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(71) Applicant: **Posco**
Pohang
Kyungsangbook-do 790-300 (KR)

(72) Inventors:
• **KIM, Ji-Hun**
Pohang-si
Kyungsangbook-do 790-360 (KR)

- **KIM, Dong-Hoon**
Pohang-si
Kyungsangbook-do 790-360 (KR)
- **KIM, Jin-Suk**
Pohang-si
Kyungsangbook-do 790-360 (KR)
- **CHOI, Sang-Kyo**
Pohang-si
Kyungsangbook-do 790-360 (KR)
- **LEE, Yong-Heon**
Pohang-si
Kyungsangbook-do 790-360 (KR)

(74) Representative: **Potter Clarkson LLP**
The Belgrave Centre
Talbot Street
Nottingham
NG1 5GG (GB)

(54) **ECO-FRIENDLY HIGH-SPEED PICKLING PROCESS FOR PRODUCING A LOW-CHROME FERRITE-BASED COLD-ROLLED STAINLESS STEEL SHEET HAVING SUPERIOR SURFACE QUALITY**

(57) The present invention relates to a method for pickling the surface of a steel sheet at high speed during the manufacturing of a ferrite-based cold-rolled stainless steel sheet that requires good surface qualities. The method for pickling a low-chrome ferrite-based cold-rolled stainless steel sheet at high speed involves pickling a ferrite-based cold-rolled stainless steel sheet which contains 14% or less of chrome and which has undergone a degreasing and annealing process, wherein the method comprises a neutral salt electrolyte treatment including the electrolytic removal of chrome-rich scale from the surface of the steel sheet using an electrolytic solution in which sodium sulfate is used as an electrolyte; a sulfuric acid electrolyte treatment including the electrolytic removal of iron-rich scale using an electrolytic solution in which sulfuric acid is used as an electrolyte; and a mixed acid treatment including immersing the steel sheet

in a mixed acid solution containing sulfuric acid, hydrofluoric acid, and hydrogen peroxide, wherein the whole pickling process is completed within 15 to 240 seconds. According to the present invention, the use of nitric acid in pickling a ferrite-based cold-rolled stainless steel sheet can be avoided, thus reducing the burden of installing an NOx removal facility and a denitrification facility, and furthermore, pickling may be adjusted in terms of the hydrogen peroxide concentration and hydrofluoric acid concentration, thus making the process easy to control and suitable for high-speed production. The quality of the steel sheet having undergone the pickling process of the present invention is improved as compared to that of the steel sheet of existing pickling process, the result being that a high-quality ferrite-based cold-rolled stainless steel sheet may be produced.

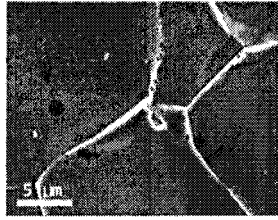


FIG. 1A

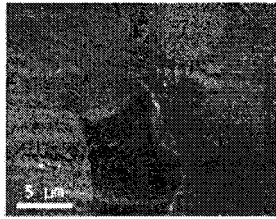


FIG. 1B

Description

[Technical Field]

[0001] The present invention relates to a high-speed steel sheet pickling process for producing a ferrite-based cold-rolled stainless steel sheet having superior surface qualities, and more particularly, to a pickling process not using nitric acid.

[Background Art]

[0002] After cold rolling, stainless steel sheets are heat-treated at a temperature of 800°C to 1150°C to obtain desired mechanical properties. However, during such a heat treatment process, the surfaces of steel sheets react with hot oxygen in a furnace and may be stained with oxide scale (e.g., SiO_2 and $(\text{Cr,Fe})_3\text{O}_4$). Such oxide scale spoils the appearance of steel sheets and reduces the quality of steel sheets. In addition, such oxide scale reduces the corrosion resistance of steel sheets because steel sheets may start to corrode from the presence of oxide scale.

[0003] Therefore, to produce cold-rolled stainless steel sheets having sleek, high-quality, and corrosion-resistant surfaces, oxide scale is removed by various methods such as: physical descaling including brushing or shot ball blasting; electrolytic descaling using a sodium sulfate electrolyte, a sulfuric acid electrolyte, or a nitric acid electrolyte; and chemical descaling using a salt bath or an acid mixture. Such a descaling process is known as a pickling process. Stainless steel is treated through a pickling process to improve surface appearance and quality and to evenly form a corrosion-resistant passive film thereon, and pickling methods for descaling stainless steel include: a nitric acid electrolytic method in which current is applied to a nitric acid solution while passing a steel sheet therethrough; and a chemical descaling method using a mixture of a nitric acid (80 g/l to 180 g/l) and a hydrofluoric acid (2 g/l to 40 g/l). Nitric acid reduces the pH level of a pickling bath to increase the activity of hydrofluoric acid, and oxidizes Fe^{2+} ions into Fe^{3+} ions to maintain the oxidation-reduction potential at a level suitable for pickling.

[0004] However, the use of nitric acid as a pickling solution results in emission of NO_x , a regulated air pollutant, and nitric nitrogen ($\text{NO}_3\text{-N}$) in waste acids and washing water. Therefore, it is necessary to add and operate pollution prevention equipment for a pickling process so as to satisfy tightened domestic and foreign environmental regulations limiting the total amount of nitrogen in effluent and the concentration of NO_x emitted from air pollutant emission facilities. However, installation and operating costs of such equipment markedly increase unit cost of production. Particularly, when producing low-chrome ferrite cold-rolled stainless steel sheets having lower levels of corrosion resistance than other stainless steel sheets due to a low chrome content of 14 weight% or less, higher amounts of low-chrome ferrite cold-rolled stainless steel sheets dissolve in an acid solution due to their low corrosion resistance, and this markedly increases the generation of NO_x and nitric nitrogen.

[0005] For these reasons, pickling methods not using nitric acid have been developed, in which hydrochloric acid or sulfuric acid is used instead of nitric acid, and insufficient oxidizing power is compensated for by hydrogen peroxide, potassium permanganate, Fe^{3+} ions, and the injection of air.

[0006] Specifically, German Patent No. 3937438 discloses a technique of using a pickling solution including sulfuric acid, hydrofluoric acid, and iron sulfate, and adding hydrogen peroxide to the pickling solution to maintain the oxidation-reduction potential of the pickling solution equal to or greater than 300 mV. Starting from the technique, techniques have been constantly proposed since the 1990s, mainly concerned with regulating appropriate amounts of hydrofluoric acid, iron ions, air, and hydrogen peroxide, or appropriate oxidation-reduction potentials (ORP) in solutions, as in US Patent No. 5154774 and European Patent No. 236354. However, the majority of such techniques are used for producing limited kinds of products such as wire rods, steel rods, and steel plates which have easy to meet quality requirements.

