Corrosion-resistant Steels, NSGP™-1, -2 for Crude Oil Tankers and their Performance

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Abstract

Nippon Steel & Sumitomo Metal Corporation (NSSMC) has firstly developed corrosion resistant steels (CRSs) for application to bottom plates (NSGP™-1: Nippon Steel & Sumitomo Metal's Green Protect-1) in association with NYK Line, and to tank head structures (NSGP™-2). And twelve years have passed since the first VLCC with NSGP-1 applied to her cargo tank bottom plate was delivered. These CRSs have already been certified by major ship's classifications. Now they have been applied to over ten tankers.

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).

This paper firstly summarizes the follow up inspection results for several vessels fitted with NSGP-1. Pit count is much less than conventional one by applying NSGP-1 to bottom plate, furthermore we found it becomes even less by combining structural countermeasure.

Secondly, this paper shows the good result of onboard trials applying NSGP-2 to cargo tank head structure after 7.5 years exposure.

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 crude oil tank (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 Fig. 1[1] [2] [3] [4]. 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, we developed CRS; NSGP-1 for the inner bottom plates and NSGP-2 for the upper deck plates.

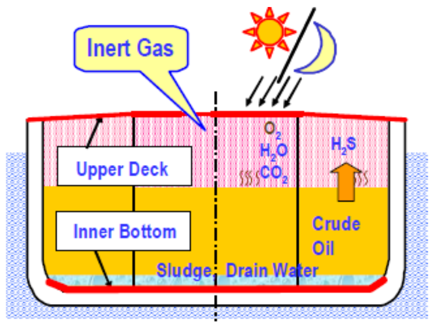

Fig. 1: Corrosion environment of COT

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 well as suitable coatings for COT. Our developed CRSs have been developed 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 [5][6][7][8].
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 IMO corrosion test for NSGP-1

In bottom plate of COT, there are some hundreds pits whose depth are up to 10mm in 2.5 years [2]. Thus, we developed CRS for COT bottom plates, known as NSGP-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 [2]. NSGP-1 has also obtained type approval for corrosion resistance steel from Class NK and ABS.

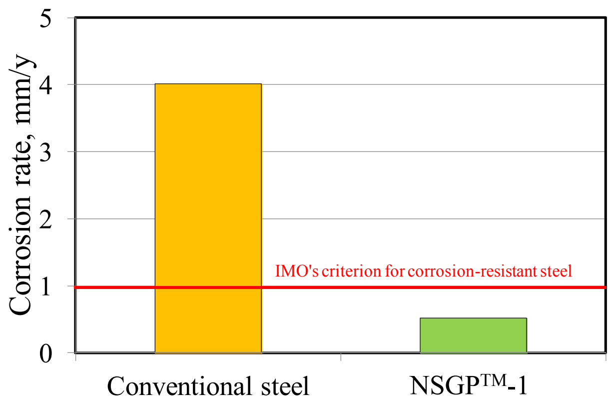

Fig. 2: Corrosion test results of the developed steel and conventional steel as per IMO Resolution MSC.289(87)

2.2 Onboard Evaluation Results for VLCCs Using NSGP-1 for COT Bottom Plates

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.
Subsequently, NSGP-1 has been applied to several VLCCs for COT bottom plates without protective paint coating since 2004. As of now, the corrosion investigations of the NSGP-1 for all COT bottom plates for the seven VLCCs (VLCC-A, VLCC-B, VLCC-C, VLCC-D, VLCC-E, VLCC-F, and VLCC-G) upon their first dock inspections were examined in detail after 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	12.2 years	Middle East / Japan	All COTs bottom Plates, 6 COTs unpainted
VLCC-B	8.0 years	Middle East / East Asia / South America / North America	All COTs bottom plates, all COTs unpainted
VLCC-C	7.6 years	Middle East / East Asia / Southeast Asia / North America	
VLCC-D	6.8 years	Middle East / East Asia	
VLCC-E	6.9 years	Middle East / Southeast Asia	
VLCC-F	5.3 years	Middle East / East Asia / Southeast Asia	
VLCC-G	5.0 years	Middle East / East Asia / Southeast Asia	

Fig. 3 shows the results of the observed pit count at over 4 mm in depth for 6 tanks with unpainted NSGP-1 upon a 10-year inspection, in comparison with the unpainted conventional steel of other VLCC upon five-year inspection [9]. In case of the VLCC-A 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 Fig.3, maximum pit number in a tank reaching approximately 1300. The above inspection results prove the effectiveness of NSGP-1 against pitting corrosion in bottom plates.

