

## DESCRIPTION

STEEL WITH EXCELLENT SULFURIC ACID DEW-POINT CORROSION  
RESISTANCE AND AIR PREHEATER

5

## Technical Field

The present invention relates to a steel material with excellent sulfuric acid dew-point corrosion resistance used for an installation, such as a flue, a  
10 smokestack, a boiler air preheater, etc., which is exposed to an exhaust gas produced by combusting heavy oil, coal, refuse and the like.

## Background Art

15 When combusting a fuel containing a sulfur component, SO<sub>x</sub> is generated in the exhaust gas, combines with water in the exhaust gas and produces sulfuric acid. When the temperature of the exhaust gas falls and reaches the dew-point of sulfuric acid, i.e. about 160°C, the  
20 sulfuric acid gas condenses, sulfuric acid having a high concentration of about 80 to 90% in terms of sulfuric acid concentration deposits on the surface of a steel material, and thus corrosion is caused. Further, when the temperature of the exhaust gas falls close to 80°C,  
25 the condensation of water occurs and sulfuric acid having relatively low concentration of about 40 to 50% in terms of sulfuric acid concentration is formed and the corrosion accelerates. That is, as conditions where a steel material is corroded by condensed sulfuric acid,  
30 there are two conditions as shown in Fig. 1; one is the condition of a relatively high temperature and high concentration and the other is the condition of low temperature and low concentration.

To cope with the problem of the sulfuric acid dew-point corrosion, a steel material which demonstrates  
35 corrosion resistance in a sulfuric acid environment has been developed. For example, as disclosed in Japanese

Examined Patent Publication No. S43-14585, a low alloy steel to which Sb and Cu, which are effective in sulfuric acid corrosion resistance, are added in combination has been practically used.

5           However, the conventional steel has not been able to secure the corrosion resistance simultaneously under the above-mentioned two corrosion conditions (one condition being near 160°C and 80 to 90% in terms of sulfuric acid concentration, the other condition being near 80°C and 40  
10       to 50% in terms of sulfuric acid concentration). For that reason, there has been a problem that the conventional steel has not always demonstrated a prescribed corrosion resistance in a plant which undergoes starting and stopping repeatedly and is  
15       frequently exposed to cycles ranging from a high temperatures to a low temperature.

#### Disclosure of the Invention

20           The present invention, in view of the above situation, provides a steel material capable of securing excellent corrosion resistance over the temperature range from a high temperature to a low temperature under a sulfuric acid dew-point corrosive environment, and an air preheater using the steel material.

25           To tackle the above challenge, the present inventors produced test materials having various steel compositions, carried out corrosion test under the total four conditions composed of: two conditions of (a) a sulfuric acid concentration of 40% and a temperature of  
30       60°C and (b) a sulfuric acid concentration of 50% and a temperature of 80°C as the low temperature conditions; and the other two conditions of (c) a sulfuric acid concentration of 80% and a temperature of 140°C and (d) a  
35       sulfuric acid concentration of 90% and a temperature of 160°C as the high temperature conditions, and evaluated the corrosion resistance of the test materials by the maximum corrosion rate under the four conditions. As a

result, the present inventors found that, with the steel compositions according to the prior art, even though the corrosion resistance was improved under either a low temperature condition or a high temperature condition, it was difficult to obtain satisfactory corrosion resistance under all conditions, and to attaining this, it was necessary to design a new steel composition exceeding that of the prior art.

The alloying elements which play major roles in the present invention are the three elements of Si, Cu and Sb. Fig. 2 shows the relation between the maximum corrosion rate and each content of Si, Cu and Sb under the above four conditions. From the figure, it is understood that, macroscopically, the corrosion rate tends to lower as the Si amount increases. However, the tendency is limited to the case where both Sb and Cu coexist, and when either Sb or Cu is not contained, even though the Si amount is abundant, it is impossible to obtain satisfactory corrosion resistance under all conditions from a low temperature to a high temperature.

That is, the present inventors found that, even though the single addition of one or more of Si, Sb or Cu was effective under any of the conditions, it was not successful to obtain the targeted corrosion resistance under the all conditions, and, for solving the above-mentioned challenge, it was indispensable to add the three elements in combination. In the present invention, the required amounts of Si, Cu and Sb are specified to be not less than 1.2%, not less than 0.05% and not less than 0.01%, respectively.

