Development of Corrosion Resistant Steels for Cargo Oil Tank of Crude Oil Tankers "JFE-SIP[™]-OT1, -OT2"

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Abstract:

JFE Steel has developed corrosion resistant steels for bottom plate "JFE-SIPTM-OT1" and upper deck "JFE- SIP^{TM} -OT2" for the cargo oil tanks of crude oil tankers. Protective corrosion products formed by the action of alloying elements reduced the pitting corrosion in bottom plates and the general corrosion of upper decks of the cargo oil tanks. In the actual bottom plate of the cargo oil tanks, the developed steel showed excellent corrosion resistance. The developed corrosion resistant steel for bottom plates satisfies corrosion resistance criterion of IMO regulations and mechanical properties of AH/DH 32/36 grades and Z35. The developed corrosion resistant steel for upper decks satisfies corrosion resistance criterion of IMO regulations and mechanical properties of AH/DH/EH 32/36/40 grades and Z35. The application of those corrosion resistant steels is expected to contribute to the improvement of the safety of crude oil tankers at low life cycle costs by omitting painting in construction and maintenance.

1. Introduction

Crude oil spills due to disruptive accidents in crude oil tankers cause serious environmental pollution. One cause of disruptive accidents was first pointed out in the latter half of the 1990s in connection with corrosion of cargo oil tanks (hereinafter, COT), and in 1999, the Shipbuilding Research Association of Japan established Ship Research Panel No. 242 (SR242), consisting of steel makers, shipbuilders, ship owners and other maritime-related parties to conduct a large-scale research study on the corrosion environment and cor-

[†] Originally published in JFE GIHO No. 46 (Aug. 2020), p. 8–14



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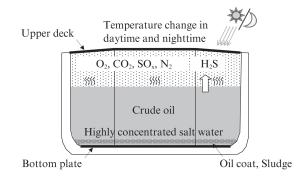


Fig. 1 Corrosion environment in COT of crude oil tanker

rosion mechanism in COT¹). Figure 1 shows a schematic illustration of the corrosion environment in a COT. Although corrosion is a problem in both the upper deck back (hereinafter, upper deck) and the bottom plate, the corrosion environments of the upper deck and bottom plate are extremely different, and different forms of corrosion also occur in these two environments. The COT upper deck is placed in a severe corrosion environment, where it is exposed to an atmosphere consisting of a mixture of hydrogen sulfide (H₂S) generated from the crude oil and combustion exhaust gas (O₂-CO₂-SO_x-N₂) which is introduced into the vapor space to prevent explosions, and corrosion occurs under cyclic wet-dry conditions accompanying day and nighttime temperature changes. General corrosion occurs under this environment. On the other hand, corrosion of the COT bottom plate proceeds by the following process: The surface of the COT bottom plate is covered by oil layer called an oil coat. Sludge, a mixed substance consisting of the solid fraction of the



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Staff Manager, Plate & Forging Sec., Products Design & Quality Control for Steel Products Dept. West Japan Works (Kurashiki), JFE Steel crude oil, iron rust and sulfur, also accumulates, and highly concentrated salt water which has separated from the crude oil stagnates above sludge and oil coat. If a break occurs in the oil coat, a macrocell (corrosion cell) is formed in this salt water environment, and pitting corrosion initiates and grows with the defective portion of the oil coat acting as a local anode and the sludge acting as the cathode. If the pH inside the pits decreases as corrosion proceeds, pitting corrosion will be accelerated, and in some cases the corrosion rate reaches 4 mm/y.

In response to the problem of corrosion in COT, in 2010, the International Maritime Organization (IMO) established performance criteria for COT from the viewpoints of improvement of ship safety and prevention of environmental pollution, and mandated corrosion protection measures. Painting and use of corrosion resistant steel are specified as corrosion protection measures².