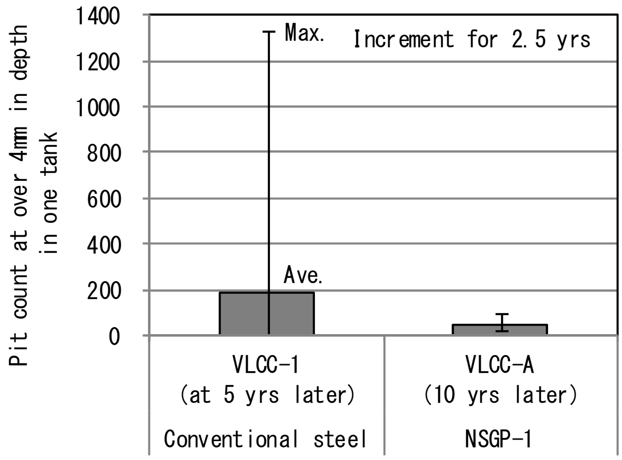

Fig. 3: Observed pit count at over 4 mm in depth for NSGP-1 VLCC and conventional VLCCs

Fig. 4 shows the results in comparison with the conventional steel of other VLCCs [9]. For the VLCCs using NSGP-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 unpainted conventional steel, the number of pits reached about 100 to 400. These inspection results made it adequately clear that the pit frequency of VLCCs using NSGP-1 was much lower than that of VLCC using conventional steel. The application of NSGP-1 to COT bottom plates is very effective in minimizing repair work.

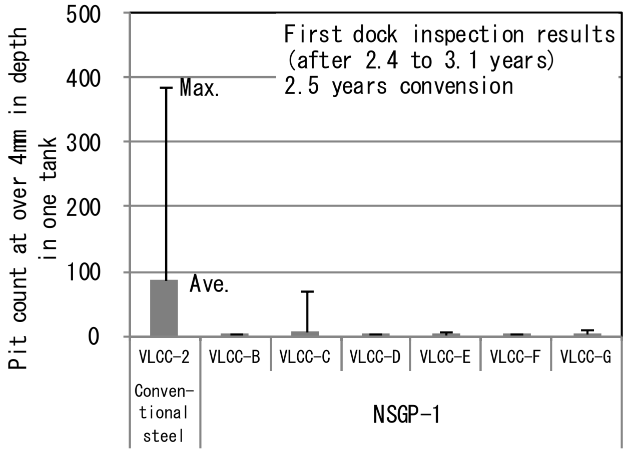

Fig.4: Observed pit count at over 4 mm in depth for the six VLCCs that used NSGP-1 and for conventional VLCC

2.3 Termination of Pit Growth

It is considered that pit growth stops after docking [2][4][5][10] as shown Fig. 5. We measured pit depth at the first docking (after 2.3 years), the second docking (after 5.0 years), the third docking (after 7.5 years) and at the fourth docking (after 10 years) in the same 5 positions from “a” to “e” of forward side in the No. 4 starboard tank[9] for VLCC-A. Pit depth at each docking is same within an error as shown Fig. 6 (a). Fig. 6(b) shows the pit “c” appearances of the second docking, the third docking and the fourth docking. These three appearances resemble closely, and the pit does not change at all. It is clearly revealed that pit growth has been halted in these studies.

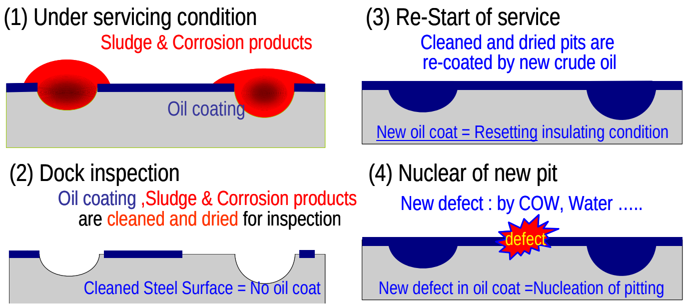

Fig.5: Mechanism of pit termination at dock inspection [2].

