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**DEVELOPMENT OF 7%Ni-TMCP STEEL PLATE
FOR LNG STORAGE TANKS**

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1. ABSTRACT

Demand of natural gas continues to increase in the recent years due to the rise of environmental issues and the drastic increase of crude oil price. These events led to the increase of constructions of Liquefied Natural Gas (LNG) storage tanks worldwide. The inner tank material for above ground LNG storage tanks have mostly been made of 9% nickel steel plate over the last 50 years as it has excellent mechanical properties under the cryogenic temperature of -160deg-C. During this period, the LNG storage tanks made of 9%Ni steel plate have been operated safely at the many LNG export and import terminals in the world. Meanwhile, technologies of steel making, refinement, design, analysis, welding and inspection have been improved significantly and enabled to enlarge volumetric capacity of the tank 2-3 times. There was a tendency for nickel price to increase in recent years. In such a circumstance lowering Ni content has focused attention on the 9%Ni steel as nickel is an expensive and valuable rare metal and a 7%Ni steel plate was eventually researched and developed by optimizing the chemical compositions and applying Thermo-Mechanical Controlled Process (TMCP). As a result, it was demonstrated that 7%Ni-TMCP steel plate had excellent physical and mechanical properties equivalent to those of 9%Ni steel plate.

In order to evaluate fitness of the 7%Ni-TMCP steel plate and its weld for LNG storage tanks a series of testing was conducted. Several different plate thicknesses, i.e. 6,10,25,40 and 50 mm, were chosen to run large scale fracture toughness tests including duplex ESSO tests, cruciform wide plate tests as well as small scale tests. It was concluded that the 7%Ni-TMCP steel plate warrants serious consideration for use in LNG storage tanks. This paper reports details of the research and development of the 7%Ni-TMCP steel plate.

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2. BODY OF PAPER

2.1 Introduction

As the global LNG demand remains high, construction of LNG storage tanks is expected to continue to increase in the future. 9%Ni steel plate¹⁻⁵ has generally been used as a primary component of aboveground LNG storage tanks for the last half century. It is well known that excellent cryogenic fracture toughness of high nickel alloy steel plate is attributed to the retained austenite and the refinement microstructure obtained by nickel content and heat treatment process. The newly developed 7%Ni-TMCP steel plate⁶⁻⁷ adopts a Thermo- Mechanical Control Process (TMCP) to succeed in obtaining the retained austenite and the refinement microstructure which bring equivalent fracture resistance to the conventional 9%Ni steel plates⁶ with a 2% nickel content reduction. Reduction of the nickel content significantly contributes to saving natural resources as well as to mitigating anticipated rising construction cost due to significant fluctuations in nickel price.

This paper introduces the basic concept of the 7%Ni-TMCP steel plate and reports the physical and mechanical properties of the plates as well as welds. This paper also reports the results of large scale fracture toughness tests conducted for assessing the safety performance of the LNG storage tank made of the 7% Ni steel plate and comparing with the study results made on the conventional 9% Ni steel, including the studies on the large capacities LNG storage tanks with heavy thickness plates⁸⁻¹⁰.

2.2 Metallurgical Basis of 7%Ni-TMCP Steel Plate

Resistance to brittle crack initiation especially in the heat affected zone (HAZ) and arrest of propagating cracks in the base plate was targeted as key properties to ensure the safe operation of LNG storage tanks (Fig. 1). Research on the effective chemical composition and production process found that a low silicon concentration and proper chromium alloying with grain refinement by TMCP leads to a 2% nickel content saving.

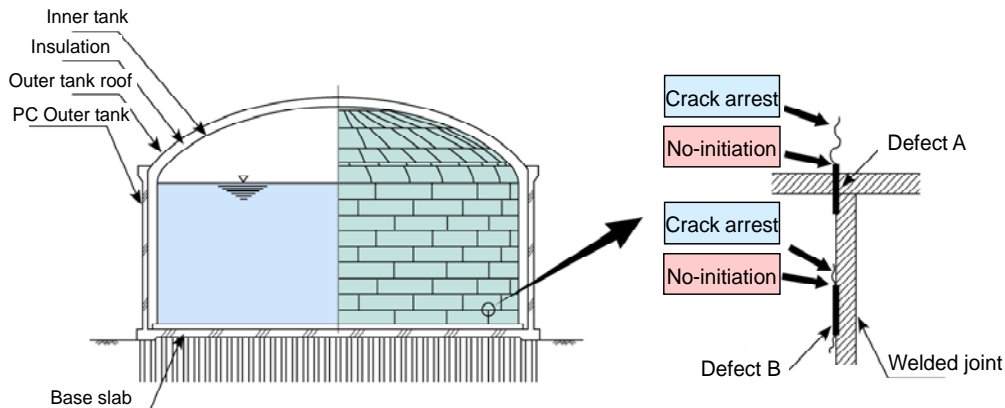


Fig. 1 Requisite properties for material of LNG tank¹¹

2.2.1 Design of Chemical Compositions for Enhancement of Brittle Crack Initiation Resistance

For 7%Ni-TMCP steel, brittle crack initiation resistance of welds was investigated. Table 1 provides chemical composition of prepared steels.

