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Corrosion Resistance Steel Plate (WELACC5) for LNG Fired Smokestacks

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Abstract

WELACC5, a new corrosion resistance steel for LNG fired smokestack, which can be used in a funnel environment of LNG-firing boiler with bare treatment and which is maintenance free over long periods of time has been developed. The developed steel has high corrosion resistance because it contains 5% of Cr and resists the spreading of rust because of the combined effect of Cu and Ni. The corrosion rate of the developed steel in the LNG funnel environment is 0.0007mm/y, which is remarkably small compared with ordinary steel. The mechanical properties, workability, weldability and weld-joint properties of the developed steel are the same as those of ordinary steel. Therefore, it is confirmed that WELACC5 easily performs as the steel plate for LNG fired smokestacks.

1. Preface

Environment protection is one of the keys to humankinds' wellbeing in the 21st century. As measures for the environmental issues after fuel diversification, power utility companies are promoting gas-fired power plants where LNG and other gases emitting little SO_x and NO_x are burned instead of heavy oil and coal.

When heavy oil or coal is burned, sulfur oxides (SO_2 and SO_3) are formed during the combustion, and at the start and stop of the boiler operation when temperature of the stack wall is low, SO_3 in the exhaust gas reacts with moisture to form sulfuric acid, causing sulfuric acid corrosion. In the case of LNG burning, sulfuric acid dew point corrosion does not occur as the fuel contains little sulfur, nevertheless water corrosion does take place due to condensation of humidity in the flue gas. As protection measures against these types of corrosion, inner surface of steel stacks is coated with organic, inorganic and metal linings. But sprayed castable lining is prone to surface deterioration and subsequent scattering and falling off of the material. Block linings can be spalled from thermal load and cause scattering as well. These problems will lead to another environmental problem in the neighboring areas.

For these reasons, the stacks are relined every 6-7 years, which causes a great amount of loss due to the plant stoppage besides the reline work being costly in itself[1)]. When conventional corrosion resistant steels such as anti-sulfuric acid steel are used for the stacks as a countermeasure, scattering of rust flakes may occur when the boilers are stopped and started frequently or after a long stoppage, which is also has an impact on the surrounding environment[2)].

A steel material for stacks of LNG-fired boilers (LNG stacks) not requiring linings and not causing rust scattering has been sought for the above reasons. If a low alloy steel material is brought to the

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market which is highly corrosion resistant and forms an adhesive rust layer under the service conditions of LNG stacks, that would meet the market demand in either economical or environmental aspects. In such a context, in cooperation with Mitsubishi Heavy Industries and Tokyo Electric Power Co., Nippon Steel developed WELACC5 (WELL Anti-Corrosion Steel Containing Cr 5% with WELdability for Advanced Combined Cycle) as a new LNG stack material which can be used without lining (meaning maintenance-free for a long period) and is more economical than stainless steels or stainless steel-clad plates.

This paper reports outlines of the development process and performances of the new plate product. The development was done in the following manner. Firstly, alloy design and methods of corrosion simulation tests were worked out based on investigations of corrosion environment of actual LNG stacks in service, then effects of alloy chemistry on corrosion resistance and rust properties were clarified through the tests. A new strain of alloy composition was formulated from these studies. Performance of the new alloy materials was confirmed through exposure tests in the environment of actually operating stacks. Then, the developed steel was trial-produced at a mill for verifying manufacturability and fabricability in various aspects.

2. Corrosion Environment of LNG Stacks

The flue gas temperature of LNG-fired boilers at the stack inlet is 373 - 383K at normal operations and around 408K at abnormal operating conditions. Typical composition of the flue gas is said to be 6 - 10 vol.% of H_2O, 3 vol.% of CO_2, 14 vol.% of O_2 and 73 - 77 vol.% of N_2. Different from the coal-burning or oil-burning boilers, condensation of sulfuric acid does not take place in the stacks as the fuel does not contain sulfur, but condensation of moisture in the combustion gas does take place causing the so-called water corrosion. During start and stop under the DSS (daily start and stop) operation regime, temperature of the internal surface of the stack is suspected to be below the dew point of water and hence, is suspected that condensation is forming.

