

Suitability Evaluation of High-strength 15% Ni Steel for Liquid Hydrogen Tank^{*1}

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Abstract

This study evaluates the suitability of using high-strength 15% Ni steel in large, liquefied hydrogen tanks. The allowable stress of the 15% Ni steel was 230 MPa based on the International Maritime Organization (IMO) Type C formula, which was 1.68 times higher than that of SUS304L. The required fracture toughness, K_{Ic} (J), at 20 K was estimated to be 171 MPa \sqrt{m} , and both the base material and weld joints of the 15% Ni steel exhibited sufficient toughness. The potential application merit of 15% Ni steel is to reduce the steel weight of a large, liquefied hydrogen tank instead of using a thicker SUS304L plate.

1. Introduction

In recent years, the expectations for using liquid hydrogen as a clean energy source have been increasing. Steel plates used in tanks for storing and transporting liquefied gases, such as liquid hydrogen, require excellent cryogenic toughness, and austenitic stainless steels, which are resistant to brittle fracture. Austenitic stainless steels have sufficient cryogenic toughness,¹⁾ but the yield stress of general-purpose materials at room temperature is approximately 200 MPa.

When austenitic stainless steel with insufficient strength is applied to liquid hydrogen tanks, the size increase is limited. If the steel yield stress is approximately 200 MPa, the plate thickness must be increased when increasing the tank size, which ultimately increases the tank weight and production cost. To address these issues, an austenitic high-Mn stainless steel with a yield stress of 450 MPa at 0.2% at room temperature has been developed.^{2,3)} However, austenitic high-Mn stainless steels have weldability issues such as weld fumes. Moreover, they have a higher coefficient of thermal expansion than ferritic steels; therefore, for large liquid hydrogen tanks, ferritic steels with a lower coefficient of thermal expansion are advantageous because of fatigue and other problems.

As ferritic steel for low-temperature applications, 9% Ni steel is used as a tank material for liquefied natural gas (LNG), which is a typical liquefied gas.⁴⁾ Although LNG is hotter than liquid hydrogen,

9% Ni steel has excellent cryogenic toughness. Various 9% and 7% Ni steels suitable for LNG tanks have been proposed previously.⁵⁻⁷⁾ The yield strength of 9% Ni steel at room temperature can be 590 MPa or higher and it can be applied to large LNG tanks. On the contrary, 9% and 7% Ni steels are unlikely to have sufficient toughness at 20 K, which is the liquid hydrogen temperature.

Therefore, we propose a Ni-containing steel for cryogenic use that has sufficient toughness at 20 K, sufficient hydrogen embrittlement resistance, and a yield stress of 590 MPa or higher at room temperature. It has a Ni content of approximately 15%, which is higher than that of conventional 9% Ni.

2. Experiments

2.1 Developed steel and material properties

An ingot was produced by laboratory vacuum melting and comprised of 15% Ni steel. 100 mm thick ingot was hot-rolled into a 20 mm thick plate. The plate was heat-treated three times (QLT) to obtain a fine microstructure and an appropriate amount of stable retained austenite. First, it was quenched from the austenite temperature to obtain a fresh martensite structure. Subsequently, it was quenched from the two-phase temperature, the so-called lamellarizing process, to obtain a sufficient amount of reverse-transformed austenite. Finally, it was tempered at a temperature near A_{c1} to concentrate austenite-stabilizing elements. As shown in **Fig. 1**, a microstructure of fine-grained tempered martensite was obtained. The area-averaged grain size, defined by the 15° orientation difference measured by electron back scattered diffraction pattern method, was

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7.0 μm. The fraction of retained austenite at room temperature, measured by X-ray analysis, was 17.3%. Only deep cooling to 20 K did not change this fraction much, but it decreased under plastic deformation near the fracture surface.

