



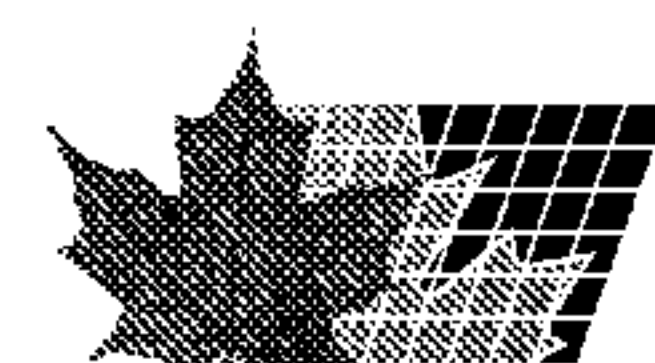
(86) Date de dépôt PCT/PCT Filing Date: 2003/03/06
(87) Date publication PCT/PCT Publication Date: 2003/12/24
(45) Date de délivrance/Issue Date: 2010/09/21
(85) Entrée phase nationale/National Entry: 2004/12/10
(86) N° demande PCT/PCT Application No.: JP 2003/002672
(87) N° publication PCT/PCT Publication No.: 2003/106726
(30) Priorité/Priority: 2002/06/12 (JP2002-170926)

(51) Cl.Int./Int.Cl. *C22C 38/04* (2006.01),
C21D 8/02 (2006.01), *C21D 8/04* (2006.01),
C22C 38/00 (2006.01)
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(54) Titre : FEUILLE D'ACIER POUR EMAILAGE VITREUX ET PROCEDE DE PRODUCTION
(54) Title: STEEL SHEET FOR VITREOUS ENAMELING AND PRODUCTION METHOD

(57) **Abrégé/Abstract:**

To provide a non-aging steel sheet for vitreous enameling, the steel sheet being excellent in resistance to bubbles and black spots, without the employment of decarbonization and denitrification annealing that raises the cost of production and also without the addition of expensive elements such as Nb, Ti, etc. that raise the cost of alloys. The steel sheet comprises, in mass, to C: 0.0050% or less, Si: 0.50% or less, Mn: 0.005 to 1.0%, P: 10x(B-11/14xN) to 0.10%, S: 0.080% or less, Al: 0.050% or less, N: 0.0005 to 0.020%, B: 0.60xN to 0.020%, and O: 0.002 to 0.0800%, and the shape of B nitrides is controlled mainly by adjusting hot-rolling conditions.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 December 2003 (24.12.2003)

PCT

(10) International Publication Number
WO 03/106726 A1

(51) International Patent Classification⁷: **C22C 38/04**,
38/00, C21D 8/02, 8/04

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(21) International Application Number: PCT/JP03/02672

(22) International Filing Date: 6 March 2003 (06.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2002-170926 12 June 2002 (12.06.2002) JP

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: STEEL SHEET FOR VITREOUS ENAMELING AND PRODUCTION METHOD

(57) Abstract: To provide a non-aging steel sheet for vitreous enameling, the steel sheet being excellent in resistance to bubbles and black spots, without the employment of decarbonization and denitrification annealing that raises the cost of production and also without the addition of expensive elements such as Nb, Ti, etc. that raise the cost of alloys. The steel sheet comprises, in mass, to C: 0.0050% or less, Si: 0.50% or less, Mn: 0.005 to 1.0%, P: 10x(B-11/14xN) to 0.10%, S: 0.080% or less, Al: 0.050% or less, N: 0.0005 to 0.020%, B: 0.60xN to 0.020%, and O: 0.002 to 0.0800%, and the shape of B nitrides is controlled mainly by adjusting hot-rolling conditions.

**WO 03/106726 A1**

DESCRIPTION

STEEL SHEET FOR VITREOUS ENAMELING AND PRODUCTION METHOD

Technical Field

The present invention relates to a steel sheet for vitreous enameling, the steel sheet being excellent in enameling properties, workability and aging properties, and a method for producing the steel sheet at a low cost.

Background Art

A steel sheet for vitreous enameling was conventionally produced by applying an annealing treatment for decarbonization and denitrification and lowering C and N contained therein to several tens of ppm or less. However, such an annealing treatment for decarbonization and denitrification had the drawbacks of low productivity and a high production cost. As a technology for avoiding an annealing treatment for decarbonization and denitrification, Japanese Unexamined Patent Publication No. H6-122938 discloses a steel sheet for vitreous enameling, the steel sheet being produced from ultra-low carbon steel obtained by lowering the C content to several tens of ppm through degassing in a steelmaking process. In such a technology, drawability and aging resistance are improved by adding Ti, Nb, etc. to avoid the adverse effects of solute C or solute N that still remains slightly in a steel sheet. However, the problems of the technology are that the defects such as bubbles and black spots are likely to be caused by carbides and nitrides and the production cost increases due to the addition of Ti, Nb, etc.

As technologies of solving the problems, steel sheets for vitreous enameling, wherein the addition amounts of Ti, Nb, etc. are decreased, though drawability

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deteriorates to some extent, and methods for producing the steel sheets have been invented and are disclosed in Japanese Unexamined Patent Publication Nos. H8-27522 and H10-102222 and other publications. These technologies are ones wherein B is used predominantly for fixing N. However, the problems of the aforementioned disclosed technologies are: that aging properties deteriorate and thus formability in pressing is impaired since the lowering of solute C is insufficient sometimes depending on the production conditions and N increases caused by the re-melting of nitrides during annealing; and that the defects such as bubbles and black spots are likely to be caused by the gases generated by the decomposition of nitrides and the like during the baking of a vitreous enamel.

