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# New S-TEN<sup>™</sup>1: An Innovative Acid-Resistant Low-Alloy Steel

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# Abstract

New S-TEN<sup>TM\*</sup>1, a corrosion resistant low alloy steel (CRLS) was developed. Based on the conventional S-TEN<sup>TM</sup>1, a classic and standard CRLS for sulfuric acid dew corrosion, its corrosion resistance against acid containing chlorides such as hydrochloric acid was drastically improved by Nippon Steel's novel alloy-design technology. As an economical countermeasure against acid dew corrosion, new S-TEN<sup>TM</sup>1 is being widely used for plants such as power stations, waste incinerators, industrial refuse furnaces, and various so-called eco-plants, in which hydrochloric acid dew corrosion as well as sulfuric acid dew corrosion is anticipated. New welding materials for new S-TEN<sup>TM</sup>1 were also developed, which show equivalent corrosion resistance and solve selective corrosion of welded metal.

#### 1. Introduction

In the flue gas system of a boiler plant, gaseous acidic substances (such as  $SO_x$  and HCl) included in high-temperature exhaust gas condense into dew, depending on the moisture content of the gas and the surface temperature of a steel material to which it comes into contact, and corrode the material. This phenomenon is called acid dew corrosion. It constitutes a problem in equipment such as the flue gas treatment and heat recovering facilities for heavy oil-fired boilers and heating furnaces of chemical plants: more specifically, economizers, air preheaters, dust catchers (electrostatic precipitators and bag filters), gas ducts, the inner ducts of smokestacks and the like <sup>1.2)</sup>. As is described below, acid dew corrosion caused by  $SO_x$  and/or HCl occurs lately also in waste incineration plants and similar<sup>3)</sup>.

The environments of acid dew corrosion are roughly classified according to the substance burned at the plant. **Table 1** shows the content levels of corrosive components in the flue gas of plants burning different substances (fuels), principal acid condensations and the ranges of their dew points<sup>3-5</sup>. Sulfuric acid dew corrosion occurs in

boilers that burn heavy oil or coal, in so-called water corrosion in boilers burning LNG, which contains little S or Cl<sup>5)</sup>, and sulfuric and hydrochloric acid dew corrosion in waste incineration and recycling plants<sup>3)</sup>.

Nippon Steel Corporation has anticipated the needs for measures against these types of corrosion, as the forerunner of the industry, and developed and commercialized corrosion-resistant steel materials for applications to plants burning various kinds of fuels. In the period of Japan's high economic growth in the 1960s and thereafter, steelmakers developed sulfuric acid-resistant steels as countermeasures against sulfuric acid dew corrosion of heavy oil-firing boilers. At that time, Nippon Steel developed a steel resistant to sulfuric acid dew corrosion, S-TEN<sup>TM</sup>1, on the basis of COR-TEN steel, and put successfully commercialized the product <sup>6,7)</sup>. In the 1990s, water corrosion newly became a problem as a result of fuel shift of thermal power plants to LNG. As a response to this, the company developed a corrosion-resistant cold-rolled steel sheet product<sup>8)</sup> for air heater elements of gas-fired boilers and a corrosion-resistant heavy plate product, WELACC5<sup>TM 9)</sup>, for combined cycle power plants, and launched them into the market.

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<sup>\*</sup> S-TEN and WELACC5 are Nippon Steel Trademarks

	Table 1 Types of	aciu uew corrosion		
	Heavy oil fired	Coal fired	LNG fired	Refuse incinerators and
	power plants	power plants	power plants	industrial refuse furnaces
Level of corrosive components in exhaust gas				
SO <sub>x</sub>	100-2,000ppm	100-2,000ppm	-	20-150ppm* <sup>3)</sup>
HCl	<1ppm	Not available	-	300-1,500ppm* <sup>3)</sup>
H <sub>2</sub> O	5-10%	5-10%	10-20%	10-50%
Acid condensation				
$H_2SO_4$	+++ *1)	+++	-	++
HCl	_ *1)	-	-	+++
H <sub>2</sub> O	-	-	+++	(++)
Cl <sup>-</sup> level in ashes / corr. products	-	Low	Low-high*2)	Extremely high
Typical ranges of dew points	100-150°C	100-150°C	50-60°C	Sulfuric acid : 100-150°C
	(sulfuric acid)	(sulfuric acid)	(water)	Hydorchloric acid : 50-80°C
Facilities nesessary for	Air preheaters	Air preheaters	Air preheaters	Rapid coolers
protection against acid dew corr.	Ducts, stacks	Ducts, GGH	Ducts, stacks	Bug-filters
				Ducts, stacks

Table 1 Types of acid dew corrosion

\*1) +++ : dominant and aggressive, - : negligible

\*2) At air-preheaters, high chlorides from air-born salt were detected. \*3) Waste incineration plant

Corrosion condtions after WFGD processes are not listed above.

