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Development of Super-9%Ni Steel Plates with Superior Low-Temperature Toughness for LNG Storage Tanks

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Abstract

Nippon Steel has developed 9%Ni thick steel plates for large LNG storage tanks by applying not only intercritical heat treatment but also decrease of Si content and small addition of Mo. The commercially produced 50mm thick plate exhibits sufficient mechanical properties for LNG storage tanks.

1. Introduction

The demands for liquefied natural gas (LNG) are increasing because it is a clean energy source from the viewpoint of global environment. 9%Ni steel was first applied to liquid oxygen tanks in 1952, and it has been used as a main material of the inner walls of LNG tanks ever since as a ferritic steel for ultra-low-temperature use. The brittle fracture properties of the steel, which are closely related to the safety of structures, among others, has been extensively studied[1)], and as a result, it has been made clear that the steel and its welded joints have sufficiently good brittle fracture properties for application to above-ground LNG tanks.

The capacity of the above-ground LNG tanks in Japan, which was conventionally about 80,000 m^3, has increased for reasons such as efficient utilization of land space and reduction of construction costs, and as a result, tanks having a 180,000 m^3-class capacity were constructed and put into operation. Whereas the thickness of the 9%Ni steel plates used for the conventional LNG tanks was 30 mm or so, the thickness of the plates used for these large tanks was often as large as 50 mm, and the lowering of fracture toughness due to increased thickness began to constitute a serous concern about the very thick 9%Ni steel plates. For this reason, it was necessary to establish a technology to stably produce steel plates having a better low-temperature toughness than conventional 9%Ni steel plates either in base metal or in welded joints.

In consideration of such market needs and for the purpose of supplying ultra-thick 9%Ni steel plates that can secure high safety of LNG tanks, Nippon Steel Corporation has developed a new 9%Ni steel plate product having excellent strength and low-temperature toughness in both base metal and welded joints (hereinafter referred to as the super-9%Ni steel plates), and the new product has been applied to LNG tanks in the country. This paper focuses on the approach to the development of the product and its material properties in base metal and welded joints.

2. Studies toward Realization of High Strength and High Toughness with Ultra-Thick Plates

2.1 Approach in development of super-9%Ni steel plates

The chemical compositions and heat treatment methods of 9%Ni steels are strictly specified in JIS, ASTM and other industrial standard systems. For this reason, in the development of the new plate product, the authors focused attention on alloying elements the contents of which were changeable within the ranges specified in the standard systems and which could realize a target strength of base metal as well as improve the toughness of welded joints, namely Si and Mo. In addition, as the heat treatment process for the developed steel, they selected the intermediate heat treatment[2-4)], which had been widely employed to greatly enhance the toughness of base metal.

2.2 Improvement of toughness by reduction of Si content

It has been known that reduction of Si content is effective in improving base metal toughness of 9%Ni steels[5)]. This is because controlling Si content to about 0.05% significantly lowers sensitivity to temper brittleness and stabilizes the austenitic phase in steel. These improve toughness after tempering.

Further, during the course of the development, the authors confirmed that the reduction of Si content was effective in improving the low-temperature toughness of welding heat affected zone (HAZ) as well as that of base metal. **Fig. 1** shows, as an example of the development studies, the results of the crack tip opening displacement (CTOD) tests of the welded joints of a 9%Ni steel with a reduced Si content and another containing 0.26% Si, which is a conventional Si content. The test pieces were prepared as follows: steels having a basic chemical composition of 0.05%C-0.55%Mn-0.001%S-