The object of the present invention is to overcome the above-mentioned problems of a conventional steel sheet for vitreous enameling, to provide a non-aging and low-cost steel sheet for vitreous enameling, the steel sheet being excellent in resistance to bubbles and black spots, and to provide a method for producing the steel sheet.

Disclosure of the Invention

The gist of the present invention is as follows:

(1) A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties, said steel sheet containing, in mass,

C: 0.0050% or less,
Si: 0.50% or less,
Mn: 0.005 to 1.0%,
P: $10 \times (B - 11/14 \times N)$ to 0.10%,
S: 0.080% or less,
Al: 0.050% or less,
N: 0.0005 to 0.020%,
B: $0.60 \times N$ to 0.020%, and
O: 0.002 to 0.0800%.

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(2) A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties, said steel sheet containing, in mass,

5 C: 0.0025% or less,
Si: 0.050% or less,
Mn: 0.10 to 0.50%,
P: $10 \times (B - 11/14 \times N)$ to 0.030%,
S: 0.030% or less,
10 Al: 0.010% or less,
N: 0.0035 to 0.0060%,
B: $0.60 \times N$ to 0.0060%, and
O: 0.005 to 0.0450%.

15 (3) A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties, said steel sheet containing, in mass,

C: 0.0025% or less,
Si: 0.050% or less,
20 Mn: 0.10 to 0.50%,
P: $10 \times (B - 11/14 \times N)$ to 0.030%,
S: 0.030% or less,
Al: 0.010% or less,
N: 0.0005 to 0.0033%,
25 B: $0.60 \times N$ to $0.90 \times N\%$, and
O: 0.005 to 0.0450%.

(4) A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties
30 according to any one of the items (1) to (3), said steel sheet further containing one or more of Nb, V, Ti, Ni, Cr, Se, As, Ta, W, Mo and Sn at 0.030 mass percent or less in total.

35 (5) A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties according to any one of the items (1) to (4), said steel

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sheet satisfying the following expression:

(the amount of N existing as BN)/(the amount of N existing as AlN) $\geq$ 10.0.

5 (6) A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties according to any one of the items (1) to (5), said steel sheet satisfying the following expression:

10 (the amount of N existing as BN)/(N content) $\geq$ 0.50.

(7) A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties according to any one of the items (1) to (6), wherein,
15 with regard to simple or compound nitrides, that contain B or Al and are 0.02 to 0.50 μm in diameter:

the average diameter of said nitrides is 0.080 μm or larger; and
the proportion of the number of the nitrides 0.050 μm or
20 smaller in diameter to the total number of said nitrides is 10% or less.

(8) A method for producing a steel sheet for vitreous enameling excellent in workability, aging
25 properties and enameling properties, characterized by: retaining a slab containing the components according to any one of the items (1) to (4) in the temperature range from 900 to 1,100°C (Retained Temperature Range 1) for 300 min. or longer before commencing hot rolling;
30 thereafter retaining it in a temperature range not less than 50°C higher than said retained temperature (Retained Temperature Range 2) for 10 to 30 min.;
then cooling it to a temperature range not less than 50°C lower than said retained temperature (Retained
35 Temperature Range 3) at a cooling rate of 2°C/sec. or less;

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retaining it in Retained Temperature Range 3 for 10 min. or longer; and
thereafter commencing hot rolling.

(9) A method for producing a steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties according to the item (8), characterized by further controlling the time period from the time when the coiling of a hot-rolled steel sheet terminates at a temperature of 700 to 750°C in a hot-rolling process to the time when the temperature of the steel sheet reaches 550°C or lower to 20 min. or longer.

(10) A method for producing a steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties according to the item (8) or (9), characterized by:
commencing hot rolling;
after the reduction ratio reaches 50% or more, retaining the hot-rolled material in the temperature range from 900 to 1,200°C for 2 min. or longer with the temperature of the material not lowered to 900°C or lower; and thereafter commencing the hot rolling again.

(11) A method for producing a steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties characterized by:

retaining a slab containing the components according to any one of the items 1 to 4 the balance being Fe and unavoidable impurities, and the steel sheet further containing simple or compound nitrides having a diameter of 0.02 to 0.50 μm which contain B or Al, and having the average diameter of 0.080 μm or larger, and the proportion of the number of the nitrides of 0.050 μm or smaller in

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diameter to the total number of said nitrides being 10% or less in the temperature range from 900 to 1,100°C (Retained Temperature Range 1) for 300 minutes or longer before commencing hot rolling;

thereafter retaining it in a temperature range not less than 50°C higher than the retained temperature (Retained Temperature 2) for 10 to 30 minutes;

then cooling it to a temperature range not less than 50°C lower than the retained temperature (Retained Temperature 3) at a cooling rate of 2°C/sec. or less;

retaining it in the retained Temperature 3 for 10 minutes or longer;

thereafter commencing hot rolling; and

retaining the hot rolled steel sheet in the temperature range from 900 to 1,200°C for 2 minutes or longer with the temperature of the steel sheet not lowered to 900°C or lower when the reduction ratio reaches 50% or more after commencing hot-rolling, and thereafter hot-rolling is commenced again.