Stress-strain curves at various temperatures were obtained from the actual tensile tests. The specimens were collected from the middle of the plate and perpendicular to the rolling direction. In particular, the test was conducted at 20 K in liquid hydrogen. The results of the tensile tests are shown in Fig. 2. At room temperature, the yield stress, which is evaluated here as a 0.2% proof stress, was approximately 690 MPa, and the tensile stress was approximately 790 MPa. At 77 K, the yield and tensile stresses were approximately 770 MPa and 1 290 MPa, respectively. At 20 K, the yield and tensile stresses were approximately 850 MPa and 1 600 MPa, respectively. Note that

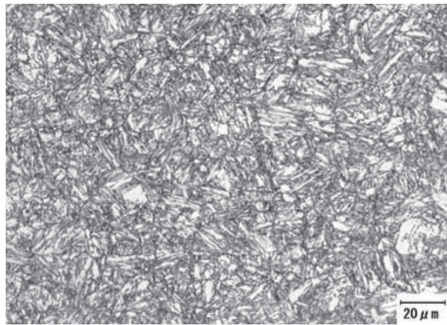


Fig. 1 Microstructure of 15% Ni steel base metal

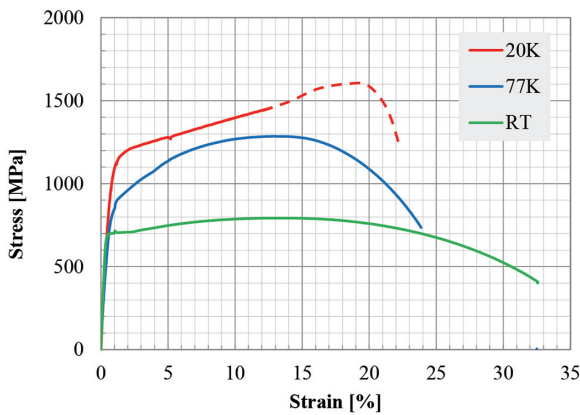


Fig. 2 Result of tensile test of 15% Ni steel (dashed lines are estimated from the strokes)

the dashed lines are estimated from the strokes owing to the measurement limits of the extensometer. As the test temperature decreased, both the yield stress and tensile stress increased; however, the increase in yield stress was not as high as the increase in tensile stress. Consequently, the yield ratio, which is the ratio of the yield stress to the tensile stress, is smaller at lower temperatures. The general properties of the 15% Ni steel compared to those of SUS304L are summarized in Table 1. The yield stress of the 15% Ni steel at room temperature was approximately three times that of SUS304L. The fracture toughness values will be discussed in detail later, but the 15% Ni steel, including the weld joints, has the same or higher toughness than SUS304L.

2.2 Hydrogen embrittlement resistance evaluation test

Tensile tests were conducted under high-pressure hydrogen using a slow strain rate technique to evaluate the hydrogen embrittlement resistance of 15% Ni steel.

The specimens were collected from the middle of the plate and perpendicular to the rolling direction. To facilitate the effect of hydrogen, the strain rate under high-pressure hydrogen at 45 MPa was assumed to be $8 \times 10^{-5} \text{ s}^{-1}$, and the strain rate in air was assumed to be $8 \times 10^{-3} \text{ s}^{-1}$. The relative Reduction of Area (RRA), which is the ratio of the Reduction of Area (RA) under high-pressure hydrogen to RA in air, was evaluated. The RA values under high-pressure hydrogen and air were 74.1% and 77.8 %, respectively. Consequently, the RRA was calculated to be 0.95. The hydrogen embrittlement resistance of 15% Ni steel was sufficiently high. The tensile fracture surface under high-pressure hydrogen is shown in Fig. 3. No brittle fracture features, characteristic of hydrogen embrittlement, were observed at fracture surface.

