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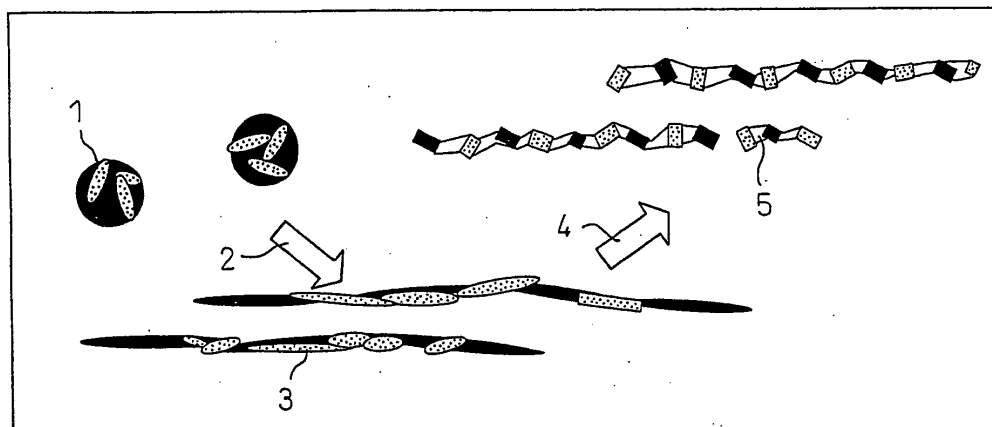
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(54) **STEEL SHEET FOR CONTINUOUS CAST ENAMELING WITH HIGHLY EXCELLENT UNSUSCEPTIBILITY TO FISHSCALING AND PROCESS FOR PRODUCING THE SAME**

(57) The present invention provides a continuously cast enameled steel sheet with remarkably excellent fish-scale resistance improving the ability to form spaces in the steel sheet so as to increase the hydrogen trap ability, and a method of production of the same, comprising a steel having as ingredients, by mass%, C: 0.010% or less, Mn: 0.03 to 1.30%, Si: 0.100% or less, Al: 0.030% or less, N: 0.0055% or less, P: 0.035% or less, S: 0.08%

or less, O: 0.005 to 0.085%, and B: 0.0003 to 0.0250% and including in the steel sheet not integral or integral oxides differing in mass concentration of B or Mn. The ratio of the maximum concentration and minimum concentration is made 1.2 or more. When not integral, they are present with a straight line distance between centers of the oxides differing in concentration of 0.10 μm to 20 μm and with an angle of the line connecting the centers of the two oxides of within $\pm 10^\circ$ from the rolling direction.

Fig.1



Description

TECHNICAL FIELD

[0001] The present invention relates to enameled steel sheet excellent in enameling characteristics (bubble and black spot defect resistance, adhesion, and fishscale resistance) and formability characteristics and a method of production of the same and particularly is characterized by being obtained by continuous casting.

BACKGROUND ART

[0002] Current day enameled steel sheet is usually produced by the continuous casting method so as to reduce the production costs. Further, both formability and enamelability are achieved by preparing the ingredients including the various additive elements. As one example, the fact that for example B (Boron) enables the production of enameled steel sheet with excellent formability is disclosed in Japanese Patent No. 3260446 and Japanese Patent No. 3358410. This art calls for adding B as an element able to fix the solute N in the steel as nitrides and impart good formability. Further, Japanese Patent No. 3260446 discloses that since the deoxidation ability of B is small, the amount of oxygen in the steel can be kept high. Japanese Patent No. 3613810 discloses that, while the details are not clear, B is effective in preventing fishscale and bubbles and that pickling by sulfuric acid before enameling is effective in preventing abnormal etching of the grain boundaries at the surface of the steel sheet.

[0003] Further, the inventors experimented with improvements to an enameled steel sheet containing B and excellent in fishscale resistance and deep drawability and filed applications for them as disclosed in Japanese Patent Publication (A) No. 2002-80934 and Japanese Patent Publication (A) No. 2004-18860. The main technical point of these is to consider not only the main nitride-controlling element B of conventional enameled steel sheet, but also the A1 and hot rolling conditions so as to control the form of the nitrides and build in optimum characteristics - features never before existing. The steel sheet resulting from these technologies not only feature excellent fishscale resistance, but also use the relatively inexpensive element B and hold down the rise in production costs and in particular feature excellent formability due to the high elongation, so are growing in use in the high grade material market. However, with the recent polarization in use of steel sheet, that is, the use of low cost materials as much as possible for general use products and, on the other hand, a higher level of characteristics than in the past for high grade products, these material have been required to offer further formability and enamelability. In particular, demands for further improvement of the fishscale resistance, which can be said to be the greatest feature of enameled steel sheet, have been becoming much stronger. To suppress fishscale of enameled steel sheet, it is known to be effective to form voids in the steel sheet and trap hydrogen invading the steel sheet during firing of the enamel, but forming the voids does not just improve the hydrogen trapping ability. For example, as shown in Japanese Patent No. 3358410 and Japanese Patent Publication (A) No. 2002-80934, there is also the clear effect of preferably controlling the form of the nitrides. However, in these conventional steels, it cannot be said that optimal control was performed from the viewpoints of the amount of spaces, form, and properties including also the form of the oxides.

DISCLOSURE OF THE INVENTION

[0004] The present invention has as its object to further advance the above-mentioned technology of enameled steel sheet and control not only the nitrides, but also the form of the oxides and thereby provide a continuously cast enameled steel sheet with excellent fishscale resistance able to further improve the fishscale resistance and enabling enameling by a single coating process with a small aging characteristic and a method of production of the same.

[0005] The present invention was obtained after various studies to optimize to the ultimate extent the conventional steel sheet and method of production of steel sheet. The inventors studied the enameling characteristics of enameled steel sheet, in particular the production conditions, especially the steelmaking conditions, for B-containing steel, and as a result newly discovered the items of 1) to 5), as described below.

[0006] That is, for enamelability, they used powder coating (dry) to coat an underglaze and overglaze to thicknesses of 100 μm for double enameling and investigated the fishscale resistance, bubble and black spot defect type surface flaws, and adhesion. As a result, they discovered the following:

- 1) The fishscale resistance tends to become better the greater the segregation of elements in the oxides.
- 2) Even if the amount of addition of B is equal, when the segregation of B in the oxides is large, the formability, in particular the r value, tends to be improved.
- 3) At this time, the yield of addition of the expensive additive element B is also improved.
- 4) For the change in concentration of elements in the oxides, the oxides extended, fractured, and separated due to rolling must also be considered.

5) The magnitude of change of the concentration of elements in the oxides can be controlled by the addition of elements at the time of steelmaking, in particular the timing of addition of the oxide-forming elements.

[0007] The present invention was completed based on the above discovery. The present invention is characterized in that the final product after a process of hot or cold rolling or both has oxides differing in composition or integral oxides having a large change in composition inside and these are present in specific preferable forms. The gist of the present invention is as follows:

(1) A continuously cast enameled steel sheet excellent in fishscale resistance characterized by comprising, by mass%,
C: 0.010% or less,
Mn: 0.03 to 1.30%,
Si: 0.100% or less,
Al: 0.030% or less,
N: 0.0055% or less,
P: 0.035% or less,
S: 0.08% or less,
O: 0.005 to 0.085%,
B: 0.0003 to 0.0250%, and
a balance of Fe and unavoidable impurities and by having, in complex oxides of 0.10 μm or more diameter comprising Fe, Mn, Si, Al, B, or other oxides combined together in a unit observation field of 100 $\mu\text{m} \times 100 \mu\text{m}$ in the sheet cross-section, any two complex oxides with different B mass concentrations and not contacting each other and with a ratio of a maximum concentration of a B mass concentration ($B_{\text{max}}\%$) and a minimum concentration of a B mass concentration ($B_{\text{min}}\%$) of $B_{\text{max}}/B_{\text{min}} \geq 1.2$.

(2) A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in (1), characterized by having, in complex oxides of 0.10 μm or more diameter comprising Fe, Mn, Si, Al, B, or other oxides combined together in a unit observation field of 100 $\mu\text{m} \times 100 \mu\text{m}$ in the sheet cross-section, any two complex oxides with different Mn mass concentrations and not contacting each other and with a ratio of a maximum concentration of an Mn mass concentration ($Mn_{\text{max}}\%$) and a minimum concentration of an Mn mass concentration ($Mn_{\text{min}}\%$) of $Mn_{\text{max}}/Mn_{\text{min}} \geq 1.2$.

(3) A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in (1) or (2), characterized by further containing, by mass%, one or both of
Nb: less than 0.004% (including zero)
V: 0.003 to 0.15%.

(4) A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of (1) to (3), characterized by further containing, by mass%, Cu: 0.01 to 0.500%.

(5) A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of (1) to (4), characterized by further containing, by mass%, one or more of Cr, Ni, As, Ti, Se, Ta, W, Mo, Sn, Sb, La, Ce, Ca, and Mg in a total of 1.0% or less.

(6) A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of (1) to (5), characterized by having, in complex oxides of 0.10 μm or more diameter comprising Fe, Mn, Si, Al, B, or other oxides combined together in the steel sheet, a distribution of the B mass concentration and a ratio of the B mass concentration of the high concentration part ($B_{\text{max}}\%$) and the B mass concentration of the low concentration part ($B_{\text{min}}\%$) of $B_{\text{max}}/B_{\text{min}} \geq 1.2$.

(7) A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of (1) to (6), characterized by having, in complex oxides of 0.10 μm or more diameter comprising Fe, Mn, Si, Al, B, or other oxides combined together in the steel sheet, a distribution of the Mn mass concentration and a ratio of the Mn mass concentration of the high concentration part ($Mn_{\text{max}}\%$) and the B mass concentration of the low concentration part ($Mn_{\text{min}}\%$) of $Mn_{\text{max}}/Mn_{\text{min}} \geq 1.2$.

