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Synopsis :

Along with the continuous increase in the size of LNG tanks, high toughness at low temperatures has been required of the main structural steels or 9% Ni steels in order to ensure the safety of tanks. Kawasaki Steel has successfully improved the products of 9% Ni steels with respect of fracture toughness at low temperatures and supplied 3000 tons of steel plates for the 80000 kl LNG tanks at Chita LNG Receiving Terminal. The present paper describes the properties of the 9% Ni steels produced recently and the main controlling items in the production. As a result of lowering phosphorus and sulfur contents and the strict control of the production line, the properties, especially the toughness at low temperatures, of the 9% Ni steel plates were much improved compared with those produced in the past. The properties of welded joints and fracture toughness showed that the 9% Ni steel plates are suited for the structural material of LNG tanks.

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Production of 9% Ni Steel Plates for Liquefied Natural Gas Tanks*

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Along with the continuous increase in the size of LNG tanks, high toughness at low temperatures has been required of the main structural steels or 9% Ni steels in order to ensure the safety of tanks. Kawasaki Steel has successfully improved the products of 9% Ni steels with respect to fracture toughness at low temperatures and supplied 3 000 tons of steel plates for the 80 000 kl LNG tanks at Chita LNG Receiving Terminal.

The present paper describes the properties of the 9% Ni steels produced recently and the main controlling items in the production. As a result of lowering phosphorus and sulfur contents and the strict control of the production line, the properties, especially the toughness at low temperatures, of the 9% Ni steel plates were much improved compared with those produced in the past. The properties of welded joints and fracture toughness showed that the 9% Ni steel plates are suited for the structural material of LNG tanks.

1 Introduction

In these past few years, imports of liquefied natural gas (LNG) have been steadily increasing, with a number of LNG bases newly built or expanded one after another. This trend is expected to persist for a while in view of the fact that LNG is a valuable energy source characterized by high calorific value and clean combustion, under the policy of diversifying energy resources. While imports of LNG in 1980 totaled 17 million tons, the figure in 1990 is estimated at 45 million tons according to the summarized target table of energy supplies¹⁾ drawn up by the Japanese Government.

Above ground LNG tanks have been mostly made of 9% Ni steel, and the demand for this steel is expected to increase further. Kawasaki Steel Corporation anticipated this tendency some time ago and has successfully developed 9% Ni steel plate KLN9 (equivalent to ASTM A 553 type I). KLN9 of thickness up to 25 mm was approved by Japan Welding Engineering Society in 1967, and that of thickness up to 40 mm in 1971. While the characteristics of KLN9 were previously reported²⁾, the product has been

greatly improved owing to progress in the manufacturing process, particularly in respect of steelmaking technology. Recently, Kawasaki Steel delivered 9% Ni steel materials for two 80 000 kl storage tanks at Chita LNG Receiving Terminal. On the basis of these experiences, the characteristics of KLN9 are described in the following with a particular emphasis on the manufacturing process, various test results and fracture toughness.

2 Key Points in the Recent Production

The 9% Ni steel plates used for LNG tanks are subjected to cryogenic temperature (-163°C). Thus they are required to have excellent low temperature toughness, weldability and workability. Since these characteristics would be greatly affected by chemical composition and manufacturing process, the following points were taken into consideration in the recent production.

2.1 Chemical Composition

The specifications for chemical composition of quenched and tempered 9% Ni steel plate by ASTM, JIS (1977) and Kawasaki Steel Standard are compared in **Table 1**. Of six elements described in the table, it is important to hold the C content at a fixed level and to minimize the contents of P and S as far as possible.

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Table 1 Specifications of 9% Ni steel

Designation	Plate thickness(mm)	Chemical composition (%)					
		C	Si	Mn	P	S	Ni
ASTM A 553 (type I)	≦50	≦0.13	0.15 - 0.30	≦0.90	≦0.035	≦0.040	8.50 - 9.50
SL 9N 60 (JIS G 3127)	≦50	≦0.12	0.15 - 0.30	≦0.90	≦0.025	≦0.025	8.50 - 9.50
KLN 9	≦40	≦0.13	0.15 - 0.30	≦0.90	≦0.035	≦0.040	8.50 - 9.50

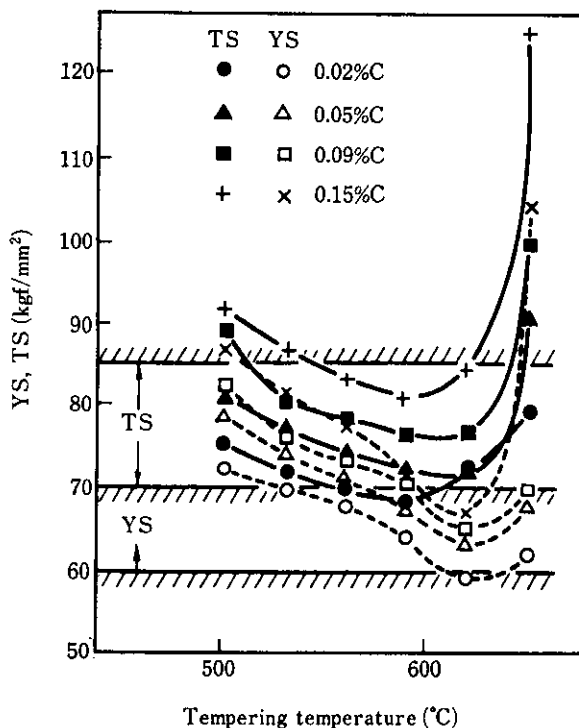


Fig. 1 Effect of C content on the strength of 9% Ni steel

2.1.1 Effect of C content

For the 9% Ni steel plates with C content varied between 0.02 and 0.15%, the yield and tensile strength and the absorbed energy at -196°C are plotted against the tempering temperature in Figs. 1 and 2, respectively. With regard to toughness, the lower the C content, the greater the range of tempering temperature at which the shear area is 100%, and hence, the greater the absorbed energy at that temperature. On the other hand, the strength falls as the C content is reduced, not attaining the specified value when the C content is 0.05% and under. Since the C content significantly affected the strength and toughness of plate as indicated above, the target content was set at 0.055% and every effort was made to suppress its fluctuation.