Towards the realization of a sustainable and recycling-based society, reduction of environmental loads and enhancement of resource productivity have come to be strongly aspired in the production and consumption sectors recently, and as a result, the subject materials of recycling have been rapidly diversified. However, many of the materials to be recycled such as waste incineration ash and waste tires contain chloride ions. While waste incineration plants and recycling plants for various materials were constructed taking advantage of the recent rapid advance in environment protection technologies, there arose an increasing number of cases where the flue gas treatment facilities of those plants were corroded because of a hydrochloric acid environment.

In October, 2002, Nippon Steel successfully developed new S-TEN<sup>TM</sup>1 as a new steel product that is resistant to the hydrochloric acid dew corrosion occurring in the flue gas treatment facilities of waste incineration plants and recycling plants for various materials. Since then, the company has sold the newly developed steel under the trade name of S-TEN<sup>™</sup>1, replacing conventional S-TEN<sup>™</sup>1. In the first year, more than 5,000 t of new S-TEN<sup>TM</sup>1 was sold to more than 100 customers and, by virtue of its new characteristics, its application is expanding to fields other than environment-related facilities as well. This paper describes the properties and advantages of new S-TEN<sup>™</sup>1.

### 2. Acid Dew Corrosion of Flue Gas Treatment Equipment

#### 2.1 Heavy oil- and coal-burning boilers (sulfuric acid dew corrosion)

Dew corrosion occurs in the flue gas treatment equipment (a gas duct, an air preheater, a smoke stack, etc.) of thermal power plants and waste incineration plants as a result of the condensation of corrosive components included in the exhaust gas. In the case of a boiler that burns heavy oil or coal, S in the fuel turns into sulfur oxide  $(SO_x)$  and, if the inner surface temperature of a steel plate of the smoke duct is lower than the dew point of sulfuric acid, sulfuric acid condenses into dew, and there occurs sulfuric acid dew corrosion. The condensation is a phenomenon resulting from the thermal and mass transport from the flue gas to the steel plate surface, and the driving force of the condensation reaction is the differences in temperature and concentration between the gas and the surface. Generally speaking, even when the concentration of SO<sub>3</sub> in flue gas is as low as 1 ppm, the dew point of sulfuric acid becomes higher than 100°C, and therefore, it is difficult to avoid the occurrence of sulfuric acid dew corrosion in flue gas treatment facilities in operation. For this reason, sulfuric acid-resistant steels such as S-TEN<sup>™</sup>1 have been widely used for this kind of equipment.

#### 2.2 Waste incineration and recycling plants (sulfuric and hydrochloric acid dew corrosion)

Fig. 1 schematically illustrates how sulfuric and hydrochloric acid dew corrosion occurs in the flue gas system of a waste incineration plant. The exhaust gas from a waste incineration plant contains  $SO_x$ (50 to 1,000 ppm), HCl (100 to several thousand ppm) and moisture by a comparatively large percentage (30 to 50%), and thus, when the steel surface temperature of the flue gas treatment equipment is sufficiently lower than the dew points of sulfuric and hydrochloric acids, these acids form.



Fig. 1 Schematic diagram of acid dew corroion mechanisms (flue gas: SO<sub>3</sub>: 6ppm, HCl: 300ppm, H<sub>2</sub>O: 30%)

Heavy hydrochloric acid dew corrosion occurred in the inner duct (made of S-TEN<sup>TM</sup>2 steel) of the smokestack of a waste incineration plant after 2 years of a revamp for countermeasures against dioxin. The flue gas condition of the plant was the same as shown in Fig. 1. The temperature of the flue gas fell from 180 to 130°C after the revamp, and penetrating corrosion of 6-mm thick plates occurred in some portions of the inner duct in the 2-year period. The portions that suffered the heavy corrosion were welded joints with horizontal support plates and the portions around nozzles for inserting environment measurement probes, namely the portions where heat radiation was structurally large. On the other hand, the equivalent corrosion rate at the portions around the heavily corroded portions was approximately 0.1 mm/y, which indicates that S-TEN<sup>TM</sup>2 was resistant to corrosion.

