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Technical Report

Development of NSSC® 260A—a Highly Corrosion-Resistant Stainless Steel for Chemical Cargo Tankers

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Abstract

High corrosion resistant stainless steel (NSSC 260A) to crude phosphoric acid, sulfuric acid and salt water was developed for chemical tankers to contribute to the improvement of the efficiency of materials handling and the decrease of environmental damage by the reduction of the tank maintenance work, such as pickling off the surface black change by crude phosphoric acid and the seawater localized corrosion. The welding material with flux for this steel was also developed, and it was confirmed that the weld joint had enough mechanical properties and corrosion resistance. This stainless steel has been applied to a chemical tanker.

1. Introduction

Formerly, carbon steel/pre-painted steel sheets were mainly used as materials for tanks in chemical tankers. Since around the mid-1970s, however, these have largely been replaced by stainless steel sheets, such as SUS304 and SUS316L sheets. Chemical tankers carry various chemicals, petroleum products, raw materials for food and cosmetics, and BTX (Benzene-Toluene-Xylene), etc. Among these, crude phosphoric acid and crude sulfuric acid are the major causes of tank corrosion.

Crude phosphoric acid is mostly manufactured using an economical wet process[1]. It is transported from phosphorus ore producing districts to phosphoric acid consuming countries in the form of a liquid obtained by treating phosphorus ore with sulfuric acid. Impurities contained in crude phosphoric acid differ widely according to where the phosphorus ore comes from. Generally speaking, at normal temperature, those impurities do not have much impact on tank corrosion: they only corrode stainless steel very slightly[2]. On the other hand, fluorides contained in crude phosphoric acid can cause the tank's inner walls that are exposed to the acidic vapor to turn black (in a phenomenon called black change) as shown in **Fig. 1**. Since such black change can hardly be prevented, the ship-owner has to undertake suitable maintenance of the tanks, such as cleaning the tank inner walls with some acid.

Crude sulfuric acid is manufactured in large quantities as a by-product of desulfurizing fossil fuels and exhausting combustion gases.

Fig. 1 Example of black change of chemical tank wall by crude phosphoric acid

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More often than not, crude sulfuric acid that resides on the tank's inner walls during unloading of the content absorbs moisture from the air to become dilute sulfuric acid (in a phenomenon known as self-dilution)[3], causing the tank material to corrode (decrease in thickness).

It is not uncommon that after the tank is emptied, a different type of load ("cargo") is put in it and transported to its destination. In this case, it is necessary to clean the tank beforehand. To clean the tank, brackish water or seawater is used. However, if salt remains on the tank wall after cleaning, it can cause local corrosion (pitting and crevice corrosion) of the tank. Because of this, the tanks are subject to periodic maintenance, including repairs as required.

Under those conditions, the authors et al. have developed a new stainless steel, NSSC 260A, that affords far superior corrosion resistance compared to conventional stainless steels for chemical tanks, with the aim of helping to improve the efficiency of transportation and decrease the impact on the environment by drastically reducing the need for various types of maintenance work.

2. How the New Stainless Steel was Developed

In developing a new stainless steel, we first specified the corrosive environment in which it would be used. Namely, in view of the types of cargoes carried by chemical tankers and the way chemical tankers are operated, we specified the following three corrosive environments that are considered to be the most harmful to stainless steels: (1) black change of stainless steel in vaporized crude phosphoric acid, (2) general corrosion (decrease in thickness) of stainless steel caused by sulfuric acid solution produced by self-dilution of crude sulfuric acid, and (3) pitting of stainless steel in a brackish water/seawater environment (neutral chloride ion environment).