Chemical analyses of water-soluble ions in deposits on the internal surface of an LNG stack and a drain from the same stack showed that either of the samples were weakly acidic mainly with sulphate ions with a pH of 3.6 - 4.4. NH_4^+ and Cl^- were identified in them. The NH_4^+ is presumed to be from the flue gas denitration system, but the origin of the Cl^- is not clear although trace element in the combustion gas or sea salt particles suspended in the air is suspected to be the origin. Other common corrosive factors such as sulfur compounds (mercaptan) formed during combustion, formaldehyde, formic acid and NO_2 formed during incomplete combustion were not detected in the corrosion investigation.

From these results it was assumed that the corrosion in the LNG stacks was caused by weakly acidic aqueous solution of combustion products in the flue gas and deposits, and it was similar to the common corrosion in the ordinary atmosphere.

3. Philosophy of Alloy Design

As it was presumed from the investigation of corrosion environment in the LNG stacks that corrosion was dominantly caused by aqueous solution of CO_2 of the flue gas, chromium, well known to enhance corrosion resistance, was selected as the main alloying element for the new product, and its amount was decided to be between 3 - 9% in order to have general corrosion covering all the steel surface rather than local corrosion. Further, for avoiding scattering of rust flakes, copper, nickel and molybdenum were considered as additional alloy elements expecting that they would help form an adhesive rust layer.

4. Study for Basic alloy composition through Corrosion Simulation Tests

4.1 Specimens

Based on the guideline delineated above, it was decided that specimens for the tests would be made of low alloy steels listed in **Table 1**. The steels were prepared in a 100 kg vacuum melting furnace, heated to 1,150°C, breakdown-rolled to 60 mm thickness, divided into three pieces, heated again to 1,150°C and hot-finish-rolled to 6 mm thickness. Specimens of conventional SM 400 B structural steel for welding use (6 mm) and SUS 304 and SUS 316 stainless steels (3 mm) (all under JIS) were also prepared as reference for comparison with the developed steels.

The test piece size was 15 × 30 × 3 mm for alternate dry/humid CO_2 gas corrosion tests, and 20 × 120 × 3 mm for intermittent immersion corrosion tests and simulation ash immersion tests. For both the sizes, test pieces of the specimens rolled to 6 mm were taken from the center of the thickness direction. Test piece surfaces were wet-polished to #600.

4.2 Corrosion test methods

4.2.1 Corrosion test methods

Corrosion conditions of LNG stacks were classified into (a) start/stop operation and (b) normal operation for the purpose of study of corrosion resistance. The condition (a) could correspond to alternate dry/humid corrosion process caused by starting and stopping of the boiler, and the condition (b) to a situation where corrosion proceeded with a small amount of water between the steel plate and surface deposits at comparatively low temperatures. The alternate dry/humid CO_2 gas corrosion test and the intermittent immersion corrosion test were carried out to simulate the condition (a) and the simulation ash immersion test was meant to simulate the condition (b)[3]. The methods of these simulation tests are described below.

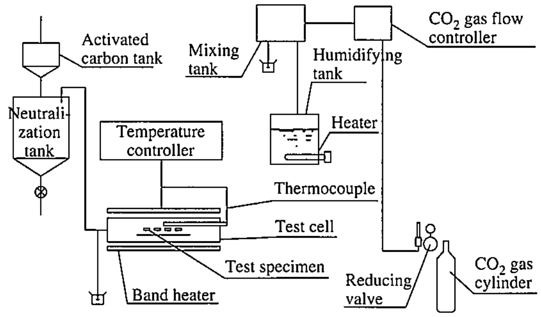
4.2.2 Alternate dry/humid CO_2 gas corrosion test

A 5.5 h cycle comprising heating, holding and cooling between 328K and 373K as shown in **Fig. 1 (b)** was set forth for simulating actual conditions of the operating stacks. Using an apparatus for alternate dry/humid CO_2 gas corrosion test shown in **Fig. 1 (a)**, the test pieces underwent said cycles for a maximum of 1,000 h (181 cycles).