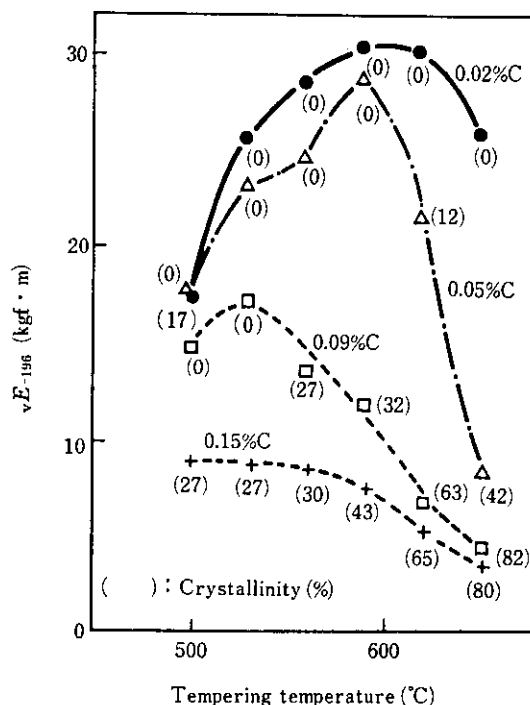


Fig. 2 Effect of C content on the notch toughness of 9% Ni steel

2.1.2 Effect of P content

A trace inclusion of P in 9% Ni steel may enhance the temper embrittlement susceptibility and deteriorate the low temperature toughness. The effect of P content on the absorbed energy at -196°C in 9% Ni steel plates cooled at different rates after tempering is shown in Fig. 3. While the P effect is relatively small in case of water-cooling after tempering (the cooling rate at the brittling region is 30°C/s), as the cooling rate is slowed down in air-cooling (35°C/min) and furnace-cooling (40°C/h), the absorbed energy declines markedly with the increase in the P content. Fig. 4 shows absorbed energy at -170°C for three types of specimens; one from a plate subjected to a weld thermal cycle simulated to that in a weld bond of about $40\,000\text{ J/cm}$ heat input and the other two, from

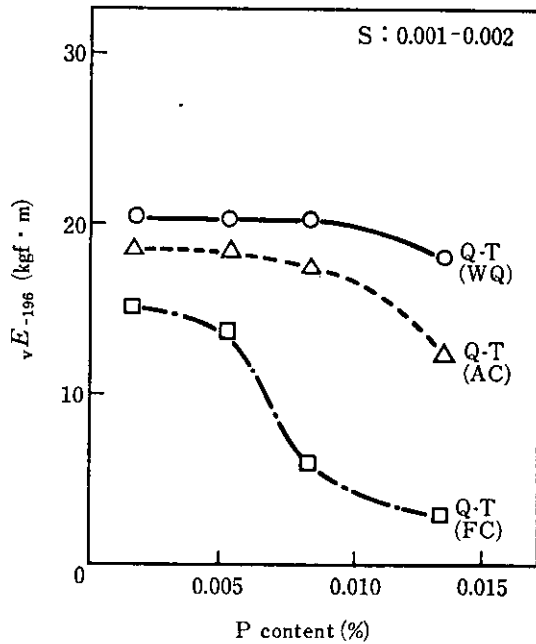


Fig. 3 Effect of P content on the notch toughness of 9% Ni steel

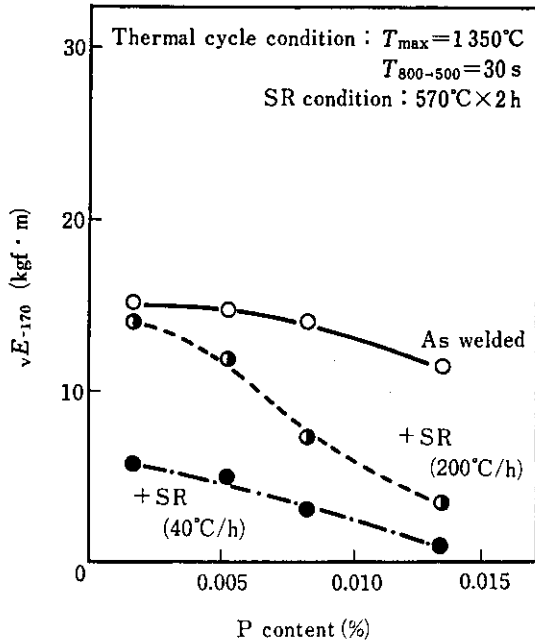


Fig. 4 Effect of P content on the notch toughness of simulated weld bond for 9% Ni steel

specimens further subjected to a 2 hr. stress-relief annealing at 570°C and subsequent cooling at different rates. While the absorbed energy increases as the P content is reduced in both cases, the effect is particularly noticeable if the specimen is cooled after stress relief at a rate higher than 165°C/h as specified in the ASTM.

