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(54) **High-strength cold-rolled steel sheet excellent in coating film adhesion**

Hochfestes, Kaltgewalztes Stahlblech mit Ausgezeichneter Adhesion von Beschichtung

Tôle d'acier à résistance élevée laminée à froid, ayant une excellente adhesivité d'une couche de revêtement

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Description

[0001] The present invention relates to a high-strength cold-rolled steel sheet excellent in coating film adhesion, and more particularly, to a cold-rolled steel sheet which has a tensile strength no lower than 550 MPa and is suitable for use as a steel sheet for automobile parts on account of its excellent coating film adhesion.

[0002] There is a growing demand for high-strength steel products necessary for automobiles with less fuel consumption and lower weight than before. This trend is prevailing also in the field of cold-rolled steel sheet. On the other hand, cold-rolled steel sheets are required to have sufficient ductility (such as elongation) because they are formed into automotive parts by pressing. Increase in strength can be effectively achieved by incorporation with alloying elements; however, they adversely affect ductility as their amount increases.

[0003] Of these alloying elements, Si is less influential in reducing ductility and is effective in increasing strength while retaining ductility. However, with an increased Si content, the resulting steel sheet is poor in chemical treatability and hence in coating film adhesion. Consequently, it was necessary to reduce Si content in the case where chemical treatability is important. Moreover, excess Si forms an Si-containing intergranular oxide on the surface of steel sheet, thereby causing cracks to occur and aggravating coating film adhesion.

[0004] One way to reconcile mechanical properties and chemical treatability is by cladding a steel sheet of high Si content with a layer of low Si content. Such a cladding layer contributes to chemical treatability without adverse effect on the mechanical properties of the steel sheet. (See Japanese Patent Laid-open No. Hei-5-787452) And the steel sheet of high Si content ensures sufficient mechanical properties. Unfortunately, cladding needs a complex process which leads to an increased production cost.

[0005] There is a conventional technology of adding a special alloying element, such as Ni and Cu, which prevents Si (detrimental to chemical treatment) from concentrating in the surface of a steel sheet. (See Japanese Patent No. JP-B2-2951480 corresponding to JP-A-6010096 and Japanese Patent No. JP-B 3266328 corresponding JP-A-6100980). This technology suffers a disadvantage of requiring expensive Ni or Cu, which leads to an increase in production cost.

[0006] The conventional technology mentioned above is concerned with so-called IF (Interstitial Free) steel. IF steel is limited in carbon content (no more than 0.005%) and has its texture controlled by a specific recrystallization temperature, so that it is improved in deep drawability. However, IF steel with a very low carbon content will not achieve the high strength intended by the present invention.

[0007] There is a technology of ensuring chemical treatability by causing NbC to separate out and function as a site for nucleation of zinc phosphate crystals. (See Japanese Patent No. 2003-3049147 corresponding JP-A-5230540). This technology is also designed to improve deep drawability by keeping the carbon content low (no more than 0.02%) for texture control. The steel of this technology has a slightly higher carbon content than the above-mentioned IF steel, but is still unsatisfactory in strength. Japanese Patent No. 3049147 discloses two inventions which respectively achieve a strength of 539 MPa (55 kgf/mm^2) and 588 MPa (60 kgf/mm^2) which is in excess of 550 MPa. This strength has been realized by increasing the content of P or Mo. Unfortunately, these elements are detrimental to weldability.

[0008] There has been proposed a retained austenite-containing steel sheet which has good chemical treatability owing to the controlled ratio of SiO_2/Mn_2SiO_4 in the surface layer. (See Japanese Patent Laid-open No. 2003-201538) To obtain this steel sheet, it is necessary to control oxides in the surface layer, to perform pickling or brushing on the surface after continuous annealing, thereby removing Si oxides and controlling the Si/Fe ratio, and to keep the dew point above -30°C at the temperature below the Ac_1 transformation point, thereby limiting the amount of Si oxides to be formed.

[0009] Unfortunately, pickling and brushing increase the number of manufacturing steps, which leads to a higher production cost. In addition, the control of dew point, which is accomplished in a continuous annealing furnace, is not very effective so long as Examples show in the document. According to data in the document, the ratio of SiO_2/Mn_2SiO_4 in the surface layer is about 1.0. This value suggests that SiO_2, which prevents the formation of film crystals due to chemical treatment, occurs as much as Mn_2SiO_4. Judging from these results, the disclosed technology will not sufficiently improve chemical treatability.

[0010] Moreover, the retained austenite-containing steel sheet mentioned above contains such alloying elements as C, Si, Mn, and A1 in large amounts so as to secure retained austenite. Therefore, it is poor in weldability.

[0011] There has been proposed another technology of improving chemical treatability, which is intended to keep below 1 the Si/Mn ratio in oxides determined by surface analysis with XPS (X-ray photoelectron spectroscopy). (See Japanese Patent Laid-open No. Hei-4-276060)

[0012] An example of steel having an Si/Mn ratio lower than 1 is mild steel nearly free of Si, which is known to have good chemical treatability. However, a certain amount of Si is necessary for steel to have both high strength and good ductility, and hence there is a limit of reducing the Si content to keep the Si/Mn ratio below 1. Further, it turned out that a steel sheet does not always exhibit good chemical treatability even though it has a Si/Mn ratio lower than 1, for a certain Si content and an adequately controlled Mn content.

[0013] The present invention was completed in view of the foregoing. It is an object of the present invention to provide a cold-rolled steel sheet characterized by a tensile strength no lower than 500 MPa and excellent coating film adhesion and weldability.

[0014] The present invention is directed to a high-strength cold-rolled steel sheet excellent in coating film adhesion, which is a DP (Dual Phase) steel sheet of ferrite-tempered martensite type containing 0.05 to 0.15 mass% of C, 0.05 to 2 mass% of Si, and 1 to 5 mass% of Mn, having a tensile strength no lower than 550 MPa, satisfying the equation (1) below, and being characterized by its surface in which there exist Si-Mn complex oxides no larger than 5 μm in diameter of the equivalent circle as many as 10 or more per 100 μm^2 and the coverage of oxides composed mainly of Si on the surface of steel sheet is no more than 10% of surface area (requirement (I)). The equivalent circle means the circle of the same area as the Si-Mn complex oxide. (This steel sheet will be referred to as Steel sheet 1 of the present invention" hereinafter.)

$$[Si]/[Mn] \leq 0.4 \quad \ldots \quad (1)$$

where [Si] denotes an Si content (in mass%) and [Mn] denotes an Mn content (in mass%).

[0015] The term "oxides composed mainly of Si" mentioned above means those oxides in which Si (as one of the constituents excluding oxygen) accounts for no less than 70% in atomic ratio. Such oxides are considered to be amorphous according to the result of analysis.

[0016] The ratio of the surface area of steel sheet which is covered by the oxides composed mainly of Si was obtained by observation under a TEM (Transmission Electron Microscope), quantitative analysis and mapping of Si, O, Mn, and Fe by EDX (Energy Dispersive X-ray), and image analysis of these data. Observation under a TEM was accomplished by using an extraction replica, which is explained in Examples given later. Observation under a TEM for an extraction replica may be replaced by surface mapping for Si, O, Mn, and Fe by AES (Auger Electron Spectroscopy) at a magnification of 2000 to 5000, and the resulting data may be used for image analysis.

[0017] The present invention is directed also to a high-strength cold-rolled steel sheet excellent in coating film adhesion, which is a DP (Dual Phase) steel sheet of ferrite-tempered martensite type containing 0.05 to 0.15 mass% of C (excluding 0 mass%), no more than 2 mass% of Si (excluding 0 mass%), and 1 to 5 mass% of Mn, having a tensile strength no lower than 550 MPa, and being characterized by its surface whose cross section does not show cracks with a width no larger than 3 μm and a depth no smaller than 5 μm in arbitrary ten fields of observation under an SEM (Scanning Electron Microscope) with a magnification of 2000 (requirement (II)). (This steel sheet will be referred to as "Steel sheet 2 of the present invention" hereinafter.)

