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# Evaluation and Development of Corrosion Resistant Materials for Smokestacks

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In this paper, evaluation and development of corrosion resistant materials for smokestacks is summarized mainly on the basis of the author's experimental results. Operating environments of smokestacks and the problems of conventional lining materials for smokestacks are described briefly. The emphasis is focused upon the evaluation and development of recently developed corrosion resistant steels such as YUS260 for heavy oil fired smokestacks, WELACC5 for LNG fired smokestacks and NSL310MoCu Clad steel for coal fired smokestacks. Corrosion resistance of these steels under laboratory corrosion testing environments and actual environments are evaluated. Finally future problems of corrosion resistant materials for smokestacks are touched on briefly.

***Keywords*** : *heavy oil fired smokestack, coal fired smokestack, LNG fired smokestack, lining material, stainless steel, low alloy steel, corrosion resistance, weldability*

## 1. Introduction

Overcoming the environmental issues on our planet earth is a critical problem for human being to live in comfort in $21^{st}$ century. The air pollution preventive technology is one of the most important key engineering technology to enable this. Technological advancement in this field is significant especially on air pollution preventive equipment such as exhaust gas desulfurizer, exhaust gas denitrizer, dust collector, smokestack and duct. Corrosion resistance of structural materials for these equipments is strongly dependent on kinds of fired fuel. In this paper, operating environments of smokestacks and ducts is briefly described. Then, conventional smokestack materials and their problems are summarized. The emphasis is placed upon the evaluation of recent developed corrosion resistant steel stack steels such as austenitic stainless steel YUS260 and YUS270 for heavy oil fired smokestacks "From the report 1)", low alloy steel WELACC5 for LNG fired smokestacks "From the report 2)"and austenitic stainless clad steel NSL310MoCu for coal fired smokestacks "From the report 3)". Finally future problems of development and evaluation for smokestack materials are briefly described.

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## 2. Operating environments in smokestacks and ducts

The internal cylinder of the smokestack is exposed to an exhaust gas including corrosive gases such as $SO_3$ and $Cl_2$ mixed with moisture. Concentration of the corrosive gas varies depending on the presence of an exhaust gas desulfurizer and reheating process, etc. Temperature of the exhaust gas is relatively low. And daily start and stop and partial load operation for steel stack are frequently associated with plant operation. Therefore the internal cylinder of the smokestack is most frequently exposed to severe corrosive environments "From the report 4)". It is well known that sulfuric acid dew point corrosion occurs at inner wall of steel stack with relatively low temperature of 313 to 423K. The relationship between boiler operating time and the wall temperature of smokestacks can be schematically illustrated in Fig. 1. In the stage (Ⅰ) and (Ⅲ) where the boiler starts and stops, wall surface temperature is low and the $SO_3$ in combustion gas reacts with moisture resulting in formation of sulfuric acid. This causes general corrosion on the lining of smokestack internal cylinder. While in higher temperature stage (Ⅱ) under normal operation, sulfate is formed and local corrosion occurs depending on the operating condition "From the report 1)".