What happened in the above case was, as is understood from Fig. 1, that, whereas the environment had been that of sulfuric acid dew corrosion only before the revamp, the condition for hydrochloric acid dew corrosion was added to the sulfuric acid dew corrosion environment at the low steel temperature portions after the revamp.

**Photo 1** shows a sectional photomicrograph of a specimen that was covered with corrosion products, and was cut out from the smokestack inner duct. The corrosion product layer contained a large amount of water-soluble metal chloride salts (CaCl<sub>2</sub>, etc.), and the pH at the boundary surface with the steel substrate was 1.8, strongly acidic <sup>10</sup>. This indicates that, even when the condensation of hydrochloric acid itself does not occur, the environment at the boundary surface of a steel substrate covered with a corrosion product layer is turned locally into a hydrochloric acid environment by metal chloride salts depositing on the surface. As described above, the acid dew corrosion of flue gas treatment equipment such as that of a waste incineration plant where substances containing chlorides (or Cl) such as vinyl chloride are burned is characterized by the coincidence of dew corrosion of both sulfuric and hydrochloric acids.

Conventional sulfuric acid-resistant steel had a problem in that although its corrosion resistance was satisfactory in a sulfuric acid dew corrosion environment with a corrosion rate generally of 0.1 to



Photo 1 SE-image of the corroded inner cylinder and distribution of chlorides

0.2 mm/y, its corrosion rate in a hydrochloric acid dew corrosion environment was sometimes as high as 1 to 2 mm/y, as seen in the above case. In the case of austenitic stainless steel excellent in corrosion resistance, on the other hand, there were problems such as the following: its use in an acidic environment at 50 to 150°C with a high chloride ion concentration required careful attention because such use could lead to the occurrence of crevice corrosion and stress corrosion cracking; and the material and construction costs were too high for ducts or casings. Development of corrosion-resistant lowalloy steel excellent in the resistance to the dew corrosion of both sulfuric and hydrochloric acids has been in high demand for these reasons.

# **3.** Characteristics of New S-TEN<sup>TM</sup>1 Steel Sheets 3.1 Specification, size range and advantages

**Table 2** shows typical examples of the chemical compositions of conventional S-TEN<sup>TM</sup>1 and new S-TEN<sup>TM</sup>1. For the purpose of realizing excellent resistance to both sulfuric and hydrochloric acids on the basis of the chemical composition of a Cu-Sb steel system of conventional S-TEN<sup>TM</sup>1, a technology for combined addition of anticorrosion elements by small amounts was newly introduced in the new steel product, and its chemical composition was also optimized by other means.

**Table 3** shows the specifications (product types, chemical composition and mechanical properties) of new S-TEN<sup>TM</sup>1. Its advantages are as follows:

- (1) Resistance to hydrochloric acid has been significantly improved from that of conventional S-TEN<sup>TM</sup>1.
- (2) Resistance to sulfuric acid equal to or better that that of conventional S-TEN<sup>™</sup>1 has been secured.
- (3) Welding materials for new S-TEN<sup>™</sup>1 have been developed at

 Table 2 Chemical compositions of new S-TEN<sup>TM</sup>1

						(	mass%)
	С	Si	Mn	Р	S	Cu	Sb
Conventional S-TEN1	0.10	0.27	0.42	0.019	0.005	0.31	0.10
New S-TEN1	0.02	0.27	0.95	0.011	0.011	0.29	0.10

Other micro-elements may be contained for purposes.

Table 3 Specifications of new S-TEN<sup>TM</sup>1

Steel type	Thickness/size
Cold-rolled sheets	0.6mm or more to 2.3mm or under
Hot-rolled sheets and plates	1.6mm or more to 20mm or under
	Wall thickness :1.8mm or more
Electric resistance welded	to 10.5mm or under
pipe and tubes	Outside diameter :19mm or more
	to 114.3mm or under
(2)Chemical compositions	(massen)

	<u>^</u>					
С	Si	Mn	Р	S	Cu	Sb
≤0.14	≤0.55	≤1.60	≤0.025	≤0.025	0.25/0.50	≤0.15

(3)Mechanical properties (sheets and plates)

Tension test						
Yield strength	Tensile strength	Elongation	Test piece			
$(N/mm^2)$	$(N/mm^2)$	(%)	(JIS)			
≥235	≥400	≥23	No.5			

the same time, and as a result, the resistance to hydrochloric and sulfuric acids of welded joints has been greatly enhanced to be virtually the same as that of the base metal.