Next, in order to set the development target, we discussed—on the basis of known facts—the corrosion indexes of the effects of alloying elements on corrosion resistance in the above corrosive environments. The corrosion that occurs in a phosphoric acid/sulfuric acid environment is basically general corrosion (uniform corrosion). To improve the resistance to general corrosion of stainless steel, it is necessary to increase the following general corrosion index:

$$GI = -[Cr] + 3.6[Ni] + 4.7[Mo] + 11.5[Cu]$$ [4]

On the other hand, stainless steel is susceptible to pitting in a saltwater environment. To improve the resistance to pitting of stainless steel, it is necessary to increase the following pitting index:

$$PI = [Cr] + 3.3[Mo] + 16[N]$$ [5]

On the basis of the above corrosion indexes, and in consideration of the economics and productivity, we decided that the development target should be to manufacture a new stainless steel plate whose chemical composition is such that the value of PI is 35 or more and the value of GI is 70 or more (see **Fig. 2**). After making strenuous efforts to design the optimum chemical composition and develop the required manufacturing technology, we successfully commercialized NSSC 260A as a stainless steel material for chemical tankers in 2003.

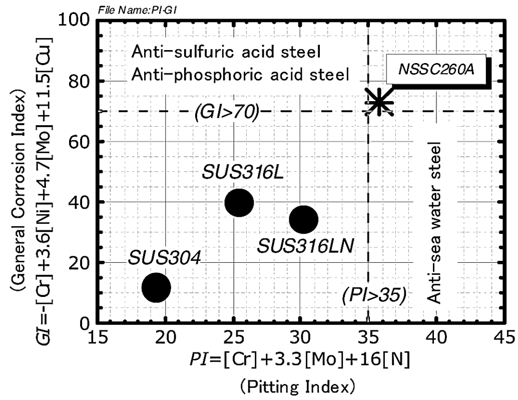

Fig. 2 Corrosion resistance position of NSSC 260A in the PI-GI diagram

In the sections that follow, we shall describe the salient characteristics of NSSC 260A—the excellent corrosion resistance in various corrosive environments and the desired weldability.

3. Corrosion Resistance of NSSC 260A

Table 1 shows the principal chemical composition and mechanical properties of NSSC 260A in comparison with those of SUS304, SUS316L and SUS316LN, which have largely been used for chemical tankers. NSSC 260A has appropriate amounts of Mo, Cu and N added to improve its resistance to pitting and general corrosion in phosphoric acid/sulfuric acid environments. It is comparable in strength to SUS316LN.

(1) Resistance to corrosion (black change) by crude phosphoric acid

Crude phosphoric acid is a black-colored liquid that always contains bluish-white sludge. **Table 2** shows the results of an analysis of typical crude phosphoric acid. The liquid contains about 73.8 percent phosphoric acid. It also contains such impurities as sulfuric acid, fluorine, chlorine and iron, which are corrosive substances. The sludge is a complex chemical compound made up of Ca, Mg, Al and F, which come from the phosphorus ore. From a sample of the sludge, $MgAlF_5 \cdot 1.5H_2O$, CaO, Al_2O_3, and $CaAl_6(SO_4)_4(OH)_2$, etc. were detected. As the gases generated from crude phosphoric acid, HF, SO_X and other corrosive gases were detected[6].

Fig. 3 shows the surface condition and corrosion rate of various stainless steels after they were exposed to the vapor phase and liquid phase, respectively, of 40℃ crude phosphoric acid for ten days. All the stainless steels, except for NSSC 260A, had a black film deposited unevenly on the surface exposed to the vapor phase. NSSC 260A was completely free from black change, that is, the deposition of a black film. Concerning the surface exposed to the liquid phase, all

Table 1 Main chemical composition and mechanical properties of NSSC 260A

Stainless steel for chemical tanker	Chemical compositions (mass%), PI value and GI value							Mechanical properties			
	Cr	Ni	Mo	Cu	N	PI	GI	YS (MPa)	TS (MPa)	EL (%)	Hardness HB
NSSC 260A	22.3	16.8	3.2	1.7	0.18	35.7	72.8	340	680	50	170
SUS304	18.5	8.5	-	-	0.05	19.3	12.1	290	635	65	160
SUS316L	17.5	12.5	2.2	0.2	0.04	25.4	40.1	265	555	62	140
SUS316LN	18.2	11	2.8	-	0.17	30.2	34.6	355	670	50	180

Table 2 Analytical result of crude phosphoric acid

(mass%, ◎ : exist, – : detection impossible)