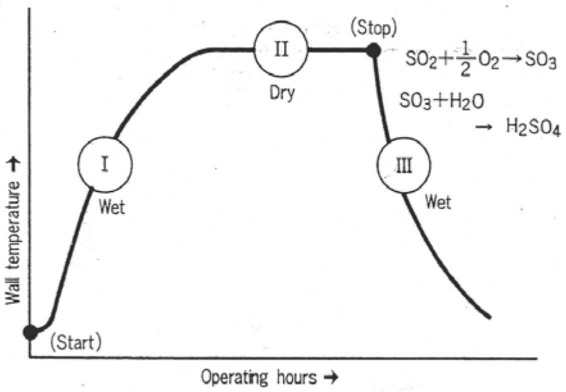


**Fig. 1.** Outline of boiler operating hours and inner wall temperature of smokestacks "From the report 1)"

## 3. Smoke stack maretials and their problems

To protect the smokestack cylinders from corrosion and heat, the internal walls of smokestacks and gas ducts are lined with inorganic, organic and metallic materials. The castable linings sometimes cause scattering and falling off due to deterioration of the surface layers. The block linings also cause spalling and scattering due to corrosion and thermal deterioration. Therefore environmental contamination sometimes occur around the smokestacks. Accordingly, maintenance of every six to seven years interval is required depending on deterioration conditions, and this requires a considerable amount of cost and period for maintenance. Furthermore, the shutdown of a plant operation causes a tremendous amount of economical loss. The used metallic lining materials are mild steel, sulfuric acid resistant steel and stainless clad steel. In case of the mild steel, sulfuric acid dew point corrosion occurs when the dryness of the wall surface cannot be maintained or heat insulation is insufficient in continuous operation. In case of the sulfuric acid resistant steel, cast pieces may scatter when the start and stop frequencies are high or shut down period is long. Under low concentrated sulfuric acid drain environment with pH value of 2 to 4 formed when the smokestack's internal wall surface temperature is lower than the water dew point temperature, conventional stainless steels such as SUS304, SUS304L, SUS316 and SUS316L or stainless clad steels are used "From the report 4)". Titanium and nickel base alloy Alloy C-276 exhibited the good corrosion resistance in a closed-loop flue gas desulfurization environment "From the report 5)". Alloy C-276 is used as a lining material for coal fired power plant stacks "From the report 5)". Titanium is also used as a lining material for flue gas desulfurization environment "From the report 7)". However, these materials are expensive and have a difficult weldability for clad materials. Therefore, it is necessary to develop the higher corrosion resistance stainless steels with excellent weldability and workability. The higher corrosion resistance means the lower general corrosion rate in a high concentration sulfuric acid environment when an exhaust gas temperature is lower than sulfuric acid dew point. The superior local corrosion resistance in an exhaust gas environment containing HCl is also necessary.

## 4. Corrosion resistant steels for smokestacks and their corrosion resistance

### 4.1 Corrosion resistant stainless steels for heavy oil fired smokestacks

Any standard corrosion test methods to evaluate corrosion resistance of smokestack materials have not been established yet. In order to determine the compositions of the simulated solutions for smokestacks, water-soluble compositions were extracted from the deposits sampled at the internal wall of the smokestack. As a results it was found that a large quantity of $SO_4^{2-}$ and $NH_4^{3+}$ were contained with hundreds to thousands ppm of $Cl^-$ and $Fe^{3+}$ in the deposits. General corrosion tests were conducted in sulfuric acid and in (sulfuric acid + $Cl^-$ + $Fe^{3+}$) solution.

Local corrosion tests were also conducted in (sulfate +$Cl^-$ + $Fe^{3+}$) solution.

Consequently, it was concluded that high corrosion resistant stainless steel requires general corrosion resistance index GI of 60 and above and local corrosion resistance index CI of 36 and above as shown in Fig. 2. Where, GI = -[Cr] + 3.6[Ni] + 4.7[Mo] + 11.5[Cu], CI = [Cr] + 0.4[Ni] + 2.7[Mo] + [Cu] + 18.7[N]. Also, in order to simulate $SO_2$/water dew point environment of actual smokestack, an alternating dry-wet gas corrosion testing apparatus was developed as shown in Fig. 3. The cyclic temperature pattern in the gas environment is shown in Fig. 4. Gas corrosion tests in alternating dry wet gas environment with $SO_2$ gas of 500 to 2000 ppm were conducted. It was concluded that corrosion resistance index SCI {[Cr] + 2.1Mo + 1.2 [Cu]} requires 20 and above (Fig. 5). Stainless steels satisfy these value are YUS260 and YUS270 with the basic composition of 20Cr-15Ni-3Mo-1.5Cu-0.15N and 20Cr-18Ni-6Mo-0.7Cu-0.2N respectively. Table 1 shows the chemical compositions and mechanical properties of both steels, in comparison of those with SUS316L. Corrosion products formed over austenitic stainless steel was dark green thin films with homogeneous thickness and high water absorbency. Chemical analysis results showed that a significant proportion of S as well as of Fe and Ni was contained in surface corrosion products formed over austenitic stainless steels. The oxide film was formed beneath

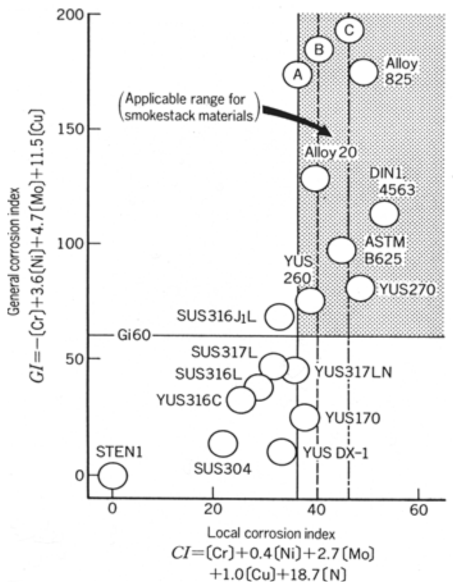


**Fig. 2.** Location of various materials and area for possible application of smokestack materials in CI-GI map "From the report 1)"