The next important element is C. Fig. 3 shows the corrosion rates of the steel materials when C contents are varied in the above compound system containing Si, Cu and Sb. From the figure, it was found that, however well the combined effect of the above-mentioned three elements might be utilized, when the C amount was inappropriate, sufficient corrosion resistance could not be obtained.

In the present invention, the C amount is specified to be suppressed to at least as low as not more than 0.20%, preferably not more than 0.10%, more preferably not more than 0.010%.

5           As explained above, the present invention can achieve satisfactory corrosion resistance in all temperature conditions under a sulfuric acid dew-point corrosion environment, for the first time, by means of introducing the factor of lowering C content in addition  
10 to the combined addition of Si, Cu and Sb. The gist of the present invention is as follows:

          (1) A steel with excellent sulfuric acid dew-point corrosion resistance, characterized by consisting of, in mass,

15           C: not more than 0.20%,  
            Si: 1.2 to 3.5%,  
            Cu: 0.05 to 1.0%,  
            Sb: 0.01 to 0.30%  
            Mn: not more than 1.0%,  
20           P: not more than 0.05%,  
            S: not more than 0.05%,  
            Al: not more than 0.10%, and  
            N: not more than 0.050%, and

the balance consisting of Fe containing incidental  
25 components and/or unavoidable impurities.

          (2) A steel with excellent sulfuric acid dew-point corrosion resistance, characterized by consisting of, in mass,

30           C: not more than 0.10%,  
            Si: 1.2 to 3.5%,  
            Cu: 0.05 to 1.0%,  
            Sb: 0.01 to 0.30%  
            Mn: 0.2 to 1.0%,  
            P: not more than 0.05%,  
35           S: not more than 0.05%,  
            Al: not more than 0.10%, and  
            N: not more than 0.020%, and

the balance consisting of Fe containing incidental components and/or unavoidable impurities.

(3) A steel with excellent sulfuric acid dew-point corrosion resistance, characterized by consisting of, in mass,

C: not more than 0.010%,

Si: 1.2 to 3.5%,

Cu: 0.05 to 1.0%,

Sb: 0.01 to 0.30%

Mn: 0.2 to 1.0%,

P: not more than 0.05%,

S: not more than 0.05%,

Al: not more than 0.10%, and

N: not more than 0.010%, and

the balance consisting of Fe containing incidental components and/or unavoidable impurities.

(4) A steel with excellent sulfuric acid dew-point corrosion resistance according to any one of the items (1) to (3), characterized by further containing one or more elements of, in mass,

Cr: not more than 1.0%,

Mo: not more than 1.0%,

Ni: not more than 0.5%,

Nb: not more than 0.1%,

V: not more than 0.1%,

Ti: not more than 0.1%,

Sn: 0.01 to 0.2%, and

B: 0.0005 to 0.010%.

(5) An air preheater characterized in that a heat transfer element is made of a steel according to any one of the items (1) to (4).

#### Brief Description of the Drawings

Fig. 1 is a graph schematically showing the sulfuric acid dew-point corrosion behavior of steel materials taking the temperature and the sulfuric acid concentration as parameters.

Fig. 2 is a graph showing the influence of Si, Cu and Sb on sulfuric acid dew-point corrosion. The corrosion rate along the vertical axis shows the maximum value of the corrosion rates under the four conditions of (a) a sulfuric acid concentration of 40% and a temperature of 60°C, (b) a sulfuric acid concentration of 50% and a temperature of 80°C, (c) a sulfuric acid concentration of 80% and a temperature of 140°C, and (d) a sulfuric acid concentration of 90% and a temperature of 160°C.

Fig. 3 is a graph showing the influence of C on sulfuric acid dew-point corrosion. The corrosion rate along the vertical axis shows the maximum value of the corrosion rates under the four conditions of (a) a sulfuric acid concentration of 40% and a temperature of 60°C, (b) a sulfuric acid concentration of 50% and a temperature of 80°C, (c) a sulfuric acid concentration of 80% and a temperature of 140°C, and (d) a sulfuric acid concentration of 90% and a temperature of 160°C.

