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(54) **METHOD FOR PRODUCING EXTREMELY LOW CARBON STEEL SHEET AND EXTREMELY LOW CARBON CAST PIECE HAVING EXCELLENT SURFACE CHARACTERISTICS, WORKABILITY AND FORMABILITY**

(57) A method of producing an extremely low carbon steel cast slab **characterized by** casting molten steel obtained by reducing the carbon concentration of the molten steel to 0.005 mass% or less, then adding Cu, Nb, and B to the molten steel, furthermore, and adjusting the concentration of dissolved oxygen in the molten steel to 0.01 mass% to 0.06 mass% and extremely low carbon

steel plate comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, and further Cu, Nb, and B, **characterized in that** the steel has fine oxides of a diameter of 0.5 μm to 30 μm dispersed in it in an amount of 1000 particles/cm² to 1,000,000 particles/cm².

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to extremely low carbon steel plate excellent in surface characteristics, workability, and formability and a method of producing extremely low carbon cast slab.

BACKGROUND ART

10 **[0002]** Molten steel refined in a converter or vacuum treatment vessel contains a large amount of dissolved oxygen. This excess oxygen is generally removed by Al which is a strong deoxidizing element with a strong affinity with oxygen. However, Al forms alumina-based inclusions by deoxidation. These aggregate and form coarse alumina clusters.

[0003] The alumina clusters become the cause of the formation of surface defects during steel plate production and greatly deteriorate the quality of the thin-gauge steel plate. In particular, in extremely low carbon molten steel, which is a material for thin-gauge steel plate having a low carbon concentration and high concentration of dissolved oxygen after refining, the amount of the alumina clusters is extremely large and the rate of formation of surface defects is extremely high, so measures for reducing the alumina-based inclusions have become major issues.

[0004] As opposed to this, in the past, the method of adding flux for adsorption of inclusions to the molten steel surface to remove alumina-based inclusions such as disclosed in Japanese Patent Publication (A) No. 5-104219 and the method of utilizing the injection flow disclosed in Japanese Patent Publication (A) No. 63-149057 to add a CaO flux in the molten steel and remove alumina-based inclusions by adsorption have been proposed and worked.

[0005] On the other hand, as a method not removing the alumina-based inclusions, but not forming them, Japanese Patent Publication (A) No. 5-302112 discloses the method of producing molten steel for thin-gauge steel plate not being deoxidized much at all by Al by deoxidizing the molten steel by Mg.

DISCLOSURE OF THE INVENTION

[0006] However, with the method of removing alumina-based inclusions as described in Japanese Patent Publication (A) No. 5-104219 and Japanese Patent Publication (A) No. 63-149057, it is extremely difficult to reduce the alumina-based inclusions formed in a large amount in extremely low carbon molten steel, to an extent not forming surface defects.

[0007] Further, with the Mg deoxidation not forming any alumina-based inclusions at all such as described in Japanese Patent Publication (A) No. 5-302112, the vapor pressure of the Mg is high and the yield to molten steel is extremely low, so deoxidizing molten steel with a high concentration of dissolved oxygen such as with extremely low carbon steel by just Mg requires a large amount of Mg. Considering the production costs, the process cannot be said to be practical.

[0008] Considering these problems, the present invention has as its object to provide extremely low carbon steel plate reliably preventing surface defects and superior in workability and formability by finely dispersing oxides at the time of solidification without forming almost any inclusions in the molten steel and a method of production of the same.

[0009] In order to solve the aforeexplained problems, the present invention has the following as its gist:

40 (1) A method of producing an extremely low carbon steel cast slab characterized by casting molten steel obtained by reducing the carbon concentration of the molten steel to 0.005 mass% or less, then adding Cu, Nb, and B to the molten steel, furthermore, and adjusting the concentration of dissolved oxygen in the molten steel to 0.01 mass% to 0.06 mass%.

45 (2) A method of producing an extremely low carbon steel cast slab characterized by casting molten steel obtained by reducing the carbon concentration of the molten steel to 0.005 mass% or less, then adding Cu, Nb, and B to the molten steel to make the molten steel include Cu by 0.01 to 3.0 mass% and Nb and B by respectively

$$-0.02 \leq \text{Nb} - (93/12) \times \text{C} \leq 0.1$$

$$-0.0023 \leq \text{B} - (11/14) \times \text{N} \leq 0.0045$$

55 and further adjusting the concentration of dissolved oxygen in the molten steel to 0.01 mass% to 0.06 mass%.

(3) A method of producing an extremely low carbon steel cast slab characterized by casting molten steel obtained by reducing the carbon concentration of the molten steel to 0.005 mass% or less, adding Cu, Ni, Nb, and B to the

molten steel to make the molten steel include Cu by 0.01 to 3.0 mass%, Ni by 0.5xCu concentration or less, and Nb and B by respectively

$$-0.02 \leq Nb - (93/12) \times C \leq 0.1$$

$$-0.0023 \leq B - (11/14) \times N \leq 0.0045$$

and further adjusting the concentration of dissolved oxygen in the molten steel to 0.01 mass% to 0.06 mass%.

