Development of Corrosion-resistant Steels and their Application to Crude Oil Tankers

Taizo Yoshida <Taizo_Yoshida@jp.nykline.com>
NYK Line, Tokyo, Japan
Jun Kato <jun_kato@jp.nykline.com>
NYK Line, Tokyo, Japan
Minoru Ito <ito.4et.minoru@jp.nssmc.com>
Nippon Steel & Sumitomo Metal Corporation, Futtsu, Japan
Seiji Nishimura <nishimura.9fc.seiji@jp.nssmc.com>
Nippon Steel & Sumitomo Metal Corporation, Tokyo, Japan
Kazuyuki Kashima <kashima.cx7.kazuyuki@jp.nssmc.com>
Nippon Steel & Sumitomo Metal Corporation, Amagasaki, Japan

Abstract

To cope with extensive corrosion occurring in ship structures resulting in wastage in thickness, Nippon Steel & Sumitomo Metal Corporation (NSSMC) has developed corrosion-resistant steels (CRSs) for application to bottom plates (NSGP™-1) in association with NYK Line, and to tank head structures (NSGP™-2), and is also developing CRS to water ballast tanks.
The IMO has developed requirements aimed at inhibiting corrosion in cargo oil tanks by way of performance standards. These performance standards are now being made mandatory by an amendment to SOLAS: *regulation II-1/3-11, Corrosion Protection of Cargo Oil Tanks of Crude Oil Tankers, adopted by Resolution MSC. 291(87).*
Eight years have passed since the first VLCC with NSGP™-1 applied to her cargo tank bottom plate was delivered. This paper firstly summarizes the follow up inspection results for several vessels fitted with NSGP™-1. Secondly, a new type of CRS, which was specially developed for cargo tank head structure, named NSGP™-2, is introduced including its corrosive environment, mechanism of general corrosion in the ullage space, laboratory simulation tests and the result of onboard trials after 5 years exposure. Finally, a brief report is given on a new series of CRS under development that is designed for water ballast tank structure.
The application of such CRSs has been very effective in minimizing repair work and the risk of failure in structural integrity. Furthermore, CRS does not require application of protective coating, which also benefits not only ship builders but also the global environment by reducing the use of volatile organic compounds.

1 Introduction

In a COT, the following are present: Inert gas (preventing explosions), H_2S-originated crude oil, sludge, and drain water containing concentrated sodium chloride below the crude oil, as shown in Figure 1[1] [3] [5] [6]. There are two types of corrosion involved in this case: The pitting corrosion of inner bottom plates and the general corrosion of upper deck plates. To resist this corrosion, CRS may be used; NSGP™-1 for the former and NSGP™-2 for the latter. To aid in protecting steel from such corrosion, the statutory IMO requirements came into effect in 2013. These requirements allow for protection through the use of CRS as

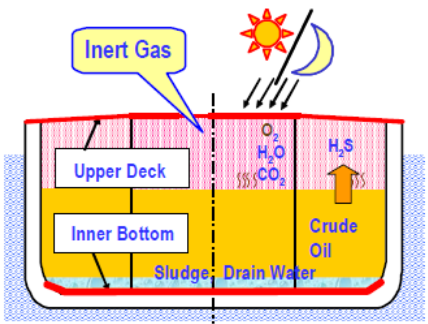


Fig. 1: Corrosion environment of COT

well as suitable coatings for COT. CRSs have been developed for upper deck plates and inner bottom plates by conducting a study of the effects of alloying elements on the corrosion behavior of steel. Such CRSs have already been applied to several crude oil tankers. Further, they have shown favorable corrosion resistance [4][7][8][16].
In addition, steel construction members in water ballast tanks (WBT) must undergo use in a severely corrosive environment, due to seawater. Therefore, the performance standard for protective coating (PSPC) adopted by the IMO was made mandatory from 2008. However, this painting standard is for 15 years of durability, while 25-year durability equivalent to the life of the ship is becoming increasingly expected. We are also developing CRS for WBT aiming at 25 years with/without protective coating. One such type of CRS has been applied to certain parts of the deck longitudinals of a WBT.
In this paper, the onboard investigation results of the ships using these types of CRS are introduced.

