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New Steel Plate for LNG Storage Tank

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Abstract

A new low-nickel (6.0–7.5%Ni) steel plate for LNG storage tanks has been developed with performance equivalent to 9% Ni steel, which has been used for LNG storage tanks for several decades. This excellent performance equivalent to 9% Ni steel was achieved by reducing the amount of added nickel, optimizing the chemical composition, and by applying the latest Thermo-mechanical controlled process (TMCP) technology to the steel plate, in order to contribute to cost savings and natural resource savings. Developed steel has been practically applied through joint research with customers and committees, and the expansion of its applications is progressing.

1. Introduction

Natural gas has attracted wide attention as a clean energy source with low environmental load in combustion since many years. Furthermore, its importance as the primary energy source is growing further, encouraged by the recent development of shale gas exploitation in North America. In line with the expansion of demand for LNG in the future, construction of above ground type LNG tanks is considered to increase. 9%Ni steel, excellent in strength and low temperature toughness under ultralow temperature, is used for the material of the inner tank of a above ground type LNG tank. The 9%Ni steel was developed by the International Nickel Company (INCO)[1] and has been used for longer than half a century, and therefore, its high safety is recognized. For LNG tanks, a double-integrity structure has been proposed to prevent peremptory fracture. Hence, in addition to the properties that suppress the initiation of a brittle crack, the properties that arrest the propagation of a brittle crack, even when a crack contingently takes place, are required of steel materials (**Fig. 1**).

Although high safety is demanded for such steel plates, from the viewpoint of saving construction cost of an LNG tank, the need of reducing the amount of costly Ni used, of which price often fluctuates, has risen. Nippon Steel & Sumitomo Metal Corporation had tackled the development of a steel plate with reduced composition of Ni since 1960s and completed its development in 2010, and the new steel plate was applied to the No.5 LNG tank of Senboku Terminal 1 of Osaka Gas Co., Ltd., the largest of its kind in Japan, in 2011 after approval of Ministry of Economy, Trade and Industry (METI).

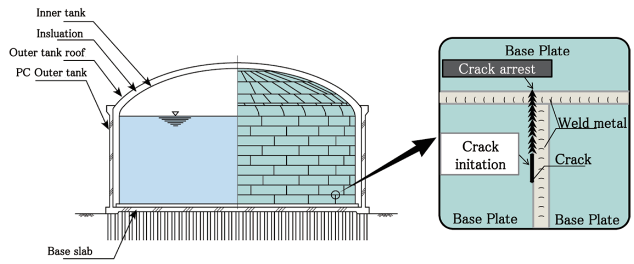

Fig. 1 Prescribed properties for material of LNG tank

This article reports the detail of the development, properties of the steel plate, status of its practical application, standardization, and future prospect about the new steel plate for LNG tanks. Furthermore, hereafter in this report, the steel of 7.1%Ni composition is termed as Heat A and the steel of 6.3%Ni composition is termed as Heat B.

2. Development of New Steel for LNG Tank

2.1 Detail of development of new steel for LNG tank

In **Table 1**, the chemical compositions and the outline of the production process are shown. Different from the C-Si-Mn-Ni system of 9%Ni steel compositions, new steel for an LNG tank has the chemical compositions of reduced Ni, increased Mn, and added Cr

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Table 1 Chemical compositions and production process

		Chemical compositions (mass%)						Production process
		C	Si	Mn	**Ni**	Cr	Mo	
Developed steel	Heat A (7.1%Ni-steel)	0.05	0.05	0.8	**7.1**	Added	Added	TMCP (DQ-L-T)
	Heat B (6.3%Ni-steel)	0.05	0.06	1.0	**6.3**	Added	Added	TMCP (DQ-L-T)
Conventional steel	9%Ni-steel	0.05	0.22	0.65	9.2	Tr.	Tr.	RQ-T

DQ: Direct quenching, RQ: Reheat quenching
L: Lamellarizing, T: Tempering

and Mo. Furthermore, different from the main production process of 9%Ni steel of Reheat Quenching-Tempering (RQ-T), the new steel for the LNG tank is produced in the production process of Thermo Mechanical Control Process-Lamellarizing-Tempering (TMCP-L-T). TMCP is a production process in which rolling temperature and cooling rate after rolling are controlled and enables the refining of the microstructure. The details of the development of Heat A and Heat B are introduced time-serially hereafter.

