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(54) PICKLING METHOD FOR STEEL PLATES

BEIZVERFAHREN FÜR STAHLPLATTEN

PROCÉDÉ DE DÉCAPAGE POUR DES TÔLES D'ACIER

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Description

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

[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 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 "Nobuhiro Shibatomi et al., Mitsubishi Heavy Industries Technical Review, Vol. 129, No. 1, 24-29 (1992)", 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.

[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 "Kazunori Hata et al., Hitachi Hyoron, Vol. 6 No. 4, 41-46 (1985)". 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.

[0005] 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 (see JP H10-8298A, JP S55-48421A and JP S58-64400A).

[0006] 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 (see JP H9-78273A).

[0007] 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 (see JP 2001-20086A).

[0008] 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 (see JP 2001-191108A).

[0009] 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 JP H9-87871A.

[0010] 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 (see JP H10-183251A).

[0011] 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 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 (see JP S62-243788A)

[0012] 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.

[0013] 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.

[0014] 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.

[0015] 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.

[0016] 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 according to claim 1 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.

[0017] 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 pickiling, the speed of dissolution of the oxide scale is remarkably improved.

[0018] 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 the object above can be achieved by the features defined in the claims.

[0019] According to the present invention, it is possible to efficiently remove oxide scale and to remarkably raise the speed of removal of oxide scale from steel sheet containing Si.

[0020] Further, the steel sheet after pickling process obtained by the present invention has a clean surface free of pickling scars.

[0021] The invention is described in detail in conjunction with the drawings, in which: FIG. 1 shows 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 shows 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 shows schematic views of blowing gas from a nozzle to the surface of steel sheet,
FIG. 4 shows an example of a pickling facility provided with a pickling system,
FIG. 5 shows an example of the case of providing a plurality of stages of nozzles, and
FIG. 6 shows views of arrangements of nozzles showing the case of a nozzle with a slit in the width direction of the steel sheet and the case of swinging a nozzle.

[0022] Below, the present invention will be explained in detail.

[0023] 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.

[0024] 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.

[0025] JP S62-243788A 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 JP S62-243788A, 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.

[0026] 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.

[0027] Further, 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.

[0028] 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.

[0029] 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.

[0030] The effect of improvement of the pickling efficiency is 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.

[0031] 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. According to the invention the angle θ (°) formed between the blowing direction and the surface of the steel sheet is $1° \leq \theta \leq 75°$ 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.

[0032] 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.

[0033] 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.

[0034] 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°.

[0035] 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.

[0036] 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.

[0037] 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.

[0038] 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.

[0039] 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 used to achieve the present invention.

[0040] 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.

[0041] 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.

[0042] The pickling solution of the pickling tank used to achieve 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.

[0043] 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.

[0044] 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.

[0045] 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

[0046] Below, the present invention will be explained more specifically using examples, but the present invention is not limited to these examples in any way. 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.

[0047] 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°C).

[0048] 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 mm$\times$50 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".

[0049] 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.

Table 1

	Si content of steel sheet (mass%)	Type of gas	Gas pressure at blowing port (MPa)	Blowing angle θ (°)	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
Ref. Ex. 20	3.6	Air	1.0	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. 21	0.3	Air	0.2	60	Good
Ref. Ex. 22	0.006	Air	0.1	60	Good
Inv. Ex. 23	0.3	Air	0.4	60	Good
Inv. Ex. 24	0.3	Air	1.1	60	Good
Ref. Ex. 25	3.6	Air	0.5	60	Good
Ref. Ex. 26	0.05	Air	0.8	60	Good
Ref. Ex. 27	0.3	Air	0.8	0.5	Fair
Ref. Ex. 28	0.3	Air	0.8	80	Fair
Ref. Ex. 29	0.3	Air	0.8	90	Fair
Ref. Ex. 30	0.3	Air	0.8	95	Fair
Comp. Ex. 1	0.3	No gas blown			Poor

Example 2

[0050] 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.

[0051] 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.