Crack initiation property was evaluated by three point bend Crack Tip Opening Displacement (CTOD) testing compliant with BS7448¹² at the Fusion Line (FL) and the weld toe where Gas Tungsten Arc Welding (GTAW) was employed with use of 70% nickel welding consumable as that used in the 9%Ni steel welding.

Fig.2 shows CTOD test results. Effects of decrease Si and Cr bearing are not only improvement of the critical CTOD value at FL and toe but also enhancement of the critical CTOD value comparable to the conventional 9%Ni steel, while Ni simply decreased steel had low critical CTOD value at toe.

To improve toughness of HAZ at the weld toe in the 7%Ni steel welds, it was considered to be effective to optimize hardenability of the steel by tempering the microstructure of HAZ by following welding passes¹³. "Tempering" is known as an effective process to precipitate cementite particles in the microstructure and mitigate the hardness of matrix to suitable level.

As mentioned above microstructure just under weld toe is unable to be tempered in the absence of following passes. Therefore, chemical composition was designed so that microstructure of HAZ should be automatically tempered without following welding passes. It is known that lowering Si content is effective for auto-temper phenomenon at Coarse grained HAZ (CGHAZ) and decreasing Martensite-Austenite constituent (MA) for Inter-critical coarse grained HAZ (ICCGHAZ)¹⁴. Cr is also effective to raise hardenability without inhibition of formation of retained austenite.

As a result of these studies, a low Si concentration and Cr bearing was applied to the chemical composition of 7%Ni-TMCP steel plate

Table 1 Chemical composition of steels [mass%]

| Mark | C | Si | Mn | Ni | Cr | Mo |
|---------------------------------|------|-------------|------|------------|-------------|------|
| Ni simply decreased 7%Ni | 0.06 | 0.25 | 1.20 | 7.0 | Tr. | Tr. |
| Decrease Si and Cr bearing 7%Ni | 0.05 | 0.05 | 0.80 | 7.1 | 0.41 | 0.04 |
| Conventional 9%Ni ⁷⁾ | 0.05 | 0.22 | 0.65 | 9.2 | Tr. | Tr. |

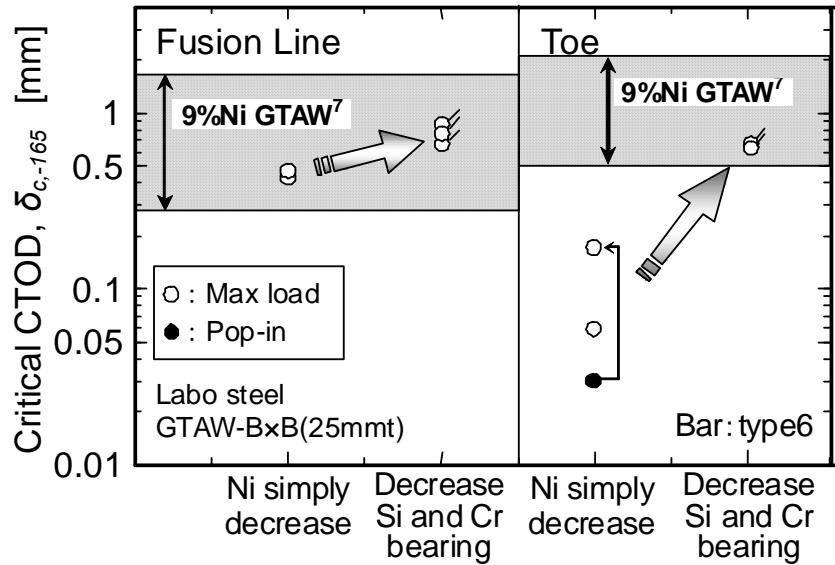


Fig. 2 Improvement of CTOD property in welded joint by decrease Si and Cr bearing on 7%Ni-TMCP steel plate

2.2.2 Application of TMCP for Enhancement of Arrestability of Propagating Brittle Crack

TMCP with large reduction just above A_{r3} is known as an effective process for enhancement of toughness due to refinement of microstructure^{6-7,15}. The TMCP with an addition of intermediate heat treatment could achieve finer microstructure for the 7%Ni steel production (Fig. 3).