(8) A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of (1) to (7), characterized by having separate complex oxides with a B mass concentration 1.2 times or more or 1/1.2 times or less of the B mass concentration (%) of the complex oxides comprising the Fe, Mn, Si, Al, Nb, B, V, Cr, or other oxides combined together in the sheet with a straight line distance between centers of the two complex oxides of 0.10 μm to 20 μm and with an angle of the line connecting the centers of the two oxides of within $\pm 10^\circ$ from the rolling direction.

(9) A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of (1) to (8), characterized by having separate complex oxides with an Mn mass concentration 1.2 times or more or 1/1.2 times or less of the Mn mass concentration (%) of the complex oxides comprising the Fe, Mn, Si, Al, Nb, B, V, Cr, or other

oxides combined together in the sheet with a straight line distance between centers of the two complex oxides of 0.10 μm to 20 μm and with an angle of the line connecting the centers of the two oxides of within $\pm 10^\circ$ from the rolling direction.

(10) A method of production of a continuously cast enameled steel sheet excellent in fishscale resistance characterized by making and casting steel comprising, by mass%

C: 0.010% or less,

Mn: 0.03 to 1.3%,

Si: 0.100% or less,

Al: 0.030% or less,

N: 0.0055% or less,

P: 0.035% or less,

S: 0.08% or less,

O: 0.005 to 0.085%,

B: 0.0003 to 0.0250%, and

a balance of Fe and unavoidable impurities, during which adding the Mn and B into the molten steel in the order of adding Mn in a total amount of addition of 80% or more, then allowing 1 minute or more to elapse, adding B in a total amount of addition of 80% or more, and casting within 60 minutes.

(11) A method of production of a continuously cast enameled steel sheet excellent in fishscale resistance as set forth in (10), characterized by further including, by mass%, one or both of

Nb: less than 0.004% (including zero) and

V: 0.003 to 0.15%

(12) A method of production of a continuously cast enameled steel sheet excellent in fishscale resistance as set forth in (10) or (11), characterized by further including, by mass%, Cu: 0.01 to 0.500%.

(13) A method of production of a continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of (10) to (12), characterized by further including, by mass%, one or more of Cr, Ni, As, Ti, Se, Ta, W, Mo, Sn, Sb, La, Ce, Ca, and Mg in a total of 1.0% or less.

(14) A method of production of continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of (10) to (13), characterized by casting by a cooling rate at the time of solidification of $\leq 10^\circ\text{C}/\text{sec}$ at 1/4 the sheet thickness of the slab.

(15) A method of production of continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of (10) to (14), characterized by hot rolling a slab with oxides of an average diameter of 1.0 μm or more and with a thickness of 50 mm or more at 600°C or more during which rolling under conditions of 1000°C or more and a strain rate of 1/sec or more to a total of the true strain of 0.4 or more, then rolling under conditions of 1000°C or less and a strain rate of 10/sec or more to a total of the true strain of 0.7 or more.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008]

FIG. 1 is a view explaining the state of oxides when rolling steel containing coarse complex oxides with large differences in concentration of B and Mn.

FIG. 2 is a view explaining the state of oxides in the conventional steel containing coarse oxides.

FIG. 3 is a view explaining the state of oxides in the rolled steel containing fine oxides.

FIG. 4 is a view explaining that the voids around complex oxides become larger in the rolled steel containing coarse complex oxides with large differences in concentration of B and Mn.

FIG. 5 is a view explaining that the voids around complex oxides are small in the rolled steel containing coarse complex oxides with no differences in concentration.

BEST MODE FOR WORKING THE INVENTION

[0009] Below, the present invention will be described in detail.

[0010] First, the diameter of the oxides covered by the control in the present invention is made 0.10 μm or more. With oxides smaller than this range, the fishscale resistance constituting the major feature in the characteristics of the present invention steel, that is, the effect of improving the ability to inhibit the hydrogen diffusion, becomes smaller, so there is no particular need to cover this by the control. Preferably, the features of the oxides explained below are recognized even if covering oxides of 0.50 μm or more, more preferably 1.0 μm or more, more preferably 2.0 μm or more. The upper limit of the diameter does not have to be particularly limited if considering the effect of the present invention. While depending on the amount of oxygen contained; if the amount of coarse oxides increases, the number density of the

oxides decreases and the effect of inhibiting hydrogen diffusion becomes smaller. Further, overall coarse oxides, as is generally known, form the starting points of cracks of the steel sheet at the time of forming sheet products and obstruct the formability. Considering these facts, the average diameter of the oxides is kept to 15 μm or less, preferably 10 μm or less, more preferably 5 μm or less.

[0011] One of the features of oxides defined by the present invention is the B concentration of the oxides. In the present invention, it is necessary to specify ones with high concentration and ones with low ones. In a 100 $\mu\text{m} \times 100 \mu\text{m}$ field, 100 of a size of 0.1 μm or more are measured. That is, there are nonintegral oxides differing in B concentration in terms of the concentration measured for oxides in a 100 $\mu\text{m} \times 100 \mu\text{m}$ observation field in the sheet cross-section, and the ratio of the high concentration of the B concentration (B_{max}) and the low concentration of the B concentration (B_{min}) is $B_{\text{max}}/B_{\text{min}} \geq 1.2$. If this B concentration ratio becomes 1.2 or more, as explained later, the change in form of the oxides during rolling and the accompanying formation of voids become efficiently performed and as a result the fishscale resistance is remarkably improved. The ratio is preferably 1.5 or more, more preferably 2.0 or more, more preferably 4.0 or more, more preferably 6.0 or more.

[0012] Further, the sheet is characterized in that there is a similar difference in composition for the amount of Mn as well. That is, it is characterized in that the steel sheet includes nonintegral oxides differing in Mn concentration in a 100 $\mu\text{m} \times 100 \mu\text{m}$ observation field in the sheet cross-section and in that the ratio of the high concentration of the Mn concentration (Mn_{max}) and low concentration of the Mn concentration (Mn_{min}) is $Mn_{\text{max}}/Mn_{\text{min}} \geq 1.2$. If this Mn concentration ratio becomes 1.2 or more, in the same way as B, the change in form of the oxides during rolling and the accompanying formation of voids become more efficient and as a result the fishscale resistance is remarkably improved. Preferably, the concentration ratio is 1.5 or more, more preferably 2.0 or more, more preferably 4.0 or more, more preferably 6.0 or more. The method of measuring the concentrations of the elements in the oxides for defining the present invention is not particularly limited, but the concentrations of the oxides have to be specified. Further, as explained later, the change in concentration in single oxides also has to be defined, so for example use of an energy dispersive X-ray detector (EDAX) is convenient. The measurement method may be an ordinary method, but it is necessary to determine a particularly fine region, so care is required to make the beam diameter of the electron beam sufficiently small. Further, the absolute value of the Nb concentration does not have to be determined. It is sufficient that the relative value be known. When using an EDAX, it is sufficient to use the ratio of the heights of the detected peaks. Caution is required in that the smaller the size of the measurement area, the larger the ratio of concentration of the high concentration part and low concentration part tends to become. In extreme cases, if measuring the concentration of a region of a size of individual atoms, a situation where the high concentration part has a ratio of 100% and the low concentration part has a ratio of 0% may also be envisioned. In the present invention, considering the irradiation area of the electron beam of an ordinarily used general TEM or SEM, the inventors decided to use the average value in the region of 0.01 to 0.1 μm or so. Precisely speaking, there is a spread in the electron beam in the irradiated object. The obtained information is therefore from a region broader than the set diameter of the electron beam. In the present invention, it is also possible to use a value able to be set to a diameter of the same extent as a region envisioning the diameter of an electron beam and possible to scan a certain extent of fine regions by the electron beam and use the average value.

[0013] The reason why when there is a difference in concentration in the composition of the oxides in this way, the fishscale resistance, that is, the ability to inhibit hydrogen diffusion, is improved is unclear, but the following may be considered. In the steel of the present invention, the dispersed oxides, as explained later, are believed to have originally been integral oxides. That is, when casting the molten steel finished being adjusted in ingredients, they were large single oxides, but they were extended and fractured and became finely dispersed. This extension and fracture mainly occurred in the rolling process. In particular, in the hot rolling process, the oxides were mainly extended, while in the cold rolling process, they were mainly fractured. In such a process, if there is a difference in composition in the oxides, the extent of extension will differ depending on the location in the oxides and therefore the shapes of the oxides will become complicated. Further, it is believed that the finer (thinner) locations fracture first and further that locations with large changes in shape fracture first due to the concentration of deformation stress. As a result, locations differing in composition efficiently fracture and disperse. At the time of this efficient fracture, a large number of voids are formed. These become hydrogen trap sites in the steel and are believed to remarkably improve the ability to inhibit hydrogen permeation, that is, the fishscale resistance, considered necessary for an enameled steel sheet. The above will be explained in detail using the drawings. If there is a large difference in concentration of B and Mn in the oxides, as shown in FIG. 1, the coarse complex oxides 1 are fractured by the hot rolling 2, extension 3, and cold rolling 4, fracture voids 5 are efficiently formed in the steel sheet, and the fishscale resistance is improved. As opposed to this, with steel sheet just containing simple complex oxides like in the past, as shown in FIG. 2, the coarse oxides 6 are hard to extend 3 and fracture by the hot rolling 2 and cold rolling 4, so even if fracture spaces 7 are formed, preferable fracture voids cannot be obtained like in the present invention steel. As shown in FIG. 3, at the slab stage, fine complex oxides 8 are not extended 9 and are not fractured that much by the hot rolling 2 and cold rolling 4, so voids 10 are hard to form. Further, FIGS. 1 and 2 show the case where the distance between the crushed complex oxides is relatively short and voids effectively remain between the complex oxides, but the effect of the present invention can be sufficiently obtained even when the voids between

the complex oxides formed by the extension and fracture due to the hot rolling and cold rolling are crushed closed by the rolling in the same hot rolling and cold rolling process. This situation is shown schematically in FIGS. 4 and 5. Even if the complex oxides themselves are the same in size and arrangement, in steel of the invention as shown in FIG. 4 where the complex oxides include large differences in concentration of B and Mn and the ability to form voids is large, the voids 11 around the complex oxides become larger and the improvement in the fishscale resistance becomes better. In oxides with the same concentration shown in FIG. 5, the voids are small. Further, complex oxides with different compositions have specific relative positional relationships in steel sheet. That is, complex oxides exhibiting a high B concentration and complex oxides exhibiting a low B concentration are present at a concentration ratio of 1.2 or more with an angle of the straight line connecting the centers of the complex oxides from the rolling direction of within $\pm 10^\circ$ and with a straight line distance between centers of the complex oxides of 0.10 μm to 20 μm . The angle is characterized by being preferably within an angle of $\pm 7^\circ$, more preferably within an angle of $\pm 5^\circ$, and more preferably within an angle of $\pm 3^\circ$. The oxides are arranged in lines in the rolling direction.

