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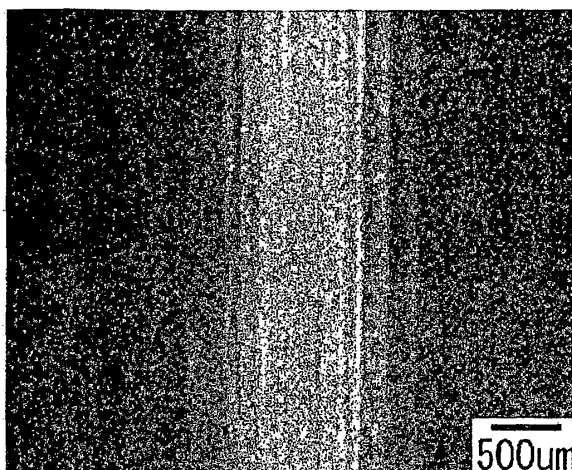
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(54) **STEEL SHEET, SURFACE-TREATED STEEL SHEET, AND METHOD FOR PRODUCING THE SAME**

(57) A high-strength steel sheet having a tensile strength of at least 590 MPa and excellent bending properties has a chemical composition containing C: 0.03 - 0.20 %, Si: 0.005 - 2.0 %, Mn: 1.2 - 3.5 %, P ≤ 0.1 %, S: ≤ 0.01 %, sol. Al: 0.001 - 1.0 %, N: ≤ 0.01 %, and Bi: 0.0001 - 0.05 %, optionally Ti: ≤ 0.3 %, Nb: ≤ 0.3 %, V: ≤ 0.3 %, Cr: ≤ 1 %, Mo: ≤ 1 %, Cu: ≤ 1 %, Ni: ≤ 1 %, Ca:

≤ 0.01 %, Mg: ≤ 0.01 %, REM: ≤ 0.01 %, Zr: ≤ 0.01 %, and B: ≤ 0.01 %, wherein the Mn segregation ratio ( $Mn_{max}/Mn_{av}$ ) calculated from the average Mn concentration ( $Mn_{av}$ ) and the maximum Mn concentration ( $Mn_{max}$ ) at a depth of 1/20 of the sheet thickness from the surface of the steel sheet is less than 1.30.

**Fig. 1**



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**Description**

## Technical Field

5     **[0001]** This invention relates to a steel sheet, a surface-treated steel sheet, and methods for their manufacture. More specifically, the present invention relates to a high-strength steel sheet and surface-treated steel sheet which are suitable as materials for members such as reinforcing members for automobiles or seat components for automobiles and methods for their manufacture.

## 10     Background Art

**[0002]** There has been an increasing interest in the automotive industry in high-strength steel sheets having excellent formability since they are effective at increasing the safety of automobiles and decreasing weight, which leads to decreased fuel consumption. In recent years, the number of components per automobile which are manufactured from high-strength steel sheets has been increasing. Therefore, an extremely high level of bend formability (formability by bending) is also required of high-strength steel sheets having a tensile strength of at least 590 MPa. In particular, members having bent portions with a small radius such as seat rails or side sills need to have better bend formability and a higher strength than in the past.

20     **[0003]** Techniques for controlling the structure of high-strength steel sheets have been employed in the past with the object of improving bend formability. Patent Document 1 discloses a high-strength steel sheet in which the hardness of hard bainitic and martensitic phases is decreased so as to reduce the difference in hardness with respect to the low-hardness ferritic phase surrounding the bainitic phase and the martensitic phase. Patent Document 2 and Patent Document 3 disclose cold-rolled steel sheets and hot-dip galvanized steel sheets which have both a high strength and satisfactory stretch flange formability for which good local deformability is required as for bending properties.

25     **[0004]** High-strength steel sheets generally contain a large amount of Mn in order to increase strength. Mn tends to segregate in steel. Therefore, the chemical composition of high-strength steel sheets locally varies due to the segregation of Mn. This local variation in the chemical composition results in the formation of a nonuniform structure in a high-strength steel sheet. As a result, it is extremely difficult from a practical standpoint to perform fine control of the hardness of the ferritic phase, the bainitic phase, and the martensitic phase over the entirety of a high-strength steel sheet in the manner disclosed in Patent Document 1.

30     **[0005]** Figure 1 is an explanatory view showing the surface condition after bending deformation of a high-strength steel sheet. As shown in Figure 1, if a nonuniform structure is formed in a high-strength steel sheet, marked surface irregularities which can be visually observed develop in the surface of worked portions of the high-strength steel sheet. These irregularities promote nonuniform deformation at the time of bending, thereby inducing the formation of cracks in worked portions and worsening bending properties. Even when cracks do not develop, surface irregularities present in worked portions remain in a member which is manufactured from the high-strength steel sheet and worsen the impact properties of the member.

35     **[0006]** Segregation of Mn causes the transformation behavior to locally vary. As a result, a high-strength steel sheet has a nonuniform grain diameter. For this reason, the methods disclosed in Patent Documents 2 and 3 cannot improve the bending properties of a high-strength steel sheet. The steel sheets disclosed in Patent Documents 1 3 have a steel composition containing a large amount of Mn and Ni which easily segregate in steel, so for the above-described reasons, there is a concern of a deterioration in the bending properties and impact properties of members formed from the steel sheets.

