-T6 aluminum alloys at low temperatures have also been reported in previous studies [45–47]. The improvement in the performance of Al-Mg alloys at low temperatures is attributed to an increase in dislocation density, and an increase in screw dislocation, which results from the reduced dynamic recovery [48–50]. Table 3 quantitatively summarizes the mechanical performance of the tensile specimens at 300 K and 20 K.

The major difference between the mechanical behaviors of stainless steel and aluminum alloy at 20 K is the discontinuous yielding phenomenon. A temporary decrease in stress was observed in the aluminum alloy during plastic deformation, which was insignificant compared with stainless steel. The stress decreased due to increasing discontinuous yielding resulting from the accumulation of the plastic deformation of stainless steel. Discontinuous yielding occurred due to the local catastrophic failure of the lattice barrier in stress fields associated with accumulated edge dislocations [51,52]. Serration shape yielding increased temperature with a sudden decrease in stress as the metallic material deformed, which occurred at specific combinations of strain rate and temperature of the metallic material type [53,54]. The thermal conductivity coefficient and thermal expansion coefficient decreased at very low temperatures, accompanied by adiabatic heating in the specimen. This thermal instability resulted in a random local deformation throughout the
specimen. As the strain rate increased, the local temperature continuously increased, and the serrated phenomenon temporarily disappeared [55].

Figure 4. Effect of temperature on mechanical behavior of (a) austenite stainless steels and (b) aluminum alloys.

Figure 5. Force and temperature time history at 20 K of (a) 304L and (b) 316L stainless steel, (c) 5083-H112 and (d) 6061-T6 aluminum alloy.
This section discusses the study of the effect of hydrogen pre-charging on the mechanical behavior at cryogenic temperatures. The temperature rise was limited within ±0.2 K with cooling down of the G-M cryocooler against heating by discontinuous yielding. We observed a series of temperature increments due to discontinuous yielding, Figure 5 illustrates the time history of the load from the load cell and with the temperature at 20 K. Furthermore, 304L stainless steel showed discontinuous yielding immediately after yielding. In contrast, 316L stainless steel exhibited intermittent serrated yielding in the plateau range. As the plastic deformation of stainless steel accumulated, the amplitude of the stress decreased and the temperature change increased. For the aluminum alloys, discontinuous yielding was not noticeable, and no temperature change was observed.

Table 3. Mechanical performance of target materials at 300 K and 20 K.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. (K)</th>
<th>Yield Strength (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STS 304L</td>
<td>300</td>
<td>299.0</td>
<td>2.6</td>
<td>765.3</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>682.0</td>
<td>7.1</td>
<td>1943</td>
</tr>
<tr>
<td>STS 316L</td>
<td>300</td>
<td>313.5</td>
<td>2.1</td>
<td>660.5</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>777.0</td>
<td>18.4</td>
<td>1824</td>
</tr>
<tr>
<td>Al 5083-H112</td>
<td>300</td>
<td>294.0</td>
<td>2.8</td>
<td>313.5</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>353.5</td>
<td>0.7</td>
<td>470.5</td>
</tr>
<tr>
<td>Al 6061-T6</td>
<td>300</td>
<td>269.5</td>
<td>3.5</td>
<td>291.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>331.0</td>
<td>1.4</td>
<td>461.0</td>
</tr>
</tbody>
</table>

We observed a series of temperature increments due to discontinuous yielding, Figure 5 illustrates the time history of the load from the load cell and with the temperature at 20 K. Furthermore, 304L stainless steel showed discontinuous yielding immediately after yielding. In contrast, 316L stainless steel exhibited intermittent serrated yielding in the plateau range. As the plastic deformation of stainless steel accumulated, the amplitude of the stress decreased and the temperature change increased. For the aluminum alloys, discontinuous yielding was not noticeable, and no temperature change was observed.