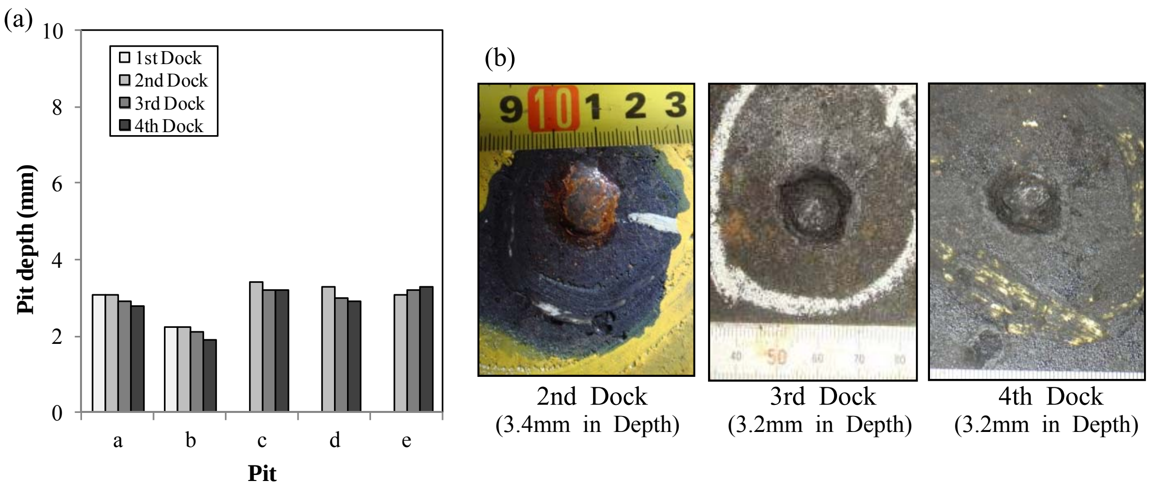

Fig.6:(a) Pit depth at the first, the second, the third and fourth dockings.
(b) Appearances of pit “c” at the second, the third and fourth docking.

2.4 Prevention against Pits by Combining Structural Countermeasure

According to the 242nd Research Committee of the Shipbuilding Research Association of Japan [1], pits often occurred under superstructure in COT. Throughout our investigations it has been clear that pits exist under drain hole of horizontal girder and side longitudinal. So we made some VLCCs with no drain hole on the lowest horizontal girder and on the lowest side longitudinal in all COTs as structural countermeasure. There is no pit in the VLCC with structural countermeasure. These results prove the effectiveness of combining structural countermeasure with NSGP-1 on prevention of pit occurring under side longitudinal and horizontal girder.

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

NSSMC developed another type of CRS for tank head structures, NSGP-2 [8][11][12][13].

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. Fig. 7 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 [14][15].

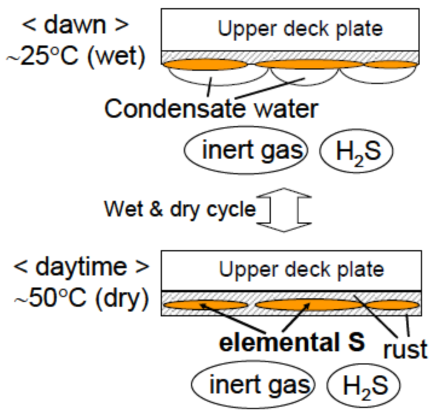

Fig7: Corrosion mechanism at the upper deck of COT

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 Fig. 8. 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°C (20 hours) and 25°C (four hours), which is a typical temperature change on an upper deck [16]. 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 [15]. Fig. 9 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.

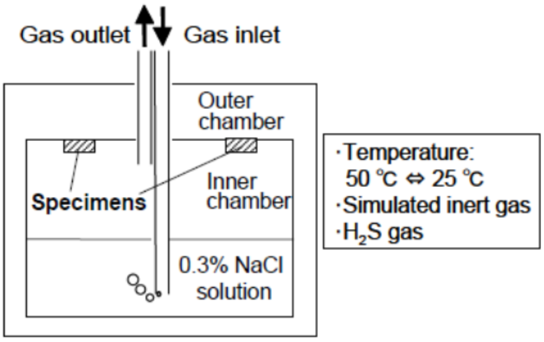

Fig. 8: Simulated corrosion test apparatus for the upper deck of a COT

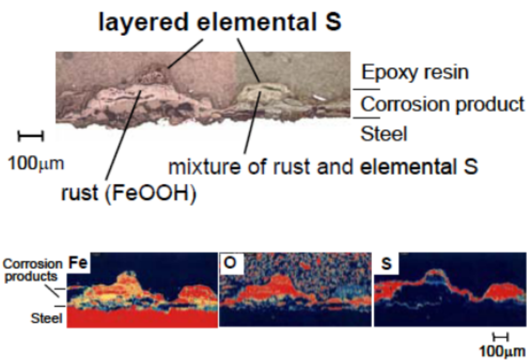

Fig. 9: Cross sectional morphology and distribution of elements by the Electron Probe Microanalysis in the corrosion products of specimen after a simulated corrosion test for the upper deck

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. 10. Corrosion loss, CL, was calculated using the following fomula; $ECL=A\cdot t^B$, where t is test period (days), A and B are coefficients. Coefficients A and B were determined by least squares method. The increments of the corrosion of NSGP-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-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-2 has also obtained type approval for corrosion resistance steel from LR, Class NK and ABS classification.