The development of Heat B commenced in 1960s, when 9%Ni steel was first placed into practical application in Japan. Basic concept comprises two points: to add Mn, an austenite forming element same as Ni, to supplement the reduction of Ni, and to add Mo, W, and so on to suppress the development of temper embrittlement caused by the increased Mn composition.[2] Effects of various elements were studied, and in 1970s, basic compositions of 6Ni-1–2Mn-0.2Mo or 0.45W were introduced.[3] Its production process is quenching and tempering. Although the steel successfully exhibited excellent base metal toughness at liquefied nitrogen temperature at the time, its optimum tempering temperature range problematically remained very narrow.

The problem was solved by an intermediate treatment[4] (L treatment, lamellarizing treatment or termed as special treatment). Tempering brittleness is greatly suppressed by the stratified reverse-transformed austenite developed during the intermediate treatment and covering the prior austenite grain boundary. The austenite once formed in the intermediate heat treatment is transformed to martensite by water cooling and transformed to a large quantity of stable and fine austenite in the subsequent tempering process. Thus, the steel exhibits excellent toughness in a wide tempering temperature range (**Fig. 2**). Furthermore, when the toughness of a welded joint is considered, deterioration of the toughness of a welded joint of thin plates, which basic composition system is 0.06C-5.5Ni-1.1Mn-0.2Mo, was found and the system was changed to Cr-added compositions (**Fig. 3**[5]). Later on, committees including academic experts studied its applicability to above ground type tank and ship tank,[6, 7] and it was judged as applicable to LNG tanks. However, it was in the 1970s, the time of emergence of the 9%Ni steel, when the study was conducted but the steel was not put into practical application. Later on in 2008, the study aiming at practical application was restarted, and the compositions and the production process were reviewed. For the steel to exhibit excellent toughness even in the crack tip opening displacement (CTOD) test, Ni composition was increased from 5.5% to 6.3%, and other element compositions were optimized, such as Si was decreased to lower susceptibility to temper embrittlement. Combination of the aforementioned intermediate heat treatment and direct quenching, TMCP+L+T, was adopted as the production process.[8] Based on the review of the compositions and the production process, high strength together with excellent low temperature toughness could be secured. As explained later, Heat B satisfies not only the strength level of the existing steel (American Society for Testing and Materials (ASTM) A841 Grade G Class[9] but also conforms to ASTM A841 Grade G Class 10, which has higher strength.

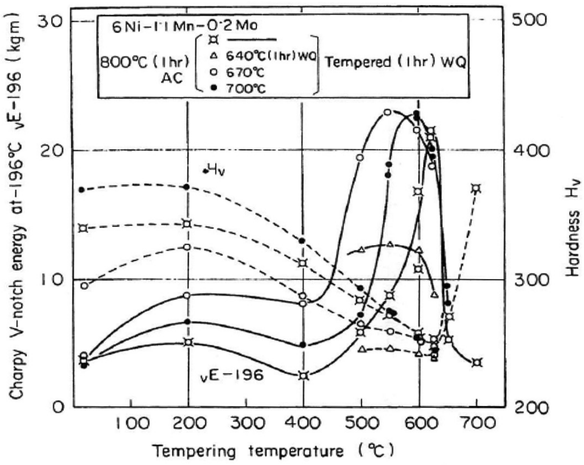

Fig. 2 Toughness improvement by intermediate heat treatment[4]

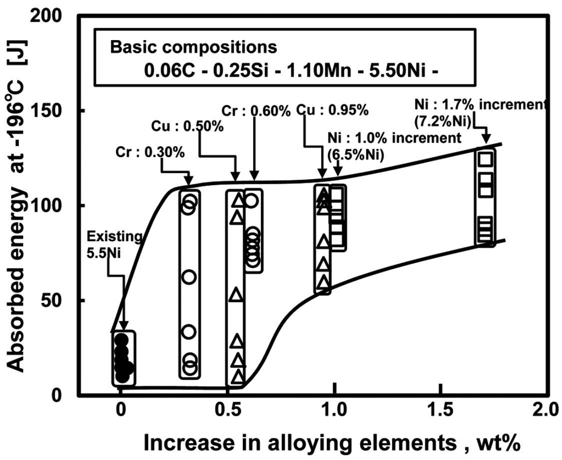

Fig. 3 Effects of substances on HAZ toughness[5]