40     **[0007]** The absolute technology in the form of a single-phase structure has been proposed in order to obtain a uniform structure. Patent Document 4 discloses a high-strength cold-rolled steel sheet having improved bending properties due to having a martensitic single-phase structure which is an essentially uniform structure. However, if the steel structure is made a martensitic single-phase structure, the flatness of a high-strength steel sheet is worsened, and this makes it difficult to use the sheet as a material for automotive parts requiring high dimensional accuracy.

45     **[0008]** Patent Document 5 discloses a thin steel sheet having an increased hole expansion ratio with an increased strength by employing a matrix with a single-phase ferritic structure. When manufacturing a high-strength cold-rolled steel sheet or a high-strength hot-dip galvanized steel sheet based on the technology disclosed in that document, it is necessary to perform cold rolling and annealing in order to improve the surface roughness and the accuracy of the sheet thickness of a product. Because the steel composition which is disclosed in that document contains a large amount of carbonitride-forming elements, the steel has an increased recrystallization temperature, and it is necessary to carry out annealing at a high temperature of not lower than the  $A_{c3}$  point. Annealing at such a high temperature promotes coarsening of precipitates and makes it impossible to attain a high strength. In addition, the grain diameter of the steel becomes nonuniform, and it is not possible to improve bending properties.

55     **[0009]** Therefore, in order to achieve good bending properties along with a high strength in a steel sheet, it is necessary

for the steel sheet to achieve the mutually incompatible goals of obtaining a uniform structure and increasing the strength by addition of a large amount of Mn.

**[0010]** Technology for eliminating segregation, which is the cause of a nonuniform structure, by means of diffusion has been proposed. Patent Document 6 discloses a heat treatment method for steel in which segregation is diffused by performing homogenization in which a steel material is maintained at a high temperature of at least 1250° C for a long period of at least 10 hours. However, that method cannot completely eliminate segregation. As a result, segregation produces a nonuniform structure, and surface irregularities in worked portions are not removed, so bending properties cannot be adequately improved.

**[0011]** Patent Document 7 and Patent Document 8 disclose a hot-dip galvanized steel sheet having reduced segregation and excellent hole expandability manufactured by carrying out continuous casting under conditions in which cooling is performed from the liquidus temperature to the solidus temperature such that the average cooling rate is at least 100° C per minute at a depth of 1/4 of the slab thickness  $t_s$ . However, this cooling rate can only be achieved with a thin slab having a thickness of 30 - 70 mm, and this technique cannot be applied to continuous casting of a usual slab having a thickness of 200 - 300 mm.

Prior Art Documents

Patent Documents

**[0012]**

Patent Document 1: JP 62-13533A

Patent Document 2: JP 2004-211126A.

Patent Document 3: JP 2004-250774A

Patent Document 4: JAP 2002-161336A

Patent Document 5: JP 2002-322539A

Patent Document 6: JP 4-1913 22A

Patent Document 7: JP 2007-70649A

Patent Document 8: JP 2007-70659A

Summary of the Invention

**[0013]** The object of the present invention is to provide a steel sheet and a surface-treated steel sheet having a tensile strength of at least 590 MPa and excellent bending properties and methods for the manufacture of such sheets.

**[0014]** In the present invention, excellent bending properties mean that the smallest bending radius for which cracks do not develop in a 180° bending test in which the axis for bending is in the rolling direction is not greater than 1.0t and that surface irregularities cannot be visually observed in a portion which has been bent after 90° V bending with a bending radius of 1.0t in the same bending direction as above. Accordingly, unless otherwise specified, bending properties in this description are evaluated by the above-described properties of a steel sheet and by visual observation of a member manufactured by bending of such a steel sheet. When a steel sheet according to the present invention is used as a material for seat rails which have strict requirements concerning bending properties, it is preferable that the smallest bending radius in a 180° bending test be not greater than 0.5t and that irregularities be not visually observed in the surface of the bent portion after 90° V bending with a bending radius of 0.5t.

**[0015]** The present invention is based on the finding that a desired distribution of the Mn concentration can be achieved by optimizing the chemical composition and the manufacturing conditions of a high-strength steel sheet. As a result, the formation of a nonuniform structure caused by Mn segregation can be suppressed to obtain a uniform structure, whereby a high-strength steel sheet having a tensile strength of at least 590 MPa and excellent bending properties can be manufactured.

**[0016]** The present invention is a steel sheet characterized by having a chemical composition in which, the contents of C, Si, Mn, P, S, sol. Al, N, Bi, Ti, Nb, V, Cr, Mo, Cu, Ni, Ca, Mg, REM, Zr, and B (in this description, unless otherwise specified, % with respect to chemical composition means mass %) is C: 0.03 - 0.20 %, Si: 0.005 - 2.0 %, Mn: 1.2 - 3.5 %, P ≤ 0.1 %, S: ≤ 0.01 %, sol. Al: 0.001 - 1.0 %, N: ≤ 0.01 %, Bi: 0.0001 - 0.05 %, Ti: 0 - 0.3 %, Nb: 0 - 0.3 %, V: 0 - 0.3 %, Cr: 0 - 1 %, Mo: 0 - 1 %, Cu: 0 - 1 %, Ni: 0 - 1 %, Ca: 0 - 0.01 %, Mg: 0 - 0.01 %, REM: 0 - 0.01 %, Zr: 0 - 0.01 %, and B: 0 - 0.01 %, and by the Mn segregation ratio ( $Mn_{max}/Mn_{av}$ ) calculated from the average Mn concentration ( $Mn_{av}$ ) and the maximum Mn concentration ( $Mn_{max}$ ) at a depth of 1/20 of the sheet thickness from the surface of the steel sheet being less than 1.30.

