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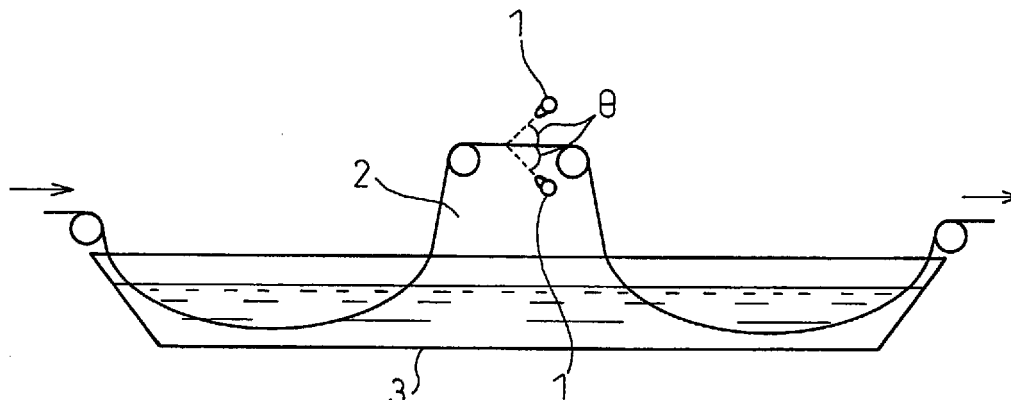
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(54) **PICKLING METHOD FOR STEEL PLATES, AND PICKLING APPARATUS**

(57) The present invention provides a pickling method of steel sheet and pickling system of steel sheet able to efficiently remove oxide scale from steel sheet. That is, it provides a continuous pickling method of steel sheet having a step A of pickling the steel sheet in a pickling tank, a step B of blowing gas toward at least part of the surfaces of the steel sheet in the air after the step A, and

a step C of pickling the steel sheet in a pickling tank after the step B, wherein at step B, the steel sheet is temporarily taken out from the pickling solution and gas is blown to at least part of the surfaces of the steel sheet in the air so as to evaporate the acid solution deposited on the surface of the steel sheet and locally increase the acid concentration to thereby efficiently remove even the stubborn Si oxides included in the oxide scale.

Fig.1



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a pickling method and a pickling system of steel sheet for removing oxide scale from the surface of the steel sheet.

BACKGROUND ART

10 **[0002]** In the process of production of steel sheet, the surface of the steel sheet is cleaned for various purposes. For example, cleaning of the steel sheet before plating or coating, pickling for removing oxide scale from hot rolled steel sheet, etc. may be mentioned. Usually, in the process of steel sheet being heat treated and rolled, oxide scale is formed on the surface of the steel sheet. This oxide scale is caught up at the rolling rolls at the time of the next step of cold rolling and often becomes a cause of damage to the surface of the steel sheet, so removal of oxide scale is becoming
15 an essential step.

[0003] In conventional oxide scale removal, the steel sheet is immersed in a plurality of acid solutions and continuously run through them to pickle it. For example, as described in Non-Patent Document 1, there is the method of removing oxide scale by providing a weir in a box-shaped pickling tank, placing a spray nozzle in it, and spraying acid on the steel sheet.

20 **[0004]** As methods for mechanically removing oxide scale, there are the rolling method, polishing method, shot blasting method, repeated bending method, etc. as described in Non-Patent Document 2. In practice, these are often combined for use. These arts mechanically remove the oxide scale and also mechanically form cracks at the oxide scale and immerse the sheets in a pickling solution to efficiently dissolve the oxide scale.

25 There is also the method of using a pickling solution to which hydrochloric acid or iron chloride has been added and applying voltage in the solution to the steel sheet to run a current through it and thereby improve the speed of dissolution of the oxide scale (Patent Documents 1, 2, and 3).

[0005] There is also the method of jointly using an induction heating system to apply heat so that cracks in the oxide scale progress down to the surface of the base metal and jointly using a system for blowing a pickling solution into them (Patent Document 4).

30 There is also the method of providing the entry side and exit side of the pickling tank with nozzles for blowing an acid solution and providing side nozzles for blowing an acid solution from the side parts so as to secure the pickling solution during the pickling process, convert the flow of pickling solution contributing to the reaction from a laminar state to a turbulent state, and destroy the boundary layer to raise the pickling efficiency (Patent Document 5).

35 **[0006]** There is also the method of using electrolysis to remove the oxide scale, then bending the steel strip by rolls and blowing high pressure water to the bent projecting surface to promote the removal of the oxide scale (Patent Document 6).

As a system for pickling pretreatment of stainless steel strip, the art of running the stainless steel strip through a salt bath tank, then cooling the front and back surfaces of the steel strip by air from an air header, then running the cooled steel strip through a rinse tank to rinse it is disclosed in Patent Document 7.

40 **[0007]** In the production of grain-oriented electrical steel sheet, as a method of mechanically removing molten deposits after using a laser beam to form grooves, the method of utilizing compressed air in addition to brushes, abrasives, wipers, and high pressure water has been illustrated (Patent Document 8).

