Onboard Evaluation of Low Alloy Corrosion Resistant Steel for Cargo Oil Tank of Crude Oil Tanker

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ABSTRACT

A new type of low-alloy corrosion-resistant steel has been developed as a countermeasure to the pitting corrosion problem with the cargo oil tank (COT) bottom plate of crude oil tankers. The corrosion tests for inner bottoms in the IMO rule revealed that the corrosion rate of the developed steel was less than 1.0 mm/y and no discontinuous surface between the base metal and weld metal was observed. The type approval for corrosion-resistant steel of COT bottom has been acquired from ClassNK. Developed steel without coating was applied to the COT bottom plates of crude oil tankers to clarify the validity. At the dock inspections, the pitting corrosion of the developed steel was found to be lower in comparison with conventional steel and there was no need for repair. Moreover, the shallow pits which do not need repairing at dock inspection did not appear after the docking. It is apparent that the developed steel has the potential ability to be repair free for the working lifetime of the ship. The application of the developed steel will reduce the risk of crude oil leakage due to pitting corrosion of the COT bottom plate and reduce the life cycle cost for crude oil tankers.

Key words: steel, tanker, oil tank, corrosion, pit, onboard evaluation

ABBREVIATIONS

COT	Cargo Oil Tank
COW	Crude Oil Washing
E_{corr}	Corrosion Potential
EL	Elongation
IACS	International Association of Classification Societies
i_{corr}	Corrosion Current Density
IMO	International Maritime Organization
SAW	Submerge Arc Welding
SR242	The Shipbuilding Research Association of Japan Panel #242
TEM	Transmission Electron Microscopy
TS	Tensile Strength
vE_{-20}	Absorbed Energy at 253 K
VLCC	Very Large Crude Carrier
YP	Yielding Point

INTRODUCTION

Pitting corrosion on the inner bottom plates of cargo oil tanks (COT) is one of the most serious corrosion problems with oil tankers, because environmental pollution may be caused by a major crude oil spill. Pits with a depth of up to 10mm were observed at dock inspection of certain oil tankers. Moreover there was a case in which the total number of pits to be repaired reached several thousand at dock inspection. For safety improvement and maintenance cost reduction, an appropriate countermeasure to the pitting corrosion on COT bottom is a strong requirement.

The pitting corrosion mechanism of COT bottom was scientifically clarified in a study which was carried out by 'The Shipbuilding Research Association of Japan Panel #242 (SR242) committee' for 3 years, supported by the Nippon Foundation[1, 2, 3]. The mechanism proven in the SR242 studies is as follows:
At the inner bottom of COT, corrosion of steel plate is suppressed, since it is covered by an oil coat with high insulating resistance. However, a partial defect in the oil coat may be caused by crude oil washing (COW) irradiation. If so, the inner bottom plate is exposed to a corrosive environment with concentrated chloride ions and H_2S and pitting corrosion is generated at the defect. Furthermore, the pH of the solution within the pit is lowered by a hydrolysis reaction of dissolved Fe^{2+} and the Cl^- concentration in the pit increases to satisfy the electrical neutral condition. These environmental conditions serve to exacerbate the pitting corrosion on COT bottom plates.

Recently, corrosion-resistant steel has drawn notice to its suitability as a countermeasure to the corrosion problem of COT with high practicability[4]. The International Maritime Organization (IMO) developed a performance standard for corrosion-resistant steels which specifies maintaining a certain required structural integrity for 25 years in the corrosive environment of COT[5]. In the performance standard of the IMO, corrosion-resistant steel is required to have mechanical properties and weldabilities which are equivalent to ship hull structural steel. Moreover, the ClassNK developed guidelines on corrosion resistant steels for COT specifying several matters for suitable application of these steels[6].

Based on the knowledge of SR242 studies, a low-alloy corrosion resistant steel KPAC-1[(1)] which satisfies the IMO performance standard for corrosion resistant steels for COT bottom was developed[7]. The mechanical properties and the weldability of the developed steel also satisfy the class rule. Moreover, the type approval for corrosion resistant steel of COT bottom has been acquired form ClassNK.

This paper describes the corrosion resistance by laboratory corrosion tests and the mechanical properties of the developed steel. Based on the results of the onboard evaluation of the corrosion of the developed steel applied to the actual ship, the validity of the development was discussed.

DEVELOPMENT CONCEPTS

The targets of the development were to offer a type of corrosion-resistant steel which satisfies the IMO performance standard for corrosion-resistant steels for COT bottom and can be applied with conventional welding materials by conventional welding process.

One of the acceptance criteria for corrosion-resistant steel of COT bottom by the IMO rule is that the average corrosion rate of base metal specimens does not exceed 1.0mm/y in the simulated solution inside the pit. In this development, the reduction in the corrosion rate in the simulated solution was examined by the micro alloying design within the ship's classification rule.