[0014] While the reason is not clear, in the hydrogen diffusion inhibiting ability considered required for the steel sheet, it is important that hydrogen diffusion from the center of the thickness of the steel sheet toward the surface be effectively prevented. For this reason, for example, if the complex oxides end up arranged in the sheet thickness direction, a flow of hydrogen is formed through the complex oxides in the sheet thickness direction. This is inconvenient for the purpose of the present invention. For this reason, it is believed that the complex oxides characterizing the present invention are arranged parallel to the steel sheet surface and thereby enable further improvement of the characteristics. Note that if parallel to the steel sheet surface, of course the oxides are not limited to any specific angle from the rolling direction as explained above, but in ordinary methods of production, for example it is difficult to make the complex oxides align in the sheet thickness direction. The rolling is believed to cause the complex oxides to disperse. The present invention defines the arrangement by the angle from the rolling direction.

[0015] Further, the complex oxides covered are present at a distance between each other, in straight line distance, of 0.10 μm to 20 μm . If outside this range, the fishscale resistance deteriorates. The distance is preferably 0.20 μm or more, more preferably 0.30 μm or more, more preferably 0.40 μm or more, more preferably 0.50 μm or more. The reason why the lower limit of the distance influences the effect of the invention is not clear, but it is believed that complex oxides covered may have fine complex oxides or complex oxides with small differences of concentration present between them and that the ability to inhibit hydrogen diffusion is affected by these complex oxides. That is, when the complex oxides covered are too close, the overall length of a column of complex oxides having a hydrogen trap ability becomes shorter, so a large number of voids are formed stopping the flow of hydrogen toward the surface and the ability to inhibit hydrogen diffusion falls. Further, the upper limit is preferably 20 μm or less, more preferably 10 μm or less, more preferably 5 μm or less, more preferably 1 μm or less. The reason for defining the upper limit is that when the complex oxides covered are too far apart, this runs counter to the idea of the present invention of extension and fracture of originally integral coarse complex oxides. According to the ordinary method of production, the oxides are usually arranged within 0.5 μm of each other.

[0016] Further, the effect of the present invention is exhibited even without the different composition complex oxides being completely separated. That is, it is sufficient that an individual complex oxide present in a steel sheet have fluctuations in the B concentration and that the ratio of the B concentration of the high concentration part (B_{max}) and the B concentration of the low concentration part (B_{min}) be $B_{\text{max}}/B_{\text{min}} \geq 1.2$. The ratio is preferably 1.5 or more, more preferably 2.0 or more, more preferably 2.5 or more, more preferably 3.0 or more. Further, similarly, it is sufficient that an individual complex oxide present in a steel sheet have fluctuations in the Mn concentration and that the ratio of the Mn concentration of the high concentration part (Mn_{max}) and the Mn concentration of the low concentration part (Mn_{min}) be $Mn_{\text{max}}/Mn_{\text{min}} \geq 1.2$. The ratio is preferably 1.5 or more, more preferably 2.0 or more, more preferably 4.0 or more, more preferably 6.0 or more.

[0017] The reason is believed to be, as explained above, in the process of extension and fracture of the integral coarse complex oxides, even if not completely separated, they are partially bonded at least under ordinary observation. In this case as well, the complex oxides become extremely complicated in shape, and voids are effectively formed around them and act as hydrogen trap sites. The defects formed along with changes of the deformability due to mainly the changes in concentration of the complex oxides trap hydrogen and enable the effect of the present invention to be detected.

[0018] In the present invention, it is believed that the particularly desirable complex oxides are present as B-Mn-Fe complex oxides. Optimum control of the composition and form (arrangement) of these complex oxides is the feature of the present invention. That is, a difference in composition of the complex oxides means a difference in the characteristics of the complex oxides, for example, the hardness or ductility. The preferable form is controlled to by the large effect of hot rolling and cold rolling on the state of extension and fracture of the complex oxides.

[0019] When the composition or production conditions of the steel, in particular the steelmaking conditions and hot rolling heating conditions, result in the complex oxides containing Si, Al, V, Nb, and other numerous types of elements, the situation becomes more complex. Controlling the contents of the different elements in the complex oxides is extremely important in improving the characteristics of steel sheet. Further, if increasing the amount of S, MnS coprecipitates in

the complex oxides. Due to the large difference in extensibility and fracturability between sulfides and oxides, the effect of the present invention can be made more conspicuous. In particular, the interactive effect of MnS and oxides on the fishscale resistance appears more in steel containing B than conventional steel, so this is considered a feature of MnS whose precipitation is promoted using as a nuclei complex oxides containing Mn and B.

[0020] Next, the steel composition will be explained in detail.

[0021] With C, it has been known in the past that the lower the content, the better the formability. In the present invention, the content is made 0.010% or less. To obtain a high elongation and r value, it is preferably made 0.0025% or less. The more preferable range is 0.0015% or less. The lower limit does not particularly have to be limited, but if making the amount of C on the low side, the steelmaking cost is increased, so 0.0003% or more is preferable.

[0022] Si can be included in a small amount to control the composition of oxides. To obtain this effect, the content is made 0.001% or more. On the other hand, excessive content not only tends to inhibit the enameling characteristics, but also a large amount of Si oxides poor in ductility in the hot rolling are formed and the fishscale resistance is lowered in some cases, so the content is made 0.100% or less. The content is preferably 0.030% or less, more preferably 0.015% or less. From the viewpoint of improving the bubble resistance and black spot defect resistance etc. and obtain further better enamel surface properties, the preferable range is 0.008% or less.

[0023] Mn is an important ingredient affecting the changes in composition of oxides relative to the amounts of addition of oxygen and Nb. Simultaneously, it is an element preventing hot embrittlement due to S at the time of hot rolling. In the present invention where oxygen is included, the content is made 0.03% or more. It is desirably 0.05% or more. In general, if the amount of Mn becomes higher, the enamel adhesion becomes poor and bubbles and black spot defects easily occur. In the steel of the present invention which actively uses Mn to the maximum extent as an oxide, there is only little deterioration of these characteristics due to the addition of Mn. Of course, addition of Mn facilitates control of the compositions of the oxides, so Mn is positively added. That is, the upper limit of the amount of Mn is specified as 1.30%. The upper limit is desirably 0.80%, more preferably the upper limit of Mn is 0.60%.

[0024] O is an element which directly affects the fishscale resistance and the formability and simultaneously, linked with the amounts of Mn and Nb, affects the fishscale resistance, so is an essential element in the present invention. To obtain these effects, 0.005% or more is necessary. Preferably, the content is 0.010% or more, more preferably 0.015% or more, more preferably 0.020% or more. On the other hand, if the amount of oxygen becomes higher, the high content of oxygen directly causes the formability to deteriorate, the amount of addition of Nb required for the present invention also increases, and the indirect cost of addition rises, so the upper limit is preferably made 0.085%. Preferably, the content is 0.065% or less, more preferably 0.055% or less.

[0025] Al is an oxide-forming element. To improve the fishscale resistance of the enameling characteristics, it is preferable to include a suitable amount of the oxygen in the steel as oxides in the steel material. To obtain this effect, 0.0002% or more is included. On the other hand, Al is a strong deoxidizing element. If added in a large amount, it becomes difficult to keep the amount of oxygen required by the present invention in the steel. Not only this, a large amount of Al oxides poor in ductility in the hot rolling are formed and the fishscale resistance is lowered in some cases. Therefore, the Al is made 0.030% or less. The content is preferably 0.015% or less, more preferably 0.010% or less, more preferably 0.005% or less.

[0026] N, like C, is a penetration type solid solution element. If included in a large amount, even if Nb, and further V, B, or other nitride-forming elements are added, the formability tends to deteriorate and production of a nonaging steel sheet becomes difficult. For this reason, the upper limit of N is made 0.0055%. Preferably the content is made 0.0045% or less. The lower limit does not particularly have to be set, but in the current steelmaking technology, production with less than 0.0010% would be costly, so the content is made 0.0010% or more.

[0027] If the content of P increases, it has an effect on the reaction between the glass and steel at the time of firing the enamel. In particular, the P precipitating in a high concentration at the grain boundaries of the steel sheet causes deterioration of the enamel appearance due to the bubbles and black spot defects etc. in some cases. In the present invention, the P content is made 0.035% or less, preferably 0.025% or less, more preferably 0.015% or less, more preferably 0.010% or less.

[0028] S forms Mn sulfides. In particular, coprecipitation of these sulfides with oxides has the effect of making the formation of voids at the time of rolling more efficient and improving the fishscale resistance. This element need not be contained at all, that is, 0% is also possible, but to obtain the above effect, 0.002% or more is necessary. The content is preferably 0.005% or more, more preferably 0.010% or more, more preferably 0.015% or more. However, if the content is too high, the effect of the Mn required for control of the composition of the oxides important in the present invention is sometimes lowered, so the upper limit is made 0.080%. The content is preferably 0.060% or less, more preferably 0.040% or less.