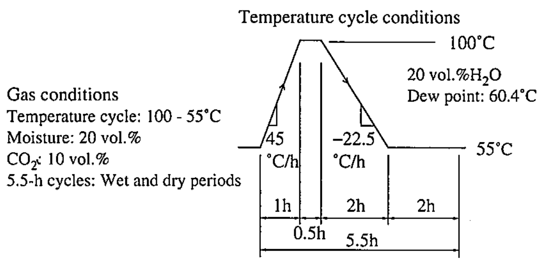
4.2.3 Intermittent immersion corrosion test

Table 1 Chemical composition of steels prepared by a laboratory melting furnace (mass %)

Steels	C	Si	Mn	P	S	Cu	Ni	Cr	Mo
3Cr	0.030	0.21	0.48	0.006	0.001	—	—	3.03	—
5Cr	0.032	0.19	0.50	0.001	0.001	—	—	5.04	—
7Cr	0.030	0.20	0.49	0.005	0.001	—	—	6.97	—
9Cr	0.028	0.21	0.49	0.005	0.001	—	—	8.56	—
3Cr-0.5Mo	0.030	0.20	0.49	0.001	0.001	—	—	2.99	0.52
5Cr-0.5Mo	0.030	0.20	0.50	0.005	0.001	—	—	5.11	0.52
5Cr-1.5Ni	0.030	0.20	0.49	0.001	0.001	—	1.48	4.93	—
5Cr-0.3Cu-0.3Ni	0.029	0.20	0.51	0.001	0.001	0.34	0.30	5.02	—
SM 400 B	0.120	0.19	0.85	0.013	0.009	0.01	0.02	—	—
SUS 304	0.060	0.48	0.86	0.028	0.007	—	8.65	18.26	—
SUS 316 L	0.020	0.48	0.85	0.026	0.001	—	12.21	17.35	2.18



(a) Test apparatus



(b) Test condition

Fig. 1 Alternately wet and dry CO_2 gas corrosion test

Based on the analysis of the deposit ash and drain of the LNG stack, a simulation solution was prepared on the basis of distilled water, adding 440 ppm of $(NH_4)_2SO_4$, 140 ppm of Na_2SO_4 and 40 ppm of NaCl, and adjusting to a pH of 4.0 with diluted sulfuric acid. 2 min immersion and 58 min drying was defined as 1 cycle (1 h) and the test pieces were immersed and dried for a maximum of 236 h (cycles).

4.2.4 Simulative deposited ash immersion corrosion test

A simulation deposit ash containing 0.8 gram equivalent of $(NH_4)_2SO_4$, 0.2 gram equivalent of Na_2SO_4, 0.002 gram equivalent of NaCl and 40 mass % of moisture was prepared and the test pieces were immersed in it and a condition of constant temperature and moisture (353K, 70% relative humidity) was maintained for 1 month. As no significant change of specific density of the simulation ash related to evaporation and condensation of moisture was observed, it was considered reasonable to suppose that the moisture of the simulated ash was virtually constant during the test period.

4.2.5 Evaluation methods of rust characteristics

When the developed low alloy steel is used for inner tube of stacks without protective linings, it is desirable that the rust generation is small and its layer is adhesive and evenly distributed on the steel surface.

In this respect characteristics of the rust after the corrosion tests were investigated and effects of alloy composition on the rust characteristics studied. The test pieces after 236 cycles of the intermittent immersion corrosion test were used for this purpose and the following analyses were carried out:

(1) Evaluation of rust generation by measurement of rust weight on the steel surface
(2) Evaluation of rust adhesion by tape test (Rust was peeled off by adhesive tape and what came with the tape was classified as "peeled rust" and what remained on the steel surface as "adherent rust" and each of them were weighed.)
(3) Evaluation of formation of relatively easily peelable rust by stereomicroscopy of the rust surface
(4) Evaluation of homogeneity of rust formation by sectional observation over interface of rust layer and steel substrate
(5) Evaluation of grain density of rust layer by TEM observation
(6) Element analysis of the rust layer/steel substrate section by EPMA.