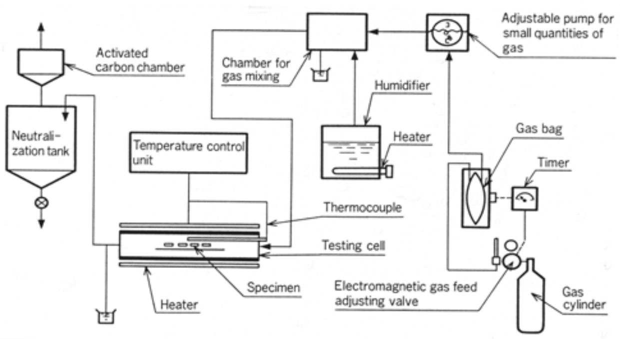


**Fig. 3.** Alternating dry-wet gas corrosion testing apparatus "From the report 1)"

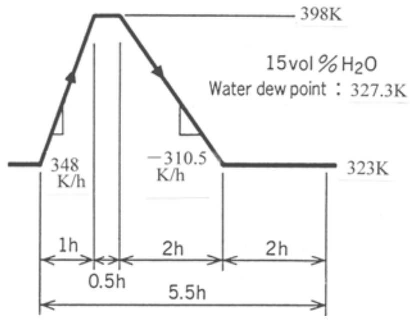


**Fig. 4.** Cyclic temperature pattern in the testing cell "From the report 1)"

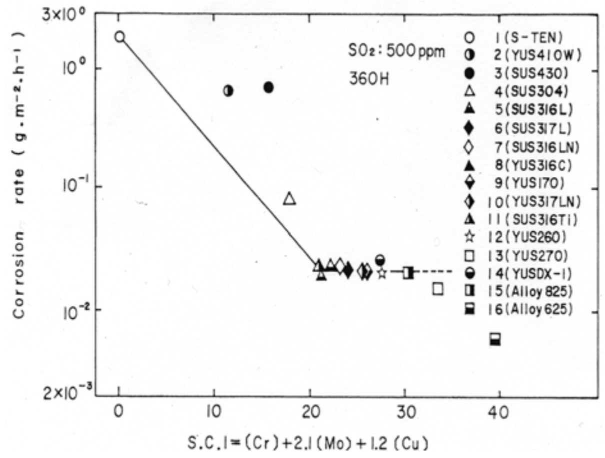


**Fig. 5.** Relation between corrosion rate and SCI of tested materials "From the report 8)"

the S rich surface. Fig. 6 shows the AES analysis of surface film formed over austenitic stainless steels after eliminating corrosion products from surface. AES analysis results indicated that the thickness of oxide film for YUS260 and SUS304 was 350 and 1200 Å, respectively. The YUS260 with a thinner oxide film layer exhibited better corrosion resistance than the SUS304 with a thicker oxide film layer. The ratios of Cr and Ni to Fe in the oxide film were appreciably higher than those in the substrate for SUS304. The S level of surface films formed over YUS260 was 2 at% and was only one six that formed over SUS 304. It can be concluded that YUS260 with super corrosion resistance against corrosion in alternating dry wet environment with $SO_2$ gas yielded a thin surface film with shallow S penetration "From the report 8)". Stress corrosion cracking resistance was evaluated by SSRT and U bend test. Fig. 7 shows SSRT testing results of stainless steel in solution simulating heavy oil and coal

**Table 1. Chemical compositions and mechanical properties of YUS260 andYUS270 "From the report 1)"**

| Material | Chemical compositions (%) | | | | | | | | | | Mechanical properties | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | P | S | Ni | Cr | Mo | N | Cu | 0.2% proof stress (MPa) | Ultimate tensile strength (MPa) | Elongation (%) | Hardness (HB) |
| YUS 260 | 0.020 | 0.50 | 0.50 | 0.022 | 0.001 | 15.31 | 20.37 | 3.20 | 0.19 | 1.70 | 382 | 736 | 50 | 172 |
| YUS 270 | 0.014 | 0.55 | 0.57 | 0.017 | 0.001 | 17.98 | 20.19 | 6.26 | 0.22 | 0.67 | 363 | 755 | 51 | 170 |
| SUS 316L | 0.020 | 0.54 | 0.83 | 0.026 | 0.004 | 12.15 | 17.50 | 2.20 | - | - | 255 | 549 | 57 | 164 |

**Table 2. Chemical compositions of welding material for YUS260 "From the report 1)"**

| Welding material | Welding method | Chemical compositions | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | Si | Mn | P | S | Ni | Cr | Mo | Cu | N |
| YUS 260 Flux cored wire $\phi$1.2 | FCAW | 0.036 | 0.61 | 0.90 | 0.024 | 0.003 | 16.98 | 19.48 | 3.87 | 1.50 | 0.10 |
| YUS 260 Welding rod $\phi$3.2 | SMAW | 0.037 | 0.24 | 1.47 | 0.022 | 0.009 | 15.28 | 20.07 | 4.30 | 1.54 | 0.10 |