Since the junction between the corrosion-resistant steel and conventional steel is inevitable in practical use on a ship, it is necessary that there is no galvanic corrosion due to potential difference between the corrosion-resistant steel and conventional steel. Then, it aimed at leveling the corrosion potential of the developed steel with conventional steel from the viewpoint of galvanic corrosion. In the alloy design of the development, the following were examined:
1) Control of the anodic reaction by improving the protection property of the corrosion product (the surface film) , 2) Control of the cathodic reaction by increasing the pH of the solution on the steel surface. Thus, it is thought that the corrosion potential change resulting from the alloying elements addition can be minimized by suppressing both the anodic reaction and the cathodic reaction.

In addition, the corrosion-resistant steel was designed to make use of 1% or less of total additive alloying elements for corrosion-resistant improvement in order to preserve good weldability.

EXPERIMENTAL PROCEDURE

LABORATORY TEST METHOD

The corrosion tests of the developed steel and the conventional steel were carried out according to the performance standard for corrosion-resistant steels by the IMO rule[5]. The specimens of the developed steel and the conventional steel were sampled from steel plates

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[(1)] Trade name

which were manufactured by the Thermo Mechanical Control Process (TMCP) at Kakogawa Works of Kobe Steel. Figure 1 shows the specimen used. The weld joint specimens with 15 mm width of weld metal were sampled from the submerged arc welding (SAW) joint of the developed steel plates. The surface of all specimens was polished with emery paper grade #600.

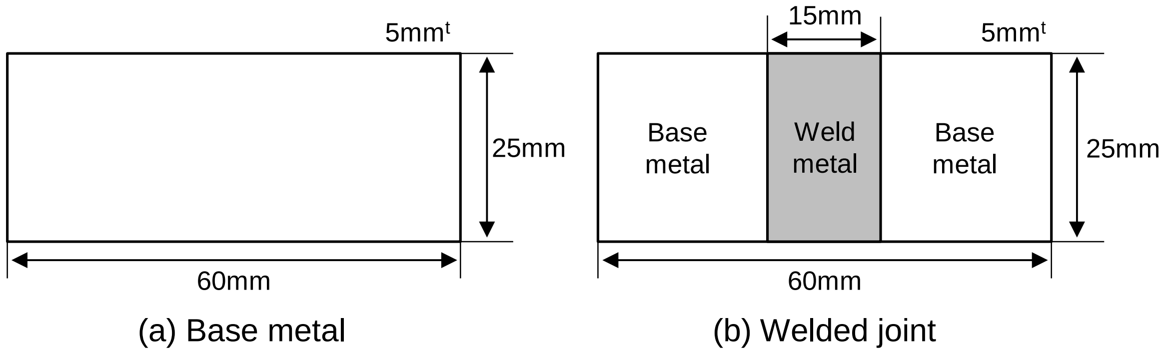


Figure 1: Specimens of corrosion tests.

A 10 mass % NaCl aqueous solution was prepared for the immersion corrosion tests. The pH of the solution was 0.85, adjusted by a HCl solution. The test solution was replaced with a new one every 24 hours in order to minimize changes in the pH of the test solution. The temperature of the test solution was maintained at 303 ± 2 K by means of a water bath.

The acceptance criteria for corrosion-resistant steel of COT bottom by the IMO rule are that the average corrosion rate of base metal specimens does not exceed 1.0mm/y and there is no discontinuous surface between the base metal and weld metal for weld joint specimens. The base metal specimens and the weld joint specimens of the developed steel were immersed in the test solutions for 72 hours and 168 hours, respectively. The weight loss of the base metal specimens was measured and the average corrosion rate was calculated from the test results. In addition, cross-sectional observation of the weld zone of the weld joint specimen was carried out.

Moreover, time-dependence of the corrosion rate of the base metal specimens was also investigated by the immersion corrosion tests. The potentio-dynamic polarization curves in the same solution as the IMO test were measured for corrosion-resistant verification of the developed steel by an electrochemical characteristic evaluation.

ONBOARD EVALUATION METHOD

In order to verify the corrosion-resistance and the practicability of the developed steel, an onboard evaluation on the actual ships was carried out. Figure 3 and Figure 4 show the application area of the developed steel on Ship A and on Ship B, respectively. The developed steel without coating was applied to the 4 COTs of an Aframax tanker (Ship A) and the 6 COTs of a VLCC (Ship B). In these ships, the application areas of the developed steel were constructed using conventional welding materials by a conventional welding process.

The corrosion of the developed steel including the weld zone was investigated at the dock after

2.5 years and 5 years. At the dock, all COTs were cleaned and dried for inspection and investigation. In the investigation, the corrosion morphology on the COT bottom was visually observed and the pitting corrosion depth and the number of pits over 2 mm in depth were measured.