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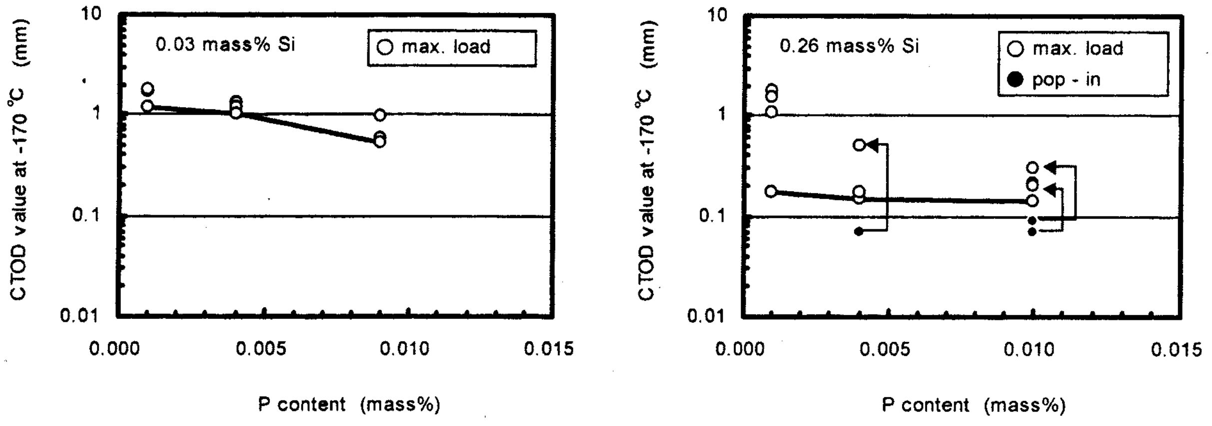

(a) 0.03 mass% Si steel (b) 0.26 mass% Si steel

Fig. 1 The influence of Si and P content on the CTOD value at HAZ/base metal boundary (GTAW, K-groove)

9.2%Ni and different contents of Si and P were melted using laboratory equipment, and hot rolled into plates 32 mm in thickness; the plates were quenched and tempered; and then they were welded by gas tungsten arc welding (GTAW) at a heat input of 3.9 kJ/mm to form welded joints. K groove was used for the welding so that the influence of local brittle structures in HAZ could easily show. The notches were cut at the boundary between the base metal and HAZ.

It is generally known that an increase in P content lowers HAZ toughness, however, as is clear from Fig. 1, when Si content is low, pop-in does not occur and HAZ toughness markedly increases even if P content is as high as about 0.009%. This is because the formation of martensite-austenite constituents, which are brittle structures likely to form locally at the boundaries between base metal and a HAZ, decreases as a result of the low Si content.

2.3 Realization of high strength and high toughness by small-amount addition of Mo

Even with highly hardenable steels such as 9%Ni steel, it is difficult to stably realize a high strength in ultra-heavy plates more than 50 mm in thickness as far as conventional chemical compositions are employed. What is more, when Si content is lowered for the purpose of improving low-temperature toughness, the strength of base metal decreases, and as a result, it becomes necessary to introduce new strengthening measures that do not adversely affect toughness.

In consideration of the above, the authors focused attention on Mo, which had the effects of improving hardenability and lowering sensitivity to temper brittleness, and studied its effects in detail. **Fig. 2** shows the influences of the contents of Mo and Si over the base metal strength of quenched and tempered steel plates 32 mm in thickness. Here, the ordinate shows relative strength with respect to the strength of a conventional 9%Ni steel (0.25 mass % Si, no Mo addition). It is understood from the graph that an addition of Mo as small as 0.09 mass % brings about an increase in strength as large as approximately 80 MPa. Although a decrease in Si content (from 0.25 to 0.01 mass %) leads to a decrease in strength by approximately 40 MPa, the small-amount addition of Mo more than compensates the strength decrease and results in a strength higher than that of the conventional steel by approximately 40 MPa.

Next, as an example of studies on the influence of Mo addition over HAZ toughness, **Fig. 3** shows the influence of Mo content over the CTOD characteristics of welded joints of a low-Si steel. The welding condition was the same as that of Fig. 1, and therefore the notches were cut also at the boundary between the base metal and HAZ. It is seen from the graph that an addition of Mo by up to 0.1

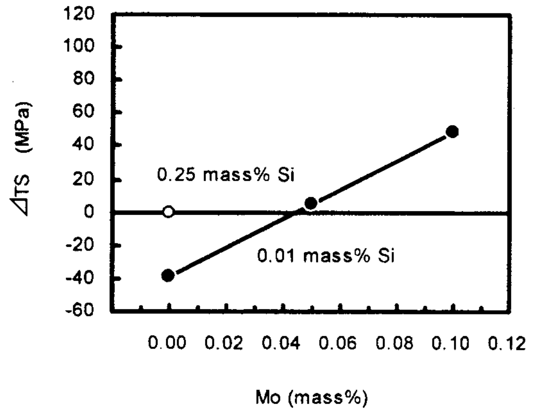

Fig. 2 The influence of Mo and Si content on the tensile strength (TS) of base plate