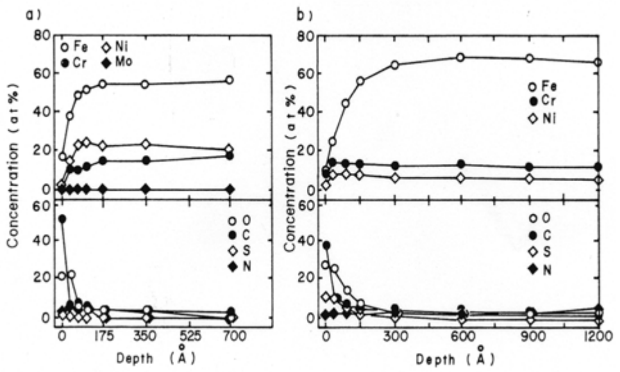

**Fig. 6.** AES analysis of surface film formed over austenitic stainless steels after eliminating corrosion products from surface, 500ppm $SO_2$, 360h, a)YUS260, b)SUS304 "From the report 8)"

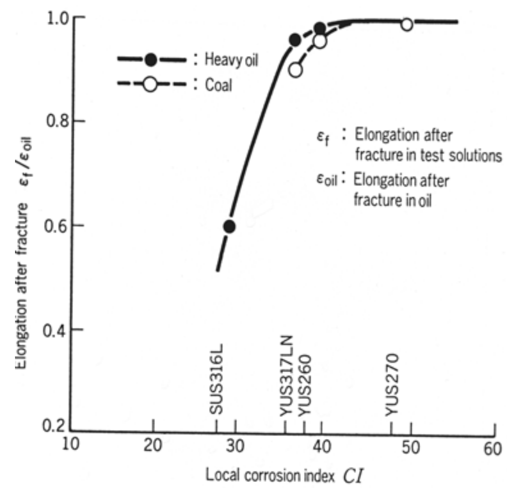

**Fig. 7.** SCC susceptibility of stainless steels in Simulated solutions for smokestack "From the report 1)"

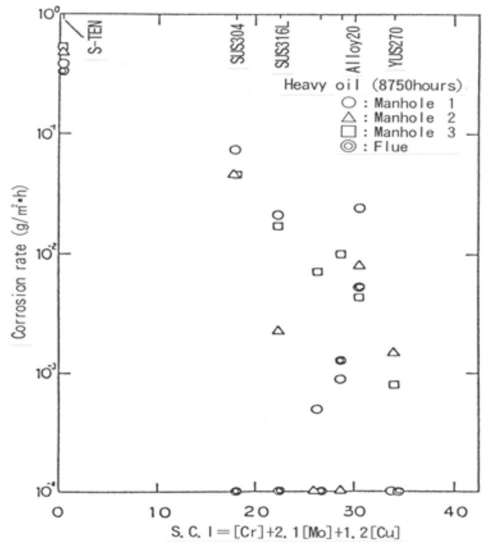

**Fig. 8.** Relation between corrosion rate in heavy oil fired steel stack, 8760h "From the report 9)"

fired smokestacks. It is apparent from this figure that $\varepsilon_f / \varepsilon_{oil}$ reaches to 1 for YUS260 and YUS270 in both solutions and that the SCC susceptibility is extremely low. Further, it was confirmed that the stress corrosion crack was not initiated after 1440 hrs in a result of stress corrosion crack test using U bend specimen.

In the case of the use of both stainless steels as the lining material, the thickness of the stainless steels is 3 to 5 mm. The semi-automatic $CO_2$ gas shielded arc welding method is considered to be suitable from the view points of economy and workability. A flux cored wire FCW and a shielded arc welding rod with chemical compositions similar with YUS260 base metal were developed "From the report 1)". Chemical compositions of the welding materials are shown in Table 2. Furthermore the results of the tensile tests, bending tests and impact tests on welded joints made by FCAW and SMAW were all satisfactory. Corrosion resistance of the welded joint is as high as that of base metal.

Results of field exposure testings for both steels under actual smokestack environment at each smoke source are compared with those of other steels. Fig. 8 shows that corrosion Index SCI gained from alternating wet and dry environment with $SO_2$ gas is well applicable for evaluation of steel stack steels in actual environments. It is also apparent from Fig. 9 that corrosion rates of both steels are very low at the top, manhole and duct and are evaluation of steel stack steels in actual environments. It is also apparent from Fig. 9 that corrosion rates of both steels are very low at the top, manhole and duct and are less than 0.001 mm/year. They are applicable to the top of the smokestack, bottom hopper, manhole, general stack cylin-