On the other hand, as for Heat A adopted by Osaka Gas, basic research commenced in 1990s. Since simply reducing Ni alone causes deterioration of toughness, safety of high degree was secured with application of TMCP and by adding Mn to cover the reduction of Ni.[9] **Figure 4** shows the production process of the new steel for an LNG tank and its microstructure. When compared with the microstructure of RQ-T9%Ni, it is found that a remarkable refining effect is obtained. Very fine martensitic microstructure is obtained by controlling the prior austenite grain size in the heating process, precisely controlling the amount of reduction in the uncrystallized zone in the rolling process, and direct-quenching in the accelerated cooling process. Then, by applying heat treatment in a dual phase region and tempering heat treatment, volume of retained austenite (retained γ) exceeding that of RQ-T9%Ni steel is secured, as shown in **Fig. 5**.

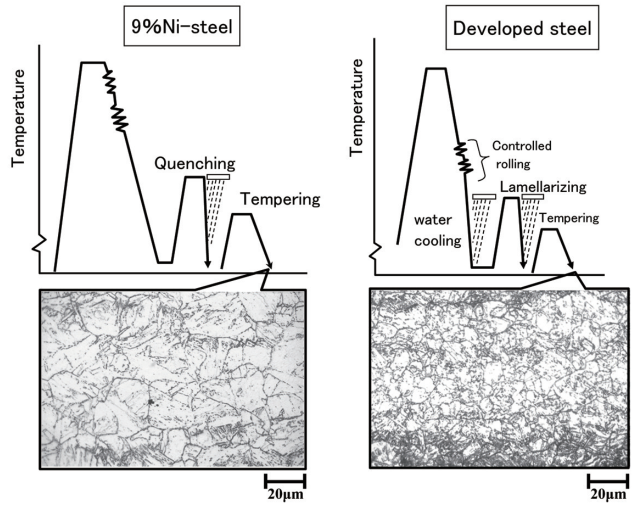

Fig. 4 Production process and microstructure

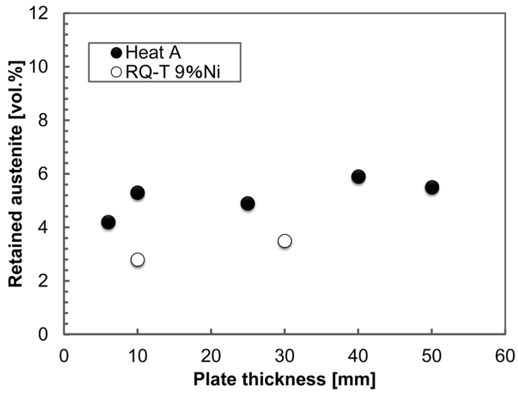

Fig. 5 Amount of retained austenite

Fine and stable retained austenite is said to be effective in improving low temperature toughness.[4, 10]

Reduction of Ni also causes the deterioration of toughness not only of the base metal but also of the Heat Affected Zone (HAZ). It is concerning for HAZ that the property-improving effect obtained by applying TMCP is invalidated by retransformation caused by welding heat cycle. The fundamental compositions of Heat A that secure the toughness of HAZ at its most highly embrittled part were decided by reducing Si and adding Cr and Mo.[11] A result of CTOD evaluation test of the gas tungsten arc welding (GTAW) welded joint, conducted to evaluate the brittle crack initiation suppressing properties of Heat A, is shown in **Fig. 6** together with the range of CTOD values of 9%Ni steel. In the test piece of A1 steel, where Ni was simply reduced and with a notch positioned on the fusion line (FL), the amount of deterioration of toughness is slight as compared with that of 9%Ni steel; however, in the test piece, where a notch is positioned at the toe of the welded joint, remarkable deterioration of toughness is noticed. The initiation point of the brittle crack in the toe notch test piece is right below the toe. The point is adjacent to the last pass and is in the coarse grain HAZ (CGHAZ), which is not favored by the thermal history rendered by subsequent passes.