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

(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. 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
Ref. Ex. 45	0.3	Air	0.4	90	Fair
Ref. Ex. 46	0.3	Air	0.4	0.8	Fair
Ref. Ex. 47	0.3	Air	0.4	80	Fair
Comp. Ex. 2	0.3	No gas blown			Poor

[0052] 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.

[0053] 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.

[0054] Reference signs used in the description and drawings are listed below:

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 for removing oxide scale of a steel sheet (2) with a content of Si of 0.1 to 3.5 mass%, **characterized by** having a step A of pickling the steel sheet (2) with a pickling solution in a pickling tank (3, 4), a step B consisting of taking out the steel sheet (2) from the pickling tank (3, 4) and then blowing gas toward at least part of the surfaces of the steel sheet (2) in the air after said step A such that the pickling solution deposited on the surface of the steel sheet (2) at the part blown upon partially evaporates and its acid concentration becomes higher with allowing the deposited pickling solution to remain at the surface of the steel sheet to be concentrated, and a step C of pickling said steel sheet (2) subsequently after said step B, wherein an angle θ (°) formed between a blowing direction of said gas and at least part of the surfaces of the steel sheet (2) is $1° \leq \theta \leq 75°$.

2. A pickling method of a steel sheet as set forth in claim 1, **characterized by** blowing said gas against a direction of movement of the steel sheet (2).

3. A pickling method of a steel sheet as set forth in claim 1 or 2, **characterized in that** a blowing pressure of said gas is 0.5 to 1.0 MPa.

4. A pickling method of a steel sheet as set forth in any one of claims 1 to 3, **characterized in** the pickling of said step A is performed in a first pickling tank (4) and the pickling of said step C is performed in a second pickling tank (5).

Patentansprüche

1. Beizverfahren zum Entfernen von Oxidzunder von einem Stahlblech (2) mit einem Si-Gehalt von 0,1 bis 3,5 Massenprozent, **gekennzeichnet durch** einen Schritt A, bei dem das Stahlblech (2) mit einer Beizlösung in einem Beiztank (3, 4) gebeizt wird, einen Schritt B, bei dem das Stahlblech (2) aus dem Beiztank (3, 4) entnommen wird und dann Gas nach Schritt A gegen zumindest einen Teil der Oberflächen des Stahlblechs (2) in der Luft geblasen wird, so dass die Beizlösung, die sich an dem Teil, gegen den geblasen wird, an der Oberfläche des Stahlblechs (2) angelagert hat, zumindest teilweise verdampft wird und ihre Säurekonzentration höher wird, wodurch ermöglicht wird, dass die abgelagerte Beizlösung, die an der Oberfläche des Stahlblechs (2) verblieben ist, konzentriert wird, und einen Schritt C, bei dem das Stahlblech (2) nach Schritt B gebeizt wird, wobei ein zwischen einer Blasrichtung des Gases und zumindest einem Teil der Oberflächen des Stahlblechs (2) gebildeter Winkel θ (°) $1° \leq \theta \leq 75°$ beträgt.

2. Verfahren zum Beizen von Stahlblech nach Anspruch 1, **dadurch gekennzeichnet, dass** das Gas gegen die Bewegungsrichtung des Stahlblechs (2) geblasen wird.

3. Verfahren zum Beizen von Stahlblech nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** der Blasdruck des Gases 0,5 bis 1,0 MPa beträgt.

4. Verfahren zum Beizen von Stahlblech nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** das Beizen aus Schritt A in einem ersten Beiztank (4) ausgeführt wird und das Beizen aus Schritt C in einem zweiten Beiztank (5) ausgeführt wird.