[0007] US Patent No. 5908511 discloses a technique for performing a pickling process using a pickling solution including: sulfuric acid, hydrofluoric acid, ferric salt, periodically added hydrogen peroxide, a wetting agent, a polishing agent, and a corrosion inhibitor while controlling concentrations of the wetting agent, the polishing agent, and the corrosion inhibitor and automatically managing the pickling solution based on the amount of Fe(III) and ORP related to the amount of Fe(III) . The pickling solution was commercialized as CLEANOX352, and has become the most widely used product in the art to which the present invention pertains. This technique is practically used for producing wire rods and hot-rolled products, but increases unit cost in production by 20% or more and requires a complicated solution and control method. Furthermore, the technique has a slow pickling weight reduction rate of about 1.5 g/m²-min to about 3 g/m²-min, and thus, is not suitable for a high-speed pickling process that has to be performed within 10 seconds to 100 seconds.

[0008] Advanced versions of the technique are disclosed in European Patent No. 1040211 and US Patent Application Publication No. 2000-560982, in which copper and chlorine ions are added to a pickling composition to increase the pickling rate. However, since the open circuit potential (OCP) of the surface of a ferrite-based stainless steel sheet is lower than the ORP of copper ions (0.1 V), copper particles may be deposited to stain the surface of the ferrite-based stainless steel sheet. In addition, if the concentration of chlorine ions in a pickling solution is higher than a certain value,

pitting corrosion may occur.

[0009] As described above, many pickling techniques not using nitric acid have been introduced. However, a pickling technique suitable for high-speed production of ferrite-based cold-rolled steel sheets has not yet been introduced.

[Disclosure]

[Technical Problem]

[0010] Aspects of the present invention provide a pickling process for rapidly producing a low-chrome ferrite-based cold-rolled stainless steel sheets having high quality by using an electrolyte solution not including nitric acid, and a pickling process for rapidly removing Si oxide by using a mixed acid solution.

[0011] Another aspect of the present invention provides a mixed acid solution not including nitric acid and suitable for the pickling processes.

[0012] Another aspect of the present invention provides a low-chrome ferrite-based cold-rolled stainless steel sheet produced by the pickling processes.

[Technical Solution]

[0013] According to an aspect of the present invention, there is provided a pickling process for rapidly removing Si oxide from a surface of a low-chrome ferrite-based cold-rolled stainless steel sheet having a content of chrome of 14% or less by using a mixed acid solution not containing nitric acid, the pickling process including immersing the cold-rolled stainless steel sheet in the mixed acid solution including hydrogen peroxide, wherein the mixed acid solution includes 70 g/l to 200 g/l of sulfuric acid and 1 g/l to 10 g/l of free hydrofluoric acid, wherein the mixed acid solution initially includes 7 g/l or more of the hydrogen peroxide but no Fe ions, and the pickling process is performed at a rate of 3 g/m²-min to 15 g/m²-min.

[0014] The hydrogen peroxide and Fe ions may satisfy the following concentration formula:

$$[\text{H}_2\text{O}_2] \geq 0.74 + 3.1e^{-[\text{Fe}]/1.1} + 3.2e^{-[\text{Fe}]/15}.$$

[0015] An open circuit potential of the cold-rolled stainless steel sheet immersed in the mixed acid solution may be maintained within a range of -0.2 V to 0.2 V, and the cold-rolled stainless steel sheet may be immersed in the mixed acid solution for 10 seconds to 100 seconds.

[0016] According to another aspect of the present invention, there is provided a process for pickling a low-chrome ferrite-based cold-rolled stainless steel sheet having 14% or less of chrome after a degreasing treatment and an annealing treatment, the process including: performing a sulfuric acid electrolyte treatment to remove (Fe,Cr) scale from the low-chrome ferrite-based cold-rolled stainless steel sheet by a sulfuric acid electrolyte solution comprising sulfuric acid as an electrolyte; and performing a mixed acid treatment in which the low-chrome ferrite-based cold-rolled stainless steel sheet is immersed in a mixed acid solution comprising sulfuric acid, a free hydrofluoric acid, and hydrogen peroxide, wherein the process has a pickling rate of 3 g/m²-min to 15 g/m²-min.

[0017] The process may further include performing a neutral salt electrolyte treatment to remove Cr-rich scale from the steel sheet using a neutral salt electrolyte solution comprising a sodium sulfate electrolyte.

[0018] The neutral salt electrolyte treatment may be performed by immersing the steel sheet in the neutral salt electrolyte solution maintained at 50°C to 90°C and applying a current of 10 A/dm² to 30 A/dm² to the steel sheet for a period of time longer than 0 seconds but not longer than 90 seconds so that open circuit potentials are applied to the steel sheet in order of positive (+), negative (-), and positive (+), and the neutral salt electrolyte solution may include 100 g/l to 250 g/l of the sodium sulfate electrolyte.

[0019] After the steel sheet is treated through the annealing treatment or a neutral salt electrolyte treatment, the sulfuric acid electrolyte treatment may be performed by immersing the steel sheet in the sulfuric acid electrolyte solution maintained at 30°C to 60°C and applying a current of 10 A/dm² to 30 A/dm² to the steel sheet for 5 seconds to 50 seconds so that open circuit potentials are applied to the steel sheet in order of positive (+), negative (-), and positive (+), and the sulfuric acid electrolyte solution may include 50 g/l to 150 g/l of the sulfuric acid.

[0020] The mixed acid treatment may be performed by immersing the steel sheet in the mixed acid solution for 10 seconds to 100 seconds, and the mixed acid solution may include 70 g/l to 200 g/l of the sulfuric acid, 1 g/l to 10 g/l of the free hydrofluoric acid, and initially 7 g/l or more of the hydrogen peroxide and substantially no iron ions.

[0021] An open circuit potential of the steel sheet may be maintained within a range of -0.2 V to 0.2 V during the mixed acid treatment.

[0022] During the process, the hydrogen peroxide and iron ions in the mixed acid solution may satisfy the following concentration formula:

$$[H_2O_2] \geq 0.74 + 3.1e^{-[Fe]/1.1} + 3.2e^{-[Fe]/15}.$$

[0023] The steel sheet may have a gloss value of 130 or greater after being pickled through the process.

[0024] According to another aspect of the present invention, there is provided a mixed acid solution not including a nitric acid for removing Si oxide from a ferrite-based cold-rolled stainless steel sheet having 14% or less of chrome after a degreasing treatment and an annealing treatment, the mixed acid solution including 70 g/l to 200 g/l of sulfuric acid, 1 g/l to 10 g/l of free hydrofluoric acid, and hydrogen peroxide, wherein the hydrogen peroxide and iron ions in the mixed acid solution satisfy the following concentration formula:

$$[H_2O_2] \geq 0.74 + 3.1e^{-[Fe]/1.1} + 3.2e^{-[Fe]/15}.$$

[Advantageous Effects]

[0025] According to the present invention, a ferrite-based cold-rolled stainless steel sheet can be pickled using the mixed acid solution not including nitric acid, and thus NO_x and nitric nitrogen are not generated. Therefore, costs necessary for installing equipment for removing NO_x and nitrogen can be saved.

[0026] In addition, since the pickling process can be controlled by adjusting the concentrations of hydrogen peroxide and hydrofluoric acid, control manipulations can be easily performed and high-speed production is possible. Furthermore, ferrite-based cold-rolled stainless steel sheets pickled according to the present invention have higher quality than those pickled by methods according to the related art.

