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Technical Report

Development of HYDLIQUID™: Satisfies the High Strength, Hydrogen Embrittlement Resistance, and Cryogenic Toughness Required for Liquefied Hydrogen from Transport to Gasification

Takahiro IZAWA* Takahiro OSUKI
Kana JOTOKU Jun NAKAMURA

Abstract

Amid global efforts toward a decarbonized society, there have been remarkable technological advances in the construction of supply chains utilizing hydrogen. Nippon Steel Corporation has developed the austenitic stainless steel with good hydrogen embrittlement resistance, high strength, and good weldability, called HYDREXEL™, for hydrogen gas application. HYDREXEL has already been applied in many hydrogen gas stations in Japan. On the other hand, hydrogen gas stations feeding the liquefied hydrogen with better transportation efficiency compared to high pressure hydrogen gas are increasing because of the increase of Fuel Cell Vehicles. Excellent low-temperature toughness is required in addition to both high strength and hydrogen embrittlement resistance for the utilized stainless steel in hydrogen gas application using liquefied hydrogen. Therefore, we have developed a new austenitic stainless steel containing high nitrogen content with superior hydrogen gas embrittlement over −253°C and good low-temperature toughness called HYDLIQUID™.

1. Introduction

Hydrogen is attracting attention as a next-generation energy source that can replace fossil fuels such as coal and oil without CO_2 emissions, and efforts toward the realization of a hydrogen society are accelerating as a national strategy. The number of household fuel cells installed since their market launch in 2009 has been steadily increasing. About 20% of Japan's CO_2 emissions come from the transportation sector, and the automobile industry, which accounts for about 85% of CO_2 emissions, is actively working to expand the use of electric vehicles and fuel cell vehicles, which have zero CO_2 emissions. In 2014, commercial sales of fuel cell battery vehicles which use hydrogen as the power source started, and the construction of hydrogen stations, the fuel supply base, is now being promoted at a rapid pace. According to Japan H_2 Mobility (JHyM),[1] as of May 17th in 2023, 156 hydrogen stations were in operation at 167 sites, and under construction at 320 sites by 2025, and in the Green Growth Strategy of the Ministry of Economy, Trade and Industry, construction at 1 000 sites by 2030 is respectively targeted.

Figure 1 shows the configuration of a hydrogen gas station. There are two types of hydrogen gas stations. One is the off-site type wherein hydrogen gas is transported to the station by tank lorries, and the other is the on-site type wherein hydrogen gas is produced by the hydrogen gas generator installed in the hydrogen station. Hereafter, along with the increase of the utilization of hydrogen gas stations by fuel cell battery vehicles, transportation of hydrogen in a great quantity becomes necessary, and the poor efficiency of hydrogen gas transportation becomes a problem. Therefore, it is highly probable that transportation of hydrogen in liquefied form which is about one 800th in volume that of gaseous hydrogen will be studied in earnest.

On the other hand, in the case where liquefied gas is handled in hydrogen stations, gasifiers which convert liquefied hydrogen to gaseous hydrogen are needed, and the steel materials used therein are required to have excellent cryogenic toughness and good hydrogen embrittlement resistance properties in the cryogenic region at

* Manager, OCTG & Line Pipe Planning Dept., Quality Management Div., Kansai Works
1 Higashimukojima Nishino-cho, Amagasaki City, Hyogo Pref. 660-0856

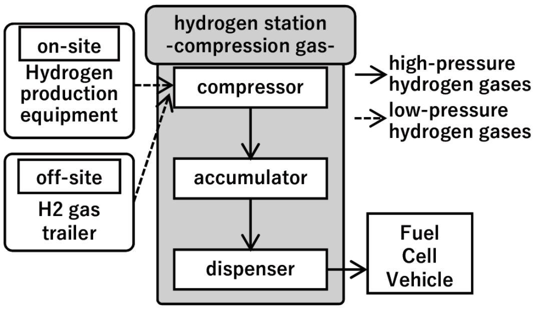

Fig. 1 Configuration of hydrogen gas station utilizing high pressure hydrogen gas and hydrogen gas flow