Against the backdrop of these conditions, JFE Steel developed corrosion resistant steel for COT bottom plates: JFE-SIPTM-OT1^{3,4)} and corrosion resistant steel for upper decks: JFE-SIPTM-OT2 which remarkably reduce corrosion of COT bottom plates and upper decks, respectively, while also possessing excellent mechanical properties, utilizing corrosion resistance design and material quality design technologies accumulated over the course of many years. This article describes the corrosion resistant steels, together with the statuses of ship classification approval and the benefits of application.

2. Corrosion Resistant Steel for Bottom Plate: JFE-SIPTM-OT1

2.1 Corrosion Mechanism and Corrosion Resistance Design

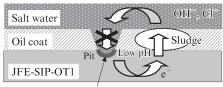
As described above, the COT bottom plate is covered with an oil layer called an oil coat, sludge accumulates in this area, and highly concentrated salt water stagnates above the sludge and oil coat. Here, macrocells form with defective portions of the oil coat as local anodes and the sludge as a cathode, and pitting corrosion initiates and grows. Thereafter, it is thought that the pH in the pits decreases as pitting corrosion proceeds, and this further accelerates pit growth. The corrosion test for COT bottom plates prescribed by the IMO regulations²⁾ simulates the acidic environment in pits after pit growth. Considering this unique step-bystep corrosion mechanism of the COT bottom plate, JFE Steel conducted not only the corrosion test in an acidic environment in the IMO regulations, but also an original JFE Steel laboratory corrosion test that simulates the macrocell, which is the initiation and growth step in pitting corrosion, in order to investigate the effect of added elements on corrosion resistance. A steel plate for COT bottom plates which satisfies both high corrosion resistance and sufficient mechanical properties was successfully developed by selecting effective elements for improving corrosion resistance based on these studies and further adjustment of the optimum steel composition.

Figure 2 shows the corrosion protection mechanism of JFE-SIP-OT1. In this steel, a protective corrosion product that contains a hardly-soluble film and fine rust particles is formed by the action of the abovementioned added elements. This protective corrosion product prevents formation of a macrocell between the defective portion of the oil coat and the sludge, thereby suppressing initiation and growth of pitting. Moreover, because the corrosion product is acid resistant, it also suppresses the acceleration of pitting growth associated with pH decrease.

2.2 Corrosion Resistance of JFE-SIPTM-OT1

2.2.1 Experimental method

Figure 3 shows a schematic diagram of the corrosion test method simulating a macrocell at the COT bottom plate (JFE Steel method). As the test material, test specimens with dimensions of 5 mm^t × 25 mm^W × 60 mm^L were taken from JFE-SIP-OT1 and the conventional steel (DH36 grade), and the specimen surface was then shot blasted and coated with an inorganic zinc primer (film thickness: 15 μ m). Portions other



Protective corrosion product



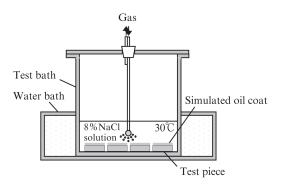


Fig. 3 Corrosion test method with simulated oil coat

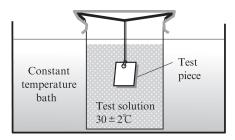


Fig. 4 Corrosion test method of immersion in hydrochloric acid (IMO regulations)

than the test surface were coated with epoxy having an adequate film thickness, and the test surface was coasted with a simulated oil coat, which was prepared using paraffin, iron rust and sulfur, referring to the sludge composition reported by SR242¹⁾. An area which is not coated with the simulated oil coat is also created on the test surface as the point of origin of pitting corrosion in order to simulate a defect of the oil coat. The specimen was immersed in an 8% NaCl solution with the evaluation surface upward and held at 30°C. A corrosive gas simulating the atmosphere of the vapor space at the back side of the upper deck was bubbled at a rate of 20 cc/min, and the depth of the pitting that had occurred on the surface of the specimen after 28 days was measured.