In the steels A2 and A3, where Si is reduced, cementite precipitating effect specific to low Si system is exhibited and autotempering progresses during cooling in the CGHAZ and toughness is recovered. Furthermore, from the hardenability perspective, according to the research made for general high tensile strength steel,[12] HAZ microstructure comprising a mixture of martensitic microstructure and lower-bainitic microstructure is considered to be the best. The same trend is noticed in the Ni-reduced steel. Namely, when hardenability is very high, a microstructure comprising only martensitic microstructure is formed and autotempering is suppressed. In case hardenability is lower, upper-bainitic microstructure appears and deterioration of toughness is confirmed. In A3 steel, HAZ toughness not inferior to that of 9%Ni steel is secured by promoting autotempering by reducing Si and optimizing hardenability by adding Cr and Mo.

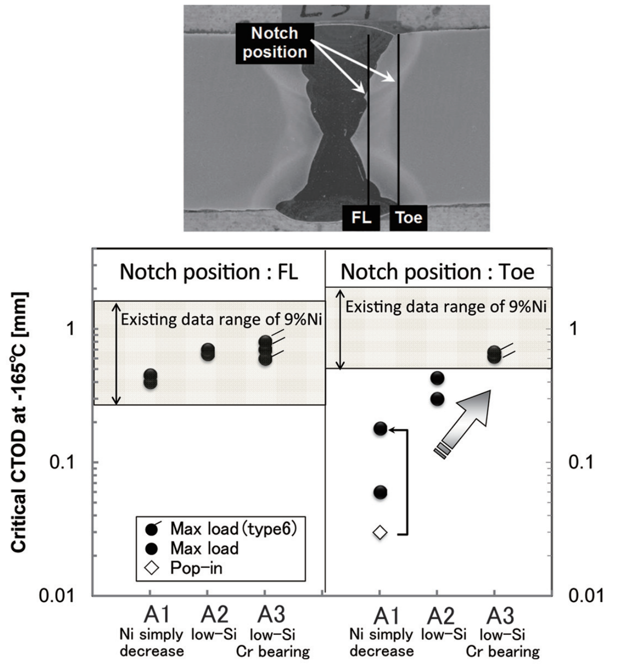

Fig. 6 Improvement of CTOD properties of weld joint by decreased Si and increased Cr

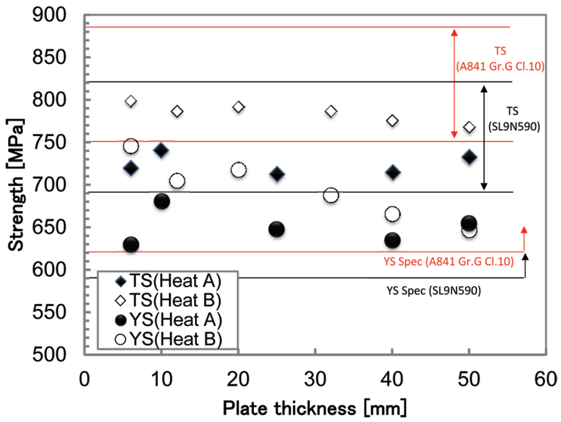

Fig. 7 Tensile results of base plates

2.2 Properties of new steel for LNG tank

2.2.1 Basic properties of base metal

Properties of Heat A and Heat B manufactured at Kashima works and Nagoya works are introduced hereunder. In **Figs. 7** and **8**, results of tensile test and Charpy impact test of the base metal are shown. Both test results sufficiently satisfy the JIS Standard specification; yield strength (YS) ≧ 590 MPa and 690 MPa ≦ tensile strength (TS) ≦ 830 MPa. Heat B also conforms to higher strength of ASTM A841 Grade G Class 10.