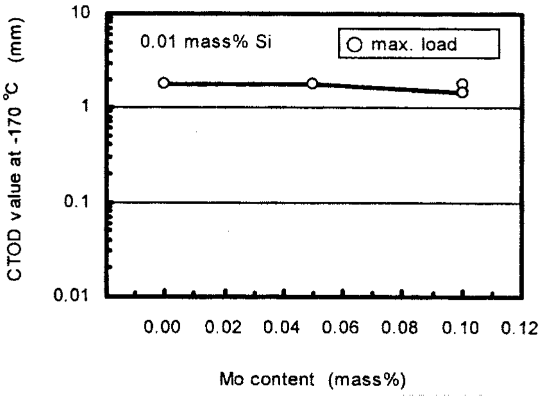

Fig. 3 The influence of Mo content on the CTOD value (GTAW, K-groove, notch location : HAZ/base metal boundary)

mass %, approximately, does not adversely affect the HAZ toughness improvement effect of low Si content.

On the basis of the above findings and other examinations in detail, the authors discovered that, even with steel plates more than 50 mm in thickness having a reduced Si content, a small-amount addition of Mo could bring about some strength of the base metal and a low-temperature toughness of base metal and welded joints good enough for JIS SL9N 590 steel.

3. Production Results of 50-mm Thick High-Toughness Super-9%Ni Steel Plates

3.1 Production method and test results of base metal properties

Based on the laboratory studies described in the preceding section, the authors conducted a mass production test of super-9%Ni steel plates 50 mm in thickness on commercial production facilities. **Table 1** shows the chemical compositions and the results of mechanical tests of the base metal of specimen plates. The fundamental characteristic of the produced super-9%Ni steel plates was that, based on the study results explained in the preceding section, the addition amount of Si was smaller than that of conventional 9%Ni steels and Mo was added by as little as 0.08 mass %. The test steel was melted in the converter, cast into slabs by the new casting method⁶⁾, and then reheated and rolled into plates. The plates then underwent quenching (Q), intermediate heat treatment (L) and tempering (T) before being submitted to tests for performance evaluation.

The strength and toughness of the specimen steel plates fully satisfied the respective specifications under JIS, and especially their Charpy absorbed energy values were as high as more than 250 J; the fracture surfaces of all the test pieces were 100% shear fracture.

3.2 Test results of welded joint properties

This subsection describes the results of performance tests of welded joints of the super-9%Ni steel plate specimens 50 mm in thickness.

Table 2 shows the welding condition applied to the welding of the test pieces. The joints were welded by automatic GTAW in a vertical position using an austenitic filler wire containing 70% Ni.

The tensile test results of the welded joints were as high as 726 MPa or more; all the test pieces broke at the weld metal the strength of which was lower than that of the base metal.

Fig. 4 shows the Charpy test results of the welded joints at –196°C. Since the strength of the 70%Ni welding wire was lower than that of the base metal, the crack deviated toward the weld metal (WM) at tests near a fusion line (FL), and for this reason, the absorbed energy values in those tests were significantly influenced by the value of the weld metal. Whereas the absorbed energy of the weld metal at 1/2 t (t: thickness) was approximately 130 J, that of HAZ was far higher than 130 J both at 1/2 and 1/4 t, and the fracture surfaces of all the test pieces were 100% shear fracture.

3.3 Test results of fracture toughness

Next, for the purpose of evaluating the safety performance of the steel plates against brittle fracture of large LNG tanks, the authors examined the ability of the base metal and welded joints to prevent the initiation of brittle fracture and that of the base metal to arrest the propagation of a brittle crack. The results are described below.

3.3.1 Resistance to initiation of brittle fracture

Test pieces of the base metal were subjected to CTOD tests at –165°C, the temperature of LNG, in accordance with BS 5762-1979. None of the test pieces machined from either the rolling direction (L) or the transverse direction (T) showed brittle fracture; the critical CTOD values of the test pieces of the developed steel plates were 1.0 mm or more in type V fracture.