[0029] B is an essential element in the present invention. B is necessary for fixing the solute N and improving the deep drawability and for nonaging and imparting formability. Further, there is also the effect of improvement of adhesion, but in the present invention, it is included for imparting a special effect completely different from this. That is, the B added bonds with the oxygen in the steel to form oxides and acts effectively to prevent fishscale. To obtain this effect, 0.0003%

or more is necessary. The content is more preferably 0.0008% or more, more preferably 0.0012% or more, more preferably 0.0015% or more, more preferably 0.0020% or more. However, if the amount of addition becomes higher, at the time of addition of B, deoxidation occurs and it becomes difficult to keep oxides in the steel. Not only this, the bubble and black spot defect resistance deteriorates. Therefore, the upper limit is made 0.0250%. The content is preferably

0.0150% or less, more preferably 0.0080% or less.

[0030] As elements having similar effects to B, there are Nb and V. Nb has the remarkable effect of improving the r value when added alone, but the deterioration in the elongation becomes great and improvement of the formability is obstructed in some respects. In the steel of the present invention which contains B, the recrystallization temperature remarkably rises. To obtain a good formability after cold rolling and annealing, annealing at an extremely high temperature becomes necessary, so the productivity of the annealing is reduced. For this reason, the content is preferably kept low. It should not be allowed to exceed 0.0040%. The content is more preferably 0.0025% or less, more preferably 0.0015% or less. If O, there is no need to consider the detrimental effect of Nb. Further, V is similar to Nb in the effect on the formability, but due to the balance with the amount of oxygen remaining in the steel, the upper limit is higher. Even when co-added to the B-containing steel covered by the present invention, the effect of raising the recrystallization temperature is smaller than Nb. Further, by co-adding it with B to form complex oxides, there is the effect of remarkably improving the fishscale resistance. To obtain the effect relating to V, 0.003% or more is necessary. The content is preferably 0.006% or more, more preferably 0.010% or more, more preferably 0.015% or more. From the viewpoint of the cost of addition and the bubble and black spot defect resistance, the upper limit is made 0.15%. When the amount of B is 0.0015% or more and B alone is enough to obtain the effect of the invention, 0.060% or less, further 0.040% or less, is sufficient.

[0031] Cu is included for controlling the reaction of the glass and steel when firing the enamel. In single enameling, the Cu precipitated on the surface at the time of pretreatment has the effect of promoting microscopic changes in the reaction and improving adhesion. In double enameling, it has little action due to the surface precipitation, but affects the microscopic reaction between the underglaze and steel. To obtain this effect, 0.01% or more is added in accordance with need. Unintentional excess addition not only inhibits the reaction between the glass and steel, but also causes the formability to deteriorate in some cases, so to avoid this detrimental effect, making the content 0.500% or less is preferable. The preferable range is 0.015 to 0.200%.

[0032] Other unavoidable impurities sometimes have a detrimental effect on the material characteristics and the enameling characteristics, so are preferably kept low. The content of the one or more of Cr, Ni, As, Ti, Se, Ta, W, Mo, Sn, Sb, La, Ce, Ca, and Mg is made 1.0% or less, preferably 0.5% or less, more preferably 0.1% or less. If included in a large amount, the reaction with the oxide-forming elements can no longer be ignored and the oxides become unpreferable in composition and form. However, even if a greater amount is added, the effect of the present invention is not lost. Merits in production or quality other than those envisioned by the present invention can be expected. It is also possible to deliberately add larger amounts.

[0033] Next, an example of the method of production of the steel sheet according to the present application will be explained. In the present invention, inclusion of B in the oxides becomes necessary. The main technical point of the steel of the present invention is to bond B, not N, with O so as to control the form of the oxides in the steel, but there are diverse methods for achieving this control. For this reason, the present application is not limited to the following method of production.

[0034] To impart the change in composition of the complex oxides characterizing the present invention, in the process of melting and casting the steel, regarding the order of addition of Mn and B to the molten steel, it is advantageous in terms of productivity to add 80% or more of the total amount of addition of Mn, wait one minute or more, add 80% or more of the total amount of addition of B, then cast the steel within 60 minutes. When adding V and Nb having effects similar to B, basically it is preferable to add the elements in the order of the weakest deoxidation ability. By adding them in the order of Mn, V, Nb, and B, the effect of the present invention can be brought out more remarkably. Here, "addition" means adding 80% or more of the total amount of addition of an element, then adding the next element. However, the amount added of less than 10% of the total amount of addition for final preparation of the ingredients after adding each element is excluded from consideration of this amount of addition. The timing of addition of each element is preferably after the elapse of 1 minute or more. The timing is more preferably after the elapse of 2 minutes or more, more preferably 3 minutes or more. Further, after all of the elements are added, the steel is cast within 60 minutes. Preferably, it is cast within 40 minutes, more preferably within 20 minutes. Further, in the casting process, the effect of the invention appears more conspicuously with a cooling rate at the time of solidification at the layer of 1/4 the thickness of the slab of $\leq 10^\circ\text{C}/\text{sec}$. The rate is preferably $5^\circ\text{C}/\text{sec}$ or less, more preferably $2^\circ\text{C}/\text{sec}$ or less, more preferably $1^\circ\text{C}/\text{sec}$ or less, more preferably $0.5^\circ\text{C}/\text{sec}$ or less, more preferably $0.1^\circ\text{C}/\text{sec}$ or less.

[0035] Note that to form the complex oxides so that the effect of the present invention can be enjoyed to the maximum, it is preferable to add B in the order of Mn, V, Nb, and B as explained above. The present invention inherently calls for effectively forming B oxides and optimally combining them with other oxides. If possible to maintain a good balance between the concentration of oxygen in the molten steel and the ratio of concentration of Mn, V, and Nb and B and temperature during refining, the effect of the present invention can be obtained even if adding the Mn, V, Nb, B all at

once in the total amounts of addition, adding any two or more elements all at once, or further adding the elements separately. When adding Mn, V, Nb, and B all at once in the total amounts of addition, adding any two or more at one time, or adding them separately, it is necessary to adjust the concentration of oxygen in the molten steel to 0.010 to 0.070% in range. Sometimes the hit rate and efficiency fall.

[0036] Further, preparing B-based complex oxides having distributions of concentration in advance and adding them to the continuous casting tundish or mold enclosed in wire etc. is one method of producing B-based complex oxides having a characteristic distribution of concentration of the present application. The above-mentioned patent document does not disclose the timing of addition of additive elements, the solidification conditions, or any other matter relating to the production of complex oxides with large changes in composition as defined in the present application. Just adding B alone cannot give the sufficient effects.

[0037] That is, in the conventional known enameled steel sheet production technology, just B is added. Further, in the prior art, formation of B nitrides is one of the objects, so the added B ends up bonding with the N having a high affinity with the B so as to form B nitrides. Sufficient B oxides for function as hydrogen trap sites are not effectively formed.

[0038] Still further, in the conventional known enameled steel sheet production technology, it was not known that oxides having an effective distribution of concentration was important, so there was never any art calling for preparing and adding such oxides having a distribution of concentration itself.

[0039] For this reason, it was not possible to use the conventionally known enameled steel sheet production technology to form oxides containing B and having large changes in composition as defined in the present application. Note that nitrides, compared with oxides, have little effect of improvement of fishscale resistance as aimed at by the present invention.

[0040] On the other hand, in the present invention, the oxides have to contain B. Therefore, in the present application, for example, as in the above-mentioned method of production, first Mn is added to form Mn oxides, then B is added or oxides having an effective distribution of concentration themselves are prepared, then added, so as to form the oxides with large changes in composition defined in the present invention having B combined with oxides of Mn etc.

[0041] The above optimum complex oxides are not formed just by the change or ingredients due to the addition of elements or the elapsed time. The temperature is also highly relevant. In particular, after the elements or oxides finish being added, the control of the high temperature reaction up until the start of solidification becomes important. In particular, when the steel turns from a liquid to a solid, the solubility of the various types of elements in the steel also greatly changes. This also has quite an effect on the change in composition. For this reason, the cooling rate at the point of solidification becomes important for sufficiently obtaining the effect of the invention. If too fast, fine oxides and precipitates are formed separate from the original coarse complex oxides and the effect of the invention is inhibited. On the other hand, if cooling too slowly, the composition becomes even, the effect of the invention becomes smaller, and the productivity also falls. In general, the cooling rate of a slab during casting differs depending on the position in the thickness direction, so in the present invention, this is defined by the cooling rate at the layer at 1/4 the thickness as a representative value. The 1/4 layer cooling rate is generally recognized and is found by calculations on heat transmission used in operational control etc. as well.

[0042] When the complex oxides covered by the present invention have an average diameter of 1.0 μm or more at the time of the completion of solidification of the slab, the effect of the invention can be remarkably obtained. Preferably, the diameter is 4.0 μm or more, more preferably 10 μm or more, more preferably 15 μm or more, more preferably 20 μm or more. The oxides are preferably coarse at the time of completion of the casting because if fine, the extensibility of the oxides at the time of forming the the slab becomes poor and fracture also becomes difficult to occur. What is defined here is the average diameter. Ordinarily, complex oxides of a size able to be observed by an optical microscope or a low power scan electron microscope are covered by the measurement.

[0043] In the process of production of ordinary steel sheet, the complex oxides are extended and fractured by rolling to obtain the targeted characteristics and change them to the more preferable forms. For this reason, a certain extent of work is required. The thickness of the slab after completion of casting is preferably made 50 mm or more. In the production process, the slab is rolled by hot rolling to 1 to 8 mm or so and further by cold rolling to 2 to 0.2 mm or so, therefore the total strain becomes a logarithmic strain of 3 to 5 or more. Further, to obtain a better fishscale resistance, it is effective in the hot rolling at 600°C or more to roll under conditions of 1000°C or more and a strain rate of 1/sec or more for a total of the true strain of 0.4 or more, then roll under conditions of 1000°C or less and a strain rate of 10/sec or more for a total of the true strain of 0.7 or more. This is believed to be because the process of formation of the complex oxides with different compositions present in the steel and the accompanying voids is controlled to obtain the preferable form and properties of the complex oxides and voids. The mechanism is not clear, but below the mechanism by which the present invention is realized will be explained. The voids functioning as hydrogen trap sites are mainly formed by the fracturing of the complex oxides in the cold rolling process after the hot rolling, but in the hot rolling process before that, control of the shape of the complex oxides is important. That is, in the hot rolling process, since the temperature is high, the complex oxides also soften. The difference in hardness from the matrix phase, that is, the iron, becomes small. In the approximately 1000°C or more temperature range, the rolling causes almost no fracturing of the complex

oxides - the complex oxides are just extended. Further, when the temperature is lower than 1000°C and becomes approximately 900°C or less, complex oxides become hard to extend, but no remarkable fracturing occurs such as with cold rolling. There is just some cracking of an extent forming fine cracks. To suitably extend the oxides in this way and obtain complex oxides having fine cracks before cold rolling, control of the temperature during hot rolling and control of the strain rate so that remarkable recovery occurs in the iron and composite oxides deformed due to the amount of strain in the temperature range and the hot working.