[0027] In addition, since Fe and Cr oxides can be completely removed through the pickling treatments using electrolytes, Si oxide can easily be removed at a high rate of 3 g/m²-min to 15 g/m²-min in a mixed acid bath containing the mixed acid solution. Therefore, removing of Si oxide and flattening by the mixed acid solution can only be performed within 10 seconds to 100 seconds.

[0028] Furthermore, since the solutions used in the pickling process of the present invention have simple compositions, the solutions can be easily handled and controlled to prevent reactions with substances other than surfaces of steel sheets. Therefore, cold-rolled stainless steel sheets having high surface qualities can be obtained, and high-speed production for improving productivity is possible.

[Description of Drawings]

[0029] FIGS. 1(a) and 1(b) are images of the surfaces of low-chrome ferrite-based cold-rolled stainless steel sheets which are heat-treated in Embodiment 1 taken with a scanning electron microscope, FIG. 1(a) showing the surface of a steel sheet (Inventive Sample 2), FIG. 1(b) showing the surface of a steel sheet (Comparative Sample 4).

[0030] FIGS. 2(a) and 2(b) are images of sections of low-chrome ferrite-based cold-rolled stainless steel sheets after a heat treatment, taken with a scanning electron microscope, FIG. 2(a) showing a section of a steel sheet treated through an electrolytic process, FIG. 2(b) showing a section of a steel sheet not treated through an electrolytic process.

[0031] FIGS. 3(a) and 3(b) are graphs showing open circuit potential with respect to oxidation-reduction potential (ORP) and the concentration of hydrogen peroxide when low-chrome ferrite-based cold-rolled stainless steel sheets are immersed in an acid mixture, FIG. 3(a) showing the relationship between open circuit potential and ORP, FIG. 3(b) showing the relationship between open circuit potential and the concentration of hydrogen peroxide.

[0032] FIG. 4 is a graph showing the minimally required concentration of hydrogen peroxide according to the concentration of iron ions.

[0033] FIG. 5 is a graph showing the gloss of low-chrome ferrite-based cold-rolled stainless steel sheets pickled according to Embodiment 8.

[Best Mode]

[0034] The present invention provides a method of removing oxide scale from the surface of a low-chrome ferrite-based cold-rolled stainless steel sheet by immersing the steel sheet in a neutral salt electrolyte bath containing sodium sulfate as an electrolyte, a sulfuric acid electrolyte bath containing sulfuric acid as an electrolyte, and a mixed acid bath containing a pickling composition in which nitric acid is not included.

[0035] The present invention will now be described in detail.

[0036] Oxide scale having a thickness of 100 nm to 300 nm is generally formed on a low-chrome ferrite-based cold-rolled stainless steel sheet after a heat treatment, and such oxide scale has a multilayer structure including a Cr-rich scale layer having more Cr oxide than Fe oxide, a Fe-rich scale layer having more Fe oxide than Cr oxide, and a Si-oxide layer formed between the oxide scale layers and the steel sheet.

[0037] The Cr-rich scale layer is removed in the neutral salt electrolyte bath. The neutral salt electrolyte bath includes: a neutral salt electrolyte solution having sodium sulfate as an electrolyte; and electrodes to apply a current to the surface of the steel sheet. The electrodes are arranged so that surfaces of the steel sheet can be charged with potentials in order of positive (+), negative (-), and positive (+).

[0038] If a current is applied to the neutral salt electrolyte solution having a pH of 3 to 6, Cr of the Cr-rich scale layer is first dissolved as Cr^{6+} , and thus the Cr-rich scale layer can be removed from the surface of the steel sheet. At this time, sodium sulfate may be used as an electrolyte. The sodium sulfate electrolyte increases the electrical conductivity of the electrolyte solution, which causes more current to flow in the steel sheet and thus facilitates dissolution of the Cr-rich scale layer.

[0039] The electrolyte solution may include 100 g/l to 250 g/l of a sodium sulfate electrolyte. If the concentration of the sodium sulfate electrolyte is 100 g/l or more, conductivity suitable for dissolving chrome can be obtained. However, if the concentration of the sodium sulfate electrolyte is greater than 250 g/l, sodium sulfate may precipitate in the electrolyte solution to clog equipment pipes and cause errors. Therefore, the concentration of the sodium sulfate electrolyte may be 250 g/l or less.

[0040] The electrical conductivity of the electrolyte in the neutral salt electrolyte bath is closely related to the temperature of the electrolyte solution. At a temperature of 50°C or higher, a conductivity level suitable for dissolving chrome may be obtained, and the conductivity increases as temperature increases. However, if the temperature of the electrolyte solution is greater than 90°C, it is difficult to practically control the temperature. Therefore, the temperature of the electrolyte solution in the neutral salt electrolyte bath may be set to be within a range of 50°C to 90°C.

[0041] A current of 10 A/dm² or higher may be applied through the electrodes for sufficiently eluting Cr of the Cr-rich scale layer. However, since a large rectifier is necessary to apply a current greater than 30 A/dm², a current of 10 A/dm² to 30 A/dm² may be applied so as not to increase initial equipment costs.

[0042] This neutral salt electrolyte treatment is performed within 90 seconds. In some cases, the neutral salt electrolyte treatment may be omitted, and Fe and Cr oxide scale may only be removed by a sulfuric acid electrolyte treatment. In this case, however, it may be necessary to perform the sulfuric acid electrolyte treatment and the next acid mixture treatment for longer periods of time. That is, the neutral salt electrolyte treatment may be necessary to decrease the total process time of a pickling treatment. If the neutral salt electrolyte treatment is performed for more than 90 seconds, over-pickling may occur to erode the steel sheet.

[0043] The Fe-rich scale layer is removed in the sulfuric acid electrolyte bath. The sulfuric acid electrolyte bath includes: a sulfuric acid electrolyte solution having sulfuric acid as an electrolyte; and electrodes to apply a current to the surface of the steel sheet. The electrodes are arranged so that the surface of the steel sheet can be charged with potentials in order of positive (+), negative (-), and positive (+).

[0044] If a current is applied to the sulfuric acid electrolyte solution having a pH of 0 to 1, Fe dissolves as Fe^{2+} . At this time, H^+ and SO_4^{2-} of the sulfuric acid increases the electrical conductivity of the electrolyte solution and thus causes more current to flow from the electrodes to the steel sheet, and owing to the lower pH value, Fe of the Fe-rich scale layer is chemically dissolved.

[0045] The electrolyte solution may include 50 g/l to 150 g/l of sulfuric acid. If the concentration of the sulfuric acid is 50 g/l or more, appropriate conductivity may be maintained to maintain the amount of current flowing in the surface of the steel sheet at an appropriate level. However, if the concentration of the sulfuric acid is greater than 150 g/l, chemical dissolving may be dominant to roughen the surface of the steel sheet.