(12) A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties, said steel sheet containing, in mass,

C: 0.0050% or less,

Si: 0.50% or less,

Mn: 0.005 to 1.0%,

P: $10 \times (B - 11/14 \times N)$ to 0.10%,

S: 0.080% or less,

Al: 0.050% or less,

N: 0.0005 to 0.020%,

B: $0.60 \times N$ to 0.020%, and

O: 0.002 to 0.0800%,

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and the balance being Fe and unavoidable impurities, and the steel sheet further containing simple or compound nitrides having a diameter of 0.02 to 0.50 μm which contain B or Al, and having the average diameter of 0.080 μm or larger, and the proportion of the number of the nitrides of 0.050 μm or smaller in diameter to the total number of said nitrides being 10% or less, said steel sheet optionally further containing one or more of Nb, V, Ti, Ni, Cr, Se, As, Ta, W, Mo and Sn at 0.030 mass % or less in total.

(13) A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties, said steel sheet containing, in mass,

C: 0.0025% or less,
Si: 0.050% or less,
Mn: 0.10 to 0.50%,
P: $10 \times (\text{B} - 11/14 \times \text{N})$ to 0.030%,
S: 0.030% or less,
Al: 0.010% or less,
N: 0.0035 to 0.0060%,
B: $0.60 \times \text{N}$ to 0.0060%, and
O: 0.005 to 0.0450%,

and the balance being Fe and unavoidable impurities, and the steel sheet further containing simple or compound nitrides having a diameter of 0.02 to 0.50 μm which contain B or Al, and having the average diameter of 0.080 μm or larger, and the proportion of the number of the nitrides of 0.050 μm or smaller in diameter to the total number of said nitrides being 10% or less, said steel sheet optionally further containing one or more of Nb, V, Ti, Ni, Cr, Se, As, Ta, W, Mo and Sn at 0.030 mass % or less in total.

(14) A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties, said steel sheet containing, in mass,

C: 0.0025% or less,
Si: 0.050% or less,
Mn: 0.10 to 0.50%,
P: $10 \times (B - 11/14 \times N)$ to 0.030%,
S: 0.030% or less,
Al: 0.010% or less,
N: 0.0005 to 0.0033%,
B: $0.60 \times N$ to $0.90 \times N\%$, and
O: 0.005 to 0.0450%,

and the balance being Fe and unavoidable impurities, and the steel sheet further containing simple or compound nitrides having a diameter of 0.02 to 0.50 μm which contain B or Al, and having the average diameter of 0.080 μm or larger, and the proportion of the number of the nitrides of 0.050 μm or smaller in diameter to the total number of said nitrides being 10% or less, said steel sheet optionally further containing one or more of Nb, V, Ti, Ni, Cr, Se, As, Ta, W, Mo and Sn at 0.030 mass % or less in total.

Best Mode for Carrying out the Invention

The present invention is hereafter described in detail. In the first place, the chemical composition of a steel is explained in detail.

It is known that, in steel, the lower the C content is, the better the workability is. In the present invention, it is necessary to control C content to 0.0050% or less in order to secure a good aging resistance, a good workability and good enameling properties. The preferable range of C content is 0.0025% or less. Though it is not necessary to specify the lower limit of C content, the practical lower limit thereof is

0.0005%, as a further reduction of the C content increases the cost of steelmaking.

Si is not required to be added intentionally and should be as low as possible as Si deteriorates enameling properties. In the present invention, as the deterioration of enameling properties is insignificant even with a comparatively high Si content, the upper limit of Si content is set at 0.50%. A preferable Si content is 0.050% or less, similarly to the case of a usual steel sheet for vitreous enameling, and a yet more preferable Si content is 0.010% or less.

Mn is a component that influences enameling properties in combination with the amounts of oxygen and S. Mn is also an element which prevents hot shortness caused by S during hot rolling and, in a steel of the present invention, the steel containing a large amount of oxygen, Mn content is required to be 0.005% or more. On the other hand, when the content of Mn is high, enamel adhesiveness is adversely affected and bubbles and black spots are likely to occur and, therefore, the upper limit is determined to be 1.0%, preferably 0.1 to 0.5%.

P, when its content is low, coarsens the grain sizes of crystals and deteriorates aging properties, but the lower limit of the content is determined in relation to the contents of B and N. On the other hand, when P content exceeds 0.10%, P not only hardens a material and deteriorates press workability but also accelerates the rate of pickling during a post-treatment for enameling and increases smuts that cause bubbles and black spots. Therefore, in the present invention, it is specified that the P content is in the range from $10 \times (B - 11/14 \times N)$ to 0.10%, preferably from $10 \times (B - 11/14 \times N)$ to 0.030%.

S increases the amount of smuts in pickling during a post-treatment for enameling and makes bubbles and black spots tend to occur. Therefore, the content of S is set at 0.080% or less, preferably 0.030% or less.

Al, when too much is contained, makes it impossible

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to control the amount of O in steel within a regulated range. Further, in the control of nitrides too, Al nitrides generate gases by the reaction with water during the baking of vitreous enamel and tend to cause bubble defects, and therefore, Al is not desirable. For those reasons, the content of Al is restricted to 0.050% or less, preferably 0.010% or less.

