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Weldability of High-strength Stainless Steel HYDREXEL™ for High Pressure Gaseous Hydrogen Environments

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Abstract

The construction of gaseous hydrogen refueling stations for fuel cell vehicles (FCV) is being globally promoted to realize the hydrogen society. In recent years, higher pressure stations with a design pressure of 70 MPa are required from the viewpoint of increasing loading efficiency. To increase gas pressure without enlarging equipment, higher strength material for piping is mandatory. HYDREXELTM, which has a high nitrogen content, has been developed as the material to satisfy high strength over 800 MPa, excellent resistance for hydrogen embrittlement and good weldability. It was practically used as piping in a high pressure station in 2014. Then, in 2015, a high pressure gaseous hydrogen refueling station was constructed by welding for the first time. Currently, HYDREXELTM is being widely used in high pressure gaseous hydrogen refueling stations in Japan.

1. Introduction

Hydrogen is expected to be the next generation core energy. Hydrogen infrastructures have been developed toward the realization of the hydrogen society. The number of home fuel cells that were first put on the market in 2009 has been steadily increasing. Commercial sales of fuel cell vehicles (FCVs) started in December 2014. The Japanese government is constructing gaseous hydrogen refueling stations as fuel supply bases, aiming at providing a total of 160 stations by FY2020. A hydrogen town at the 2020 Tokyo Olympics is being discussed, so more gaseous hydrogen refueling stations may be constructed. Figure 1 shows the configuration of a hydrogen refueling station. Metal materials used for hydrogen refueling stations are exposed to high pressure hydrogen, so they must be highly resistant to hydrogen embrittlement. Hydrogen embrittlement refers to a phenomenon in which hydrogen atoms retained in metal materials hinder the materials from deforming and cause embrittlement (degradation of elongation and reduction of area) as shown in Fig. 2. Meanwhile, FCVs have 70 MPa class hydrogen tanks to increase the travel distance, which requires that the pressure of hydrogen to be loaded at gaseous hydrogen refueling stations be higher than the current level of 35 MPa. In addition, hydrogen needs to be loaded quickly.



Fig. 1 Illustration of hydrogen gas supply in high pressure hydrogen refueling station

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Fig. 2 Schematic illustration of hydrogen embrittlement

To this end, the area of passages, or the inner diameters of pipes, where hydrogen gas flow needs to be secured. To meet these requirements without upsizing equipment (increase in the major diameter and thickness of pipes), high strength metal materials that can restrain the increase in the material thickness of pipes required based on the pressure resistance property and that can secure the inner diameter are required (the solid line arrows in Fig. 1 indicate that high strength materials are essential).

Type 316L for which the chemical compositions are specified has been used for 70 MPa level high pressure hydrogen refueling stations as will be described later. However, solution treated Type 316L cannot secure the required inner diameter of pipes and thereby the equipment unavoidably needs to be larger. Therefore, materials whose strength has been improved by cold working are often used, but when such materials are welded, the strength decreases due to the influence of the weld thermal cycles. Accordingly, mechanical joints like cone and thread joints have been used for connecting. However, there is some concern of reliability on these joints, such as looseness due to vibration and thermal stress during the long term usage, so construction by welding has been strongly demanded. Therefore, to satisfy the needs for weldable high strength stainless steel with excellent resistance to hydrogen embrittlement, we have developed high strength stainless steel for high pressure gaseous hydrogen HYDREXELTM and put it on the market. This report describes the development concepts of the steel and various characteristics-mainly regarding weldability.

2. Development Concepts of High Strength Stainless Steel HYDREXEL[™] for High Pressure Gaseous Hydrogen

Table 1 shows the characteristics of HYDREXEL[™] and Table 2 lists the chemical compositions. The resistance to hydrogen embrit-

tlement is expressed by Ni equivalent (Ni equivalent = [Ni]+0.65[Cr]+0.98[Mo]+1.05[Mn]+0.35[Si]+12.6[C], [x] is the mass% of each element) that refers to the stability of austenite structure.¹⁾ The Japanese High Pressure Gas Safety Act stipulates that the Ni equivalents of materials to be used at -45°C or higher at hydrogen refueling stations shall be equal to or higher than 28.5% (required value at which Type 316L does not cause hydrogen embrittlement at -45° C). For HYDREXEL[™], the quantity of Ni added has been reduced to the level of that of Type 316L and the quantities of Mn, Cr, and N added, which are less expensive compared to Ni, have been optimized, achieving Ni equivalents equal to or higher than 32.09%. Regarding the strength, the targeted tensile strength (TS) of 800 MPa or higher has been achieved by increasing the N content compared to the existing stainless steel. In addition, the high strength has been achieved in the solution treatment status, so the steel can be welded for construction.