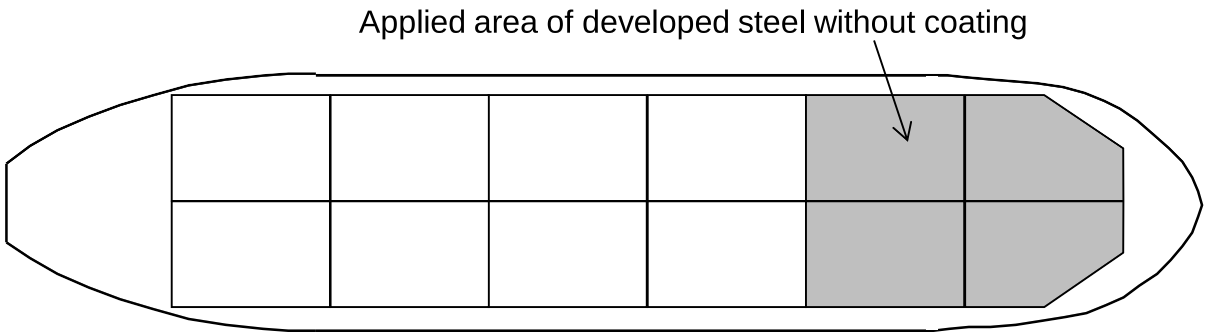


Figure 2: Applied area of developed steel in crude oil tanker (Ship A).

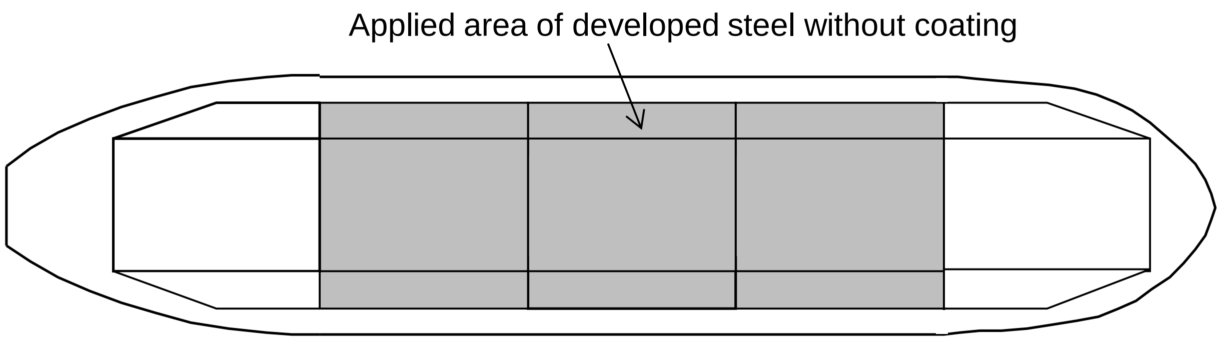


Figure 3: Applied area of developed steel in crude oil tanker (Ship B).

RESULTS AND DISCUSSION

CORROSION RESISTANCE

As shown in Figure 4, the IMO corrosion tests for COT inner bottoms revealed that the corrosion rate of the developed steel is reduced in 1/10 of that of conventional steel and the developed steel has excellent corrosion-resistance in the simulated solution in the pit. It is clear that the corrosion rate of the developed steel was less than 1.0 mm/y. Moreover, it was confirmed that the corrosion rate of the base material and the weld metal in the welded specimen was the same as the result of the cross-sectional observation shown in Figure 5. Thus, no discontinuous surface between the base metal and weld metal was observed in the welded zone. As mentioned above, the corrosion-resistance performance of the developed steel obviously satisfies the performance standard of corrosion-resistant steel for inner bottom of COT of the IMO.

Although the corrosion rate of the conventional steel increased over time, that of the developed steel gradually decreased in the early stages of the corrosion test. It is suggested that the formation of the corrosion product on the surface contributes to the corrosion-resistant improvement of the developed steel.

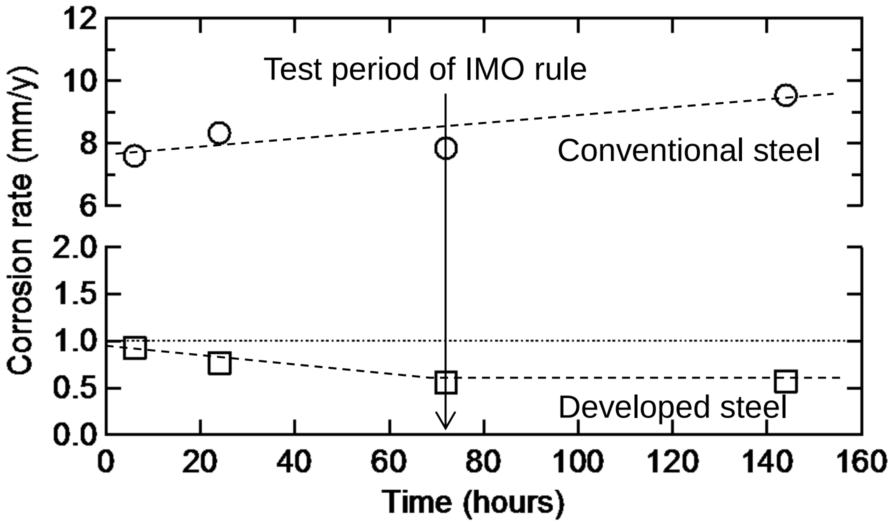


Figure 4: Corrosion-resistant property of base metal of developed steel.