Fig. 4 consists of views showing an outline of the structure of an air preheater.

#### Best Mode for Carrying out the Invention

The reasons for restricting the steel compositions according to the present invention will be described hereunder.

C: Since C deteriorates corrosion resistance, it is preferable to suppress its content to as low as possible. If the content exceeds 0.20% in particular, it is impossible to obtain sufficient corrosion resistance simultaneously under both conditions of a low temperature and a high temperature. Therefore, the upper limit is set at 0.20%. Here, a preferable C content is not more than 0.10%, and a more preferable C content is not more than 0.010%.

Si, Cu and Sb: It is indispensable to effect the combined effect of the three elements to secure good

sulfuric acid corrosion resistance under both a low temperature condition and a high temperature condition. The smallest contents of those elements required for securing the above effect are; 1.2% for Si, 0.05% for Cu, and 0.01% for Sb. The upper limits of the contents of those elements desirable in the practical use are as follows.

10       The upper limit of Si: It is desirable to contain as much Si as possible as an element effective for improving corrosion resistance under both a low temperature condition and a high temperature condition. However, if Si is contained in excess of 3.5%, the effect of improving corrosion resistance is saturated, and therefore the upper limit is set at 3.5%.

15       The upper limit of Cu: Cu is effective for improving corrosion resistance mainly under a low temperature condition. However, if Cu is contained in excess of 1.0%, the hot working property deteriorates, and therefore the upper limit is set at 1.0%.

20       The upper limit of Sb: Sb is effective for improving corrosion resistance under a low temperature condition. However, if Sb is contained abundantly, not only corrosion resistance under a high temperature condition but also a hot working property deteriorates, and therefore the upper limit is set at 0.30%.

25       Mn: Mn is an element effective for strengthening a steel and is contained in an appropriate amount in the case where the compensation for strength deterioration caused by the decrease of C, which is the case of the present invention, is required. A desired content is not less than 0.2%, but if it is contained in excess of 1.0%, corrosion resistance deteriorates and, therefore, the upper limit is set at 1.0%.

30       P: P is an impurity which remains in a steel during a refining process. If it remains in excess of 0.05%, corrosion resistance deteriorates, and therefore the upper limit is set at 0.05%.

S: S is an impurity like P. If it remains in excess of 0.05%, a hot working property and corrosion resistance deteriorate and, therefore, the upper limit is set at 0.05%.

5 Al: Al may be contained for the purpose of deoxidation during a refining process. However, if it is contained in excess of 0.10%, a hot working property deteriorates, and therefore the upper limit is set at 0.10%.

10 N: N is an impurity like P and S, and it is desirable to suppress the content as much as possible. Therefore, the upper limit is set at 0.050%, preferably not more than 0.020%, more preferably not more than 0.010%.

15 A steel according to the present invention contains above elements as its fundamental components, and, in addition to those elements and Fe, may contain the following elements for the purposes of further improving corrosion resistance, adjusting mechanical properties and  
20 improving hot working property.

Cr and Mo: Cr and Mo are effective for enhancing strength, but are not favorable to corrosion resistance under the condition of a low temperature. The preferable range of each element considering the balance of the  
25 strength and the corrosion resistance is not more than 1.0%.

Ni: Ni is utilized to prevent the deterioration of hot working property caused by Cu. However, if it is contained in excess of 0.5%, corrosion resistance tends  
30 to deteriorate and, therefore, it is desirable to add Ni by setting the upper limit at 0.5% when it is added.

Nb, V and Ti: Nb, V and Ti are elements effective for forming precipitates and enhancing toughness. However, if each of them is contained in excess of 0.1%,  
35 corrosion resistance tends to deteriorate, and therefore it is desirable to add each of them by setting the upper limit at 0.1% when it is added.

Sn: Sn is an element effective for improving corrosion resistance. However, if the content is less than 0.01%, the effect does not appear, and if it exceeds 0.2%, a hot working property tends to deteriorate.

5 Therefore, it is desirable to control the content in the range of 0.01 to 0.2% when it is added.

B: B is effective as an element capable of suppressing the deterioration of hot working property in the case where the elements which improve corrosion resistance such as Sb, Cu and Sn are contained abundantly. If the content is less than 0.0005%, sufficient effect cannot be obtained, and if it exceeds 0.010%, a hot working property rather tends to deteriorate. Therefore, it is desirable to control the content in the range of 0.0005 to 0.010% when it is added.