4.3 Test results and discussions

4.3.1 Effects of alloy composition on corrosion rate

Fig. 2 shows effects of Cr addition amount on the steel corrosion rate as observed in the alternate dry/humid CO_2 gas corrosion test. It is clear from this result that an addition of Cr is very effective for enhancing corrosion resistance, and that only a 5% addition of Cr results in a sufficiently high corrosion resistance. SUS 304 and SUS 316 showed little corrosion weight loss at any of the tests, either. Similarly, the 5% Cr addition showed its corrosion resistance enhancement effect also in the intermittent immersion corrosion test and the simulation ash immersion test.

Fig. 3 compares corrosion rates of the specimens at the alternate dry/humid CO_2 gas corrosion test. Corrosion rate was improved by

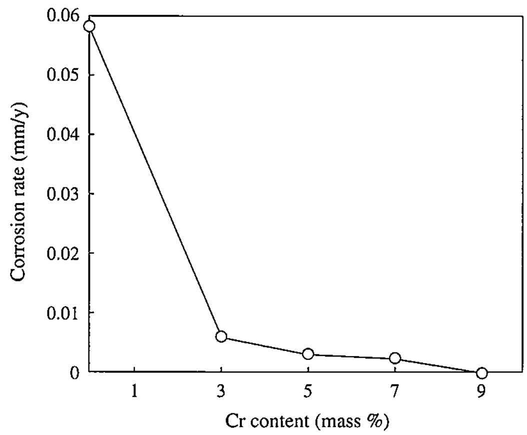


Fig. 2 Effect of chromium content on corrosion rate (after 248 h of alternately wet and dry CO_2 gas corrosion test)

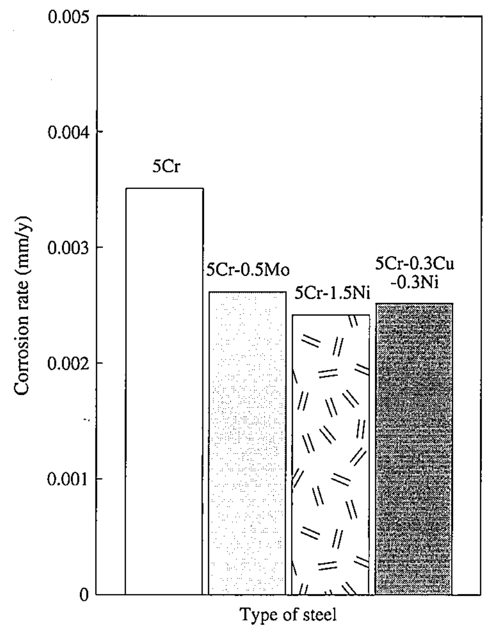


Fig. 3 Effects of alloying elements on corrosion rate of 5Cr steel (after 1,000 h of alternately dry and wet CO_2 gas corrosion test)

approximately 20% through an addition of Ni, Mo or a combination of Cu-Ni to the simple 5% Cr added steel (5Cr steel). But the addition of these elements did not show any meaningful decrease of corrosion rate compared with the 5Cr steel at either of the other two tests.

From the above results it was concluded that the corrosion resistance improving effect of the addition of Ni, Mo or a combination of Cu-Ni to the 5Cr steel depended on the corrosion conditions but it would not do any harm at any rate.

4.3.2 Rust characteristics

Fig. 4 shows effects of Cr content on the rust amount (total weight of the peeled rust and the adherent rust). The total amount of rust depended dominantly on the amount of Cr and showed a good correlation with corrosion weight loss. Stereomicroscopy of corroded steel surfaces revealed that SM 400 B steel was covered with coarse, granular and peelable loose rust, and formation of this kind of rust decreased as the amount of Cr increased. Further, the amount of the same kind of rust was smaller in the 5% Cr steel samples added with Cu, Ni and/or Mo in various amounts compared with the simple 5Cr steel.

Fig. 5 shows evaluation result of rust adhesion of SM 400 B, 5Cr steel and 5Cr-0.3Cu-0.3Ni steel. Both 5Cr steel and 5Cr-0.3Cu-0.3Ni steel had nearly the same total amount of rust but the latter had more adhesive rust and less peelable rust than the former. 5Cr-1.5Ni steel and 5Cr-0.5Mo steel also showed an increase in adhesive rust similar to the 5Cr-0.3Cu-0.3Ni steel.