[0018] The width and depth of cracks are shown in Fig. 1 (which is a schematic sectional view of the steel sheet). They are found by observing the vicinity of the surface of the steel sheet under an SEM with a magnification of 2000 (Model S-4500 of Hitachi Ltd.).

[0019] The present invention is directed also to a high-strength cold-rolled steel sheet excellent in coating film adhesion, which is a DP (Dual Phase) steel sheet of ferrite-tempered martensite type containing 0.05 to 0.15 mass% of C (excluding 0 mass%), 0.05 to 2 mass% of Si, and 1 to 5 mass% of Mn, having a tensile strength no lower than 550 MPa, satisfying the equation (1) above, and meeting the above-mentioned requirements (I) and (II). (This steel sheet will be referred to as "Steel sheet 3 of the present invention" hereinafter.)

[0020] The steel sheets of the present invention should preferably have a composition specified by the equations (2) and (3) below as an additional requirement, so that they exhibit good weldability.

$$[P] + 3[S] + 1.54[C] < 0.25 \quad \ldots \quad (2)$$

$$[C] + [Si]/30 + [Mn]/20 + 2[P] + 4[S] < 0.34 \quad \ldots \quad (3)$$

where [C], [Si], [Mn], [P], and [S] denote the content (in mass%) of these elements.

[0021] The steel sheet according to the present invention has a high strength in excess of 550 MPa, exhibits good chemical treatability, and/or good coating film adhesion owing to controlled fine cracks, and provides good weldability. It is suitable for automotive parts. It can be produced without cladding or expensive elements.

Fig. 1 is a schematic diagram showing cracks in the cross section of the steel sheet.
Fig. 2 is a diagram illustrating (part of) one manufacturing process in Examples.
Fig. 3 is a diagram illustrating (part of) another manufacturing process in Examples.

Fig. 4 is an electron micrograph (TEM) of sample in experiment No. 1 in Examples. (Extraction replica, x15000)
Fig. 5 is an electron micrograph (TEM) of sample in experiment No. 29 in Examples. (Extraction replica, ×15000)
Fig. 6 is an electron micrograph (TEM) of sample in experiment No. 34 in Examples. (Extraction replica, ×15000)
Fig. 7 is an electron micrograph (SEM) showing the cross section near the surface of the steel sheet in experiment No. 1 in Examples.
Fig. 8 is an electron micrograph (SEM) showing the cross section near the surface of the steel sheet in experiment No. 29 in Examples.
Fig. 9 is an electron micrograph (SEM) showing the cross section near the surface of the steel sheet in experiment No. 34 in Examples.
Fig. 10 is an electron micrograph (SEM) showing the surface of the steel sheet (after chemical treatment) in experiment No. 1 in Examples.
Fig. 11 is an electron micrograph (SEM) showing the surface of the steel sheet (after chemical treatment) in experiment No. 29 in Examples.
Fig. 12 is an electron micrograph (SEM) showing the surface of the steel sheet (after chemical treatment) in experiment No. 34 in Examples.

[0022] The results of investigation carried out to obtain a steel sheet excellent in coating film adhesion revealed that the object is achieved if the following requirements (I) and/or (II) are met. This finding led to the present invention. The steel sheet that meets these requirements and has a high strength (in excess of 550 MPa) and good ductility can be produced in specific compositions under specific manufacturing conditions as mentioned later.

(I) In the surface of steel sheet:

(i) there should exist Si-Mn complex oxides no larger than 5 μm in diameter of the equivalent circle as many as 10 or more per 100 μm^2, and
(ii) the coverage of oxides composed mainly of Si on the surface of steel sheet should be no more than 10% of the surface area. ("Mainly" means that Si accounts for no less than 70% (in atomic ratio) in the constituents of oxides other than oxygen.)

(II) The cross section of the surface of steel sheet should not show cracks with a width no larger than 3 μm and a depth no smaller than 5 μm in arbitrary ten fields of observation under an SEM with a magnification of 2000.

[0023] The above-mentioned requirements (I) and (II) were established for the following reasons.

- Requirement that in the surface of steel sheet, there should exist Si-Mn complex oxides no larger than 5 μm in diameter of the equivalent circle as many as 10 or more per 100 μm^2.
The present inventors have carried out a series of researches to obtain a high-strength steel sheet excellent in coating film adhesion and proposed a technique for improving the chemical treatability of a steel sheet containing Si in a comparatively large amount. (See Japanese Patent Application No. 2003-106152 or JP-A-2004393969). This technique is , intended to improve chemical treatability by finely dispersing amorphous Si oxides detrimental to chemical treatability while controlling the annealing atmosphere. However, major oxides that occur when the Si content is relatively low (Si content: 0.05 to 2% as defined in the present invention) are Si-Mn complex oxides rather than amorphous Si oxides. It is considered that these complex oxides are also detrimental to coating film adhesion. With this in mind, the present inventors searched for the possibility of positively using Si-Mn complex oxides for improvement of chemical treatability.
As the result, it turned out that chemical treatability improves if Si-Mn complex oxides are finely dispersed into iron oxides formed in the surface layer of steel sheet, so as to form the "inhomogeneous field of oxide interface" which functions as the nucleating site for zinc phosphate crystals (as mentioned later). It is not yet elucidated why the Si-Mn complex oxides specified in the present invention function as the nucleating site for zinc phosphate crystals. A probable reason is as follows.
It is known that zinc phosphate crystals tend to form during chemical treatment in the "electrochemical inhomogeneous field" originating from the grain boundary or the periphery of the Ti colloid which has been attached to the surface of steel sheet at the time of surface preparation. It is considered that the Si-Mn complex oxides specified in the present invention also create the electrochemical inhomogeneous field around them, thereby helping zinc phosphate crystals to stick easily at the time of chemical treatment, which leads to improved chemical treatability.
It is considered that zinc phosphate crystals after chemical treatment should preferably be no larger than several micrometers from the standpoint of coating film adhesion. Consequently, it is also considered that the electrochemical inhomogeneous field mentioned above should preferably be of the same size. For this reason, the present invention

specifies that there should exist Si-Mn complex oxides no larger than 5 μm in diameter of the equivalent circle as many as 10 or more per 100 μm^2 (or 1 per 10 μm^2 or more on average), with the average distance between particles of complex oxides being several micrometers. This condition is necessary for easy formation of the electrochemical inhomogeneous field of the above-specified size.

The number of particles of Si-Mn complex oxides should preferably be 50 or more per 100 μm^2, more preferably 100 per or more 100 μm^2, and most desirably 150 or more per 100 μm^2, because the electrochemical inhomogeneous field does not necessarily occur in every particle of the Si-Mn complex oxides which are present. An example of the Si-Mn complex oxides is Mn_2SiO_4. It is considered that about 50 nm is the maximum observable size of Si-Mn complex oxides.

- Requirement that the coverage of oxides composed mainly of Si on the surface of steel sheet should be no more than 10% of surface area.

  The Si-Mn complex oxides functioning as nucleating sites for zinc phosphate crystals will not contribute to good chemical treatability if there exist other substances detrimental to chemical treatment. Hence, the resulting steel sheet will be poor in coating film adhesion.

  If oxides composed mainly of Si are present on the surface of steel sheet, zinc phosphate crystals do not form on them, which leads to considerably poor chemical treatability. Consequently, the present invention requires that the coverage of oxides composed mainly of Si on the surface of steel sheet should be no more than 10% of surface area.

  The present inventors had previously proposed a technique of improving chemical treatability by finely dispersing oxides composed mainly of Si, as mentioned above. However, it turned that that the presence of oxides should be minimized in the present invention which is intended to utilize the action of Si-Mn complex oxides as mentioned above. Therefore, the coverage of oxides composed mainly of Si on the surface of steel sheet should preferably be no more than 5% of surface area, most desirably 0% of surface area.