Retained austenite is also known to contribute for improving toughness of high nickel steels. As nickel depresses M_s transformation temperature and serves to stabilize austenite thermally, the decrease of nickel generally reduces retained austenite fraction. However, it is clearly shown that the 7%Ni steel plates manufactured by the TMCP with an intermediate heat treatment achieve higher retained austenite volume than that of 9%Ni steel (Fig. 4)

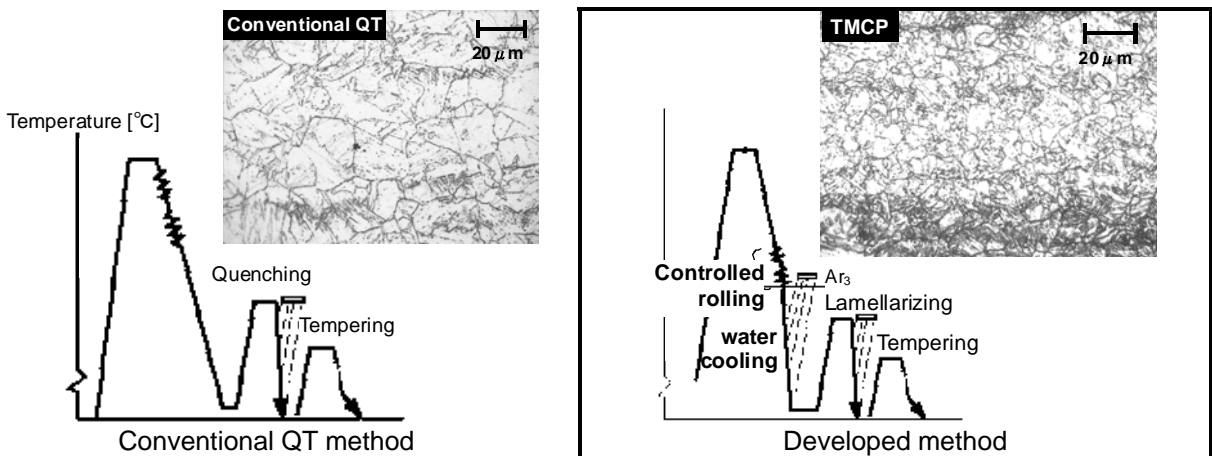


Fig. 3 Generals of production process and typical microstructure

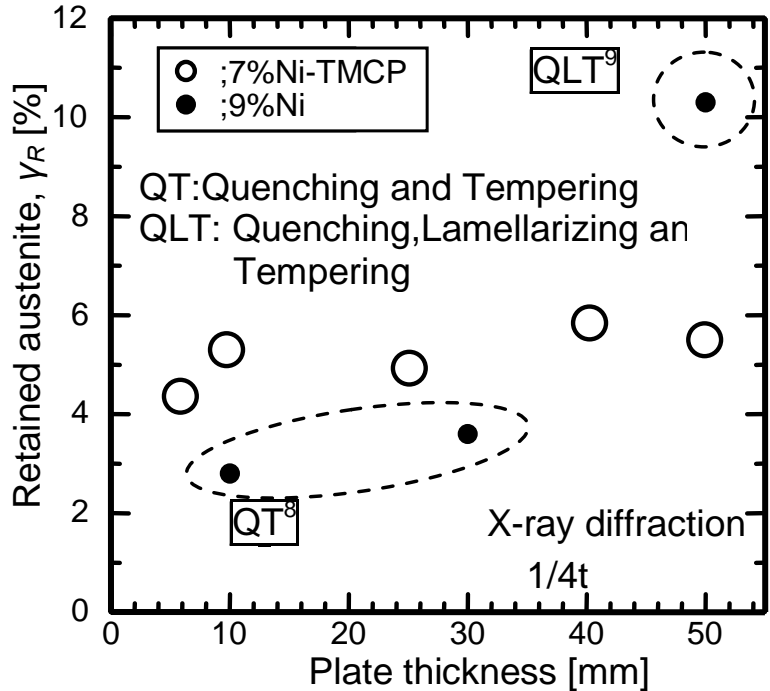


Fig. 4 Evaluation result of retained austenite

2.3 Mechanical Properties of 7%Ni-TMCP Steel Plate

Table 2 shows the test items conducted to evaluate fitness of the 7%Ni-TMCP steel plate and its weld for inner tank of LNG storage tanks. The evaluation program is set to be the same as a previous study in order to evaluate 38~55 mm heavy thick 9 %Ni steel plate⁸⁻⁹. Test plate thicknesses were 6, 10, 25, 40 and 50 mm, which were manufactured in actual production equipment.