(4) A method of producing an extremely low carbon steel cast slab according to any one of (1) to (3) characterized by decarburizing said molten steel by vacuum degassing.

(5) A method of producing an extremely low carbon steel cast slab according to any one of (1) to (4) characterized by casting said molten steel by casting it while electromagnetically stirring it.

(6) A method of producing an extremely low carbon steel cast slab according to (5) characterized by casting said molten steel by casting it while electromagnetically stirring it to make the molten steel at the meniscus position swirl by an average flow rate of 40 cm/s to 100 cm/s.

(7) Extremely low carbon steel plate having excellent surface characteristics, workability, and formability comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, and further Cu, Nb, and B, characterized in that the steel has fine oxides of a diameter of 0.5 μ m to 30 μ m dispersed in it in an amount of 1000 particles/cm² to 1,000,000 particles/cm².

(8) Extremely low carbon steel plate having excellent surface characteristics, workability, and formability comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, Cu: 0.01 to 3.0 mass%, and further Nb and B of respectively

$$-0.02 \leq Nb - (93/12) \times C \leq 0.1$$

$$-0.0023 \leq B - (11/14) \times N \leq 0.0045$$

characterized in that the steel has fine oxides of a diameter of 0.5 μ m to 30 μ m dispersed in it in an amount of 1000 particles/cm² to 1,000,000 particles/cm².

(9) Extremely low carbon steel plate having excellent surface characteristics, workability, and formability comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, Cu: 0.01 to 3.0 mass%, Ni: 0.5xCu mass% or less, and further Nb and B of respectively

$$-0.02 \leq Nb - (93/12) \times C \leq 0.1$$

$$-0.0023 \leq B - (11/14) \times N \leq 0.0045$$

characterized in that the steel has fine oxides of a diameter of 0.5 μ m to 30 μ m dispersed in it in an amount of 1000 particles/cm² to 1,000,000 particles/cm².

(10) Extremely low carbon steel plate having excellent surface characteristics, workability, and formability comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, and further Cu, Nb, and B, characterized in that at least 40% of the number of oxides present in the steel include at least Si, Mn, and Fe.

(11) Extremely low carbon steel plate having excellent surface characteristics, workability, and formability comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, Cu: 0.01 to 3.0 mass%, and further Nb and B of respectively

$$-0.02 \leq Nb - (93/12) \times C \leq 0.1$$

$$-0.0023 \leq B - (11/14) \times N \leq 0.0045$$

characterized in that at least 40% of the number of oxides present in the steel include at least Si, Mn, and Fe.

(12) Extremely low carbon steel plate having excellent surface characteristics, workability, and formability comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, Cu: 0.01 to 3.0 mass%, Ni: 0.5xCu mass% or less, and further Nb and B of respectively

$$-0.02 \leq Nb - (93/12) \times C \leq 0.1$$

$$-0.0023 \leq B - (11/14) \times N \leq 0.0045$$

characterized in that at least 40% of the number of oxides present in the steel include at least Si, Mn, and Fe.

(13) An extremely low carbon steel plate having excellent surface characteristics, workability, and formability according to any one of (10) to (12) characterized in that the contents of the at least Si oxides, Mn oxides, and Fe oxides which at least 40% of the number of oxides present in the steel include is 20 mass% or more.

[0010] According to the present invention, oxides can be made to finely precipitate in the molten steel at the time of solidification without causing formation of almost any inclusions, so it is possible to reliably prevent surface defects and fix the C and N in the steel plate and possible to control the texture of the hot rolled steel plate, so it is possible to produce a thin-gauge steel plate excellent in workability and formability.

BEST MODE FOR CARRYING OUT THE INVENTION

[0011] Below, the present invention will be explained in detail.

[0012] The method of production of the present invention adds Cu, Nb, and B to molten steel refined in a converter, electric furnace, or other steelmaking furnace or treated by vacuum degassing or the like to reduce the carbon concentration in the molten steel to 0.005 mass% or less and adjusts the concentration of dissolved oxygen to 0.01 to 0.06 mass%.

[0013] The basic idea of this melting method is to reduce the carbon concentration to an extent where it does not react with the oxygen during casting to generate CO gas and leave behind a large amount of dissolved oxygen without adding almost any Al so as to prevent the formation of almost all inclusions in the molten steel and to add Cu, Nb, and B extremely weak in deoxidizing power to fix the C and N and control the texture control and thereby secure quality as steel plate for sheet use.