Furthermore, a steel may contain other incidental components, such as W (W of not more than 0.5% tends to improve strength at high temperatures) and Ca, Mg and REM (they have the effect of improving hot working property when the addition amount is not more than 50 ppm in total), in a range where corrosion resistance, strength and workability do not deteriorate.

A steel comprising the above composition may be refined and cast by a usual method and, after that, processed into the shape of a sheet, a pipe or a bar by a conventional hot working method such as forging or rolling, and then put into practical use. Further, a steel, after hot working, may be subjected to a heat treatment such as annealing or, after that, to pickling and then cold-rolling, as the need arises. The corrosion resistance of a steel material produced through the above-mentioned production processes is not influenced by the process conditions, and the steel material can be produced in the processes similar to those employed in the production of a conventional carbon steel material.

As the applications of a steel comprising the above

composition, various kinds of members for equipment used in a sulfuric acid environment, such as facilities around a boiler in a thermal power plant, sulfuric acid purification facilities and storage tanks in a chemical plant and pickling tanks in a steelmaking plant, are possible. In particular, the steel is preferably used as the material of a heat transfer element in an air preheater close to a boiler. An outline of an air preheater is shown in Fig. 4. The arrow indicated with the reference numeral 1 means the flow of the exhaust gas, the arrow with the numeral 2 the flow of the air supplied into a boiler, the arrow with the numeral 3 the direction of the rotation of the rotor, the numeral 4 the rotor, the numeral 5 the baskets housed in the rotor, and the numeral 6 the heat transfer elements (which are fabricated using steel sheets formed into a corrugated shape) loaded in the baskets. The air preheater is structured so as to accumulate the sensible heat of exhaust gas in the heat transfer elements and preheat the air supplied into a boiler, and the heat transfer elements are the members which attach importance to sulfuric acid dew-point corrosion resistance because they are repeatedly exposed to the exhaust gas including SOx and, therefore, are appropriate for the application of the present invention.

#### Example

Steels having the chemical compositions shown in Table 1 were melted and refined in a vacuum melting furnace and cast into 50 kg ingots. After that, the ingots were hot-rolled into plates 12 mm in thickness, and strip test pieces 3 mm in thickness, 20 mm in width and 40 mm in length were prepared and subjected to sulfuric acid corrosion test. A dip test, for four hours, was conducted under the four conditions of (a) a sulfuric acid concentration of 40% and a temperature of 60°C, (b) a sulfuric acid concentration of 50% and a

temperature of 80°C, (c) a sulfuric acid concentration of 80% and a temperature of 140°C, and (d) a sulfuric acid concentration of 90% and a temperature of 160°C, which were adopted as the conditions representing a low  
5 temperature range and a high temperature range in a sulfuric acid dew-point corrosive environment, and their corrosion rates were measured.

The test results are shown in Table 2. As seen in the table, the maximum corrosion rate among the four  
10 conditions of (a) to (d) is 60 to 99 g/m<sup>2</sup>/hr in the case of the inventive example Nos. 1 to 10, while it is 145 to 4,890 g/m<sup>2</sup>/hr in the case of the comparative example Nos. 11 to 18, and the former is apparently superior to the latter.

15 Further, the difference between the maximum value and the minimum value among the corrosion rates of the four conditions is smaller in the case of the inventive examples than in the case of the comparative examples. Therefore, a steel according to the present invention can  
20 contribute to expanding the degree of freedom in a plant design from the viewpoint that the variation of the corrosion rate of the steel caused by the variation of temperatures and sulfuric acid concentrations is small.

Here, comparative example No. 11 does not satisfy  
25 the range of the Sb content specified in the present invention, and likewise, C and Si contents in the case of the comparative example No. 12, Si content in No. 13, Si and Cu contents in No. 14, Cu content in No. 15, Si and Mn contents in No. 16, C content in No. 17, and Si, Cu  
30 and Sb contents in No. 18 are outside the ranges respectively specified in the present invention. Therefore, the comparative examples result in the severe corrosion under any of the four conditions.