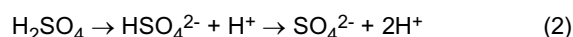
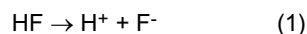
[0046] Like the electrolyte solution in the neutral salt electrolyte bath, the sulfuric acid electrolyte solution may be maintained at 30°C or higher for maintaining conductivity equal to or higher than a lower limit. However, if the temperature of the sulfuric acid electrolyte solution is greater than 60°C, chemical dissolution may proceed excessively to roughen the steel sheet and stain the steel sheet with black smut. Therefore, the temperature of the electrolyte solution in the sulfuric acid electrolyte bath may be set to be within a range of 30°C to 60°C.

[0047] A current of 10 A/dm² to 30 A/dm² may be applied to the sulfuric acid electrolyte bath. If a current of 10 A/dm² or lower is applied, the steel sheet may start to dissolve and become rough. In addition, since a large rectifier is necessary to apply a current greater than 30 A/dm², a current of 10 A/dm² to 30 A/dm² may be applied so as not to increase initial equipment costs.

[0048] This sulfuric acid electrolyte treatment may be performed for 5 seconds to 50 seconds. If the sulfuric acid electrolyte treatment is performed for less than 5 seconds, pickling may be insufficient, and if the sulfuric acid electrolyte treatment is performed for longer than 50 seconds, over-pickling may occur. Thus, the sulfuric acid electrolyte treatment may be performed for the above-mentioned period of time.

[0049] After the neutral salt electrolyte treatment and the sulfuric acid electrolyte treatment, only the Si-oxide layer remains on the steel sheet. The Si-oxide layer may be removed by a mixed acid solution not including nitric acid and nitrogen. The mixed acid solution includes sulfuric acid, free hydrofluoric acid, and hydrogen peroxide. After the neutral salt electrolyte treatment and the sulfuric acid electrolyte treatment, the steel sheet is immersed in the mixed acid bath containing the mixed acid solution to remove the Si-oxide layer.

[0050] In the mixed acid solution, the hydrofluoric acid and the sulfuric acid dissociate as shown in Reaction Formulas (1) and (2) below. In the mixed acid solution, the hydrofluoric acid dissolves and dissociates, and the chemical equilibrium of the hydrofluoric acid is varied according to the concentration of H^+ generated by dissociation of the sulfuric acid, that is, according to the acidity of the mixed acid solution.

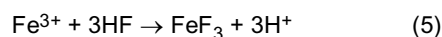
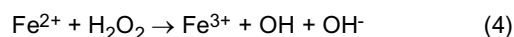


[0051] The hydrofluoric acid in its free state (non-dissociating state, free HF) has acidity to dissolve Si oxide and dissolve Fe by permeating between the Si-oxide layer and the steel sheet. Dissolved Fe and Si ions are removed from the surface of the steel sheet in the form of $FeF_x^{(3-x)}$, H_2SiF_6 , etc. The concentration of the hydrofluoric acid in the mixed acid solution may be within the range of 1 g/l to 10 g/l, more specifically, within the range of 1 g/l to 5 g/l. If the concentration of the hydrofluoric acid is less than 1 g/l, the concentration of free hydrofluoric acid is not enough to dissolve Si, and thus the surface of the steel sheet may not be pickled. If the concentration of the hydrofluoric acid is greater than 10 g/l, the steel sheet may erode rapidly and become rough after pickling.

[0052] As described above, since acidity necessary for removing the Si-oxide layer from the surface of the steel sheet is provided by hydrofluoric acid, it may be necessary to maintain the concentration of free hydrofluoric acid at a level effective to obtain a predetermined acidity value or higher. Therefore, in the mixed acid solution, the concentration of the sulfuric acid is maintained at a predetermined value or above so as to prevent or reduce dissociation of the hydrofluoric acid. The concentration of the sulfuric acid may be maintained within the range from 50 g/l to 150 g/l. If the concentration of the sulfuric acid is less than 50 g/l, it is difficult to maintain an effective concentration of free hydrofluoric acid, and thus acidity decreases as a result of hydrofluoric acid dissociation. In this case, pickling may be insufficiently performed. On the contrary, if the concentration of the sulfuric acid is greater than 150 g/l, heat generated during sulfuric acid dilution may worsen working conditions. Therefore, the concentration of the sulfuric acid may be maintained within the above-mentioned range.

[0053] All the Si oxide of the oxide scale is formed on the surfaces and boundaries of ferrite grains of the ferrite-based stainless steel sheet, and the portion of the Si oxide formed on the boundaries of the ferrite grains is located deeper within the steel sheet than the other Si oxide. Austenitic stainless steel starts to erode at its grain boundaries because of high corrosion resistance at grains. However, the erosion rate of a ferrite-based steel sheet is not different at the insides and boundaries of grains because of low corrosion resistance at grains, and thus the surfaces and boundaries of grains are not selectively dissolved but dissolved together. Therefore, a considerable amount of the stainless steel sheet may dissolve until all the Si oxide is removed.

[0054] In this case, Fe^{2+} comes out from the stainless steel sheet and is oxidized to Fe^{3+} by reaction with hydrogen peroxide. The Fe^{3+} combines with HF to produce a complex, $FeF_x^{(3-x)}$. In this way, Fe is removed from the stainless steel sheet. These reactions can be expressed by Reaction Formulas (3) to (6) below, and the pickling process can be rapidly performed when the reactions smoothly occur.



[0055] According to experiments carried out by the inventors, about 3 g/m² to about 5 g/m² of scale and a steel sheet has to be removed in a mixed acid bath. In addition, to rapidly produce cold-rolled steel sheets, a pickling rate of about 3 g/m²-min to about 15 g/m²-min has to be guaranteed so that Si scale can be removed from a steel sheet by immersing the steel sheet in a mixed acid bath only for 10 seconds to 100 seconds or for 20 seconds to 60 seconds.

[0056] Each kind of stainless steel has a unique potentiodynamic curve indicating a potential-current relationship, and the rate of pickling can be expressed according to current. That is, the maximum rate of pickling can be obtained by adjusting open circuit potential. To obtain a pickling rate of 3 g/m² to 15 g/m², required to rapidly produce cold-rolled

steel sheets, the open circuit potential of a cold-rolled steel sheet may be maintained at a range of - 0.2 V to 0.2 V. If the open circuit potential of a cold-rolled steel sheet is outside of this range, the cold-rolled steel sheet may not be pickled or may be defectively pickled, and even in the case that the cold-rolled steel sheet is pickled, the surface qualities thereof may be deteriorated.

[0057] In the related art, a pickling process is performed while controlling the oxidation-reduction potential (ORP) of a pickling solution by varying the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the pickling solution. However, there is no relationship between open circuit potential and ORP as shown in FIG. 3(a). That is, ORP is not an important factor for open circuit potential in a pickling process. On the contrary, in the case where a low-chrome ferrite-based stainless steel sheet is treated with a mixed acid solution, open circuit potential relates to the concentration of metal ions generating in a mixed acid bath in a pickling process. That is, open circuit potential relates to the concentration of ions of iron, a parent material, and the concentration of hydrogen peroxide remaining in the mixed acid solution, especially, to the concentration of the remaining hydrogen peroxide.