[0014] The molten steel decarburized in the converter or vacuum treatment vessel contains a large amount of dissolved oxygen. This dissolved oxygen forms a large amount of alumina-based inclusions since almost all of it is removed by addition of Al (reaction of Formula 1):



[Formula 1]

[0015] The alumina-based inclusions aggregate immediately after deoxidation to become coarse alumina-based inclusions which become the cause of formation of surface defects at the time of steel plate production. However, if not adding any Al in the molten steel after decarburization or, even if adding it, adding a small amount and not removing much oxygen at all, a large amount of dissolved oxygen is contained in the molten steel, but almost no inclusions are formed and molten steel of an extremely high cleanliness can be obtained.

[0016] Usually, if casting molten steel in which dissolved oxygen is contained in a large amount, CO gas is generated during solidification, a severe bubbling phenomenon occurs, and a large amount of bubbles are trapped in the cast slab, so not only is the castability deteriorated, but also the quality of the cast slab greatly decreases.

[0017] Consequently, the present invention has focused attention on not adding Al at all or not adding much at all and leaving dissolved oxygen, but instead greatly lowering the C concentration so as to suppress formation of CO gas during solidification. As a result, from experimental studies, it was learned that if the C concentration is made 0.005 mass% or less, the rate of formation of CO gas during solidification drops by an extremely large margin.

[0018] In order to raise the workability in steel plate for thin-gauge steel plate, it is important to reduce the C concentration as much as possible and fix the C and N in solid solution in the steel by the addition of other elements. Usually, Al, Ti,

etc. are used as elements fixing C and N in the steel, but if adding sufficient amounts of these elements for fixing the C or N, the molten steel ends up becoming strongly deoxidized.

[0019] In the present invention, it was discovered to add Nb and B as elements where even if amounts of an extent able to sufficiently fix N or C are added, the deoxidizing power is so weak that the molten steel is not deoxidized much at all.

[0020] Nb and B function to increase the workability of the steel plate by fixing mainly C and mainly N respectively as precipitates.

[0021] However, with just the compound addition of Nb and B, the total elongation of the obtained steel plate is greatly improved, but the Lankford value (referred to as the "r value") becomes a somewhat low value compared with Al-deoxidized Ti-added extremely low carbon steel.

[0022] Therefore, when the present inventors examined in detail the additive elements which easily cause the formation of texture in the plate surface orientation {111} suited for r value improvement in the steel plate, whereupon they discovered that Cu addition is the most effective in the steel plate of the present invention with the high oxygen concentration.

[0023] Consequently, in the present invention, to raise the workability of the steel plate, that is, both the total elongation and the r value, it is necessary to add the three elements of Nb, B, and Cu in the molten steel.

[0024] In the above way, even if reducing the C concentration to 0.005 mass% or less, if the concentration of dissolved oxygen in the molten steel is too high, production of the CO gas during solidification cannot be suppressed. By experimental study, if the concentration of dissolved oxygen is over 0.06 mass%, even if lowering the C concentration to 0.005 mass% or less, CO bubbles end up being trapped in the cast slab, so bubble-based defects are generated after rolling.

[0025] On the other hand, in order to suppress production of CO gas, it is possible to remove the excess concentration of dissolved oxygen by Al, Ti, or the like, but from experimental studies, if deoxidized to lower than a concentration of dissolved oxygen of 0.01 mass%, alumina, titania, and other inclusions become excessive and end up remaining in the molten steel without floating up and being removed.

[0026] Accordingly, the concentration of dissolved oxygen in the molten steel has to be 0.01 mass% to 0.06 mass%.

[0027] However, when adding Nb, B, and Cu, if the concentration of dissolved oxygen is in the range of the present invention, Al, Ti, etc. need not be added at all. Note that the concentration of dissolved oxygen in the molten steel can be analyzed by an oxygen sensor using a solid electrolyte, while the concentration of C can be analyzed by the molten steel sampling method.

[0028] Next, the preferred concentrations in the molten steel of Nb and B added to the molten steel will be explained. As explained earlier, Nb and B increase the workability of the steel plate by fixing mainly C and mainly N respectively as precipitates.

[0029] However, if adding more than required, they are present as solid solution Nb and solid solution B in the steel and raise the recrystallization temperature, so unless treated at the annealing temperature corresponding to this, a hot worked structure easily results and the ductility easily decreases.

[0030] Therefore, the preferred range of addition of Nb and B to the molten steel can be suitably expressed if using the middle part of the following formulas described using the chemical equivalents of the elements as indicators. Here, the middle part of [Formula 2] means the amount of free Nb not bonding with C and forming a carbide, while the middle part of [Formula 3] means the amount of free N not bonding with N and forming a nitride.

[0031] That is, in the case of Nb, if the value of the middle part of [Formula 2] is less than -0.02 or over 0.1, or, in the case of B, if the value of the middle part of [Formula 3] is less than -0.0023 or over 0.0045, the ductility easily decreases.