N is an important element for controlling the state of BN in the present invention. It is preferable that the content of N is as low as possible from the viewpoint of aging properties and resistance to bubbles and black spots. However, when the content is less than 0.0005%, good properties can be obtained even without the B addition that is a requirement in the present invention. Therefore, N content in the present invention is set at 0.0005% or more. The upper limit of N is determined to be 0.020% in relation to B content that is determined based on the relationship with oxygen amount in steel. A preferable upper limit is 0.0050%. Note that, in order to control nitrides to a desirable shape, it is preferable that N content is 0.0035 to 0.0060%, more preferably 0.0005 to 0.0033%.

B is also an important element for controlling the state of BN in the present invention. Though it is preferable to contain B as much as possible in order to control BN in a good state, when it is intended to add B abundantly, the yield in a steelmaking process tends to deteriorate in the case of a steel according to the present invention that contains O abundantly. Therefore, the upper limit of B content is set at 0.020%, preferably 0.0060% or 0.90 times the N content. The lower limit thereof is set at 0.60 times the N content.

O has a direct influence on fish scale resistance. It also affects enamel adhesiveness and resistance to bubbles and black spots in combination with the content of Mn. O content of 0.002% or more is necessary to exhibit such effects. On the other hand, a high O

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content makes the yield of B addition during steelmaking low, makes a good state of B nitrides difficult to maintain, and deteriorates workability, aging properties and resistance to bubbles and black spots. For these
5 reasons, the upper limit of O content is determined to be 0.0800%. Therefore, the content of O is set at 0.002 to 0.0800%, preferably 0.005 to 0.0450%.

An important condition of the present invention is the control of the kind and amount of B nitrides and a
10 steel according to the present invention should satisfy one of the following expressions:

(the amount of N existing as BN)/(the amount of N existing as AlN) $\geq$ 10.0, and

(the amount of N existing as BN)/(N content) $\geq$
15 0.50, preferably,
(the amount of N existing as BN)/(the amount of N existing as AlN) $\geq$ 20.0, and

(the amount of N existing as BN)/(N content) $\geq$
0.70. The reason is not clear yet, but it is estimated
20 that, fixing N as nitrides, particularly as stable B nitrides that are thought to be hardly decomposable during annealing or during the baking of vitreous enamel, is effective in securing aging resistance and resistance to bubbles and black spots. Here, (the amount of N
25 existing as BN) and (the amount of N existing as AlN) are the values obtained by analyzing B and Al amounts in a residue when a steel sheet is dissolved in an iodine alcohol solution and then calculating N amounts regarding the whole B and Al amounts as constituents of BN and AlN,
30 respectively.

The distribution of the sizes of nitrides is also an important factor for improving aging resistance and resistance to bubbles and black spots. With regard to simple or compound nitrides, that contain B or Al, 0.02
35 to 0.50 μm in diameter, the present invention restricts

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the average diameter of the nitrides to 0.080 μm or larger and the proportion of the number of the nitrides 0.050 μm or smaller in diameter to the total number of said nitrides to 10% or less. The reason is not clear yet, but it is thought that B nitrides, though they are stable in the state of a high temperature such as in the process of annealing or vitreous enamel baking, are likely to decompose when they are fine and therefore deteriorate aging resistance and resistance to bubbles and black spots. Here, the number and diameter of the precipitates are the values obtained by observing an extraction replica obtained from a steel sheet by the SPEED method using an electron microscope and measuring the number and diameter of the precipitates in a visual field not having deviation. The distribution of the sizes of the precipitates can be obtained by photographing several visual fields and applying image analysis to the photographs. The reason why the diameter of the objective BN is determined to be 0.02 μm or larger is that the quantitative and qualitative analyses of fine precipitates are not said to be perfect even with the latest measurement technology and thus large errors may occur. Further, the reason why the diameter of the objective nitrides is determined to be 0.50 μm or smaller is that, when B, Al or N is contained in large oxides that are contained abundantly in a steel according to the present invention, it may also be measured undesirably and may create errors in the measurement results of the objective nitrides. For those reasons, in the present invention, the range of nitrides is specified in relation to the precipitates having the sizes that allow yet smaller measurement errors to be expected. A precipitate whose shape is elongated is sometimes observed particularly among the precipitates that are compounded with MnS. In such a case, where the shape is not isotropic, the average of the length and breadth is used

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as the diameter of the precipitate.

It is well known that Cu has the functions of suppressing the rate of pickling during a post-treatment for enameling and of improving adhesiveness. To add Cu
5 by about 0.02% in order to effectuate the functions of Cu in a one-coat enameling treatment does not hinder the effects of the present invention. However, the amounts of solute C and N are very small in case of the present invention, and therefore, when the function of
10 suppressing pickling is excessively strong, the adhesiveness in the duration of low pickling deteriorates. For that reason, the upper limit of Cu content should be restricted to about 0.04% even when Cu is added.

15 Ti, Nb, V, Ni, Cr, Se, As, Ta, W, Mo and Sn do not hinder the effects of the present invention as long as one or more of them are contained at 0.030% or less in total. In other words, as long as the total content of them is within aforementioned range, it is possible to
20 add them actively, in addition to such an amount thereof as to be unavoidably included from iron ore, scraps and others, with the expectation that the advantages in a production method or in quality, other than the advantages envisaged in the present invention, may be
25 obtained.