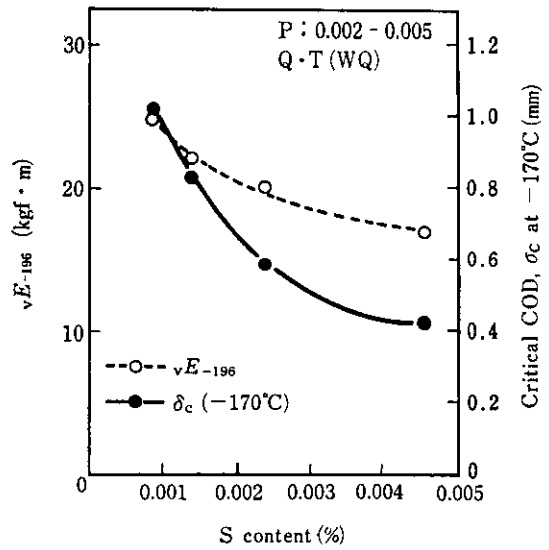


Fig. 5 Effect of S content on vE_{-196} and critical COD, δ_c , for 9% Ni steel

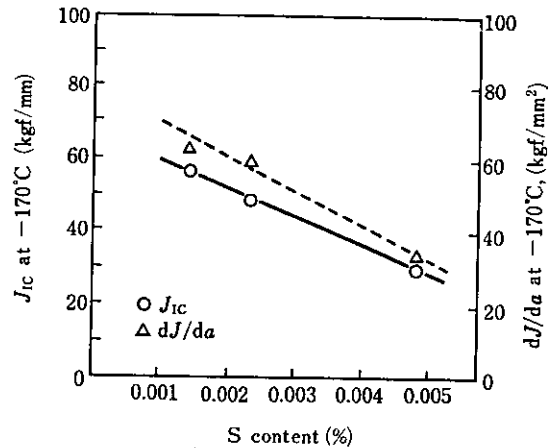


Fig. 6 Effect of S content on J_{IC} and dJ/da for 9% Ni steel

2.1.3 Effect of S content

Fig. 5 shows the effect of S content on absorbed energy at -196°C and on the critical COD (δ_c) at -170°C . In this range of S content, the Charpy test piece presents a 100% shear area, and the COD test indicates no initiation of brittle fracture until the load reaches maximum. The reduction of S content markedly increases the absorbed energy in the ductile region and the critical COD through the decrease in the amount of nonmetallic sulfide inclusions. Fig. 6 shows the resistance to ductile crack initiation, J_{IC} , and that to ductile crack extension (dJ/da , where a is the length of crack) as revealed by the J_{IC} test at -170°C for specimens of different S contents³⁾. Both resistances increase as the S content is reduced.

2.2 Manufacturing Process

2.2.1 Manufacture of very low P, very low S Steel

As described in the preceding paragraph, the low temperature toughness of 9% Ni steel can be effectively improved through the reduction of P and S contents. For this reason, the hot metal pretreatment method with the bottom-blown converter (Q-BOP) was developed and adopted in the present manufacturing process, in place of the conventional double slag method. The Q-BOP is characterized by faster dephosphorization in the high carbon region (earlier stage of refining) than the top-blown converter owing to the adequate mixing of flux with hot metal and increased reaction area, because the intensive stirring within the furnace shortens the time required for uniform mixing to about 10 seconds⁴⁾ and fine lime powder is blown from the tuyere at the furnace bottom into the hot metal together with oxygen gas flow. An example of dephosphorization pretreatment of hot metal in a 230 t Q-BOP is shown in Fig. 7. When fine powder of lime and spar with oxygen are blown into the charged hot metal, the P content can be reduced from 0.14 to 0.008% in a few minutes, while keeping the C content as high as 3.7–4.0%. Fig. 8 shows the relationship between the P content in hot metal and that at tapping in the final refining with the LD converter⁵⁾. It is evident that the present method can reduce the P content more drastically than the conventional method⁴⁾. Besides the Q-BOP, the dephosphorization pretreatment has been developed and adopted as a routine process with the top/bottom-blown converter (K-BOP) in which a part of oxygen is blown from the bottom.

Since the pretreatment of molten pig iron with the Q-BOP is conducted in the region of lower oxygen potential, desulfurization is performed at the same time, with the final S content as low as 0.002%. The main refining with the LD converter and the subsequent treatments reduce the S content to 0.001% and under.

2.2.2 Manufacturing process and major controlling items

In order to produce 9% Ni steel plates of excellent strength and toughness, manufacturing processes specifically suited for 9% Ni steel should be selected not only in the pretreatment and refining process described above, but also in heating, rolling and heat treatment, and each process must be strictly controlled. The manufacturing processes and major controlling items adopted at Chiba Works for the present production are shown in Fig. 9.

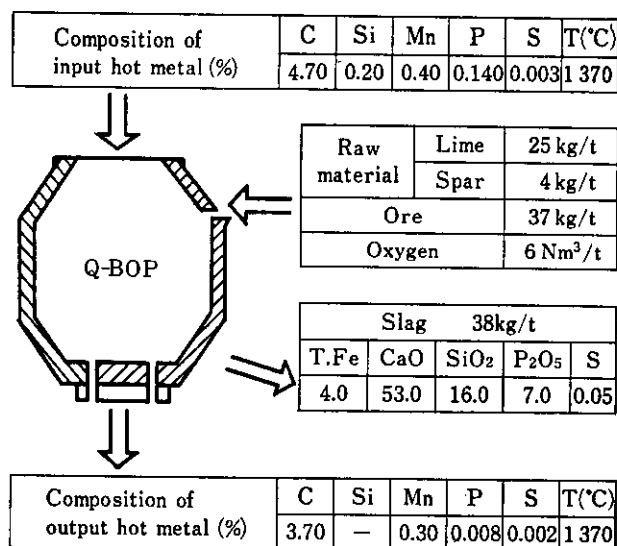


Fig. 7 An example of dephosphorization pretreatment of hot metal by the use of Q-BOP

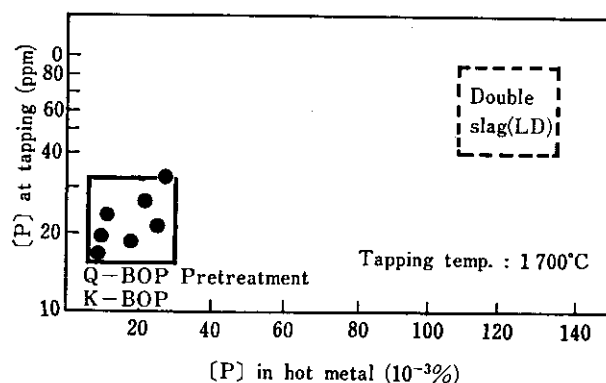


Fig. 8 Relation of P contents between hot metal and steel at blow end with various methods

3 Manufacture of 9% Ni Steel Plates for LNG Tanks

Some 3 000 tons of 9% Ni steel plates manufactured by the process shown in Fig. 9 were tested for chemical composition and other various properties. The results are outlined as follows.

3.1 Chemical Composition

Fig. 10 shows the results of chemical analysis of 32 charges by 150 t converter in histogram form. For the purpose of improving the low temperature toughness, the C content was kept within a narrow range of 0.05–0.06%, while the P and S contents were reduced.