	Solution	Sludge	Gas	Solid
Phosphoric acid (H_3PO_4)	73.8	8	–	–
Sulfuric acid (H_2SO_4)	2.6	20	◎	–
Hydrofluoric acid (HF)	0.2	20	◎	◎
Cl	0.1	0.1	◎	–
Si	0.06	3.4	–	◎

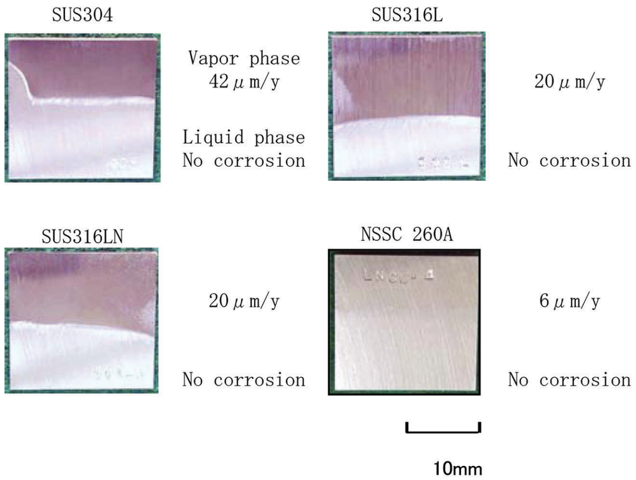

Fig. 3 Surface appearance and corrosion rate of specimens after 10 days crude phosphoric acid half immersion test at 40℃

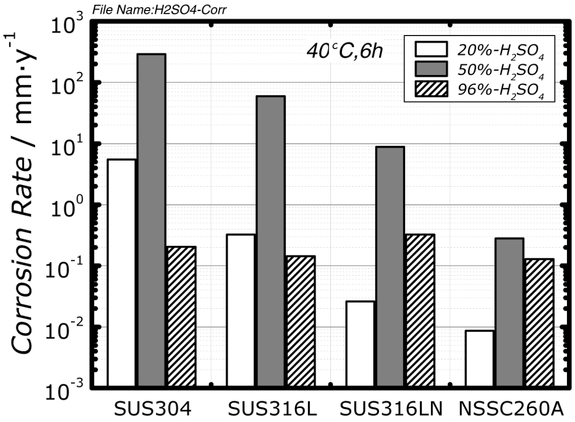

Fig. 4 Corrosion rate of stainless steels in sulfuric acid

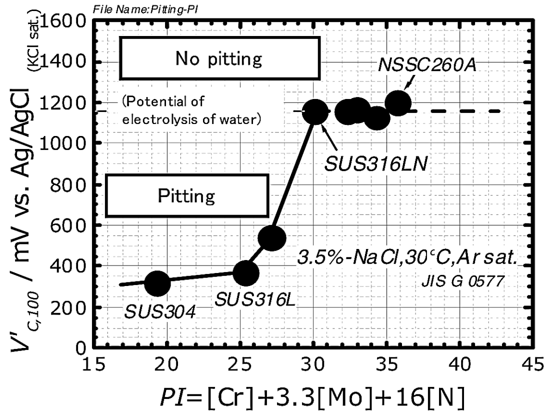

Fig. 5 Relationship between pitting potential and pitting index

the stainless steels were free from corrosion, maintaining their original metallic luster. From the results of the exposure test, it was found that the black change of stainless steel in the presence of crude phosphoric acid occurs in the vapor phase but not in the liquid phase. The black film was estimated to be the product of a corrosion reaction between a fluoride-based gas/SO_x gas generated from crude phosphoric acid and the stainless steel.

(2) Resistance to general corrosion in sulfuric acid solution

It is known that the corrosion resistance of stainless steel in sulfuric acid declines most when the sulfuric acid concentration is about 50 percent[7]. Therefore, concerning the corrosion resistance of chemical tank materials in sulfuric acid, it is necessary to understand it under each of these sulfuric acid conditions: high concentration (96% sulfuric acid), medium concentration reached by self-dilution (50% sulfuric acid), and very low concentration (20% sulfuric acid). **Fig. 4** shows the corrosion rate of various stainless steels in sulfuric acid of varying concentrations. All the stainless steels show the highest corrosion rate when the sulfuric acid concentration is 50 percent. Even in that environment, the corrosion rate for NSSC 260A is the lowest of all.