**[0017]** In a preferred embodiment of a steel sheet according to the present invention, the above-described chemical composition includes at least one of the following (a) - (d):

- (a) at least one of Ti: 0.003 - 0.3 %, Nb: 0.003 - 0.3 %, and V: 0.003 - 0.3%;
- (b) at least one of Cr: 0.01 - 1 %, Mo: 0.01 - 1 %, Cu: 0.01 - 1 %, and Ni: 0.01 - 1. %;
- (c) at least one of Ca: 0.0001 - 0.01 %, Mg: 0.0001 - 0.01 %, REM: 0.0001 - 0.01 %, and Zr: 0.0001 - 0.01 %; and
- (d) B: 0.0003 - 0.01 %.

**[0018]** From another aspect, the present invention is a surface-treated steel sheet characterized by having a plating layer formed on the surface of at least one side of the above-described steel sheet.

**[0019]** From another aspect, the present invention is a method of manufacturing a steel sheet characterized by including the following steps (A) - (C):

(A) a continuous casting step in which molten steel having the above-described chemical composition is cast to form a slab with a thickness of 200 - 300 mm under conditions such that the rate of solidification at a depth of 10 mm from the surface is 100 - 1000° C per minute;

(B) a rolling step including hot rolling and cold rolling in which the slab obtained in the above-described continuous casting step is hot rolled to obtain a hot-rolled steel sheet and the hot-rolled steel sheet is then cold rolled to obtain a cold-rolled steel sheet; and

(C) a continuous annealing step in which the cold-rolled steel sheet obtained in the rolling step is subjected to recrystallization annealing in a temperature range of 750 - 950° C.

**[0020]** From another aspect, the present invention is a method of manufacturing a surface-treated steel sheet characterized in that the steel sheet obtained by the above-described manufacturing method is subjected to plating which forms a plating layer on the surface of at least one side of the steel sheet.

**[0021]** The present invention can provide a high-strength steel sheet having a strength of at least 590 MPa and excellent bending properties. A steel sheet according to the present invention can be widely used in various industrial fields and particularly in the automotive field.

#### Brief Explanation of the Drawings

**[0022]**

Figure 1 is an explanatory view showing the surface condition after bending deformation.

#### Embodiments of the Invention

**[0023]** The chemical composition of a steel sheet according to the present invention is as follows.

C: 0.03 - 0.20 %

**[0024]** C contributes to increasing the strength of a steel sheet. The C content is at least 0.03 % in order to make the tensile strength of a steel sheet at least 590 MPa. If the C content exceeds 0.20 %, weldability worsens. Therefore, the C content is made at most 0.20 %. The C content is preferably at least 0.05 % in order to easily obtain a tensile strength of at least 980 MPa.

Si: 0.005 - 2.0 %

**[0025]** If the Si content is at least 0.005 %, it is possible to increase the strength of a steel sheet without significantly degrading bending properties. If the Si content exceeds 2.0 %, the ability of an unplated steel sheet to undergo chemical conversion treatment is degraded, and in the case of a hot-dip galvanized steel sheet, wettability at the time of plating, the ability to undergo alloying treatment, and plating adhesion deteriorate. Therefore, the Si content is at least 0.005 % and at most 2.0 %.

**[0026]** If the Si content exceeds 1.5 %, Si-containing oxides may be formed on the surface of the steel sheet to such a degree that the surface condition worsens. Therefore, the Si content is preferably at most 1.5 %. When manufacturing a hot-dip galvanized steel sheet which is more difficult to increase in strength than a cold-rolled steel sheet due to restrictions on the manufacturing process, a tensile strength of at least 980 MPa can be easily obtained if the Si content is at least 0.4 %. Therefore, the Si content is preferably at least 0.4 %.

Mn: 1.2 - 3.5 %

**[0027]** Mn contributes to increasing the strength of a steel sheet. In order to make the tensile strength of a steel sheet at least 590 MPa, it is necessary for the Mn content to be at least 1.2 %. If the Mn content exceeds 3.5 %, it not only becomes difficult to melt and refine steel in a converter, but weldability also worsens. Therefore, the Mn content is at least 1.2 % and at most 3.5 %. Mn promotes the formation of a nonuniform structure in steel, but as stated below, when Bi is contained in the steel, this adverse effect of Mn is alleviated and the structure becomes uniform, so a worsening of bending properties is suppressed and strength is increased. In order to achieve a tensile strength of at least 980 MPa, the Mn content is preferably at least 1.8 %.

$P \leq 0.1 \%$

**[0028]** P is typically contained as an unavoidable impurity. However, P is a solid solution strengthening element, and it is effective for strengthening a steel sheet, so it may be deliberately contained. Weldability deteriorates if the P content exceeds 0.1%. Therefore, the P content is at most 0.1 %. In order to strengthen a steel sheet with greater certainty, the P content is preferably at least 0.003 %.