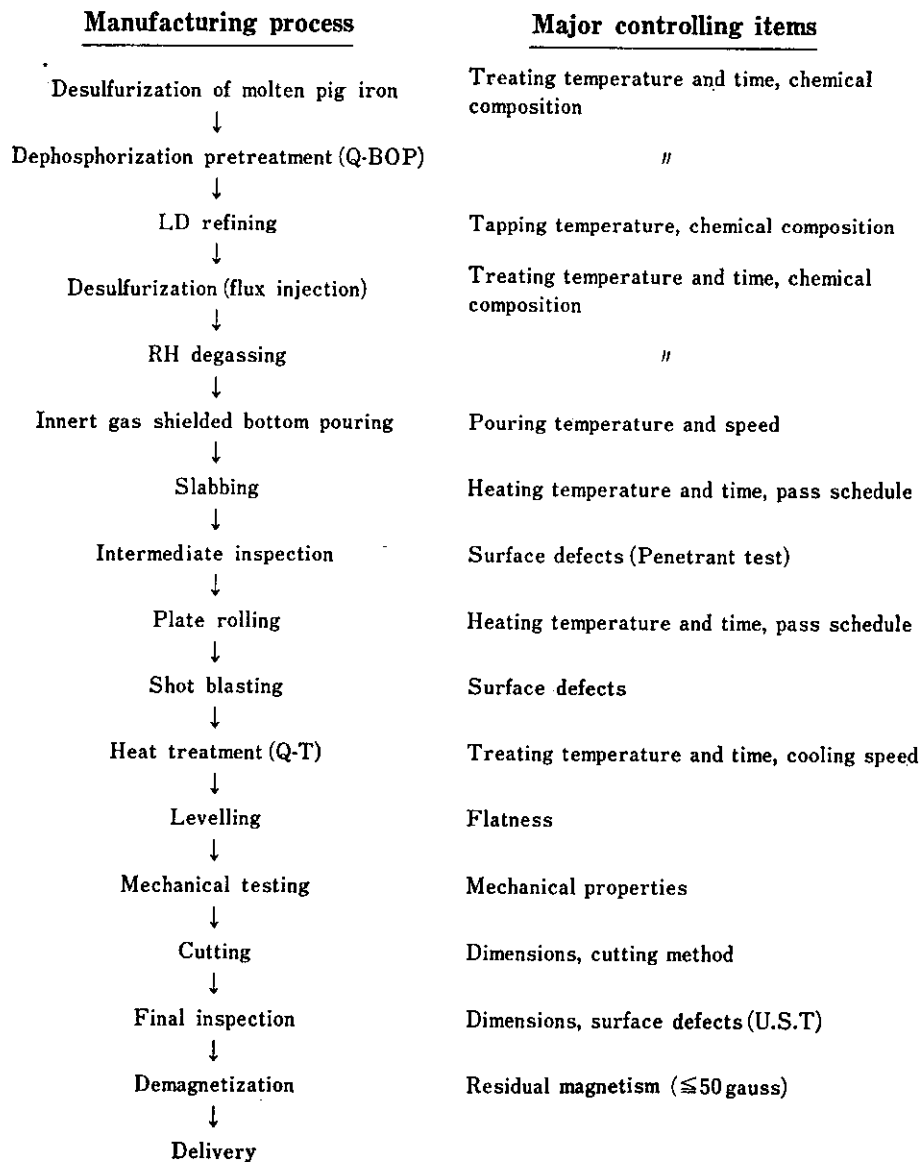


Fig. 9 Manufacturing process and major controlling items of 9% Ni steel plates at Chiba Works

The hatched areas in the figure represent the high grade steels to be used for annular plates and a part of the bottom-most side plates, with the P and S contents held at 0.004% and under and 0.001%, respectively, through particular consideration in the manufacturing process.

3.2 Tensile Test

Fig. 11 shows the results of tensile test with JIS No. 5 test pieces sampled from 11–20 mm thick steel plates in the transverse direction. All of steel plates

tested satisfied the specifications with respect to yield point (0.2% proof stress), tensile strength and elongation. The properties fluctuated little among test pieces sampled from different sites. The bending test also provided good results.

3.3 Charpy Impact Test

Fig. 12 shows the results of 2 mm V-notch Charpy impact test with JIS No. 4 test pieces sampled from the same steel plates. All the test pieces presented 100% shear area at -196°C , showed little difference in