Figure 4 shows the acid resistance evaluation test method, which conforms to the corrosion test method for COT bottom plates in the IMO regulations ²⁾. (Hereinafter, this method is called the hydrochloric acid immersion corrosion test method in this paper.) As the test materials, specimens with dimensions of 5 mm^t × 25 mm^W × 60 mm^L were taken from JFE-SIP-OT1 and the conventional steel (DH36 grade) and polished to a #600 finish. The test solution used in this test was 10% NaCl adjusted to pH = 0.85 with hydrochloric acid. This test solution simulated the pH decrease in pits. The test temperature was 30°C, and the corrosion rate was measured after immersion for 72 h.

A corrosion test of welded joints was also conducted because corrosion resistance equal to that of the base metal is required in welded joints in the IMO regulations. The welded joints were prepared using JFE-SIP-OT1 and various welding consumables, and welded joint corrosion test specimens were taken. The cross sections of the specimens were observed after immersion for 168 h by the hydrochloric acid immersion corrosion test method, and the difference in level of the base metal and weld metal boundary region ("depth step" caused by corrosion of the weld metal) was measured.

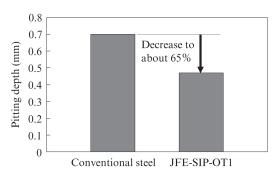


Fig. 5 Corrosion test results with simulated oil coat

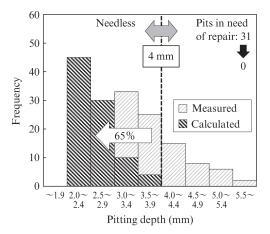


Fig. 6 Pitting depth distribution on actual tanker and distribution after JFE-SIPTM-OT1 applied

2.2.2 Experimental results

Figure 5 shows the results of the corrosion test using the simulated oil coat. The pitting depth of JFE-SIP-OT1 decreased to about 65% in comparison with the conventional steel. As shown in Fig. 6, if this pitting depth suppression effect is applied to the pitting depth distribution obtained in a survey of an actual tanker with a conventional steel primer specification (that is, if the respective pitting depths of all pits in need of repair measured in the actual tanker are multiplied by a uniform pitting depth reduction of 65%), the number of pits in need of repair is zero in the case of JFE-SIP-OT1. Since the pitting depth distribution is not the same in all actual ships, it cannot be said that the number of pits requiring repair will be zero in all ships. Nevertheless, it is clear that JFE-SIP-OT1 has a large pitting suppression effect.

Figure 7 shows the results of hydrochloric acid immersion corrosion test method in the IMO regulations. The corrosion rate of JFE-SIP-OT1 is approximately 0.39 mm/y, which is about 1/20 that of the conventional steel, and amply satisfies the IMO performance standard criterion (corrosion rate ≤ 1.0 mm/y)².

Photo 1 shows an example of the results of the cor-

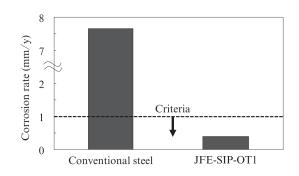


Fig. 7 Corrosion test results of immersion in hydrochloric acid resistance of JFE-SIP[™]-OT1

Welding method: SAW	Welding method: GMAW			
Welding consumables:	Welding consumables:			
US-36(×3)/PF-I55E/RR-2/RF-1*	DW-50JST*			
Base metal Weld metal	Base metal Weld metal			
<u>200 µm</u>	2 <u>00 μm</u>			
SAW: Submerged arc welding	*Kobe Steel, Ltd.			

SAW: Submerged arc welding GMAW: Gas metal arc welding

Photo 1 Cross section view of welded joints of JFE-SIP[™]-OT1 after corrosion test of immersion in hydrochloric acid

rosion test of welded joints. The photos show the results of cross-sectional observation of a SAW joint (welding consumable: Kobe Steel, Ltd. US-36 (×3)/PF-I55E/RR-2/RF-1) and a GMAW joint (welding consumable: Kobe Steel, Ltd. DW-50JST, welding consumable developed for JFE-SIP-OT1 and -OT2 D class steels), which were prepared using JFE-SIP-OT1. In the joints using JFE-SIP-OT1, no depth step occurred in the boundary region between the base metal and the weld metal, and the joints amply satisfy the IMO performance standard criterion for welded joints (the depths of both steps at the boundary region between the base metal and weld metal are less than or equal to $30 \,\mu$ m, or are less than or equal to $50 \,\mu$ m and the angles are less than or equal to 15°).