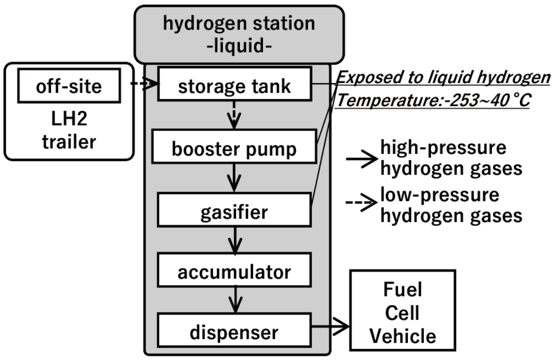

Fig. 2 Configuration of hydrogen gas station utilizing liquefied hydrogen and hydrogen gas flow

−253°C or above. Furthermore, for the compactification and the reduction of the construction cost of hydrogen stations, a liquefied hydrogen station as shown in **Fig. 2** wherein transported liquefied hydrogen is raised to a high pressure gas by booster pumps is also under study. In this case, high strength becomes necessary in addition to cryogenic toughness and hydrogen embrittlement resistance properties. Therefore, we developed a new high-nitrogen stainless steel HYDLIQUID applicable to the abovementioned environment by utilizing the knowledge of HYDREXEL developed for hydrogen stations handling compressed hydrogen gas.

2. Development Concept of HYDLIQUID

2.1 Performance required for steel material for use in cryogenic environment

Hydrogen embrittlement resistance properties of stainless steels under high-pressure hydrogen gas environments influence the amount of deformation-induced martensite which increases and the hydrogen diffusivity which decreases as temperatures decrease, and hydrogen embrittlement resistance properties are lowest at about −80°C.[2] In the gasifiers in liquefied hydrogen stations, since temperature variations from −253°C to room temperature take place, it is necessary to ensure excellent hydrogen embrittlement resistance properties at around −80°C.

Furthermore, for the high-pressure gas specified equipment like gasifiers in the liquefied hydrogen stations, steel materials are usable when they are specified in the ASME Section VIII Division 1 (1998) mentioned in Appendix 1 Article 4 Paragraph 3 of the Collection of Exemplified Standards pertaining to specified facility inspection regulations established by the High Pressure Gas Safety Institute of Japan. Furthermore, when the minimum design metal temperature (MDMT) is −196°C or lower, in the Charpy impact test at −196°C, a lateral expansion of 0.46 mm or above needs to be satisfied. Therefore, steel materials used for gasifiers of liquefied hydrogen stations need to satisfy the above requirement.

2.2 Design concept to secure hydrogen embrittlement resistance properties

In order to develop a high-strength stainless steel having excellent hydrogen embrittlement resistance properties and cryogenic toughness, we focused on HYDREXEL, which was developed based on XM-19, a high-nitrogen stainless steel specified in ASME Section VIII Division 1 (1998) Part UHA. HYDREXEL is a high nitrogen stainless steel having excellent hydrogen embrittlement resistance properties realized by the cell-encapsulation of dislocation microstructure by optimizing the contents of Cr and Mn to prevent the deterioration of hydrogen embrittlement resistance properties due to planarization of dislocations during plastic deformation attributed to high nitrogen.[3–6] It has been reported that such dislocation structure changes are correlated with stacking fault energy, and we considered that it is possible to secure hydrogen embrittlement resistance properties at −80°C by employing the composition design based on XM-19 which is capable of securing the stacking fault energy equivalent to or above that of HYDREXEL having hydrogen embrittlement resistance properties superior to that of SUS316L and the stability of the austenitic structure which suppresses the formation of deformation-induced martensite. (Ni equivalent=[Ni]+0.65[Cr]+0.98[Mo]+1.05[Mn]+0.35[Si]+12.6[C], [ ] shows mass% of each element.)