[0032] From the above reasons, it is desirable to satisfy the relationships of

$$-0.02 \leq \text{Nb} - (93/12) \times \text{C} \leq 0.1 \quad [\text{Formula 2}]$$

$$-0.0023 \leq \text{B} - (11/14) \times \text{N} \leq 0.0045 \quad [\text{Formula 3}]$$

[0033] Further, if the amounts of addition of Nb and B of this range, the oxygen concentration balanced with Nb and B is 0.01 mass% or more. Even if adding Nb and B, dissolved oxygen of 0.01 mass% or more can be secured.

[0034] Further, the preferable concentration of the Cu added to the molten steel in the molten steel will be explained. Cu has the effect of promoting the formation of a texture of the {111} orientation where a high r value is easily obtained in the steel plate. At the minimum, if adding 0.01 mass% or more, this effect does not easily appear, so the amount of addition is preferably made 0.01 mass% or more.

[0035] On the other hand, if the amount of addition of Cu is over 3.0 mass%, the surface properties of the steel plate after hot rolling easily deteriorate due to Cu-embrittlement, so the upper limit is preferably made 3.0 mass%.

[0036] Ni has the effect of easing the deterioration of the hot rolled surface characteristics due to Cu. On a mass base,

it is general to add the equivalent of more than half of the Cu as a rule. It was discovered in steel plate with a high oxygen concentration of the present invention, when the concentration of dissolved oxygen in the molten steel is 0.01 mass% or more, Cu-embrittlement is inhibited by smoothing the scale and ferrite boundaries of the hot rolled plate and improving the scale peelability.

[0037] Because of this, in the present invention, even in a state where Ni is not added, the surface characteristics of the hot rolled plate become good and the features of the present invention can be extracted to the maximum, but when it is necessary, it is sufficient to add Ni in an amount of less than half of the Cu. Originally, in steel plate with good surface characteristics of the hot rolled plate, even if adding Ni to same extent as conventional Cu steel, only a rise in cost is incurred. The upper limit of Ni is preferably made less than 1/2 of the Cu concentration.

[0038] The action of the other ingredients in the molten steel will be alluded to next.

[0039] The Si concentration in the molten steel is preferably 0.005 mass% to 0.03 mass%. If Si concentration is less than 0.005 mass%, the strength of the steel plate easily becomes insufficient, while if the Si concentration is over 0.03 mass%, the workability of the steel plate decreases.

[0040] Further, if the Si concentration is 0.03 mass% or less, the equilibrium oxygen concentration also becomes more than 0.02 mass%. By just adjusting the Si concentration, it is possible to secure a concentration of dissolved oxygen of over 0.02 mass% to 0.06 mass%. Furthermore, by adding elements having deoxidizing power, a concentration of dissolved oxygen in the molten steel of 0.01 mass% to 0.06 mass% can be secured.

[0041] When the Mn concentration in the molten steel is less than 0.08 mass%, scab flaws are easily formed at the time of hot rolling of the slab. Further, if the Mn concentration is over 0.3 mass%, the workability of the steel plate decreases. Because of this, the Mn concentration in the molten steel is preferably 0.08 mass% to 0.3 mass%.

[0042] Further, Mn has an extremely weak deoxidizing power compared to Si, because the Mn concentration is 0.3 mass%, the equilibrium oxygen concentration is in excess of 0.1 mass%, furthermore, by adding elements having deoxidizing power, a concentration of dissolved oxygen in the molten steel no less than 0.01 mass% and no greater than 0.06 mass% can be guaranteed.

[0043] Furthermore, because Mn has an extremely weak deoxidizing power, if the Mn concentration is 0.3 mass% or less, almost no Mn oxides are formed under equilibrium conditions, but if adding Mn in high oxygen molten steel after converter blowing or after vacuum degassing, the Mn is adding in the form of large clumps of ferromanganese or manganese ore, so sometimes regions of high Mn concentration are locally formed in the molten steel. In such regions, while small in amount, Mn oxides end up being formed.

[0044] In the present invention, it is more preferable not to form inclusions in the molten steel, so it is more preferable to adjust the Mn concentration under operating conditions with no addition of Mn after converter blowing or after vacuum degassing.

[0045] Usually, molten iron contains Mn. Even without the addition of Mn, by the operating conditions, it is possible to obtain an Mn concentration of about 0.15 mass%. Consequently, if considering even the inclusions in addition to the quality, the more preferable range of Mn concentration is 0.08 to 0.15 mass% where production is possible without the addition of Mn after converter blowing or after vacuum degassing.

[0046] In the present invention, to prevent the formation of the easily aggregating alumina-based inclusions, Al is not added to the molten steel or almost not added at all. In experimental studies, if the acid soluble Al concentration of the steel plate exceeds 0.005 mass%, the alumina-based inclusions in the steel plate increase, so the upper limit was made 0.005 mass%. Since no addition of Al in the molten steel is preferable, of course the lower limit of Al concentration includes 0 mass%.