[0058] If the concentration of hydrogen peroxide remaining in the mixed acid solution is low, the reaction expressed by Reaction formula (4) may not occur to increase the concentration of Fe^{2+} locally on the surface of the steel sheet, and the reaction expressed by Reaction Formula (3) may mainly take place in the reverse direction. In this case, substances such as Cu that had existed in the steel sheet or Fe as additives or impurities are re-deposited on the surface of the steel sheet as shown in Reaction Formula (6) to form black smut. Therefore, it is necessary to maintain the concentration of remaining hydrogen peroxide at a certain value or higher.

[0059] The concentration of the remaining hydrogen peroxide has a relationship with the concentration of iron ions in the mixed acid solution. FIG. 3 shows the relationship between the open circuit potential of a cold-rolled steel sheet and the concentration of iron ions, and the minimum concentration of hydrogen peroxide necessary to maintain the open circuit potential of the cold-rolled steel sheet equal to or greater than -0.2 V in a mixed acid bath for performing a high-speed pickling process.

[0060] At the same concentration of hydrogen peroxide, the open circuit potential of a steel sheet increases gradually as the concentration of iron ions increases. The reason for this is that Fe^{3+} ions function as an oxidant, and as the concentration of Fe^{3+} ions increases, the concentration of hydrogen peroxide necessary for maintaining the open circuit potential of the steel sheet is decreased. However, although the concentration of Fe^{3+} ions is equal to or greater than a certain value, if the concentration of hydrogen peroxide is insufficient, the open circuit potential of the steel sheet becomes equal to or lower than -0.2 V to lower the surface qualities of the steel sheet. Based on the above-described relationships, the minimum concentration of hydrogen peroxide for maintaining the open circuit potential of a steel sheet equal to or higher than -0.2 V according to the concentration of iron ions can be expressed by the following formula.

$$[\text{H}_2\text{O}_2]_{\min} = 0.74 + 3.1e^{-[\text{Fe}]/1.1} + 3.2e^{-[\text{Fe}]/15}$$

[0061] In detail, if the concentration of iron ions is zero, the concentration of hydrogen peroxide may be at least 7 g/l, and if the concentration of iron ions is 40 or higher, the concentration of hydrogen peroxide may be 1.0 g/l or higher. As the concentration of hydrogen peroxide is sufficiently high, it is unnecessary to add more hydrogen peroxide, simplifying the process. However, since hydrogen peroxide is expensive, the use of hydrogen peroxide increases costs. In addition, since pickling efficiency does not increase in proportion to the concentration of hydrogen peroxide, the concentration of hydrogen peroxide may be kept lower than 30 g/l.

[0062] In the present invention, the temperature of the mixed acid solution is not limited to a certain value. An operator can select an appropriate temperature range, for example, 20°C to 95°C, 25°C to 80°C, or 25°C to 65°C.

[0063] As described above, in the mixed acid bath, the concentrations of sulfuric acid, hydrofluoric acid, and remaining hydrogen peroxide are the most important factors increasing the effect and speed of the pickling process. Therefore, it is necessary to control the concentrations thereof. For example, the concentrations of sulfuric acid and hydrofluoric acid may be controlled using a typical acid analyzer, and the concentration of remaining hydrogen peroxide may be analyzed and controlled using a near-infrared analysis method or an automatic titration method.

[0064] According to the present invention, a pickling process can be rapidly performed within about 15 seconds to about 240 seconds to markedly reduce the time necessary for pickling, and low-chrome ferrite-based cold-rolled stainless steel sheets having superior quality can be produced.

[Mode for Invention]

[0065] Examples of the present invention will now be described in detail.

Example 1

[0066] The effects of a neutral salt electrolyte treatment and a sulfuric acid electrolyte treatment in a pickling process for removing oxide scale were checked. For this, a Cr-rich scale layer and a Fe-rich scale layer were removed from a ferrite-based cold-rolled stainless steel sheet having 14% or less of chrome through the neutral salt electrolyte treatment and the sulfuric acid electrolyte treatment. In the treatments, a neutral salt electrolyte solution including 150 g/l of sodium sulfate as an electrolyte was maintained at 60°C, and a current of 150 A/dm² was applied for 40 seconds. A pH-1 sulfuric acid electrolyte solution including 85 g/l of sulfuric acid was maintained at 50°C, and a current of 20 A/dm² was applied for 15 seconds in a manner such that the steel sheet was charged with potentials in order of positive (+), negative (-), and positive (+).

[0067] The surface of the steel sheet treated with the neutral salt electrolyte treatment and the sulfuric acid electrolyte treatment, and the surface of a non-treated steel sheet were captured with a scanning electron microscope (SEM) and shown in FIGS. 1(a) and 1(b). FIG. 1(a) shows the surface of the electrolyte-treated steel sheet, and FIG. 1(b) shows the surface of the non-treated steel sheet.

[0068] Referring to in FIGS. 1(a) and 1(b), both (Cr,Fe)₃O₄ and silicon oxide remain on the surface of the steel sheet not treated through the neutral salt electrolyte treatment and the sulfuric acid electrolyte treatment. However, only silicon oxide remains on the surface of the treated steel sheet.

Example 2

[0069] Ferrite-based cold-rolled stainless steel sheets having 14% or less of chrome and treated as explained in Example 1 to remove Fe-rich and Cr-rich scale layers were heat-treated at 900°C and used as samples for observing a relationship between the surface states and open circuit potentials of the samples.

[0070] The samples were immersed in a mixed acid solution maintained at 45°C and including 150 g/l sulfuric acid and 5 g/l of free hydrofluoric acid, and a pickling process was performed by applying potentials of -0.5 V to 0.5 V to the samples for 150 seconds as shown in Table 1.

[0071] After the pickling process, the surface states of the samples were observed using a SEM, and pickling and surface roughness of the samples were evaluated. If scale remained on a sample, the sample was determined as being not pickled. If the surface roughness of a sample was 3 μm or greater, the sample was determined as having bad surface roughness, indicated by "X," and if the surface roughness of a sample is 3 μm or less, the sample was determined as having good surface roughness, indicated by "O." Samples determined as being not pickled were not evaluated in surface roughness.

[0072] Evaluation results are shown in Table 1 below. The surfaces of Inventive Sample 2 and Comparative Sample 4 to which 0.1 V and -0.3 V were applied were captured using a SEM and shown in FIGS. 2(a) and 2(b).

[Table 1]

	Applied potential (V)	Pickling	Surface Roughness
Comparative Sample 1	0.6	X	-
Comparative Sample 2	0.4	X	-
Comparative Sample 3	0.3	X	-
Inventive Sample 1	0.2	○	○
Inventive Sample 2	0.1	○	○
Inventive Sample 3	-0.2	○	○
Comparative Sample 4	-0.3	○	X
Comparative Sample 5	-0.4	X	-
Comparative Sample 6	-0.6	X	-

[0073] As shown in Table 1, if the open circuit potential was -0.3 V to 0.2 V, pickling was possible in the mixed acid solution (Inventive Samples 1 to 3, and Comparative Sample 3). However, Comparative Sample 3 had poor surface roughness. That is, it can be understood that the surface of Inventive Sample 2 dissolved uniformly along grains as shown in FIG. 2(a) but the surface of Comparative Sample 3 had poor surface qualities due to separation of grains along grain surfaces as shown in FIG. 2 (b) .