Further, regarding a method and system for continuous pickling of steel strip, a method and system of removing (destroying and reducing) the layer of acid solution (boundary film layer) moving together with the steel strip by blowing air from above the pickling tank and bringing the layer into contact with a partition strip has been disclosed. By using the above
45 method to remove the boundary film layer, it is possible to not only prevent the acid solution of the preceding tank from being brought into the succeeding tank, but also to prevent the boundary film layer from blocking contact of new acid solution with the steel sheet in a succeeding tank (Patent Document 9)

50 PRIOR ART DOCUMENTS

Patent Documents

[0008]

55 Patent Document 1: Japanese Patent Publication (A) No. 10-8298
Patent Document 2: Japanese Patent Publication (A) No. 55-48421
Patent Document 3: Japanese Patent Publication (A) No. 58-64400

Patent Document 4: Japanese Patent Publication (A) No. 9-78273
 Patent Document 5: Japanese Patent Publication (A) No. 2001-20086
 Patent Document 6: Japanese Patent Publication (A) No. 2001-191108
 Patent Document 7: Japanese Patent Publication (A) No. 9-87871
 Patent Document 8: Japanese Patent Publication (A) No. 10-183251
 Patent Document 9: Japanese Patent Publication (A) No. 62-243788
 Non-Patent Documents

[0009]

Non-Patent Document 1: Nobuhiro Shibatomi et al., Mitsubishi Heavy Industries Technical Review, Vol. 129, No. 1, 24-29 (1992)
 Non-Patent Document 2: Kazunori Hata et al., Hitachi Hyoron, Vol. 6 No. 4, 41-46 (1985)

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0010] In the case of steel sheet containing Si - a leading type of high strength steel, it is known through experience that if using the usual pickling method for treatment, the speed of dissolution will become slower. In the case of steel sheet containing Si, the Si in the steel will sometimes concentrate as oxides at the base iron side of the oxide scale layer making it necessary to dissolve the Si oxide layer formed between the oxide scale layer and base iron to remove the oxide scale as a whole.

Further, Si oxides once dissolved simultaneously with oxide scale have a small solubility in the pickling solution, so while Fe ions from the oxide scale can be present in the solution, sometimes only Si oxides are redeposited. Sometimes too, the concentration of the Si ions in the pickling solution causes a change to a gel state in the solution. The deposition of this gel on the surface of the steel sheet has also been observed.

[0011] Up to now, scale has been dissolved away by conventional pickling methods, but the speed of dissolution is not being raised at the present. Therefore, the line speed of pickling has not been raised and efficient pickling has not necessarily been performed.

Further, in steel sheet not containing Si as well, no measures are being taken to deal with the redeposition of oxide scale and the partial specific ingredients of oxide scale, so the problem of achieving efficient removal of oxide scale has not been completely solved.

[0012] The present invention was made so as to solve the above problem and has as its object the provision of a continuous pickling method of steel sheet and a continuous pickling system of steel sheet enabling efficient removal of oxide scale from steel sheet. In particular, the invention has as its object the provision of a pickling method of steel sheet and a pickling system of steel sheet able to effectively remove Si oxides contained in oxide scale for steel sheet containing Si and to greatly improve the speed of dissolution of the oxide scale.

MEANS FOR SOLVING THE PROBLEMS

[0013] The inventors engaged in intensive studies on means for solving the above problems and as a result discovered that in the process of dissolution of oxide scale of steel sheet by pickling, by temporarily taking the steel sheet out from the pickling solution and blowing gas to at least part of the surfaces of the steel sheet in the air, part of the acid solution deposited on the surface of the steel sheet is made to evaporate and the acid concentration is locally raised. They confirmed that due to this, even stubborn Si oxides contained in the oxide scale can be efficiently removed. Further, they discovered that by later repeating the pickling, the speed of dissolution of the oxide scale is remarkably improved.

[0014] Furthermore, the inventors discovered that by blowing the gas in a direction facing the direction of movement of the steel sheet, the effect becomes more remarkable. Furthermore, they discovered that by blowing the gas from a direction facing the direction of movement of the steel sheet and at a slant from the surface of the steel sheet, the effect becomes even more remarkable. The present invention was made based on these discoveries and has as its gist the following:

[0015] (1) A pickling method of steel sheet comprising a pickling method for removing oxide scale of steel sheet characterized by having a step A of pickling the steel sheet, a step B of blowing gas toward at least part of the surfaces of the steel sheet in the air after the step A, and a step C of pickling the steel sheet after the step B.

[0016] (2) A continuous pickling method of steel sheet as set forth in (1), characterized by blowing the gas against a direction of movement of the steel sheet.

[0017] (3) A pickling method of steel sheet as set forth in (2), **characterized in that** an angle θ ($^{\circ}$) formed between a

blowing direction of the gas and at least part of the surfaces of the steel sheet is $1^\circ \leq \theta \leq 75^\circ$.

[0018] (4) A pickling method of steel sheet as set forth in any one of (1) to (3), **characterized in that** a blowing pressure of the gas is 0.5 to 1.0 MPa.

[0019] (5) A pickling method of steel sheet as set forth in any one of (1) to (4), characterized in the pickling of the step A is performed in a first pickling tank and the pickling of the step C is performed in a second pickling tank.

[0020] (6) A pickling system of steel sheet characterized by having at least one pickling tank and means for blowing gas toward at least part of the surfaces of the steel sheet in the air.

[0021] (7) A continuous pickling system of steel sheet as set forth in (6), **characterized in that** the means for blowing gas is a means for blowing it facing the direction of movement of the steel sheet.

[0022] (8) A pickling system of steel sheet as set forth in (6) or (7), **characterized in that** an angle θ ($^\circ$) formed between a blowing direction of the gas and at least part of the surfaces of the steel sheet is $1^\circ \leq \theta \leq 75^\circ$.

[0023] (9) A pickling system of steel sheet as set forth in any one of (6) to (8), **characterized in that** the means for blowing gas is a nozzle.

[0024] (10) A pickling system of steel sheet as set forth in (9), **characterized in that** the nozzle has an angle changing means.

[0025] (11) A pickling system of steel sheet as set forth in (9) or (10), **characterized in that** a pressure at a blowing port of the nozzle is 0.5 to 1.0 MPa.

[0026] (12) A pickling system of steel sheet as set forth in any one of (9) to (11), characterized two or more of the nozzles are arranged in the direction of movement of the steel sheet.

[0027] (13) A pickling system of steel sheet as set forth in (6), **characterized in that** the pickling tank is two or more pickling tanks.

