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DEVELOPMENT OF 6% NICKEL STEEL FOR LNG STORAGE TANKS

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ABSTRACT

9% Ni steel has been used for LNG storage tanks for more than four decades although 5.5% Ni steel (N-TUF CR196) was developed in the 1970's using a special heat treatment method named L-treatment. The reason why the actual application of 5.5% Ni steel has not been attained to LNG storage tanks is mainly because the requirement of fracture properties is not confirmed for the tanks. Under the circumstances of expanding demand for natural gas and double-integrity in LNG storage tanks, we restarted developing low Ni steel for LNG storage tanks by using both conventional and advanced techniques.

For the application of low Ni steel to the present LNG storage tanks, both fracture initiation and propagation properties of base metal plates and welded joints should be concerned. The fracture initiation and propagation properties of base metal were compensated with the intercritical reheating process (L-treatment), and the propagation property was additionally enhanced by combining TMCP with L-treatment. In addition, the chemical composition adjustment and the homogenization treatment of solute elements were conducted for improving the fracture initiation and propagation properties of welded joints.

6% Ni steel plates were manufactured by the process of continuous casting, reheating, hot rolling, direct quenching (TMCP), L-treatment, and tempering, and their chemical composition was 0.05C-0.06Si-1.0Mn-6.3Ni-Cr-Mo. As the results of fracture property evaluation including large-scale fracture tests such as the duplex ESSO test and the wide plate tensile test, it was demonstrated that 6% Ni steel has good characteristics regarding brittle fracture initiation and propagation in base metal plates and welded joints.

INTRODUCTION

9% Ni steel, which was developed in the 1940's, has high fracture toughness values at extremely low temperatures such as -196 °C [1-3], and it is mostly used for the inner tank of LNG storage tanks. In Japan, it has a long track record of operating more than 40 years since the first LNG tank manufacture in 1967. 9% Ni steel has been used as the major material of LNG storage tanks through the improvement of various characteristics and the clarification of superior resistance to fracture by large-scale fracture tests [4-9].

While the commercial service of 9% Ni steel to LNG storage tanks was proceeding, much research effort of reducing nickel content had been already conducted in the 1950's. 5.5% Ni steel was developed by Nippon Steel Corporation in the 1970's [10-12]. This was caused by the invention of a special heat treatment called L-treatment (the intercritically reheating treatment), which leads to good toughness in base metal with less Ni content than 9%. A group of industry, academic and government researchers carried out the extensive evaluation of steel for LNG storage tanks, and concluded that 5.5% Ni steel can be used for the tanks [13]. Because the fracture toughness requirement of 9% Ni steel was not confirmed for LNG storage tanks at that time, low Ni steel was not practically applied to any LNG storage tanks. Around or after that, a few low Ni steels for LNG storage tanks were investigated by various research groups, where 5% Ni steel [12] and 8% Ni steel [14] were early presented, and 7% Ni steel [15] was recently introduced. This might be attributed to the enhanced reliability of 9% Ni steel, the increase in the nickel price, and the expanding demand for natural gas. The authors have restarted the development of low Ni steel for LNG storage tanks, where the L-treatment is indispensable for the compensation for a fracture toughness decline caused by decreasing nickel content. In addition to the L-treatment, the advanced technology of the Thermo-Mechanical Control Process (TMCP) was applied to the low Ni content steel, which is suitable for present LNG storage tanks.

Structural integrity is quite important for LNG storage tanks because a fracture accident can lead to an enormous disaster [16]. The evaluation of fracture properties should be carefully conducted for the development of low Ni steel for LNG storage tanks. This paper firstly describes four steel design concepts according to the comprehensive investigation into previous research papers and the experimental data of Nippon Steel in the last several decades, secondly introduces newly developed 6% Ni steel and the results of its fracture tests, and finally concludes that 6% Ni steel is suitable for LNG storage tanks.