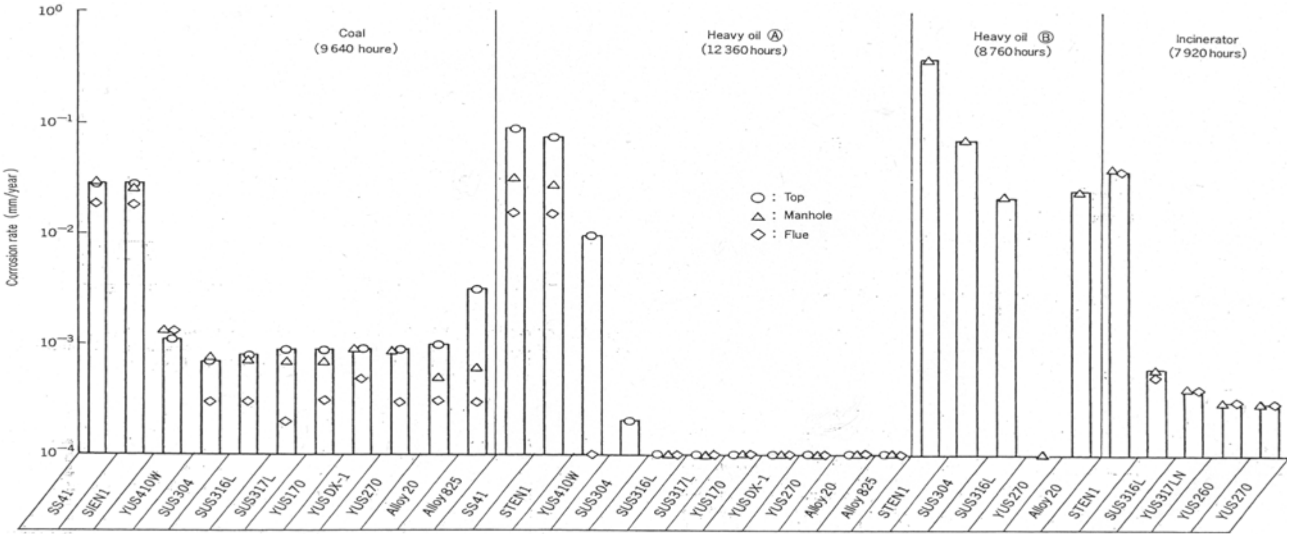


**Fig. 9.** Corrosion rates of various materials exposed in various kind of actual steel stacks "From the report 1)"

der and inner cylinder of RC smokestack.YUS260 has been applied mostly to heavy oil fired smokestacks in quantity of over than 500 tons. YUS270 has been applied to coal fired smokestacks. They are applicable to the top of the smokestack, bottom drain hopper, manhole, general stack cylinder and inner cylinder of RC smokestack. YUS260 has been applied mostly to heavy oil fired smoke-stacks in quantity of over than 500 tons. YUS270 has been applied to coal fired smokestacks.

### 4.2 Newly developed corrosion resistant steel for LNG fired smokestacks

In recent years the LNG fired combined cycle thermal power generation plant has been constructed because of environmental problems, fuel diversification, etc. The LNG fired smokestacks conventionally use cylinders lined with corrosion resistant inorganic materials or those with stainless steel clad steel. However, cylinders with in-organic material lining require considerable cost and time for maintenance, while the stainless steel clad cylinders with high corrosion requires a large amount of initial investment. Therefore, we have developed new corrosion resistant steel, WELACC5 which can be used for long term with maintenance free and its economically efficient with initial investment. This steel is a low alloy steel with basic composition of 5Cr-0.3Cu-0.3Ni as shown in Table 3. Corrosion resistance can be improved by adding Cr, and resistance for rust spreading by adding Cu and Ni. The main composition of an exhaust gas from the LNG combined cycle smokestack is 6 to 10 Vol. % for $H_2O$, 3 Vol. % for $CO_2$ 14 Vol. % for $O_2$, and 73 to 77 Vol. % for $N_2$. The inlet temperature of smokestack is 373 to 383 K in steady state operation and about 408 K in by pass operation.

If alternating dry-wet cycle is loaded with DSS operation, corrosion caused primarily due to $CO_2$. Therefore, corrosion resistance was evaluated by various corrosion tests conducted for developed steels based on alloy design under water dew point corrosion environment in by pass operation and alternating dry-wet corrosive environment.

**Table 3. Chemical compositions and mechanical properties of WELACC5 "From the report 2)"**

| Material | Chemical compositions (mass %) | | | | | | | | Mechanical properties | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | P | S | Cu | Ni | Cr | 0.2% proof strength (MPa) | Tensile strength (MPa) | Elonga-tion (%) | Charpy impact energy 273 K (J) |
| WELACC 5 | 0.03 | 0.20 | 0.50 | 0.006 | 0.004 | 0.28 | 0.34 | 5.00 | 311 | 463 | 28 | L: 245<br>T: 206 |
| Spec. | ≦0.09 | ≦0.05 | 0.30/0.60 | ≦0.030 | ≦0.0030 | 0.15/0.50 | 0.15/0.50 | 4.00/6.00 | 245≦* | 400-510* | 18≦* | 27≦* |

* JIS rolled steel for welded structure SM 400 B (thickness: 12 mm)

Fig. 10 shows the effect of Cr content on corrosion rate on the basis of the results of alternating dry-wet $CO_2$ gas corrosion test. It can be indicated from this figure that addition of Cr is extremely effective to corrosion resistance of low alloy steel and that an addition of 5% Cr ensures corrosion resistance effectively "From the report 10)". From the surface observation results of exposed specimens after 14400 hrs in LNG fired smokestacks it can be considered that Cr suppress the dissolution of oxide film formed over the 5Cr steel "From the report 10)".