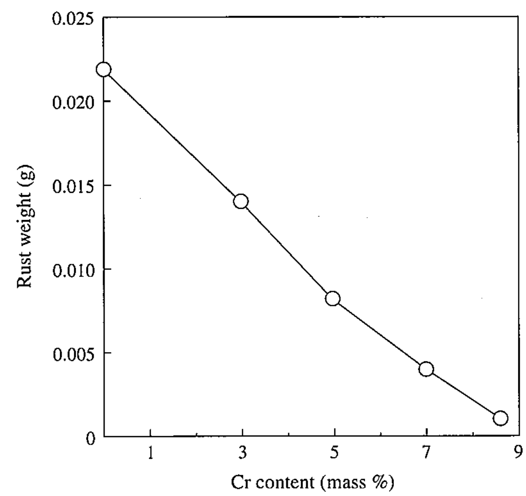


Fig. 4 Effect of chromium content on rust weight (after 236 h of intermittent immersion corrosion test)

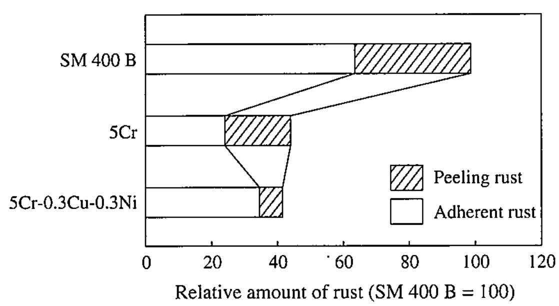


Fig. 5 Effects of alloying elements on rust weight (after 236 h of intermittent immersion corrosion test)

Sectional observation of steel substrate and rust layer by optical microscope[3)] revealed that the rust layer of SM 400 B was uneven, more than 100 μm thick locally, comprising granular and peelable rust. Rust layers of steels containing 3% or more Cr were found to be thin (10 - 30 μm) and even. It was confirmed that the 5% Cr steel added with Cu, Ni or Mo had more even and adhesive rust layers than the simple 5Cr steel.

Through TEM observation[3)], it was found out that the rust particles were composed of colloidal condensate of iron oxide hydroxide, comprising needle-shaped, crystallized coarse particles and fine particles. Whereas SM 400 B rust contained a considerable amount of coarse particles more than 1 μm large, formation of these particles was limited in the 5% Cr steels. This trend was seen more clearly in the 5Cr-0.3Cu-0.3Ni and 5Cr-0.5Mo steels.

Sectional observation of steel substrate and rust layer by EPMA[3)] disclosed that, in the 5% Cr steel rust, Cr was evenly and more densely distributed in the rust layer than in the steel substrate. The 5% Cr steels added with Cu-Ni, Ni or Mo also showed these elements in the rust, though to lesser extents than the Cr condensation.

From the above results, it was presumed that Cr would decrease rust formation amount by slowing corrosion rate and that addition of Ni, Mo or combination of Cu-Ni would enhance adhesion and homogeneity of rust and reduce the formation of peelable rust by restricting crystallization and growth of the coarse rust particles through dissolution of Cu, Ni and/or Mo into the rust together with Fe and Cr.

4.4 Selection of basic alloy chemistry

Based on the investigation of the effects of Cr on corrosion resistance, it was concluded that, on the basis of 5% Cr addition, 5Cr-0.3Cu-0.3Ni steel would be most suitable as the LNG stack material for economically obtaining yet better corrosion resistance and enhanced adhesion of rust to the steel substrate.

5. Evaluation of Characteristics of the Developed Steel

5.1 Trial production conditions

The new corrosion resistant 5Cr-0.3Cu-0.3Ni steel having the chemical composition as per **Table 2** was trial-produced on a commercial mill. 4.5, 12, 21 and 30 mm thick plates were manufactured through converter tapping, ladle refining, casting, slab conditioning, reheating, plate rolling and heat treatment, and various aspects of product properties were assessed.