Next, the production method is explained hereunder. The effects of the present invention can be obtained under any of the casting methods.

A temperature history during hot rolling largely
30 affects the control of B precipitates as described above. In order to control the value of (the amount of N existing as BN)/(the amount of N existing as AlN) to 10.0 or more, it is desirable, for example: to retain a slab in the temperature range from 900 to 1,100°C (Retained
35 Temperature Range 1) for 300 min. or longer before commencing hot rolling; thereafter to retain it in a temperature range not less than 50°C higher than the

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retained temperature (Retained Temperature Range 2) for 10 to 30 min.; then to cool it to a temperature range not less than 50°C lower than the retained temperature (Retained Temperature Range 3) at a cooling rate of 2°C/sec. or less; to retain it in Retained Temperature Range 3 for 10 min. or longer; and thereafter to commence hot rolling.

On the other hand, it is also possible to control the state of B precipitates by a temperature history after hot rolling.

In order to control the value of (the amount of N existing as BN)/(N content) to 0.50 or more, it is desirable, for example, to control the time period from the time when the coiling of a hot-rolled steel sheet terminates at a temperature of 700 to 750°C to the time when the temperature of said steel sheet lowers and reaches 550°C or lower to 20 min. or longer.

Further, it is possible to optimize the distribution of the sizes of precipitates by controlling a temperature history and a reduction ratio during hot rolling.

In order to satisfy the condition that, with regard to simple or compound nitrides, that contain B or Al, 0.02 to 0.50 μm in diameter: the average diameter of said nitrides is 0.080 μm or larger; and the proportion of the number of the nitrides 0.050 μm or smaller in diameter to the total number of said nitrides is 10% or less, it is desirable, for example: to commence hot rolling; after the reduction ratio reaches 50% or more, to retain the hot-rolled material in the temperature range from 900 to 1,200°C for 2 min. or longer with the temperature of said material not lowered to 900°C or lower; and thereafter to commence the hot rolling again.

That is, the object of specifying hot-rolling conditions as explained above is to control the shape of precipitates in a desirable state.

The higher the temperature before the commencement

of hot rolling is, the more the precipitates dissolve. Then, as the temperature lowers with the progress of the succeeding hot rolling, the possibility that dissolved elements may precipitate at undesirable element ratios or in undesirable shapes increases.

If the temperature lowers excessively, not only cannot the composition ratio of precipitates be controlled in a preferable state but also the dispersion of precipitate-forming elements during the retention of the temperature is decelerated, and that makes the growth of the precipitates not as expected.

Considering the growth of precipitates during the retention of the temperature in particular, it is necessary to take the influence of not only the temperature but also the time into consideration. The control of a cooling rate is important in order to suppress the fining of the precipitates that are formed as the elements having dissolved during the retention of the temperature precipitate with the drop of the temperature.

It is desirable to strictly control a heat pattern including a heating temperature, a heating time and a cooling rate in order to ideally control precipitates.

Further, with respect to precipitation behavior, a precipitation promotion phenomenon (strain induced precipitation) caused by introducing a strain during the precipitation is well known, and when the strain induced precipitation is applied to a steel according to the present invention, the composition ratio of the precipitates becomes in a preferable state. The reason is not clear yet, but it is estimated that: a strain caused by the consistency with a parent phase varies with the kind of precipitates; therefore the interaction with the work induced strain also varies with the precipitates; and thus, in a steel according to the present invention, the precipitates preferable to workability and aging properties grow preferentially.

The aforementioned temperature control is applied in the state wherein a parent phase of a steel sheet is predominantly composed of an austenite phase, and the temperature history after a parent phase has transformed
5 into ferrite due to a temperature drop at the latter half stage of a hot-rolling process is also important.

It is thought that the reason is that, in the present invention, though the solubility of the main objective precipitates may decrease with the parent phase
10 transforming from austenite to ferrite and the precipitation may proceed rapidly, stable precipitates vary with the parent phase.

That is, as the precipitates that have been stable up to that time are decomposed and new precipitates that
15 are newly stabilized are formed by the transformation of a parent phase, the composition of the precipitates varies consecutively.

From this viewpoint, the temperature history in a coiling process wherein a steel sheet is retained at a
20 relatively high temperature in a ferrite phase is important.

It is desirable that the cold reduction ratio is 60% or more in order to obtain a steel sheet having a good drawability. When a yet higher drawability is required
25 in particular, it is preferable that the cold reduction ratio is 75% or more.

With respect to annealing, the effects of the present invention do not change with either box annealing or continuous annealing and they are exhibited as long as
30 the temperature is not lower than the recrystallization temperature. From the viewpoint of the cost reduction that is a feature of the present invention in particular, continuous annealing is preferable. A steel according to the present invention is not necessarily annealed at a
35 high temperature since it is characterized by completing recrystallization at 630°C even with short-time annealing.

Skin-pass rolling is carried out for the purpose of correcting the shape of a steel sheet or suppressing generating yield-point elongation during working. Skin-pass rolling is applied usually at the reduction ratio of about 0.6 to 2% in order to suppress yield point elongation while the deterioration of workability (elongation) due to rolling working is avoided. However, in the present invention, the generation of yield point elongation is suppressed even without the application of skin-pass rolling, and the deterioration of workability is low even with a relatively high reduction ratio in skin-pass rolling. When skin-pass rolling is applied, it is desirable to set the range of the reduction ratio at 5% or lower.