EFFECTS OF THE INVENTION

[0028] According to the present invention, it is possible to efficiently remove oxide scale from steel sheet. In particular, it is possible to remarkably raise the speed of removal of oxide scale from steel sheet containing Si. Further, the steel sheet after pickling process obtained by the present invention has a clean surface free of pickling scars.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029]

FIG. 1: An example of blowing gas to the surface of the steel sheet in a single pickling tank during pickling and performing the subsequent pickling in the same pickling tank as the above.

FIG. 2: An example of pickling, then blowing gas to the surface of the steel sheet in a first pickling tank and performing the subsequent pickling in a second pickling tank.

FIG. 3: Schematic views of blowing gas from a nozzle of the present invention to the surface of steel sheet.

FIG. 4: An example of a pickling facility provided with a pickling system of the present invention.

FIG. 5: An example of the case of providing a plurality of stages of nozzles.

FIG. 6: Views of arrangements of nozzles according to the present invention showing the case of a nozzle with a slit in the width direction of the steel sheet and the case of swinging a nozzle.

EMBODIMENTS OF THE INVENTION

[0030] Below, the present invention will be explained in detail.

The inventors discovered that when removing oxide scale formed on the surface of steel sheet, if temporarily blowing gas to at least part of the surfaces of the steel sheet in the air in the process of dissolving the oxide scale by a pickling solution, the pickling efficiency (efficiency of removal of oxide scale) is improved.

[0031] That is, if once taking out the steel sheet from the pickling tank and blowing gas to at least part of the surfaces of the steel sheet, the pickling solution deposited on the surface of the steel sheet at the part blown upon partially evaporates and is concentrated, so the acid concentration becomes higher (pH becomes lower). At the recessed part at the interface between the oxide scale layer just being peeled off and the surface of the steel sheet, the deposited pickling solution becomes locally higher in acid concentration, so the adhered part of the oxide scale layer and steel sheet is selectively dissolved. When again immersed in the pickling solution, the oxide scale is easily removed. Regarding the blowing of the gas, if blowing the gas at a slant with respect to the surface of the steel sheet, the effect is obtained more remarkably.

[0032] Patent Document 9 also discloses a method of blowing air on to a steel strip. However, inherently, this method is aimed at the removal of the layer of acid solution (boundary film layer) deposited on the steel strip. Therefore, this

requires using air to blow away the acid solution and bringing an end of a partition plate having elasticity into contact with the steel strip to wipe away the remaining the acid solution. Allowing the deposited pickling solution to remain at the surface of the steel sheet to be concentrated as explained above is neither described nor suggested. Therefore, even if using the method or system of Patent Document 9, the deposited pickling solution ends up being removed, so it is not possible to concentrate the deposited pickling solution to raise the acid concentration as explained above and an effect like the present invention cannot be obtained. Rather, the pickling solution ends up being removed, so new spot like patterns (patterns formed at surface of steel sheet due to uneven acid solution) are liable to form.

Here, "at least part of the surfaces of the steel sheet" (below, called "the surface of the steel sheet") may mean one surface of the steel sheet, both (front and back) surfaces, the side surfaces, or all surfaces. The surfaces are not particularly limited so long as surfaces on the steel sheet.

[0033] Further, more remarkable effects are obtained in steel sheet containing Si. If investigating in detail the process by which oxide scale in steel sheet containing Si dissolves in a pickling solution, it is learned that the oxide scale on the surface of the steel sheet gradually dissolves and at the final stage when reaching near the interface of the oxide scale and steel sheet, there is a layer where Si oxides concentrate. It is learned that at this concentrated layer part, the remaining oxide scale is difficult to separate from the surface of the steel sheet. This concentrated layer of Si oxides is sometimes dissolved by the pickling solution, then forms a gel. It has been observed that the gel-like Si oxides are freed from the surface of the steel sheet in the process of dissolution of the oxide scale, but cannot be separated (removed) from the interface between the oxide scale and base iron and therefore remain there.

[0034] In the present invention, the dissolved and freed gel-like Si oxides and the oxide scale having the layer where Si oxides concentrate can be removed by blowing a gas. For removal of Si oxides and oxide scale, while the dynamic action of blowing the gas also is effective in removal, above and beyond that, as explained above, it is believed that these are efficiently removed by the superposed chemical effect due to the concentration of the pickling solution deposited at the surface. Further, the concentrated pickling solution concentrates at the interface of the steel sheet and oxide scale due to the surface tension to selectively dissolve it the more the solution evaporates. This is believed because there is a concentrated layer of Si oxides at the interface of the steel sheet and oxide scale, so removal of the Si oxides is promoted and, accordingly, the efficiency of removal of the oxide scale is increasingly improved.

[0035] That is, the gel-like Si oxides and the interface of the oxide scale and the surface of the steel sheet are selectively dissolved whereby removal of Si oxides is promoted. The Si oxides interfering with the removal of the oxide scale are efficiently removed as explained above, so if the steel sheet is again immersed in the pickling solution, the oxide scale is also efficiently removed. That is, the dissolution speed of the oxide scale is improved. This has a large effect when the Si oxides are gel-like.

[0036] The effect of improvement of the pickling efficiency is more remarkable in steel sheet with a content of Si of 0.1 to 3.5 mass%. If the content of Si contained in the steel sheet becomes 0.1 mass% or more, a layer where Si oxides concentrate is easily formed, so a remarkable effect of improvement of the pickling efficiency is obtained. If the content of Si increases, the effect of improvement of the pickling efficiency becomes greater, but if the content of Si contained in the steel sheet exceeds 3.5 mass%, no further improvement in the pickling efficiency is seen any longer and the efficiency remains constant.