2.3 Mechanical Properties of JFE-SIPTM-OT1

Table 1 shows the mechanical properties of the base metal of JFE-SIP-OT1 (thickness: 40 mm), and **Table 2** shows an example of the mechanical properties of a welded joint prepared using JFE-SIP-OT1. In order to evaluate the mechanical properties of welded joints when using large heat input welding, the joint was prepared by FCB (flux copper backing) welding with a heat input of approximately 26 kJ/mm. Both the base metal and welded joints of this steel amply satisfy the properties required in DH36 grade steel for shipbuild-

Table 1	Mechanical properties of base metal of JFE-SIP [™] -
	OT1

	Tensile property (Direction : T)			Charpy impact property (Direction : L)	Through thickness tensile property
	YP (MPa)	TS (MPa)	El (%)	vE-20 (J)	RA (%)
JFE-SIP-OT1 (40 mm ^t)	431	548	24	271	73 (Each 70,74,76)
Spec. (DH36-Z35)	≥355	490 - 620	≥20	≥34	≥35 (Each≥25)

Table 2 Mechanical properties of welded joint of JFE-SIPTM-OT1

	Welding method	Ten prop		Charpy impact property		
		TS (MPa)		Face, vE ₀ (J)		
		Start	End	WM	FL	FL+2 mm
JFE-SIP-OT1 (40 mm ^t)	FCB, Heat input : 26 kJ/mm	548	557	116	107	187
Spec. (DH36)		≧490		≥34		

ing. As shown in Table 1, this steel displayed a high reduction of area (RA) value in the through thickness tensile test, and thus has high lamellar tearing resistance.

2.4 Example of Application of JFE-SIPTM-OT1 to Ships

In order to verify the corrosion resistance of JFE-SIP-OT1 in actual ship environments, application to crude oil tankers was started in 2007, and the conditions of the bottom plates was investigated each time the vessels were in dock at intervals of 2.5 years. Figure 8 shows the results of the investigation of the number of pits for the actual ships. Here, the pits of three oil tankers (AFRA (Average Freight Rate Assessment) Max: 1 tanker, and VLCC (Very Large Crude Oil Carrier): 2 tankers) in which JFE-SIP-OT1 was applied were measured in the inspection docks of the 5th year and 10th year. The number of pits with depths of 4 mm or more in all tank bottom plates was totaled, and the number of pits per one tank was obtained. For comparison, a similar investigation was carried out with 8 oil tankers in which the conventional steel was applied. All object ships of this investigation were constructed before corrosion protection measures were made mandatory in the IMO, and were in service with the bottom plates in an unpainted condition. Since the growth of pitting corrosion is thought to have been arrested by tank cleaning when the ships were in dock

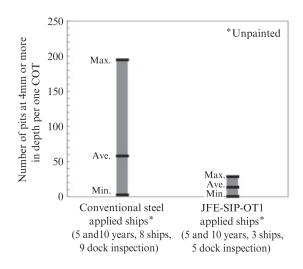


Fig. 8 Number of pits on bottom plate of actual COT

every 2.5 years ¹⁾, a comparative investigation of the number of pits occurring in the tank bottom plates of actual ships based on the investigation data when the ships are in dock is considered possible. Regarding the number of pits with depths of 4 mm or more, i.e., pits in need of repair, in case of the conventional steel, the maximum number was 195, and the average was 58. These numbers decreased dramatically when JFE-SIP-OT1 was applied, as the maximum number was 29 and the average was 14. These results confirmed that JFE-SIP-OT1 shows excellent pitting corrosion resistance in actual ship environments.