STEEL DESIGN CONCEPTS

Brittle Crack Initiation Properties of Base Metal Plates

The brittle fracture initiation property of base metal is of extreme importance as a basic characteristic. The superior property of 9% Ni steel in terms of brittle fracture initiation at cryogenic temperature is attributed to the toughness improvement of its matrix given by solute nickel, microstructure refinement due to lowering transformation temperature, microstructures mainly composed of well tempered martensite, and the existence of stable retained austenite [17,18]. If the nickel content is decreased, a part of those effects are diminished, and resistance to brittle fracture initiation is deteriorated. Nagashima et al. [10] investigated the effect of alloying elements on the brittle crack initiation property of 6% Ni steel, and concluded that the low temperature toughness of 6% Ni steel was not as high as that of 9% Ni steel in the industrial scatter range of heat treatment temperature. This means that 6% Ni steel dose not have enough fracture toughness for LNG storage tanks when the Ni content of steel is simply reduced from 9%. On the other hand, Yano et al. [11] found out that 6% Ni steel had the almost same fracture toughness as 9% Ni steel at cryogenic temperature in the wide range of heat treatment temperature by conducting L-treatment. This improvement was attributed to the formation of a lot of stable retained austenite, the depression of temper embrittlement sensitibity, and the refinement of microstructures [19-23]. In the development of new 6% Ni steel, both L-treatment and TMCP were utilized.

Brittle Crack Arrest Properties of Base Metal Plates

An opinion that steel for LNG inner tanks should hold the ability to arrest a brittle crack has its roots in the fracture accidents of LPG tanks in the 1960's and the 1970's. Various evaluation methods such as the short crack arrest (SCA) test were developed after the active research work in the 1980's [24-30]. As for 5.5% Ni steel, the evaluation of crack arrestability was confined to some limited conditions because the requirement of arrestability was vague in the 1970's [31]. LNG storage tanks must be double integrity tanks [32], and the newly developed 6% Ni steel has to be applicable to the tanks; the steel has the ability to arrest the brittle running crack within a short distance.

As the deterioration of crack arrestability was anticipated with decreasing nickel content, the optimization of the manufacture process was studied. The adjustment of TMCP condition was experimentally researched with the combination of L-treatment in accordance with the fact that TMCP enhances the crack arrestability of 9% Ni steel [33].

Brittle Crack Initiation Properties of Welded Joints

When 5.5% Ni steel was developed, the content of Mn was increased to compensate the loss of strength and stability of austenite. Although Mn is a substitute element for Ni as the basic concept of hardening, Mn has some negative effects on fracture toughness such as promoting the temper embrittlement and increasing the brittle martensite-austenite(MA) constituents. Whereas the brittle fracture toughness of base metal was confirmed to be improved with low-Ni and high-Mn compositions, that of welded joints deteriorated. Then, Mo and Cr were also added to with Mn. Mo is a quite important element from the viewpoint of depressing the temper embrittlement, as is used for the high grade 9% Ni steel [9]. The addition of Cr is also considered to be essential for enhancing the hardenability without deteriorating the brittle crack initiation property of welded joints [11,34]. Moreover, Lowering Si is well known as an effective way of improving brittle fracture toughness by means of decreasing temper embrittlement sensitivity [9]. The decrease of Si content and the small addition of Mo have been adopted for the high grade 9% Ni steel of Nippon Steel. As mentioned above, in addition to the concept of 5.5% Ni steel, which includes Mn, Mo and Cr, the adequate amounts of Ni, Si, Mn, Cr and Mo were investigated for each thickness and fracture toughness necessary for the present LNG storage tanks. As the results of these investigations, 6% Ni steel with low-Si, Cr and Mo was developed.

Brittle Crack Arrest Properties of Welded Joints

The Gas Research Institute (GRI) committee had conducted various fracture tests to evaluate the brittle crack arrest properties of 9% Ni steel welded joints, and concluded that the arrest property of HAZ did not need to be high when the HAZ was located between high toughness base metal and 70% Ni undermatched austenitic weld metal [35]. This is because the running crack along the welded bond deviates to base metal or weld metal and arrests [30]. By contrast, there were some cases in which the running crack went through the welded bond and penetrated the specimen width when the arrestability of HAZ was poor [35]. In the case of 6% Ni steel, it is probable that the running crack deviates and arrests in a similar way to 9% Ni steel welded joints when 70% Ni austenitic welding consumable is used. However, the overall performance of welded joints is affected by the balance of strength and toughness among base metal, weld metal and HAZ. Since the brittle crack arrest property of HAZ can change with the variation of brittle crack initiation toughness in the HAZ, the total arrest performance of welded joints can be also changeable. The evaluation of crack arrestability in weld joints was conducted by using the same arrest test method as that of 9% Ni steel welded joints.

Since the crack arrest property of welded joints was supposed to be deteriorated with decreasing Ni content, the homogenization treatment was also conducted in addition to the chemical composition adjustment as described above. This treatment involves the relief of segregation through the preliminary thermo-mechanical treatment of a steel slab. This was motivated from the fact that closely-spaced MA exists at the brittle fracture initiation point of each fracture toughness test specimen sampled from 6% Ni steel made in a laboratory, and the MA possibly causes brittle crack propagation. This treatment is also considered to be effective in the improvement of brittle fracture property in base metal through the homogenization during the L-treatment.