Table 2 Evaluation program

| Thick. [mm] | Subject | Basic mechanical test | Fracture toughness test |
|---------------------------|--------------|--|---|
| 6 10 25 40 50 | Base metal | Chemical compositions, Macrostructure, Microstructure, Sulfur print, Non-metallic inclusions, Hardness, Side bend test, Tensile test, Low temp. tensile test, 2mmV Charpy test Strain aged Charpy test | CTOD test*, Dynamic tear test ***, Duplex ESSO test *** |
| | Welded joint | Macrostructure, Microstructure, Hardness, Longitudinal bend test, Tensile test, 2mmV Charpy test | CTOD test*, Cross weld notched wide plate test** |

*other than 6mm thickness, **other than 10mm thickness,
 ***other than 6 and 10mm thickness

2.3.1 Results of Basic Mechanical Tests on Base Metal

Table 3 shows results of chemical composition analysis. Impurity elements are kept to be very low by the latest steel making technology. Table 4 shows results of tensile tests and Charpy impact tests. All of them met the requirements of ASTM A553M-Type1

Table 3 Chemical compositions [mass%]

| | C | Si | Mn | P | S | Cu | Ni | Cr | Mo | Sol.Al |
|-------|------|------|------|-------|-------|------|------|------|------|--------|
| Ladle | 0.05 | 0.05 | 0.80 | 0.001 | 0.001 | 0.03 | 7.13 | 0.41 | 0.04 | 0.030 |

Table 4 Results of tensile test and Charpy impact test

| Thick. [mm] | Tensile property(avg.) | | | | Charpy impact property(avg.) | | | |
|------------------------|------------------------|------|----------------|-------------|------------------------------|------|--|-----------|
| | Posi. | Dir. | 0.2YS [MPa] | TS [MPa] | Posi. | Dir. | vE_{-196} [J] | BA [%] |
| 6 | Full | T | 630 | 720 | 1/4t* | L | 110* | 0 |
| 10 | Full | T | 681 | 741 | 1/4t** | L | 179** | 0 |
| 25 | 1/4t | T | 648 | 713 | 1/4t | L | 259 | 0 |
| 40 | 1/4t | T | 635 | 715 | 1/4t | L | 255 | 0 |
| 50 | 1/4t | T | 655 | 733 | 1/4t | L | 237 | 0 |
| ASTM A553M Type1 | - | - | 585 min. | 690 /825 | - | - | $\geq 21(6\text{mm})$ $\geq 26(10\text{mm})$ $\geq 34(25\sim 50\text{mm})$ | - |

* 1/2 sub size specimen ** 3/4 sub-size specimen

2.3.2 Results of Fracture Toughness Tests on Base Metal

CTOD tests¹² were performed for evaluation of resistance to brittle crack initiation. All critical CTOD values show extremely high level.

Duplex ESSO tests (Fig. 5) were performed under the applied load of 393 MPa at -196 deg.C to directly evaluate the arrest toughness. Results of both 25 mm, 40 mm and 50mm thick plate specimens showed "No-Go". Example of fracture surface of duplex ESSO test is shown in Fig. 6.