[0044] If the temperature range of the hot working is too high, the recovery is too fast and enough strain for forming cracks can not be imparted to the complex oxides. Further, if too low, the form of the complex oxides becomes not flattened, but close to spherical, so cracks become difficult. Suitable elongation and less thickness are required for formation of cracks. For this, in hot rolling, control is necessary to impart extension of complex oxides by suitable deformation at a higher temperature range and formation of cracks in the lower temperature range. Further, the form of the complex oxides forming these cracks, as explained above, becomes more complicated and enables formation of effective voids efficiently compared with the case where there is a difference in concentration in complex oxides and a difference in deformability.

[0045] The hot rolling heating temperature, the coiling temperature, etc. may be set as usual in the usual range of operation. The hot rolling heating temperature may be 1000°C or less, but to sufficiently obtain the effect of extension of the complex oxides by the above hot rolling, should be 1050 to 1300°C for rolling at 1000°C or more. The coiling temperature is 400 to 800°C.

[0046] The cold rolling is preferably performed by a cold rolling rate of 60% or more for sufficient fracture of the complex oxides and for obtaining steel sheet with a good deep drawability. In particular, when a deep drawability is required, a cold rolling rate of 75% or more is preferable.

[0047] The annealing may be box annealing or continuous annealing. The features of the present invention remain the same. The features of the present invention are exhibited so long as the temperature is the recrystallization temperature or more. In particular, to bring out the features of the present invention such as excellent deep drawability and good enameling characteristics, continuous annealing is preferable. Box annealing can be performed at 650 to 750°C, while continuous annealing can be performed at 700 to 890°C.

[0048] As explained above, steel sheet controlled in change of composition of complex oxides as in the present invention is given extremely excellent fishscale resistance not only by direct single enameling, but also double enameling. Further, no bubbles, black spot defects, etc. occur and an enameled steel sheet with excellent enamel adhesion is obtained. The method of application of the glaze includes enameling of not only a wet glaze, but also a dry powder without problem. Further, the applications etc. are not limited in any way. The invention exhibits its characteristics in bathtubs, eating utensils, kitchen utensils, building materials, household electrical appliance panels, and other products in the technical field of classification of enameled steel sheet.

EXAMPLES

[0049] Continuously cast slabs having various chemical compositions were hot rolled, cold rolled, and annealed under various production conditions. Next, they were temper rolled by 1.0%, then examined for enameling characteristics. The ingredients are shown in Table 1, the added oxides in Table 1-2, the production conditions in Table 2, and the results of examination in Table 3. In the examples, the inventors studied the effects of the conditions of addition of elements at the time of steelmaking. Even in steel aiming at the same ingredients, slight differences in ingredients occur. Therefore, the inventors compared characteristics assuming equivalent ingredients. Steels judged to have equivalent ingredients were assigned the same letter of the alphabet and given consecutive numbers after the letters in the steel code. The inventors studied the effects of the production conditions using these. Note that in the "rolling" column of Table 2, A indicates the total of the true strain given at 1000°C or more and a strain rate of 1/sec or more, while B indicates the total of the true strain at 1000°C or less and a strain rate of 10/sec or more. Further, in the "separate oxide distribution" column in Table 3, the relative position for the oxides exhibiting a high concentration/low concentration ratio means A: an angle of within $\pm 5^\circ$ and a distance within 0.5 μm , B: the A conditions not satisfied, an angle of within $\pm 10^\circ$, and a distance within 20 μm , and C: the B conditions not satisfied. (Here, the "oxides" means Fe, Si, Mn, Al, Nb, V, B, and other oxides combining together to form complex oxides. "Separate oxides" means any two complex oxides not contacting each other. "Same oxide" means any one not separate complex oxide".)

[0050] The enameling was performed by using the powder electrostatic coating method to dry coat an underglaze to 100 μm and an overglaze to 100 μm and firing in an atmosphere with a condensation point of 60°C at 850°C for 3 minutes.

[0051] The fishscale resistance was evaluated by placing the fired sheet into a 160°C constant temperature tank for 10 minutes for a fishscale promotion test and visually judging the state of formation of fishscale by the five stages of A to E of A: extremely excellent, B: excellent, C: slightly excellent, D: ordinary, and E: problematic. Table 3 shows this as the fishscale resistance.

[0052] The surface characteristics of the bubbles and black spot defects were visually judged in five stages of A to E

including A: extremely excellent, B: excellent, C: slightly excellent, D: ordinary, and E: problematic and are shown in Table 3.

[0053] The enamel adhesion was evaluated by dropping a 2 kg spherical weight from a 1 meter height, measuring the state of peeling of enamel at the deformed part by 169 contact probes, and determining the area ratio of the unpeeled parts since there was no difference in adhesion by the ordinarily performed P.E.I. adhesion test method (ASTM C313-59) .

[0054] As clear from the results of Table 3, the steel sheet of the present invention is an enameled steel sheet with extremely excellent enameling characteristics, in particular fishscale resistance. In particular, there is a clear effect of improvement of the fishscale resistance by control of the method of production for control of the difference of concentration of the complex oxides.

[0055] That is, among steel sheets satisfying the steel ingredients defined by the present invention, as shown in Table 3, steel sheets of the steel codes satisfying all of the requirements defined by the present invention, that is, the max/min ratio of B of separate oxides (defined in claim 1), the max/min ratio of Mn of separate oxides (defined in claim 2), the separate oxide distribution (defined in claim 8 for B, defined in claim 9 for Mn), and the max/min ratio in the same oxide (defined in claim 6 for B, defined in claim 7 for Mn) had adhesions of 80 to 100% and enameling characteristics of bubbles and black spot defect resistance, adhesion, and fishscale resistance evaluated most highly overall.

[0056] Further, the steel sheets of the steel codes (a2, a5, c4, d5, e2, h1, k1) satisfying the requirement of the max/min ratio of B of the separate oxides (defined in claim 1) but not satisfying one of the other above requirements had adhesions of 75 to 85% and had enameling characteristics of a bubble and black spot defect resistance, adhesion, and a fishscale resistance evaluated as excellent (B) or slightly excellent (C), but were evaluated as overall excellent and gave the effects aimed at by the present invention.

[0057] As opposed to this, the comparative examples (l1 to n2) do not satisfy the requirement of the max/min ratio of B of the other oxides (defined in claim 1) and even if satisfying the other requirements, are inferior in enameling characteristics (bubble, and black spot defect resistance, adhesion, and fishscale resistance), so the effects targeted by the present invention cannot be obtained.

[0058] In the "rolling" column, A means the total of the true strain imparted at 1000°C or more and a strain rate of 1/sec or more, while B means the total of the true strain imparted at 1000°C or less and a strain rate of 10/sec or more.

[0059] In the "separate oxide distribution" column, the relative position for the oxides exhibiting a high concentration/low concentration ratio means A: an angle of within $\pm 5^\circ$ and a distance within 0.5 μm , B: the A conditions not satisfied, an angle of within $\pm 10^\circ$, and a distance within 20 μm , and C: the B conditions not satisfied. (Here, the "oxides" means Fe, Si, Mn, Al, Nb, V, B, and other oxides combined together to form complex oxides. "Separate oxides" means any two non-contacting composite oxides. "Same oxide" means any single complex oxide not separated.)

[0060] The fishscale resistance was judged in five stages of A to E including A: extremely excellent, B: excellent: C: slightly excellent, D: ordinary, and E: problematic.

[0061] The surface characteristics of the bubble/black spot defects were visually judged in five stages of A to E including A: extremely excellent, B: excellent, C: slightly excellent, D: ordinary, and E: problematic.

Table 1

Steel code	Ingredient (mass%)												
	C	Si	Mn	P	S	Al	N	B	V	Nb	O	Cu	other elements
a1	0.0015	0.004	0.28	0.005	0.0006	0.0014	0.0025	0.0035	-	-	0.020	0.022	-
a2	0.0015	0.004	0.28	0.005	0.0006	0.0014	0.0025	0.0035	-	-	0.024	0.025	-
a3	0.0015	0.004	0.28	0.005	0.0006	0.0014	0.0025	0.0035	-	-	0.023	0.025	-
a4	0.0013	0.004	0.29	0.005	0.0008	0.0018	0.0025	0.0033	-	-	0.020	0.022	-
a5	0.0015	0.005	0.27	0.006	0.0010	0.0011	0.0025	0.0038	-	-	0.020	0.020	-
b1	0.0006	0.002	0.15	0.003	0.014	0.0024	0.0016	0.0059	-	-	0.031	0.034	-
b2	0.0006	0.002	0.18	0.003	0.019	0.0027	0.0015	0.0065	-	-	0.039	0.035	-
b3	0.0009	0.003	0.20	0.004	0.012	0.0023	0.0022	0.0077	-	-	0.043	0.038	-
b4	0.0006	0.002	0.14	0.003	0.016	0.0032	0.0016	0.0069	-	-	0.033	0.033	-
b5	0.0006	0.005	0.15	0.003	0.014	0.0025	0.0016	0.0073	-	-	0.036	0.030	-
b6	0.0006	0.005	0.14	0.003	0.014	0.0025	0.0016	0.006	-	-	0.035	0.040	-
c1	0.0011	0.038	0.61	0.007	0.059	0.0035	0.0008	0.0014	0.040	0.0015	0.014	0.010	-
c2	0.0011	0.038	0.61	0.007	0.059	0.0035	0.0008	0.0012	0.037	0.0015	0.017	0.012	-
c3	0.0012	0.034	0.58	0.007	0.057	0.0035	0.0007	0.0012	0.040	0.0015	0.015	0.016	-
c4	0.0010	0.035	0.59	0.005	0.058	0.0048	0.0014	0.0016	0.041	0.0013	0.011	0.015	-
d1	0.0013	0.007	0.03	0.010	0.046	0.0005	0.0041	0.0023	-	-	0.026	-	-
d2	0.0013	0.007	0.03	0.010	0.046	0.0005	0.0041	0.0023	-	-	0.026	-	-
d3	0.0012	0.009	0.05	0.011	0.044	0.0009	0.0031	0.0021	-	-	0.029	-	-
d4	0.0012	0.009	0.05	0.011	0.044	0.0009	0.0031	0.0021	-	-	0.029	-	-
d5	0.0014	0.007	0.04	0.010	0.044	0.0008	0.0033	0.0020	-	-	0.020	-	-
e1	0.0015	0.013	0.30	0.020	0.016	0.0091	0.0044	0.0113	-	-	0.047	-	Mo: 0.021
e2	0.0013	0.013	0.32	0.021	0.014	0.0074	0.0034	0.0114	-	-	0.048	-	Mo: 0.021
f1	0.0015	0.004	0.45	0.011	0.035	0.0019	0.0020	0.0181	0.048	-	0.024	0.133	-
f2	0.0015	0.005	0.47	0.011	0.033	0.0016	0.0022	0.0199	0.038	-	0.025	0.094	-