3. Corrosion Resistant Steel for Upper Deck: JFE-SIPTM-OT2

3.1 Corrosion Mechanism and Corrosion Resistance Design

As clarified by the survey research by SR242¹⁾, the corrosion that occurs in COT upper plates is general corrosion, which is caused by exposure to a mixed atmosphere consisting of hydrogen sulfide (H₂S) generated from the crude oil and the combustion off-gas (O₂-CO₂-SO_x-N₂) used for explosion-proofing, in combination with a repeated wet-dry cycle of moisture condensation and drying due to night-and-day temperature changes. Because the upper deck is placed in a completely different corrosion environment from that of the COT bottom plates described above, a new corrosion resistance design was necessary in the development of a corrosion resistant steel for the COT upper deck. JFE Steel conducted the simulated corrosion test²⁾ in the IMO regulations, which reproduces the characteristic corrosion mechanism of the upper deck, and selected effective added elements for enhancing the corrosion resistance of the COT upper deck. By

designing and adjusting the optimum composition, focusing on elements which have the effect of preventing corrosion factors (HS⁻, $SO_4^{2^-}$, etc.) in condensed moisture from approaching the base steel, JFE Steel succeeded in satisfying both high corrosion resistance and the mechanical properties necessary in steel for use in the COT upper deck.

Figure 9 shows the corrosion protection mechanism of JFE-SIP-OT2. Hardly-soluble compounds consisting mainly of sulfides are formed on the steel surface by the action of the added alloying elements. Because the protective corrosion product including these hardlysoluble compounds prevents corrosion factors from approaching the base steel, the Fe dissolution reaction is reduced and high corrosion resistance is realized.

3.2 Corrosion Resistance of JFE-SIPTM-OT2

3.2.1 Experimental method

Figure 10 shows the schematic diagram of the simulated corrosion test ²⁾ apparatus in the IMO regulations. The environment of the upper deck is simulated by blowing a gas (containing O_2 , CO_2 , SO_2 and H_2S), which simulate the corrosive gas in the vapor space on the underside of the upper deck, into a closed container partially filled with distilled water. In order to simulate the back side of the upper deck, the test piece is attached to the underside of the test bath ceiling, and the condensation and wet-dry cycle are reproduced by applying a temperature cycle of 25°C-50°C. The test of JFE-SIP-OT2 was conducted for 21-, 49-, 77- and

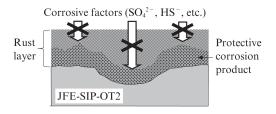


Fig. 9 Protection mechanism of JFE-SIP[™]-OT2

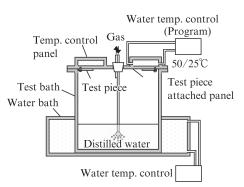


Fig. 10 Simulated corrosion test apparatus for upper deck of COT (IMO regulations)

98-day periods and the test of conventional steel was conducted for 98-day period using JFE-SIP-OT2 and the conventional steel as the test materials. After the test, corrosion loss after 25 years was estimated by extrapolation by applying the least-squares method to the corrosion test data for JFE-SIP-OT2 in accordance with the IMO rules ²). Under the IMO rules, a test is judged to be appropriate if the corrosion rate of the conventional steel after the 98 day test is within the range of 0.2 to 0.4 mm/y.

As with the bottom plate, the corrosion resistance of welded joints was also evaluated, as the IMO regulations require that welded joints possess the same corrosion resistance as the base metal. Welded joints were prepared using JFE-SIP-OT2 and various welding consumables, and welded joint corrosion test specimens were taken. The cross-sections of the welded joint test specimens were observed after the 98 day period by the simulated corrosion test method for the upper deck of COT, and the depth step at the boundary between the base metal and weld metal was measured.