2. CRS FOR BOTTOM PLATES (NSGP™-1) AND ONBOARD EVALUATION RESULTS

2.1 Evaluation Results of a VLCC that Partially Used NSGP™-1

In bottom plate of COT, there are some hundreds pits whose depth are up to 10mm in 2.5 years [3]. We developed CRS for COT bottom plates, known as NSGP™-1 (Nippon Steel & Sumitomo Metal's Green Protect-1), through investigation into the effect of alloy elements on corrosion resistance. The results of a corrosion test, which was adopted for subsequent SOLAS II-1 Cargo Oil Tank Corrosion Protection of NSGP™-1 and conventional steel are shown in Fig. 2.The corrosion rate for NSGP™-1 is as low as approximately 0.5 mm/y, i.e., far superior than that of conventional steel. Moreover, the composition of NSGP™-1 fully satisfies IACS standards. NSGP™-1 has also obtained type approval for corrosion resistance steel from Class NK.

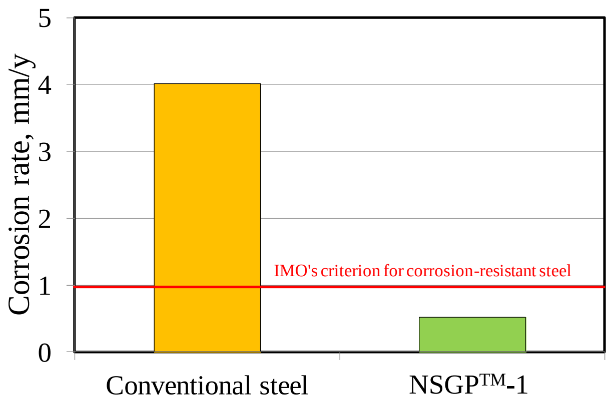


Fig. 2: Corrosion test results of the developed steel and conventional steel as per IMO Resolution MSC.289(87)

NSGP™-1 was first applied to VLCCs on a trial basis from 2004 for all bottom plates of COT as AH32 grade with conventional weld material that meets the criterion of SOLAS. The NSGP™-1 steel caused no problems whatsoever in terms of application, and the ship's construction was as smooth as that of any ordinary vessel. Notably in the cases of six tanks in the No. 3 and No. 4 COTs at the center of the hull, the steel was used without a protective coating.
Figure 3 shows the results of the observed pit count at over 4 mm in depth upon a 7.5-year inspection, in comparison with the conventional steel of other VLCCs upon 2.5-year or five-year inspections. In case of the VLCC applying NSGP™-1, there were only tens of pits per tank, at most. Based on the authors' investigation of ordinary VLCCs, the number of pits at over 4 mm in depth reached several hundred as shown in the figure —the number being over 1,000 in some cases. The above inspection results prove the effectiveness of NSGP™-1 against pitting corrosion in bottom plates.

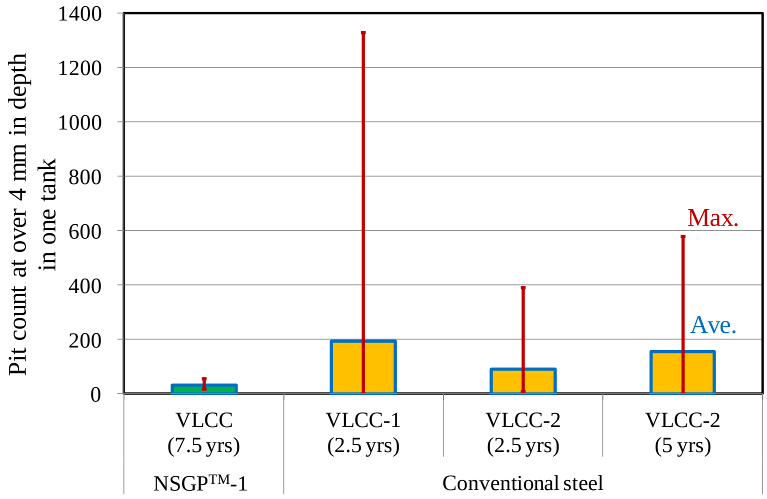


Fig. 3: Observed pit count at over 4 mm in depth for CRS VLCC and conventional VLCCs

2.2 Termination of Pit Growth

It is considered that pit growth stops after docking [2][3][4][6]. However, a direct observation of pit termination has not been obtained. We measured pit depth at the second docking (after 5.0 years) and at the third docking (after 7.5 years) in the same positions of the No. 4 starboard tank. Figure 4 shows the relationship of pit depth at the second and third dockings. Those plots are situated around the line showing that the pits terminate upon dock inspection. It is clearly revealed that pit growth has been halted in these studies.