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(continued)

Steel code	Ingredient (mass%)												
	C	Si	Mn	P	S	Al	N	B	V	Nb	O	Cu	other elements
g1	0.0010	0.005	0.28	0.008	0.033	0.0022	0.0025	0.0059	-	-	0.040	0.024	Cr: 0.33 Mg: 0.004
h1	0.0018	0.024	0.86	0.011	0.015	0.0018	0.0020	0.0020	-	-	0.065	-	Ni: 0.54 Sn: 0.015
i1	0.0025	0.003	0.27	0.026	0.018	0.0110	0.0020	0.0050	-	0.0025	0.008	-	Ca: 0.005
j1	0.0072	0.000	0.18	0.024	0.036	0.0011	0.0020	0.0047	-	-	0.040	0.057	Ce: 0.005
k1	0.0003	0.011	0.13	0.004	0.043	0.0082	0.0015	0.0033	-	-	0.033	-	Ti: 0.021
l1	0.0024	0.004	0.20	0.005	0.024	0.0035	0.0009	-	-	-	0.048	0.024	
l2	0.0024	0.004	0.20	0.005	0.024	0.0035	0.0009	-	-	-	0.048	0.024	
m1	0.0012	0.014	0.35	0.008	0.041	0.0460	0.0024	-	-	-	0.008	0.031	Ti: 0.058
m2	0.0012	0.014	0.35	0.008	0.041	0.0460	0.0024	-	-	-	0.008	0.031	Ti: 0.058
n1	0.0015	0.007	0.21	0.006	0.007	0.0022	0.0022	0.0002	-	0.0450	0.035	-	
n2	0.0015	0.007	0.21	0.006	0.007	0.0022	0.0022	0.0002	-	0.0450	0.035	-	
o1	0.0011	0.036	0.6	0.007	0.059	0.0033	0.0008	0.0008	0.035	-	0.004	0.01	-

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Table 1-2

	SiO ₂	MnO	Al ₂ O ₃	B ₂ O ₃	V ₂ O ₃	Nb ₂ O ₅
Content %	14.79	44.55	1.30	6.59	25.37	7.40
Concentration ratio (maximum concentration/ minimum concentration in complex oxides)	1.3	1.4	1.1	1.5	1.2	1.3
Note) The above oxides are added to just steel code o1 by wire in a continuous casting mold Average particle size: 21 μm						

Table 2																
	Steelmaking (casting)						Slab		Hot rolling					Cold roll.	Annealing	
	Order of add. of Mn, B	Initial am't of add.		Add. inter (min)	Time after add. (min)	Cool at solid. (°C/sec)	Thick mm	Oxide dia. (μm)	Slab heating (°C)	Rolling		Fin. temp (°C)	Coil. temp (°C)	Red. rate (%)	Temp (°C)	Time (min)
		Mn	B							A	B					
a1	Mn→B	100	100	10	5	1.0	250	110	1250	1.7	1.6	860	660	73	890	1
a2	Mn→B	100	100	10	10	0.5	250	50	1250	1.7	1.6	860	660	73	890	1
a3	Mr→B	100	100	10	10	1.0	250	50	1250	1.7	1.6	860	660	73.	890	1
a4	Mn→B	100	100	1	10	1.0	250	10	1250	1.7	1.6	860	660	73	890	1
a5	Sim.	100	100	-	10	1.0	250	5	1250	1.7	1.6	860	660	73	890	1
b1	Mn→B	90	90	60	5	2.0	200	180	1050	0.9	2.3	900	700	80	830	3
b2	Mn→B	90	90	30	5	2.0	200	100	1050	0.9	2.3	900	700	80	830	3
b3	Mn→B	90	90	15	5	2.0	200	40	1050	0.9	2.3	900	700	80	830	3
b4	Mn→B	90	90	5	5	2.0	200	10	1050	0.9	2.3	900	700	80	830	3
b5	Mn→B	90	90	3	5	2.0	200	5	1050	0.9	2.3	900	700	80	830	3
b6	Mn→B	90	90	3	5	0.2	200	2	1050	0.9	2.3	900	700	80	830	3
c1	Mn→B	70	100	30	20	5.0	100	60	1150	0.6	1.9	850	750	88	720	0.5
c2	Mn→B	70	100	30	50	5.0	100	20	1150	0.6	1.9	850	750	88	720	0.5
c3	Mn→B	70	100	30	120	5.0	100	50	1150	0.6	1.9	850	750	88	720	0.5
c4	Sim.	70	100	-	20	5.0	100	5	1150	0.6	1.9	850	750	88	720	0.5
d1	Mn→B	100	90	10	5	1.0	200	120	1200	1.3	2.8	930	720	80	750	1
d2	Mn→B	100	90	10	20	1.0	200	60	1200	1.3	2.8	930	720	80	750	1
d3	Mn→B	100	90	3	5	1.0	200	30	1200	1.3	2.8	930	720	80	750	1
d4	Mn→B	100	90	3	20	1.0	200	50	1200	1.3	2.8	930	720	80	750	1
d5	Sim.	100	90	-	60	1.0	200	5	1200	1.3	2.8	930	720	80	750	1
e1	Mn→B	80	80	5	5	0.3	250	30	1100	1.8	1.0	960	780	93	800	1

(continued)

	Steelmaking (casting)						Slab		Hot rolling				Cold roll.	Annealing		
	Order of add. of Mn, B	Initial am't of add.		Add. inter (min)	Time after add. (min)	Cool at solid. (°C/sec)	Thick mm	Oxide dia. (μm)	Slab heating (°C)	Rolling		Fin. temp (°C)	Coil. temp (°C)	Red. rate (%)	Temp (°C)	Time (min)
		Mn	B							A	B					
e2	B→Mn	80	80	5	5	0.3	250	1	1100	1.8	1.0	960	780	93	800	1
f1	Mn→B	100	100	20	30	15	50	20	1150	0.3	1.8	900	670	75	860	1
f2	B→Mn	100	100	20	30	15	50	5	1150	0.3	1.8	900	670	75	860	1
g1	Mn→B	100	100	1	20	0.1	300	30	1100	2.4	1.6	880	710	80	830	1
h1	Mn→B	50	90	1	40	0.5	250	20	1100	1.0	3.2	800	590	77	900	1
i1	Mn→B	100	100	60	40	2.0	250	20	1000	-	1.3	900	740	80	780	1
j1	Mn→B	80	80	10	30	0.5	200	10	1100	1.2	0.5	810	600	87	830	2
k1	Mn→B	100	100	10	30	1.0	200	40	1050	0.4	1.4	840	730	85	770	2
11	-	80	-	-	20	1.0	200	70	1150	1.6	2.3	890	700	80	830	1
12	-	80	-	-	60	1.0	200	20	1150	1.6	2.3	890	700	80	830	1
m1	-	100	-	-	10	0.5	250	10	1150	1.0	1.6	920	730	87	850	1
m2	-	100	-	-	30	0.5	250	10	1150	1.0	1.6	920	730	87	850	1
n1	Sim.	100	100	-	40	1.0	250	30	1150	1.5	1.2	890	690	80	820	1
n2	Sim.	100	100	-	40	10	100	2	1150	0.7	1.2	890	690	80	820	1
o1	Oxide mold add.	70	100	30	20	5.0	100	60	1150	0.6	1.9	850	750	88	720	0.5