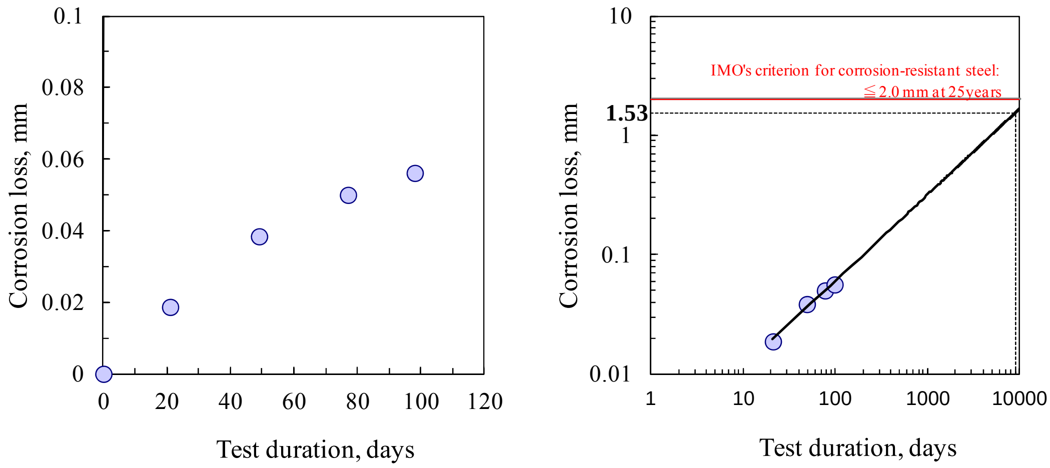

Fig. 10: Corrosion test results of NSGP-2

NSGP-2 was also applied to an Aframax tanker for the upper deck plate of COT without protective coating. Fig. 11 shows the results of an exposure test after 7.5 years. It was found that the corrosion loss of the developed steel at the upper deck was under 0.6 mm. The corrosion rate of NSGP-2 was less than 0.08 mm/y at 7.5 years, and it is thought that the corrosion loss of the developed steel will not exceed 2 mm after 25 years.

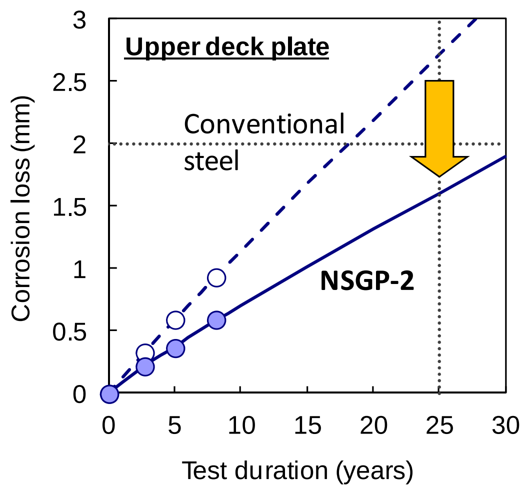

Fig. 11: Results of the exposure test on the upper deck of an Aframax tanker

4. Conclusions

The developed CRS for COT bottoms, NSGP-1, was applied to more than ten 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. Furthermore we found it becomes even less by combining structural countermeasure.
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.

NSGP-1 has obtained type approval for corrosion resistance steel from Class NK and ABS, and NSGP-2 has also obtained type approval for corrosion resistance steel from LR, Class NK and ABS classification. Due to the above peculiarities of NSGP-1 and NSGP-2, there are many benefits for a ship owner to apply CRS. For example, CRS does not require protective paint coating, this is one benefit for the global environment by reducing the use of volatile organic compounds. Furthermore, there is no concern about dispersion of coating quality before completion of ship building. And, protective paint damages doesn't occur at sludge removal work, it lead to minimize repair work of coating and maintenance cost which are heavy in periodical dock inspection/expense items for ordinary VLCCs. Considering these merits, NYK decided to use CRS on our new tankers from 2004 and shares the continuous dock inspection result with NSSMC to contribute for improvements of CRS.

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