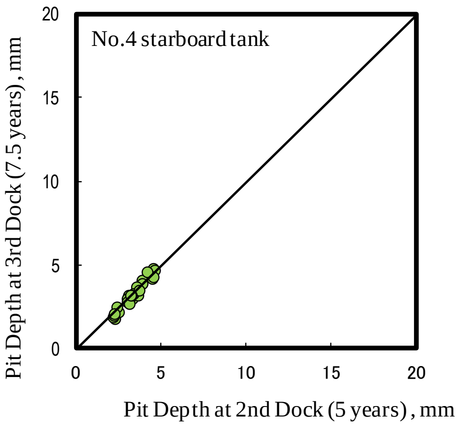


Fig.4: Relationship of pit depth at the second and third dockings

2.3 Evaluation Results for VLCCs Using NSGP^{TM}-1 for All COT Bottom Plates

As mentioned above, the favorable corrosion resistance of NSGP^{TM}-1 was confirmed through onboard investigation. Subsequently, NSGP^{TM}-1 has been applied to several VLCCs for all COT bottom plates without protective paint coating since 2008. As of now, the corrosion investigations of the NSGP^{TM}-1 for all COT bottom plates for the four VLCCs (VLCC-A, VLCC-B, VLCC-C, and VLCC-D) upon their first dock inspections were examined in detail after 2.4 to 3.1 years from their start of service. The routes of these vessels are different, as shown in Table 1.

Table 1: List of VLCCs provided with CRS

	Service period	Main route	Application of CRS
VLCC-A	2.4 years	Middle East / East Asia / South America / North America	All COT bottom plates
VLCC-B	3.1 years	Middle East / East Asia / Southeast Asia / North America	
VLCC-C	2.8 years	Middle East / East Asia	
VLCC-D	2.9 years	Middle East / Southeast Asia	

Figure 5 shows the results in comparison with the conventional steel of other VLCCs. For the VLCCs using NSGP^{TM}-1 for the bottom plates of COT, the average number of pits seen at more than 4 mm in depth was only a few tens per tank, at the most. For conventional steel, the number of pits reached about 100 to 200. These inspection results made it adequately clear that the pit frequency of VLCCs using NSGP^{TM}-1 was much lower than that of VLCCs using conventional steel. The application of NSGP^{TM}-1 to COT bottom plates is very effective in minimizing repair work.

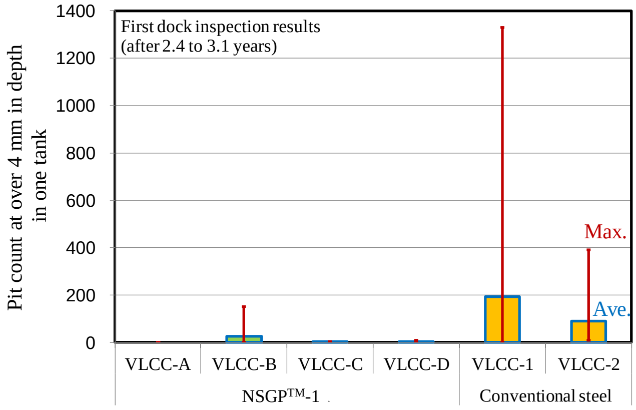


Fig.5: Observed pit count at over 4 mm in depth for the four VLCCs that used NSGP^{TM}-1 and for conventional VLCCs

3. CRS FOR TANK HEAD STRUCTURES (NSGP^{TM}-2) AND ONBOARD EVALUATION RESULTS

NSSMC developed another type of CRS for tank head structures, NSGP^{TM}-2 [16].