$S \leq 0.01\%$

**[0029]** S is contained in steel as an unavoidable impurity. The S content is preferably as low as possible from the standpoint of bending properties and weldability. Therefore, the S content is made at most 0.01 %. The S content is preferably at most 0.005 % and more preferably at most 0.003 %.

sol. Al: 0.001 - 1.0%

**[0030]** Al is contained in steel for deoxidation of steel. Al is effective for increasing the yield of carbonitride-forming elements such as Ti. The content of sol. Al which is necessary for this effect is at least 0.001 %. If the sol. Al content exceeds 1.0 %, weldability is degraded, and oxide inclusions in the steel increase, leading to a deterioration in the surface condition. Therefore, the sol. Al content is made at least 0.001 % and at most 1.0 %. The sol. Al content is preferably at least 0.01 % and at most 0.2 %.

$N < 0.01 \%$

**[0031]** N is contained in steel as an unavoidable impurity. From the standpoint of bending properties, the N content is preferably as low as possible, so it is made at most 0.01 %. The N content is preferably at most 0.006 %.

Bi: 0.0001 - 0.05 %

**[0032]** Bi performs an important function in the present invention. Bi when contained in steel refines the solidification structure of a slab, and even if the steel contains a large amount of Mn, the structure of the steel sheet becomes uniform and a deterioration in bending properties is suppressed. Accordingly, in order to guarantee the desired excellent bending properties, it is necessary for the Bi content to be at least 0.0001 %. However, if the Bi content exceeds 0.05 %, hot workability is degraded and hot rolling becomes difficult. Therefore, the Bi content is at least 0.0001 % and at most 0.05 %. In order to further improve bending properties, the Bi content is preferably at least 0.0010 %.

**[0033]** At least one element selected from Ti:  $\leq 0.3 \%$ , Nb:  $\leq 0.3 \%$ , and V:  $\leq 0.3 \%$

**[0034]** Ti, Nb, and V each contribute to increasing the strength of a steel sheet, so they are optional elements which can be contained in steel as necessary. Containing at least one of Ti, Nb, and V in steel is effective for guaranteeing a tensile strength of at least 980 MPa. In order to obtain this effect with greater certainty, the content of at least one of Ti, Nb, and V is preferably at least 0.003 %. If the content of any of Ti, Nb, and V exceeds 0.3 %, inclusions containing Ti, Nb, or V increase and the surface condition of the steel sheet deteriorates. Therefore, when at least one of Ti, Nb, and V is contained, the content of each which is added is preferably at most 0.3 %.

**[0035]** At least one element selected from Cr:  $\leq 1 \%$ , Mo:  $\leq 1 \%$ , Cu:  $\leq 1 \%$ , and Ni:  $\leq 1\%$

**[0036]** Cr, Mo, Cu, and Ni each contribute to increasing the strength of a steel sheet, so they are optional elements which can be contained in the steel as necessary. Containing at least one of Cr, Mo, Cu, and Ni in a steel is effective for guaranteeing a tensile strength of at least 980 MPa when manufacturing a cold-rolled steel sheet such that the temperature at the completion of cooling in continuous annealing is at least 300° C and at most 420° C or when manufacturing a hot-dip galvanized steel sheet. In order to obtain this effect with greater certainty, at least one of Cr, Mo, Cu, and Ni is preferably contained in an amount of at least 0.01. %. However, if the content of any of Cr, Mo, Cu, and Ni

exceeds 1 %, the above-described effect saturates and the addition becomes economically wasteful. In addition, the hot-rolled steel sheet at the completion of hot rolling becomes hard, and it becomes difficult to perform cold rolling on the hot-rolled steel sheet. Therefore, when at least one of Cr, Mo, Cu, and Ni is contained, the content of each added element is made at most 1 %.

**[0037]** At least one element selected from Ca:  $\leq 0.01$  %, Mg:  $\leq 0.01$  %, REM:  $\leq 0.01$  %, and Zr:  $\leq 0.01$  %

**[0038]** Each of Ca, Mg, REM, and Zr contributes to controlling inclusions in steel and particularly to finely dispersing inclusions, thereby further improving the bending properties of a steel sheet. Therefore, they are optional elements which can be contained in steel as necessary. However, if an excessive amount of Ca, Mg, REM, or Zr is contained, the surface condition of a steel sheet deteriorates. Therefore, when at least one of Ca, Mg, REAM, and Zr is contained, the content of each which is added is at most 0.01 %. In order to obtain the above-described effect with certainty, the content of any of Ca, Mg, REM, and Zr which is added is preferably at least 0.0001 %.

B:  $\leq 0.01$  %

**[0039]** B not only contributes to improving the bending properties of a steel sheet, but it is effective at guaranteeing a tensile strength of at least 980 MPa when manufacturing a hot-dip galvanized steel sheet. Therefore, it is an optional element which can be contained in steel as necessary. However, if the B content exceeds 0.01 %, a hot-rolled steel sheet becomes hard, and it becomes difficult to carry out cold rolling on the hot-rolled steel sheet. Therefore, the B content is preferably at most 0.01 %. In order to obtain the above-described effect with greater certainty, the B content, when B is contained, is preferably at least 0.0003 %.