[0047] Here, the acid soluble Al is the amount of Al dissolved in acid. Usually, this corresponds to the dissolved Al concentration (concentration of Al not forming Al_2O_3).

[0048] Further, the alumina-based inclusions inevitably entering from the refractories etc. do not pose a problem. This is because with a small amount of alumina-based inclusions, the dissolved oxygen in the molten steel is high, so the boundary energy of the molten steel and alumina-based inclusions decreases and almost no texture is formed.

[0049] Furthermore, the Ti in the molten steel fixes the C and N as TiN or TiC, so is effective in improving the workability, but if the amount of addition of Ti also becomes greater, for example, if the Ti concentration becomes more than 0.01 mass%, the equilibrium oxygen concentration becomes less than 0.01 mass%, so a sufficient concentration of dissolved oxygen cannot be secured. Consequently, when adding Ti from the necessity of further raising the workability, it should be added in the range of 0.01 mass% or less.

[0050] Recently, continuous casting machines have been equipped with in-casting mold electromagnetic stirring devices or magnetic coils. By using these, it was discovered that casting is possible without allowing CO bubbles to be trapped in the cast slab.

[0051] The present inventors discovered that if securing a molten steel flow rate at the meniscus in the casting mold at the time of electromagnetic stirring during solidification of 40 to 100 cm/s, casting is possible with almost no CO bubbles trapped in the cast slab even if making the concentration of dissolved oxygen about 0.06 mass%, so this is more preferable.

[0052] Note that if the swirl flow rate of the molten metal by electromagnetic stirring is less than 40 cm/s, a sufficient cleansing effect of CO bubbles is difficult to obtain, while if the swirl flow rate is over 100 cm/s, the CO bubbles are cleansed, but mold powder at the surface of the molten steel is entrained and surface defects easily are formed.

[0053] In the present invention, molten steel reduced in C concentration to 0.05 mass% or so by converter blowing is further reduced in C concentration to 0.005 mass% by a vacuum degassing apparatus. The concentration of dissolved oxygen in the molten steel is controlled to approach 0.01 to 0.06 mass% after the end of decarburization considering the amount of decarburization.

[0054] After the end of decarburization in the vacuum degassing apparatus, Mn and Si are not added or not added as much as possible, but Cu, Nb, B, Ni, and the like are added. Further, when it is necessary to finely adjust the concentration of dissolved oxygen in the molten steel to the target value, simultaneously small amounts of Al and Ti are added to adjust the ingredients. The melted steel produced in this way is continuously cast to produce a cast slab using continuous casting or electromagnetic stirring.

[0055] Next, the steel plate of the present invention will be explained. Note that the hot rolled steel plate obtained by hot rolling the cast slab produced by the above method, cold rolled steel plate obtained by cold rolling, or other steel plate obtained by working the cast slab is defined as the "steel plate" in the present invention.

[0056] Therefore, the steel plate of the present invention contains Cu, Nb, and B. As other elements, for example, it is possible to include Si, Mn, etc. from the viewpoint of securing the strength and a trace amount of Ti and acid soluble Al at 0.005 mass% or less from the viewpoint of securing workability.

[0057] Further, if making the C concentration in the molten steel extremely low, the dissolved oxygen precipitates during the casting as Fe oxide-based inclusions. The Fe oxide-based inclusions are not formed in the molten steel, but precipitate during solidification, so disperse finely in the cast slab without aggregating together.

[0058] Note that the "Fe oxide-based inclusions" are not just pure Fe oxides and also contain oxides of Si oxides, Mn oxides, etc. combined.

[0059] Therefore, in steel plate of an extremely low carbon steel like the present invention, at least Si, Mn, and Fe are included as oxides. In other words, at least one type of oxide of Si, Mn, and Fe is included. Here, other than the oxides of Si, Mn, and Fe, various oxides such as oxides of Mg, Ca, and Al may also be included.

[0060] Further, when evaluating the state of dispersion of inclusions in the steel plate of the present invention, fine oxides of a size of 0.5 μm to 30 μm are dispersed in the steel plate in an amount of 1000 particles/cm² to 1,000,000 particles/cm². By finely dispersing inclusions in this way, prevention of surface defects can be attained.

[0061] Note that the size of the fine oxides is made from 0.5 μm to 30 μm because the size of the inclusions in the steel plate of the present invention falls in the range of about 0.5 μm to 30 μm . If the inclusions are of a size of 30 μm or so, surface defects can be sufficiently prevented.

[0062] Further, the state of dispersion of inclusions was made 1000 particles/cm² to 1,000,000 particles/cm² because if the inclusions of the steel plate in the present invention are in this range of particle density, surface defects are not formed.