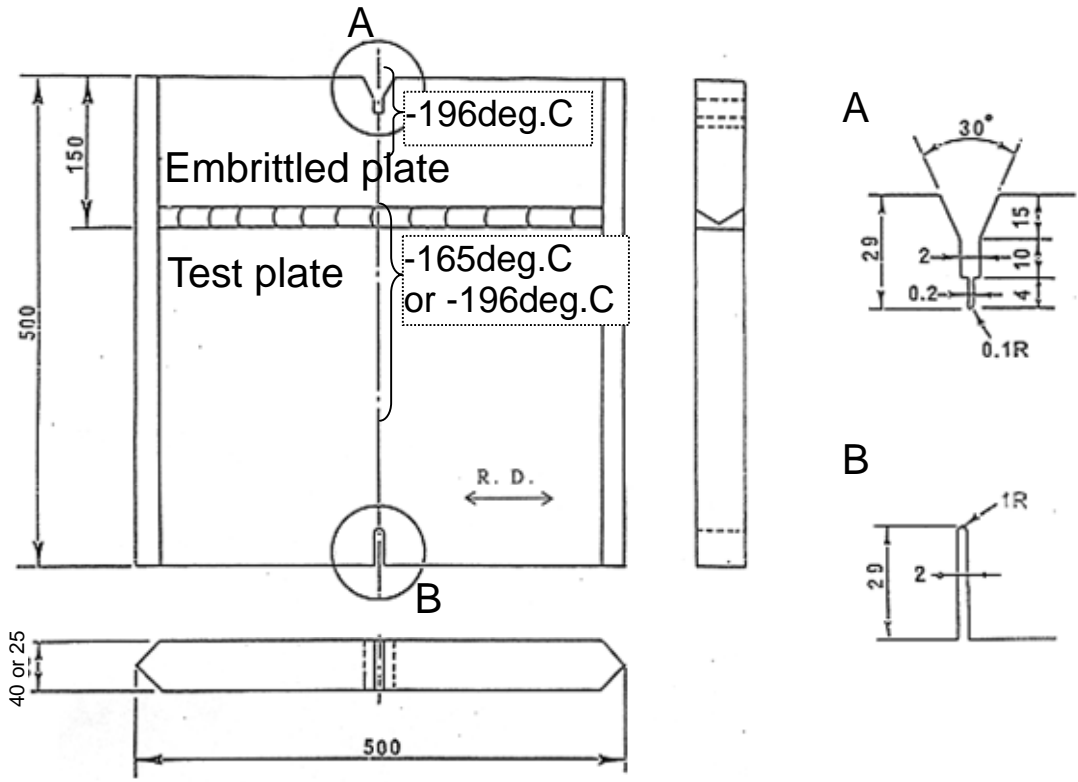


Fig. 5 Duplex ESSO specimen

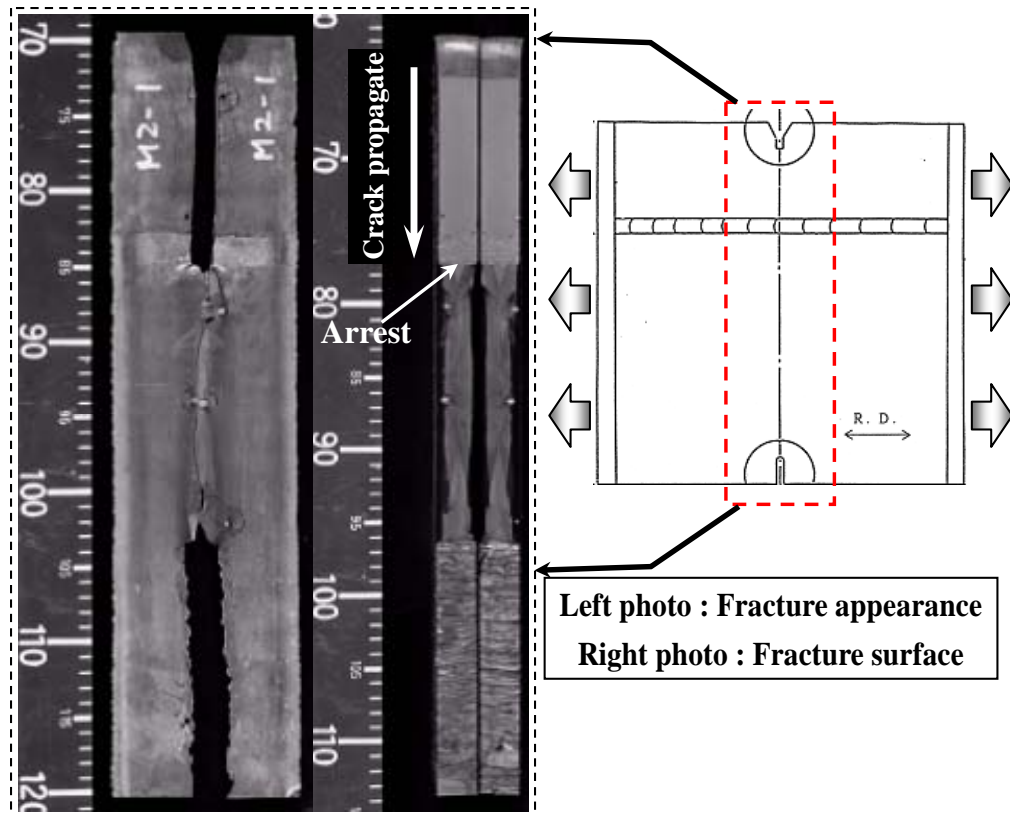


Fig. 6 Example of fracture surface of duplex ESSO test (25mmt, -196deg.C)

2.3.3 Results of Basic Mechanical Tests on Welded Joints

Welded joints of 7%Ni-TMCP steel plates were prepared in three different welding methods; SMAW, GTAW and SAW (Table 5). V groove in case of 6 and 10mm thick plate and double-V groove in case of 25,40 and 50mm were applied for edge preparation similar to actual tank fabrication. 70% nickel type welding consumables were used. Thus, welding conditions including the edge preparations and the welding consumables are all the same as that of the actual fabrications using 9%Ni steel plates.

In every thickness and welding condition, tensile strengths show more than 690 MPa which is specified minimum value of A553M-Type1. Fracture path run through or across weld metals corresponding to that the hardness distributions provided a typical profile of an under-matching welded joint¹⁶⁻¹⁷.

Also, all of absorbed energy of Charpy impact test whose notch position is at WM, FL, HAZ1mm, HAZ3mm and HAZ5mm was evaluated sufficiently high against the requirement of ASTM A553M.

Table 5 Welding conditions

| Thick. [mm] | Welding Method | Welding material | Position of weld | Max. Heat Input [kJ/mm] |
|-------------|----------------|------------------|------------------|-------------------------|
| 6 | SMAW | 70%Ni type | Vertical | 3.1 |
| 10-50 | SMAW | 70%Ni type | Vertical | 4.8 |
| | GTAW | | Vertical | 4.4 |
| | SAW | | Horizontal | 2.0 |

2.3.4 Results of Fracture Toughness Tests on Welded Joints

CTOD tests¹² were performed on four different thicknesses i.e. 10, 25, 40 and 50 mm and three different welding methods that were SMAW, GTAW and SAW. The critical CTOD value of all conditions at -165 deg. C was evaluated sufficiently high. Table 6 shows results of welded joint of 50 mm thick plate, that is maximum thickness, as an example. The critical CTOD value at -165 deg. C shows 0.4 mm in minimum. The results of thinner plate from 10 to 40 mm are comparable.