[0037] When blowing gas to the surface of the steel sheet, it is more effective if blowing it from a direction slanted with respect to the surface of the steel sheet. When blowing gas from a slant, as shown in FIG. 1 or FIG. 2, it is more preferable to blow it facing the direction of movement of the steel sheet. More preferable is the case where the angle θ ($^{\circ}$) formed between the blowing direction and the surface of the steel sheet is $1^{\circ} \leq \theta \leq 75^{\circ}$ in range. FIG. 3 schematically shows an enlarged view of blowing gas to the surface of the steel sheet (only one surface shown). FIG. 3 schematically shows the case where the surface of the steel sheet has an oxide scale layer 6 and where, between the oxide scale layer 6 and the steel sheet 2, there is a layer 7 where Si oxides are concentrated.

[0038] The Si oxides pass once through the pickling tank, so are dissolving. At this time, as shown in FIG. 3, blowing the gas slanted with respect to the surface of the steel sheet makes it directly strike the interface between the oxide scale layer and steel sheet, so a sufficient effect is obtained. If the angle θ is less than 1° , even if raising the gas blowing pressure, the gas striking the surface of the steel sheet disperses, so the gas will not strike the surface of the steel sheet with a sufficiently high pressure in some cases. If the angle θ exceeds 75° , the blown gas will increasingly no longer directly strike the interface of the oxide scale layer and steel sheet and the above effect will no longer be sufficiently obtained in some cases.

[0039] The means for blowing the gas may use any method, but for example the method of using a blower, nozzle, etc. may be mentioned. In particular, it is preferable to use a nozzle to blow the gas.

If considering the size of the nozzle, the distance over which the gas is blown from the nozzle to the surface of the steel sheet, etc., the angle θ is preferably 10° to 60° . More preferably, to make the blown gas concentrate at the interface between the oxide scale layer and steel sheet, the angle θ is preferably made 15° to 45° .

[0040] The width of the blowing nozzle port shown in FIG. 3 is preferably at least the width of the surface of the steel sheet. The nozzle port may be a slit in the width direction or independent nozzle ports may be aligned in the width

direction. Further, as shown in FIG. 6, it is also possible to make the nozzle port swing in a plane parallel to the surface of the steel sheet.

[0041] FIG. 1 and FIG. 2 show one gas blowing nozzle 1 arranged at each of the two surfaces of the steel sheet, but there is no need to limit the gas blowing nozzles to one for each surface of the steel sheet. As shown in FIG. 5, it is also possible to arrange two or more gas blowing nozzles in the direction of movement of the steel sheet and blow gas in multiple stages. By using multistage gas blowing nozzles, it is possible to remove the oxide scale more efficiently.

[0042] A gas blowing nozzle is preferably provided at each of the two surfaces of the steel sheet, but may also be provided at only one surface. Of course, there is no need to simultaneously blow the gas at the two surfaces. It is also possible to blow the gas alternately at one surface at a time.

The angle θ formed by the nozzle gas blowing direction and the surface of the steel sheet is preferably variable. For example, when the speed of movement of the steel sheet is large, even if making the angle θ large, a sufficient gas blowing effect is obtained, but when the speed of movement of the steel sheet is small, the angle θ may be reduced to obtain a sufficient gas blowing effect. Therefore, it is possible to make the angle variable in accordance with the speed of movement of the steel sheet.

[0043] As explained above, in the middle of the oxide scale being dissolved by the pickling, the gas is blown at the surface of the steel sheet, so, for example, as shown in FIG. 1, it may be considered to use a single pickling tank to pickle the steel sheet, take out the pickled steel sheet once from the pickling tank and blow gas at it, and further use the same pickling tank for repeat pickling. Alternatively, a plurality of pickling tanks may be arranged in a line to form a pickling facility (FIG. 2 shows an example of two pickling tanks) and a steel sheet pickled between one tank and another may be taken out from the pickling tank once and gas blown at it. FIG. 4 schematically shows a pickling facility according to the present invention.

[0044] The gas used in the present invention is not particularly limited, but for example, air, nitrogen, argon, or another gas may be used. Further, mixed gases of these may also be used. The pressure of the blown gas at the blowing port may be made 0.5 to 1.0 MPa or more to obtain the effect of the present invention. If less than 0.5 MPa, the pickling speed sometimes cannot be improved. Further, the reason why the upper limit is defined as 1.0 MPa is that if blowing gas over 1.0 MPa, the facilities relating to the pressurizing system become larger in size and the economic effect cannot be obtained in some cases.

[0045] Further, the gas blowing nozzle port is preferably a distance of 2 cm to 80 cm from the surface of the steel sheet. Therefore, when inclining the gas blowing nozzle port, the distance becomes the shortest straight line distance between the gas blowing nozzle port and the surface of the steel sheet multiplied by $1/\sin\theta$. If less than 2 cm, vibration of the running steel sheet causes contact with the gas blowing nozzle port. If over 80 cm, the gas blown toward the surface of the steel sheet sometimes will not sufficiently reach the surface of the steel sheet. While depending on the state of the peripheral facilities etc., with a distance of 5 cm to 30 cm, a high effect can be obtained.

[0046] The pickling solution of the pickling tank according to the present invention is a pickling solution for removing ordinary oxide scale. For example, an aqueous hydrochloric acid solution, aqueous sulfuric acid solution, aqueous fluoric acid solution (hydrofluoric acid), or aqueous solutions of these solutions further containing nitric acid, acetic acid, formic acid, etc. may be used. The concentration of the acid of the pickling solution is not particularly limited, but is 2 mass% to 20 mass% in range. If less than 2 mass%, a sufficient speed of dissolution of the oxide scale sometimes cannot be obtained. If over 20 mass%, the pickling tank becomes remarkably corroded in some cases or the rinse tank has to be made larger in some cases.

[0047] Further, the pickling solution may have Fe^{2+} ions added to it. The concentration of Fe^{2+} ions is more preferably 30 to 150 g/L. If less than 30 g/L, stable pickling is not possible in some cases. If over 150 g/L, the pickling speed becomes slower in some cases. Further, the pickling solution may also have Fe^{3+} ions added to it.