CHARACTERISTICS OF 6% NICKEL STEEL

Chemical Composition and Manufacturing Process

According to the concept mentioned above, steel plates, whose thicknesses were 6 to 50mm, were manufactured at the steel plate mill of Nippon Steel Corporation in Nagoya, Japan. The chemical composition and the manufacturing process are shown in the table 1. In this paper, the mechanical test results of a plate of 32mm in thickness are shown.

Table 1 Chemical composition and manufacturing process.

Chemical composition (wt%)							Manufacturing process
C	Si	Mn	P	S	Ni	Others	
0.05	0.06	1.0	0.003	0.001	6.3	Cr, Mo	Continuous casting, Heating, Hot rolling, Direct quenching(TMCP), L-treatment, Tempering

Base Metal Plate Properties

The results of tensile tests and Charpy impact tests are shown in Tables 2 and 3, respectively. They meets the standard of JIS G3127 SL9N590.

Table 2 Results of tensile tests.

Specimen	Position	Direction	YS (MPa)	TS (MPa)	EL (%)
JIS4	1/4t	Transverse	693	785	30
JIS G3127 SL9N590			min.590	690～830	≧21(t>20)

Table 3 Results of Charpy impact tests.

Specimen	Size (mm)	Direction	Absorbed energy (J)	Crystallinity (%)
JIS V notch	10x10	Longitudinal	233	0
JIS G3127 SL9N590			min.41	

The results of base metal plate CTOD tests are shown in Fig. 1, where the range of 9% Ni steel test data [36-38] was also exemplified. The CTOD tests were based on BS7448. It was demonstrated that the critical CTOD of 6% Ni steel was almost equivalent to that of 9% Ni steel in base metal .

The results of dynamic tearing (DT) tests are shown in Table 4, where the range of 9% Ni steel data was also exhibited. The DT tests were based on ASTM E604. It was confirmed that the DT absorbed energy of 6% Ni steel was similar to that of 9% Ni steel in base metal.

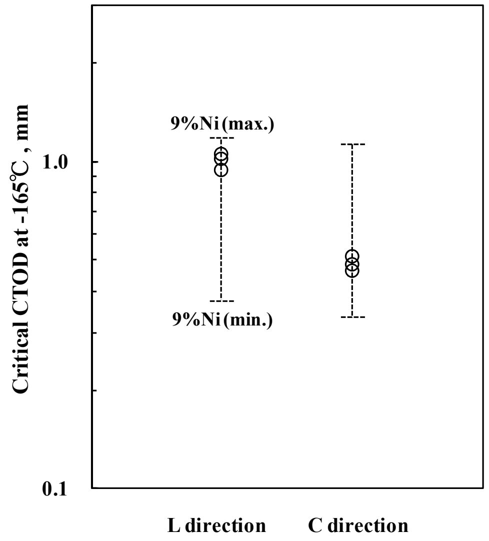

Fig. 1 Results of CTOD tests (Base metal).

Table 4 Results of DT tests.

Thickness (mm)	Position, Direction	Temp. (℃)	Absorbed energy (J)		Absorbed energy (J) Example of 9%Ni	Shear fracture (%)	
			each	ave.		each	ave.
32	1/2t, L	-196	1890-2328	2095	1197-2088	94-100	97

L=Longitudinal

The result of a base metal plate duplex ESSO test is shown in Table 5 and Fig.2. It was verified that 6% Ni steel has the ability to arrest the brittle running crack under the uniform tensile stress of 392 MPa.

Table 5 An example of duplex ESSO test results.

Thickness (mm)	Direction	Temp. (℃)	Stress (MPa)	Result	
				Judgement	Crack length
32	Longitudinal	-165	392	No-Go(Arrest)	167mm

Brittle plate width : 150mm, Test plate width : 350mm
Test temperature : -165℃ or -196℃
Stress : 294MPa (Moderate condition),
392MPa (Severe condition)

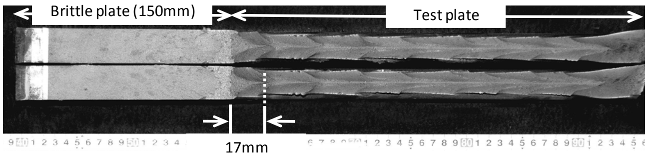

Fig. 2 Fracture surface appearance of a duplex ESSO test specimen (Base metal,-165℃,392MPa).