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Table 3

Steel code	max/min ratio (separate oxides)		Separate oxide distribution		Max/min ratio (in same oxide)		Enamel characteristics			Remarks
	B	Mn	B	Mn	B	Mn	Bubble/ black spot defect resistance	Adhesion %	Fishscale resistance	
a1	4.5	2.7	A	A	3.3	2.2 2	A	100	A	Inv. ex.
a2	1.5	1.9	B	A	1.1	1.7	A	85	B	Inv. ex.
a3	2.4	2.4	A	A	3.4	2.2	A	95	A	Inv. ex.
a4	1.8	2.3	A	A	2.0	1.4	A	85	B	Inv. ex.
a5	1.3	1.4	C	B	1.1	1.5	A	85	C	Inv. ex.
b1	1.5	1.9	C	B	1.2	1.7	A	80	B	Inv. ex.
b2	1.9	1.4	B	B	1.5	1.3	A	90	A	Inv. ex.
b3	4.1	3.6	A	A	2.1	1.5	A	95	A	Inv. ex.
b4	9.5	5.9	A	A	4.1	2.3	A	100	A	Inv. ex.
b5	3.1	4.0	B	A	2.5	1.2	B	90	B	Inv, ex.
b6	1.5	1.8	A	B	2.0	1.3	B	80	B	Inv. ex.
c1	>10	4.4	A	A	7.7	3.8	B	80	A	Inv. ex.
c2	7.1	7.4	A	A	3.9	5.5	A	80	A	Inv. ex.
c3	2.2	3.1	B	A	2.2	1.9	A	85	B	Inv. ex.
c4	1.5	1.3	C	C	1.4	1.3	B	75	C	Inv. ex.
d1	3.0	4.3	A	B	2.1	1.7	C	95	B	Inv. ex.
d2	2.5	2.1	B	A	1.4	2.0	C	90	C	Inv. ex.
d3	1.8	1.5	A	A	1.4	1.4	B	80	B	Inv. ex.
d4	1.4	1.6	A	A	1.6	1.4	C	80	C	Inv. ex.
d5	1.3	1.1	B	C	1.2	1.1	C	80	C	Inv. ex.
e1	2.5	1.8	B	A	2.2	2.5	A	100	A	Inv. ex.
e2	1.2	1.3	C	B	1.1	1.2	B	80	C	Inv. ex.
f1	3.5	4.1	A	A	1.5	3.1	C	100	A	Inv. ex.
f2	1.3	1.3	B	B	1.3	1.4	C	90	B	Inv. ex.
g1	>10	2.5	A	B	3.7	2.6	A	85	B	Inv. ex.
h1	3.2	1.5	A	C	2.2	2.0	B	75	A	Inv. ex.
i1	>10	2.2	B	A	3.0	1.5	C	85	A	Inv. ex.
j1	>10	3.0	A	B	7.2	4.0	A	90	A	Inv. ex.
k1	5.1	1.8	B	A	1.1	1.7	B	80	C	Inv. ex.
11	-	1.4	-	C	-	1.4	C	70	D	Comp. ex.
12	-	1.1	-	C	-	1.1	D	75	D	Comp. ex.

(continued)

Steel code	max/min ratio (separate oxides)		Separate oxide distribution		Max/min ratio (in same oxide)		Enamel characteristics			Remarks
	B	Mn	B	Mn	B	Mn	Bubble/ black spot defect resistance	Adhesion %	Fishscale resistance	
m1	-	2.0	-	B	-	2.0	E	65	E	Comp. ex.
m2	-	2.6	-	B	-	1.9	E	70	E	Comp. ex.
n1	1.0	1.4	C	C	-	1.3	C	80	D	Comp. ex.
n2	1.0	1.2	C	C	-	1.1	C	75	D	Comp. ex.
o1	>10	4.4	A	A	7.7	3.8	B	80	A	Inv. ex.

INDUSTRIAL APPLICABILITY

[0062] The enameled steel sheet of the present invention satisfies all of the fishscale resistance, bubble and black spot defect resistance, enamel adhesion, and surface characteristics required for an enameled steel sheet. In particular, the fishscale resistance is remarkably improved, the defect rate in the process of production of an enamel product greatly falls, and therefore the industrial significance is large.

Claims

1. A continuously cast enameled steel sheet excellent in fishscale resistance **characterized by** comprising, by mass%,
C: 0.010% or less,
Mn: 0.03 to 1.30%,
Si: 0.100% or less,
Al: 0.030% or less,
N: 0.0055% or less,
P: 0.035% or less,
S: 0.08% or less,
O: 0.005 to 0.085%,
B: 0.0003 to 0.0250%, and
a balance of Fe and unavoidable impurities and having, in complex oxides of 0.10 μm or more diameter comprising Fe, Mn, Si, Al, B, or other oxides combined together in a unit observation field of 100 $\mu\text{m} \times 100 \mu\text{m}$ in the sheet cross-section, any two complex oxides with different B mass concentrations and not contacting each other and with a ratio of a maximum concentration of a B mass concentration ($B_{\text{max}}\%$) and a minimum concentration of a B mass concentration ($B_{\text{min}}\%$) of $B_{\text{max}}/B_{\text{min}} \geq 1.2$.
2. A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in claim 1, **characterized by** having, in complex oxides of 0.10 μm or more diameter comprising Fe, Mn, Si, Al, B, or other oxides combined together in a unit observation field of 100 $\mu\text{m} \times 100 \mu\text{m}$ in the sheet cross-section, any two complex oxides with different Mn mass concentrations and not contacting each other and with a ratio of a maximum concentration of an Mn mass concentration ($Mn_{\text{max}}\%$) and a minimum concentration of an Mn mass concentration ($Mn_{\text{min}}\%$) of $Mn_{\text{max}}/Mn_{\text{min}} \geq 1.2$.
3. A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in claim 1 or 2, **characterized by** further containing, by mass%, one or both of
Nb: less than 0.004% (including zero)

V: 0.003 to 0.15%.

4. A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of claims 1 to 3, **characterized by** further containing, by mass%, Cu: 0.01 to 0.500%.
5. A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of claims 1 to 4, **characterized by** further containing, by mass%, one or more of Cr, Ni, As, Ti, Se, Ta, W, Mo, Sn, Sb, La, Ce, Ca, and Mg in a total of 1.0% or less.
6. A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of claims 1 to 5, **characterized by** having, in complex oxides of 0.10 μm or more diameter comprising Fe, Mn, Si, Al, B, or other oxides combined together in the steel sheet, a distribution of the B mass concentration and a ratio of the B mass concentration of the high concentration part (Bmax%) and the B mass concentration of the low concentration part (Bmin%) of $B_{\text{max}}/B_{\text{min}} \geq 1.2$.
7. A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of claims 1 to 6, **characterized in** one of the Fe, Mn, Si, Al, Nb, B, V, Cr, and other oxides in the steel sheet join together to form complex oxides in which the Mn concentration fluctuates, and a ratio of the Mn mass concentration of the high concentration part (Mnmax%) and the Mn mass concentration of the low concentration part (Mnmin%) is $Mn_{\text{max}}/Mn_{\text{min}} \geq 1.2$.
8. A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of claims 1 to 7, **characterized by** having separate complex oxides with a B mass concentration 1.2 times or more or 1/1.2 times or less of the B mass concentration (%) of the complex oxides comprising the Fe, Mn, Si, Al, Nb, B, V, Cr, or other oxides combined together in the sheet with a straight line distance between centers of the two complex oxides of 0.10 μm to 20 μm and with an angle of the line connecting the centers of the two oxides of within $\pm 10^\circ$ from the rolling direction.
9. A continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of claims 1 to 8, **characterized by** having separate complex oxides with an Mn mass concentration 1.2 times or more or 1/1.2 times or less of the Mn mass concentration (%) of the complex oxides comprising the Fe, Mn, Si, Al, Nb, B, V, Cr, or other oxides combined together in the sheet with a straight line distance between centers of the two complex oxides of 0.10 μm to 20 μm and with an angle of the line connecting the centers of the two oxides of within $\pm 10^\circ$ from the rolling direction.
10. A method of production of a continuously cast enameled steel sheet excellent in fishscale resistance **characterized by** making and casting steel comprising, by mass%
 C: 0.010% or less,
 Mn: 0.03 to 1.3%,
 Si: 0.100% or less,
 Al: 0.030% or less,
 N: 0.0055% or less,
 P: 0.035% or less,
 S: 0.08% or less,
 O: 0.005 to 0.085%,
 B: 0.0003 to 0.0250%, and
 a balance of Fe and unavoidable impurities, during which adding the Mn and B into the molten steel in the order of adding Mn in a total amount of addition of 80% or more, then allowing 1 minute or more to elapse, adding B in a total amount of addition of 80% or more, and casting within 60 minutes.
11. A method of production of a continuously cast enameled steel sheet excellent in fishscale resistance as set forth in claim 10, **characterized by** further including, by mass%, one or both of
 Nb: less than 0.004% (including zero) and
 V: 0.003 to 0.15%
12. A method of production of a continuously cast enameled steel sheet excellent in fishscale resistance as set forth in claim 10 or 11, **characterized by** further including, by mass%, Cu: 0.01 to 0.500%.

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13. A method of production of a continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of claims 10 to 12, **characterized by** further including, by mass%, one or more of Cr, Ni, As, Ti, Se, Ta, W, Mo, Sn, Sb, La, Ce, Ca, and Mg in a total of 1.0% or less.

5 14. A method of production of continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of claims 10 to 13, **characterized by** casting by the cooling rate at the time of solidification of $\leq 10^{\circ}\text{C}/\text{sec}$ at 1/4 the sheet thickness of the slab.

10 15. A method of production of continuously cast enameled steel sheet excellent in fishscale resistance as set forth in any one of claims 10 to 14, **characterized by** hot rolling a slab with oxides of an average diameter of $1.0\text{ }\mu\text{m}$ or more and with a thickness of 50 mm or more at 600°C or more during which rolling under conditions of 1000°C or more and a strain rate of 1/sec or more to a total of the true strain of 0.4 or more, then rolling under conditions of 1000°C or less and a strain rate of 10/sec or more to a total of the true strain of 0.7 or more.