**[0040]** The remainder of the composition other than the above-described components is essentially Fe and impurities.

Mn segregation ratio: less than 1.30

**[0041]** A steel sheet according to the present invention has a prescribed Mn distribution. Namely, the Mn distribution of the steel sheet satisfies the condition that the Mn segregation ratio ( $Mn_{\max}/Mn_{\text{av}}$ ) is less than 1.30. The Mn segregation ratio ( $Mn_{\max}/Mn_{\text{av}}$ ) is determined by analysis with an EPMA (electron probe microanalyzer) at a depth of 1/20 of the sheet thickness from the surface of the steel sheet in a region which does not contain MnS. The segregation ratio is calculated as the ratio of the maximum Mn concentration ( $Mn_{\max}$ ) to the average Mn concentration ( $Mn_{\text{av}}$ ). A Mn segregation ratio of less than 1.30 indicates that the structure is uniform, as a result of which the bending properties of the steel sheet are improved, and it becomes difficult for surface irregularities to develop in a portion which has undergone bending. The Mn segregation ratio of a steel sheet can be made less than 1.30 by containing Bi in the chemical composition of the steel and, as described below, by satisfying prescribed conditions for the casting speed. In order to further improve bending properties, the Mn segregation ratio is preferably less than 1.20.

**[0042]** The bending properties of a steel sheet are affected by the Mn distribution in the surface layer of the steel sheet. Deformation during bending is larger in the surface layer of a steel sheet than in the center of the thickness of the steel sheet, and bending properties are controlled by the deformability in the surface layer of the steel sheet. However, it may not be possible to accurately measure the Mn distribution in the surface of the steel sheet and immediately beneath it due to the influence of surface oxidation of the steel sheet and other factors. Accordingly, in the present invention, the Mn concentration is measured at the above-described depth near the surface of the steel sheet to determine the Mn segregation ratio. Analysis by EPMA is preferably performed by measurement in an area sufficient to adequately evaluate local variations in the Mn distribution such as a rectangular region measuring 500 micrometers in the rolling direction by a total of 4 mm in a direction perpendicular to the rolling direction, as shown in the examples.

Plating Layer

**[0043]** A steel sheet according to the present invention can also be used as a surface-treated steel sheet by forming a plating layer on the surface of one or both sides thereof with the object of increasing corrosion resistance or the like.

**[0044]** The plating layer which is formed may be an electroplated layer or a hot-dip plated layer. Examples of an electroplated layer are an electroplated zinc layer and an electroplated Zn-Ni alloy layer. Examples of a hot-dip plated layer are a hot-dip galvanized (zinc) layer, a galvanized layer, a hot-dip aluminum plated layer, a hot-dip Zn-Al alloy plated layer, a hot-dip Zn-Al-Mg alloy plated layer, a hot-dip Zn-Al-Mg-Si alloy plated layer, and the like. The coating weight (or thickness) of these plated layers may be that typically used for this type of plated steel sheet. If desired, there may be two or more plated layers.

**[0045]** Next, a preferable manufacturing method for a steel sheet according to the present invention will be explained.

## Continuous Casting Step

**[0046]** Molten steel having the above-described chemical composition is prepared by a known melting method using a converter, an electric furnace, or the like. The molten steel is continuously cast to form a slab with a thickness of 200 - 300 mm under conditions such that the rate of solidification at a depth of 10 mm from the slab surface is 100 - 1000° C per minute.

Rate of solidification: 100 - 1000° C per minute

**[0047]** If the solidification rate at a depth of 10 mm from the slab surface in the continuous casting step is less than 100° C per minute, the primary dendrite arm spacing at a depth of 1/20 of the slab thickness from the slab surface cannot be refined, and segregation of Mn is not sufficiently prevented. As a result, it is sometimes not possible to improve the bending properties of a steel sheet. A solidification rate exceeding 1000° C per minute may induce surface cracking of the slab. Therefore, the solidification rate is at least 100° C per minute and at most 1000° C per minute.

Slab Thickness: 200 - 300 mm

**[0048]** If the slab thickness is less than 200 mm, it becomes difficult to guarantee an overall rolling reduction of at least 99.0 % in the below-described hot rolling and cold rolling. If the slab thickness exceeds 300 mm, it becomes difficult to guarantee an Mn segregation ratio of less than 1.30 at a depth of 1/20 of the sheet thickness from the surface of the steel sheet. Therefore, the slab thickness is at least 200 mm and at most 300 mm.

## Rolling Step

**[0049]** A slab obtained by the above-described continuous casting step is subjected to hot rolling to prepare a hot-rolled steel sheet, and then the hot-rolled steel sheet is subjected to cold rolling to obtain a cold-rolled steel sheet.

**[0050]** Preferably, a slab which is obtained by the continuous casting step is subjected to homogenization by holding in a temperature range of 1200 - 1350° C for at least 20 minutes and then to hot rolling with a finishing temperature of 800 - 950° C and a coiling temperature of 400 - 750° C to obtain a hot-rolled steel sheet. The hot-rolled steel sheet is then cold rolled to obtain a cold-rolled steel sheet, with the overall rolling reduction in hot rolling and cold rolling being at least 99.0 %.