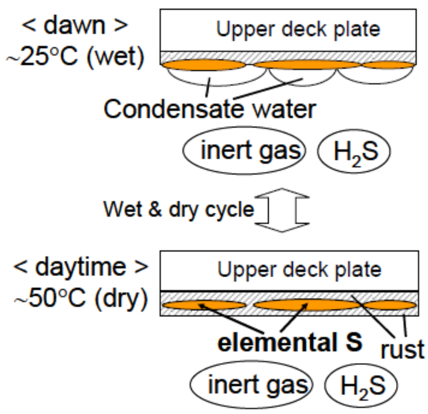


Fig.6: Corrosion mechanism at the upper deck of COT

The vapor space of crude oil tanks is composed of H_2O, inert gas containing O_2 (<5 vol. %), CO_2, SO_2, and H_2S originating from crude oil. According to the field examination of several VLCCs by "The Shipbuilding Research Association of Japan Panel #242" (SR242 committee)", H_2S gas was detected in high concentration in the vapor space. The maximum concentration of H_2S was over 0.2 vol. % at a full load condition. This coexistence of O_2 and H_2S is a very rare case from the standpoint of corrosion science because of the reducing property of H_2S. Thus, the corrosion environment in a cargo oil tank is quite complicated and unique. Figure 6 shows the corrosion mechanism in the upper deck plate. The underside of the upper deck is exposed to cyclical wet and dry conditions through the temperature change over the course of the day and night, and then the pH of the condensate water becomes lower (approx. pH 2−4) with the existence of CO_2 and SO_2 in the inert gas. Moreover, elemental sulfur is generated by the oxidation of H_2S with oxygen. The corrosion product on the upper deck plate mainly consists of α-FeOOH and elemental sulfur, and features a layered structure of rust and elemental sulfur. According to the field examination by the SR242 committee, a maximum of 60 wt. % of elemental sulfur was detected in corrosion products at the upper deck. This indicates that the amount of corrosion products does not correspond to the corrosion loss at the upper deck. It seems that the existence of H_2S in the vapor space does not substantially affect corrosion, but mainly generates elemental sulfur and increases the volume of corrosion products. This means that the general corrosion of the upper deck plate was progressed by the condensate water with a low pH [11][12].

From the corrosion mechanisms mentioned above, simulated corrosion test methods in a laboratory were studied to reproduce the corrosion that was observed in the actual cargo oil tanks of oil tankers. The upper deck plates of cargo oil tanks are exposed to a corrosion environment that contains O_2, CO_2, SO_2 in inert gas, H_2S from crude oil, and condensation due to temperature change. The simulated test method is shown in Figure 7. The test apparatus consists of two chambers－the outer chamber corresponds to the atmosphere and the inner chamber corresponds to the cargo oil tank. Specimens were set on the upper surface of the inner chamber to simulate upper deck plates. The temperature of the outer chamber varied between 50 ℃ (20 hours) and 25 ℃ (four hours), which is a typical temperature change on an upper deck. The surface of the specimens was condensed through this temperature change. Gas A (13%CO_2-5%O_2-0.01%SO_2-bal.N_2, simulated inert gas) and gas B (gas A + 0.2%H_2S) were blown alternatively every 14 days into the inner chamber to simulate conditions at ballast and full load. The pH of the condensate water of this simulated test was about 2.7, which is similar to the pH measured in actual cargo oil tanks [12]. Figure 8 shows the cross-section of corrosion products after the simulated test for 28 days. The corrosion products consisted of rust layers, mixtures of rust and sulfur, and layered elemental sulfur. The structure of corrosion products after this test was quite similar to that of a cargo oil tank. Futher, the composition of the corrosion products was similar to that of a cargo oil tank as shown in Table 2.

These results suggest that the structure and composition of the corrosion products were reproduced using the laboratory corrosion test. In addition, this test method became the basis of the corrosion test of COT upper decks for SOLAS II-1 Cargo Oil Tank Corrosion Protection.