[0063] Here, the state of dispersion of inclusions was evaluated by observing the polished surface of the steel plate by an optical microscope at 100X and 1000X power and assessing the distribution of particle size of the inclusions in a unit area. The particle size of the inclusions, that is, the diameter, was obtained by measuring the major axis and minor axis and calculating (major axis \times minor axis)^{0.5}.

[0064] Further, if 40% or more of the number of oxides present in the steel plate contain at least Si, Mn, and Fe, almost all inclusions will be formed during solidification and the time for them to aggregate will be short, so they can finely disperse and surface defects will be difficult to form. This is therefore preferable.

[0065] Here, "contain at least Si, Mn, and Fe" means at least one type of Si, Mn, and Fe. This is used in a similar sense later as well.

[0066] Further, if 40% or more of the number of oxides present in the steel plate have a content of at least Si oxides, Mn oxides, and Fe oxides of 20 mass% or more, more preferably 50 mass% or more, almost all of the oxides will be formed at a timing close to the end of solidification and the time for them to aggregate will be extremely short, so the inclusions will finely disperse and surface defects will be difficult to form. This is therefore more preferable.

[0067] A steel plate having this kind of dispersed state of oxides and composition is resistant to the formation of surface defects.

[0068] From the above results, according to the present invention, the Fe oxide-based inclusions can be made to precipitate and finely disperse during solidification without allowing the formation of almost any inclusions in the molten steel, so the inclusions do not become the cause of formation of surface defects at the time of production of the steel plate. Further, the workability is greatly improved due to the Nb, B, and Cu in the steel plate, so the quality and material of the steel plate for sheet use can be greatly improved.

[0069] Steel plate for sheet use is used for automobile external sheet and other applications where processing is harsh, so workability must be added. In order to raise the workability of the steel plate for sheet use, decreasing the C concentration as much as possible and further fixing the C and N in solid solution in the steel by the addition of other elements are important.

[0070] The C concentration is made 0.01 mass% or less, preferably 0.005 mass% or less, from the viewpoint of workability. However, the condition for prevention of the formation of CO bubbles during solidification is a C concentration of 0.005 mass% or less, so in the present invention, the C concentration determined from the condition of workability is sufficiently satisfied. Note that the lower limit of the C concentration is not particularly limited.

EXAMPLES

[0071] Below, examples and comparative examples will be given to explain the present invention.

Example 1

[0072] 300 t of molten steel with a C concentration of 0.0019 mass% was produced by refining at a converter and treatment at a rotary flow type vacuum degassing apparatus.

[0073] To the molten steel, alloys of Cu, Nb, and B were added, without adding Al, to give 0.011 mass% Si, 0.16 mass% Mn, 0.014 mass% Nb, 0.003 mass% B, 0.07 mass% Cu, 0.0016 mass% N, 0.043 mass% dissolved oxygen, and 0.001 mass% or less acid soluble Al.

[0074] This molten steel was cast into a slab of a thickness of 250 mm and a width of 1800 mm by continuous casting. The cast slab was cut into 8500 mm lengths for use as coil units.

[0075] The thus obtained slab was hot rolled and cold rolled by ordinary methods to finally obtain a coil of cold rolled steel plate of 0.7 mm thickness and a width of 1800 mm. The quality was visually examined on an inspection line after cold rolling and the number of surface defects formed per coil was evaluated.

[0076] As a result, no surface defects were formed and no cracking due to Cu-embrittlement was observed either. Further, the inclusions in the cold rolled steel plate were examined, whereupon fine oxides of a diameter of 0.5 μm to 30 μm were dispersed in the steel plate in an amount of 35,000 particles/cm². 70% of this included Si oxides, Mn oxides, and Fe oxides in a total of 60 mass% or more.

[0077] Further, the obtained cold rolled steel plate was evaluated for workability. It was high workability steel plate with a total elongation of 57% and an r value of 2.6.

Example 2

[0078] 300 t of molten steel with a C concentration of 0.003 mass% was produced by refining at a converter and treatment at a rotary flow type vacuum degassing apparatus.

[0079] To the molten steel, alloys of Cu, Nb, B, and Ni were added, without adding Al, to give 0.01 mass% Si, 0.15 mass% Mn, 0.035 mass% Nb, 0.005 mass% B, 1.8 mass% Cu, 0.5 mass% Ni, 0.0025 mass% N, 0.004 mass% Ti, 0.015 mass% dissolved oxygen, and 0.001 mass% acid soluble Al.

[0080] This molten steel was cast to a slab of a thickness of 250 mm and a width of 1800 mm using a continuous casting machine with an in-mold electromagnetic stirring device while electromagnetically stirring the molten metal by an average flow rate of 50 cm/s at the meniscus. The cast slab was cut into 8500 mm lengths for use as coil units.