(3) Resistance to pitting in saltwater

If the tank is incompletely cleaned and salt remains stuck to the tank inner wall, pitting can occur on the stainless steel surface. Since resistance to pitting in saltwater is also important, we measured the pitting resistance (V'_{C100}) of various stainless steels in accordance with JIS G 0577. **Fig. 5** shows the measurement results in terms of the relationship between pitting potential and pitting index (PI). With the increase in PI value, the pitting potential shifts toward the noble side. When the value of PI is about 30 or more (as in the case of SUS316LN and NSSC 260A), pitting does not occur. Instead, the electrolysis of water begins to take place.

From the above results, it was confirmed that NSSC 260A displays sufficient corrosion resistance in the abovementioned three corrosive environments that are critical to chemical tanks.

4. Welding Operation and Properties of Welded Joints

When applying NSSC 260A to a chemical tanker, it is advantageous from the standpoint of economics and work efficiency to employ the CO_2 semiautomatic welding method using a flux-cored wire (FCW). Therefore, we developed an FCW welding material for NSSC 260A[8]. The chemical composition of the newly developed welding material is shown in **Table 3**. Using this welding material, we evaluated the efficiency of the welding operation, the resistance to cracking, and the performance of welded joints in the case of NSSC 260A. As a result, it was found that the efficiency of welding operation, including arc resistance and slag removal, was quite satisfactory. With respect to its resistance to cracking as well, NSSC 260A was comparable to ordinary austenitic stainless steels. In addition, welded joints were subjected to tensile, bending and impact tests. The test results showed that they had sufficient mechanical properties. The results of a corrosion resistance test on NSSC 260A including welds also

Table 3 Chemical compositions of FCW FC 317LNCU weld metal

(mass%)

Brand	Welding process	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	N
FC-317LNCU	FCAW	0.03	0.34	1.48	0.01	0.005	13.24	22.68	2.63	2.24	0.06

showed good corrosion resistance comparable to the base metal.

5. Commercial Production of NSSC 260A and Application of NSSC 260A to Chemical Tankers

The manufacturing target we aimed at was a wide NSSC 260A plate with excellent corrosion resistance. Since NSSC 260A contains considerable proportions of Cr, Mo and Cu, at the stage of trial production, we unexpectedly experienced many surface defects due to the precipitation of brittle phases, etc. Accordingly, the causes of these surface defects were thoroughly investigated by means of experiments in the laboratory and production tests in the field. The investigation results and suitable countermeasures were fed back to the individual manufacturing processes, including the refining, continuous casting and hot rolling processes. Eventually, we were able to establish the technology to manufacture wide NSSC 260A plates (exceeding 3,000 mm).

NSSC 260A was first manufactured on an actual production line in 2004. In June of the same year, it was applied to a 115-ton chemical tank of a newly built chemical tanker. **Fig. 6** shows the appearance of the chemical tanker to which NSSC 260A was applied. At the end of February 2009, we confirmed that the tank made from NSSC 260A had no corrosion problems, including black change, and that the maintenance load for the tank had been reduced compared with SUS316LN tanks.

Fig. 6 Chemical tanker to which NSSC 260A stainless steel was applied

Incidentally, we won the 28th Japan Institute of Metals Award for the development of NSSC 260A[9].

6. Conclusion

Herewith, we have described the process of development, corrosion resistance, welding operation efficiency, welded joint performance, commercial production, application, etc. of NSSC 260A. From the standpoint of improving the efficiency and economics of cargo transportation, the application of NSSC 260A to chemical tankers is expected to increase in the future. In addition, in view of its excellent corrosion resistance with regard to sulfuric acid, NSSC 260A is expected to be increasingly used for smokestacks, flues, flue-gas desulfurization equipment, and sulfuric acid storage tanks, etc.

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