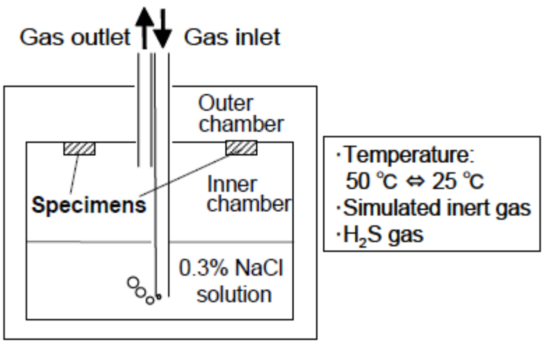


Fig. 7 Simulated corrosion test apparatus for the upper deck of a COT

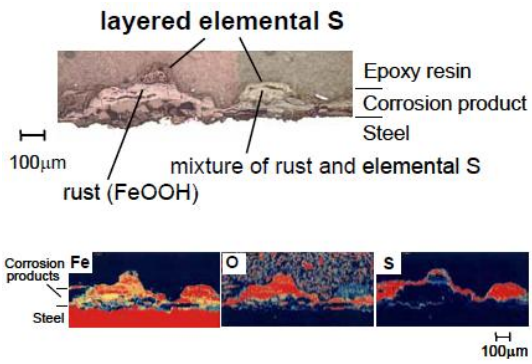


Fig. 8 Cross sectional morphology and distribution of elements by the Electron Probe Microanalysis in the corrosion products of specimen after a simulated corrosion test for the upper deck

Table 2: Composition of the corrosion products formed on the simulated test specimen for the upper deck analyzed by the X-ray diffraction method (mass %)

	α-FeOOH	β-FeOOH	γ-FeOOH	Fe_3O_4	Elemental S	Others
Cargo oil tank	37	0	8	0	12	43
Simulated test	30	0	3	8	21	38

The results of the SOLAS corrosion test for COT upper decks are shown in Fig. 9. The increments of the corrosion of NSGP^{TM}-2 decrease with the progress of time, and the estimated corrosion loss for 25 years is less than 2 mm, which is the criterion for CRS.
Moreover, the tensile and impact properties of NSGP^{TM}-2 were equivalent to conventional steel and satisfied the specification for DH36-grade classes. Further, it also exhibited good weldability. Regarding these results, and in appreciation of these favorable properties, NSGP^{TM}-2 was certified for LR, NK, and ABS classification.

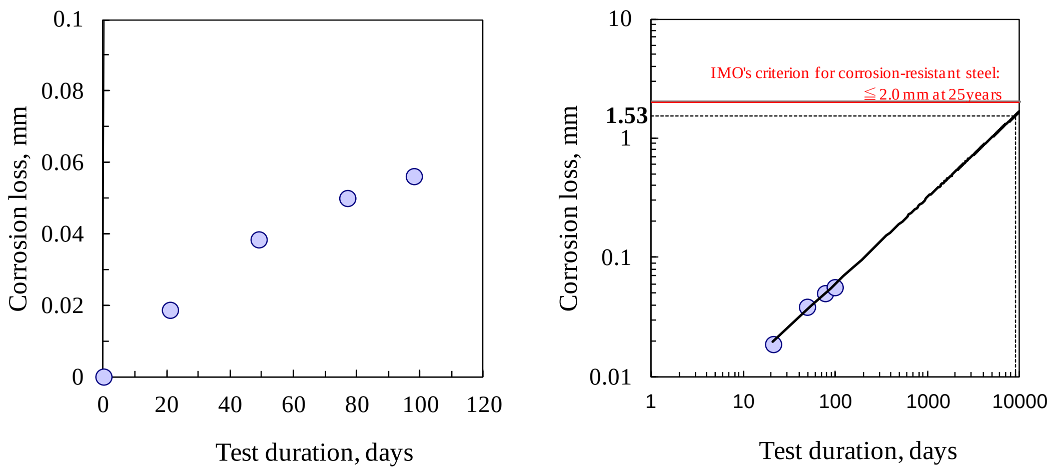


Fig. 9: Corrosion test results of NSGP^{TM}-2

NSGP^{TM}-2 was also applied to an Aframax tanker for the upper deck plate of COT without protective coating. Figure 10 shows the results of an exposure test after five years. It was found that the corrosion loss of the developed steel at the upper deck was under 0.4 mm. The corrosion rate of NSGP^{TM}-2 was 0.07 mm/y at five years, and it is thought that the corrosion loss of the developed steel will not exceed 2 mm after 25 years.