Table 1 Chemical compositions of test materials (mass %)

| Classification          | No. | C      | Si   | Mn   | P     | S     | Cu   | Al    | Sb   | N      | Others               |
|-------------------------|-----|--------|------|------|-------|-------|------|-------|------|--------|----------------------|
| Inventive<br>examples   | 1   | 0.0029 | 1.21 | 0.35 | 0.009 | 0.010 | 0.32 | 0.025 | 0.09 | 0.0091 |                      |
|                         | 2   | 0.0028 | 1.55 | 0.35 | 0.009 | 0.010 | 0.32 | 0.026 | 0.10 | 0.0051 | Ni: 0.15%            |
|                         | 3   | 0.0029 | 1.61 | 0.28 | 0.009 | 0.010 | 0.29 | 0.024 | 0.11 | 0.0213 | Cr: 0.31%            |
|                         | 4   | 0.0029 | 3.37 | 0.25 | 0.009 | 0.010 | 0.33 | 0.026 | 0.03 | 0.0111 |                      |
|                         | 5   | 0.0069 | 1.51 | 0.33 | 0.010 | 0.011 | 0.33 | 0.025 | 0.11 | 0.0089 | Sn: 0.05%            |
|                         | 6   | 0.0029 | 1.33 | 0.21 | 0.009 | 0.010 | 0.31 | 0.025 | 0.10 | 0.0071 | B: 0.0035%           |
|                         | 7   | 0.0028 | 1.30 | 0.32 | 0.008 | 0.011 | 0.32 | 0.026 | 0.11 | 0.0039 | Ti: 0.03%, Nb: 0.03% |
|                         | 8   | 0.0027 | 1.60 | 0.31 | 0.008 | 0.011 | 0.50 | 0.018 | 0.12 | 0.0045 | Mo: 0.5%, V: 0.03%   |
|                         | 9   | 0.0215 | 1.22 | 0.63 | 0.011 | 0.009 | 0.27 | 0.031 | 0.08 | 0.0078 |                      |
|                         | 10  | 0.1590 | 1.22 | 0.63 | 0.011 | 0.009 | 0.27 | 0.031 | 0.08 | 0.0065 |                      |
| Comparative<br>examples | 11  | 0.0079 | 1.45 | 0.51 | 0.009 | 0.011 | 0.31 | 0.032 | 0.00 | 0.0039 |                      |
|                         | 12  | 0.2231 | 0.27 | 0.35 | 0.014 | 0.006 | 0.27 | 0.027 | 0.10 | 0.0080 | Ni: 0.15%            |
|                         | 13  | 0.0078 | 0.84 | 0.87 | 0.011 | 0.006 | 0.28 | 0.033 | 0.13 | 0.0078 | Ni: 0.20%            |
|                         | 14  | 0.0020 | 0.26 | 0.34 | 0.020 | 0.004 | 0.01 | 0.043 | 0.10 | 0.0065 |                      |
|                         | 15  | 0.0122 | 1.43 | 0.35 | 0.015 | 0.011 | 0.02 | 0.033 | 0.09 | 0.0036 |                      |
|                         | 16  | 0.0212 | 0.07 | 0.35 | 0.015 | 0.015 | 0.28 | 0.004 | 0.00 | 0.0189 |                      |
|                         | 17  | 0.2102 | 1.22 | 0.63 | 0.011 | 0.009 | 0.27 | 0.031 | 0.08 | 0.0056 |                      |
|                         | 18  | 0.0031 | 0.80 | 0.31 | 0.009 | 0.009 | 0.00 | 0.031 | 0.00 | 0.0068 |                      |

Underlined amount of element in the table indicate the values outside the range specified in the present invention.