3.2.2 Test results

Figure 11 shows the results of the simulated corrosion test of the upper deck. Figure 12 shows the result of the calculation of corrosion loss after 25 years by extrapolation by the least-squares method as provided in the IMO rules ²⁾. In Fig. 12, the line indicated as "Conventional steel" shows the data for cumulative 98% plate thickness loss ⁶⁾ published by Nippon Kaiji Kyokai (ClassNK). The estimated corrosion loss of JFE-SIP-OT2 after 25 years is 1.39 mm, which sufficiently satisfies the criterion of the IMO performance standard ($\leq 2.0 \text{ mm/25 y}$)²⁾.

Photo 2 shows examples of the results of the joint corrosion test. The photos show the results of cross-sectional observation of a SAW joint (welding consumable: Kobe Steel, Ltd. US-36 (×3)/PF-I55E/RR-2/RF-1) and a GMAW joint (welding consumable: Kobe Steel, Ltd. DW-50JSTB, welding consumable developed for JFE-SIP-OT1 and -OT2 E class steels), which

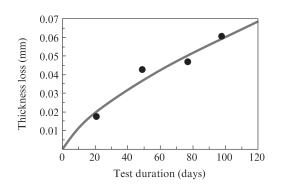


Fig. 11 Simulated corrosion test result of JFE-SIP[™]-OT2

were prepared using JFE-SIP-OT2. No depth step can be observed in the boundary region between the base metal and the weld metal, confirming that the corrosion resistance of the joints is excellent.

3.3 Mechanical Properties of JFE-SIPTM-OT2

Table 3 shows the mechanical properties of the base metal (plate thickness: 40 mm) of JFE-SIP-OT2. **Table 4** shows an example of the mechanical properties of a large heat input welded joint (FCB welding, heat input: approx. 26 kJ/mm) in which this steel plate was used. Both the base metal and the welded joint of JFE-SIP-OT2 amply satisfy the mechanical properties required in EH40 grade steel for ship structural use. As in the case of the bottom plate, this steel also showed a high value for reduction of area (RA) in the through thickness tensile test, demonstrating that it also possesses excellent lamellar tearing resistance.

4. Statuses of Classification Approval

In addition to classification approval by Nippon Kaiji Kyokai (ClassNK), both corrosion resistant steels have successively received classification approval from foreign ship classification societies including the American Bureau of Shipping, DNV GL, Bureau Veritas and

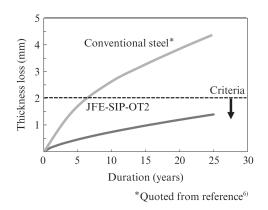


Fig. 12 Estimation of corrosion loss of JFE-SIP[™]-OT2 after 25 years (Extrapolated from the data in Fig. 11)

Welding me	thod: SAW	Welding method: GMAW		
Welding co	nsumables:	Welding consumables:		
US-36(×3)/PF-I5	5E/RR-2/RF-1*	DW-50JSTB*		
Base metal	Weld metal	Base metal	Weld metal	
SAW: Submerge	ed arc welding	*	Kobe Steel, Lto	

Photo 2 Cross section view of welded joints of JFE-SIPTM-OT1 after simulated corrosion test

GMAW: Gas metal arc welding

	Tensile property (Direction : T)			Charpy impact property (Direction : L)	Through thickness tensile property
	YP (MPa)	TS (MPa)	El (%)	vE -40 (J)	RA (%)
JFE-SIP-OT2 (40 mm ^t)	460	544	26	353	76 (Each 80,72,77)
Spec. (EH40-Z35)	≥390	510 - 650	≥19	≥39	$ \ge 35 \\ (Each \ge 25) $