- Requirement that the cross section of the surface layer of the steel sheet does not show cracks with a width no larger than 3 μm and a depth no smaller than 5 μm in arbitrary ten fields of observation under an SEM with a magnification of 2000.

  Sharp cracks present on the surface of the steel sheet prevent zinc phosphate crystals from sticking to them at the time of chemical treatment. As the result, corrosion readily proceeds there, aggravating coating film adhesion. For this plausible reason, it is important to minimize the occurrence of sharp cracks in order to improve coating film adhesion.

[0024] The present inventors had previously proposed a technique of improving coating film adhesion by restricting to 10 μm or less the depth of linear oxides (narrower than 30 nm) composed of Si and oxygen. This technique is based on the assumption that continuous annealing will not be followed by pickling. However, in common practice, continuous annealing is followed by pickling, and pickling removes linear oxides, thereby causing cracks to occur.

[0025] How the depth of cracks relates with linear oxides is not yet quantitatively elucidated. It is considered that linear oxides dissolve in acid or mechanically drop off, thereby giving rise to cracks. It is also considered that such cracks are deeper than the size of linear oxides because they dissolve further in acid even after linear oxides have been removed.

[0026] With the foregoing in mind, the present inventors conceived that it would be possible to improve coating film adhesion more by controlling cracks than by regulating the depth of linear oxides (as in the technology they had previously proposed) and they investigated the shape of cracks to be controlled. As the result, it was found that zinc phosphate crystals hardly stick to cracks having a width approximately equal to or smaller than their particle diameter. This holds true particularly for cracks deeper than 5 μm. Thus, according to the present invention, cracks to be controlled are limited to those which are narrower than 3 μm and deeper than 5 μm.

[0027] Based on the foregoing is established the requirement that the cross section of the surface layer of the steel sheet should not show the above-specified cracks in arbitrary ten fields of observation under an SEM with a magnification of 2000.

[0028] The steel sheet according to the present invention is required to have the following chemical composition so that it has controlled cracks for efficient deposition of the above-mentioned oxides and it exhibits the characteristic properties of high-strength steel sheet.

$$[Si]/[Mn] \leq 0.4 \quad \ldots \quad (1)$$

where [Si] denotes an Si content (in mass%) and [Mn] denotes an Mn content (in mass%).

[0029] Since oxides composed mainly of Si adversely affect chemical treatability, it is more desirable to suppress them as much as possible rather than finely dispersing them. The object of suppressing such oxides can be achieved if the [Si]/[Mn] ratio in the chemical composition is no larger than 0.4, preferably no larger than 0.3.

C : 0.05 to 0.15 1 mass%

[0030] Carbon is essential for strength. The minimum carbon content is 0.05 mass%. An excess carbon content aggravates weldability. Therefore, the carbon content is no larger than 0.15 mass%.

Si : 0.05 to 2 mass% (for steel sheets 1 and 3)

Si no larger than 2 mass% (excluding 0 mass%) (for steel sheet 2)

[0031] Since Si increases strength without decreasing ductility, it may be contained in the steel sheet. A certain amount of Si is necessary for the Si-Mn complex oxides with a diameter of the equivalent circle no larger than 5 μm to form as much as specified by the requirement (I) mentioned above. A minimum amount of Si for this purpose is 0.05 mass%. An adequate amount should be no less than 0.15 mass%, preferably no less than 0.3 mass%, and more preferably no less than 0.5 mass%. Si in an excess amount brings about solid solution hardening more than necessary, which leads to an increased rolling load. Therefore, the content of Si should be no larger than 2 mass%, preferably no larger than 1.5 mass%.

Mn : 1 to 5 mass%

[0032] Mn is also essential for strength; however, excess Mn is detrimental to ductility. An adequate content of Mn should be no less than 1 mass%, preferably no less than 2 mass%, and no more than 5 mass%, preferably no more than 3.5 mass%.

[0033] The steel sheet according to the present invention should contain the above-mentioned elements, with the remainder being substantially iron. It may contain A1 no more than 1 mass%, N no more than 0.01 mass%, and O no more than 0.01 mass%, originating from raw materials or incorporated depending on production conditions. It may be positively incorporated with additional elements, such as Cr, Mo, Ni, Ti, Nb, V, P, and B, in an amount not harmful to the effect of the present invention.

[0034] The amount of these additional elements to strengthen the steel sheet is specified as follows.
Cr : 0.1 to 1 mass%
Mo : 0.1 to 1 mass%
Ni : 0.1 to 1 mass%
Ti : 0.005 to 0.1 mass%
Nb : 0.005 to 0.1 mass%
V : 0.0005 to 0.01 mass%
P : 0.005 t0 0.1 mass%
B : 0.0003 to 0.01 mass%
These additional elements will aggravate ductility and weldability when added in an excess amount.

$$[P] + 3[S] + 1.54[C] < 0.25 \quad \ldots \quad (2)$$

$$[C] + [Si]/30 + [Mn]/20 + 2[P] + 4[S] < 0.34 \quad \ldots \quad (3)$$

where [C], [Si], [Mn], [P], and [S] denote the content (in mass%) of these elements.

[0035] The left side of each of the equations (2) and (3) above is known as the parameter to evaluate spot weldability. {Tanaka et al., Nippon Koukan Gihou, No. 105 (1984); Heuschkel, J. : Weld J26 (10), P560 S(1947)} The more the parameter increases, the more the weldability decreases. It was found in the present invention that spot weldability decreases when the left hand in (2) and (3) exceeds 0.25 and 0.34, respectively.

[0036] The present invention covers a steel sheet having a strength no lower than 550 MPa (preferably no lower than 750 MPa, more preferably no lower than 900 MPa). The steel sheet should contain C, Si, and Mn (and optionally P) in an adequate amount as specified below according to strength and weldability desired.

[0037] For tensile strength from 550 to 650 MPa.

$$[P] + 3[S] + 1.54[C] < 0.14$$

$$[C] + [Si]/30 + [Mn]/20 + 2[P] + 4[S] < 0.21$$

[0038] For tensile strength from 650 (exclusive) to 750 MPa.

$$[P] + 3[S] + 1.54[C] < 0.18$$

$$[C] + [Si]/30 + [Mn]/20 + 2[P] + 4[S] < 0.27$$

[0039] For tensile strength from 750 (exclusive) to 1050 MPa.

$$[P] + 3[S] + 1.54[C] < 0.22$$

$$[C] + [Si]/30 + [Mn]/20 + 2[P] + 4[S] < 0.30$$

[0040] For tensile strength in excess of 1050 MPa.

$$[P] + 3[S] + 1.54[C] < 0.25$$

$$[C] + [Si]/30 + [Mn]/20 + 2[P] + 4[S] < 0.34$$

[0041] The present invention covers a DP (Dual Phase) steel sheet of ferrite-tempered martensite type. The steel may be composed solely of ferrite and tempered martensite, or it may additionally contain pearlite, bainite, and retained austenite in an amount not harmful to the effect of the present invention. They inevitably remain in the manufacturing process, but they should be as little as possible.

[0042] For the steel sheet to have good chemical treatability, the shape of the oxides that separate out on the surface thereof should be controlled according to the requirement (I) mentioned above. This object is achieved not only by the controlled steel composition as mentioned above but also by pickling (that follows hot rolling) with hydrochloric acid (1 to 18 mass%) at 70 to 90°C for about 40 seconds or more (preferably 60 seconds or more) and continuous annealing in an atmosphere with a dew point no higher than -40°C, preferably no higher than -45°C. Incidentally, in the case of pickling with several acid baths for intermittent dipping, the total dipping time should be 40 seconds at the minimum. Thus, in order to control the formation of the oxides so as to satisfy the requirement (I), the hot rolled steel sheet need undergo pickling.