Table 2 Results of sulfuric acid corrosion test

| Classification       | No. | Corrosion rate (g/m <sup>2</sup> /hr)                  |                                                        |                                                         |                                                         |
|----------------------|-----|--------------------------------------------------------|--------------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------|
|                      |     | Sulfuric acid concentration: 40% and temperature: 60°C | Sulfuric acid concentration: 50% and temperature: 80°C | Sulfuric acid concentration: 80% and temperature: 140°C | Sulfuric acid concentration: 90% and temperature: 160°C |
| Inventive examples   | 1   | 42                                                     | 60                                                     | 55                                                      | 59                                                      |
|                      | 2   | 38                                                     | 64                                                     | 49                                                      | 75                                                      |
|                      | 3   | 37                                                     | 55                                                     | 35                                                      | 66                                                      |
|                      | 4   | 23                                                     | 18                                                     | 29                                                      | 69                                                      |
|                      | 5   | 40                                                     | 61                                                     | 58                                                      | 61                                                      |
|                      | 6   | 41                                                     | 79                                                     | 59                                                      | 78                                                      |
|                      | 7   | 42                                                     | 76                                                     | 55                                                      | 77                                                      |
|                      | 8   | 45                                                     | 89                                                     | 60                                                      | 88                                                      |
|                      | 9   | 45                                                     | 76                                                     | 58                                                      | 76                                                      |
|                      | 10  | 68                                                     | 78                                                     | 73                                                      | 99                                                      |
| Comparative examples | 11  | 202                                                    | 264                                                    | 93                                                      | 106                                                     |
|                      | 12  | 83                                                     | 146                                                    | 76                                                      | 184                                                     |
|                      | 13  | 121                                                    | 251                                                    | 119                                                     | 130                                                     |
|                      | 14  | 105                                                    | 146                                                    | 101                                                     | 212                                                     |
|                      | 15  | 144                                                    | 154                                                    | 101                                                     | 128                                                     |
|                      | 16  | 209                                                    | 219                                                    | 97                                                      | 69                                                      |
|                      | 17  | 115                                                    | 105                                                    | 73                                                      | 145                                                     |
|                      | 18  | 2810                                                   | 4890                                                   | 101                                                     | 190                                                     |

23 August 2006

- 14 -

#### Industrial Applicability

According to the present invention, a steel material which can demonstrate excellent corrosion resistance in all the temperature range from a low temperature to a  
5 high temperature in a sulfuric acid dew-point corrosion environment can be obtained.

CLAIMS

1. A steel with excellent sulfuric acid dew-point corrosion resistance, characterized by consisting of, in mass,

5 C: not more than 0.01%,  
Si: 1.2 to 3.5%,  
Cu: 0.05 to 1.0%,  
Sb: 0.01 to 0.30%  
Mn: not more than 1.0%,  
10 P: not more than 0.05%,  
S: not more than 0.05%,  
Al: not more than 0.10%, and  
N: not more than 0.050%, and

15 the balance consisting of Fe containing incidental components and/or unavoidable impurities.

2. A steel with excellent sulfuric acid dew-point corrosion resistance, characterized by consisting of, in mass,

20 C: not more than 0.01%,  
Si: 1.2 to 3.5%,  
Cu: 0.05 to 1.0%,  
Sb: 0.01 to 0.30%  
Mn: 0.2 to 1.0%,  
P: not more than 0.05%,  
25 S: not more than 0.05%,  
Al: not more than 0.10%, and  
N: not more than 0.020%, and

the balance consisting of Fe containing incidental components and/or unavoidable impurities.

30 3. A steel with excellent sulfuric acid dew-point corrosion resistance, characterized by consisting of, in mass,

35 C: not more than 0.010%,  
Si: 1.2 to 3.5%,  
Cu: 0.05 to 1.0%,  
Sb: 0.01 to 0.30%  
Mn: 0.2 to 1.0%,

P: not more than 0.05%,  
S: not more than 0.05%,  
Al: not more than 0.10%, and  
N: not more than 0.010%, and

5 the balance consisting of Fe containing incidental components and/or unavoidable impurities.

4. A steel with excellent sulfuric acid dew-point corrosion resistance according to any one of claims 1 to 3, characterized by further containing one or more  
10 elements of, in mass,

Cr: not more than 1.0%,  
Mo: not more than 1.0%,  
Ni: not more than 0.5%,  
Nb: not more than 0.1%,  
15 V: not more than 0.1%,  
Ti: not more than 0.1%,  
Sn: 0.01 to 0.2%, and  
B: 0.0005 to 0.010%.

5. An air preheater characterized in that a heat  
20 transfer element is made of a steel according to any one of claims 1 to 4.