[0074] Comparative Samples 1, 2, 4, and 5 were not pickled.

[0075] Therefore, it can be understood that open circuit potentials of -0.2 V to 0.2 V are suitable for dissolving Si oxide layers.

Example 3

[0076] This example is for checking the relationship between the concentrations of hydrogen peroxide and iron ions for obtaining an open circuit potential of -0.2 V in a mixed acid treatment for a ferrite-based cold-rolled stainless steel sheet.

[0077] The ferrite-based cold-rolled stainless steel sheet having 14% or less of chrome and treated as explained in Example 1 to remove Fe-rich and Cr-rich scale layers was heat-treated at 900°C and used as a sample.

[0078] The sample was immersed in a mixed acid solution maintained at 45°C and including 150 g/l sulfuric acid and 5 g/l of free hydrofluoric acid, and the open circuit potential of the sample was measured while adding metal ions (Fe^{3+}) and hydrogen peroxide to the mixed acid solution.

[0079] The open circuit potential of the sample was measured with respect to the concentration of iron ions, and the minimum concentration of hydrogen peroxide for maintaining the open circuit potential equal to or greater than -0.2 V was measured with respect to the concentration of iron ions. FIG. 3 shows the measured results.

[0080] FIG. 4 is a graph showing a relationship between the minimum concentration of hydrogen peroxide and the concentration of iron ions for maintaining the open circuit potential of the sample equal to or greater than -0.2 V. Referring to FIG. 4, as the concentration of iron ions increases, the minimum concentration of hydrogen peroxide for maintaining the open circuit potential of the sample is reduced. However, although the concentration of iron ions increases to 40 g/l or greater, the minimum concentration of hydrogen peroxide is not reduced to 1 g/l or less. From this, the relationship between the minimum concentration of hydrogen peroxide and the concentration of iron ions for maintaining the open circuit potential equal to or greater than -0.2 V can be expressed as follows.

$$[\text{H}_2\text{O}_2]_{\min} = 0.74 + 3.1e^{-[\text{Fe}]/1.1} + 3.2e^{-[\text{Fe}]/15}$$

Example 4

[0081] This example is for checking appropriate conditions for a neutral salt electrolyte treatment.

[0082] A neutral salt electrolyte treatment was performed in the same method as in Example 1. However, the temperature of an electrolyte solution in a bath, a current, and the concentration of sodium sulfate were varied as shown in Table 2.

[0083] After the neutral salt electrolyte treatment, the surface states of steel sheets were observed as shown in Table 2. A good surface state is indicated by "O," and a bad surface state such as chrome oxide scale is indicated by "X."

[Table 2]

	Temperature (°C)	Current (A/dm ²)	Concentration of Sodium Sulfate	Surface Qualities
Comparative Sample 1	30	20	250	X
Comparative Sample 2	50	5	250	X
Comparative Sample 3	50	10	50	X
Inventive Sample 1	50	10	100	○
Inventive Sample 2	90	30	250	○

[0084] As shown in Table 2, the surface qualities of the steel sheets were good when the neutral salt electrolyte treatment was performed under conditions where the temperature of the electrolyte solution was from 50°C to 90°C, the concentration of sodium sulfate in the electrolyte solution was from 100 g/l to 250 g/l, and current density was 10 A/dm² to 30 A/dm².

Example 5

[0085] This example is for checking appropriate conditions for a sulfuric acid electrolyte treatment.

[0086] A sulfuric acid electrolyte treatment was performed in the same manner as in Example 1. However, the temperature of an electrolyte solution in a bath, a current, and the concentration of sulfuric acid were varied as shown in Table 3.

[0087] After the sulfuric acid electrolyte treatment, the surface states of steel sheets were observed as shown in Table 3. A steel sheet surface where Fe oxide scale and Cr oxide scale were removed and only Si oxide scale remained was determined as good and indicated by "O," and a steel sheet surface where Fe oxide scale or Cr oxide scale remained was determined as bad and indicated by "X."

[Table 3]

	Temperature (°C)	Current (A/dm ²)	Concentration of Sodium Sulfate	Surface Qualities
Comparative Sample 1	30	5	50	X
Comparative Sample 2	70	5	150	X
Comparative Sample 3	70	30	150	X
Comparative Sample 4	30	10	30	X
Inventive Sample 1	30	10	50	○
Inventive Sample 2	60	20	150	○

[0088] As shown in Table 3, the surface quality of the steel sheets was good when the sulfuric acid electrolyte treatment was performed under the conditions where the temperature of the electrolyte solution was from 30°C to 60°C, the concentration of sulfuric acid in the electrolyte solution was from 50 g/l to 150 g/l, and the current density was 10 A/dm² to 30 A/dm².

Example 6

[0089] This example is for checking appropriate treatment periods of time for a neutral salt electrolyte treatment and a sulfuric acid electrolyte treatment.

[0090] A neutral salt electrolyte treatment and a sulfuric acid electrolyte treatment were performed in the same method as in Example 1 except that treatment periods of time were as shown in Table 4.

[0091] Pickling was observed while varying the treatment periods of time of the neutral salt electrolyte treatment and the sulfuric acid electrolyte treatment. In Table 4, the case where Si oxide scale remained but no chrome oxide scale and Fe oxide scale remained is indicated by "O," the case where Si oxide remained and Cr oxide scale or Fe oxide scale remained is indicated by "X," and the case where a parent steel sheet eroded is indicated by "X (over-pickling)."

[Table 4]

	Period of time of neutral salt electrolyte treatment (s)	Period of time of sulfuric acid electrolyte treatment (s)	Pickling
Comparative Sample 1	0	5	X
Comparative Sample 2	0	60	X (over- pickling)
Comparative Sample 3	90	0	X
Comparative Sample 4	90	60	X (over- pickling)
Inventive Sample 1	0	15	○
Inventive Sample 2	0	50	○
Inventive Sample 3	30	5	○
Inventive Sample 4	90	50	○

[0092] As shown in Table 4, when the neutral salt electrolyte treatment was performed within 0 to 120 seconds and the sulfuric acid electrolyte treatment was formed within 5 to 50 seconds, only Si oxide remained on cold-rolled stainless steel sheets as shown in FIG. 2(a). However, in the case of Comparative Samples 1 to 4 treated for different periods of time, (Cr,Fe)₃O₄ scale remained as shown in FIG. 2(b). Based on this, the treatment period of time in a mixed acid bath can be minimized.

Example 7

[0093] This example is for checking appropriate treatment conditions for a mixed acid bath.

[0094] Steel sheets treated through a neutral salt electrolyte treatment and a sulfuric acid electrolyte treatment as explained in Example 1 were treated using a mixed acid solution under the conditions shown in Table 5. The mixed acid solution was maintained at room temperature, and the concentration of hydrogen peroxide was controlled as explained in Example 3.