Further, in order to secure enamel adhesiveness, it is preferable, for example, to apply Ni plating of about 0.01 to 2 g/m² after cold rolling or after annealing.

Example

The continuously cast slabs consisting of the various chemical compositions shown in Table 1 were subjected to hot rolling, cold rolling, annealing and skin-pass rolling under the conditions shown in Table 2. The state of nitrides, mechanical properties and enameling properties of the steel sheets are shown in Table 3.

The mechanical properties were evaluated by the tensile tests specified in JIS No. 5 Test. An aging index (AI) was obtained by imposing a prestrain of 10% with a tension and measuring the difference of the stresses between before and after the aging at 100°C for 60 min.

The enameling properties were evaluated after the process steps shown in Table 4. Among the enameling properties, the surface properties of bubbles and black spots were evaluated by the visual observation under the condition of a long pickling time of 20 min. The

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enameling adhesiveness was evaluated under the condition of a short pickling time of 3 min. Because the commonly employed P.E.I. adhesiveness test method (ASTM C313-59) was incapable of detecting small difference in the enamel
5 adhesiveness, the enamel adhesiveness was evaluated by dropping a 2.0-kg weight with a spherical head on a test piece from a height of 1 m, measuring the exfoliation state of the enameling film at the deformed area using 169 probing needles, and calculating the percentage of
10 the non-exfoliated area. The fish scale resistance was evaluated by carrying out the accelerated fish scale test, wherein three steel sheets were pre-treated through 3-min. pickling without Ni immersion, glazed with a glaze for direct one-coat enameling, dried, baked for 3 min. in
15 a baking furnace kept at 850°C and having a dew point of 50°C, and then held for 10 h. in a constant temperature tank kept at 160°C., and by visually judging the occurrence or otherwise of fish scales.

As is clear from the results shown in Table 3, the
20 steel sheets according to the present invention are the steel sheets for vitreous enameling excellent in workability (elongation), aging resistance and enameling properties.

25 [Tables 1 to 4]

Table 1

No.	Chemical components (mass%)								
	C	Si	Mn	P	S	Al	N	B	O
1	0.0020	0.011	0.32	0.009	0.018	0.002	0.0034	0.0023	0.041
2	0.0012	0.45	0.15	0.088	0.012	0.003	0.0029	0.0020	0.035
3	0.0008	0.005	0.30	0.002	0.011	0.001	0.0032	0.0025	0.062
4	0.0015	0.008	0.26	0.041	0.015	0.002	0.0045	0.0070	0.026
5	0.0016	0.005	0.28	0.015	0.026	0.005	0.0115	0.0075	0.033
6	0.0022	0.003	0.44	0.007	0.052	0.002	0.0035	0.0033	0.044
7	0.0027	0.39	0.80	0.023	0.015	0.003	0.0020	0.0024	0.008
8	0.0018	0.006	0.30	0.083	0.015	0.006	0.0022	0.0034	0.010
9	0.0016	0.004	0.33	0.012	0.015	0.008	0.0041	0.0028	0.007
10	0.0011	0.022	0.06	0.006	0.011	0.002	0.0052	0.0039	0.039
11	0.0006	0.005	0.26	0.019	0.023	0.001	0.0049	0.0055	0.024
12	0.0020	0.004	0.27	0.004	0.024	0.005	0.0057	0.0041	0.011
13	0.0014	0.002	0.38	0.026	0.016	0.003	0.0050	0.0040	0.034
14	0.0012	0.005	0.04	0.028	0.014	0.004	0.0042	0.0057	0.036
15	0.0035	0.008	0.22	0.010	0.011	0.003	0.0049	0.0033	0.029
16	0.0013	0.009	0.17	0.009	0.008	0.003	0.0054	0.0034	0.035
17	0.0012	0.004	0.12	0.009	0.002	0.002	0.0016	0.0013	0.022
18	0.0011	0.031	0.27	0.008	0.015	0.007	0.0032	0.0027	0.015
19	0.0016	0.005	0.30	0.004	0.012	0.002	0.0018	0.0013	0.026
20	0.0011	0.005	0.35	0.022	0.011	0.003	0.0020	0.0017	0.035
21	0.0022	0.003	0.30	0.010	0.019	0.008	0.0028	0.0022	0.008
22	0.0014	0.004	0.24	0.010	0.022	0.004	0.0022	0.0018	0.031
23	0.0018	0.005	0.18	0.009	0.015	0.002	0.0023	0.0016	0.042
24	0.0010	0.003	0.21	0.013	0.014	0.004	0.0020	0.0013	0.030
25	0.0060	0.003	0.32	0.015	0.012	0.003	0.0034	0.0015	0.031
26	0.0022	0.003	0.35	0.015	0.008	0.012	0.0016	0.0032	0.001