2.3 Design concept for improving cryogenic toughness

In general, austenitic stainless steels have good cryogenic toughness because they undergo ductile fracture even at cryogenic temperatures.[7] However, high nitrogen stainless steels with high nitrogen solid solutions like XM-19 are known to exhibit cryogenic embrittlement in spite of austenitic structure.[8] Various hypotheses have been proposed as to the cause of this phenomenon, and the following have been reported:[9–12] for example, occurrence of deformation twinning, and crack growth due to stress concentration at the intersection,[9] occurrence of slip-plane-separated fracture of the austenite phase due to accumulation of slip zones on the $\{111\}_{\gamma}$ slip plane,[10] and the pile-up of dislocations at the intersections of cross-slip and/or grain boundaries due to suppression of cross-slip by the planarization of dislocations, forming fracture initiation points, leading to embrittlement-like fracture.[11, 12] These indicate that stress relaxation by increasing the density of movable dislocations is effective in suppressing cryogenic embrittlement of high-nitrogen stainless steels, and the promotion of cross-sliding by increasing the stacking fault energy and the reduction of coarse inclusions/precipitates that inhibit dislocation migration and serve as the origin of stress concentration are effective.[13, 14]

Therefore, in this development, we considered that, based on HYDREXEL, it would be possible to secure cryogenic toughness by further increasing the stacking fault energy by reducing the N content and reducing coarse nitrides by optimizing the Nb and V contents and manufacturing conditions.[15]

2.4 Target compositions and mechanical properties of HYDLIQUID

Table 1 shows the chemical compositions of HYDLIQUID thus developed based on the above concept, and the mechanical proper-

Table 1 Nominal composition of materials used

(mass%)

	C	Si	Mn	P	S	Ni	Cr	Mo	V	Nb	N	Ni equivalent
HYDLIQUID	0.005 –0.060	0.20 –1.00	4.30 –6.00	≤0.030	≤0.001	12.00 –13.50	21.50 –23.50	1.50 –3.00	0.10 –0.20	0.10 –0.20	0.20 –0.40	≥32.09
ASME XM-19	≤0.06	≤1.00	4.0 –6.0	≤0.045	≤0.030	11.5 –13.5	20.5 –23.5	1.50 –3.00	0.10 –0.30	0.10 –0.30	0.20 –0.40	N.A.
HYDREXEL	0.005 –0.060	0.20 –1.00	4.30 –6.00	≤0.030	≤0.001	12.00 –13.50	21.50 –23.50	1.50 –3.00	0.15 –0.30	0.15 –0.30	0.25 –0.40	≥32.09

Table 2 Mechanical property

	Tension testing at room temperature (Tensile Strength)	Impact testing at −196°C (Lateral Expansion)
HYDLIQUID	Min 690 MPa	Min 0.46 mm
ASME XM-19	Min 690 MPa	N.A.
HYDREXEL	Min 800 MPa	N.A.

ties are shown in **Table 2**. The chemical compositions of HYDLIQUID satisfy those of XM-19, and compared with those of HYDREXEL, the contents of N, Nb, and V are lower. The guaranteed Ni equivalent of HYDLIQUID is the same as that of HYDREXEL, and is 32.09 mass% or above, and HYDLIQUID secures the suppression effect on deformation-induced martensite equivalent to that of HYDREXEL. Since the stacking fault energy increases along with the decrease of the N content, HYDLIQUID exhibits hydrogen embrittlement resistance properties at least equal to that of HYDREXEL or above. Furthermore, as strengthening of solid solution and/or precipitation reduce compared with that of HYDREXEL due to lowered N, Nb, and V contents, although the guaranteed tensile strength is the same as that of XM-19 equal to or above 690 MPa, owing to the increase of stacking fault energy by lowered nitrogen content, and the suppression effect on the coarsening of nitrides by the reduction of Nb and V contents, the guarantee of lateral expansion of 0.46 mm or above in the Charpy impact test at −196°C required by ASME Section VIII Division 1 (1998) Part UHA has become possible.