[0043] For the steel sheet to be free of cracks as provided in the requirement (II) mentioned above, the manufacturing process is specified as follows:

[0044] The winding temperature for hot rolling should be no higher than 500°C, preferably no higher than 480°C; The hot rolled steel sheet should be dipped in hydrochloric acid (1 to 18 mass%) at 70 to 90°C for 40 seconds or more, preferably 60 seconds or more; Continuous annealing should be performed in an atmosphere with a dew point no higher than -40°C, preferably no higher than -45°C; The hardening start temperature at the time of annealing (which may be referred to as "slow cooling end temperature") should be no higher than 550°C, preferably from 400 to 450°C. Thus, in order to restrict the formation of the cracks and to satisfy the requirement (II),the production conditions should be such that generation of grain boundary oxides which can become start points for the cracks is restrained.

[0045] The present invention does not specify other manufacturing conditions than mentioned above. Thus the steel sheet may be produced in the usual way by melting, casting, and hot rolling. Although the manufacturing process in Examples that follow involves pickling that follows continuous annealing, pickling is not mandatory in the present invention.

EXAMPLES

[0046] The invention will be described in more detail with reference to the following examples, which are not intended to restrict the scope thereof, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

[0047] In each example, a steel with the chemical composition shown in Table 1 was prepared by melting, and the resulting steel was cast into a slab, which underwent hot rolling, followed by pickling. Winding and pickling were performed under the conditions shown in Tables 2 and 3. Pickling involved an aqueous solution of hydrochloric acid (1 to 18 mass%) at 70 to 90°C. Pickling was followed by cold rolling, which gave a 1.4 mm thick steel sheet.

[0048] The steel sheet underwent continuous annealing by either of the processes shown in Figs. 2 and 3. The process shown in Fig. 2 involves cooling with water quenching (WQ) that follows soaking and slow cooling. The process shown in Fig. 3 involves cooling with mist, gas blowing (GJ), or water-cooled roll quenching (RQ).

[0049] The heating temperature, slow cooling end temperature, and tempering temperature shown in Tables 2 and 3 correspond to those shown in Figs. 2 and 3. The dew point is that of the atmosphere in the continuous annealing furnace. After cooling, the steel sheet underwent tempering. In the process shown Fig. 2, pickling was carried out before and/or after tempering.

[0050] The thus obtained steel sheet was examined for mechanical properties and coating film adhesion. All of the steel sheet samples were found to be composed mainly of ferrite and tempered martensite.

[0051] Mechanical properties were determined by measuring the tensile strength (TS), total elongation (El), and yield ratio (YP) of specimens (conforming to JIS No. 5) taken from the steel sheet. A discoid specimen measuring 100 mm in diameter and 1.4 mm thick was tested for stretch-flanging performance. The test method consists of punching a hole (10 mm in diameter) in the specimen and expanding the hole by a 60° conical punch, with the burr upward. The bore expanding ratio (λ) was measured when the conical punch passed through with cracking. (according to JFST 1001 provided by The Japan Iron and Steel Federation).

[0052] For evaluation of coating film adhesion, samples were examined for chemical treatability and the presence of cracks in the following manner. After chemical treatment, the surface of the treated steel sheet was observed under an SEM with a magnification of 1000 to confirm the presence of zinc phosphate crystals in ten fields of observation. The result was rated according to the following criterion. O : Zinc phosphate crystals are present uniformly in all of ten fields of observation.

× : There is at least one field of observation in which zinc phosphate crystals are not present.

[0053] Method for chemical treatment

- Chemical treating solution : "Parbond L3020" from Nihon Parkerizing Co., Ltd.
- Process of chemical treatment : degreasing → water washing → surface conditioning → chemical treatment

Method of counting the number of Si-Mn oxide particles

[0054] First, an extraction replica is prepared from the surface of the steel sheet. Then, it is observed under a TEM (Model H-800 of Hitachi, Ltd.) with a magnification of 15000. An average number of particles (per 100 μm^2) is counted in arbitrary 20 fields of observation.

[0055] The ratio of the surface area of steel sheet which is covered by the oxides composed mainly of Si was obtained by observation of a sample under a TEM and ensuing image analysis. The sample was prepared by the extraction replica method consisting of four steps (a) to (d) as explained in the following.

(a) Vacuum deposition of carbon on the surface of steel sheet.
(b) Cross-cutting (2 to 3 mm square each) of the sample surface.
(c) Corrosion with an etching solution composed of 10% acetylacetone and 90% methanol. This corrosion brings carbon into relief.
(d) Storing the sample in alcohol for observation.

[0056] The treated sample was photographed in ten fields of observation (each measuring 13 by 11 cm) through a TEM with a magnification of 15000. The resulting electron micrograph was examined to measure the area covered by oxides composed mainly of Si (or oxides in which Si as the constituents excluding oxygen accounts for no less than 70% in atomic ratio). In this way there was obtained the coverage of oxides composed mainly of Si.

[0057] The presence of cracks (width : no larger than 3 μm, depth : no smaller than 5 μm) was examined by observing the cross section of the surface layer of the steel sheet in ten fields of observation (each measuring 13 by 11 cm) under an SEM (Model S-4500 of Hitachi Ltd.) with a magnification of 2000.

Table 1

Type of steel	Composition (mass%)																
	C	Si	Mn	P	S	Al	Cr	Mo	Ti	Nb	V	B (ppm)	N (ppm)	O (ppm)	Si/Mn	P+3S+1.54C	C+Si/3O+ Mn/ 20+2P+4S
1	0.08	0.69	2.45	0.001	0.001	0.029	--	0.2	--	--	--	--	18	21	0.282	0.13	0.23
2	0.08	1.01	3.11	0.008	0.003	0.033	--	--	--	--	--	--	9	15	0.325	0.14	0.30
3	0.08	0.21	2.91	0.008	0.003	0.014	--	--	--	--	--	--	18	31	0.072	0.14	0.26
4	0.08	0.59	2.99	0.007	0.003	0.015	--	--	--	--	--	--	22	36	0.197	0.14	0.27
5	0.08	1.01	3.04	0.007	0.002	0.015	--	--	--	--	--	--	23	32	0.332	0.13	0.29
6	0.10	0.47	1.61	0.011	0.002	0.024	--	0.19	--	--	--	--	30	28	0.292	0.17	0.23
7	0.10	0.66	2.10	0.013	0.003	0.026	--	0.18	--	--	--	--	28	23	0.314	0.18	0.27
8	0.13	0.19	2.68	0.010	0.011	0.019	--	--	0.050	--	--	--	34	24	0.071	0.22	0.30
9	0.08	0.73	2.39	0.006	0.002	0.047	--	0.2	--	0.001	0.003	5	15	20	0.305	0.13	0.24
10	0.08	0.96	2.95	0.008	0.003	0.038	--	--	--	0.003	0.005	6	20	23	0.325	0.14	0.29
11	0.05	1.02	2.98	0.003	0.005	0.066	--	--	--	--	--	--	12	16	0.324	0.10	0.28
12	0.05	0.98	2.92	0.003	0.006	0.062	0.20	--	--	--	--	--	15	15	0.336	0.10	0.27
13	0.05	0.98	2.87	0.002	0.007	0.060	0.40	--	--	--	--	--	8	11	0.341	0.11	0.27
14	0.05	1.00	2.87	0.003	0.007	0.066	0.59	--	--	--	--	--	13	12	0.341	0.11	0.28
15	0.05	1.00	3.05	0.011	0.007	0.064	0.80	--	--	--	--	--	11	10	0.328	0.11	0.29
16	0.05	0.99	3.09	0.010	0.005	0.043	--	0.19	--	--	--	--	24	22	0.320	0.11	0.28
17	0.05	0.99	3.08	0.010	0.005	0.048	--	0.47	--	--	--	--	22	22	0.321	0.11	0.28
18	0.05	0.99	2.91	0.010	0.007	0.049	0.20	0.19	--	--	--	--	22	23	0.340	0.11	0.28
19	0.05	0.98	2.85	0.010	0.006	0.044	0.21	0.47	--	--	--	--	21	21	0.343	0.11	0.27
20	0.11	1.01	2.93	0.011	0.007	0.092	--	--	--	--	--	--	33	8	0.345	0.11	0.27
21	0.07	0.19	2.00	0.004	0.006	0.039	--	--	--	0.020	--	--	37	30	0.095	0.13	0.22
22	0.05	0.48	1.98	0.004	0.005	0.033	-	--	--	0.022	--	--	41	31	0.242	0.13	0.22