2.2.2 Brittle crack initiation suppressing properties

Figure 9 shows the result of the CTOD test of the base plates conducted in accordance with BS 7448 Part 1. Critical CTOD at −165°C is at the same level with that of 9%Ni steel. **Figure 10** shows the results of the CTOD test of welded joints. These figures show that the properties of the steel are not inferior to those of 9%Ni steel of respective thickness and notched location.

Furthermore, cross weld notch wide plate test as large-scale fracture test assuming a welded joint of LNG tank was conducted. Schematic illustration of the specimen is shown in **Fig. 11** and the results of the test are shown in **Table 2** and **Fig. 12**. On the fusion line of the vertical welded joints of GTAW or shielded metal arc welding (SMAW), a notch of a length twice of the thickness and penetrating through the entire thickness was introduced. The fracture stress at −165°C was above 750 MPa and equivalent to the properties of 9%Ni steel. Furthermore, in either test piece, the crack

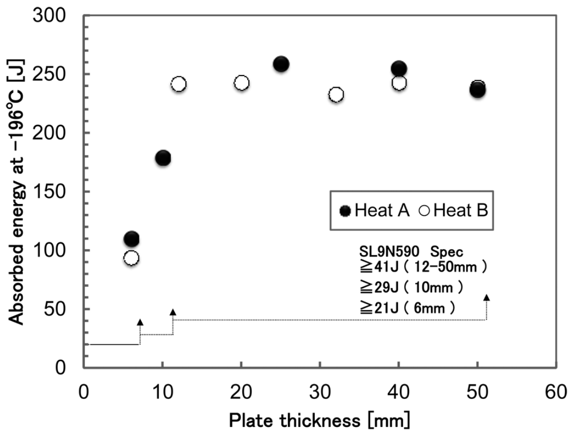

Fig. 8 Charpy impact results of base plates

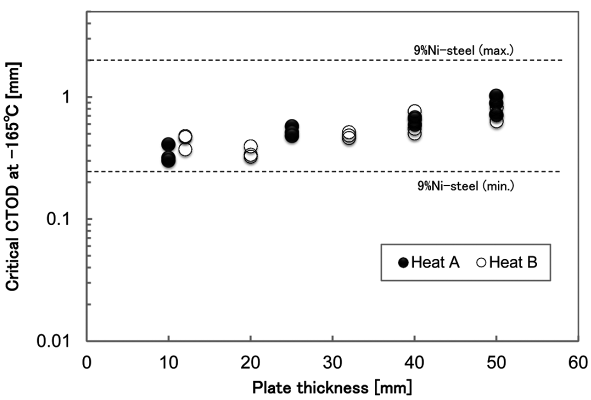

Fig. 9 CTOD results of base plates

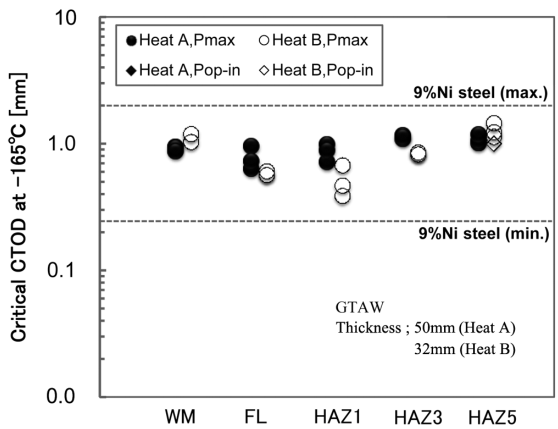

Fig. 10 CTOD test of welded joints

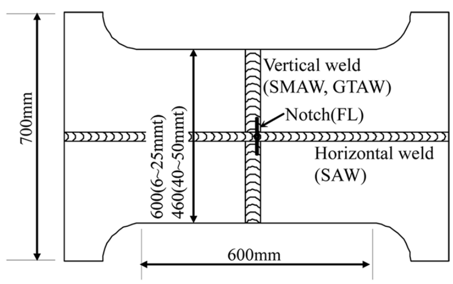

Fig. 11 Specimen of cross weld notch wide test

Table 2 Results of cross weld notch wide test

	Thickness (mm)	Width (mm)	Welding method	Notch Position	Notch Length (mm)	Temperature (°C)	Fracture stress (net) (MPa)
Heat A (7.1%Ni)	6	600	SMAW	Fusion line	36	−166	822
	25	600	GTAW	Fusion line	50	−167 ~ −181	752
	25	600	SMAW	Fusion line	50	−168 ~ −185	756
	40	460	GTAW	Fusion line	80	−165 ~ −179	768
	40	460	SMAW	Fusion line	80	−166 ~ −179	812
	50	460	GTAW	Fusion line	100	−163 ~ −173	807
Heat B (6.3%Ni)	6	600	SMAW	Fusion line	36	−165	1 002
	12	600	SMAW	Fusion line	24	−165	954