Revendications

1. Procédé de décapage pour éliminer la calamine d'une tôle d'acier (2) ayant une teneur en Si de 0,1 à 3,5 % en

masse, **caractérisé par le fait qu'**il comporte une étape A de décapage de la tôle d'acier (2) à l'aide d'une solution de décapage dans un bac de décapage (3,4), une étape B consistant à retirer la tôle d'acier (2) du bac de décapage (3, 4) puis à souffler un gaz vers au moins une partie des surfaces de la tôle d'acier (2) dans l'air après ladite étape A de manière à ce que la solution de décapage déposée sur la surface de la tôle d'acier (2) au niveau de la partie ayant reçu le gaz soufflé s'évapore partiellement et à ce que sa concentration en acide devienne supérieure en laissant la solution de décapage déposée rester à la surface de la tôle d'acier pour être concentrée, et une étape C de décapage de ladite tôle d'acier (2) ensuite après ladite étape B, dans lequel un angle θ (°) formé entre une direction de soufflage dudit gaz et au moins une partie des surfaces de la tôle d'acier (2) est $1° \leq \theta \leq 75°$.

2. Procédé de décapage d'une tôle d'acier selon la revendication 1, **caractérisé par** le soufflage dudit gaz à l'opposé d'une direction de mouvement de la tôle d'acier (2).

3. Procédé de décapage d'une tôle d'acier selon la revendication 1 ou 2, **caractérisé en ce qu'**une pression de soufflage dudit gaz est de 0,5 à 1,0 MPa.

4. Procédé de décapage d'une tôle d'acier selon l'une quelconque des revendications 1 à 3, **caractérisé en ce que** le décapage de ladite étape A est réalisé dans un premier bac de décapage (4) et le décapage de ladite étape C est réalisé dans un second bac de décapage (5).