3. Resistance to Hydrogen Embrittlement

A slow strain rate test (SSRT) was used to study the metal materials' resistance to hydrogen embrittlement in a high pressure hydrogen environment.²⁻⁴⁾ **Figure 3** illustrates the configuration of the tester. In an SSRT, a plate-like or round bar shaped tensile test piece is pulled at a slow strain rate in hydrogen and air (or in inert gas) to compare the reduction of area and elongation. As the relative reduction of area that indicates the ratio of the reduction of area in hydrogen to that in the air (or in inert gas) is higher, the resistance to hydrogen embrittlement is superior. A tester with the rated load of 10 kN was used in the test. SSRT was carried out in an autoclave pressurized with 90 MPa gaseous hydrogen at the temperature range



Fig. 3 Schematic illustration of SSRT apparatus

	[True 2161	HYDREXEL™	
Performance	Specification	1ype 3161		
renormance	Specification	Solution heat treatment	Cold work	Solution heat treatment
Resistance to hydrogen embrittlement	Ni equivalent $\geq 28.5\%$	0	0	0
High-strength material	$TS \ge 800 MPa$	×		0
Weldability	TS of welded joint $\ge 800 \text{ MPa}$	×	×	0

Table 1 Characteristics of HYDREXEL™

 \bigcirc : Outstanding, \bigcirc : Good, \triangle : Acceptable, \times : Not acceptable

Table 2 Nominal compositions of HYDREXELTM (mass%)

С	Si	Mn	Р	S	Ni	Cr	Мо	V	Nb	Ν	Ni equivalent
0.005-0.06	0.2-1.0	4.3-6.0	≤ 0.03	≤ 0.001	12.0-13.5	21.0-23.5	1.5-3.0	0.15-0.30	0.15-0.30	0.25-0.40	≥ 32.09



Fig. 4 Effect of temperature on relative reduction of area

from -40 to 150°C. The strain rate was 3×10^{-6} s⁻¹ at the cross head speed referred to the original gage length 20 mm.

Figure 4 shows the SSRT results in high pressure hydrogen. The figure also shows the results of Type 316L with the Ni equivalent of 28.9% for comparison. The figure shows that the relative reduction of the area of HYDREXELTM with the Ni equivalent exceeding 32% surpasses 90% in a wide range of −50 to +150°C and thereby HYDREXELTM has excellent resistance to hydrogen embrittlement equal to or higher than that of Type 316L.

4. Weldability of HYDREXELTM

4.1 Welded joints without filler wire

Steel sheets 2.2 mm thick were used as samples. An I-groove was provided at the edges of the test samples by machining and the sheets were butted to form welded joints by gas tungsten arc welding (GTAW) without using filler wires. The weld heat input was varied from 0.3 to 0.5 kJ/mm. The pure Ar or Ar+2 to 8 vol%N₂ were used as the shielding gas and the pure N₂ was also used as the back shielding gas.

Figure 5 shows the tensile test results of welded joints prepared under various welding conditions such that the nitrogen content in the shielding gas and weld heat input were changed. For all the heat input values, the tensile strength increases until the nitrogen content in the shield gas reaches 2 vol% and then results in saturation. Meanwhile, when the nitrogen content in the shielding gas is the same, the tensile strength of the welded joints with 0.3 to 0.4 kJ/mm is higher, satisfying 800 MPa that is the guaranteed tensile strength



Fig. 5 Tensile test results of no-filler welded joints

of the base metal. **Figure 6** shows the measured fraction of δ ferrite in the weld metals on the joints with 0.4 to 0.5 kJ/mm. When pure Ar was used as the shielding gas, some δ ferrite remained. When the nitrogen gas content in the shielding gas exceeded 5 vol%, the structure became austenite (single phase) in most parts. The strengthening by fine dispersion of the δ ferrite phase disappears, which is offset by the solute strengthening due to an increase in the nitrogen content. Therefore, the tensile strength reached saturation against the increase in the nitrogen content in the shielding gas.