The temperature rise was limited within ±0.2 K with cooling down of the G-M cryocooler against heating by discontinuous yielding. However, according to a previous study, 304 stainless steel was observed to instantaneously exceed 20 K with discontinuous yielding during tensile testing at 4.2 K [56]. The temperature time history illustrated in Figure 5 was measured using a silicon diode close to the tensile specimen. A silicon diode was installed to measure the ambient temperature of the specimen to control the test vessel temperature using a cryocooler and heater. The temperature change in the cryostat responded quickly to slight heating because of the high specific heat of gaseous helium at 20 K [57, 58]. Hence, the measured temperature provided an indirect temperature of the specimen.
3.2. Effect of Hydrogen Embrittlement

This section discusses the study of the effect of hydrogen pre-charging on mechanical behavior. Figure 6 shows the stress–strain relationship for ambient and cryogenic environments to evaluate the effect of hydrogen pre-charging on 304L and 316L stainless steel. Changes in the yield strength were observed for both 304L and 316L stainless steel at room temperature; however, the changes were not significant. After yielding, the strain hardening rate decreased compared to that of the as-received specimen for the pre-charged stainless steel. The tensile strength and elongation also decreased. The low strain-hardening rate presumably resulted from the suppressed strain-induced \( \alpha' \) martensite formation in the presence of hydrogen [59–61]. Koyama et al. (2019) reported that hydrogen charging increases the critical stress for \( \varepsilon \)-martensite nucleation and promotes the dislocation motion-related nucleation process [62]. Additionally, the tensile strength decreased when the hydrogen-induced cracking was dominant [23].

No significant difference was found in the yield strength and tensile strength at 20 K compared to the specimen without hydrogen charging. However, strain hardening occurred earlier, allowing tensile strength to be reached with less plastic deformation. The change in the mechanical behavior presumably resulted from hydrogen-induced martensite formation during cathodic hydrogen charging [63,64].

The effect of hydrogen on the mechanical behavior at cryogenic temperatures has been reported. Merket et al. (2021) performed a tensile test at 20 K by cooling gaseous helium after thermal hydrogen charging 304L stainless steel [17]. The pre-charged specimen had reduced ductility by 60% in terms of reduction in area. At Stuttgart University, Germany, tensile tests were performed on 304LN and 316LN stainless steel in liquid hydrogen and gaseous helium at the same temperature. In liquid hydrogen, the elongation decreased by \( \sim 2–4\% \). Furthermore, the relative reduction in areas in liquid hydrogen was 61% and 77% for 304LN and 316LN, respectively, compared to that in gaseous helium [18].

Table 4 summarizes the effects of hydrogen loading on the strength and elongation for quantitative analysis. The ratio in Table 4 indicates the relative ratio of each mechanical performance index between the as-received and hydrogen-charged specimens to determine the influence of hydrogen pre-charging.

<table>
<thead>
<tr>
<th>Material</th>
<th>H(_2) Charging</th>
<th>Testing Temp. (K)</th>
<th>Yield Strength (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Avg.</td>
<td>Std.</td>
<td>Ratio (%)</td>
</tr>
<tr>
<td>STS 304L</td>
<td>AR</td>
<td>300</td>
<td>299</td>
<td>2.6</td>
<td>99.7</td>
</tr>
<tr>
<td></td>
<td>PC</td>
<td>300</td>
<td>298</td>
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<td>97.4</td>
</tr>
<tr>
<td></td>
<td>AR</td>
<td>20</td>
<td>682</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PC</td>
<td>20</td>
<td>664</td>
<td>26.9</td>
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<tr>
<td>STS 316L</td>
<td>AR</td>
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<td>313</td>
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<td>20</td>
<td>768</td>
<td>8.5</td>
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</tr>
</tbody>
</table>

3.3. Macroscopic Analysis

The effect of hydrogen pre-charging and test temperature on the ductility of the material was evaluated by observing the fractured surface and measuring the reduction in area. Only the fracture surface was observed as a function of the temperature for the aluminum alloy that was not charged with hydrogen. All length and fracture shape measurements were obtained using a stereomicroscope (Leica M165C).
Figure 7 shows the fracture morphologies of the aluminum alloy with respect to the temperature. The left and right sides of the photograph show the top and side views of the fractured specimen, respectively. In both the aluminum alloys, wrinkles in the same direction as the loading direction were observed near the fractured part. Moreover, the wrinkling tendency was consistent with the elongation. At room temperature, wrinkles were only observed near the fracture area. Wrinkles appeared throughout the specimen as the elongation of the aluminum alloy increased at low temperatures. A sharp decrease in the cross-sectional area near the fractured part was observed for both the aluminum alloys subjected to tension at room temperature, whereas the cross-sectional area of the tensile specimen did not decrease significantly at 20 K. The decrease in the cross-sectional area with temperature can be confirmed again through the stress–strain diagram (see Figure 4). At room temperature, the aluminum alloy reached the tensile strength within 10% of plastic deformation and underwent a long necking section. At 20 K, the aluminum alloy reached the tensile strength after 25% of the plastic deformation and suffered a short necking section.