Fig. 11 shows that addition of Mo, Cu and Ni is effective to corrosion rate of this steel. Fig. 12 shows results of rust adhesion evaluation test. According to the figure, it is apparent that WELACC5 has higher rate of the sticky rust and lower rate of exfoliated rust than mild steel and 5Cr steel. It was revealed by observation of rust particles using transmission electron microscope that the rust is an agglomerate of the colloidal particles of ferroxi hydro oxide, and is composed of coarse particles with proceeded acicular crystallization and primary agglomerate with fine particles. It has further been confirmed that WELACC5 tends to produces fewer coarse particles than 5Cr steel. The EPMA analysis of the rust layer section that the sticky rust in WELACC5 contains the condensed Cu and Ni in addition to Cr."From report 6)". It can be concluded that 5Cr efficiently reduces corrosion rate and that 0.3Cu-o.3Ni improves adhesive property of corrosion products.

The WELACC5 was tapped in a converter before being subjected to rolling and heat treatment for the manufacture by way of trial with 4.5-30 mm thick steel plates and showed an excellent manufacturability. Mechanical properties of WELACC5 satisfy the standard value of SM400B steel (JIS G 3106 weld structural rolled steel plate) and is excellent for workability and cutability. As to welding materials, SUS309 of austenititic stainless steel is selected on the basis that weld strength is equivalent to that of SM400A. and no cold cracks occur without preheating. As for welding process, MAG, SMAW, EG and $CO_2$ gas semi-automatic welding process are applicable. There is no anxiety for hot crack of weld metal due to dissimilar

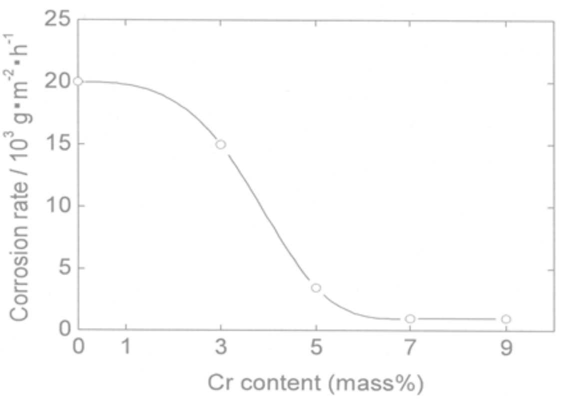


**Fig. 10.** Effect of Cr content on corrosion rate in alternating wet and dry $CO_2$ gas environment after 1000h.[10] "From report 10)"