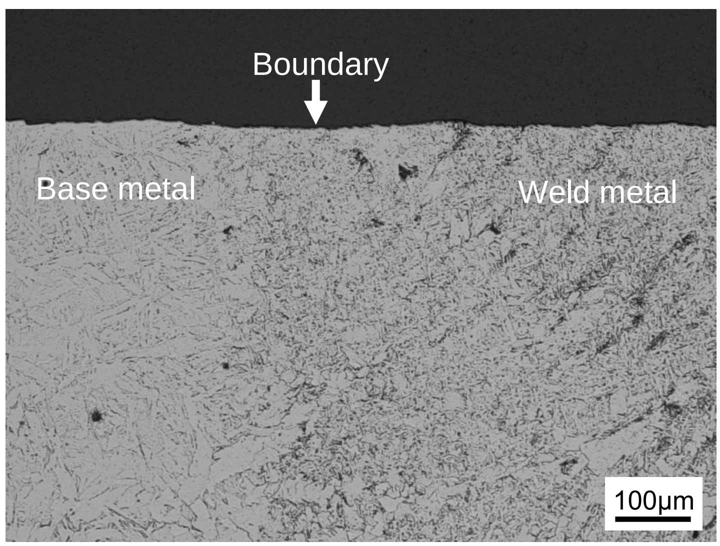
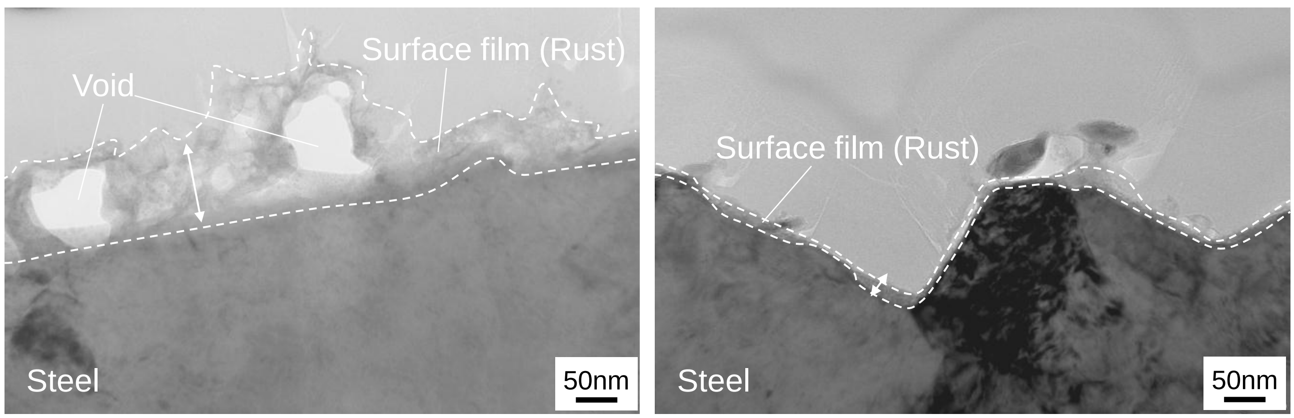


Figure 5: Corrosion-resistant property of weld zone of developed steel.

Figure 6 shows TEM observation results of the surface film on the specimen after the corrosion tests. Although a coarse surface film (rust) including voids was generated on the conventional steel, a fine surface film was observed on the developed steel by the TEM observations. This fine surface film on the developed steel is considered to have improved the protection property and have inhibited the anodic reaction of the corrosion.

As is shown in Figure 7, it became clear that both the anodic reaction and the cathodic reaction of the developed steel are reduced more than those of the conventional steel in the simulated solution on the polarization curves. It is thought that the control of the anodic reaction of the developed steel is caused by the formation of the fine rust as shown in Figure 6, and the control of the cathodic reaction is due to the rise in pH on the steel surface. In addition, the corrosion current density (i_{corr}) of the developed steel was suppressed in 1/10 of that of the conventional steel in Figure 7. It is in agreement with the above-mentioned corrosion tests results shown in Figure 4. Moreover, the corrosion potential (E_{corr}) of the developed steel was almost the same as that of the conventional steel. It was assumed that there was no problem with galvanic corrosion at the junction of the developed steel and conventional steel. Thus, it also became clear that the corrosion-resistance of the developed steel is practically excellent in the electrochemical evaluation in the simulated solution.



(a) Conventional steel (b) Developed steel

Figure 6: TEM observation results of surface film on specimen after corrosion tests.

