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Sulfuric Acid Dew Resistant Steel S-TEN 1 Tube

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Abstract

S-TEN 1, a corrosion resistant steel for sulfuric acid dew, has been widely used in flue gas treating equipment such as air preheaters, smoke stacks and ducts as a countermeasure for low temperature corrosion caused by sulfur oxides. The steel also shows excellent corrosion resistance to the corrosion problem at waste incinerating facilities, where hydrochloric acid dew corrosion resulting from lower-temperature waste gas, is anticipated. S-TEN 1 tube is a high-quality, economical steel tube made of the steel material having such high corrosion resistance and produced under the same quality control as that for power station boiler tubes. This paper outlines qualitative characteristics of S-TEN 1 tube.

1. Introduction

When sulfur (S) -containing fuels, including heavy oil, LNG, and coal, are burnt, sulfur oxides (SO_x) are produced, part of which is turned to SO_3. When exhaust gas temperature drops to below a dew point or when the gas is in contact with a low-temperature wall, SO_3 and H_2O, contained in the gas, are combined to form highly-concentrated sulfuric acid that corrodes steel. This is sulfuric acid dew corrosion, which severely corrodes not only carbon steel but also stainless steel unlike normal atmospheric corrosion.

It was discovered in the U.S. that Cu-added weatherproof steel can be used stably even in the sulfuric acid dew corrosion environment. In Japan as well, much research has been done on the influence of alloy elements on sulfuric acid dew corrosion using atmospheric corrosion resistant steel in around 1960. This resulted in developing more excellent corrosion-resistant steel[1)]. Particularly, S-TEN 1 steel[2)], developed by Nippon Steel, is most effective for use in the acid dew corrosion environment, because Cu and Sb, contained in the steel, respectively inhibit not only anodic reaction but also cathodic reaction by forming the film of Cu_2Sb on the steel surface. S-TEN 1 steel has been extensively used as steel plate and sheet products, and expanded its application to steel tubes since around 1980.

S-TEN 1 pipes are mostly used for large-diameter spiral pipes for stacks. However, small-diameter electric resistance welding (ERW) tubes are extensively applied to the air preheaters of boilers for power plants, waste incineration plants, and various heating furnaces. This ERW tube is a high-quality steel manufactured under strict quality control as in boiler tube for power generation. Additionally, with the intention of applying this steel not only to non-pressure sections but also to pressure sections, such as fuel economizers, Nippon Steel has obtained a permit to use this material based on “Technical standards for thermal power plants by Ministry of Economy and Trade and Industry (METI),” in 2001. This material was standardized as material “KA-STB380J1” in May, 2002.

This paper deals with the properties of S-TEN 1 ERW tube, of which demand is rapidly increasing.

2. Properties of S-TEN 1 Tube

2.1 Chemical composition, mechanical properties, and fracture tests

Table 1 (a) and **Table 1 (b)** respectively give the examples of the chemical composition and the mechanical properties of S-TEN 1 tube. Its tensile strength (TS) is designed over 380 N/mm^2, an intermediate strength between STB340 and STB410.

Photo 1 shows the flattening, reverse flattening, flaring, and flanging test results of S-TEN 1 tube, 45.0 mm in outside diameter and 3.2 mm in wall thickness. In all cases, it is found to have a good formability with no crack occurring in weld portion.

2.2 Tensile properties at elevated temperatures and stress-rupture properties

Fig. 1 (a) shows the results of the tension test of S-TEN 1 tube at

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Table 1 (a) Chemical composition of S-TEN 1 (analytical values of ladle steel)

(mass%)

	C	Si	Mn	P	S	Cu	Sb	Ni
Standard	≤0.14	≤0.55	≤0.70	≤0.025	≤0.025	0.25-0.50	≤0.15	≤0.50
Example	0.096	0.19	0.35	0.009	0.006	0.26	0.096	0.18

Table 1 (b) Mechanical properties of S-TEN 1 tube

	0.2% offset strength (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Hardness (HRB)
Standard of STB340	≥215	≥340	≥35	≤77
Standard of STB410	≥245	≥410	≥35	≤79
Standard of S-TEN 1	≥230	≥380	≥35	—
Example	281	415	52	70

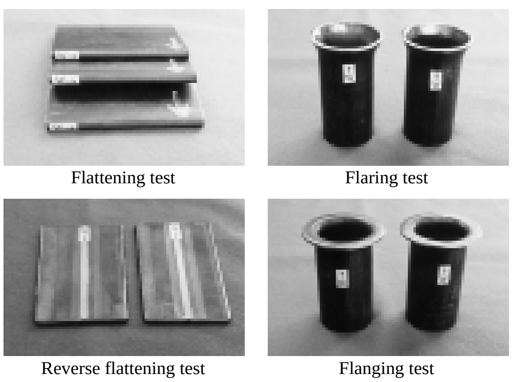


Photo 1 Fracture tests of S-TEN 1 steel tubes

temperatures from room temperature to 500˚C. Still more, the figure shows the minimum tensile strength and minimum 0.2% offset strength of S-TEN 1 tube, obtained at each temperature according to the technical standards of the thermal power plant by METI.