[0095] Thereafter, pickling results were observed and indicated by "O" and "X" as shown in Table 5. The case where Si oxide did not remain is indicated by "O," the case where Si oxide remained is indicated by "X," and the case where a parent steel sheet eroded is indicated by "X (over-pickling)."

[Table 5]

	Sulfuric acid (g/l)	Hydrofluoric acid (g/l)	Period of time (s)	Pickling
Comparative Sample 1	50	5	100	X
Comparative Sample 2	200	0.5	100	X
Comparative Sample 3	200	0.5	5	X
Comparative Sample 4	250	5	100	X (over- pickling)
Comparative Sample 5	200	15	100	X (over- pickling)
Comparative Sample 6	200	5	150	X (over- pickling)
Inventive Sample 1	70	1	10	○
Inventive Sample 2	100	3	30	○
Inventive Sample 3	200	5	100	○
Inventive Sample 4	150	10	100	○

[0096] As shown in Table 5, steel sheets may properly pickled when the steel sheets are immersed for 10 seconds to 100 seconds in a mixed acid solution including 70 g/l to 200 g/l of sulfuric acid, 1 g/l to 10 g/l of free hydrofluoric acid, and at least 1.0 of hydrogen peroxide, although the concentration of hydrogen peroxide varies according to the concentration of iron ions.

Example 8

[0097] In this example, the quality of ferrite-based cold-rolled stainless steel sheets pickled according to the present invention by using a mixed acid solution including sulfuric acid, hydrofluoric acid, and hydrogen peroxide was compared with the quality of a ferrite-based cold-rolled stainless steel sheet pickled according to a method of related art by using a mixed acid solution including nitric acid and hydrofluoric acid.

[0098] Ferrite-based cold-rolled stainless steel sheets including 14% or less of chrome were pickled using mixed acid solutions, and the gloss thereof was measured (n=15). Process conditions and compositions of the acid solutions are as follows.

[0099] Comparative Sample 1: a ferrite-based cold-rolled stainless steel sheet was treated through a neutral salt electrolyte treatment and a sulfuric acid electrolyte treatment as explained in Example 1, and was then immersed in a mixed acid solution including 100 g/l of nitric acid and 3 g/l of hydrofluoric acid for 30 seconds. Then, the gloss thereof was measured.

[0100] Inventive Sample 1: the gloss of Inventive Sample 4 of Example 7 was measured.

[0101] Inventive Sample 2: the gloss of Inventive Sample 2 of Example 7 was measured.

[0102] The measured gloss values of the samples are shown in FIG. 5.

[0103] With reference to FIG. 5, the gloss of the ferrite-based cold-rolled stainless steel sheets pickled by the mixed acid pickling method of the present invention can be compared with the gloss of the ferrite-based cold-rolled stainless steel sheet pickled by a nitric acid pickling method of the related art or the gloss of a non-pickled ferrite-based cold-rolled stainless steel sheet. In detail, the gloss of Inventive Samples is 130 or higher, greater than the gloss of Comparative Sample 1 by about 40 to about 60.

[0104] Therefore, it can be understood that the pickling method of the present invention is useful for improving the surface quality of steel sheets.

Claims

1. A pickling process for rapidly removing Si oxide from a surface of a low-chrome ferrite-based cold-rolled stainless steel sheet having a content of chrome of 14% or less by using a mixed acid solution not containing nitric acid, the pickling process comprising immersing the cold-rolled stainless steel sheet in the mixed acid solution comprising hydrogen peroxide, wherein the mixed acid solution comprises 70 g/l to 200 g/l of sulfuric acid and 1 g/l to 10 g/l of free hydrofluoric acid, wherein the mixed acid solution initially comprises 7 g/l or more of the hydrogen peroxide but no Fe ions, and the pickling process is performed at a rate of 3 g/m²-min to 15 g/m²-min.

2. The pickling process of claim 1, wherein the hydrogen peroxide and Fe ions satisfy the following concentration formula:

$$[\text{H}_2\text{O}_2] \geq 0.74 + 3.1e^{-[\text{Fe}]/1.1} + 3.2e^{-[\text{Fe}]/15}.$$

3. The pickling process of claim 1 or 2, wherein an open circuit potential of the cold-rolled stainless steel sheet immersed in the mixed acid solution is maintained within a range of -0.2 V to 0.2 V.

4. The pickling process of claim 1 or 2, wherein the cold-rolled stainless steel sheet is immersed in the mixed acid solution for 10 seconds to 100 seconds.

5. A process for pickling a low-chrome ferrite-based cold-rolled stainless steel sheet having 14% or less of chrome after a degreasing treatment and an annealing treatment, the process comprising:

performing a sulfuric acid electrolyte treatment to remove (Fe,Cr) scale from the low-chrome ferrite-based cold-rolled stainless steel sheet by a sulfuric acid electrolyte solution comprising sulfuric acid as an electrolyte; and performing a mixed acid treatment in which the low-chrome ferrite-based cold-rolled stainless steel sheet is immersed in a mixed acid solution comprising sulfuric acid, a free hydrofluoric acid, and hydrogen peroxide, wherein the process has a pickling rate of 3 g/m²-min to 15 g/m²-min.

6. The process of claim 5, further comprising performing a neutral salt electrolyte treatment to remove Cr-rich scale from the steel sheet using a neutral salt electrolyte solution comprising a sodium sulfate electrolyte.

7. The process of claim 6, wherein the neutral salt electrolyte treatment is performed by immersing the steel sheet in the neutral salt electrolyte solution maintained at 50°C to 90°C and applying a current of 10 A/dm² to 30 A/dm² to the steel sheet for a period of time longer than 0 seconds but not longer than 90 seconds so that open circuit potentials are applied to the steel sheet in order of positive (+), negative (-), and positive (+).

8. The process of claim 6, wherein the neutral salt electrolyte solution comprises 100 g/l to 250 g/l of the sodium sulfate electrolyte.

9. The process of claim 5, wherein after the steel sheet is treated through the annealing treatment or a neutral salt electrolyte treatment, the sulfuric acid electrolyte treatment is performed by immersing the steel sheet in the sulfuric acid electrolyte solution maintained at 30°C to 60°C and applying a current of 10 A/dm² to 30 A/dm² to the steel sheet for 5 seconds to 50 seconds so that open circuit potentials are applied to the steel sheet in order of positive (+), negative (-), and positive (+).

10. The process of claim 9, wherein the sulfuric acid electrolyte solution comprises 50 g/l to 150 g/l of the sulfuric acid.

11. The process of claim 5, wherein the mixed acid treatment is performed by immersing the steel sheet in the mixed acid solution for 10 seconds to 100 seconds, and the mixed acid solution comprises 70 g/l to 200 g/l of the sulfuric acid, 1 g/l to 10 g/l of the free hydrofluoric acid, and initially 7 g/l or more of the hydrogen peroxide and substantially no iron ions.