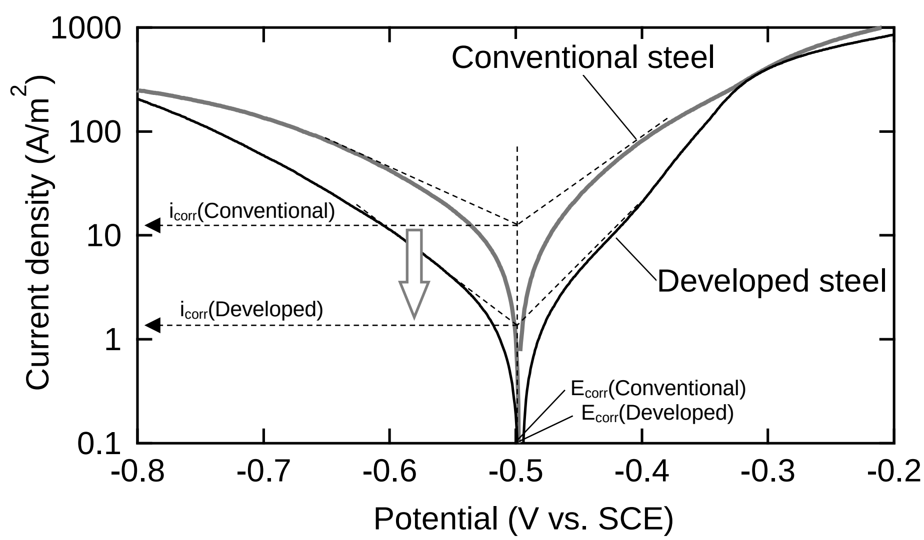


Figure 7: Electrochemical property of base metal of developed steel.

MECHANICAL AND OTHER PROPERTIES

Table 1 shows an example of the mechanical properties of the developed steel. It is clear that the developed steel satisfies the DH36 specification of classes and is equivalent to or better than that of conventional steel. Table 2 shows the Charpy impact tests of a SAW joint using a conventional welding material. It is clear that the welded joint of the developed steel also satisfies the DH36 specification of classes and has good impact properties. It was confirmed that the developed steel has the same mechanical properties and weldability as hull structural steel.

From the corrosion-resistance and the mechanical property which are shown above, the type approval for corrosion-resistant steel of COT bottom has been acquired from ClassNK.

Table 1: Mechanical properties of developed steel (Plate thickness: 30 mm)

	YP(MPa)	TS(MPa)	El(%)	vE-20(J)
Developed steel	417	521	22	260
DH36 specification	≧355	490-620	≧20	≧34

Table 2: V-Notch Charpy impact test results of SAW joint of developed steel

Notch position	WM	FL	1 mm	3 mm	5 mm
vE0(J)	141	161	177	204	260
DH32 specification	≧34				

Plate thickness: 30 mm, Heat input : 130kJ/cm

ONBOARD EVALUATION

At the dock inspection of ship A and ship B, the corrosion of the COT bottom plate was investigated in detail. Figure 8 shows a typical example of the appearance of the COT bottom. There was no uniform corrosion but only localized corrosion (pitting corrosion) on the bottom plate. All the pits were generated on the base metal and there was no pitting corrosion on the weld line. Moreover, no galvanic corrosion was found at the weld zone of the developed steel and the conventional steel. It is thought that galvanic corrosion did not occur at the junction of the developed steel and conventional steel because of the same corrosion potential, as shown in Figure 7.

Figure 9 shows a typical example of pitting corrosion on COT bottom built with conventional steel which is painted with zinc-primer on the surface. Comparatively deep pits of spherical shape were found on the conventional steel. This behavior of the pitting corrosion on the conventional steel is consistent with the result of SR242 studies. On the developed steel in COT bottom, the shape of pits was similarly spherical and the depth of the pits was generally shallow, compared with the conventional steel.

Figure 10 and Figure 11 show the results of the corrosion investigation at the dock inspection of ship A and ship B. As shown in Figure 10, the number of pits over 2 mm in depth on the developed steel is much lower than that on the conventional steel. The maximum pit depth of the developed steel is also lower than that of the conventional steel, as shown in Figure 11. The pits are usually repaired as part of dock inspection, when the depth of the pits is more than 4 mm. Some pits more than 4 mm in depth were generated on the conventional steel and these were repaired at every dock inspection. On the other hand, no pits more than 4 mm in depth were found on the developed steel on either steel surface on all ships and thus there was no need for repair. Thus, the developed steel exhibited good corrosion-resistant behaviour both on the primer painted surface and the as-rolled surface.

The number of pits on COT bottom plate changes with ships and tanks, and it was reported that average frequency of pits over 4 mm in depth on conventional steels was about 140 counts per COT[4]. As is clear from these results, the corrosion inhibition effect of the developed steel is significant.