[0081] The thus obtained slab was hot rolled and cold rolled by ordinary methods to finally obtain a coil of cold rolled steel plate of 0.7 mm thickness and a width of 1800 mm. The quality of the slab was visually examined on an inspection line after cold rolling and the number of surface defects formed per coil was evaluated.

[0082] As a result, no surface defects and no cracking due to Cu-embrittlement occurred. Further, the inclusions in the cold rolled steel plate were examined, whereupon fine oxides of a diameter of 0.5 μm to 30 μm were dispersed in the steel plate in an amount of 23,500 particles/cm². 50% of this included Si oxides, Mn oxides, and Fe oxides in a total of 40 mass% or more.

[0083] Further, the obtained cold rolled steel plate was evaluated for workability. It was high workability steel plate with a total elongation of 56% and an r value of 2.7.

Comparative Example 1

[0084] Alloys of Ti and Cu were added to molten steel in a ladle reduced in carbon concentration to 0.0015 mass% by refining at a converter and treatment at a rotary flow type vacuum degassing apparatus and the steel was deoxidized by Al to give 0.01 mass% Si, 0.15 mass% Mn, 0.02 mass% Ti, 0.3 mass% Cu, 0.002 mass% N, 0.04 mass% Al, and 0.0002 mass% concentration of dissolved oxygen.

[0085] This molten steel was cast into a slab of a thickness of 250 mm and a width of 1800 mm by continuous casting. The cast slab was cut into 8500 mm lengths for use as coil units.

[0086] The thus obtained slab was hot rolled and cold rolled by ordinary methods to finally obtain a coil of cold rolled steel plate of 0.7 mm thickness and a width of 1800 mm. The quality of the slab was visually examined on an inspection

line after cold rolling and the number of surface defects formed per coil was evaluated.

[0087] As a result, surface defects occurred at a rate of 5 defects/coil by slab average. Cracks due to Cu-embrittlement also occurred. Further, when the inclusions in the cold rolled steel plate were examined, fine oxides of a diameter of 0.5 μm to 30 μm were only found in the steel plate at a rate of 200 particles/cm². A large number of inclusions in excess of 30 μm were also observed. 95% of the inclusions in the steel plate were alumina-based inclusions.

[0088] Furthermore, when the workability of the cold rolled steel plate was evaluated, a high workability steel plate with a total elongation of 40% and an r value of 1.4 could not be obtained.

INDUSTRIAL APPLICABILITY

[0089] According to the present invention, extremely low carbon thin-gauge steel plate having excellent surface characteristics, workability, and formability can be provided, so the present invention expands the applications of thin-gauge steel plate and the industrial applicability is great.

Claims

1. A method of producing an extremely low carbon steel cast slab **characterized by** casting molten steel obtained by reducing the carbon concentration of the molten steel to 0.005 mass% or less, then adding Cu, Nb, and B to the molten steel, furthermore, and adjusting the concentration of dissolved oxygen in the molten steel to 0.01 mass% to 0.06 mass%.

2. A method of producing an extremely low carbon steel cast slab **characterized by** casting molten steel obtained by reducing the carbon concentration of the molten steel to 0.005 mass% or less, then adding Cu, Nb, and B to the molten steel to make the molten steel include Cu by 0.01 to 3.0 mass% and Nb and B by respectively

$$-0.02 \leq \text{Nb} - (93/12) \times \text{C} \leq 0.1$$

$$-0.0023 \leq \text{B} - (11/14) \times \text{N} \leq 0.0045$$

and further adjusting the concentration of dissolved oxygen in the molten steel to 0.01 mass% to 0.06 mass%.

3. A method of producing an extremely low carbon steel cast slab **characterized by** casting molten steel obtained by reducing the carbon concentration of the molten steel to 0.005 mass% or less, adding Cu, Ni, Nb, and B to the molten steel to make the molten steel include Cu by 0.01 to 3.0 mass%, Ni by 0.5xCu concentration or less, and Nb and B by respectively

$$-0.02 \leq \text{Nb} - (93/12) \times \text{C} \leq 0.1$$

$$-0.0023 \leq \text{B} - (11/14) \times \text{N} \leq 0.0045$$

and further adjusting the concentration of dissolved oxygen in the molten steel to 0.01 mass% to 0.06 mass%.

4. A method of producing an extremely low carbon steel cast slab according to any one of claims 1 to 3 **characterized by** decarburizing said molten steel by vacuum degassing.

5. A method of producing an extremely low carbon steel cast slab according to any one of claims 1 to 4 **characterized by** casting said molten steel by casting it while electromagnetically stirring it.

6. A method of producing an extremely low carbon steel cast slab according to claim 5 **characterized by** casting said molten steel by casting it while electromagnetically stirring it to make the molten steel at the meniscus position swirl by an average flow rate of 40 cm/s to 100 cm/s.