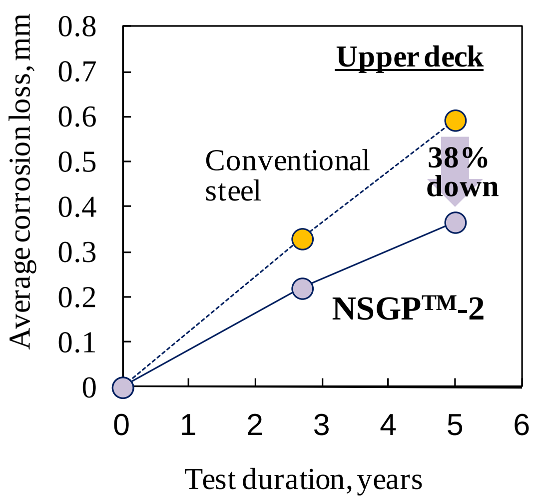


Fig. 10: Results of the exposure test on the upper deck of an Aframax tanker

4. DEVELOPING CRS FOR WATER BALLAST TANKS

The IMO has adopted the Performance Standard for Protective Coating (PSPC) for dedicated ballast tank in all types of ships, and it is now necessary for newbuild vessels to satisfy a painting specification and application in accordance with the PSPC scheme. However, a target of this painting standard is of 15-year durability, and the 25-year durability equivalent to the life of the ship is becoming increasingly expected. Therefore, we are also developing CRS for water ballast tanks.

CRS was applied to certain parts of the deck longitudinals of water ballast tanks with primer as shown in Figure 11. As shown in Table 3, CRS did not exhibit rust at even 5.5 years, whereas conventional steel rusted entirely after three years. According to a cyclic corrosion test, corrosion resistance was approximately 10 times that of the conventional steel during the period when CRS begins to rust. Therefore, it is expected that CRS performs with such durability for 30 years.

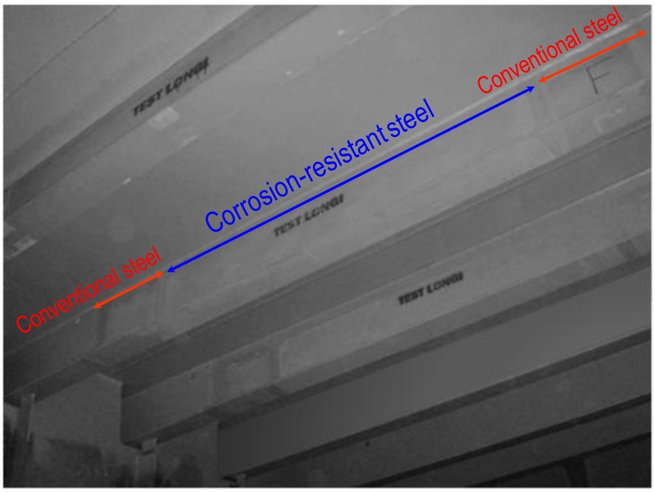
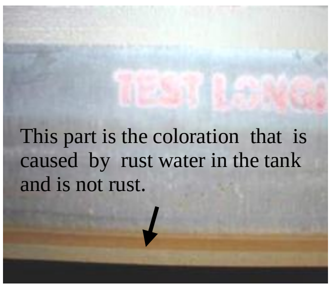


Fig. 11: Appearance of a test longitudinal for a water ballast tank

Table 3: Appearance of the test longitudinal of conventional steel and the developed steel

	3 years	5.5 years
Conventional steel		
Developed steel		

5. Conclusions

The developed CRS for COT bottoms , NSGP™-1, was applied to several VLCCs for all COT bottom plates without protective paint coating. The pit count of these VLCCs was much lower than that of VLCCs using conventional steel.
Further, another type of developed CRS for COT, NSGP™-2, was applied to an Aframax tanker for COT upper deck plates without protective coating. The corrosion rate of NSGP™-2 was less than 0.08 mm/y, and it is thought that the corrosion loss of CRS will not exceed 2 mm after 25 years.
In addition, we are developing other types of CRS for water ballast tanks. CRS applied to the deck longitudinal of water ballast tanks has shown resistance to rust even after 5.5 years. According to this result and a cyclic corrosion test, it is expected that CRS performs with such durability for 30 years.
From the above, the application of CRS is very effective at minimizing repair work due to corrosion. In addition, CRS does not require protective paint coating, which also benefits the global environment by reducing the use of volatile organic compounds.

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