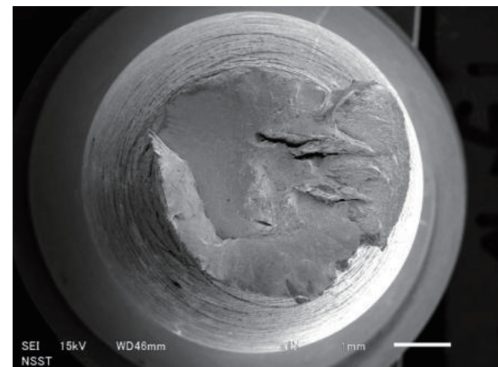


Fig. 3 Tensile fracture surface under high-pressure hydrogen

Table 1 Properties of 15% Ni steel compared to SUS304L

Steel	Component	Base metal				Weld joint		
		Strength				Toughness		
		RT		20K (in LH2)		20K (in LH2)	20K (in LH2)	
		YS (MPa)	TS (MPa)	YS (MPa)	TS (MPa)	K_{Ic} (J) (MPa√m)	K_{Ic} (J) (MPa√m)	
SUS304L	Fe-18%Cr-8%Ni steel	Austenite	175–	480–	-	-	150–200	150–200
15%Ni steel	Fe-15%Ni steel	Ferrite (a small amount of Austenite)	550–750	700–850	850–1 350	1 350–1 650	200–	150–200

2.3 J-R curve test

A J-R curve test was performed to evaluate the fracture toughness of the weld joint of 15% Ni steel based on ASTM: E1820-13.⁸⁾ A weld joint consisting of a 15% Ni steel base plate and 70% Ni welding material was fabricated under the following welding conditions: The welding method was shielded metal arc welding for a 60° X-type groove with a current of 140 A, voltage of 25 V, and heat input of 12–21 kJ/cm. Half-inch compact tension specimens (thickness: 12.7 mm and width: 25.4 mm) were collected from the middle of the weld joint and perpendicular to the rolling direction. Fusion Line (FL) notch was defined as one containing half of the welding metal at the notch tip. The heat-affected zone (HAZ) 1 notch was defined as a notch 1 mm from the FL notch on the HAZ side, and other notches were defined in a similar manner. The initial crack length was 14 mm, a tip 2 mm was introduced using the fatigue method. The test temperature was 20 K, which was achieved by evaluation using liquid hydrogen. A double-cantilever clip-in displacement gauge was mounted using integral knife-edges. The unloading compliance method was used to evaluate the crack extension. In addition, the J-integral value was calculated from the measured load and displacement. Finally, K_{Ic} was converted from J_{Ic} which was determined as the intersection of the J-R curve and 0.2 mm offset line.

The results of the J-R curve test are shown in Fig. 4. As the crack extension increased, the J-integral also increased. The J-integral was the highest in WM among the evaluated notch positions. The J-integral of HAZ had various values; the closer it was to WM, the better the value, and the further away it was from WM, the worse the value. It can be concluded that the J-integral of HAZ is supported by the preferential deformation of the soft WM.

The Converted K_{Ic} from J_{Ic} is shown in Fig. 5. Both the base material and weld joints had the same or better $K_{Ic}(J)$ at 20 K as that of SUS304L, as well as sufficient toughness to attain the ASME standard value of 132 MPa√m.⁹⁾

As shown in Fig. 6, the fracture surface of the weld joint of the 15% Ni steel was observed using scanning electron microscopy. The failure mode at all notch positions was ductile fracture, with fine dimples as the main body. Cleavage fractures were not observed.