	12	600	GTAW	Fusion line	24	−165	983
	32	600	SMAW	Fusion line	64	−165	857
	32	600	GTAW	Fusion line	64	−165	851

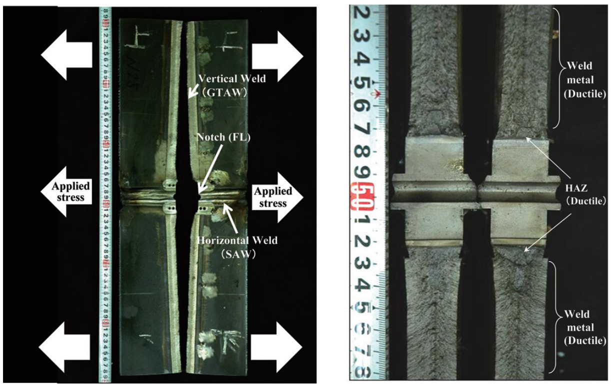

Fig. 12 Fracture path and fracture surface of cross weld notch wide test (Heat A, 25 mmt)

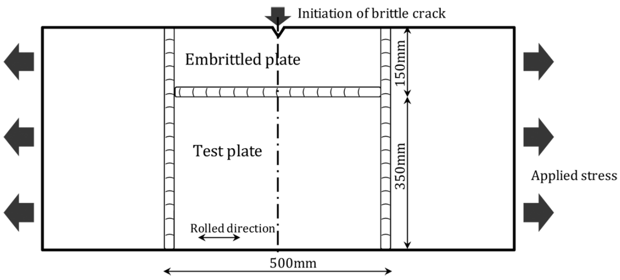

Fig. 13 Specimen of duplex ESSO test

Table 3 Results of duplex ESSO test

	Thickness (mm)	Temperature (°C)	Applied stress (MPa)	Crack length (mm)	Judgement
Heat A	25	−165	393	151	No-go
	40	−165	393	152	No-go
	50	−165	393	155	No-go
Heat B	32	−165	408	167	No-go
	40	−165	393	155	No-go
	50	−165	393	155	No-go

deviated the tip of the notch to weld metal and the test plate is fractured at maximum load after yielding. The crack deviated to weld metal.

From the above, it was confirmed that the base plate and the welded joint of the new steel for LNG tank possesses brittle crack initiation suppressing properties equivalent to that of 9%Ni steel.

2.2.3 Brittle crack propagation arresting properties

To empirically assess the brittle crack propagation arresting properties, a duplex ESSO test was conducted in the same way as for 9%Ni steel. **Figure 13** shows the form of the specimen and the test results are shown in **Table 3** and **Fig. 14**. It was confirmed that a brittle crack was immediately arrested after penetrating the test plate from an embrittled plate under the test condition of applied stress of 393 MPa, which is equivalent in level to design stress stipulated for an earthquake in the guide line for storing LNG in above ground type tank and, of temperature of −165°C. Based on the above, it was confirmed that the new steel for an LNG tank had excellent brittle crack propagation arresting properties same as those

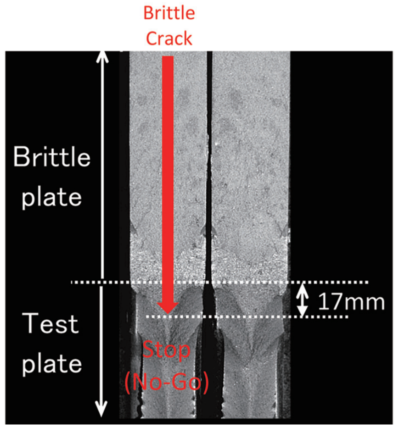

Fig. 14 Fracture path and fracture surface of duplex ESSO test (Heat B, 32 mmt)

of 9%Ni steel.