- (4) Mechanical properties and weldability as good as those of conventional S-TEN<sup>™</sup>1 have been secured.
- (5) Types of products as widely varied as those of conventional S-TEN<sup>™</sup>1 have been made available.
- (6) Marketing framework for availability as good as that of conventional S-TEN<sup>™</sup>1 such as sales from stock through distributors has been arranged.

This paper focuses mainly on the material properties of new S-TEN<sup>TM</sup>1 steel sheets and plates and their welded joints. As for the material properties of new S-TEN<sup>TM</sup>1 steel pipes, see another paper in the present issue <sup>11</sup>).

# 3.2 Physical properties

**Table 4** shows the physical properties of new S-TEN<sup>TM</sup>1. The specific heat, heat conductivity and coefficient of thermal expansion are in the same level as those of JIS SS 400, and therefore, new S-TEN<sup>TM</sup>1 is applicable to equipment designed for SS 400.

# 3.3 Chemical composition, microstructure and mechanical properties

**Photo 2** shows a typical microstructure of a hot-rolled plate of new S-TEN<sup>TM</sup>1, and **Table 5** the results of tensile and bending tests of the developed steel at room temperature. The specification of new S-TEN<sup>TM</sup>1 does not specify toughness, but it has a toughness sufficiently higher for low-alloy steel for welded structures for plant applications.

Table 4 Physical properties of new S-TEN<sup>TM</sup>1

Temp.	Youngs	Specific	Heat	Coefficient of
	modulus	heat	conductivity	thermal expansion
				20°C
(°C)	(GPa)	$(J/(kg \cdot K))$	$(W/(m \cdot K))$	(×10 <sup>-6</sup> /°C)
25	207.4	0.450	44.2	-
100	203.7	-	-	12.8
200	198.3	0.491	45.5	13.2
300	192.0	-	-	13.6
400	184.0	0.532	36.8	14.0



Photo 2 Typical microstructure of new S-TEN<sup>TM</sup>1

Table 5 Results of tension test and bending test

		Bending test			
Thickness	Yield point	Tensile	Elongation	Test	R=1.5t
	1	strength	υ		(t:thickness)
(mm)	(N/mm <sup>2</sup> )	$(N/mm^2)$	(%)	piece	
2.3	300	436	37		-
6	320	432	42	JIS	-
12	384	446	42	No.5	-
16	417	458	43		Good

## 4. Corrosion Resistance of New S-TEN<sup>TM</sup>1 Steel Sheets and Plates

#### 4.1 Corrosion resistance in sulfuric acid dew corrosion environment

**Table 6** shows the chemical compositions of the specimens used for immersion tests simulating different vapor/liquid equilibrium conditions of a sulfuric acid-water system. **Fig. 2** shows the results of the tests. The graph indicates that the resistance of new S-TEN<sup>TM</sup>1 to sulfuric acid dew corrosion is equal to or better than that of conventional S-TEN<sup>TM</sup>1. The steels were submitted to another corrosion test under the condition of 70°C and 50% sulfuric acid, where the corrosion was the largest in the tests of Fig. 2, and **Fig. 3** shows

Table 6 Chemical compositions of test coupons

							(mas	s%)
С	Si	Mn	Р	S	Cu	Cr	Sb	Ti
0.15	0.14	0.70	0.010	0.010				
0.15	0.14	0.70	0.010	0.010	-	-	-	-
0.10	0.07	0.42	0.010	0.005	0.21		0.10	
0.10	0.27	0.42	0.019	0.005	0.51	-	0.10	-
0.00	0.07	0.05	0.011	0.011	0.00		0.10	
0.02	0.27	0.95	0.011	0.011	0.29	-	0.10	-
	C 0.15 0.10 0.02	C         Si           0.15         0.14           0.10         0.27           0.02         0.27	C         Si         Mn           0.15         0.14         0.70           0.10         0.27         0.42           0.02         0.27         0.95	C         Si         Mn         P           0.15         0.14         0.70         0.010           0.10         0.27         0.42         0.019           0.02         0.27         0.95         0.011	C         Si         Mn         P         S           0.15         0.14         0.70         0.010         0.010           0.10         0.27         0.42         0.019         0.005           0.02         0.27         0.95         0.011         0.011	C         Si         Mn         P         S         Cu           0.15         0.14         0.70         0.010         0.010         -           0.10         0.27         0.42         0.019         0.005         0.31           0.02         0.27         0.95         0.011         0.011         0.29	C         Si         Mn         P         S         Cu         Cr           0.15         0.14         0.70         0.010         0.010         -         -           0.10         0.27         0.42         0.019         0.005         0.31         -           0.02         0.27         0.95         0.011         0.011         0.29         -	C         Si         Mn         P         S         Cu         Cr         Sb           0.15         0.14         0.70         0.010         0.010         -         -         -           0.10         0.27         0.42         0.019         0.005         0.31         -         0.10           0.02         0.27         0.95         0.011         0.011         0.29         -         0.10