3. Results and Discussions

3.1 Investigation of allowable stress

The allowable stresses calculated from various standards are listed in Table 2. In this study of allowable stress, the IMO Type C

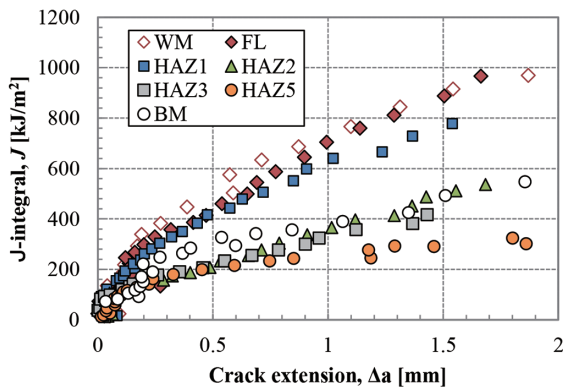


Fig. 4 J-R curve of weld joint of 15% Ni steel

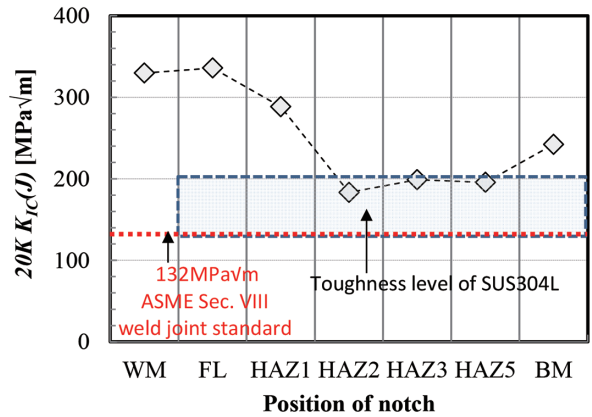
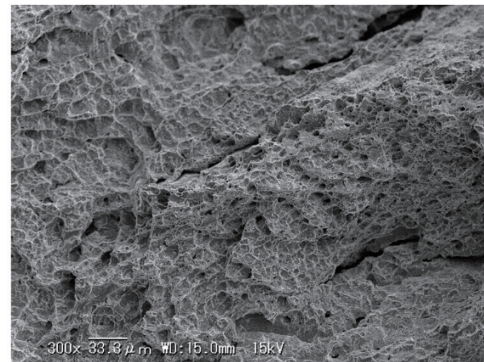
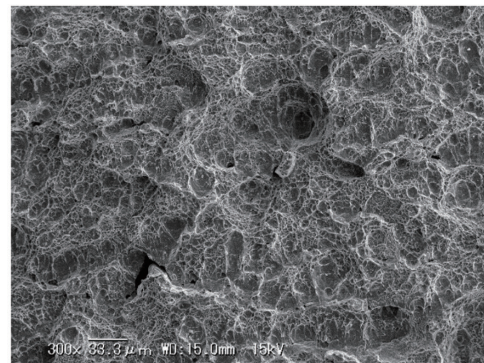


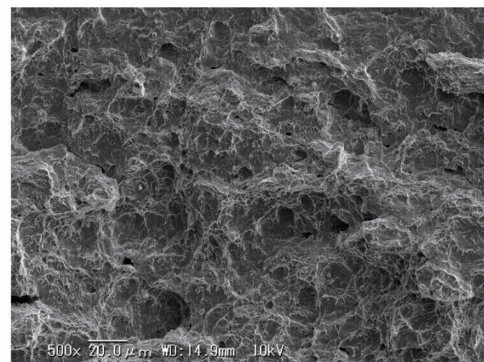
Fig. 5 20 K $K_{Ic}(J)$ of weld joint of 15% Ni steel



(a) Weld metal



(b) HAZ2



(c) Base metal; note that scale bar is different from the above two

Fig. 6 SEM images of the fracture surface of 15% Ni steel weld joint

Table 2 Allowable stresses calculated from various standards

Material	Unit: MPa				
	IMO Type C ¹⁾	IMO type B ²⁾	API 620Q ^{3,4)}	ASME Div. 1 ⁵⁾	ASME Div. 2 ⁶⁾
9Ni	230	333	230	197	267
SUS304L	137	171	154	137	137