(continued)

Type of steel	Composition (mass%)															
	C	Si	Mn	P	S	Al	Cr	Mo	Ti	Nb	V	B (ppm)	N (ppm)	O (ppm)	Si/Mn	P+3S+1.54C	C+Si/3O+ Mn/ 20+2P+4S
23	0.08	0.49	1.91	0.004	0.005	0.035	--	--	0.010	0.020	--	--	39	27	0.257	0.14	0.25
24	0.07	0.48	1.94	0.004	0.006	0.036	--	--	--	0.035	--	--	42	27	0.247	0.14	0.23
25*	0.19	1.66	2.03	0.002	0.001	0.029	--	--	--	--	--	--	22	29	0.818	0.30	0.35
26	0.10	0.82	1.86	0.010	0.002	0.067	--	--	0.066	--	--	--	27	13	0.441	0.17	0.25
27	0.14	0.24	1.87	0.011	0.007	0.055	--	--	--	--	--	--	30	17	0.128	0.25	0.29
28	0.11	1.05	2.31	0.004	0.002	0.037	--	--	0.042	--	--	--	28	26	0.455	0.18	0.28
29	0.10	0.01	2.57	0.005	0.003	0.038	0.10	0.09	0.008	0.008	--	--	25	19	0.004	0.17	0.25
30	0.10	1.96	2.49	0.004	0.003	0.040	0.09	0.10	0.009	0.010	--	--	23	20	0.787	0.17	0.31
31	0.10	0.65	1.55	0.004	0.003	0.039	0.10	0.09	0.007	0.008	--	--	20	18	0.419	0.17	0.22
32	0.10	0.63	3.53	0.006	0.003	0.040	0.11	0.09	0.009	0.009	-	--	26	18	0.178	0.17	0.32
33*	0.16	0.63	2.59	0.011	0.005	0.057	0.021	--	--	--	0.007	--	17	20	0.243	0.27	0.35

* Comparative examples

Table 2

Experiment No.	Steel Kind No.	Manufacturing conditions							Mechanical properties				Surface oxides		Film adhesion	
		Winding (°C) P	Pickling (sec)	Heating (°C)	Slow Cooling End Temp. (°C)	Cooling Method	Tempering (°C)	Dew Point (°C)	TS (MPa)	EL (%)	YP (MPa)	λ	Si-Mn oxides (number)	Si *2 oxides (%)	Chemical treatability	Cracks
1	1	450	50	850	500	WQ	180	-50	985	17	639	42	20	0	○	none
2	2	450	50	850	440	WQ	200	-50	1007	18	697	52	41	0	○	none
3	3	500	50	830	500	WQ	200	-40	849	18	560	33	16	0	○	none
4	4	500	50	830	500	WQ	200	-40	984	16	679	36	26	0	○	none
5	5	500	50	830	500	WQ	200	-40	1017	16	651	28	43	3	○	none
6	6	500	50	830	450	WQ	180	-40	633	30	396	55	12	2	○	none
7	7	500	50	830	450	WQ	180	-40	802	23	529	42	24	3	○	none
8	8	500	50	830	450	WQ	250	-40	1203	12	866	31	13	0	○	none
9	9	500	50	830	450	WQ	180	-40	1004	17	664	43	18	3	○	none
10	10	500	50	830	500	WQ	200	-40	998	17	637	34	39	2	○	none
11	11	450	60	870	400	WQ	200	-50	835	22	502	35	35	2	○	none
12	12	450	60	870	420	WQ	200	-50	871	20	545	33	34	2	○	none
13	13	450	60	870	440	WQ	200	-50	902	19	599	30	35	4	○	none
14	14	450	60	870	460	WQ	200	-50	997	16	702	35	37	5	○	none
15	15	450	60	870	400	WQ	200	-50	1008	13	734	38	36	2	○	none
16	16	450	60	870	380	WQ	250	-50	981	16	667	45	35	3	○	none
17	17	450	60	870	380	WQ	250	-50	1012	12	784	40	35	3	○	none
18	18	450	60	870	380	WQ	180	-50	987	15	658	35	31	2	○	none
19	19	450	60	870	380	WQ	180	-50	1003	13	772	41	29	5	○	none

(continued)

Experiment No.	Steel Kind No.	Manufacturing conditions							Mechanical properties				Surface oxides		Film adhesion	
		Winding (°C) P	Pickling (sec)	Heating (°C)	Slow Cooling End Temp. (°C)	Cooling Method	Tempering (°C)	Dew Point (°C)	TS (MPa)	EL (%)	YP (MPa)	λ	Si-Mn oxides (number)	Si *2 oxides (%)	Chemical treatability	Cracks
20	20	450	60	870	450	WQ	400	-50	1052	14	910	35	38	4	○	none
21	21	400	40	850	520	WQ	400	-45	617	27	523	49	13	0	○	none
22	22	400	40	850	520	WQ	400	-45	608	28	499	58	18	0	○	none
23	23	400	40	850	520	WQ	400	-45	708	25	554	43	19	0	○	none

*1 Number of particles of Si-Mn complex oxides (smaller than 1.5 μm) per 100 μm^2.
*2 Ratio of the surface area of steel sheet which is covered with oxides composed mainly of Si.

Table 3

Experiment No.	Steel Kind No.	Manufacturing conditions							Mechanical properties				Surface oxides		Film adhesion	
		Weeding Temp. (°C)	Pickling Time (sec)	Heating Temp. (°C)	Slow Cooling End Temp. (°C)	Cooling Method	Tempering Temp. (°C)	Dew Point (°C)	TS (MPa)	EL (%)	YP (MPa)	λ (%)	Si-Mn*1 oxides (number)	Si*2 oxides (%)	Chemical treatability	Cracks
24	24	400	40	850	520	WQ	400	-45	611	26	527	45	20	0	○	none
25	1	450	50	850	500	RQ	180	-45	948	18	685	44	18	0	○	none
26	1	450	50	850	500	mist	180	-40	953	17	673	40	25	0	○	none
27	1	450	50	850	500	GJ	180	-40	902	19	667	48	22	0	O	none
28	33*	480	50	850	450	WQ	200	-40	1285	13	882	25	21	0	O	none
29	25*	550	50	880	630	WQ	230	-40	1006	19	649	26	8	55	x	yes
30	26	600	50	880	630	WQ	400	-40	1215	11	972	28	9	25	x	yes
31	28	600	40	850	650	mist	250	-40	990	17	599	18	8	33	x	yes
32	27	650	50	850	650	GJ	500	-40	608	26	394	47	13	0	O	yes
33	1	450	50	850	500	WQ	180	0	972	16	659	38	5	5	x	yes
34	29	480	50	850	500	WQ	200	-45	1056	9	744	27	0	0	x	none
35	30	480	50	850	500	WQ	200	-45	1227	11	937	25	7	40	x	none
36	31	480	50	850	500	WQ	200	-45	735	20	558	42	9	20	x	none
37	32	480	50	850	500	WQ	200	-45	1327	8	1002	19	30	0	○	none
38	5	700	50	830	500	WQ	200	-40	992	16	631	30	45	8	○	yes
39	5	500	5	830	500	WQ	200	-40	1021	15	660	27	9	12	x	yes
40	5	500	50	830	700	WQ	200	-40	1217	11	1010	48	48	5	○	yes
41	5	500	50	830	500	WQ	200	-10	1007	16	654	33	8	15	x	yes

*1 Number of particles of Si-Mn complex oxides (smaller than 1.5 μm) per 100 μm^2.
*2 Ratio of the surface area of steel sheet which is covered with oxides composed mainly of Si.
* Comparative examples

[0058] The results shown in Tables 1 to 3 are discussed in the following. (No. means Experiment No.)