Fig. 1 (b) shows the relationship between load stress and fracture time relative to the stress rupture strength of S-TEN 1 base material. The test is carried out at between 400˚C and 500˚C in temperature for up to about 4,000 hours.

It is to be noted, however, that, the allowable tensile stress of S-TEN 1 tube depends not on stress rupture strength but on tensile strength at elevated temperature in the usable range of this steel material (below 425˚C), that is, in the non-stress-rupture temperature zone up to the maximum working temperature.

Fig. 1 (c) shows the allowable tensile stress of an S-TEN 1 tube (the technical standards of the thermal power plant by METI), obtained from the results of respective tests of tensile strength at elevated temperature and stress rupture strength. The allowable tensile stress is determined by tensile strength at room temperature and at elevated temperature or 0.2% offset strength at elevated temperature up to a maximum working temperature of 425˚C. The stress rupture strength is sufficiently high within this temperature range, and has no influence on the value of allowable tensile stress.

2.3 Workability of S-TEN tube[3]

S-TEN 1 steel can be welded in the same condition with ordinary steel on the same strength level, because it contains no alloy elements, such as chromium, and contains low carbon. The results of the tensile test, in which tubes were connecting-welded with each other, revealed that the tube was ruptured unexceptionally at the position of the base material, indicating good weld strength. In consideration of the corrosion resistance of the welded part, welding material FGC-55 (for atmospheric corrosion resistant steel use) made by Nippon Steel and Sumikin Welding Co., Ltd., was used.

Photo 2 shows how S-TEN 1 tubes, 31.8mm diameter × 2.9mm thickness, were 2.0D (65R) cold-bent. They showed a good work-

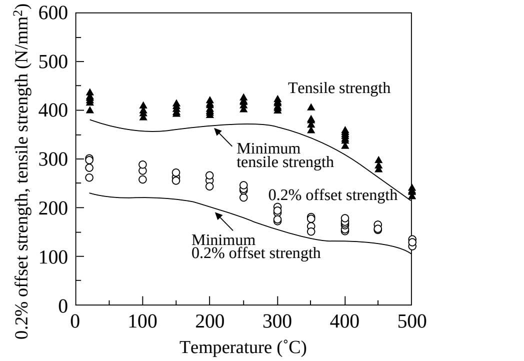


Fig. 1 (a) Tensile properties at elevated temperature for S-TEN 1 tubes

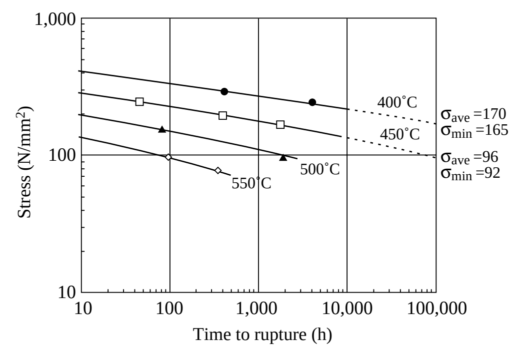


Fig. 1 (b) Stress rupture strength for S-TEN 1 steel

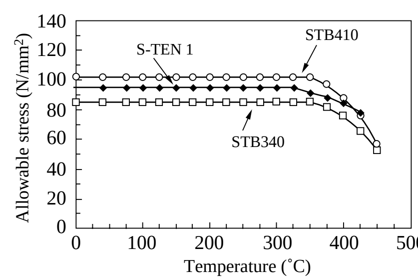


Fig. 1 (c) Comparison of allowable tensile stress of various kinds of steel

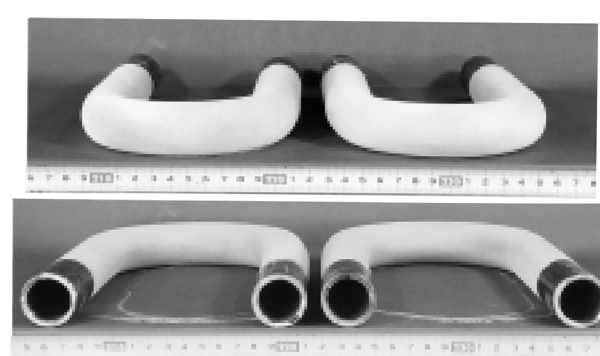


Photo 2 Cold-bending test (after color contrast penetrant examination)

ability in the color contrast penetrant examination after cold bending with neither cracking nor wrinkle observed. Since they are treated full-body normalizing, they are excellent in bendability regardless of the weld portion.