![Figure 7](image_url)

(a)

(b)

(c)

Figure 7. Cont.
The reduction in area (RA) was defined to quantitatively evaluate the cross-sectional area after fracture, as follows:

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

where $A_0$ is the cross-sectional area of the specimen before the test, and $A_f$ is the cross-sectional area of the specimen after the tensile test. The reduction in areas of 5083-H112 and 6061-T6 aluminum alloys were 53.6% and 43.0% at room temperature, respectively, and 34.6% and 23.5% at 20 K. The areas of 5083-H112 and 6061-T6 aluminum alloys decreased by 64.6% and 54.6% as the temperature decreased. As mentioned previously, the reduction in the area indicates ductility, although a decrease in the reduction in the area by half does not imply brittleness due to increasing elongation.

Figures 8 and 9 show the fracture surfaces of 304L and 316L stainless steel in accordance with the hydrogen conditions and temperature. At room temperature, a typical cup-cone shape was observed with a reduction in the cross-sectional area for as-received stainless steel. The reductions in areas of 304L and 316L stainless steel were 78.3% and 84.5%, respectively. A dimple was observed at the center of the fracture surface. The hydrogen-charged stainless-steel specimens showed cracks perpendicular to the tensile load direction throughout the specimen. These cracks appeared mainly in hydrogen-charged specimens [23,65,66].

Figure 10 shows the appearance and evolution of the surface cracks of hydrogen-pre-charged 316L stainless steel after yielding. As the stroke increased, the vertical crack grew larger and more distinct. Cracks on the surface eventually decreased the effective cross-sectional area of the tensile specimen for load-carrying. Finally, the decrease in the effective cross-sectional area contributed to the reduction in the strain-hardening rate of the hydrogen-pre-charged specimen.

Figure 11 shows the concept of effective stress based on reducing the cross-sectional area due to damage. Kachanov (1958) proposed a damage variable as the loss of the effective load-carrying cross-sectional area [67]. According to the strain equivalent principle proposed by Lemaitre (1971), effective stress, $\tilde{\sigma}$, is introduced by the relationship between a damaged volume of material under the applied stress, $\sigma$, and damage variable, $D$, as follows [68].

$$\tilde{\sigma} = \sigma \frac{\tilde{S}}{S} = \frac{\sigma}{1 - D}$$

where $\tilde{S}$ is the cross-section area of a fictitious undamaged state. The damage variable of the undamaged material was zero. The damage variable evolved with decreasing effective cross-sectional area. It is generally adopted to describe crack propagation through void nucleation, growth, and coalescence. Hence, the introduction of another damage variable
with quantitative measurements of surface crack growth could explain the decrease in flow stress caused by hydrogen pre-charging.

Figure 8. Fracture morphologies of stainless steel specimens at 300 K; (a) as-received and (b) hydrogen-pre-charged 304L stainless steel specimen and (c) as-received and (d) hydrogen-pre-charged 316L stainless steel specimen.
Figure 9. Fracture morphologies of stainless steel specimens at 20 K; (a) as-received and (b) hydrogen-pre-charged 304L stainless steel specimen and (c) as-received and (d) hydrogen-pre-charged 316L stainless steel specimen.
Figure 10. Surface crack evolution of hydrogen-charged specimen with increase in specimen deformation.

Figure 11. Schematic description of concept of effective stress.

A mixture of brittle and ductile fractures was also observed in the top view of the fracture surface. The pre-charged 304L stainless steel exhibited a distinct brittle fracture zone at the edge of the fracture surface. Wang et al. (2004) regarded it as evidence of irreversible damage after hydrogen charging [69]. This area had relatively little pre-charged 316L stainless steel. These mixed fracture surfaces have been observed on austenitic stainless steel exposed to 1 bar gaseous hydrogen in an ambient environment [26] and 10 bar gaseous hydrogen at −50 °C [24].