4.2 Welded joints with filler wire

4.2.1 Higher strength of HYDREXEL™ welded joints

Steel sheets 4 mm thick were used as samples. A U-groove was provided at the edges of the test samples by machining and the sheets were butted to form filler welded joints by GTAW using the commercially available filler wires listed in **Table 3**. The outer diameters of all the filler wires are 1.2 mm. The weld heat input was adjusted ranging from 0.4 to 0.8 kJ/ mm. The pure Ar or Ar+2 to 8 vol%N₂ were used as the shielding gas and the pure N₂ was also used as the back shielding gas.

Figure 7 shows the tensile test results of welded joints using filler



δ ferrite fraction :0.9% δ ferrite fraction :0.2% Fig. 6 Microstructures of weld metals (weld heat input: 0.4–0.5kJ/mm)

Table 3 Compositions of welding consumables (mass%)

Туре	С	Si	Mn	Ni	Cr	Мо	N
ER309LMo	0.02	0.5	1.5	13.8	23.1	2.2	0.08
ER308H	0.06	0.4	2.0	10.2	19.7	_	0.03
ER308N2	0.07	0.2	2.1	9.7	21.4	_	0.15
ER209	0.04	0.4	5.8	9.9	21.3	1.6	0.20





Fig. 8 Effect of N₂ gas content in shielding gas on tensile strength of weld metal and N content in weld metal

wire designated ER309LMo, the shielding gas was pure Ar or Ar+2 vol%N₂, and the back shielding gas was pure N₂. Some test specimens used had excessive convexity formed during the welding and the others did not. Although the test pieces with excessive convexity failed at the weld metals regardless of the shielding gas types, they satisfied 800 MPa, the guaranteed tensile strength of the base metal. When Ar+2 vol%N₂ was used as the shielding gas, the tensile strength improved compared to when pure Ar was used. On the other hand, for the test specimens without excessive convexity, when Ar+2 vol%N₂ was used as the shielding gas, the tensile strength became higher. However, they did not satisfy the guaranteed tensile strength of the base metal and failed at the weld metals. Weld metals need to have higher strength to increase the welding construction conditions.

We studied whether weld metals of austenitic stainless steel can have higher strength by adding nitrogen to shielding gas to increase the nitrogen content that contributes to solute strengthening. ER309-LMo was used and the nitrogen content in the shielding gas was changed to make welded joints. **Figure 8** shows the tensile test results and analysis results of the nitrogen content in the weld metals. All welded joints failed at the weld metals. As the nitrogen content in the shielding gas increases, the tensile strength increases. However, when the nitrogen content in the shielding gas exceeds 2 vol%, the tensile strength starts to increase more slowly. The nitrogen content in the weld metals increases as the nitrogen content in the shielding gas increases.

Figure 9 shows the results of a similar study using different filler wires. When ER308N2 was used as a welding filler, as the nitrogen content in the weld metals increases, the tensile strength of the weld metals also increases as is the case with ER309LMo. On the other hand, when ER308H was used, the tensile strength decreases once as the nitrogen content increases. Then it starts increasing when the nitrogen content further increases. The influence of nitrogen on the tensile strength varies depending on the welding filler. In addition, when ER209 was used and when the nitrogen content exceeded 0.43 mass% (when the nitrogen content in the shielding gas was more than 5 vol%), blowholes occurred in the weld metals and thereby sound welded joints could not be obtained, so the tensile strength decreased.

From the results in Fig. 9, the influence of the nitrogen content on the tensile strength of the weld metals varied only when ER308H was used. This is presumably because traditionally the tensile



N content in weld metal (mass%)

Fig. 9 Relationship between tensile strength of weld metal and N content in several weld metals

strength of austenitic stainless steel is affected by solid solution elements, δ ferrite, and twin spacing.⁵⁾ Therefore, we compared the δ ferrite fraction in the weld metals because solid solution elements and δ ferrite presumably affect weld metals whose structure has just solidified. **Figure 10** shows the results. When the nitrogen content in the weld metals is the lowest for each welding material, that is to say, when pure Ar was used for the shielding gas, the δ ferrite fraction in all the welding material is approximately 5 to 8%.