3. Performance of HYDLIQUID

3.1 Mechanical properties

Sample materials, based on HYDLIQUID with varied amounts of Nb and V, were smelted in a laboratory vacuum induction smelting furnace, hot-forged to steel bars with an outside diameter of 120 mm, and solution heat treatment was applied. Four tensile test specimens were taken in the direction parallel to the main forging direction, and four Charpy impact test specimens were taken perpendicularly to the main forging direction. **Figure 3** shows the relationship between the Nb+V content and average tensile strength obtained from tensile tests at room temperature, showing that tensile strength decreases as the Nb+V content decreases. **Figure 4** shows the relationship between the lateral expansion obtained from the Charpy impact test at −196°C and the amount of Nb+V. The amount of lateral expansion increases with the decrease in the amount of Nb+V, indicating that lowering the minimum value of Nb+V from 0.30 mass% in HYDREXEL to 0.20 mass% can ensure good cryogenic toughness.

Next, sample materials with fixed Nb+V content of approximately 0.20 mass% and varied N contents were smelted in a laboratory vacuum induction smelting furnace, hot-forged to steel bars with an outside diameter of 120 mm, and solution heat treatment was applied. Four tensile specimens were taken in the direction parallel to the main forging direction and four Charpy impact specimens were taken perpendicularly to the main forging direction. **Figure 5** shows the relationship between the average tensile strength and N content obtained from the tensile test at room temperature. Tensile strength increases as the N content increases, and the relationship between the lateral expansion obtained from the Charpy impact test at −196°C and the N content shown in **Fig. 6** indicates that the amount of lateral expansion decreases as the N content increases. Therefore, by lowering the lower limit of the N content