Fig.1

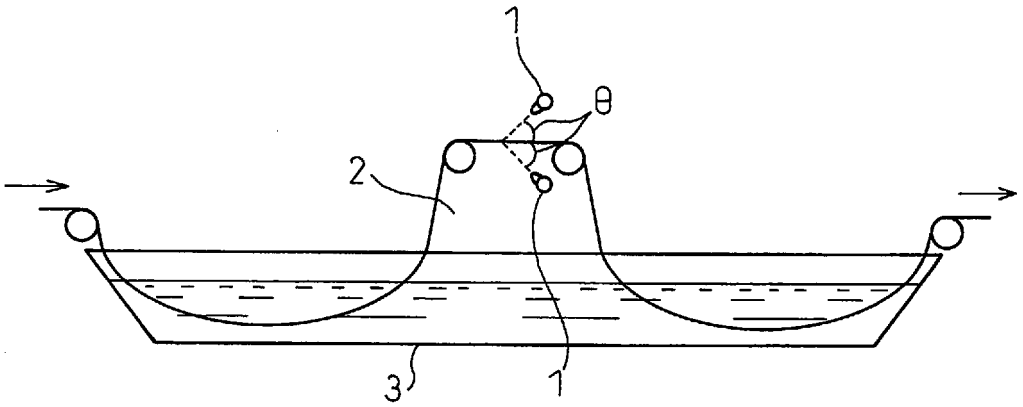


Fig.2

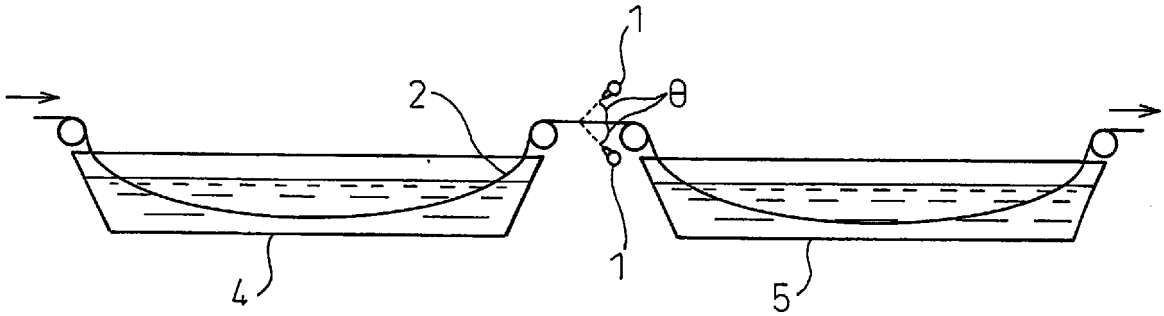


Fig.3

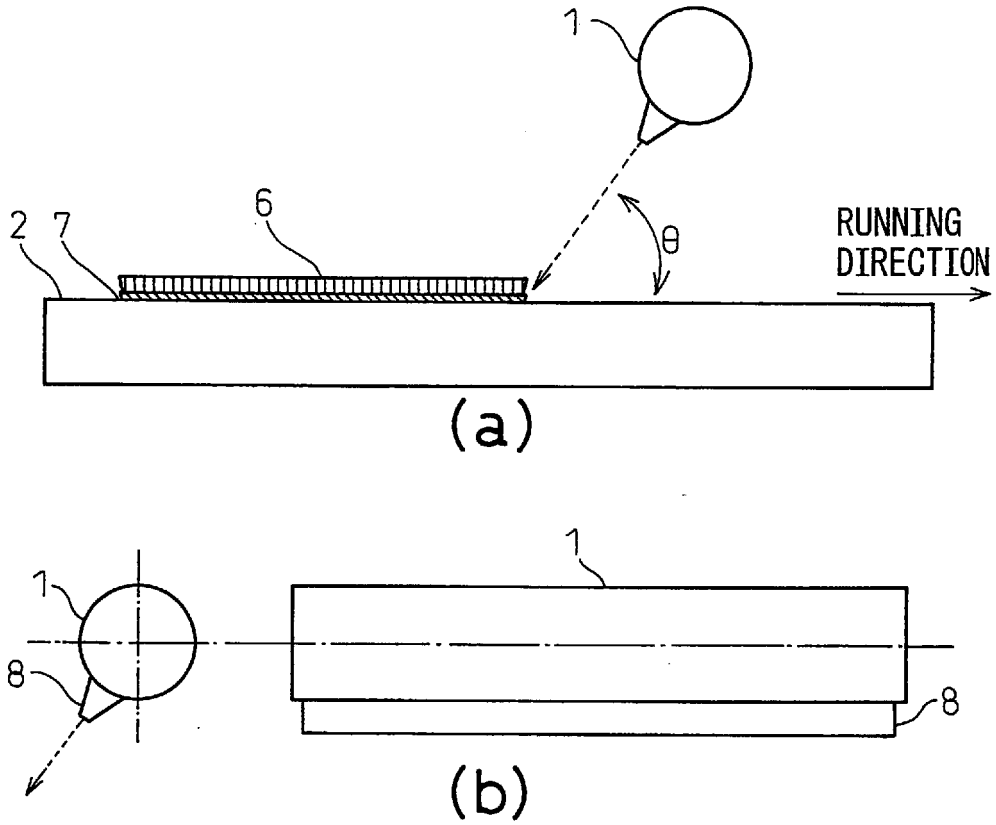


Fig.4

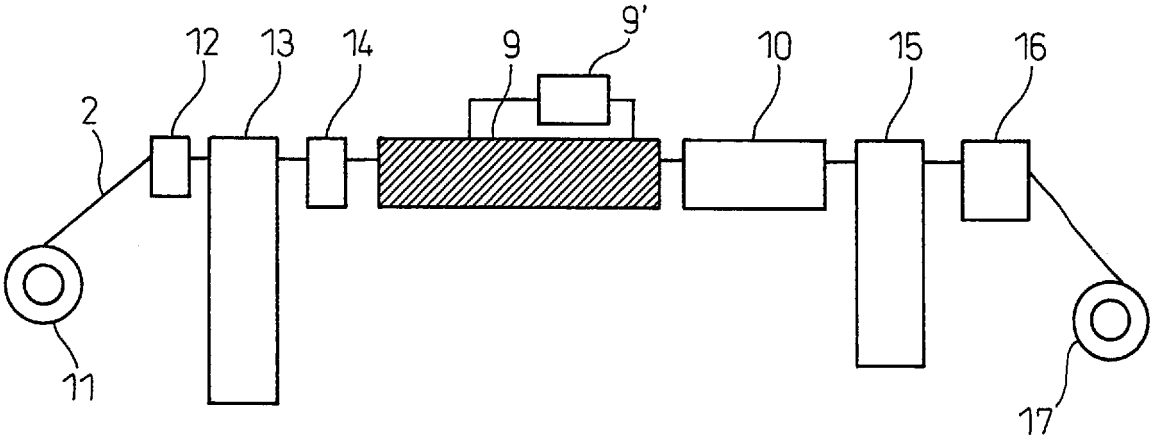


Fig.5

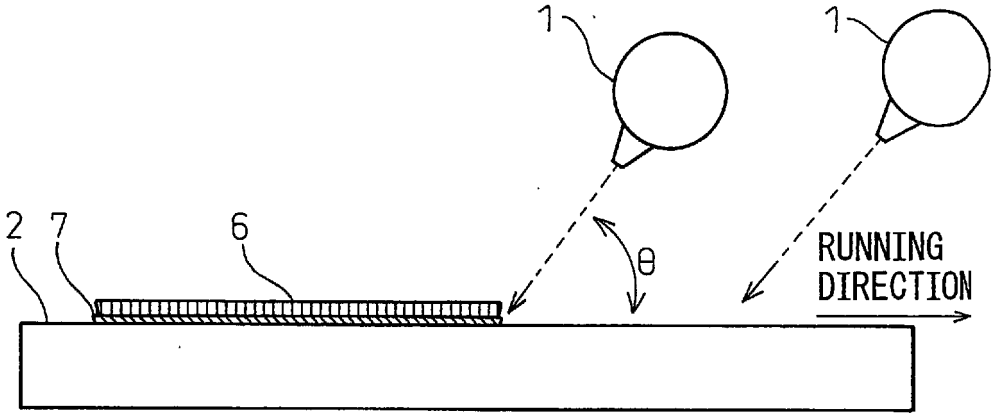