Furthermore, cross weld notch wide plate tensile tests were conducted to evaluate safety of the T-cross welded joint in LNG storage tanks. Test specimen and notch location are shown in Fig.7. Through thickness notch is prepared along the vertical weld at the intersection of welds. The radius of tip is sharpened to 0.1mm by electro discharge machining. For 25, 40 and 50mm thick plate, the length of the notch is double of the plate thickness c. For 6mm thick plate, the length is 36mm. FL is defined as the position that the portion of weld metal is 50% to notch depth.

Vertical welding were performed GTAW or SMAW according to actual tank fabrication, while horizontal welding were performed by SAW. Test temperature is set to be -165 deg.C, that is design

temperature of LNG tank.

Fracture net stresses of all specimens were more than 750 MPa and much higher values than 400 MPa, which is the design stress based on huge scenario earthquake. All specimens were fractured in a ductile manner and no brittle pop-in was observed. Cracks initiated at the HAZ deviated into weld metal with no exception in all specimens (Fig. 8 as an example). Considering the fracture stress, it is concluded that initiation and propagation of fracture occurs almost after yielding of the ligament section so there is a very high safety against fracture.

Table 6 CTOD test results of welded joints (50mm, -165deg.C)

| Welding method | Notch position | Critical CTOD, δ_c [mm] (type underline: pop-in) | Welding method | Notch position | Critical CTOD, δ_c [mm] |
|----------------|----------------|---|----------------|----------------|--------------------------------|
| SMAW | WM | 0.679(6), 0.645(6), 0.706(6) | SAW | WM | 0.463(6), 0.584(6), 0.609(6) |
| | FL | 0.691(4), 0.634(4), <u>0.402-0.627(5)</u> | | FL | 0.533(4), 0.561(4), 0.675(4) |
| | HAZ1mm | 0.741(4), 0.936(4), 0.759(4) | | HAZ1mm | 0.564(4), 0.905(4), 0.836(4) |
| | HAZ3mm | 0.990(4), 0.881(4), 0.851(4) | | HAZ3mm | 0.878(4), 0.849(4), 0.888(6) |
| | Toe | >1.212(4-6), 1.085(4), >1.213(4-6) | | Toe | 0.846(4), 0.869(4), 0.665(4) |
| GTAW | WM | 0.953(6), 0.938(6), 0.879(6) | SAW | WM | 0.463(6), 0.584(6), 0.609(6) |
| | FL | 0.638(4), 0.963(4), 0.734(4) | | FL | 0.533(4), 0.561(4), 0.675(4) |
| | HAZ1mm | 0.723(4), 0.996(4), 0.894(4) | | HAZ1mm | 0.564(4), 0.905(4), 0.836(4) |
| | HAZ3mm | 1.100(4), >1.175(4-6), 1.141(4) | | HAZ3mm | 0.878(4), 0.849(4), 0.888(6) |
| | Toe | 1.018(4), 1.066(4), 1.193(4) | | Toe | 0.846(4), 0.869(4), 0.665(4) |

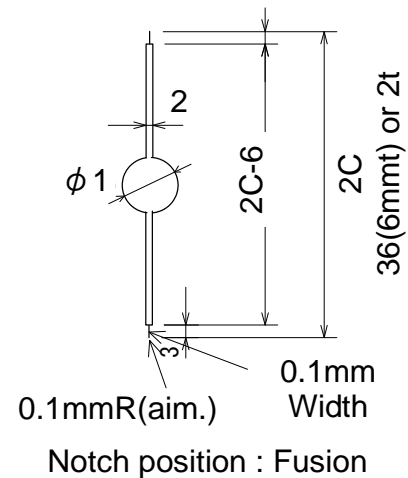
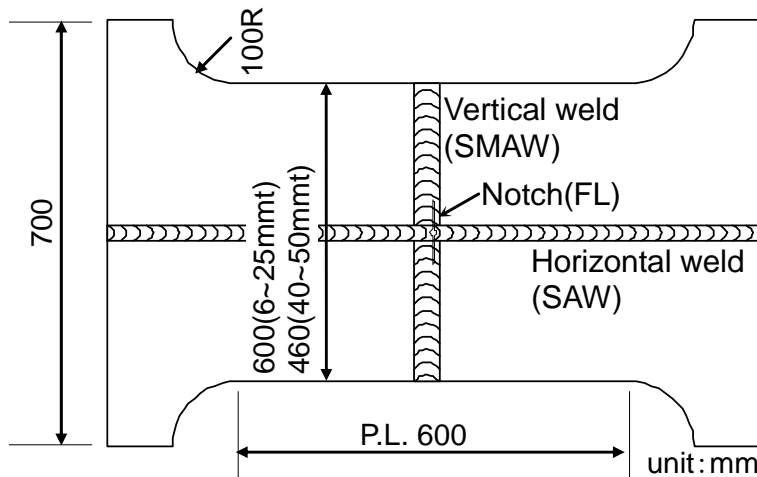
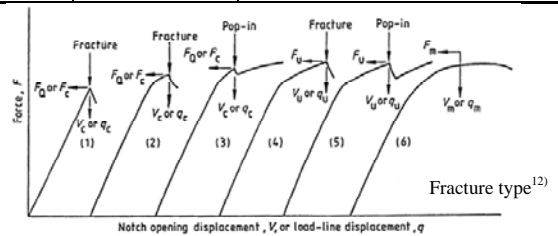