Strength standard value of each material

Materials	SMYS [MPa]	SMTS [MPa]	1) Min. (SMTS/3.0, SMYS/1.5)
			2) Min. (SMTS/2.5, SMYS/1.2)
9Ni	Base metal	590	690
	Weld metal	400	690
SUS304L	Base metal	205	515
	Weld metal	360	550

SMYS (Specified Minimum Yield Strength), SMTS (Specified Minimum Tensile Strength)

calculation formula was used.¹⁰⁾ Because the measured tensile strength of the 15% Ni steel at room temperature (700 MPa) is nearly the same as that of the 9% Ni steel, the allowable stress was assumed to be the same as that of the 9% Ni steel (230 MPa). As the TS of 70% Ni welding material at room temperature is equivalent to that of 9% Ni steel and 15% Ni steel, the allowable stress as a joint is also 230 MPa. Compared to the allowable stress of 137 MPa for SUS304L, that of the 15% Ni steel is 1.68 times higher.

3.2 Investigation of required K_{Ic} (J)

The increase in the required K_{Ic} (J) at 20 K from the ASME standard value of 132 MPa√m, owing to the increased allowable stress, was evaluated by assuming that K_{Ic} is proportional to the product of the allowable stress and square root of the assumed defect size as follows:

$$K_{Ic} (J) \propto \sigma \sqrt{a} \tag{1}$$

The defect size was assumed to be proportional to the plate thickness, as shown in Fig. 7.

It was assumed that the thickness of 15% Ni steel could be decreased until the product of the allowable stress and plate thickness of SUS304L was equal to that of the 15% Ni steel. Specifically, the plate thickness of 15% Ni steel was reduced by a factor of 0.60 times (132 MPa/230 MPa) compared to that of SUS304L because of the increased allowable stress. As a result, square root of the assumed defect size reduced to 0.77 times ($\sqrt{0.6}$) that of SUS304L. Finally, the required K_{Ic} for 15% Ni steel was estimated to be 171 MPa√m. Values used for K_{Ic} estimation are listed in Table 3. The base metal and weld joint of 15% Ni steel exhibited sufficient toughness to attain 171 MPa√m or higher. The increase in the required K_{Ic} with a decreasing plate thickness ratio to SUS304L is shown in Fig. 8. Considering the case where the thickness cannot be reduced in consideration of buckling, the change in the required K_{Ic} (J) owing to the plate thickness of 15% Ni steel was calculated using the same method as above. For example, when thinning to 0.8 times the plate thickness of SUS304L, the required K_{Ic} (J) is 148 MPa√m.

3.3 Investigation of required crack tip opening displacement

For a stand-alone Type C tank for ships, we assumed two types of defects in the weld, as shown in Fig. 9. Based on WES2805-2011,¹¹⁾ which is a method for evaluating defects against brittle fracture occurrence and fatigue crack growth of welded joints, we esti-

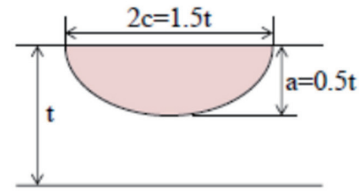


Fig. 7 Assumed defect size and shape

Table 3 Values used for K_{Ic} estimation

Steel	σ (MPa)	Thickness (mm)	\sqrt{a} (√mm)	K_{Ic} (J) (MPa√m)
SUS304L	137	1.0 t	\sqrt{t}	132
15% Ni steel	230	0.6 t	$\sqrt{0.6t} = 0.77\sqrt{t}$	$132 \times 1.68 \times 0.77 = 171$
Ratio to SUS304L	1.68	0.60	0.77	1.30