12. The process of claim 11, wherein an open circuit potential of the steel sheet is maintained within a range of - 0.2 V to 0.2 V during the mixed acid treatment.

13. The process of claim 10, wherein during the process, the hydrogen peroxide and iron ions in the mixed acid solution satisfy the following concentration formula:

$$[H_2O_2] \geq 0.74 + 3.1e^{-[Fe]/1.1} + 3.2e^{-[Fe]/15}.$$

14. The process of any one of claims 5 to 13, wherein the steel sheet has a gloss value of 130 or greater after being pickled through the process.

15. A mixed acid solution not including a nitric acid for removing Si oxide from a ferrite-based cold-rolled stainless steel sheet having 14% or less of chrome after a degreasing treatment and an annealing treatment, the mixed acid solution comprising 70 g/l to 200 g/l of sulfuric acid, 1 g/l to 10 g/l of free hydrofluoric acid, and hydrogen peroxide, wherein the hydrogen peroxide and iron ions in the mixed acid solution satisfy the following concentration formula:

$$[H_2O_2] \geq 0.74 + 3.1e^{-[Fe]/1.1} + 3.2e^{-[Fe]/15}.$$

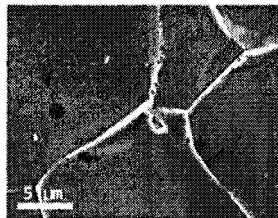


FIG. 1A



FIG. 1B

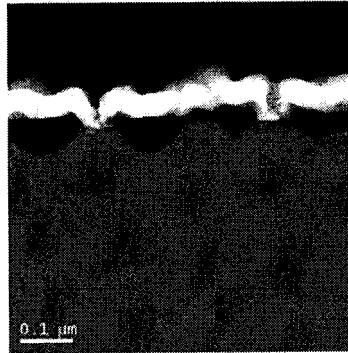


FIG. 2A

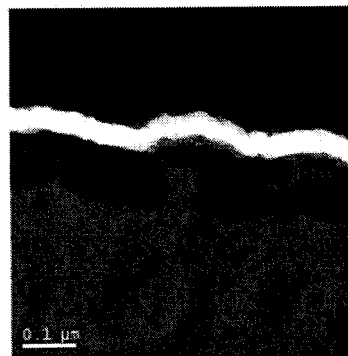


FIG. 2B

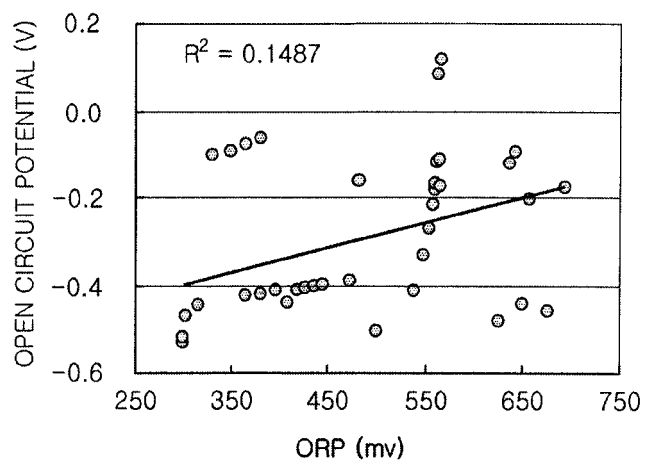


FIG. 3A

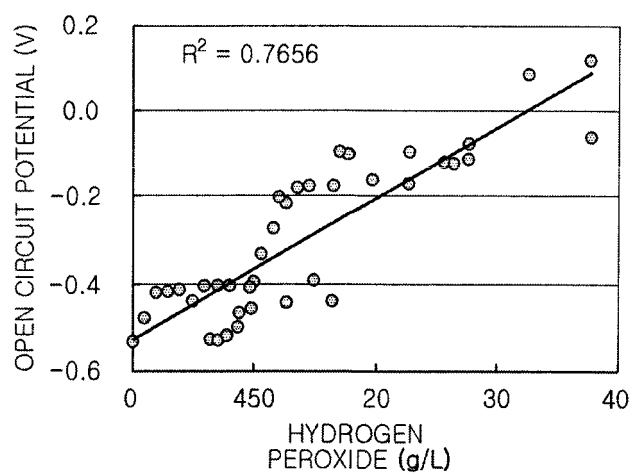


FIG. 3B

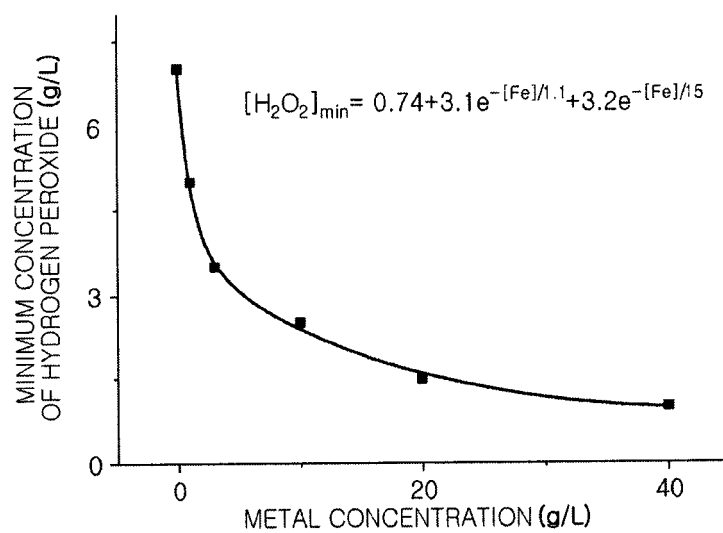


FIG. 4

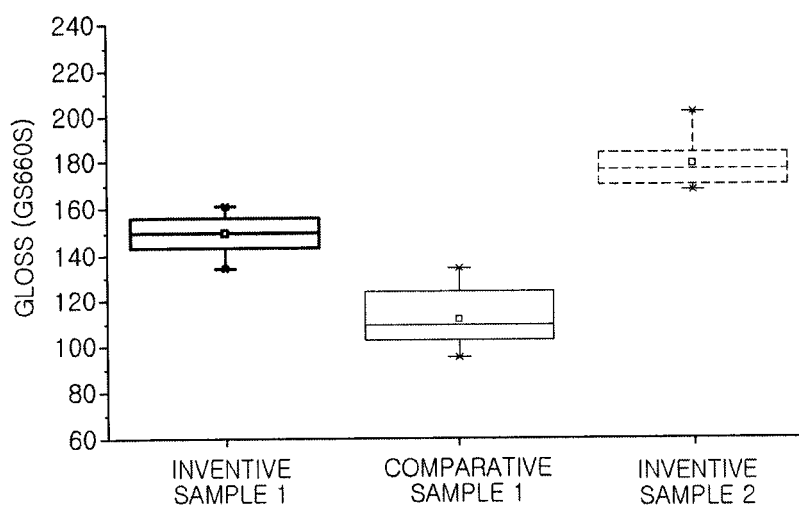


FIG. 5

REFERENCES CITED IN THE DESCRIPTION

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