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Fig.1

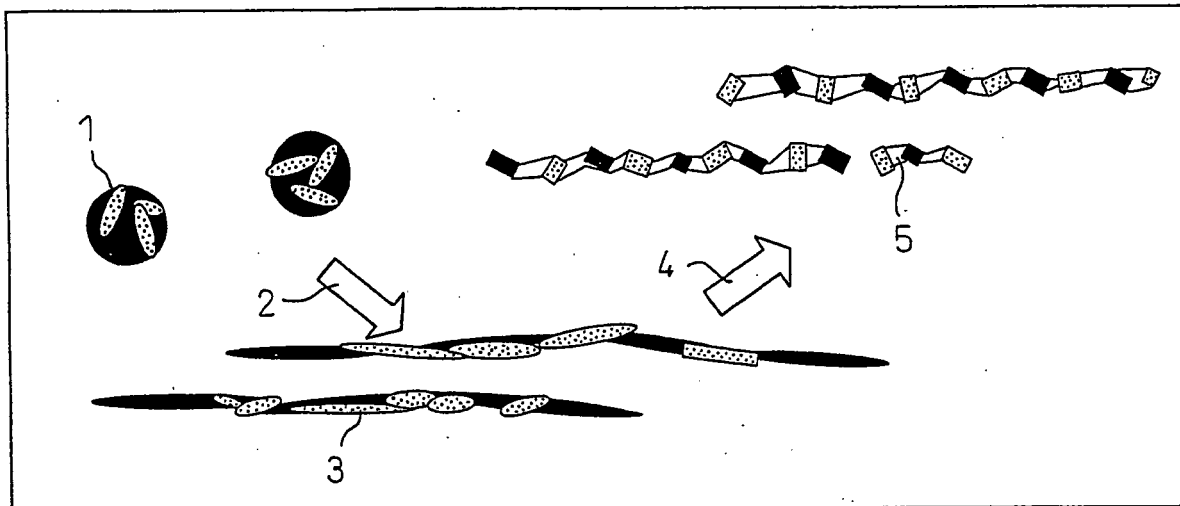


Fig.2

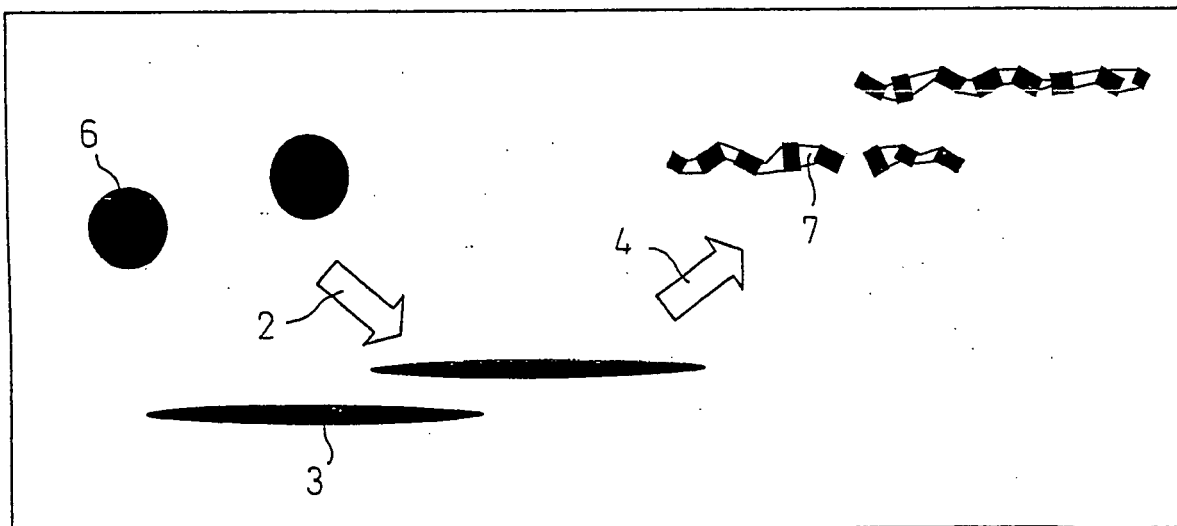


Fig.3

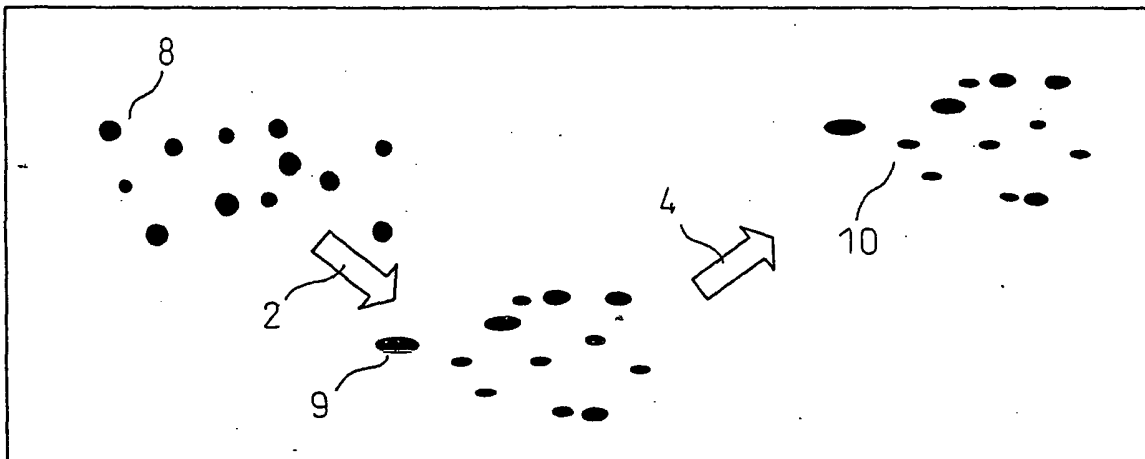


Fig.4

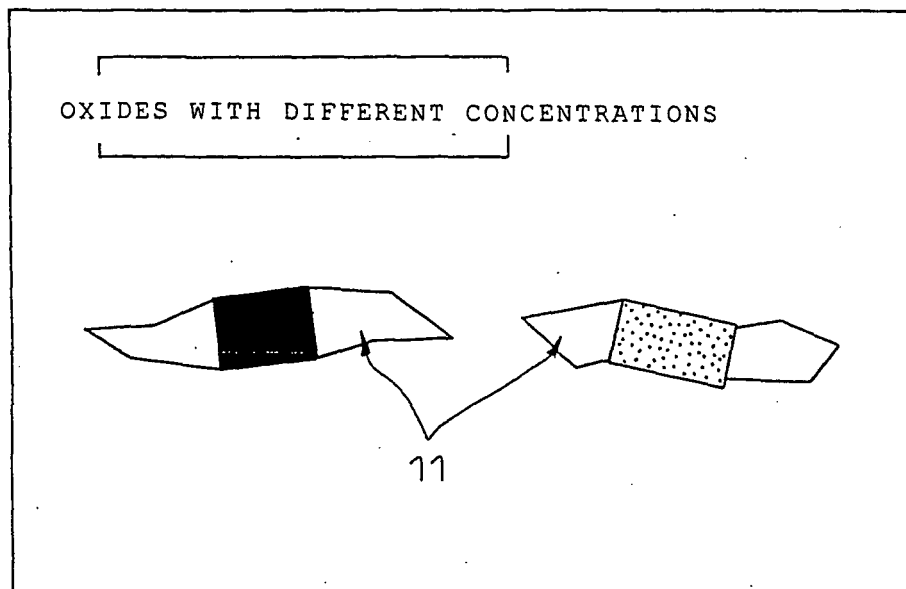
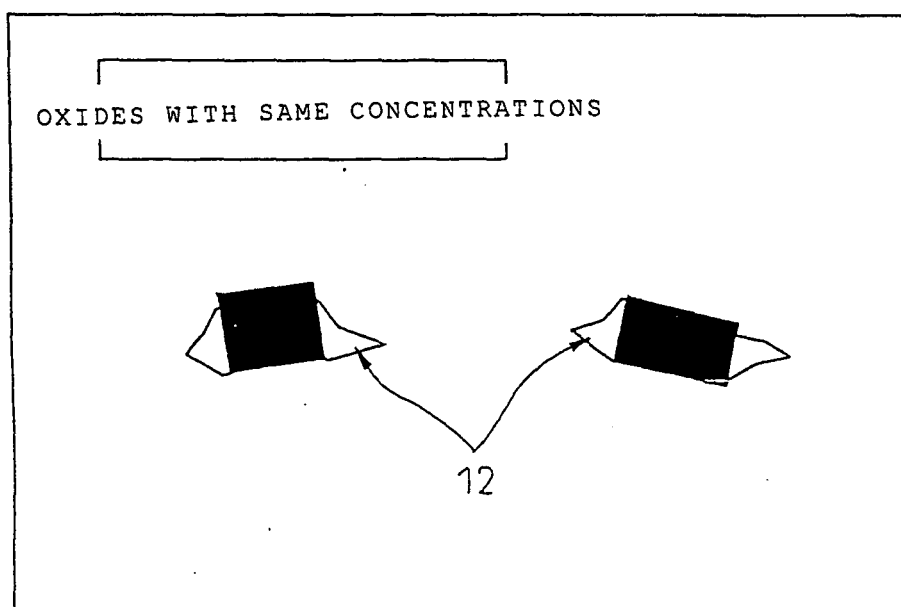


Fig.5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2006/322786

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, B22D11/124(2006.01)i, C21D9/46(2006.01)i, C22C38/60(2006.01)i, C23D5/00(2006.01)i, C21C7/04(2006.01)n, C21C7/06(2006.01)n

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)

C22C38/00, B22D11/124, C21D9/46, C22C38/60, C23D5/00, C21C7/04, C21C7/06

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 1996-2007
Kokai Jitsuyo Shinan Koho 1971-2007 Toroku Jitsuyo Shinan Koho 1994-2007

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.
A	JP 2004-18860 A (Nippon Steel Corp.), 22 January, 2004 (22.01.04), Full text & EP 1513961 A1 & US 2005/236078 A1 & WO 03/106726 A1	1-15
A	JP 2005-510624 A (Nippon Steel Corp.), 21 April, 2005 (21.04.05), Full text & EP 1442147 A1 & US 2004/244885 A1 & WO 03/38140 A1	1-15
A	JP 2001-316760 A (Sumitomo Metal Industries, Ltd.), 16 November, 2001 (16.11.01), Full text (Family: none)	1-15

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search
05 February, 2007 (05.02.07)

Date of mailing of the international search report
13 February, 2007 (13.02.07)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2006/322786

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2000-1748 A (Kawasaki Steel Corp.), 07 January, 2000 (07.01.00), Full text (Family: none)	1-15
A	JP 2001-279331 A (Kawasaki Steel Corp.), 10 October, 2001 (10.10.01), Full text (Family: none)	1-15

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2002080934 A [0003] [0003]
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