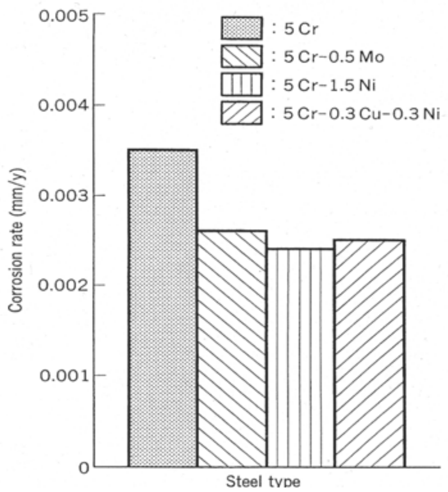


**Fig. 11.** Effect of alloying elements on corrosion rate of 5Cr steel "From the report 2)"

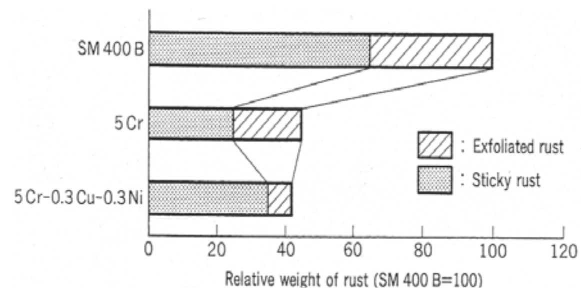


**Fig. 12.** Effect of alloying elements on rust weight "From the report 2)"

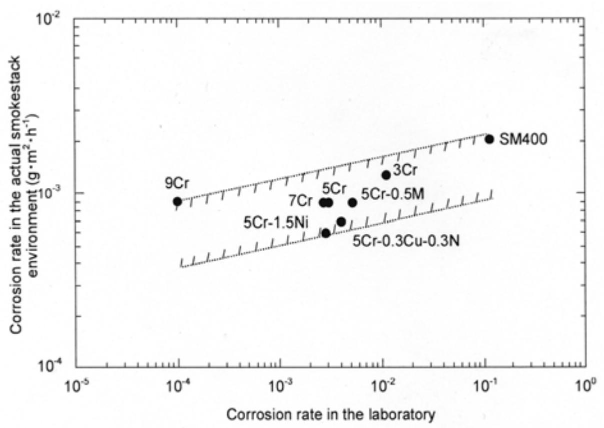


**Fig. 13.** Relation between corrosion rates under LNG fired smokestack environment and corrosion rates under alternating wet and dry $CO_2$ gas environment "From the report 2)"

metal welding and brittleness leading to crack due to martensite. Welded joint performance is in the level of SM400B steel. Fig. 13 shows results of exposure test in actual LNG fired smokestack. Corrosion rate of new corrosion resistant steel WELACC5 is 0.0007 mm/year, which is approximately one thirds of that of SM400B steel; proving the superior corrosion resistance. WELACC5 has already been applied to LNG combined actual smokestack in quantity of more than 5000 ton.

### 4.3 High corrosion resistant stainless steel for coal fired smokestacks

In coal fired thermal power station in these years, a single loop desulfurizer without cooling tower is becoming dominant to reduce cost. Accordingly, $Cl^-$ which has conventionally been absorbed by the cooling tower now may possibly be carried over into the exhaust gas, allowing chloride ions of high concentration flow into the smokestack. Seeing examples steelstacks in the world, Hastelloy C-276 clad material and Ti sheet are most frequently used for the internal cylinder of smokestacks under such high $Cl^-$ environment, material. However, as aforementioned these materials are expensive and difficulty of welding for clad materials. Therefore an austenitic stainless steel SUS310MoCu was newly developed to use in single loop desulfurization equipments. Chemical compositions and mechanical properties of NSL310MoCu are shown in Table 4. In laboratory accelerated corrosion tests, NSL310MoCu showed good corrosion resistance in smokestack simulated environments. In order to evaluate corrosion resistance of NSL310MoCu general corrosion tests were conducted in 1 to 50% $H_2SO_4$ aqueous solution with 20000 ppm$Cl^-$ which was simulated to environment for coal fired steel stack with single loop desulfurizer. Fig. 14 shows relation between corrosion rate and general corrosion Index Isc. $= -0.6[Cr]+[Ni]+1.5[Mo]+7.5[Cu]+122[N]$. In 50% $H_2SO_4$+20000ppm $Cl^-$. decrease of corrosion rate becomes smaller over the Isc value of 40. By optical microscopy general corrosion was observed on specimens after corrosion test under the environment. It can be concluded that over the 40 of corrosion index Isc. and addition of Cu is desirable against general corrosion under the sulfuric acid solution. From anodic polarization test in 5% $H_2SO_4$+20000 ppm $Cl^-$ environment it was found that NSL310MoCu was easily passivated. Multi crevice corrosion tests were also conducted under the 50% $H_2SO_4$+20000 ppm$Cl^-$ environment. Corrosion rate can be well correlated with Isc as shown in Fig. 15. Local corro-

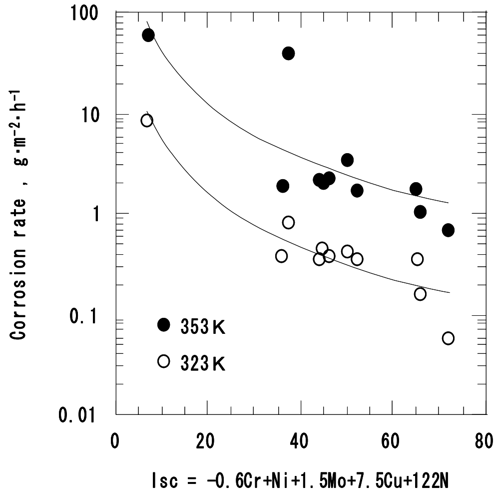


**Fig. 14.** Relation between general corrosion resistance index Isc. and corrosion rate, 50% $H_2SO_4$+20000ppm $Cl^-$, 24h "From the report 11)"