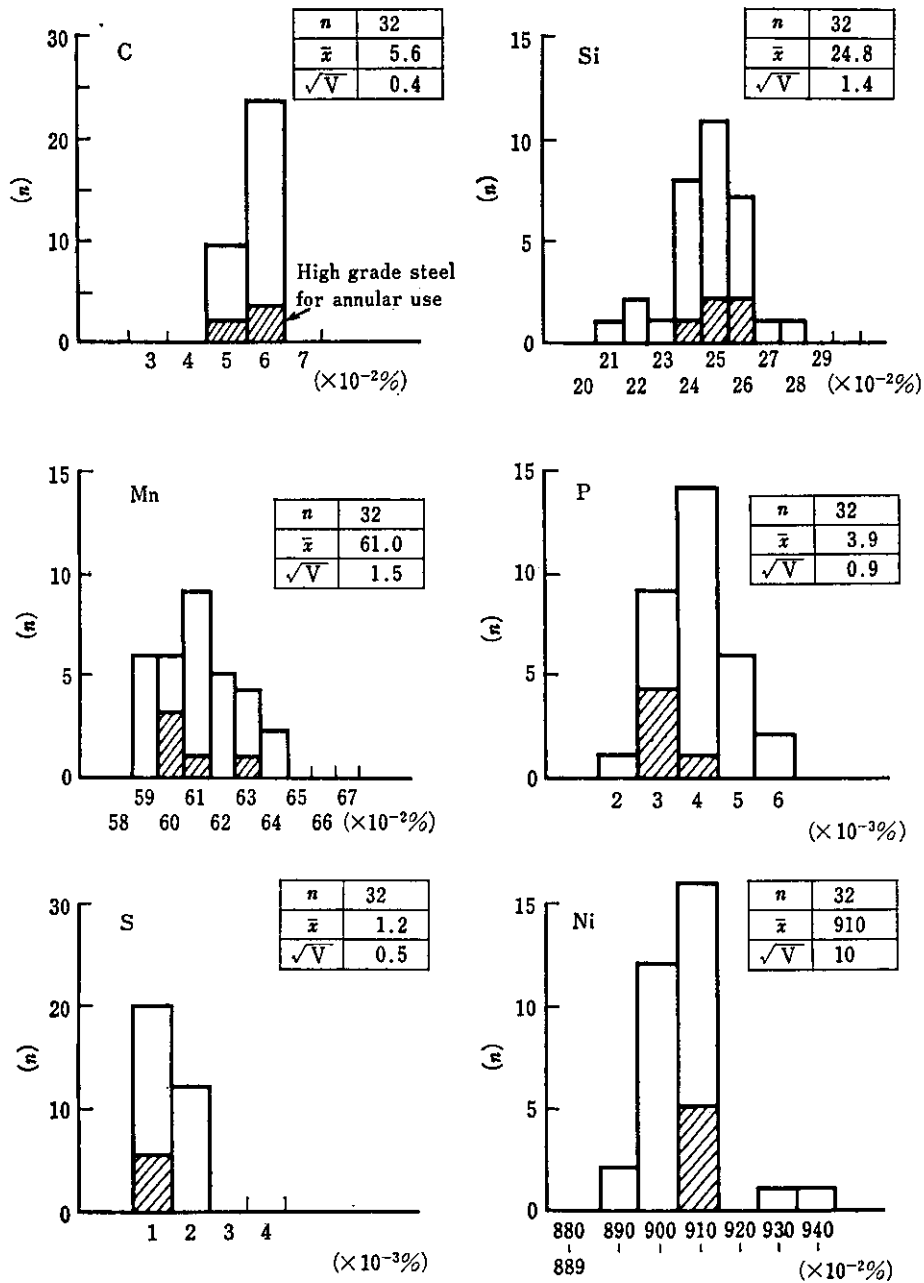


Fig. 10 Ladle analysis of molten steel for 9% Ni steel plates

values depending on rolling directions, and proved to have excellent toughness with mean absorbed energy of about 24 kgf · m in the transverse direction. The hatched portions represent the results of high grade steels to be used for 18 mm thick annular plates, in which the absorbed energy is concentrated at a higher level owing to the low P and S contents, as shown in

Fig. 10. As a part of the process tests, the Charpy impact test was conducted with 5 types of steel after strain ageing. It was proved consequently that ageing at 250°C for an hour with 7% prestrain reduced the absorbed energy very little and no brittle fracture was recognized.

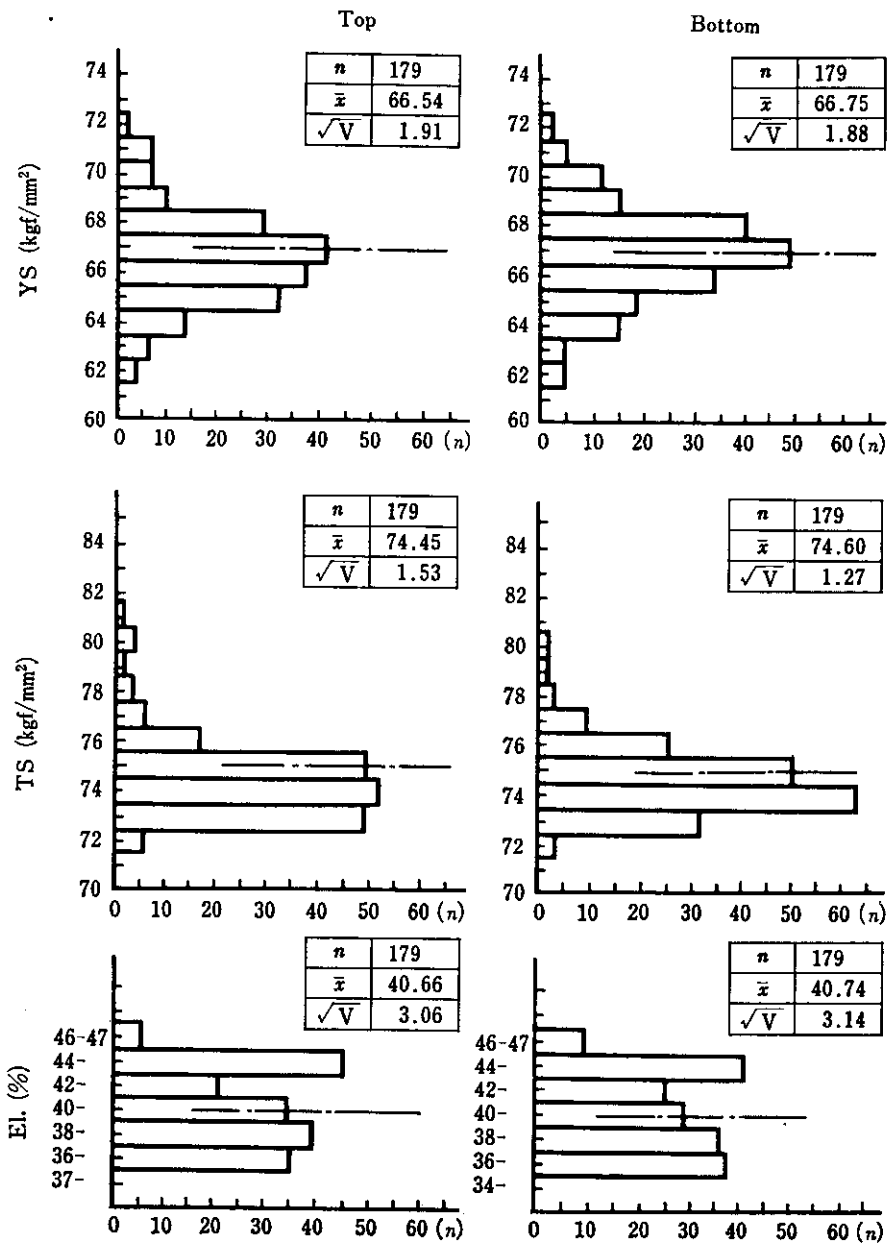


Fig. 11 Tensile properties of 9% Ni steel plates ($11 \leq t \leq 20$ mm)

3.4 COD Test

The steel plates of maximum thickness (10–31 mm) in each charge were subjected to the COD test in accordance with British Standard BS 5762. The results are shown in Fig. 13. At the test temperature (-170°C), the brittle crack did not initiate even at the maximum

load (P_{\max}), and the critical COD (δ_{\max}) was 0.4 mm or greater in the transverse direction. As in case of the Charpy impact test, the strain ageing test was conducted on 5 charges. Ageing with 7% prestrain had little effect on the critical COD value, and no brittle crack occurred up to the maximum load.