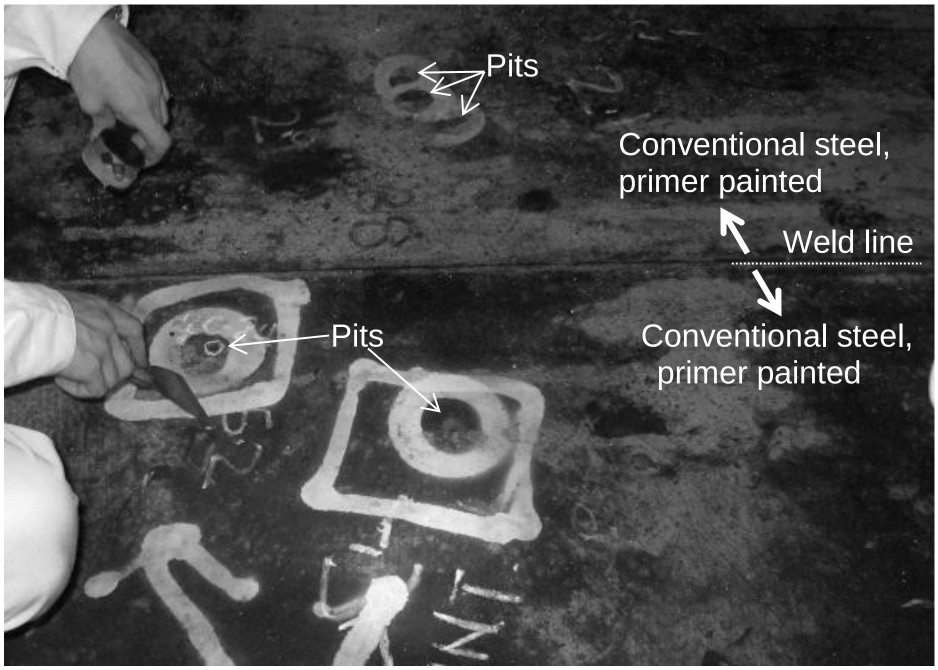


Figure 8: Typical example of condition of COT bottom plate (Ship B / 2.5 y).

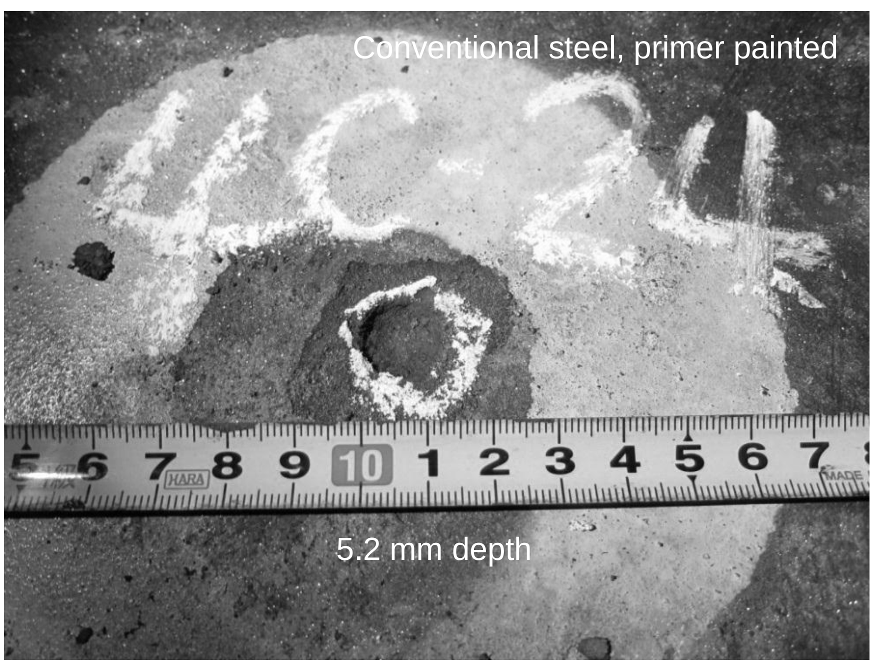


Figure 9: Typical example of pit on COT bottom plate (Ship B / 2.5 y).

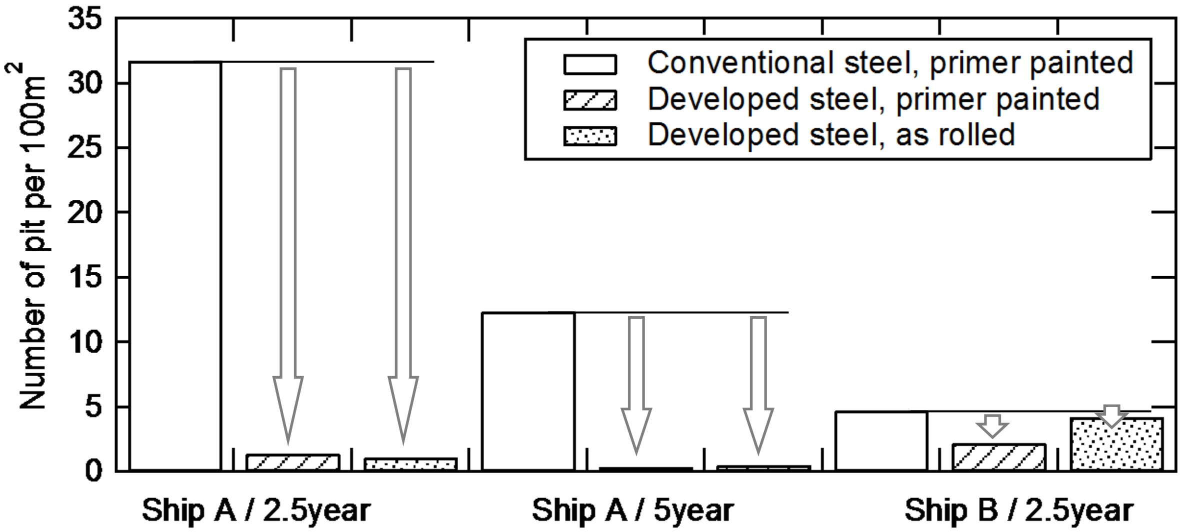


Figure 10: Number of over 2 mm depth pit observed on COT bottom plates at dock inspection.