Welded Joint Properties

The results of Charpy impact tests and CTOD tests of welded joints are shown in Figs 3 and 4, respectively, where the range of 9% Ni steel test data was also exemplified. The critical CTOD of the welded joints of 6% Ni steel is almost equivalent to that of 9% Ni steel.

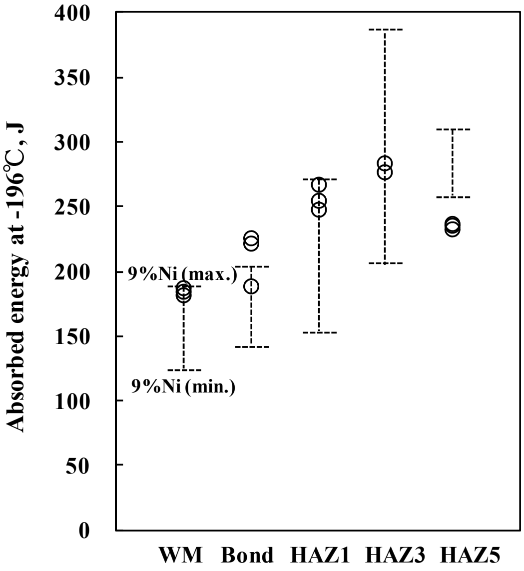

Fig. 3 Results of Charpy impact tests (GTAW, vertical, max. heat input 4.5kJ/mm, 70% Ni welding consumable).

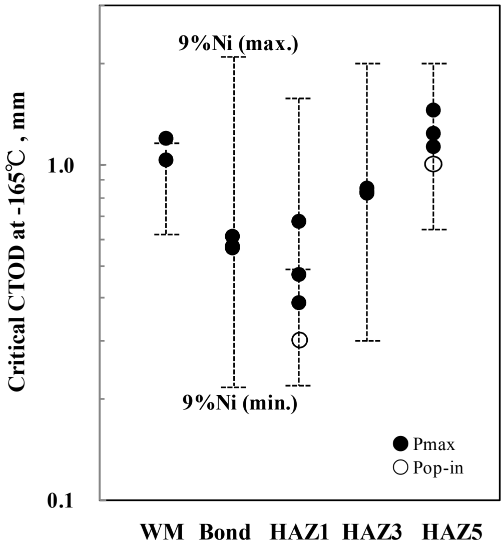

Fig. 4 Results of CTOD tests. (GTAW, vertical, max. heat input 4.5kJ/mm, 70% Ni welding consumable).

The results of wide plate tensile tests of cross welded joints are shown in Table 6. Each specimen did not fracture in the low elastic stress region, and the crack deviated from a welded bond to weld metal.

Table 6 Results of cross-welded wide plate tensile tests.

Thickness (mm)	Welding method	Temp. (℃)	Net stress (MPa)	Fracture path
32	GTAW	-165	851	BOND→WM
			838	BOND→WM

The result of a duplex ESSO test of a welded joint is shown in Table 7 and Fig.5. Good crack arrestability was confirmed.

Table 7 An example of duplex ESSO test results.

Thickness (mm)	Welding method	Groove	Temp. (℃)	Stress (MPa)	Results	
					Judgement	Crack length
32	SMAW	X	-196	294	No-Go(Arrest)	203mm

Brittle plate width : 150mm, Test plate width : 350mm
Test temperature : -165℃ or -196℃
Stress : 294MPa (Moderate condition),
392MPa (Severe condition, currently being tested)

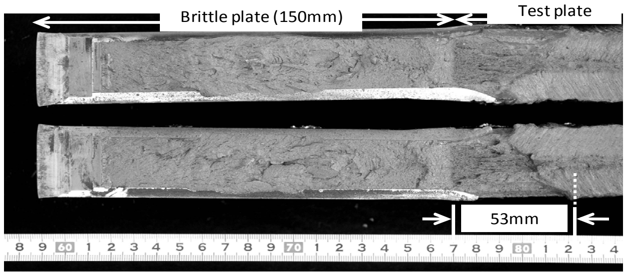

Fig. 5 Fracture surface appearance of a duplex ESSO test specimen (Welded joint, -196℃, 294MPa).

CONCLUSION

6% Ni steel has been newly developed, and its characteristics of brittle fracture initiation and propagation in base metal plates and welded joints were evaluated in this study. 6% steel has an adequate resistance to brittle fracture for the inner tank steel of LNG storage tanks.

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