On the other hand, when the nitrogen content is 2 vol% and when ER309LMo and 308N2 were used, the δ ferrite fraction is approximately 2 to 6%. However, when ER308H was used, the microstructure of the weld metal was mostly austenite (single phase). From these results, when ER308H was used, until the nitrogen content in the weld metals reached approximately 0.22 mass%, as the nitrogen content increased, the δ ferrite disappeared. Therefore, the effect of increased strength due to the δ ferrite was presumably lost and thereby it seemed that the nitrogen content exceeded approximately 0.22 mass%, the microstructure of the weld metals changed to austenite (single phase). Therefore, the microstructure has little influence and as the nitrogen content increases, the tensile strength increases. As a result of this, the ER308N2 may have behaved differently from ER309LMo and 308N2.

Therefore, using nitrogen in weld metals and considering the influence of δ ferrite and solid solution elements other than nitrogen can produce higher strength of the weld metal.

4.2.2 Improvement of tensile strength of weld metal

From the study above, increasing the nitrogen content in weld metals may be effective in increasing their strength. We studied optimization of the chemical compositions of filler wires to further increase the strength of weld metals. Many studies have been conducted on nitrogen uptake in weld metals to date. Some researchers have reported that the influence of alloying elements on the nitrogen content in weld metals is almost equal to that on the equilibrium solubility of nitrogen.⁶⁾ The equilibrium constant (*K*) in the nitrogen uptake reaction in the molten iron alloy shown with formula (1) can be expressed with formula (2).⁷⁾

$$N_2(gas) = 2N(in \ liquid \ metal) \tag{1}$$

 $K = a_N \cdot (P_{N_2})^{-1/2} = f_N \cdot [\%N]_e \cdot (P_{N_2})^{-1/2}$ (2) Where, a_N is the nitrogen activity in the molten alloy, f_N is the activity

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Fig. 10 Microstructures of weld metals



Fig. 11 Effect of activity coefficient of nitrogen on N content in weld metal and ensile strength of weld metal

coefficient of the nitrogen in the molten iron alloy, and P_{N_2} is the atmospheric nitrogen partial pressure (atm).

The solubility of nitrogen in molten iron alloy in an equilibrium state is expressed by formula (3).⁸⁾ From formulae (2) and (3), the nitrogen content dissolved in the molten metal alloy is expressed using formula (4).

$$log K = -518/T - 1.063$$
(3)
$$log [\%N] = -518/T - 1.063 - log f_N + 1/2 \cdot log \sqrt{P_{N_0}}$$
(4)

As shown above, when the temperature (T) and nitrogen partial pressure (P_{N2}) are constant, the nitrogen content dissolved in molten iron alloy increases as the f_N decreases. Therefore, when f_N is smaller, the solubility of nitrogen in weld metals may be improved. Whereas, the activity coefficient can be expressed using the interaction auxiliary coefficient of other alloying elements in molten iron alloy and their concentration as reported by Kokawa et al.7)

Various filler wires were created for which ER309LMo was used as their bases and f_N was changed to study the relationships with the nitrogen content in weld metals made by welding and with their tensile strength. **Figure 11** shows the results. As the nitrogen activity coefficient (f_N) of the welding fillers becomes smaller, the nitrogen content in the weld metals increases and the tensile strength also increases. Reducing f_N is effective for producing higher strength weld metals.

4.3 Resistance of welded joints to hydrogen embrittlement

Figure 12 shows the evaluation results of resistance to hydrogen embrittlement of no-filler welded joints (weld heat input: 0.4 to 0.5 kJ/mm, shielding gas: $Ar+8 \text{ vol}\%N_2$) and that of filler welded joints (welding material: ER309LMo, shielding gas: pure Ar). SSRT was carried out in an autoclave pressurized with 70 MPa gaseous hydrogen at -40°C and 90 MPa gaseous hydrogen at RT. The relative reduction of area of all the welded joints exceeds 90% and thereby the welded joints have excellent resistance to hydrogen embrittlement.

5. Conclusion

This report describes the development concepts of high strength stainless steel for high pressure gaseous hydrogen HYDREXELTM and its weldability. Weldable HYDREXELTM is stronger than conventional Type 316L, contributing to the downsizing of hydrogen refueling stations and enhancing their reliability. The increased use of HYDREXELTM is expected to further contribute to the hydrogen society.

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

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