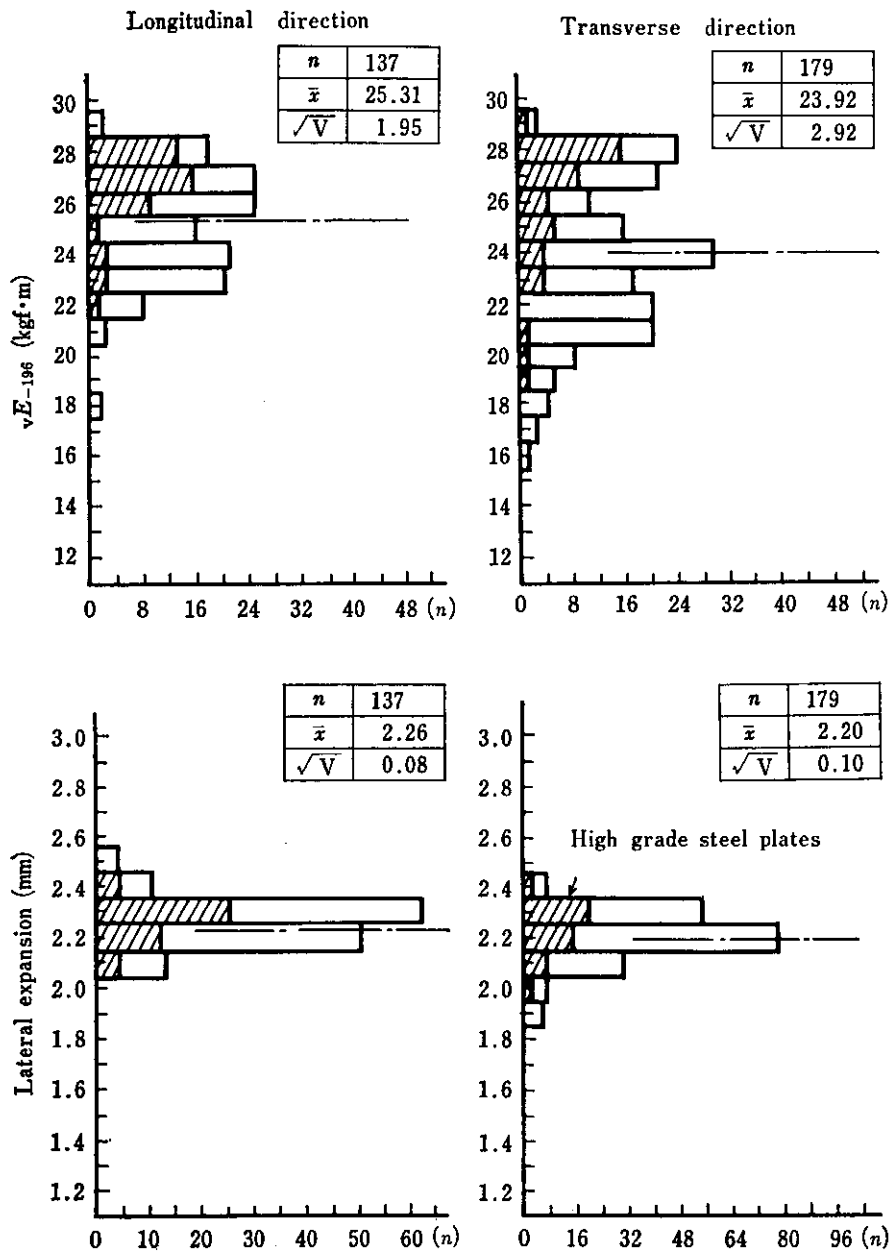


Fig. 12 Charpy impact properties of 9% Ni steel plates ($11 \leq t \leq 20$ mm)

Table 2 Chemical composition and mechanical properties in the direction perpendicular to the rolling direction of a 30 mm thick plate tested

Chemical composition (wt. %)						Tensile test at RT				V-notch Charpy test at -196°C		
C	Si	Mn	P	S	Ni	YS (kgf/mm ²)	TS (kgf/mm ²)	El (%)	YR (%)	Absorbed energy (kgf·m)	Shear area (%)	Lateral expansion (mm)
0.064	0.24	0.57	0.0016	0.0023	9.04	66.1	75.1	31	88	17.6	100	1.93

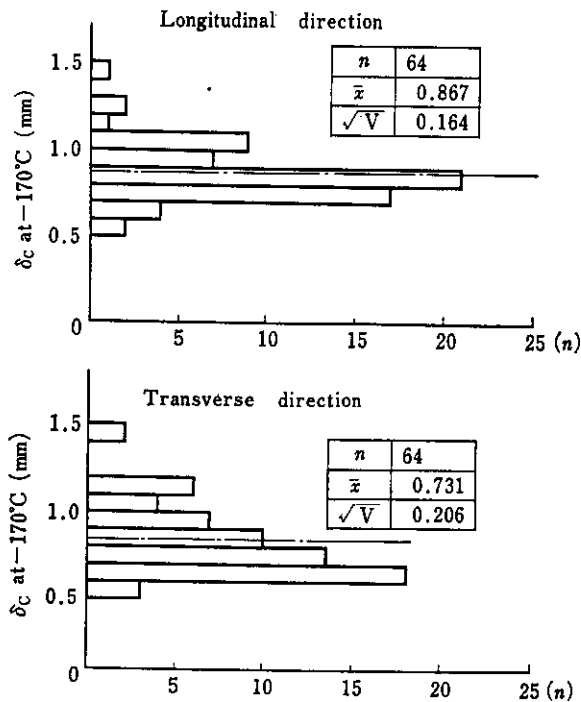


Fig. 13 COD test results of 9% Ni steel plates ($10 \leq t \leq 31$ mm)

4 Properties of Welded Joints and Fracture Toughness of 9% Ni Steel Plates

In order to secure the safety of LNG tanks, it is necessary to have adequate knowledge of the brittle crack initiation and arrest properties of welded joints. In Kawasaki Steel, these properties have been intensively studied, and some examples of testing with a 30 mm thick steel plate of relatively lower toughness in the direction perpendicular to the principal rolling direction are presented below, as taken from the previous manufacturing records.

4.1 Properties of Welded Joints

Vertical TIG and horizontal SAW welded joints were prepared with steel plates whose chemical composition and mechanical properties were given in Table 2, under the welding conditions shown in Table 3, to test the welded joint properties of test samples. The chemical composition of weld metal, the tensile test results of weld metal and welded joints, and the V-notch Charpy test results are shown in Tables 4, 5 and 6, respectively.