2.3 Practical application of new steel for LNG tank

2.3.1 Approach to the practical application of the new steel for LNG tank

Through joint research with Osaka Gas, Toyo Kanetsu K.K. and academic experts and long term deliberation of an external review committee, not only the above described basic properties of the 7%Ni Heat A steel material of plates 6–50 mm in thickness but also a number of other items that need consideration for actual construction of a tank were evaluated. Referring to the evaluation items used for evaluating the applicability of a thick 9%Ni steel plate to LNG tank, tests listed in **Table 4** were conducted in addition to the ones shown in 2.2.

Assuming that a 7%Ni steel plate and a 9%Ni steel plate are welded together, properties of a welded joint of different materials was also evaluated and the equivalence of the properties to those of the welded joint of an identical material was confirmed. Furthermore, considering the actual construction work of a tank, influence of repair welding on welded joint toughness was evaluated and no faulty result was found. Furthermore, physical properties required for tank designing (Young's modulus, Poisson's ratio, and thermal expansion rate) and fatigue properties have been evaluated and equivalence to those of 9%Ni steel was confirmed.

2.3.2 Application to above ground type LNG tank to be newly constructed

For the application of the 7%Ni steel to an LNG tank, which Osaka Gas was going to construct based on the result of the above-mentioned technical development, the subject steel was assessed by the 2010 fiscal year deliberation of the conformity assessment committee enacted by the Gas Business Act. As the result thereof, with Ni composition of 7.0%–7.5%, it was approved that the new steel for the LNG tank conforms to the ministerial ordinance that stipulates the technical specification of the relevant gas structure and, the new steel is equipped with the properties equivalent to those of 9%Ni steel of JIS G 3127 and the design stress same with that of 9%Ni steel is applicable to base plate and welded joint. The new steel was adopted by Osaka Gas for the application to the above ground type LNG tank that Osaka Gas was going to construct in Senboku Terminal 1, which has the capacity of 230 thousand m^3 and is the biggest of its kind in Japan (**Fig. 15**). At present, the construction of the tank is under way and it will be completed in 2015. In addition, adoption of 7%Ni steel in two more domestic LNG tanks has been decided.

Table 4 Evaluation program of 7%Ni steel

	Thickness (mm)	Basic property test	Fracture toughness test
Base metal	6, 10, 25, 40, 50	Chemical compositions, Macrostructure, Microstructure, Sulfur print, Non-metallic inclusions, Hardness, Side bend test, Tensile test, Low temperature tensile test, 2mmV Charpy test, Strain aged Charpy test	CTOD test*, Dynamic tear test***, Duplex ESSO test***
	10, 40	Physical constant (Young's modulus, poisson ratio, coefficient of linear expansion) fatigue properties (S-N curve)	
Welded joint	6, 10, 25, 40, 50	Macrostructure, Microstructure, Hardness, Longitudinal bend test, Tensile test, 2mmV Charpy test	CTOD test* Cross weld notched wide plate test**
Welded joint between 7%Ni and 9%Ni	40	Macrostructure, Microstructure, Hardness, Longitudinal bend test, Tensile test, 2mmV Charpy test	CTOD test Cross weld notched wide plate test
Repair welded joint	25	Macrostructure, Microstructure, Hardness, Tensile test, 2mmV Charpy test	CTOD test

* Other than 6 mm thickness
** Other than 10 mm thickness
*** Other than 6 and 10 mm thickness

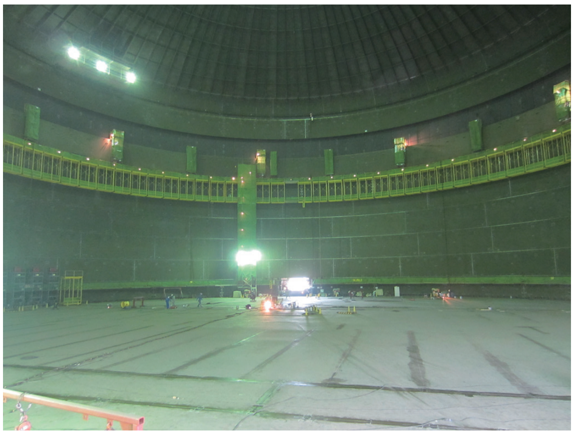

Fig. 15 LNG tank (Senboku Terminal 1 of Osaka Gas Co., Ltd)