7. Extremely low carbon steel plate having excellent surface characteristics, workability, and formability comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, and further Cu, Nb, and B, **characterized in that** the steel has fine oxides of a diameter of 0.5 μm to 30 μm dispersed in it in an amount of 1000 particles/cm² to 1,000,000 particles/cm².

8. Extremely low carbon steel plate having excellent surface characteristics, workability, and formability comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, Cu: 0.01 to 3.0 mass%, and further Nb and B of respectively

$$-0.02 \leq \text{Nb} - (93/12) \times \text{C} \leq 0.1$$

$$-0.0023 \leq \text{B} - (11/14) \times \text{N} \leq 0.0045$$

characterized in that the steel has fine oxides of a diameter of 0.5 μm to 30 μm dispersed in it in an amount of 1000 particles/cm² to 1,000,000 particles/cm².

9. Extremely low carbon steel plate having excellent surface characteristics, workability, and formability comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, Cu: 0.01 to 3.0 mass%, Ni: 0.5xCu mass% or less, and further Nb and B of respectively

$$-0.02 \leq \text{Nb} - (93/12) \times \text{C} \leq 0.1$$

$$-0.0023 \leq \text{B} - (11/14) \times \text{N} \leq 0.0045$$

characterized in that the steel has fine oxides of a diameter of 0.5 μm to 30 μm dispersed in it in an amount of 1000 particles/cm² to 1,000,000 particles/cm².

10. Extremely low carbon steel plate having excellent surface characteristics, workability, and formability comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, and further Cu, Nb, and B, **characterized in that** at least 40% of the number of oxides present in the steel include at least Si, Mn, and Fe.

11. Extremely low carbon steel plate having excellent surface characteristics, workability, and formability comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, Cu: 0.01 to 3.0 mass%, and further Nb and B of respectively

$$-0.02 \leq \text{Nb} - (93/12) \times \text{C} \leq 0.1$$

$$-0.0023 \leq \text{B} - (11/14) \times \text{N} \leq 0.0045$$

characterized in that at least 40% of the number of oxides present in the steel include at least Si, Mn, and Fe.

12. Extremely low carbon steel plate having excellent surface characteristics, workability, and formability comprised of steel containing C: 0.005 mass% or less, acid soluble Al: 0.005 mass% or less, Cu: 0.01 to 3.0 mass%, Ni: 0.5xCu mass% or less, and further Nb and B of respectively

$$-0.02 \leq \text{Nb} - (93/12) \times \text{C} \leq 0.1$$

$$-0.0023 \leq B - (11/14) \times N \leq 0.0045$$

characterized in that at least 40% of the number of oxides present in the steel include at least Si, Mn, and Fe.

13. An extremely low carbon steel plate having excellent surface characteristics, workability, and formability according to any one of claims 10 to 12 **characterized in that** the contents of the at least Si oxides, Mn oxides, and Fe oxides which at least 40% of the number of oxides present in the steel include is 20 mass% or more.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2006/303201

A. CLASSIFICATION OF SUBJECT MATTER C21C7/06 (2006.01), B22D1/00 (2006.01), B22D11/00 (2006.01), B22D11/115 (2006.01), C21C7/04 (2006.01), C21C7/068 (2006.01), C21C7/10 (2006.01), C22C38/00 (2006.01), C22C38/06 (2006.01), C22C38/14 (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C21C7/04 (2006.01) - C21C7/10 (2006.01), C22C38/00 (2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2006 Kokai Jitsuyo Shinan Koho 1971-2006 Toroku Jitsuyo Shinan Koho 1994-2006 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2004-244665 A (Nippon Steel Corp.), 02 September, 2004 (02.09.04), Claims 1 to 8; Par. Nos. [0002], [0012] to [0015] (Family: none)	1-4, 7-9 5-6
Y A	JP 2003-105432 A (Nippon Steel Corp.), 09 April, 2003 (09.04.03), Claims 1 to 8; Par. Nos. [0002], [0005], [0008] to [0010] (Family: none)	5-6 1-4, 7-9
Y A	JP 2003-119513 A (Nippon Steel Corp.), 23 April, 2003 (23.04.03), Claims 1 to 25; Par. Nos. [0002], [0005], [0015] to [0020] (Family: none)	5-6 1-4, 7-13
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 15 March, 2006 (15.03.06)		Date of mailing of the international search report 20 March, 2006 (20.03.06)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	JP 2000-144330 A (Nippon Steel Corp.), 26 May, 2000 (26.05.00), Claims 1 to 6; Par. No. [0026] (Family: none)	1-13
A	JP 2004-156116 A (Nippon Steel Corp.), 03 June, 2004 (03.06.04), Claims 1 to 3; Par. Nos. [0002] to [0014] (Family: none)	1-13

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REFERENCES CITED IN THE DESCRIPTION

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