[0048] The temperature of the pickling solution is not particularly limited, but for the pickling efficiency, temperature control, or other reasons, ordinary temperature to 97°C is preferable.

[0049] The speed of movement of the steel sheet at the gas blowing part of the present invention is not particularly limited, but is preferably 50 m/min to 400 m/min. If less than 50 m/min, the productivity (pickling efficiency) becomes lower in some cases. If over 400 m/min, the effect of improvement of the pickling efficiency by the blowing of a gas sometimes can no longer be obtained. The steel sheet running speed is particularly preferably 100 m/min to 200 m/min.

Example 1

[0050] Below, the present invention will be explained more specifically using examples, but the present invention is not limited to these examples in any way.

[0051] Steel materials were used to run tests on removal of oxide scale. As the steel materials, hot rolled steel sheets adjusted to C: 0.002 mass%, Mn: 0.53 mass%, S: 0.01 mass%, Nb: 0.006 mass%, Si in the mass% shown in Table 1, and a balance of Fe and unavoidable impurities were used. The steel sheets were shaped as test steel strips of a thickness of 4 mm and a width of 100 mm. The inventors used a pickling tank combining gas blowing shown in FIG. 1

to run each strip at a speed of 10 to 100 m/min and investigated the pickling effect while changing the pressure of the blown gas and the feed angle θ in the ranges of Table 1. The pressure of the gas at the blowing port was measured by a manometer set at the side wall of a gas blowing nozzle.

[0052] The inventors used an aqueous HCl solution as the pickling solution and adjusted and controlled it during operation to give hydrochloric acid within the range of 6 to 9 mass%. Furthermore, they added FeCl_2 so that the Fe^{2+} in the solution became 80 g/L. Further, for Fe^{3+} as well, in the same way, the inventors added FeCl_3 so that the Fe^{3+} in the solution became 1 g/L. They warmed the pickling solution to a temperature of 70°C ($\pm 5^\circ\text{C}$).

[0053] As the method of evaluation, the inventors changed the running speed (movement speed) of the steel sheet and measured the pickling time for the area ratio of removal of oxide scale to reach 90%. Here, they investigated the ratio of the area of the parts with no oxide scale in a surface of the steel sheet of 50 mmx50 mm. They averaged the values for the front and back surfaces of the steel sheet and used the result as the area ratio of removal of oxide scale. A case where the pickling time for the area ratio of removal of oxide scale to reach 90% or more exceeded 35 seconds was evaluated as "poor", a case of 30 to 35 seconds as "fair", a case of 25 to 30 seconds as "good", and a case of within 25 seconds as "very good".

[0054] Table 1 shows the results of evaluation. Compared with the case of not blowing gas, blowing gas to the surface of the steel sheet during the pickling process enabled the pickling time to be shortened. For the gas blowing angle, a range of 1° to 75° was more superior for improvement of the pickling efficiency. Further, with a pressure of the gas at the blowing port in the range of 0.5 to 1.0 MPa, the pickling efficiency was higher. The effect of gas blowing appeared remarkably in steel sheet containing 0.1 to 3.6 mass% of Si.

[0055]

Table 1

	Si content of steel sheet (mass%)	Type of gas	Gas pressure at blowing port (MPa)	Blowing angle θ ($^\circ$)	Evaluation of pickling time
Inv. Ex. 1	0.3	Argon	0.5	60	Very good
Inv. Ex. 2	0.3	Nitrogen	0.5	60	Very good
Inv. Ex. 3	0.3	Air	0.5	60	Very good
Inv. Ex. 4	0.3	Air	1.0	60	Very good
Inv. Ex. 5	0.1	Air	0.5	60	Very good
Inv. Ex. 6	0.5	Air	0.5	60	Very good
Inv. Ex. 7	0.5	Air	0.5	1	Very good
Inv. Ex. 8	0.5	Air	0.5	5	Very good
Inv. Ex. 9	0.5	Air	0.5	10	Very good
Inv. Ex. 10	0.5	Air	0.8	10	Very good
Inv. Ex. 11	0.5	Air	0.5	30	Very good
Inv. Ex. 12	0.5	Air	0.8	30	Very good
Inv. Ex. 13	0.5	Air	1.0	60	Very good
Inv. Ex. 14	0.5	Air	0.5	75	Very good
Inv. Ex. 15	0.5	Air	0.8	75	Very good
Inv. Ex. 16	0.3	Air	0.8	45	Very good
Inv. Ex. 17	0.3	Air	0.8	67	Very good
Inv. Ex. 18	0.3	Nitrogen	0.8	1	Very good
Inv. Ex. 19	0.3	Nitrogen	0.8	13	Very good
Inv. Ex. 20	3.6	Air	1.0	60	Good
Inv. Ex. 21	0.3	Air	0.2	60	Good
Inv. Ex. 22	0.006	Air	0.1	60	Good

(continued)

	Si content of steel sheet (mass%)	Type of gas	Gas pressure at blowing port (MPa)	Blowing angle θ (°)	Evaluation of pickling time
Inv. Ex. 23	0.3	Air	0.4	60	Good
Inv. Ex. 24	0.3	Air	1.1	60	Good
Inv. Ex. 25	3.6	Air	0.5	60	Good
Inv. Ex. 26	0.05	Air	0.8	60	Good
Inv. Ex. 27	0.3	Air	0.8	0.5	Fair
Inv. Ex. 28	0.3	Air	0.8	80	Fair
Inv. Ex. 29	20.3	Air	0.8	90	Fair
Inv. Ex. 30	0.3	Air	0.8	95	Fair
Comp. Ex. 1	0.3	No gas blown			Poor

Example 2

[0056] In the same way as Example 1, the inventors used test steel sheets containing C, Mn, S, and Nb and containing Si shown in Table 2 and blew a gas between the two pickling tanks shown in FIG. 2 for pickling. The pickling solutions of the two pickling tanks are the same as in Example 1. The temperature of the pickling solution was made 75°C (+5°C) by warming.