Fig. 5 shows the CTOD test results of the GTAW joint test pieces of the super-9%Ni steel plates 50 mm in thickness at –165°C, the temperature of LNG. The critical CTOD values of the developed steel plates were higher than those of conventional 9%Ni steel plates 40 mm in thickness⁴⁾ at any of the notch positions, and no pop-in was observed in the test pieces of the developed steel plates. According to a defect evaluation method in accordance with WES-2805, the critical CTOD value of a welded joint required in LNG tank applications is approximately 0.1 mm at the largest⁷⁾. The above results of the super-9%Ni steel are far higher than this both in base metal and welded joints. Thus, the developed steel is deemed to have extremely good resistance to the initiation of brittle fracture both in base metal and welded joints.

Table 1 Chemical composition and mechanical properties of steel tested (comparison with the results of conventional 45mm thick 9%Ni steel)

	Plate thickness (mm)	Chemical composition (mass%)							Mechanical properties				
										Tensile test *2			Impact test*3
		C	Si	Mn	P	S	Mo	Ni	Position Orientation*1	0.2% proof stress (MPa)	Tensile strength (MPa)	Elongation (%)	$_{v}E$(–196°C) (Average) (J)
JIS G 3127 SL9N 590	6 -100	≤0.12	≤0.30	≤0.90	≤0.025	≤0.025	–	8.50-9.50	–	590≤	690-830	21≤	34(min.)≤ 41(ave.)≤
Conventional 9%Ni steel	45	0.05	0.24	0.56	0.002	0.001	–	9.39	1/4t -L 1/2t -L	609 612	713 713	34 33	284 294
Super 9%Ni steel	50	0.05	0.08	0.59	0.003	0.000	0.08	9.35	1/4t -L 1/2t -L	632 633	747 751	33 32	277 258

*1 L : Rolling direction, *2 JIS No.4 specimens (G.L. : 50mm), *3 JIS No.4 specimens

Table 2 Test plate welding condition

Welding method	Position	Plate thickness	Current	Voltage	Speed	Heat input	Test item
GTAW	Vertical	50 mm	280 - 300 A	10 V	4.0 - 4.5 cm/min	4.0 - 4.5 kJ/mm	Tensile test Brittle fracture test

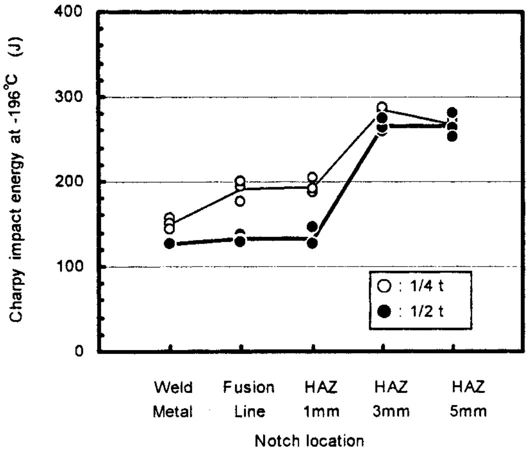

Fig. 4 Results of Charpy impact test for GTAW welded joint

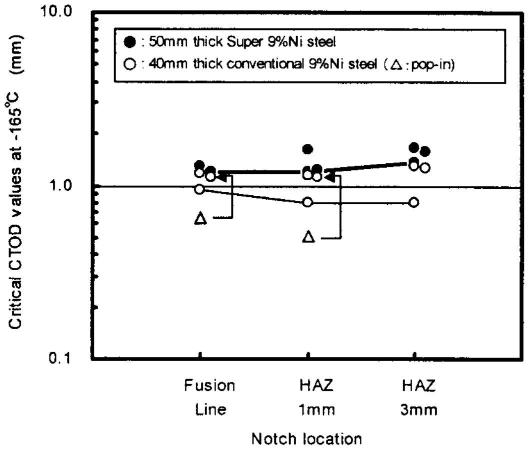

Fig. 5 Critical CTOD values at –165°C for GTAW welded joints

The authors also conducted cross weld notched wide plate tensile tests (the notch shape of the test pieces was the same as that in the reference literature[7]). As a result, they confirmed that the fracture stress of the developed steel plates at –165°C was more than twice the allowable stress at an earthquake (375 MPa) specified in the Guidelines for Above-Ground LNG Tanks[8]) of the Japan Gas Association.