The strength of welded joints satisfied the specified value for steel plate at room temperature, and the absorbed energy and lateral expansion in the impact

Table 3 Welding conditions

Thickness (mm)	Welding method	Groove dimensions	Welding conditions				
			Wire (mm ϕ)	Current (A)	Voltage (V)	Speed (cm/min)	Heat input (kJ/cm)
30	Vertical TIG		1.2	220 270	10	3.5 4.0	33.0 46.3 (41.5)**
	Horizontal SAW		2.4	300 350	25	30 65	7.5 17.5 (9.3)**

* Number of layers
** Average

Table 4 Chemical composition of weld metals

(wt %)

Welding method	C	Si	Mn	Ni	Cr	Mo	W	Fe
Vertical TIG	0.03	0.25	0.28	51.5	12.57	13.40	2.32	19.2
Horizontal SAW	0.03	0.55	0.63	67.3	0.01	18.00	2.62	10.2

Table 5 Tensile test results at RT of weld metals and welded joints

Thickness (mm)	Welding method	Weld metal					Welded joint	
		Specimen dia. (mm ϕ)	YS (kgf/mm ²)	TS (kgf/mm ²)	El (%)	RA (%)	TS (kgf/mm ²)	Failure position
30	Vertical TIG	12.5	48.3	75.1	35.6	43.4	77.6	WM
		12.5	44.8	73.8	37.8	48.1	77.9	WM
	Horizontal SAW	12.5	39.7	74.6	49.4	41.0	77.3	WM+BM
		12.5	39.7	74.6	48.6	42.3	77.2	WM

Table 6 V-notch Charpy test results at -196°C of welded joints of 30 mm thick plate

Welding method	Notch position	Absorbed energy (kgf·m)	Shear area (%)	Lateral expansion (mm)
Vertical TIG	Weld metal	10.9	100	1.62
	Bond	13.2	100	1.66
	1 mm from bond	11.6	100	1.34
	3 mm from bond	13.5	100	1.53
	5 mm from bond	14.5	100	1.60
Vertical TIG (5% prestrained plate)	Weld metal	—	—	—
	Bond	11.6	100	1.75
	1 mm from bond	12.0	100	1.43
	3 mm from bond	17.1	100	1.59
	5 mm from bond	12.1	100	1.44
Horizontal SAW	Weld metal	9.2	100	1.20
	Bond	10.1	100	1.27
	1 mm from bond	11.2	100	1.21
	3 mm from bond	17.4	100	1.88
	5 mm from bond	15.4	100	1.56

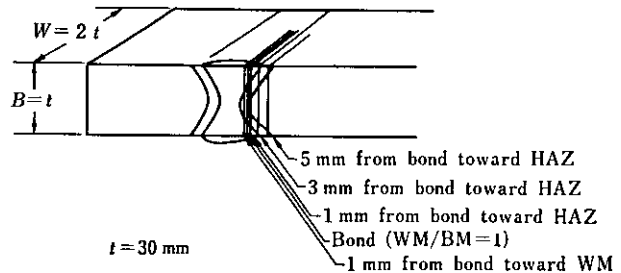


Fig. 14 Notch position of a COD specimen in the welded joint

test fully met the specified value for base metals irrespective of the notch position. The impact values of welded joints were not affected by 5% prestrain applied to the steel plates.

The COD test was conducted on the welded joints in accordance with British Standard BS 5762. Through-thickness notch was given at a position shown in Fig. 14. The COD test results are shown in Table 7. In some cases, "pop-in" occurred at 3 mm from the bond toward HAZ at -170°C , representing the fracture at a local toughness deterioration located at the notch tip within the welded joint. The "pop-in", however, did not lead to the fracture of welded joint. The load

Table 7 COD test results at -170°C of welded joint of 30 mm thick plate

Welding method	Notch position	Fracture load P (kgf)	Plastic component of clip gage displacement V_p (mm)	Critical COD δ_c (mm)
Vertical TIG	1mm from bond toward WM	9 450	1.967	0.528
		10 900	1.766	0.529
	Bond	10 900	2.014	0.593*
		10 950	1.489	0.472*
	1mm from bond toward HAZ	12 000	1.422	0.474
		12 400	1.660	0.550
	3mm from bond toward HAZ	9 650	1.438	0.415
		(10 020) 10 030	(0.722) 1.180	(0.247) 0.362
	5mm from bond toward HAZ	11 050	1.308	0.410*
		11 300	0.945	0.323*
Vertical TIG (5% prestrained plate)	1mm from bond toward WM	11 525	2.978	0.874*
		10 800	1.820	0.554*
	Bond	10 825	1.689	0.514
		11 065	2.618	0.753
	1mm from bond toward HAZ	10 275	2.382	0.653*
		10 875	1.513	0.467*
	3mm from bond toward HAZ	(11 230) 11 425	(0.523) 0.956	(0.212) 0.322
		11 575	0.967	0.337
	5mm from bond toward HAZ	11 700	1.315	0.426*
		11 350	1.022	0.343*
Horizontal SAW	1mm from bond toward WM	13 900	2.000	0.671*
		12 925	1.691	0.579*
	Bond	13 875	1.655	0.578*
		14 000	1.678	0.583*
	1mm from bond toward HAZ	13 500	1.664	0.572*
		13 200	1.573	0.536*
	3mm from bond toward HAZ	13 500	1.445	0.498*
		13 050	1.818	0.597*
	5mm from bond toward HAZ	14 400	1.761	0.612*
		14 600	1.886	0.652*

() : Pop-in * : δ_{max}

continued increasing after the occurrence of "pop-in" and the COD value was proved to be 0.3 mm and over.

In order to examine the brittle fracture initiation properties in case of a large defect existing at the butt and T-joint welds, the center-notched, wide plate tension test was conducted. The geometry of the test

piece is shown in Fig. 15. The test piece was cooled to $-170 \pm 5^{\circ}\text{C}$ and tested using an 8 000 t test rig.