3. Corrosion resistance of S-TEN 1 tubes

3.1 Resistance to sulfuric acid dew corrosion

The tube type air preheater of a heavy oil-fired boiler is the typical equipments attacked by sulfuric acid dew corrosion[4]. Generally, this corrosion is more severe on the low temperature side. Two kinds of tubes, S-TEN 1 and carbon steel STB340-EG (60.3mm diameter × 3.2mm thickness × 6,080mm length) were arranged in the front row of a tube type air preheater. **Table 2** shows the results of investigation how they were corroded by extracting part of them after one year. The tubes are so structured that they contact combustion exhaust gas inside and preheated air outside. The estimated volume of corrosion of S-TEN 1 tube in one year was 0.04 mm to 0.22 mm, about 1/5 of 0.46 to 1.13 mm in the ordinary steel tube. The corrosion products inside the tube was composed mainly of $FeSO_4 \cdot H_2O$ and $FeSO_4 \cdot 4H_2O$, peculiar to sulfuric acid dew corrosion. This induces us to think that they were in the sulfuric acid dew corrosion environment. The foregoing results reveal that S-TEN 1 tube is excellent in the resistance to sulfuric acid dew corrosion.

3.2 Resistance to hydrochloric acid dew corrosion

The dew-point temperature of hydrochloric acid is lower than that of sulfuric acid, and considered to be lower than 72˚C. In the exhaust gas system of a waste incineration facility, hydrochloric acid dew corrosion sometimes occurs as exhaust gas temperature goes lower after improvement work for anti-dioxin measures. **Fig. 2** shows the respective resistances of various kinds of steel materials. It is apparent that S-TEN 1 (added Cu, Sb) tube is more excellent in resistance to hydrochloric acid than other sulfuric acid resistant steel (added Cu, high Cr) tubes.

Table 2 Results of actual tube tests of S-TEN 1 tubes

Test place	Tube type air preheater of heavy oil-fired boiler for power plant 'A'					
Test position	Front row of air preheater reheater low-temperature layer					
Test conditions	Exhaust gas temperature	124-130˚C	Gas composition	SO_x	360 ppm	
	Sulfuric acid dew point	130˚C		H_2O	About 10 %	
	Metal temperature	70-80˚C	Test period		4,808 hours	
			Start-stop frequency		35 times	
Test results	Kind of steel	Value measured of corrosion thinning (mm/4,808h) Maximum	Value measured of corrosion thinning (mm/4,808h) Average	Estimated yearly corrosion volume (mm/y)		
	S-TEN 1	0.12	0.02	0.04-0.22		
	STB340	0.62	0.25	0.46-1.13		

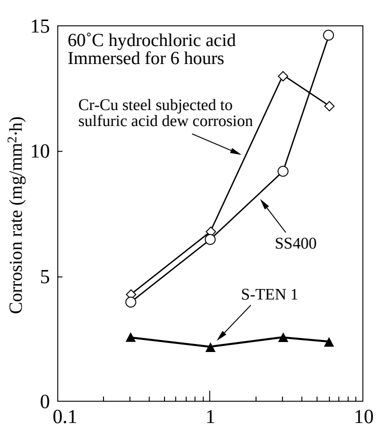
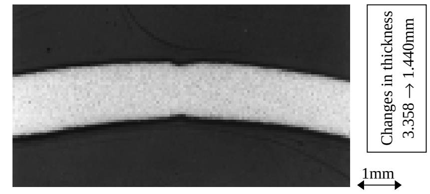
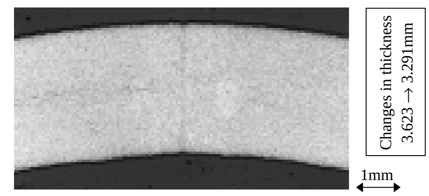


Fig. 2 Resistance to hydrochloric acid of S-TEN 1 steel



(a) ERW carbon steel (STB340) tube (after 4 hours)



(b) ERW S-TEN 1 tube (after 6 hours, 5 cycles)

Photo 3 Macro-structure after test of immersion in sulfuric acid at gas-liquid equilibrium state of sulfuric acid-water system

3.3 Acid resistance of weld portion of ERW tube

Test pieces, divided into half, with weld portions included were sampled from carbon steel tube (STB340) and S-TEN 1 tube, and immersed in a test solution of 40% H_2SO_4 at 60˚C. **Photo 3** shows how they were corroded after the immersion. Carbon steel tube STB340 was thinned by about 40%. However, S-TEN 1 ERW tube showed almost no trace of thinning with no selective corrosion observed at the weld portion.

4. Conclusion

As described above, S-TEN 1 ERW tube is economical in that it has excellent mechanical properties, workability, and corrosion resistance. Because it was standardized as material "KA-STB380J1" in Technical standards for thermal power plants by METI, it is expected to be extensively used for pressure section in the future.

Furthermore, the demand for S-TEN 1-EX, designed as fin material for extra-small-diameter tubing wound with fins, is also expanding because of its exceedingly excellent workability. In addition, a new kind of S-TEN 1 with its corrosion resistance greatly enhanced has also been developed to respond to the recent needs for resistance to chloride-induced corrosion.

As such, economical steel S-TEN 1 contributing to the environmental policy is always developing, and therefore expected to be used increasingly not only for steel tubes and plates and sheets but also for other applications in the future.

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