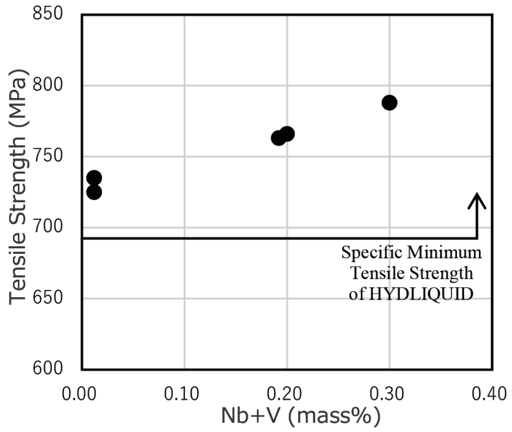

Fig. 3 Effect of Nb+V content on tensile strength at room temperature

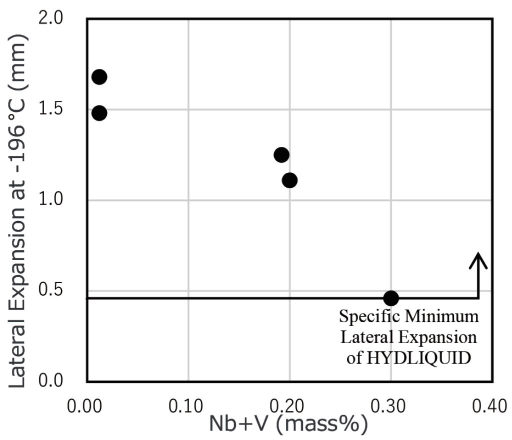

Fig. 4 Effect of Nb+V content on low-temperature toughness at −196°C

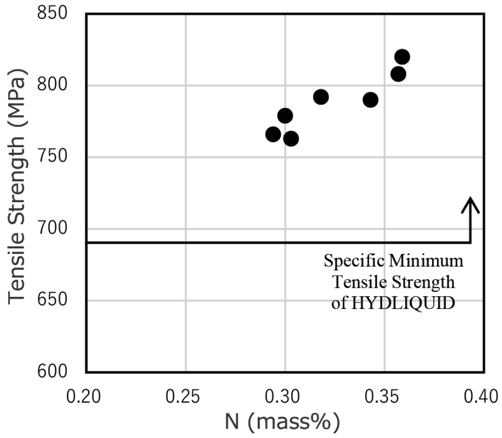

Fig. 5 Effect of N content on tensile strength at room temperature

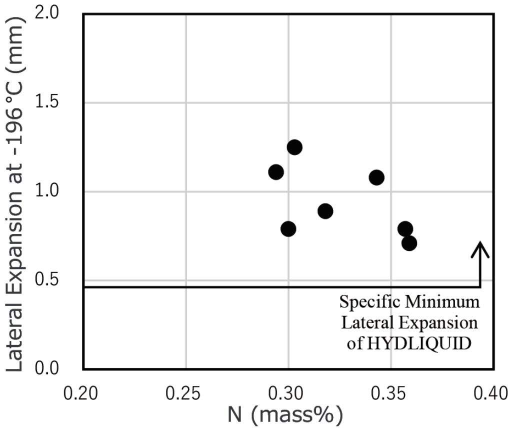

Fig. 6 Effect of N content on low-temperature toughness at −196°C

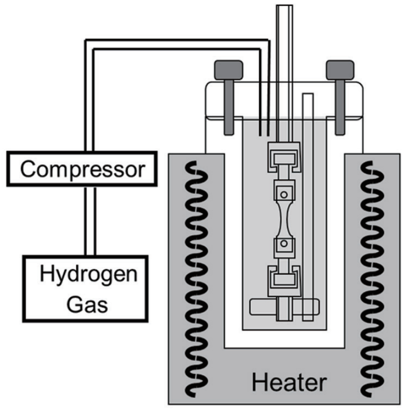

Fig. 7 Configuration of SSRT equipment[5)]

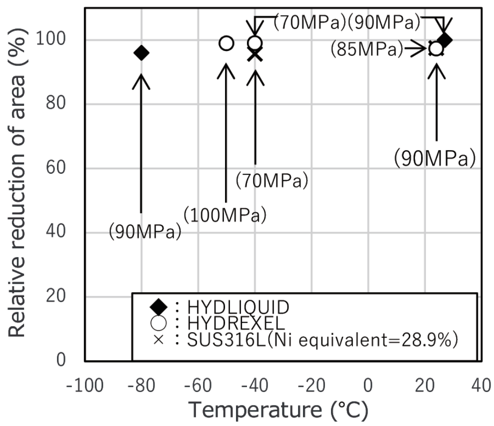

Fig. 8 Effect of temperature on relative reduction of area[5)]

from 0.25 mass% of HYDREXEL to 0.20 mass%, it is possible to secure stable cryogenic toughness while maintaining the guaranteed tensile strength of XM-19.

3.2 Hydrogen embrittlement resistance properties

For evaluation of the steel material hydrogen embrittlement resistance properties under the high-pressure hydrogen gas environment, the slow strain rate test (hereafter referred to as SSRT) is effective.[2, 6)] **Figure 7** shows the configuration of SSRT equipment. In SSRT, plate-shaped or bar type test specimens are stretched at a slow strain rate under high-pressure hydrogen gas, open air, and inert gas, and the values of fracture reduction of area and fracture elongation under the respective environments are compared. Steel materials susceptible to hydrogen embrittlement show fracture elongation and fracture reduction of area in high-pressure hydrogen gas environment values lower than those in open air or inert gas environments. Then, it is possible to evaluate relatively the hydrogen embrittlement resistance properties by using the relative fracture elongation, and relative reduction of area (hereafter referred to as RRA) which are the rations of the values of fracture elongation and fracture reduction of area in the high-pressure hydrogen environment vs. those in open air or inert gas. Namely, this means that the higher the relative fracture and the fracture reduction of area are, the higher the hydrogen embrittlement resistance properties become. Furthermore, it is reported that if these values are above 80%, the subject steel material has good hydrogen embrittlement resistance properties.[2)]