Fig. 2 Immersion test results under the  $SO_3$ -10%H<sub>2</sub>O equilibrium state of sulfuric acid



Fig. 3 Immersion test results under 50%H,SO<sub>4</sub> at 70°C

NIPPON STEEL TECHNICAL REPORT No. 90 JULY 200
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Test location		Ljungstrom type air preheater					
			at coal-fire	ed power pl	ant		
Co	upon attachment		Radial seal at cold-end side				
	Flue gas temperature	130°C	Flue	SOx	455ppm(dry)		
Conditions	Inlet air temperature	30°C	Flue	H <sub>2</sub> O	5vol%		
	Dewpoint (estimate)	128°C	gas	0 <sub>2</sub>	3.6vol%		
	Coupon temperature	Not available	composition	$CO_2$	15.5vol%		
	Test duration	5 months (3.6kh)					
	Grade	Corrosion rate		Corrosion resistance			
Results	Conventional S-TEN1	0.12	mm/y	good			
	New S-TEN1	0.11	mm.y	good			

 Table 7 Results of field test in surlfuric acid dew point corrosion

the results. Heavy corrosion occurs even in stainless steel (JIS SUS 304, SUS 316L, etc.) under such a condition, but conventional S-TEN<sup>TM</sup>1 and new S-TEN<sup>TM</sup>1 showed excellent corrosion resistance under this condition. As another exposure test, coupon test pieces of the chemical compositions shown in Table 6 were attached to a radial seal at the cold-end side of a Ljungstrom type air preheater of a coal-fired power plant. **Table 7** shows the results. It is clear from these results that new S-TEN<sup>TM</sup>1 exhibits corrosion resistance equal to or better than that of conventional S-TEN<sup>TM</sup>1 in both the laboratory test and the real sulfuric acid dew corrosion environment.

#### 4.2 Corrosion resistance in hydrochloric acid corrosion environment

**Fig. 4** shows the results of immersion tests where specimens of various steels were immersed in 10.5 and 1% sulfuric acid solutions at 80°C. It is understood from the graphs that the resistance to sulfuric acid of new S-TEN<sup>TM</sup>1 is markedly better than that of conventional S-TEN<sup>TM</sup>1 especially in the 1% solution. Comparing new S-TEN<sup>TM</sup>1 with the SUS grade steels (with the suffix SS meaning stainless steel), it is seen here that the former is superior to the latter as the temperature and the concentration increase.

Dew corrosion by sulfuric and hydrochloric acids or sulfuric acid and metal chloride salts occurs in waste incineration plants and the like, as described earlier. In consideration of this, the authors investigated the influence of the addition amount of NaCl over the corrosion rate in a dilute sulfuric acid solution (0.3 N, or 1.5 mass %), and **Fig. 5** shows the results. Chloride ions exhibit an effect to decrease



Fig. 4 Immersion test results under HCl solutions at 80°C



Fig. 5 Effect of chlorides on corrosion rate of new S-TENTM1 in dilute  $\rm H_2SO_4$  solution

the corrosion rate in a dilute sulfuric acid environment on any of the steels tested. It is seen in the figure that new S-TEN<sup>™</sup>1 demonstrates excellent corrosion resistance not only in a pure hydrochloric acid environment but also in a dilute sulfuric acid environment containing chloride ions. Whereas austenitic stainless steel may suffer stress corrosion cracking (SCC) in a corrosive environment containing chloride ions, the mode of corrosion of new S-TEN<sup>™</sup>1, which is ferritic low-alloy steel, is general corrosion and the developed steel is free from the fear of SCC. This is another significant advantage of new S-TEN<sup>™</sup>1 as a steel material for plant applications.