Table 2

No.	Hot-rolling heating conditions										Hot-rolling coiling conditions			Hot-rolling conditions		
	Retained Temperature Range 1		Retained Temperature Range 2		Cooling rate from Retained Temperature Range 1 to Retained Temperature Range 2 (°C/sec.)	Retained Temperature Range 3		Retention time (min.)	Coiling temperature (°C)	Retention time (min.)	Reduction ratio before temperature retention (%)	Retained temperature (°C)	Retention time (min.)			
	Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)		Temperature (°C)	Time (min.)									
					Temperature (°C)			Time (min.)	Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)		
1	1100	250	-	-	-	-	-	-	650	10	-	-	-			
2	1080	360	1150	15	1.5	1030	30	1030	650	10	-	-	-			
3	1080	360	1150	15	1.5	1030	30	1030	650	10	-	-	-			
4	1080	360	1150	15	1.5	1030	30	1030	650	10	-	-	-			
5	1080	360	1150	15	1.5	1030	30	1030	730	100	-	-	-			
6	1080	360	1150	15	1.5	1030	30	1030	730	100	-	-	-			
7	1080	360	1150	15	1.5	1030	30	1030	730	100	-	-	-			
8	1080	360	1150	15	1.5	1030	30	1030	730	100	75	950	10			
9	1100	250	-	-	-	-	-	-	650	10	-	-	-			
10	1080	360	1150	15	1.5	1030	30	1030	650	10	-	-	-			
11	1080	360	1150	15	1.5	1030	30	1030	650	10	-	-	-			
12	1080	360	1150	15	1.5	1030	30	1030	650	10	-	-	-			
13	1080	360	1150	15	1.5	1030	30	1030	730	100	-	-	-			
14	1080	360	1150	15	1.5	1030	30	1030	730	100	-	-	-			
15	1080	360	1150	15	1.5	1030	30	1030	730	100	-	-	-			
16	1080	360	1150	15	1.5	1030	30	1030	730	100	75	950	10			
17	1100	250	-	-	-	-	-	-	650	10	-	-	-			
18	1080	360	1150	15	1.5	1030	30	1030	650	10	-	-	-			
19	1080	360	1150	15	1.5	1030	30	1030	650	10	-	-	-			
20	1080	360	1150	15	1.5	1030	30	1030	650	10	-	-	-			
21	1080	360	1150	15	1.5	1030	30	1030	730	100	-	-	-			
22	1080	360	1150	15	1.5	1030	30	1030	730	100	-	-	-			
23	1080	360	1150	15	1.5	1030	30	1030	730	100	-	-	-			
24	1080	360	1150	15	1.5	1030	30	1030	730	100	75	950	10			
25	1100	250	-	-	-	-	-	-	650	10	-	-	-			
26	1100	250	-	-	-	-	-	-	650	10	-	-	-			

The symbol "-" shows that the condition was not applied.

Table 3

No.	Mechanical properties				Aging properties			Enameling properties		Remarks			
	NasBN / NasAlN	NasBN / N	Average grain diameter (μm) in claim 7	Proportion of fine precipitates in claim 7	YP (MPa)	TS (MPa)	EI (%)	AI (MPa)	Fish scale resistance		Adhesive-ness (%)	Surface properties	
1	5.2	0.43	0.02	90	186	316	54	30	△	95	△	Invented examples	
2	3.3	0.20	0.09	10	375	523	33	50	○	92	△		
3	6.9	0.80	0.05	60	177	308	56	5	○	92	△		
4	12	0.48	0.05	70	251	385	48	30	○	93	△		
5	14	0.52	0.07	20	217	348	51	5	○	90	○		
6	8.8	0.90	0.10	7	200	330	50	1	○	94	○		
7	16	0.33	0.12	8	295	435	25	20	○	90	○		
8	26	0.82	0.14	8	339	477	39	2	○	100	◎		
9	6.3	0.45	0.05	20	204	335	52	2	○	96	○		
10	6.8	0.45	0.24	5	160	291	60	2	○	98	○		
11	6.8	1.00	0.19	40	209	341	52	0	◎	96	○		
12	21	0.37	0.24	15	171	301	55	10	◎	96	○		
13	>50	0.90	0.12	80	220	353	49	1	◎	98	◎		
14	6.7	0.95	0.35	4	235	368	46	1	○	100	○		
15	24	0.77	0.28	2	190	320	54	3	◎	98	◎		
16	>50	1.00	0.55	2	179	309	56	0	◎	100	◎		
17	4.1	0.22	0.08	30	171	302	59	10	○	95	△		
18	8.2	0.48	0.19	10	197	328	53	8	○	98	○		
19	6.7	0.74	0.06	50	166	296	56	6	○	98	○		
20	>50	0.48	0.14	20	204	336	52	7	○	95	○		
21	25	1.00	0.06	20	205	336	45	0	○	100	○		
22	9.1	1.00	0.13	5	179	310	56	2	○	100	○		
23	14	0.41	0.31	5	181	312	57	5	◎	98	◎		
24	>50	0.83	0.14	4	182	314	56	0	◎	100	◎		
25	5.3	0.20	0.04	80	222	322	53	70	×	85	×		Comparative examples
26	8.1	0.43	0.07	30	212	312	50	40	×	80	×		

◎ : Very good, ○ : Good, △ : Conventional level, × : Poor

Table 4

Process steps		Conditions
1	Degreasing	Alkaline degreasing
2	Hot water rinse	
3	Water rinse	
4	Pickling	15% H_2SO_4 , 75°C x 3 or 20 min. immersion
5	Water rinse	
6	Ni treatment	2% $NiSO_4$, 70°C x 3 min. immersion
7	Water rinse	
8	Neutralization	2% Na_2CO_3 , 75°C x 5 min. immersion
9	Drying	
10	Glazing	Direct one-coat glaze, 100 μm in thickness
11	Drying	160°C x 10 min.
12	Baking	840°C x 3 min.