[0059] Samples in Nos. 32, 38, and 40 meet the requirement for the steel sheet 1 of the present invention and hence they are excellent in chemical treatability and coating film adhesion. The results suggest that it is necessary to control the winding temperature and slow cooling end temperature for the steel sheet to have good coating film adhesion, with cracks properly controlled.

[0060] Samples in Nos. 34 to 36 meet the requirement for the steel sheet 2 of the present invention and hence they are free of cracks and excellent in coating film adhesion. The results suggest that it is necessary to control the composition and the shape of the oxides that separate out on the surface of the steel sheet for the steel sheet to have good chemical treatability and coating film adhesion.

[0061] By contrast, samples in Nos. 29, 30, 31, 33, 39, and 41 do not meet the requirement for the steel sheets (1 to 3) of the present invention and hence they are poor in coating film adhesion. In other words, samples in Nos. 29 to 31 do not meet the requirement for [Si]/[Mn] ratio and hence they do not give oxides having the shape specified in the present invention. Moreover, they have many cracks (because they are not produced under the desired conditions) and they are poor in coating film adhesion.

[0062] Samples in Nos. 33, 39, and 41 are not produced under the desirable conditions and hence they do not have oxides with the shape specified in the present invention. They have cracks and are poor in coating film adhesion.

[0063] Sample in No. 37 meets the requirements and hence is excellent in coating film adhesion; but it cannot be formed satisfactorily on account of its poor ductility.

[0064] Samples in Nos. 1 to 27 meet the requirement for the steel sheet 3 of the present invention (or the requirements for the steel sheets (1 and 2) of the present invention) and they also satisfy the equations (2) and (3) and hence they are excellent in chemical treatability, coating film adhesion (free of cracks), and weldability.

[0065] Sample in No. 28 meets the requirements for the steel sheet 3 of the present invention; however, the results suggest that the composition should satisfy the equations (2) and (3) for the steel sheet to exhibit good weldability.

[0066] Samples in Nos. 1, 29, and 34 gave the extraction replicas whose electron micrographs (by observation under a TEM) are shown in Figs. 4 to 6. Fig. 4 indicates that sample in No. 1 has fine Si-Mn complex oxides but does not have oxides composed mainly of Si. Fig. 5 indicates that sample in No. 29 is covered with oxides composed mainly of Si. Fig. 6 indicates that sample in No. 34 does not have fine Si-Mn complex oxides although it has particulate matter (which is rust).

[0067] Samples in Nos. 1, 29, and 34 have the cross section near the surface of the steel sheet whose electron micrographs (by observation under an SEM) are shown in Figs. 7 to 9. Fig. 7 indicates that sample in No. 1 is free from cracks. Fig. 8 indicates that sample in No. 29 has cracks, 5 μm deep. Fig. 9 indicates that sample in No. 34 is free of cracks and hence excellent in coating film adhesion.

[0068] Samples in Nos. 1, 29, and 34 have the surface texture whose electron micrographs (by observation under an SEM) are shown in Figs. 10 to 12. Fig. 10 indicates that sample in No. 1 has fine zinc phosphate crystals free of interstice. Fig. 11 indicates that sample in No. 29 has small zinc phosphate crystals with large interstices. Fig. 12 indicates that sample in No. 34 has large zinc phosphate crystals with large interstices.

Claims

1. A high-strength colled-rolled steel sheet excellent in coating film adhesion, which is a DP (Dual Phase) steel sheet of ferrite-tempered martensite type containing 0.05 to 0.15 mass% of C, 0.05 to 2 mass% of Si, 1 to 5 mass% of Mn, no more than 1 mass% of Al, no more than 0.01 mass% of N, no more than 0.01 mass% of O, and optionally one or more of 0.1 to 1 mass% of Cr, 0.1 to 1 mass% of Mo, 0.1 to 1 mass% of Ni, 0.005 to 0.1 mass% of Ti, 0.005 to 0.1 mass% of Nb, 0.0005 to 0.01 mass% of V, 0.005 to 0.1 mass% of P and 0.0003 to 0.01 mass% of B, the balance being iron and inevitable impurities, having a tensile strength no lower than 550 MPa, satisfying the equations (1), (2) and (3) below, and being **characterized by** its surface in which there exist Si-Mn complex oxides no larger than 5 μm in diameter of the equivalent circle as many as 10 or more per 100 μm^2 and the coverage of oxides wherein Si accounts for no less than 70 at% in the constituents of oxides other than oxygen, on the surface of steel sheet is no more than 10% of surface area,

$$[Si]/[Mn] \leq 0.4 \qquad (1)$$

$$[P] + 3[S] + 1.54[C] < 0.25 \qquad (2)$$

$$[C] + [Si]/30 + [Mn]/20 + 2[P] + 4[S] < 0.34 \quad (3)$$

where [C], [Si], [Mn], [P], and [S] denote the content (in mass%) of these elements.

2. The high-strength cold-rolled steel sheet as defined in Claim 1, which is further **characterized by** its surface whose cross section does not show cracks with a width no larger than 3 μm and a depth no smaller than 5 μm in arbitrary ten fields of observation under an SEM with a magnification of 2000.

3. The high-strength cold-rolled steel sheet as defined in Claim 1 or 2, wherein the coverage of oxides wherein Si accounts for no less than 70 at% in the constituents of oxides other than oxygen, on the surface of steel sheet is no more than 5% of surface area,

Patentansprüche

1. Kalt-gewalztes Stahlblech mit hoher Festigkeit, ausgezeichnet in der Haftung einer Beschichtungsfolie, welches ein DP (zweiphasiges) Stahlblech vom Ferrit-getempertem Martensit-Typ ist, enthaltend 0,05 bis 0,15 Masse-% C, 0,05 bis 2 Masse-% Si, 1 bis 5 Masse-% Mn, nicht mehr als 1 Masse-% Al, nicht mehr als 0,01 Masse-% N, nicht mehr als 0,01 Masse-% O und gegebenenfalls eines oder mehrere von 0,1 bis 1 Masse-% Cr, 0,1 bis 1 Masse-% Mo, 0,1 bis 1 Masse-% Ni, 0,005 bis 0,1 Masse-% von Ti, 0,005 bis 0,1 Masse-% Nb, 0,0005 bis 0,01 Masse-% V, 0,005 bis 0,1 Masse-% P und 0,0003 bis 0,01 Masse-% B, wobei der Rest Eisen und unvermeidbare Verunreinigungen sind, mit einer Zugfestigkeit von nicht weniger als 550 MPa, genügend den nachstehenden Gleichungen (1), (2) und (3) und **gekennzeichnet durch** dessen Oberfläche, worin Si-Mn Mischoxide von nicht größer als 5 μm im Durchmesser des equivalenten Kreises so viele wie 10 oder mehr pro 100 μm^2 vorliegen, und die Oxidbedeckung, wobei Si nicht weniger als 70 Atom-% in den Bestandteilen der Oxide, verschieden von Sauerstoff, ausmacht, auf der Oberfläche des Stahlblechs nicht mehr als 10% des Oberflächenbereichs ist,

$$[Si]/[Mn] \leq 0,4 \quad (1)$$

$$[P] + 3[S] + 1,54[C] < 0,25 \quad (2)$$

$$[C] + [Si]/30 + [Mn]/20 + 2[P] + 4[S] < 0,34 \quad (3)$$

worin [C], [Si], [Mn], [P] und [S] den Gehalt (in Masse-%) dieser Elemente bezeichnen.