5.2 Material properties

Table 3 shows tensile test results. Sufficient strength for 400 MPa class welded structural steel has been verified in each of the manufactured dimensions. Simulating the fabrication of a stack, 12-mm thick plate were edge bent on a 3,000-ton press (bending load of 150 tons, 9 bends) and body bent with bending rollers (bending displacement of 10 to 20 mm, 10 bends). As a result, the worked plates showed good bend radius and straightness. Both forming accuracy and working time were the same as normal carbon steel plates or stainless

Table 2 Chemical composition of WELACC5 trial-produced at a commercial mill (mass %)

		C	Si	Mn	P	S	Cu	Ni	Cr	T-Al
Specification	Min.	—	—	0.30	—	—	0.15	0.15	4.00	—
	Max.	0.09	0.50	0.60	0.030	0.50	0.50	6.00	—	
Ladle analysis		0.03	0.20	0.50	0.006	0.004	0.28	0.34	4.89	0.033

Table 3 Tensile test results of WELACC5 plates

Thickness (mm)	Type of test specimen	No. of test pieces	Direction of tensile test	0.1% offset yield strength (MPa)	Yield point or 0.2% offset yield strength (MPa)	Tensile strength (MPa)	Elonga-tion (%)
4.5	JIS #5	3	Transverse	330 328 328	336 337 340	478 480 482	37 37 38
12	JIS #1 A	3	Transverse	307 310 311	311 311 315	463 463 464	28 29 26
21	JIS #1 A	3	Transverse	285 294 297	297 303 325	475 478 484	29 26 23
30	JIS #1 A	3	Transverse	247 248 249	262 268 268	459 462 461	32 32 32

Table 4 Welding condition of WELACC5

Welding method	Welding material	Current (A)	Voltage (V)	Speed (cm/min)	Heat input (kJ/cm)	No. of passes	Shielding gas	Interlayer temperature
SMAW	309 type 3.2 mmϕ	100	24	200	7.2	15	—	≦423
FCAW	309 type 1.2 mmϕ	220	28	300	12.3	6	80%Ar +20%CO_2	≦423

SMAW: Submerged arc welding FCAW: Flux-cored wire arc welding

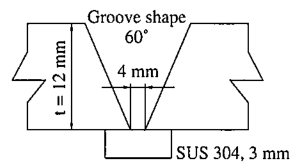


Table 5 Tensile test results of WELACC5 weld joints

Thickness	Welding method	Type of test specimen	No. of test pieces	Tensile strength(MPa)	Position of rupture
12 mm	SMAW	JIS No.1 GL = 30	2	499 494	Base metal
		JIS No.1 A GL = 68	2	480 484	Base metal
	FCAW	JIS No.1 GL = 30	2	508 503	Base metal
		JIS No.1 A GL = 68	2	483 485	Base metal

steel-clad plates. Tests of plasma cutting and gas cutting were also carried out. A good plasma cutting property was confirmed under a condition of 120 mA, straight cut at 1,600 mm/min cutting speed. The plates showed no problem for gas cutting, too.

5.3 Weldability

Welding materials for the plate thickness range of 4.5 to 30 mm were studied to meet the conditions that the weld strength should be equivalent to that of the SM 400 A steel and that cold cracking should not occur when the weldment was not preheated and post-heated. The austenitic stainless steel SUS 309 was selected as a result.

In case of using austenitic welding material, as the welding material is different from the base metal, hot cracking of the weld metal and embrittlement and cracking by martensite are feared to occur. These problems were investigated, mainly using the Schaeffler constitution diagram, according to the composition of the developed steel and the welding materials. As a result, it was found that since the dilution ratio was less than 30% for submerged arc welding (SMAW) and flux-cored wire arc welding (FCAW), martensite did not form, eliminating the fear of cold cracking. And as a few percent δ-ferrite forms, the probability of hot cracking is small. The welding condition is shown in **Table 4**.