**Fig. 6** shows the results of an exposure test at a dust collector duct of a coke oven plant. Saltwater is sprayed on stacks of coal, the raw material of coke, at coal yards near the sea in order to prevent the scattering of coal fine, and as a consequence, the exhaust gas from a coke oven plant includes fly ash containing considerable amounts of HCl and metal chloride salts, in addition to SO<sub>x</sub>. For this reason, the environment is presumed to be one of sulfuric or hydrochloric acid containing chloride ions. As seen in Fig. 6, new S-TEN<sup>TM</sup>1 has been confirmed to have corrosion resistance in a sulfuric and hydrochloric acid dew corrosion environment containing chloride ions superior to that of SS 400 and conventional S-TEN<sup>TM</sup>1.



Fig. 6 Corrosion loss in thickness of duct panels at coke oven gas, where sulfuric acid dew corrosion involving chloride-containing ashes

### 5. Welding Materials for New S-TEN<sup>TM</sup>1

#### 5.1 Welding materials<sup>12)</sup>

In order to realize excellent durability and reliability in a structure as a whole, it is essential that not only the steel materials (base metal) but also welded joints have good corrosion resistance. However, in the past, the corrosion resistance of the weld metal for S-TEN<sup>TM</sup>1 and other sulfuric acid-resistant steels was inferior to that of the base metal especially in an environment where the steel was totally immersed in a solution of sulfuric or hydrochloric acid. In consideration of this situation and starting from a concept that even matching of corrosion resistance between base metal and welded joints is ideal, Nippon Steel has developed new welding materials for new S-TEN<sup>TM</sup>1 jointly with Nippon Steel Sumikin Welding Co., Ltd. (NSSW). The developed welding materials realize corrosion resistance of weld metal equal to or better than that of base metal. NSSW sells covered arc welding electrodes (trade name: ST-16M) and flux-cored welding wires (seamless type, trade name: SF-1ST).

**Table 8** shows the mechanical properties of the welding materials in accordance with JIS Z 3111. These welding materials are characterized by having substantially the same alloy composition as the base metal of new S-TEN<sup>TM</sup>1, as seen in **Table 9**. The new welding materials bring about excellent mechanical properties, bead appearance and bendability. Their welding workability is equal to or better than that of conventional welding materials.

#### 5.2 Corrosion resistance of welded joints

Steel plates were welded using the welding materials shown in Table 9 under the conditions shown in **Table 10** to form the joints listed in **Table 11** for the purpose of comparing and evaluating the

Table 8 Mechanical pr	operties of	f welding	materials
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Welding		Tension test	Charpy impact test	
material	Yield point	Tensil strength	Elongation	Absorbed energy
	(MPa)	(MPa)	(%)	(J)
ST-16M	471	568	31	165 at 0°C
SF-1ST	581	640	27	71 at 0°C

Table 9 Chemical compositions of welded metals with new S-TEN<sup>TM</sup>1 (mass%)

Welding material	С	Si	Mn	Р	S	Cu	Sb
ST-16M	0.04	0.62	0.50	0.009	0.004	0.42	0.08
SF-1ST	0.05	0.60	1.41	0.012	0.013	0.39	0.10

corrosion resistance of the joints welded using the developed welding materials.

(1)Resistance to sulfuric and hydrochloric acids

**Photos 3** and **4** show the cross sections of the above specimen joints after an immersion test in a 20% solution of sulfuric acid at 40°C and another in a 10.5% solution of hydrochloric acid at 80°C, respectively. It is seen in the photos that the selective corrosion of weld metal observed in the joint welded with the conventional welding material (FC-1ST) after the immersion in the sulfuric and hydrochloric acid solutions did not occur in the joint welded with the developed flux-cored wire (SF-1ST).