The test results are shown in Table 8. The relationship between load and clip gage opening displacement plotted a smooth curve, and no load drop caused by brittle fracture such as "pop-in" was observed. The

Table 8 Wide plate tension test results

Test	Specimen dimensions(mm)			Prestrain (%)	Test temperature (°C)	Maximum load (t)	Maximum stress (kgf/mm ²)		K _c (kgf·√mm/mm ²)	Clip gage opening displacement V _g (mm)			Critical COD, δ _c (mm)		
	Thickness	Width	Notch length 2C				σ _{gross}	σ _{net}		1	2	Ave.	1	2	Ave.
Center notched wide plate tension test of TIG welded joint	30.83	1 000	400	0	-173	1 475	47.84	79.73	1 290	3.96	3.69	3.83	3.46	3.23	3.35
	30.85	1 000	400	5	-168	1 510	48.95	81.58	1 319	4.63	4.58	4.61	4.04	4.00	4.02
Notched wide plate tension test of T joint	30.70	1 000	400	0	-170	1 565	50.98	84.96	1 374	5.20	4.41	4.81	4.36	3.70	4.02

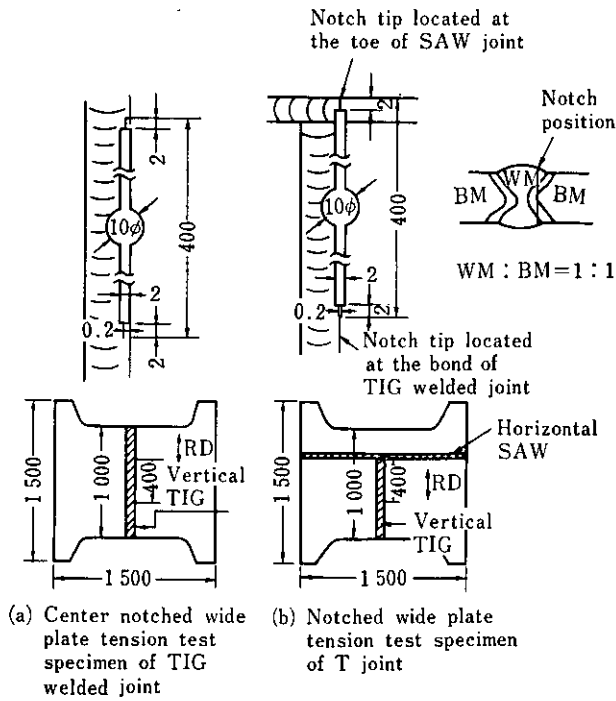


Fig. 15 Geometries of wide plate tension test specimen

maximum net section tensile stress was 79 kgf/mm² and over, exceeding the specified yield stress. The fracture occurring at the notch tip located in the bond propagated through the middle of weld metal perpendicular to the axis of tensile stress, leading to the final fracture. The propagating fracture was of ductile nature.

4.2 Brittle Crack Propagation Arrest Properties

In order to test the brittle crack propagation arrest properties of 9% Ni steel plates, the duplex ESSO test was conducted using specimens slightly larger than the standard and that of extra large scale. The geometries of test pieces are shown in Fig. 16. The

test piece was prepared by welding a 30 mm thick, 80 kgf/mm² high tensile strength steel as a crack starter to a 30 mm thick 9% Ni steel plate with the weld metal for 80 kgf/mm² high tensile strength steel plates.

The standard test piece shown in Fig. 16 (a) was cooled to -170°C ± 5°C or -196°C with and without 5% prestrain applied to 9% Ni steel plate and tested in a 1 200 t test rig, while the extra large test piece shown in Fig. 16 (b) was cooled to -170 ± 5°C and tested using an 8 000 t test rig.

Table 9 shows the results of the duplex ESSO tests. The brittle crack, which had propagated through the 80 kgf/mm² high tensile strength steel plate, failed to penetrate the 9% Ni steel plate in all cases. In the standard specimen with 0% prestrain and tested at -173°C, the brittle crack was arrested at the weld groove, while in the specimen subjected to 0% prestrain and tested at -196°C and that subjected to 5% prestrain, spearhead-shaped cracks with maximum length of 30 mm at the middle of plate thickness and 0 mm at the plate surface penetrated the test plates. In either case, however, the brittle crack was immediately arrested. In case of the extra large test

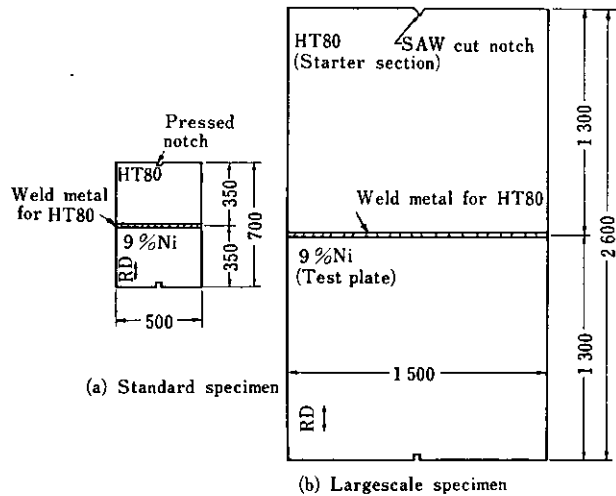


Fig. 16 Duplex ESSO specimen geometries

test, none of "pop-ins" was recognized on the load-clip gage opening displacement curve. Moreover, cracks induced at the notch tip at the welded joint bond were all ductile cracks propagating in the interior of soft weld metal. It may be said, therefore, that the probability of initiation and propagation of brittle crack in the welded joints of steel plates tested is very small.

In the duplex ESSO test, moreover, the brittle crack failed to propagate in the test steel plate at both -170°C and -196°C . Even if a long crack occurred due to some cause, therefore, the steel plates tested could arrest the propagation of brittle crack.

5 Conclusion

Excellent low temperature toughness is required of 9% Ni steel to be used for LNG tanks. Kawasaki Steel has for some time made great efforts to improve the quality of 9% Ni steel and succeeded in manufacturing and delivering about 3 000 tons of 9% Ni steel plates characterized by stable quality and excellent properties for the 80 000 k/ LNG tanks at Chita LNG Receiving Terminal, through the drastic reduction of the P and S contents and the strict control of manufacturing processes. Furthermore, it was confirmed

by various welded joint strength tests and fracture toughness tests that the steel plates were adequately applicable to the construction of LNG tanks. It is expected that the demands for 9% Ni steel plates will continue to increase, and the authors believe that their product with its excellent properties will fully meet the users' requirements.

The welded joint strength tests and fracture toughness tests reported here were conducted through the collaboration of Harima Works, Kawasaki Heavy Industries, Co., Ltd. to whom the authors would like to express their sincere gratitude for giving permission to publish the results.

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