2.4 Approach to standardization

The new steel for an LNG tank within the range of Ni composition of 6.0%–7.5% was standardized in JIS, American Society of Mechanical Engineers (ASME) and ASTM. Outline of the standardized is shown in **Table 5**. The steel was registered in JIS as SL7N590 in JIS G 3127 (Ni steel plate for pressure vessels for low temperature use). Ni composition is regulated to 6.0%–7.5% and all other specifications except chemical compositions and production process remain same as those of 9%Ni steel (SL9N590). As for standardization abroad, the new steel was registered in ASTM and ASME in 2013. In ASTM, the new steel is registered as Grade G of A841 (Standard Specification for Steel Plate for Pressure Vessels, Produced by TMCP), and all of the specifications of 9%Ni steel (A553) except chemical compositions and production process are followed. Ni composition is specified similar to JIS as 6.0%–7.5%. Furthermore, in ASTM, in addition to conventional Class 9, Class 10, which has higher strength, is specified. Aforementioned Heat B has already been made to be a steel material that conforms to Class 10, and efforts for registration of Class 10 in ASME and API will be continued sequentially. As for Class 9, the new steel is registered in ASME as "Case of ASME Boiler and Pressure Vessel Code" Code Case 2736 (Div.I) and 2737 (Div.II). The new steel is scheduled to be registered in API (API 620 Appendix.Q) in 2014. Nippon Steel & Sumitomo Metal has already obtained steel similar to the 9%Ni steel the NK Classification (May 2014) and the DNV Classification (February 2014).

2.5 Future prospect

In addition to being a steel material of ferrite system and there-

Table 5 JIS and ASTM standard

Standard	Designation		Ni [mass%]	Manufacturing process*	Mechanical properties		
					YS [MPa]	TS [MPa]	vE−196°C [J]
JIS	G3127	SL7N590	6.0-7.5	TMCP-T** (TMR-T, DQ-T)	≧ 590	690-830	≧ 41
		SL9N590	8.5-9.5	RQ-T			
ASTM	A841 Gr. G	Class 9	6.0-7.5	TMCP*** TMR-I-T, DQ(-I)-T)	≧ 585	690-825	≧ 27
		Class 10	6.0-7.5		≧ 620	750-885	≧ 27
	A553	Type I	8.5-9.5	RQ(-I)-T	≧ 585	690-825	≧ 27

* TMR; Thermo mechanical rolling, DQ; Direct quenching, RQ; Reheat quenching, I; Intermediate heat treatment, T; Tempering
** Intermediate heat treatment can be applied.
*** TMR-I-T and DQ(-I)-T are defined as TMCP.

fore superior in strength to other materials such as aluminum alloys and stainless steel, the new steel for an LNG tank is able to conform to Class 10 of ASTM A841 as mentioned above; therefore, further contribution to reduction of weight of LNG tank is expected.

3. Conclusion

A new steel plate for LNG tank that enables replacing 9%Ni steel has been developed. Owing to the application of TMCP technology and optimized composition designing, the new steel for an LNG tank is excellent in brittle crack initiation suppressing properties and brittle crack propagation arresting properties, and has been registered for the range of Ni composition of 6.0%–7.5% in JIS as JIS G 3127, ASTM as ASTM A841 Grade G, and ASME as Code Case 2736, 2737. It was confirmed that the new steel for LNG tank possesses the properties equivalent to that of 9%Ni steel, and it is being practically applied. Expansion of the application as a new inner LNG tank material of resource-saving type is further expected.

Acknowledgement

The authors wish to express deep appreciation to Messrs. Osaka Gas Co., Ltd. for its great cooperation extended in applying the 7%Ni steel to its above ground type LNG tank.

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