Figure 8 shows the result of SSRT of HYDLIQUID at −80°C to room temperature in the high-pressure hydrogen gas environment. For comparison purposes, the results of SUS316L with Ni equivalent to 28.9% and that of HYDREXEL are shown together. Tests were conducted at −80°C to room temperature at the strain rate of 3.0×10^{-6} to 2.5×10^{-5}/s under high-pressure hydrogen gas (Max. 100 MPa). At −80°C, HYDLIQUID exhibits the lowest hydrogen embrittlement resistance properties; however, RRA satisfies 80% and above, and HYDLIQUID has excellent hydrogen embrittlement resistance properties superior to that of SUS316L.

4. Performance of HYDLIQUID Welded Joint

In order to evaluate the performance of the HYDLIQUID welded joint, welded joints were prepared by gas tungsten arc welding (hereafter referred to as GTAW) using as filler metal YS316L which is the filler material of SUS316L applied to liquid hydrogen tanks and/or gasifiers. A plate material was used as the base metal which had been vacuum-smelting processed, hot-forged, and hot-rolled, and solution heat treatment was applied. Multi-layer welding was applied to the beveling of the HYDLIQUID plate as shown in **Fig. 9**, using a 1.2 mm in diameter welding material wire of 28.6%Ni equivalent YS316L. Heat input was 7–12 kJ/cm, Ar was used as the