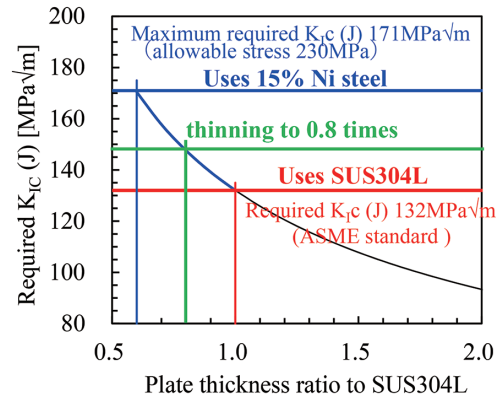
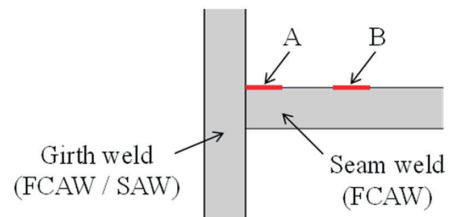


Fig. 8 Relationship between required K_{Ic} and plate thickness ratio to SUS304L



FCAW (Flux Cored Arc Welding), SAW (Submerged Arc Welding)

Fig. 9 Two types of defects in the weld

estimated the effect of the increase in the yield point (YP) on the required crack tip opening displacement (CTOD) value, as shown in Fig. 10. The required CTOD values estimated from YP (20 K) = 1100 MPa of 15% Ni steel were estimated to be 0.09 mm for 40 mm thick plate and 0.06 mm for 25 mm thick plate. The CTOD values of the base metal and weld joint of 15% Ni steel were calculated from the maximum load and plastic component of the clip gauge displacement of the J-R curve and exhibited sufficient toughness to attain 0.09 mm or higher.

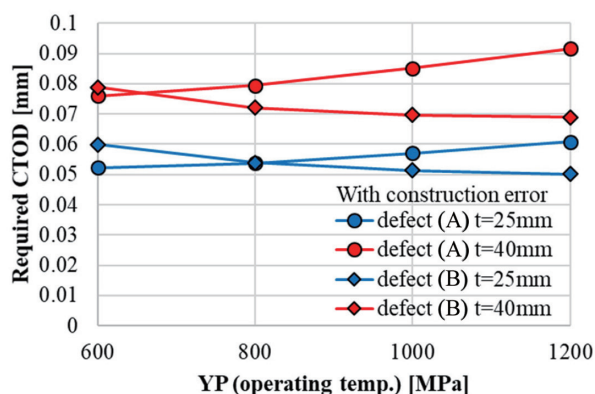


Fig. 10 Effect of the YP increase on the required CTOD value

4. Application Merit of 15% Ni Steel

The advantages of employing 15% Ni steel were determined for simple application to the inner tank material (30000 m³×4 units) of a large carrier. For example, the steel weight of a large liquefied hydrogen tank can be reduced by replacing a 40 mm thick SUS304L plate with a 24 mm thick 15% Ni steel plate, as shown in **Table 4**.

5. Conclusions

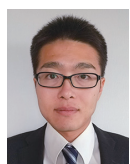
As a material for large liquefied hydrogen tanks, we roughly estimated the merits of applying high-strength 15% Ni steel, which has the potential to increase the allowable stress compared to SUS304L and make the tank thinner and lighter. By applying 15% Ni steel, the allowable stress of 15% Ni steel can be increased to 1.68 times that of SUS304L and the plate thickness of 15% Ni steel can be reduced to 0.6 times that of SUS304L. The required K_{Ic} for 15% Ni steel was estimated to be 171 MPa√m. The base metal and weld joint of 15% Ni steel exhibited sufficient toughness to attain 171 MPa√m or higher. Moreover, it was found that the hydrogen embrittlement resistance of 15% Ni steel was sufficiently high. For example, the steel weight of a large liquefied hydrogen tank can be reduced by replacing a 40 mm thick SUS304L plate with a 24 mm thick 15% Ni steel plate.

Table 4 Values used for the application merit estimation of 15% Ni steel

Steel	Allowable stress (MPa)	Thickness (mm)	Steel weight (ton)	Reduced weight (ton)
SUS304L	137	40	5891	▼2356
15% Ni steel	230	24	3534	

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