The steel sheets according to the present invention have good workability and further satisfy all of the fish scale resistance, enamel adhesiveness and surface properties that are required of a steel sheet for vitreous enameling. In particular, the present invention makes a considerable cost reduction possible and has a great industrial significance, because it makes it viable to produce a steel sheet excellent in workability and aging resistance with decarbonization annealing or decarbonization and denitrification annealing that can be applied to a conventional high-oxygen steel without containing expensive elements such as Ti or Nb.

CLAIMS

1. A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties, said steel sheet containing, in mass,

C: 0.0050% or less,
Si: 0.50% or less,
Mn: 0.005 to 1.0%,
P: $10 \times (B - 11/14 \times N)$ to 0.10%,
S: 0.080% or less,
Al: 0.050% or less,
N: 0.0005 to 0.020%,
B: $0.60 \times N$ to 0.020%, and
O: 0.002 to 0.0800%,

and the balance being Fe and unavoidable impurities, and the steel sheet further containing simple or compound nitrides having a diameter of 0.02 to 0.50 μm which contain B or Al, and having the average diameter of 0.080 μm or larger, and the proportion of the number of the nitrides of 0.050 μm or smaller in diameter to the total number of said nitrides being 10% or less, said steel sheet optionally further containing one or more of Nb, V, Ti, Ni, Cr, Se, As, Ta, W, Mo and Sn at 0.030 mass % or less in total.

2. A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties, said steel sheet containing, in mass,

C: 0.0025% or less,
Si: 0.050% or less,
Mn: 0.10 to 0.50%,
P: $10 \times (B - 11/14 \times N)$ to 0.030%,

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S: 0.030% or less,
Al: 0.010% or less,
N: 0.0035 to 0.0060%,
B: 0.60xN to 0.0060%, and
O: 0.005 to 0.0450%,

and the balance being Fe and unavoidable impurities, and the steel sheet further containing simple or compound nitrides having a diameter of 0.02 to 0.50 μm which contain B or Al, and having the average diameter of 0.080 μm or larger, and the proportion of the number of the nitrides of 0.050 μm or smaller in diameter to the total number of said nitrides being 10% or less, said steel sheet optionally further containing one or more of Nb, V, Ti, Ni, Cr, Se, As, Ta, W, Mo and Sn at 0.030 mass % or less in total.

3. A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties, said steel sheet containing, in mass,

C: 0.0025% or less,
Si: 0.050% or less,
Mn: 0.10 to 0.50%,
P: $10 \times (B - 11/14 \times N)$ to 0.030%,
S: 0.030% or less,
Al: 0.010% or less,
N: 0.0005 to 0.0033%,
B: 0.60xN to 0.90xN%, and
O: 0.005 to 0.0450%,

and the balance being Fe and unavoidable impurities, and the steel sheet further containing simple or compound nitrides having a diameter of 0.02 to 0.50 μm which contain B or Al, and having the average diameter of

0.080 μm or larger, and the proportion of the number of the nitrides of 0.050 μm or smaller in diameter to the total number of said nitrides being 10% or less, said steel sheet optionally further containing one or more of Nb, V, Ti, Ni, Cr, Se, As, Ta, W, Mo and Sn at 0.030 mass % or less in total.

4. A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties according to any one of claims 1 to 3, wherein the steel sheet further containing one or more of Nb, V, Ti, Ni, Cr, Se, As, Ta, W, Mo or Sn at 0.030 mass % or less in total.

5. A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties according to any one of claims 1 to 4, said steel sheet satisfying the following expression:

$$\frac{(\text{the amount of N existing as BN})}{(\text{the amount of N existing as AlN})} \geq 10.0.$$

6. A steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties according to any one of claims 1 to 5, said steel sheet satisfying the following expression:

$$\frac{(\text{the amount of N existing as BN})}{(\text{N content})} \geq 0.050.$$

7. A method for producing a steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties characterized by:

retaining a slab containing the components

according to any one of claims 1 to 4 in the temperature range from 900 to 1,100°C (Retained Temperature Range 1) for 300 minutes or longer before commencing hot rolling;

thereafter retaining it in a temperature range not less than 50°C higher than said retained temperature (Retained Temperature 2) for 10 to 30 minutes;

then cooling it to a temperature range not less than 50°C lower than said retained temperature (Retained Temperature 3) at a cooling rate of 2°C/sec. or less;

retaining it in said retained Temperature 3 for 10 minutes or longer;

thereafter commencing hot rolling; and

retaining the hot rolled steel sheet in the temperature range from 900 to 1,200°C for 2 minutes or longer with the temperature of said steel sheet not lowered to 900°C or lower when the reduction ratio reaches 50% or more after commencing hot-rolling, and thereafter hot-rolling is commenced again.

8. A method for producing a steel sheet for vitreous enameling excellent in workability, aging properties and enameling properties according to claim 7, wherein hot-rolling is controlled under the condition of the time period from the time when the coiling of a hot-rolled steel sheet terminates at a temperature of 700 to 750°C in a hot-rolling process to the time when the temperature of said steel sheet reaches 550°C or lower for 20 minutes or longer.