**[0051]** Homogenization Temperature: 1200 - 1350° C, Duration of Homogenization: at least 20 minutes

**[0052]** By holding a slab to be subjected to hot rolling at a temperature of at least 1200° C for at least 20 minutes, a nonuniform structure caused by segregation of Mn is further eliminated and the bending properties of the steel sheet are further improved. The homogenization temperature is preferably at most 1350° C from the standpoints of suppressing scale loss, preventing damage to the heating furnace, and increasing productivity.

**[0053]** The duration of homogenization is more preferably at least 1.0 hours and at most 3 hours. By making the duration of homogenization at least 1.0 hours, the Mn segregation ratio can be made less than 1.20 and the bending properties of the steel sheet can be further improved. By making the duration of homogenization at most 3 hours, scale loss is suppressed and productivity can be increased which leads to a decrease in manufacturing costs.

Finishing Temperature: 800 - 950° C

**[0054]** If the finishing temperature of hot rolling is at least 800° C, the resistance to deformation during hot rolling can be made small and operations can more easily be carried out. If the finishing temperature is at most 950° C, flaws due to scale can be suppressed with greater certainty, and a good surface condition can be guaranteed.

Coiling Temperature: 400 - 750° C

**[0055]** If the coiling temperature in hot rolling is at least 400° C, the formation of hard bainite or martensite is suppressed, and subsequent cold rolling can be easily carried out. By making the coiling temperature at most 750° C, oxidation of the surface of a steel sheet is suppressed and a good surface condition can be guaranteed.

**[0056]** In a hot rolling step, a rough bar after rough rolling and before finish rolling is preferably heated by induction heating or the like so as to allow the rough bar to have a uniform temperature over its entire length, whereby variations in the properties of the steel sheet can be suppressed.

Overall Rolling Reduction in Hot Rolling and Cold Rolling: At least 99.0 %

**[0057]** The hot-rolled steel sheet which is obtained by the above-described hot rolling step usually undergoes descaling by a usual method such as pickling before it is subjected to cold rolling to obtain a cold-rolled steel sheet. The overall rolling reduction in the hot rolling and cold rolling is preferably at least 99.0 %. The overall rolling reduction is calculated using the following formula.

$$\text{Overall rolling reduction (\%)} = \{1 - (\text{thickness of cold-rolled steel sheet}) / (\text{thickness of slab subjected to hot rolling})\} \times 100$$

**[0058]** Surface irregularities in bent portions which develop after bending of a steel sheet are affected not only by the Mn segregation ratio but also by the thickness in the sheet thickness direction of Mn concentrated bands, which are ribbon-shaped regions in which Mn segregated portions which developed by segregation during solidification are elongated in the rolling direction in the subsequent rolling step. Decreasing the thickness of these Mn concentrated bands can suppress surface irregularities after working with greater certainty, and as a result, the bending properties of a steel sheet can be improved. For this purpose, it is effective to make the overall reduction at least 99.0 %.

**[0059]** The reduction in cold rolling is preferably at least 30 % in order to make the structure of a steel sheet after continuous annealing uniform. It is preferable from the standpoint of guaranteeing the flatness of a steel sheet that light rolling with a reduction of at most 5 % be carried out before or after pickling to rectify the shape. Carrying out this light rolling before pickling improves the processability of pickling so as to promote removal of elements which concentrate at the surface. As a result, adhesion of a plated layer is improved in the case of a hot-dip galvanized sheet or the surface condition is improved in the case of a cold-rolled steel sheet.

#### Continuous Annealing Step

**[0060]** A cold-rolled steel sheet obtained by the rolling step including the above-described hot rolling and cold rolling undergoes continuous annealing. The annealing temperature is preferably at least 750° C and at most 950° C. From the standpoint of productivity, the rate of temperature increase up to the recrystallization annealing temperature is preferably at least 1° C per second.

Annealing Temperature: 750 - 950° C

**[0061]** By making the annealing temperature at least 750° C, the possibility that an unrecrystallized structure remains is suppressed and a uniform structure can be obtained with certainty, which results in further improvements in bending properties. Making the annealing temperature at most 950° C suppresses damage to the annealing furnace and increases productivity.

**[0062]** The annealing time is preferably at least 10 seconds in order to completely remove an unrecrystallized structure and stably guarantee good bending properties. From the standpoint of productivity, the annealing time is preferably at most 300 seconds.

**[0063]** In order to limit the addition of alloying elements which lead to cost increases while guaranteeing a high tensile strength of at least 590 MPa, cooling after annealing is preferably carried out with an average cooling rate of at least 5° C per second in the region from 650° C to 550° C.

**[0064]** Temper rolling is preferably carried out on the steel sheet after annealing (after plating when hot-dip galvanizing has been carried out). Temper rolling can suppress the occurrence of yield elongation and prevent fouling and galling at the time of press forming. The elongation in temper rolling is preferably at least 0.05 % and at most 1 %.

#### Plating Step

**[0065]** When the surface of the steel sheet is subjected to hot-dip galvanizing, it is preferable that cooling after annealing in the annealing step be stopped at a temperature of at least 460° C and at most 550° C and that the annealed steel sheet be immediately immersed in a hot-dip plating bath to carry out continuous plating. If cooling after annealing is stopped at a temperature lower than 460° C, there is a large amount of heat dissipation at the time of immersion in the plating bath, as a result of which plating operation sometimes becomes difficult. If it is stopped at a temperature exceeding 550° C, plating operation sometimes becomes difficult.