(2)Corrosion resistance in hydrochloric acid pickling tank of hot dip galvanizing line

Hydrochloric acid pickling tanks used to be made of rubber-lined steel plates or FRP in most cases, but they have recently come to be made of S-TEN<sup>TM</sup>1 steel plates without coating for reasons of economical efficiency and ease of maintenance. Joints of new S-TEN<sup>TM</sup>1 steel plates welded under the conditions of Table 10 were immersed

Table 10 Welding conditions

Welding method	Diameter (mm)	Current (A)	Voltage (V)	Speed (mm/min)	Heat input (kJ/mm)	Shielding gas
SMAW	4.0	170	24	140	1.7	-
FCAW	1.2	280	30	300	1.7	CO <sub>2</sub>

Table 11 Welding joints tested

Welding method	Welding material	Base metal	Remarks
Shield metal	ST-16M	New S-TEN1	New
arc welding	ST-16	Conv. S-TEN1	-
(SMAW)	S-16	Mild steel (JIS SS 400)	-
Flux cored	SF-1ST	New S-TEN1	New
arc welding	FC-1ST	Conv. S-TEN1	-
(FCAW)	SF-1	Mild steel (JIS SS 400)	-



Photo 3 Cross-sectoin of welded joints after HCl immersion tests



Photo 4 Cross-sectoin of welded joints after 20%H<sub>2</sub>SO<sub>4</sub> immersion

in the hydrochloric acid pickling tank of a hot dip galvanizing line at the portion above a point where the acid bath in the tank was heated. **Photo 5** shows the appearance of the welded joint specimens after



Photo 5 Appearance of welded joints after 4 months immersion test in a HCl pickling pot



Photo 6 Cross-section of welded joints after 4 months immersion test in HCl pickling pot



Fig. 7 Corrosion loss in thickness of welded joints in acid pickling bath

### NIPPON STEEL TECHNICAL REPORT No. 90 JULY 2004

the above test, and **Photo 6** their cross sections. **Fig. 7** shows the corrosion thickness loss of the specimens. The authors have confirmed that the combination of new S-TEN<sup>TM</sup>1 and the developed new welding material, ST-16M, will solve most of the problems of the selective corrosion of weld metal that occurred in conventional welded joints.

# 6. Mechanism of Hydrochloric Acid Resistance of New S-TEN<sup>TM</sup>1

In an environment of a non-oxidizing acid such as sulfuric or hydrochloric acid, low-alloy steel dissolves in most cases actively, that is, without forming a protective coating film such as a passive film or a protective rust layer. The electrochemical impedance responses of new S-TEN<sup>TM</sup>1 and SS 400 in a 1-N solution of hydrochloric acid are plotted in **Fig. 8**. The plotting forms a clear semicircle for each of the steels, demonstrating that the rate of corrosion is determined by charge transfer reactions resulting from active dissolution, and the radius of the semicircle corresponds to the resistance to the corrosion reactions. The fact that the radius of the semicircle of new S-TEN<sup>TM</sup>1 is more than five times larger than that of SS 400 indicates that the corrosion reaction rate in the active anodic dissolution of new S-TEN<sup>TM</sup>1 is very low.

**Fig. 9** shows examples of polarization curves of the steels in a hydrochloric acid solution. It is seen here that both the anodic and cathodic reactions of new S-TEN<sup>™</sup>1 are more restrained. Studies of the authors have clarified that the restriction is strong especially on the active anodic dissolution. Whereas the excellent corrosion resistance of stainless and weathering steels owes to protective oxide films, the excellent hydrochloric acid resistance of new S-TEN<sup>™</sup>1



Fig. 8 Cole-Cole plots of new S-TEN<sup>TM</sup>1 in 1N HCl solution by EIS



Fig. 9 Polarization curves of new S-TEN<sup>TM</sup>1 in HCl solution

is realized not because of oxide films but directly controlling and inhibiting the dissolution reactions of the steel substrate using micro-alloying elements.

#### 7. Closing - Principal Applications

Because of its new characteristic of resistance to acids containing chloride ions, the developed new S-TEN<sup>TM</sup>1 steel has far wider fields of application than conventional sulfuric acid-resistant steels, which are resistant to a corrosive environment of sulfuric acid only. Thus, its application is expanding to such equipment as flue gas treatment facilities where acids containing chloride ions form and storage and/or transportation facilities for sulfuric and hydrochloric acids. There have been many cases of corrosion by sulfuric and/or hydrochloric acids especially among the flue gas treatment facilities in the field of resource recycling, and the developed steel is being used for the plant facilities in this field. New S-TEN<sup>TM</sup>1 is expected to further expand its application taking advantage of its unique characteristic of being excellent in resistance to hydrochloric acid, despite the small amounts of alloying elements, and yet as highly usable and readily available as mild steel (SS 400) products.

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