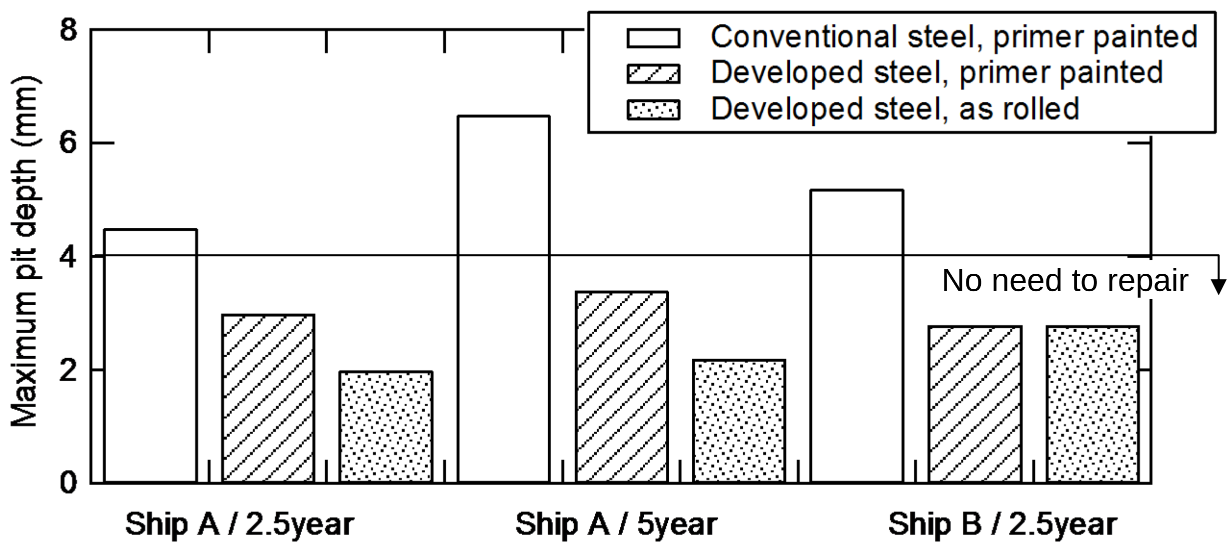
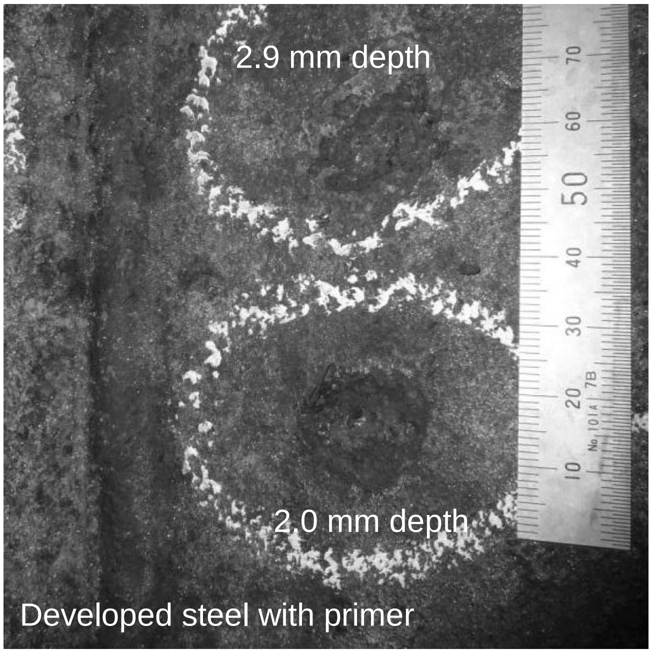


Figure 11: Maximum pit depth observed on COT bottom plates at dock inspection.

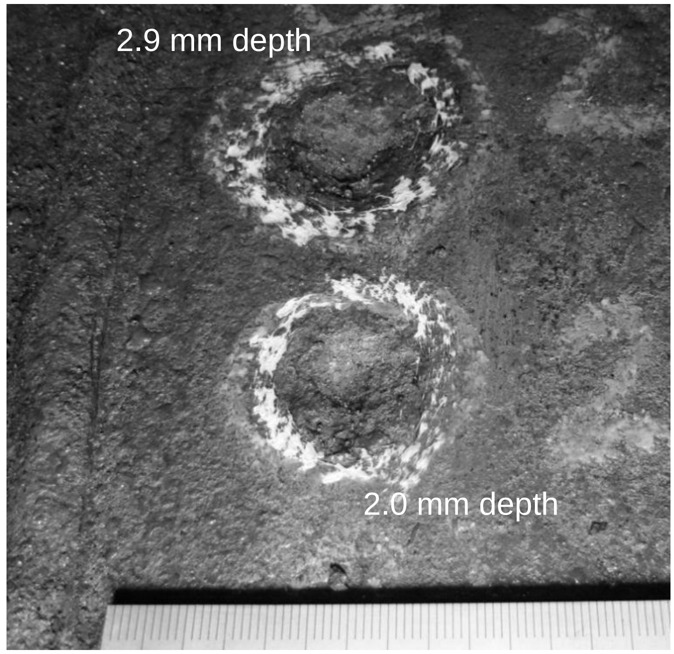
A follow-up survey of the unrepaired pits on the COT bottom was conducted on ship A. Figure 12 shows examples of the observation results of the pits on the developed steel. It seems that these pits do not exhibit growth tendencies between 2.5 years and 5 years. Figure 13 shows a comparison between the depths of the unrepaired pits after 2.5 years and 5 years. The depth of the pits is unchanged after 2.5 years and 5 years.