**[0066]** Hot-dip galvanizing can be carried out by usual methods. For example, a steel sheet can be immersed in a hot-dip galvanizing bath at a temperature of at least 410° C and at most 490° C, and the coating weight of plating can

be controlled with a gas wiping nozzle or the like immediately after the steel sheet leaves the plating bath.

**[0067]** Alloying heat treatment to manufacture a galvanized steel sheet may be carried out on the resulting galvanized steel sheet after immersion in the hot-dip galvanizing bath. When alloying heat treatment is performed, a preferable temperature for alloying heat treatment is at least 460° C and at most 600° C. If this temperature is less than 460° C, portions which have not undergone alloying may develop and it becomes easy for the surface condition of the steel sheet to deteriorate. If the temperature for alloying heat treatment exceeds 600° C, powdering of the plating easily develops.

**[0068]** When manufacturing an electroplated steel sheet, a steel sheet which was cooled after annealing is electroplated in a conventional manner after it has been subjected to appropriate surface preparation treatment.

**[0069]** After hot-dip plating or electroplating, depending upon the use, conventional post-treatment (such as chemical conversion treatment, lubricating treatment, or the like) may be performed on the resulting plated steel sheet.

**[0070]** A manufacturing method according to the present invention can easily manufacture a steel sheet and a surface-treated steel sheet having a high strength while having excellent bending properties with an Mn segregation ratio at a depth of 1/20 of the sheet thickness from the surface of the steel sheet of less than 1.30.

#### Example 1

**[0071]** Steels having the chemical compositions shown in Table 1 were prepared by melting in a converter. Slabs having a thickness of 245 mm were then prepared by continuous casting such that the solidification rate at a depth of 10 mm from the surface of the slabs satisfied the conditions shown in Table 2.

**[0072]** The slabs were subjected to hot rolling under the conditions shown in Table 2 followed by pickling and then cold rolling under the conditions shown in Table 2 to obtain cold-rolled steel sheets with a thickness of 1.2 mm.

55 50 45 40 35 30 25 20 15 10 5

Tablet 1

Steel Type	Chemical composition (mass %, remainder. Fe and impurities)															
	C	Si	Mn	P	S	sol. Al	N	Bi	Ti	Nb	V	Cr	Mo	Cu	Ni	Other
A1	0.10	0.75	2.44	0.012	0.001	0.031	0.0039	0.0033	0.102							
B1	0.10	0.12	2.49	0.011	0.002	0.031	0.0046	0.0006	0.063	0.035						B:0.0013
C1	<u>0.02</u>	0.62	2.38	0.013	0.001	0.042	0.0043	0.0015	0.064							
D1	0.15	0.59	2.22	0.011	0.002	0.023	0.0028	tr.	0.061			0.51				
E1	0.10	0.36	2.43	0.011	0.001	0.032	0.0038	0.0053	0.072	0.042						
F1	0.12	0.10	<u>1.10</u>	0.012	0.001	0.031	0.0037	0.0022	0.053							
G1	0.15	0.20	1.68	0.010	0.002	0.038	0.0052	0.012	0.044	0.029						REM:0.0028
H1	0.12	0.87	2.12	0.012	0.001	0.032	0.0038	0.021	0.053		0.11					
I1	0.13	0.02	2.47	0.012	0.002	0.036	0.0041	0.016	0.074				0.17			
J1	0.16	0.45	2.42	0.012	0.001	0.036	0.0043	0.0083	0.045	0.092						
K1	0.07	0.03	2.40	0.011	0.001	0.15	0.0040	0.030	0.053				0.23			
L1	0.12	0.96	1.52	0.011	0.001	0.029	0.0047	0.0067								
M1	0.12	0.96	1.54	0.009	0.001	0.038	0.0052	tr.								
N1	0.10	1.42	2.02	0.009	0.002	0.037	0.0041	0.011								Mg:0.002
O1	0.03	1.42	1.74	0.014	0.001	0.035	0.0028	0.0042								
P1	0.14	1.32	2.05	0.011	0.001	0.028	0.0035	0.0097								Ca:0.002
Q1	0.09	0.01	2.53	0.011	0.001	0.028	0.0036	0.016								
R1	0.12	1.35	1.57	0.011	0.001	0.028	0.0041	0.017				0.25				
S1	0.09	0.74	2.11	0.013	0.002	0.025	0.0043	0.0004					0.17			
T1	0.09	0.03	2.53	0.011	0.001	0.028	0.0036	0.0072								
U1	0.10	0.32	1.01	0.010	0.001	0.029	0.0036	0.0038								
V1	0.06	1.22	1.63	0.011	0.002	0.038	0.0032	0.0006								
W1	0.07	0.52	2.13	0.021	0.002	0.031	0.0042	0.018								Mg:0.001
X1	<u>0.02</u>	0.21	1.54	0.013	0.003	0.036	0.0045	0.0047								

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(continued)