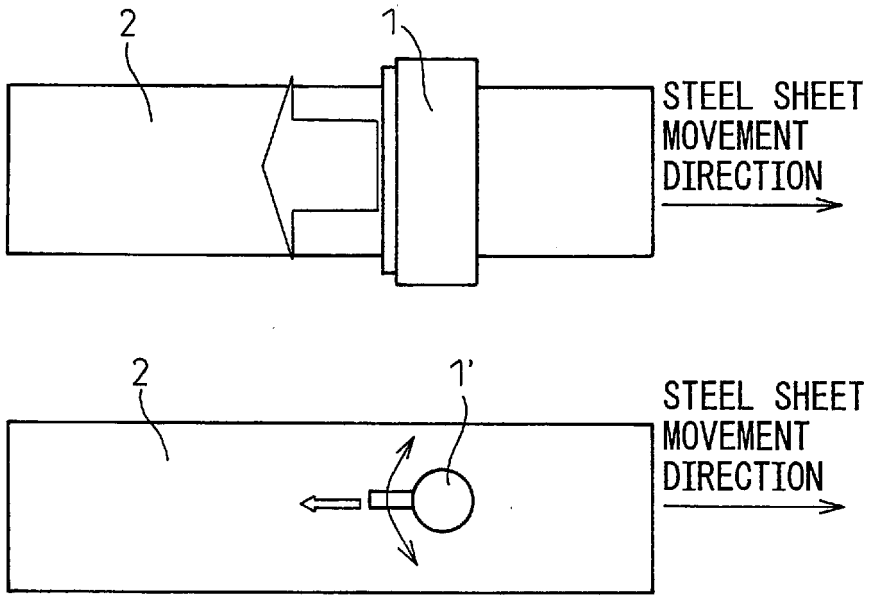

1
1
2
7
6
θ
RUNNING
DIRECTION

Fig.6


2
1
STEEL SHEET
MOVEMENT
DIRECTION
2
1'
STEEL SHEET
MOVEMENT
DIRECTION

REFERENCES CITED IN THE DESCRIPTION

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