The method of evaluation is the same as in Example 1. Table 2 shows the results of evaluation. Compared with when not blowing gas, blowing gas to the surface of the steel sheet during the pickling process enabled the pickling time to be shortened. Regarding the blowing angle of the gas, a range of 1° to 75° was better for improvement of the pickling efficiency. Further, with a pressure of the gas at the blowing port of 0.5 to 1.0 MPa in range, the pickling efficiency was higher.

[0057]

Table 2

	Si content of steel sheet (mass%)	Type of gas	Gas pressure at blowing port (MPa)	Blowing angle θ (°)	Evaluation of pickling time
Inv. Ex. 31	0.5	Air	0.5	1	Very good
Inv. Ex. 32	0.5	Air	0.5	5	Very good
Inv. Ex. 33	0.5	Air	0.5	10	Very good
Inv. Ex. 34	0.5	Air	0.5	30	Very good
Inv. Ex. 35	0.5	Air	1.0	30	Very good
Inv. Ex. 36	0.5	Air	0.5	60	Very good
Inv. Ex. 37	0.5	Air	0.5	75	Very good
Inv. Ex. 38	0.5	Air	1.0	75	Very good
Inv. Ex. 39	0.3	Air	1.0	45	Very good
Inv. Ex. 40	0.3	Air	1.0	67	Very good
Inv. Ex. 41	0.3	Nitrogen	1.0	1	Very good
Inv. Ex. 42	0.3	Nitrogen	1.0	13	Very good
Inv. Ex. 43	0.3	Air	0.4	60	Good
Inv. Ex. 44	0.3	Air	1.1	60	Good

(continued)

	Si content of steel sheet (mass%)	Type of gas	Gas pressure at blowing port (MPa)	Blowing angle θ (°)	Evaluation of pickling time
Inv. Ex. 45	0.3	Air	0.4	90	Fair
Inv. Ex. 46	0.3	Air	0.4	0.8	Fair
Inv. Ex. 47	0.3	Air	0.4	80	Fair
Comp. Ex. 2	0.3	No gas blown			Poor

INDUSTRIAL APPLICABILITY

[0058] The present invention can be utilized in the iron and steel industry. According to the present invention, it becomes possible to efficiently remove oxide scale of steel sheet. In particular, it is possible to remarkably improve the speed of removal of oxide scale (pickling speed) from Si-steel sheet - a leading type of high strength steel. Further, the steel sheet after pickling process obtained by the present invention has a clean surface free of pickling scars. Due to this, it is possible to strikingly improve the productivity of hot rolled steel sheet, in particular automobile steel sheet and other high strength steel sheet. The inventors are confident that this can contribute to the supply of good quality, low cost steel sheet.

EXPLANATION OF REFERENCES

[0059]

- 1, 1' gas blowing nozzle
- 2 running steel sheet
- 3 pickling tank
- 4 first pickling tank
- 5 second pickling tank
- 6 oxide scale layer
- 7 Si oxide layer
- 8 gas blowing nozzle port
- 9 pickling unit
- 9' gas blowing unit
- 10 rinse tank
- 11 uncoiler
- 12 welding machine
- 13 entry side looper
- 14 tension leveler
- 15 exit side looper
- 16 oil coater
- 17 coiler

Claims

1. A pickling method of steel sheet comprising a pickling method for removing oxide scale of steel sheet **characterized by** having a step A of pickling the steel sheet, a step B of blowing gas toward at least part of the surfaces of the steel sheet in the air after said step A, and a step C of pickling said steel sheet after said step B.
2. A continuous pickling method of steel sheet as set forth in claim 1, **characterized by** blowing said gas against a direction of movement of the steel sheet.
3. A pickling method of steel sheet as set forth in claim 2, **characterized in that** an angle θ (°) formed between a blowing direction of said gas and at least part of the surfaces of the steel sheet is $1^\circ \leq \theta \leq 75^\circ$.
4. A pickling method of steel sheet as set forth in any one of claims 1 to 3, **characterized in that** a blowing pressure

of said gas is 0.5 to 1.0 MPa.

- 5 5. A pickling method of steel sheet as set forth in any one of claims 1 to 4, **characterized in** the pickling of said step A is performed in a first pickling tank and the pickling of said step C is performed in a second pickling tank.
6. A pickling system of steel sheet **characterized by** having at least one pickling tank and means for blowing gas toward at least part of the surfaces of the steel sheet in the air.
- 10 7. A continuous pickling system of steel sheet as set forth in claim 6, **characterized in that** said means for blowing gas is a means for blowing it facing the direction of movement of the steel sheet.
8. A pickling system of steel sheet as set forth in claim 6 or 7, **characterized in that** an angle θ (°) formed between a blowing direction of said gas and at least part of the surfaces of the steel sheet is $1^\circ \leq \theta \leq 75^\circ$.
- 15 9. A pickling system of steel sheet as set forth in any one of claims 6 to 8, **characterized in that** said means for blowing gas is a nozzle.
10. A pickling system of steel sheet as set forth in claim 9, **characterized in that** said nozzle has an angle changing means.
- 20 11. A pickling system of steel sheet as set forth in claim 9 or 10, **characterized in that** a pressure at a blowing port of said nozzle is 0.5 to 1.0 MPa.
12. A pickling system of steel sheet as set forth in any one of claims 9 to 11, **characterized** two or more of said nozzles are arranged in the direction of movement of the steel sheet.
- 25 13. A pickling system of steel sheet as set forth in claim 6, **characterized in that** said pickling tank is two or more pickling tanks.