3.3.2 Resistance to propagation of brittle crack

Needless to say, with a storage tank of a highly evaporative liquid such as LNG, it is imperative to prevent the occurrence of fracture. Further, should a brittle crack occur, it is essential to stop its propagation within as short a distance as possible. On the other hand, it has been known that, in the unlikely even that a brittle crack starts from HAZ of a welded joint of a 9%Ni steel plate, it deviates to the weld metal within a short distance because the strength of the weld metal is low, and therefore the fracture does not propagate along the HAZ[1]). For this reason, the properties of base metal to arrest the propagation of a brittle crack are of higher importance.

From this standpoint, the properties to stop the propagation of a crack (short crack arrest) have been used for evaluation of 9%Ni steels, and the properties have been the subjects of various studies[9,10]). As a result of such studies, the duplex ESSO test has been found effective in evaluating the crack arresting performance in actual use. In view of the above, the authors conducted the duplex ESSO tests of the base metal of the super-9%Ni steel plates 50 mm in thickness. **Fig. 6** shows the shape of the test pieces used, and **Table 3** the test results. In consideration of the stress intensity factor calculated from the crack starter plate width of 150 mm, the developed steel plate has a brittle crack arresting capacity of 280 MPa m$^{1/2}$ or more even at –196°C.

Machida et al.[7]) have calculated the value of K_{ca} required for arresting a crack 5.5 t (t: thickness) in length, taking the influence of residual stress into consideration, and obtained 167 MPa m$^{1/2}$ as the value of base metal under an earthquake. The authors' duplex ESSO tests of the base metal demonstrated that the super-9%Ni steel plates had a toughness superior to the above calculation result.

As a conclusion from the above, the super 9%Ni steel plates fully satisfy the brittle crack arresting capacity required for the base metal of steel plates used for large LNG tanks.

4. Summary

In response to the market demands for thicker gauges of 9%Ni steel plates for LNG tank application, Nippon Steel has newly developed super-9%Ni steel plates having excellent strength and low-temperature toughness in base metal and welded joints. By reducing Si content in steel, adding Mo by a small amount and employing a new casting method and intermediate heat treatment, super-9%Ni steel plates 50 mm in thickness were produced on commercial production facilities. The authors confirmed that the steel plates thus produced had, despite the very large thickness, excellent resistance

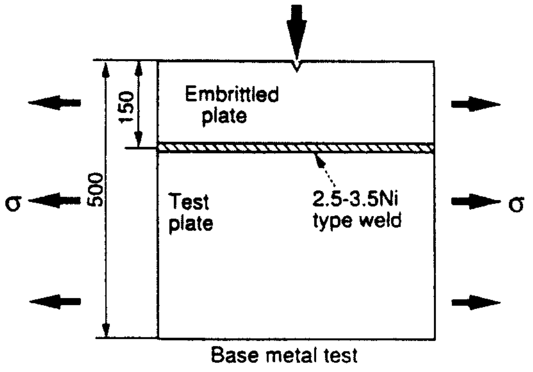

Fig. 6 Duplex ESSO test specimen geometry

Fig. 3 Results of duplex ESSO test for base plate

Test location	Plate thickness	Test temperature	Applied stress	Judgement	K_{ca}
Base plate	50 mm	–196°C	392MPa	No - Go	>280MPa m$^{1/2}$

Note 1) Crack starter plate width is 150mm and test plate width is 350mm.
2) Driving force (K-value) of a crack when it reaches the test plate is 280 MPa m$^{1/2}$

to the initiation of brittle fracture in both base metal and welded joints and high ability of base metal to arrest a brittle crack, superior to those of conventional 9%Ni steel.

It has to be noted that the super-9%Ni steel plates are applicable not only to large LNG tanks but also to various types of ultra-low-temperature vessels, and available in an ultra-large thickness range of up to approximately 100 mm.

The developed steel plate product is expected to expand its application to vessels and facilities for ultra-low-temperature use in the industrial fields such as energy-related industries where high level of safety is essential.

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