At 20 K, no significant difference was observed between the hydrogen-pre-charged and as-received specimens. An oblique fracture pattern without a fibrous area or secondary cracks on the fracture surface was observed regardless of the hydrogen charging condition and steel type. Localized necking-shaped cross-sectional shrinkage was observed throughout the specimen as evidence of discontinuous yielding observed at cryogenic temperatures.

The relative reduction in area (RRA) was adopted to quantitatively evaluate the brittleness caused by hydrogen pre-charging. RRA is the ratio of the reduction in the area of the hydrogen-affected specimen to that of the as-received specimen in the reference environments, such as ambient and helium environment, as follows.

$$RRA = \frac{RA_{H_2}}{RA_{air}} \times 100(\%)$$  \hspace{1cm} (3)

where \(RA_{H_2}\) is the reduction in area of the hydrogen-pre-charged specimen; \(RA_{air}\) is the reduction in area of the as-received specimen.
At ambient temperature, the reductions in areas of 304L and 316L stainless steel after hydrogen charging were 66.4% and 71.4%, respectively, which were 84.8% and 89.0% compared to the non-charged specimens. The area was further reduced during the tensile tests at 20 K compared to that at 300 K owing to hydrogen embrittlement, but the difference is not significant such that it can be used to determine further brittleness. Table 5 lists the reduction in the area of the aluminum alloys and austenitic stainless steel in accordance with the test temperature and hydrogen charging. In the table, the relative reduction in the area of aluminum alloys is not provided because of the lack of hydrogen pre-charging on aluminum alloys.

Table 5. Macroscopic analysis with testing temperature and hydrogen charging condition.

<table>
<thead>
<tr>
<th>Material</th>
<th>Testing Temp. (K)</th>
<th>Hydrogen Charging</th>
<th>Reduction in Area (%)</th>
<th>Relative RA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Avg.</td>
<td>Std.</td>
</tr>
<tr>
<td>STS 304L</td>
<td>300</td>
<td>As-received</td>
<td>78.3</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pre-charged</td>
<td>66.4</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>As-received</td>
<td>47.2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pre-charged</td>
<td>42.0</td>
<td>4.6</td>
</tr>
<tr>
<td>STS 316L</td>
<td>300</td>
<td>As-received</td>
<td>84.5</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pre-charged</td>
<td>71.4</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>As-received</td>
<td>38.6</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pre-charged</td>
<td>32.4</td>
<td>2.3</td>
</tr>
<tr>
<td>Al 5083-H112</td>
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<td>As-received</td>
<td>53.6</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>As-received</td>
<td>34.6</td>
<td>0.0</td>
</tr>
<tr>
<td>Al 6061-T6</td>
<td>300</td>
<td>As-received</td>
<td>43.0</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>As-received</td>
<td>23.7</td>
<td>1.3</td>
</tr>
</tbody>
</table>

4. Conclusions

A uniform distribution of high concentrations of hydrogen in metallic materials is difficult in liquid hydrogen systems subjected to cryogenic temperatures and low pressures of gaseous hydrogen. A tensile cryostat and hydrogen-charging apparatus were developed based on the localized hydrogen concentration and difficulty of hydrogen diffusion at 20 K. The main results of this study are summarized as follows:

- Cathodic charging with high current density at high temperature (80 °C) resulted in intensive hydrogen concentration on the surface of tensile specimen owing to the low diffusion properties of 304L and 316L stainless steel. A high concentration on the surface caused hydrogen-induced cracking on the surface of the tensile specimen, which is the same as the effect of reducing the load-carrying area; it is considered to decrease tensile strength.

- The tensile hydrogen-pre-charged specimen did not show any significant change in the yield strength and flow stress of the hydrogen-charged specimen up to 20% engineering strain. After 20% plastic deformation of stainless steel, hydrogen pre-charging affected strain-hardening behaviors, such as a decrease in tensile strength and elongation.

- Discontinuous yielding of austenitic stainless steel was observed at 20 K. This phenomenon was accompanied by multiple onset of localized necking and temperature rise. The increase in the yield strength of the hydrogen-pre-charged specimens at 20 K is attributed to hydrogen-induced martensite formation.

- The mechanical performance of the aluminum alloys improved at 20 K in terms of strength and elongation. However, serrated yielding and temperature rise were not observed for the aluminum alloys.
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