Fig.1

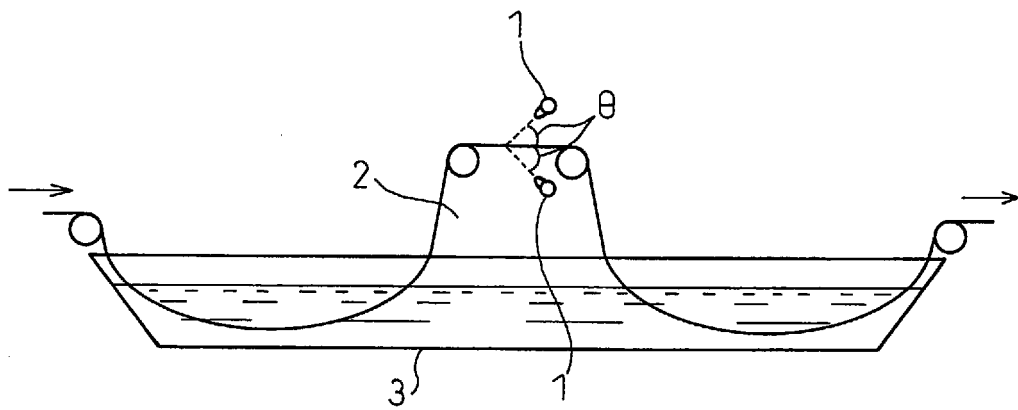


Fig.2

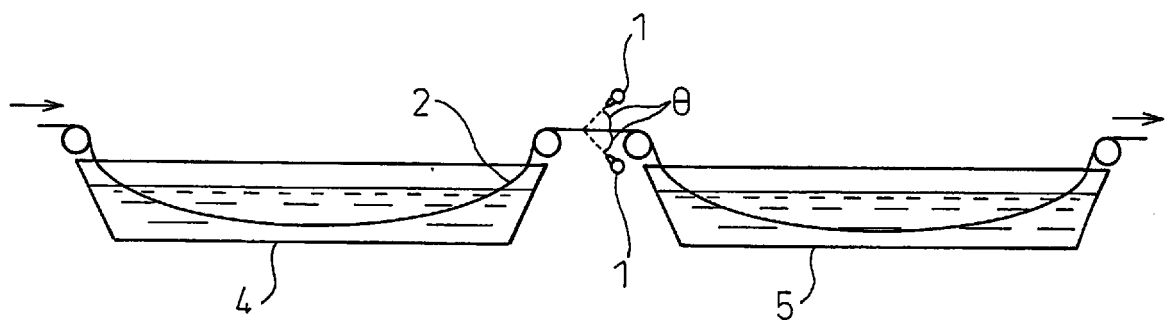


Fig.3

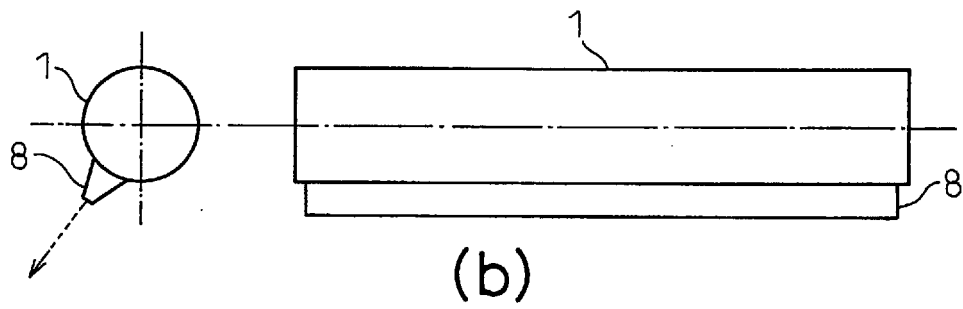
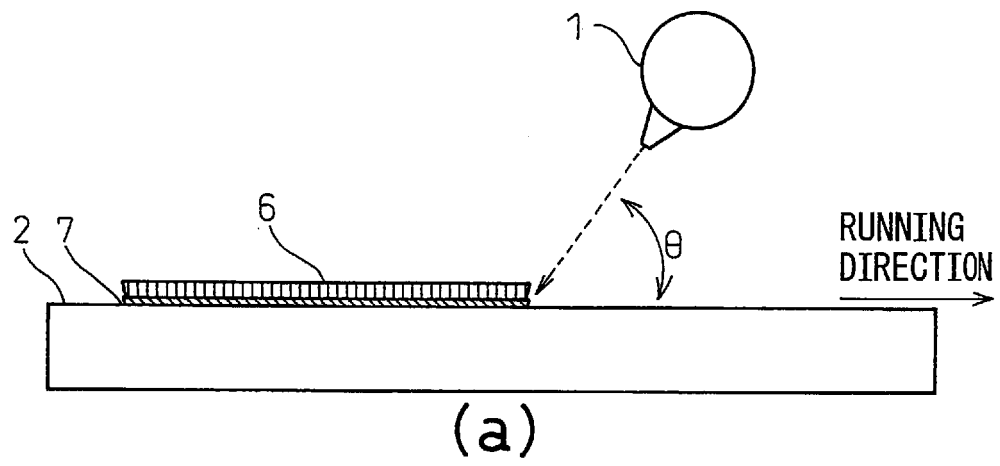