Table 3 Mechanical properties of base metal of JFE-SIPTM- OT2

Table 4 Mechanical properties of welded joint of JFE-SIPTM-OT2

	Welding	Tensile property		Charpy impact property		
	method	TS (MPa)		F	Face, $vE_{-20}(J)$	
		Start	End	WM	FL	FL+2 mm
JFE-SIP-OT2 (40 mm ^t)	FCB, Heat input : 26 kJ/mm	548	556	111	99	117
Spec. (EH40)		≥510		≥39		

others. The corrosion resistant steel for bottom plates JFE-SIP-OT1 has received Z35 (lamellar tearing resistance) approval for a maximum plate thickness of 50 mm under the ship classification standards "AH32-RCB," "DH32-RCB," "AH36-RCB" and "DH36-RCB," and the corrosion resistant steel for upper decks JFE-SIP-OT2 has received Z35 approval for a maximum thickness of 40 mm under the standards "AH32-RCU," "DH32-RCU," "EH32-RCU," "AH36-RCU," "DH36-RCU," "DH36-RCU," "EH36-RCU," "AH40-RCU," "DH40-RCU" and EH40-RCU." A large number of approvals for applications of welding consumables have also been obtained for both corrosion resistant steels.

5. Benefits of Application of JFE-SIPTM-OT1 and -OT2

Pitting corrosion can be greatly reduced by applying JFE-SIP-OT1 to COT bottom plates, and general corrosion can be greatly reduced by applying JFE-SIP-OT2 to the COT upper deck. Because both corrosion resistant steels conform to IMO standards, COT bottom plates and upper deck plates can be used without painting, thereby reducing the cost and time associated with painting during construction of crude oil tankers. After tankers are put into service, these steels can also contribute to shortening the time spent in dock by simplifying repair work. Since these steels provide both corrosion resistance and high mechanical properties, and particularly lamellar tearing resistance, application

to welds which are subject to tensile stress in the plate thickness direction in COT structural members is possible ⁷). In addition, a reduction in volatile organic components (VOC) generated during painting can also be expected because these steels are used without painting.

In the bottom plate corrosion environment, the corrosion resistant steel material itself provides corrosion resistance. Although abnormal corrosion can occur at painting defects when painted conventional steel plates are used, this is not an issue with JFE-SIP-OT1, which does not required painting, and as a result, stable corrosion resistance performance can be expected.

Among the advantages of using JFE-SIP-OT2 in upper deck plates, human safety is improved because painting work in high places is not necessary during ship repairs, and it is not necessary to use care to avoid burn-out of the paint at the back side of the upper deck when performing work with fire on the upper deck. On the other hand, it is also possible to use painting in combination with the corrosion resistant steels in corrosion protection design, and in this case, a further enhancement of corrosion resistance is considered possible, even with simple painting.

As outlined above, in responding to the recent heightened needs for labor-saving, JFE-SIP-OT1 and -OT2 can contribute to improving the safety of crude oil tankers at a low life cycle cost, and also make an important contribution to protection of the global environment.

6. Conclusion

Corrosion resistant steel for the bottom plates of crude oil tanker cargo oil tanks (COT) "JFE-SIP-OT1" and corrosion resistant steel for the COT upper deck "JFE-SIP-OT2" were developed. The main features of the developed steels may be summarized as follows.

- (1) The developed steels suppress pitting corrosion of COT bottom plates and general corrosion of the COT upper deck by formation of protective corrosion products by the action of alloying elements.
- (2) In COT bottom plates of actual ships, the developed steel displayed excellent pitting resistance performance, and the number of pits with depths that required repair decreased remarkably.
- (3) The developed steels conform to IMO standards; the corrosion resistant steel for bottom plates satisfies the corrosion resistance requirement in the IMO regulations and the mechanical properties requirements of AH/DH 32/36-Z35, while the corrosion resistant steel for upper deck plates satisfies the corrosion resistance requirement in the IMO regulation and the mechanical properties require-

ments of AH/DH/EH 32/36/40-Z35.

- (4) The developed steels have received approval from a number of ship classification societies, and have also received a large number of approvals for applications of welding consumables.
- (5) Various benefits can be expected by applying the developed steels, including enhanced ship safety, reduction of the cost and time associated with painting and reduction of VOC emissions.

Acknowledgement

The COT survey of actual ships was conducted with the cooperation of Mitsui O.S.K. Lines. The authors wish to express their deep appreciation to all concerned.

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