It was reported that the pits which had been observed at dock inspections did not exhibit further growth at the next dock inspections4. This fact can be explained as follows:
At a dock, COT is cleaned and dried for inspection. After inspection, COT will be filled with crude oil and an oil coating will be formed on the surface of the bottom plates. Since the thickness of the oil coating at the already-generated pits is thicker than that of the surface

without pits, the corrosion prevention effect of the oil coat at the already generated pits is higher than on the surrounding normal surface. Thus, the growth of the pitting corrosion on COT bottom is halted at a dock with COTs cleaning. The fact was also confirmed in this study.



(a) 2.5 years



(b) 5years

Figure 12: Follow-up of shallow pit without repair on COT bottom plate (Ship A).

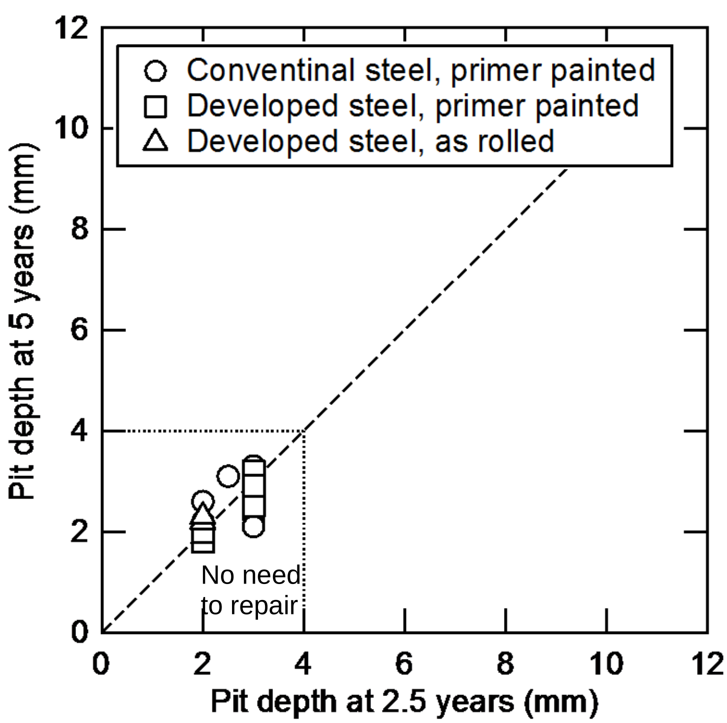


Figure 13: Comparison between depths of unrepaired pits at 2.5 y and 5 y (Ship A).

CONCLUSIONS

A new type of low-alloy corrosion-resistant steel has been developed as a countermeasure to the pitting corrosion problem of COT bottom plate of crude oil tanker. The IMO corrosion tests for inner bottoms revealed that the corrosion rate of the developed steel was less than 1.0 mm/y and no discontinuous surface between the base metal and weld metal was observed with the SAW joint specimens. The mechanical properties and the weldabilities of the developed steel are equivalent to or better than that of conventional steel. Thus, it was confirmed that the developed steel satisfies the performance standard for corrosion-resistant steels for inner bottom by the IMO. Moreover, the type approval for corrosion-resistant steel of COT bottom has been acquired from ClassNK.

It became clear that both the anodic reaction and the cathodic reaction of the developed steel are lower than the conventional steel and the corrosion resistance of the developed steel is excellent in the electrochemical evaluation in the simulated solution. It was assumed that there was no problem with galvanic corrosion in the junction of the developed steel and conventional steel because of the same corrosion potential.

The developed steel without coating was applied to the COT bottom plates of the crude oil tankers in order to verify the corrosion resistance and the practicability. At the dock inspections after 2.5 years and 5 years, the number of the pits and the maximum pit depth of the developed steel are sufficiently lower than those of the conventional steel. No pit needing repair was found on the developed steel on any of the ships. In addition, it was confirmed that there was no problem with galvanic corrosion on the weld zone. As is clear from the onboard evaluation, the corrosion inhibition effect of the developed steel is significant.

In this study, it has also been confirmed that the pitting corrosion growth stops at a dock with COTs cleaning by the follow-up of the unrepaired pits on the COT bottom. These results suggest a possibility of being repair-free throughout the working life of the ship to which the developed steel is applied. The application of the developed steel to COT bottom plate will contribute to an improvement in the safety record and a reduction in the life cycle cost of oil tankers.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Mitsui O.S.K.Lines, Ltd., IMABARI SHIPBUILDING CO., LTD. and TSUNEISHI SHIPBUILDING Co., Ltd. for the complete cooperation in the application of the developed steel to the vessels and the onboard investigations.

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