Fig. 7 Specimen of cross weld notch wide plate test

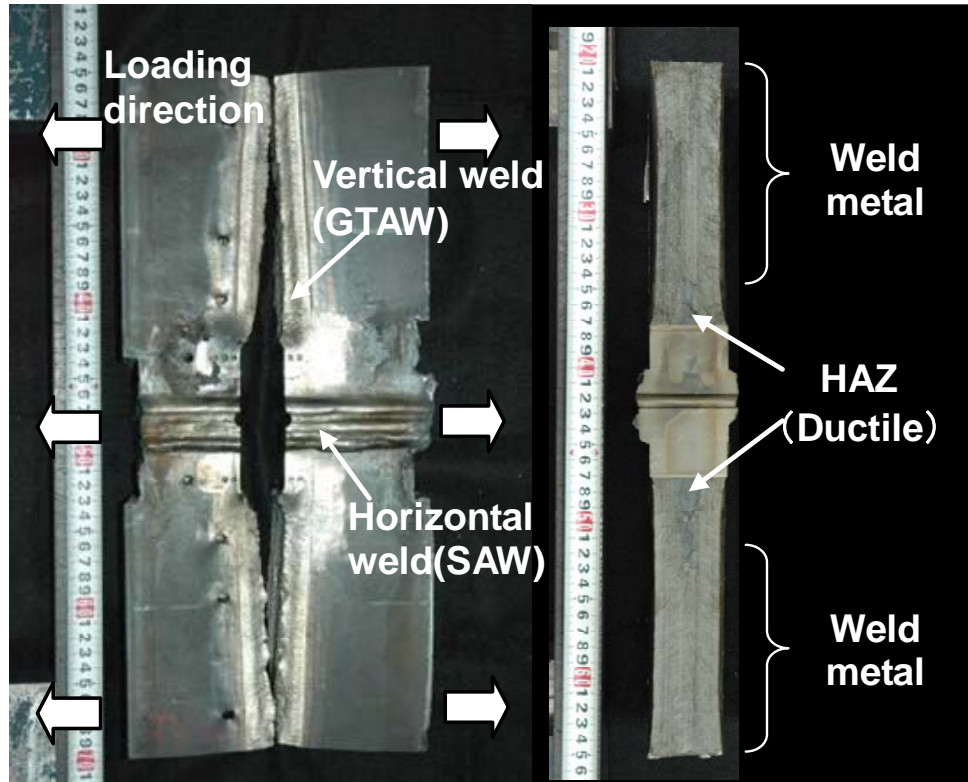


Fig. 8 Fracture path and fracture surface of cross weld notch wide plate test (50mm, GTAW)

2.4 Comparison with Properties to Existing 9%Ni Steel Plate

As shown in the preceding section, properties of 7%Ni-TMCP steel plate were widely evaluated. In this section, safety against fracture of 7%Ni-TMCP steel plate is evaluated compared with properties of existing 9%Ni steel plate.

2.4.1 Brittle Crack Initiation Properties

Comparison of the critical CTOD values of welds is shown in Fig. 9 except for the fully ductile weld metal. All results including pop-ins are distributed within the range of the 9%Ni CTOD test results.

Furthermore, the cross weld notch tensile tests were conducted for the evaluation of safety of the T-cross welded joint in LNG storage tanks in case a very long defect exists nearby FL. The net stresses of the 7%Ni-TMCP steel seems to be comparable to that of the 9 %Ni steel. As all specimens show a ductile fracture manner in those of austenitic weld metal a brittle fracture property cannot be evaluated (or compared). It can be said that the welds of the 7%Ni-TMCP steel has a quite high safety against brittle fracture as same as that of the 9 %Ni steel⁸⁻⁹.