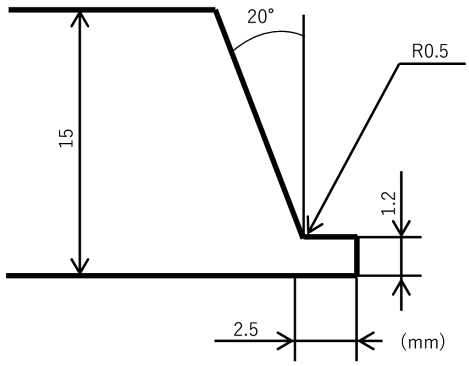

Fig. 9 Groove shape of weld evaluation

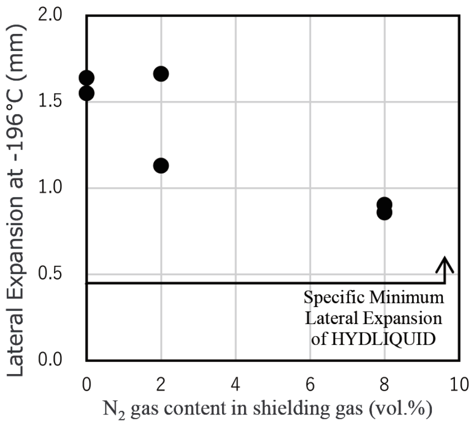

Fig. 10 Low-temperature toughness of welded joints

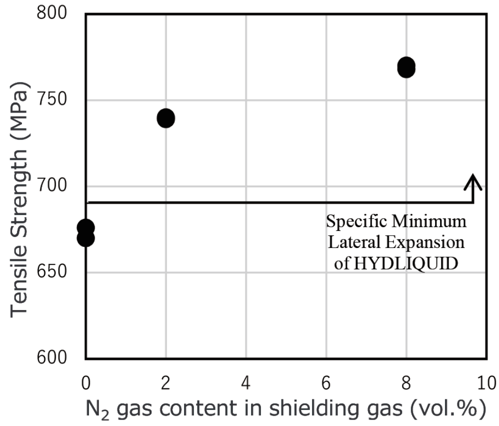

Fig. 11 Tensile strength of welded joints

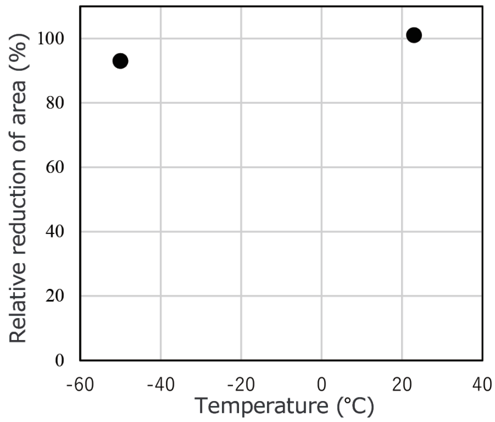

Fig. 12 Effect of temperature on relative reduction of area in welded joints

back shielding gas, and interpass temperature difference was controlled to below 150°C, and without preheating and post heating. Since the strength of the deposit metal of YS316L is lower than the guaranteed strength of the base metal of HYDLIQUID, for the main test, nitrogen gas was mixed into the Ar shielding gas by 0%, 2%, and 8%, and welded joints were prepared respectively. Then, perpendicularly to the weld line, tensile strength test specimens and Charpy impact test specimens (notch position at weld metal) were taken.

Figure 10 shows the result of the Charpy impact test of the HYDLIQUID welded joints at −196°C. Although the cryogenic toughness of the HYDLIQUID welded joints deteriorates as the mixture ratio of nitrogen gas in the Ar shielding gas increases, even in the case of 8% nitrogen gas mixture, the lateral expansion satisfies the specified minimum of 0.46 mm.

Figure 11 shows the result of the tensile test of HYDLIQUID welded joints at room temperature. Although in the case of 100% Ar shielding gas being used, it is difficult for the weld metal to satisfy the base metal guaranteed strength of 690 MPa or above, the welded joint tensile strength of 690 MPa or above can be satisfied at least by securing the nitrogen gas mixture of 2% or above.

Figure 12 shows the result of SSRT of the HYDLIQUID welded joints prepared by using the Ar+2%N_2 mixed shielding gas. The test was conducted under the conditions of test temperatures and hydrogen gas pressures at −50°C under 70 MPa and at room temperature under 90 Mpa, respectively at the stain rate of 3×10^{-6}/s. Hydrogen embrittlement resistance properties of the HYDLIQUID welded joints satisfy 80% or above of RRA, and excellent hydrogen embrittlement resistance properties are exhibited.

5. Conclusion

We have developed a high-strength, high-nitrogen stainless steel HYDLIQUID securing hydrogen embrittlement resistance properties and cryogenic toughness at −253°C required of steel materials used for hydrogen stations handling liquid hydrogen. HYDLIQUID has already been shipped for actual use in hydrogen stations handling liquid hydrogen, and we wish to contribute to the dissemination of hydrogen stations together with HYDREXEL.

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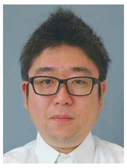
Takahiro IZAWA
Manager
OCTG & Line Pipe Planning Dept.
Quality Management Div.
Kansai Works
1 Higashimukojima Nishino-cho, Amagasaki City, Hyogo Pref. 660-0856

Kana JOTOKU
Former Researcher,
Material Research Dept., Kansai R&D Lab.
Current Specially Appointed Assistant Professor,
Joining and Welding Research Institute,
Osaka University
(Nippon Steel Future Manufacturing Research Alliance Laboratories)

Takahiro OSUKI
Ph.D, Principal Researcher, Head of Dept.
High Toughness Steel Research Lab.
Steel Research Laboratories



Jun NAKAMURA
Former Senior Researcher,
Pipe & Tube Research Lab., Steel Research Laboratories
Current Deputy Director, Environment Dept.,
New Energy and Industrial Technology Development Organization