2. Kalt-gewalztes Stahlblech mit hoher Festigkeit, wie in Anspruch 1 definiert, welches weiter durch dessen Oberfläche gekennzeichnet ist, dessen Querschnitt keine Risse mit einer Breite von nicht größer als 3 μm und einer Tiefe von nicht geringer als 5 μm in willkürlichen zehn Beobachtungsfeldern unter einem SEM mit einer Vergrößerung von 2.000 zeigt.

3. Kalt-gewalztes Stahlblech mit hoher Festigkeit wie in Anspruch 1 oder 2 definiert, wobei die Oxidbedeckung, wobei Si nicht weniger als 70 Atom-% in den Bestandteilen der Oxide, verschieden von Sauerstoff, ausmacht, auf der Oberfläche des Stahlblechs nicht mehr als 5% des Oberflächenbereichs ist.

Revendications

1. Tôle d'acier haute résistance laminée à froid présentant une excellente adhérence du film de revêtement, qui est une tôle d'acier biphasée (DP) de type ferrite-martensite revenue contenant de 0,05 à 0,15 % en masse de C, de

0,05 à 2 % en mase de Si, de 1 à 5 % en masse de Mn, pas plus de 1 % en masse d'Al, pas plus de 0,01 % en masse de N, pas plus de 0,01 % en masse de O, et éventuellement un ou plusieurs éléments parmi 0,1 à 1 % en masse de Cr, 0,1 à 1 % en masse de Mo, 0,1 à 1 % en masse de Ni, 0,005 à 0,1 % en masse de Ti, 0,005 à 0,1 % en masse de Nb, 0,0005 à 0,01 % en masse de V, 0,005 à 0,1 % en masse de P et 0,0003 à 0, 01 % en masse de B, le reste étant du fer et des impuretés inévitables, possédant une résistance à la traction non-inférieure à 550 MPa, satisfaisant aux équations (1), (2) et (3) ci-dessous, et étant **caractérisée en ce qu'**elle possède une surface dans laquelle il existe des oxydes complexes de Si-Mn d'un diamètre non supérieur à 5 μm du cercle équivalent et jusqu'à 10 ou plus pour 100 μm^2, et la couverture des oxydes, où le Si représente pas moins de 70 % en atomes des constituants desdits oxydes autres que l'oxygène, sur la surface de la tôle d'acier n'est pas supérieure à 10 % de la superficie,

$$[Si]/[Mn] \leq 0,4 \quad (1)$$

$$[P] + 3[S] + 1,54[C] < 0,25 \quad (2)$$

$$[C] + [Si]/30 + [Mn]/20 + 2[P] + 4[S] < 0,34 \quad (3)$$

où le [C], le [Si], le [Mn], le [P], et le [S] indiquent la teneur (en % en masse) de ces éléments.

2. Tôle d'acier haute résistance laminée à froid selon la revendication 1, **caractérisée en outre par** sa surface dont la coupe transversale ne montre aucune fissure d'une largeur non supérieure à 3 μm et d'une profondeur non inférieure à 5 μm dans dix champs d'observation arbitraires sous microscope électronique à balayage à un grossissement de 2000.

3. Tôle d'acier haute résistance laminée à froid selon la revendication 1 ou 2, dans laquelle la couverture d'oxydes, où le Si représente pas moins de 70 % en atome des constituants desdits oxydes autres que l'oxygène, sur la surface de la tôle d'acier n'est pas supérieure à 5 % de la superficie.

FIG. 1

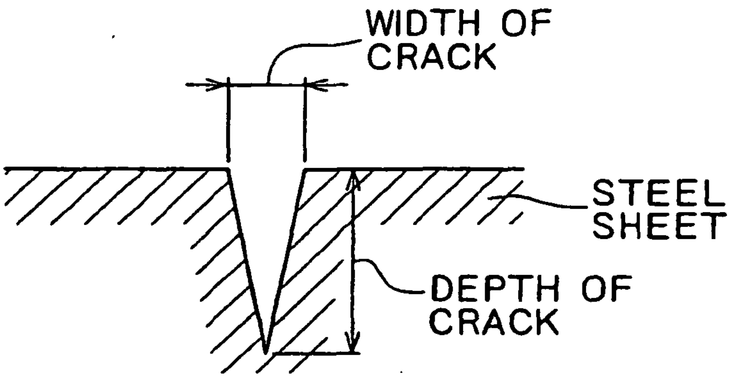

WIDTH OF CRACK
STEEL SHEET
DEPTH OF CRACK

FIG. 2

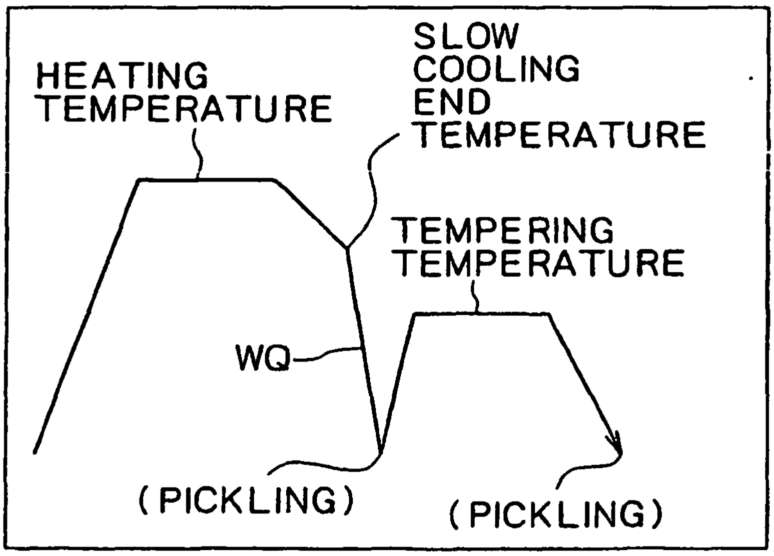

HEATING TEMPERATURE
SLOW COOLING END TEMPERATURE
TEMPERING TEMPERATURE
WQ
(PICKLING)
(PICKLING)

FIG.3

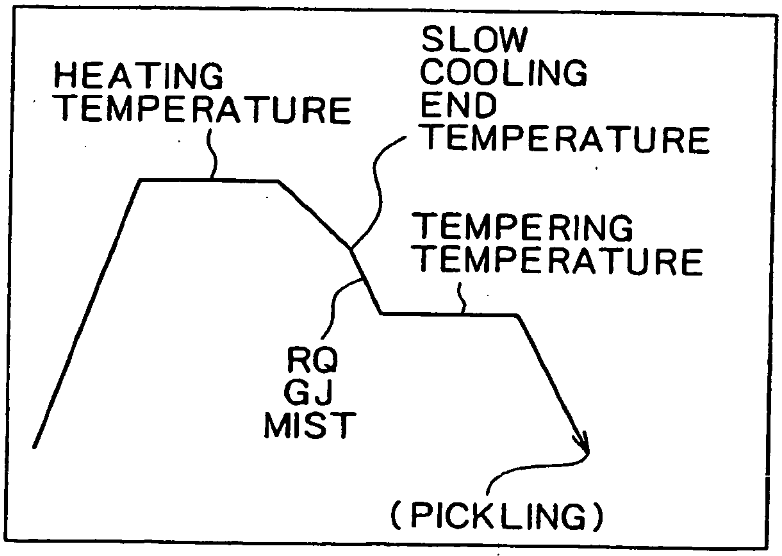

HEATING
TEMPERATURE
SLOW
COOLING
END
TEMPERATURE
TEMPERING
TEMPERATURE
RQ
GJ
MIST
(PICKLING)