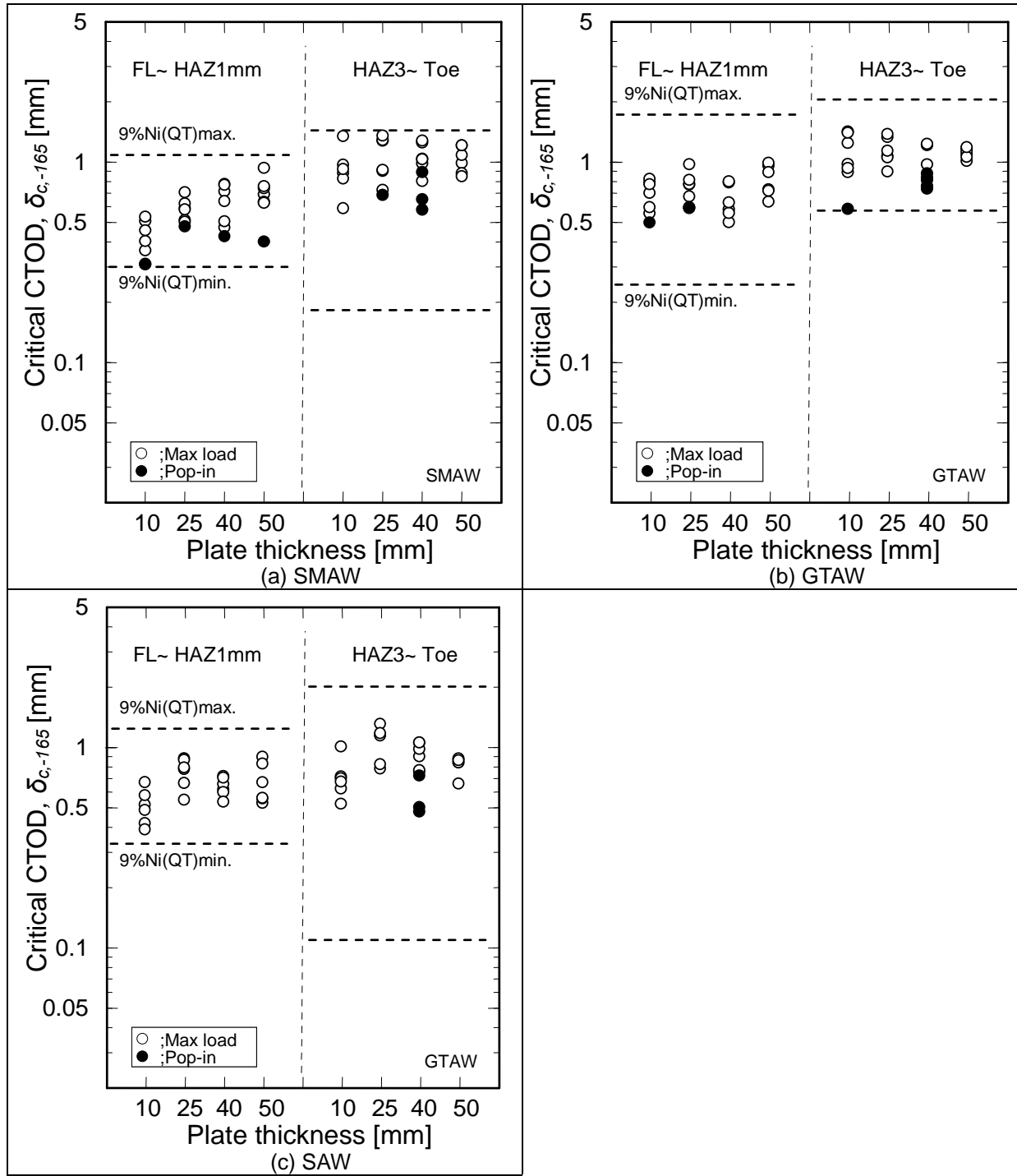


Fig.9 Comparison of CTOD test results of welded joint between 7%Ni-TMCP and 9%Ni steel

2.4.2 Brittle Crack Propagation Properties

In Duplex ESSO test, “No-Go” is obtained under loading 393 MPa at -196 deg.C, which is more severe condition compared to the actual operation. This is the result that is equal to conventional 9% Ni

steel plate. The reason why 7%Ni-TMCP steel plate has superior propagation property in spite of lowering nickel by 2 % is thought to be effect of retained austenite produced by TMCP with intermediate heat treatment.

2.5 Conclusions

Properties of the 6, 10, 25, 40 and 50mm thick 7%Ni -TMCP steel plates were evaluated by the various fracture toughness tests to confirm their fitness for use in the above-ground LNG storage tanks. As a result, including its welds, it was demonstrated that the 7%Ni-TMCP steel plate has an excellent resistance to brittle fracture of the inner tank steel exposed to the cryogenic temperature of LNG. Another evaluation of the 7%Ni-TMCP steel plate was done in its equivalency to the conventional 9%Ni steel plate which is used in the current LNG storage tank constructions. It was demonstrated that both steels had equivalent resistance to the aimed brittle fracture by comparison of their mechanical properties. Hence, it is considered that the 7%Ni-TMCP steel plate warrants a sufficiently high safety level for use in LNG storage tanks.

2.6 Acknowledgements

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