Fig.4

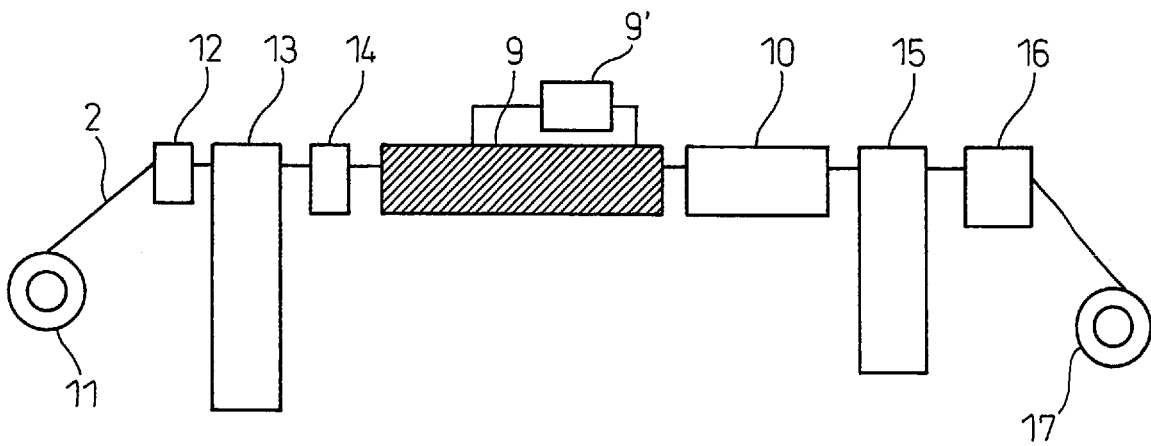


Fig.5

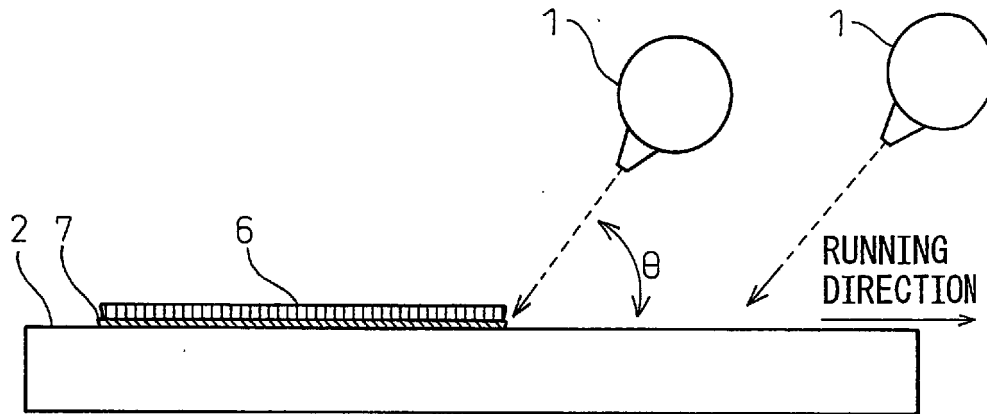
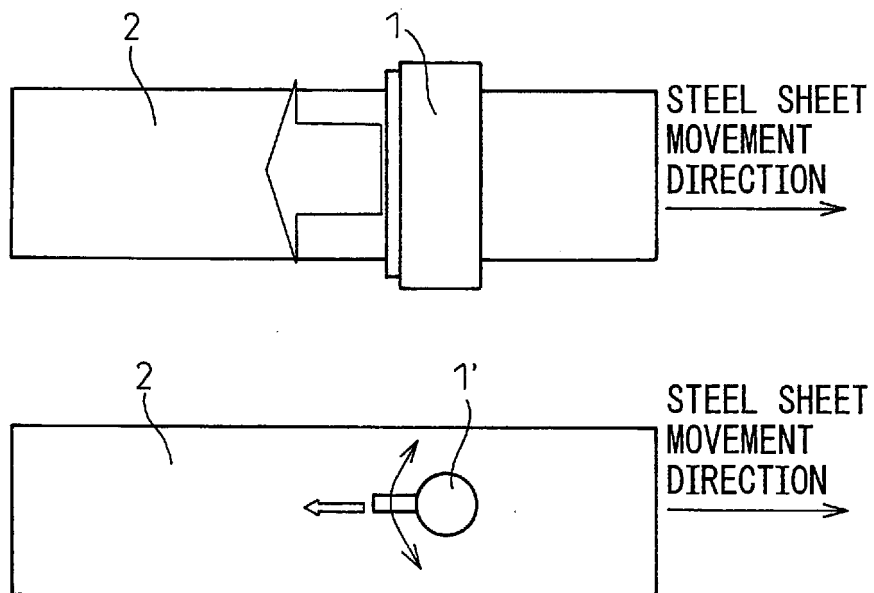


Fig.6



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/060205

A. CLASSIFICATION OF SUBJECT MATTER

C23G1/08(2006.01)i, C23G3/00(2006.01)i, C23G3/02(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23G1/00-5/06, B21B45/00-45/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2009

Kokai Jitsuyo Shinan Koho 1971-2009 Toroku Jitsuyo Shinan Koho 1994-2009

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<u>X</u>	JP 62-243788 A (Sumitomo Metal Industries, Ltd.),	<u>1, 5, 6, 9, 12,</u>
Y	24 October, 1987 (24.10.87), Claims 1, 2; page 1, right column, line 15 to page 2, upper left column, line 2; page 2, lower left column, line 6 to page 3, upper right column, line 15; Figs. 1, 3, 5, 6 (Family: none)	<u>13</u> 2-4, 7, 8, 10, 11
Y	JP 2000-140929 A (NKK Corp.), 23 May, 2000 (23.05.00), Claims 1, 2; Par. Nos. [0012], [0023]; Fig. 2 (Family: none)	2-4, 7, 8, 10, 11

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
19 June, 2009 (19.06.09)Date of mailing of the international search report
30 June, 2009 (30.06.09)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 10008298 A [0008]
- JP 55048421 A [0008]
- JP 58064400 A [0008]
- JP 9078273 A [0008]
- JP 2001020086 A [0008]
- JP 2001191108 A [0008]
- JP 9087871 A [0008]
- JP 10183251 A [0008]
- JP 62243788 A [0008]

Non-patent literature cited in the description

- **Nobuhiro Shibatomi et al.** *Mitsubishi Heavy Industries Technical Review*, 1992, vol. 129 (1), 24-29 [0009]
- **Kazunori Hata et al.** *Hitachi Hyoron*, 1985, vol. 6 (4), 41-46 [0009]