FIG. 4

EXPERIMENT NO. 1

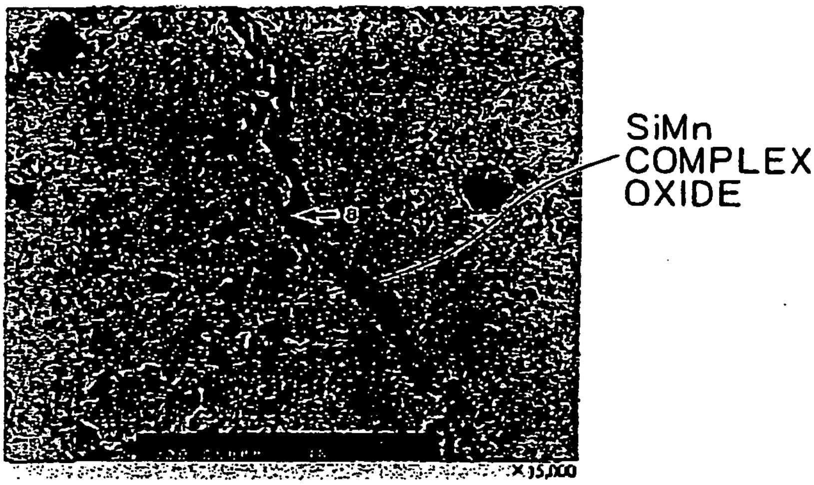


FIG. 5

EXPERIMENT NO. 29

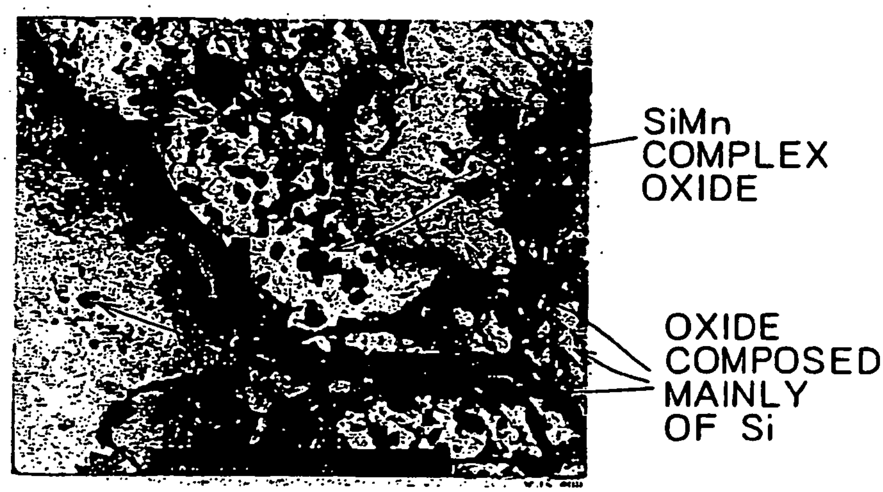


FIG.6

EXPERIMENT NO. 34

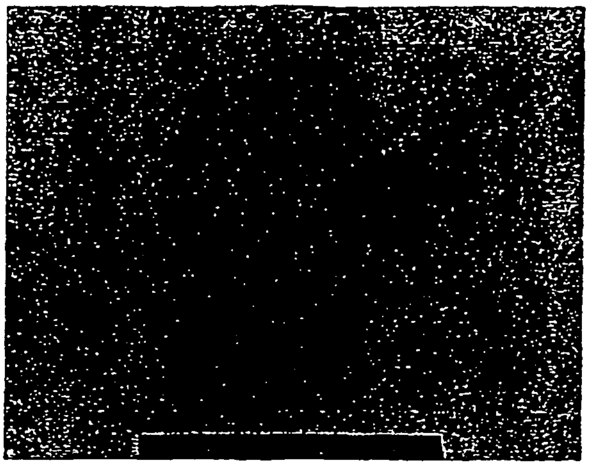


FIG.7

EXPERIMENT NO. 1

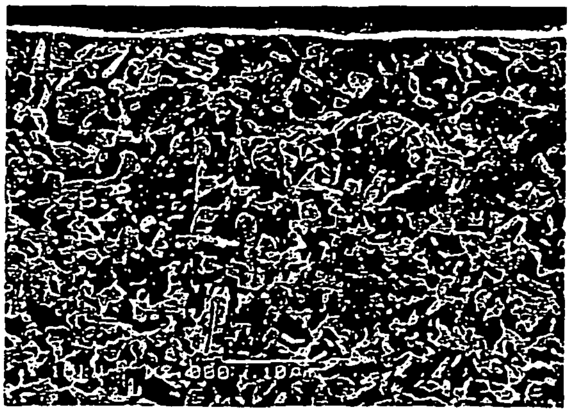


FIG. 8

EXPERIMENT NO. 29

FIG. 9

EXPERIMENT NO. 34

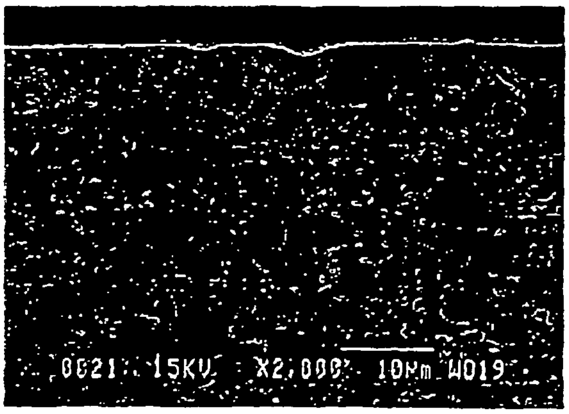


FIG.10

EXPERIMENT NO. 1

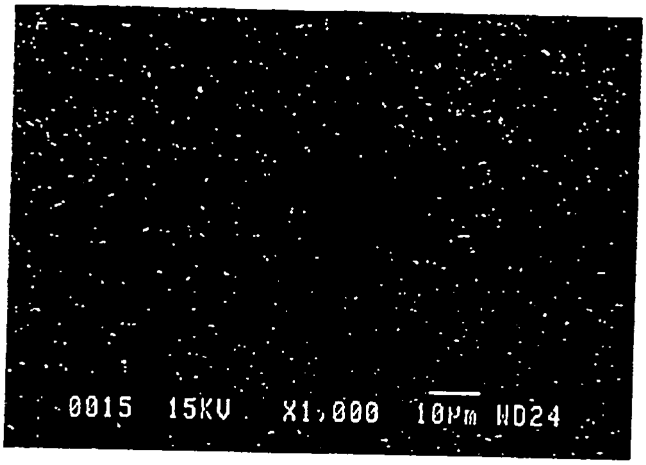
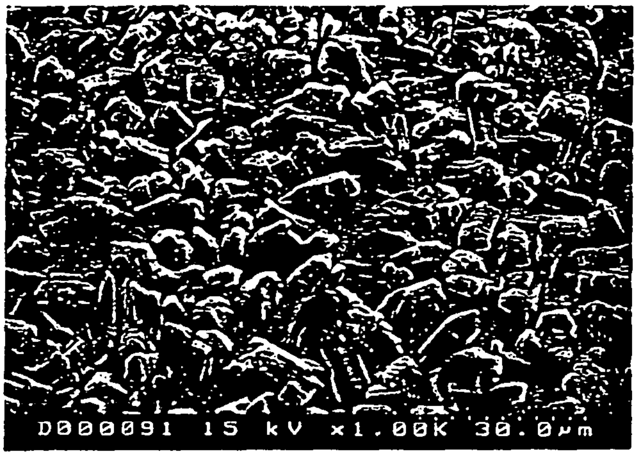


FIG.11

EXPERIMENT NO. 29

FIG. 12

EXPERIMENT NO. 34



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