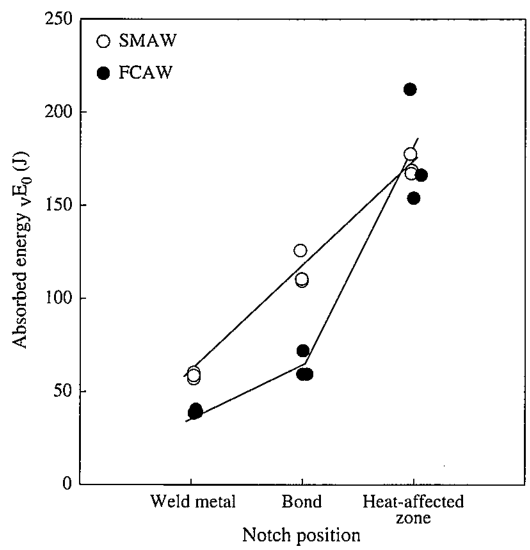


Fig. 6 Impact test results of weld joints of WELACC5

Oblique y-groove restraint weld crack test was carried out with regards to weld crack sensitivity and it was confirmed that use of the austenitic welding material for the developed steel would offer good weldability not causing any cracks without any need for pre-heating. Tensile strength, toughness and bendability of the weld joint were confirmed to be equal or superior to SM 400 B. **Table 5** shows tensile test results and **Fig. 6** the results of 2 mm V-notch Charpy tests.

6. Exposure Tests in Operating Stack

Fig. 7 shows result of an exposure test for 5,760 h in the duct of an LNG stack in service. Corrosion rate of the developed 5Cr-0.3Cu-0.3Ni type steel was as low as 0.0007 mm/y, about 1/3 that of SM 400 B. The surface of the specimen was slightly covered with a small amount of brown corrosion products, wherein $(NH_4)_3H(SO_3)_2$ and $(NH_4)_2SO_4$ were identified by X-ray diffraction. These matters are deposits and are also found in the deposits of LNG-fired boiler stacks. Test pieces of weld joints were also exposure-tested in the same stack and no local corrosion was identified in any of weld metal, heat-affected zone and the base metal at an evaluation after 8,640 h exposure.

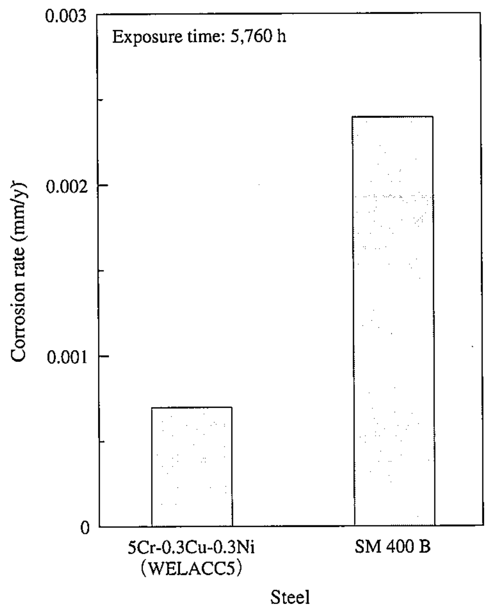


Fig. 7 Exposure test result of WELACC5 in stack environment of LNG-fired power plant

No problem was found with regards to rust scattering but, since the exposure time was only 5,760 h and little rust had been formed as of the time of the evaluation, a longer exposure test would be necessary for a definitive evaluation in this respect.

7. Conclusion

A new corrosion resistant plate product WELACC5 was developed for use in LNG stacks for a maintenance-free operation for a long term. The developed product contains 5% Cr for enhancing corrosion resistance and small amounts of Cu and Ni for the purpose of further enhancing corrosion resistance and improving adhesion of rust (anti-rust-scattering). Its manufacturing process was designed for obtaining mechanical properties and weldability equivalent to JIS SM 400 B.

At exposure tests in an operating LNG stack, WELACC5 showed a corrosion rate as small as 0.0007 mm/y and its anti-rust-scattering property was also satisfactory. The product has mechanical properties equal to JIS SM 400 B and by the use of an austenitic welding material good welding workability is secured with no problem at all regarding crack resistance and strength, toughness and corrosion resistance of the welded joint without requiring pre-heating. It has also been confirmed through fabrication tests that the plate material has good practical workability for forming into stack components.

Approximately 3,300 t of WELACC5 has been applied to stacks since 1997 and further 1,600 t will be used for the application. The product is expected to expand its market in the stacks for LNG-fired boilers thanks to its economic and environmental advantages.

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