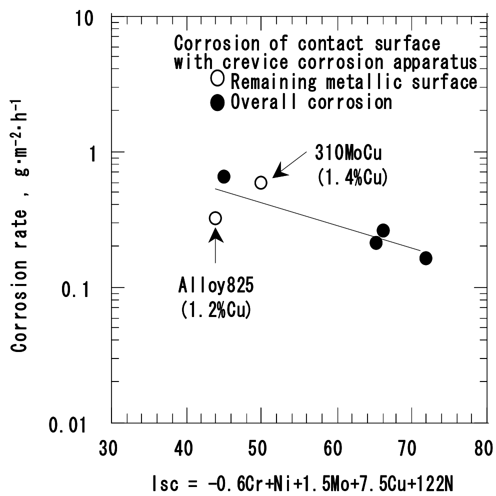


**Fig. 15.** Relation between general corrosion resistance index Isc and corrosion rate, 50% $H_2SO_4$+20000ppm$Cl^-$ "From the report 11)"

**Table 4. Chemical compositions and mechanical properties of NSL310MoCu "From the report 3)"**

| Material | Chemical compositions (mass %) | | | | | | | | | | Mechanical properties | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | P | S | N | Cu | Ni | Cr | Mo | $\sigma_{0.2}$ (MPa) | $\sigma_B$ (MPa) | E (%) | Hv HV(10kg) |
| NSL310MoCu | 0.005 | 0.28 | 1.60 | 0.004 | 0.001 | 0.22 | 1.51 | 21.80 | 25.00 | 4.41 | 346 | 702 | 63 | 154 |

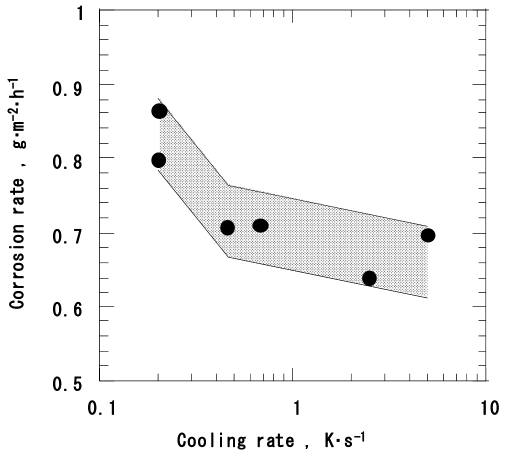


**Fig. 16.** Relation between cooling rate and corrosion rate 50% $H_2SO_4$+20000ppm $Cl^-$, 323K, 24h "From the report 11)"

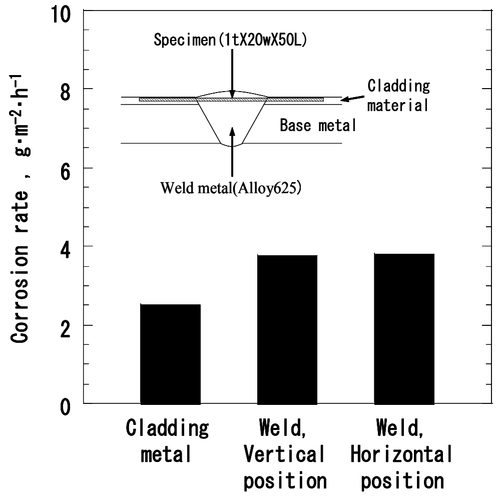


**Fig. 17.** Corrosion rate of clad metal "From the report 11)"

sion index was expressed CI=[Cr]+4.1[Mo]+24[N]. Effective value for local corrosion Index in 3% $H_2SO_4$ with 20000 ppm $Cl^-$ environment is 48. The corrosion rate of this steel in an operating coal fired smoke stack was 0.0001 mm/year and no crevice corrosion was observed. The corrosion resistance of the clad former with heat history was the same as that of the base metal, and it is fully applicable to low cost cladding. From Fig. 16 increase of corrosion rate with cooling rate over 0.4K/s-is small and applicable for clad steel with thickness of 15 mm.Inconel 625 was used for welding material. The weldability and properties of welded joints were reliable. The NSL310MoCu clad steel has successfully applied to coal fired smokestacks.

## 4. Summary

The environment in the internal cylinder of the smokestack varies significantly depending on the kind of fuel and the operating conditions. Since the smokestack is located at the end of downstream among air pollution preventive units, it is strongly affected by the type of upper stream equipment. If the maintenance free is a major premised, it is reasonable to apply corrosion resistant steels, such as stainless steels, that are superior in workability and weldability. In this paper newly developed steels such as YUS260 and YUS 270 for heavy oil fired steel stack, low alloy steel,WELACC5 for LNG fired steel stack and NSLMoCu for coal fired steel stack were evaluated. These steels have successfully applied for actual steel stacks. Development of low cost new corrosion resistant steels must be further continued in future. Among steel stack environments environment in incinerator is very complex and most aggressive. Correlation between the testing results by an alternating dry-wet gas corrosion testing and the testing results in an actual smokestacks must be examined further to establish an definite acceleration test method for evaluating corrosion resistance of internal cylinder materials under the smokestack environment.

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