Steel Type	Chemical composition (mass %, remainder. Fe and impurities)															
	C	Si	Mn	P	S	sol. Al	N	Bi	Ti	Nb	V	Cr	Mo	Cu	Ni	Other
Y1	0.14	1.06	1.73	0.011	0.001	0.33	0.0047	0.011						0.22	0.62	
Z1	0.15	0.12	1.48	0.012	0.001	0.032	0.0042	0.0028								Zr:0.0042
A2	0.06	0.04	2.62	0.011	0.004	0.038	0.0032	0.0070					0.41			B:0.0016
B2	0.09	0.03	2.53	0.011	0.001	0.028	0.0036	0.0072								
C2	0.12	0.93	1.51	0.012	0.001	0.52	0.0039	0.0083								REM:0.0027
D2	0.06	0.22	2.42	0.013	0.002	0.038	0.0032	tr.								
E2	0.06	1.22	1.63	0.011	0.002	0.038	0.0032	0.0006								

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Table 2

	Test steel No.	Steel type	Solidification rate in continuous casting (°C/min)	Homogenization		Hot rolling		Reduction in cold rolling (%)	Overall rolling reduction (%)
				Temp. (°C)	Duration (min)	Finishing temp. (°C)	Coiling temp. (°C)		
5	1	A1	120	1250	150	900	600	50	99.5
10	2	B1	120	1250	90	900	600	50	99.5
	3	B1	120	1250	90	900	600	50	99.5
	4	B1	<u>93</u>	1250	90	900	600	50	99.5
15	5	C1	120	1250	150	900	600	50	99.5
	6	D1	130	1250	90	900	600	50	99.5
	7	E1	150	1250	90	900	600	50	99.5
20	8	E1	150	1250	90	900	600	50	99.5
	9	F1	140	1250	90	900	600	50	99.5
	10	G1	150	1250	90	900	600	50	99.5
25	11	H1	140	1250	90	900	600	50	99.5
	12	I1	150	1250	90	900	600	50	99.5
	13	I1	150	1250	90	900	600	50	99.5
30	14	J1	130	1250	90	900	600	50	99.5
	15	J1	130	1250	90	900	600	50	99.5
	16	K1	150	1250	90	900	600	50	99.5
35	17	L1	120	1250	90	900	600	50	99.5
	18	L1	<u>95</u>	1250	90	900	600	50	99.5
	19	M1	120	1250	90	900	600	50	99.5
40	20	N1	120	1250	90	900	600	50	99.5
	21	O1	120	1250	90	900	600	50	99.6
	22	P1	120	1250	90	900	600	50	99.5
45	23	Q1	120	1250	90	900	600	50	99.5
	24	R1	120	1250	90	900	600	50	99.5
	25	S1	120	1250	90	900	600	50	99.5
50	26	T1	120	1250	90	900	600	50	99.5
	27	T1	120	1250	90	900	600	50	99.5
	28	U1	120	1250	90	900	600	50	99.5
55	29	V1	120	1250	90	900	600	50	99.5
	30	W1	120	1250	90	900	600	50	99.5
	31	W1	120	1250	90	900	600	50	99.5
	32	X1	120	1250	90	900	600	50	99.5
	33	Y1	120	1250	90	900	600	50	99.5
	34	Y1	120	1250	30	900	600	50	99.5

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(continued)

Test steel No.	Steel type	Solidification rate in continuous casting (°C/min)	Homogenization		Hot rolling		Reduction in cold rolling (%)	Overall rolling reduction (%)
			Temp. (°C)	Duration (min)	Finishing temp. (°C)	Coiling temp. (°C)		
35	Z1	120	1250	90	900	600	50	99.5
36	A2	120	1250	150	900	600	50	99.5
37	B2	120	1250	90	900	600	50	99.5
38	B2	120	150	90	900	600	50	99.5
39	C2	120	1250	90	900	600	50	99.5
40	C2	120	1250	90	900	600	50	99.5
41	D2	120	1250	90	900	600	50	99.5
42	E2	120	1250	90	900	600	50	99.5

**[0073]** Test specimens for heat treatment were taken from the resulting cold-rolled steel sheets, and as shown in Table 3, the test specimens underwent heat treatment corresponding to the heat pattern in a continuous annealing apparatus or a hot-dip galvanizing apparatus.

Table 3

Test steel No.	Continuous annealing step						Heat treatment simulating continuous annealing equipment (cold rolled steel sheet)				Heat treatment simulating hot dip galvanized equipment (hot dip galvanized steel sheet)				Elongation in temper rolling (%)		
	Heating rate (°C/min)	Anneal-ing temp. (°C)	Anneal-ing time (s)	Slow cooling (°C/s)	Temp. at start of rapid cooling (°C)	Cooling rate (°C/s)	Stopping temp. (°C)	Holding temp. (°C)	Holding time (s)	Cooling rate after holding (°C/s)	Stopping temp. (°C)	Holding temp. (°C)	Holding time (s)	Immersion temp. (°C)		Alloying temp. (°C)	Cooling rate after heating (°C)
1	10	880	60	None		25	400	400	250	10							0.1
2	10	860	60	None		20	400	400	250	10							0.1
3	10	860	60	None		20					500	500	20	460	500	10	0.1
4	10	880	60	None		20	400	400	250	10							0.1
5	10	900	60	None		25	280	280	250	10							0.1
6	10	860	60	None		25	320	320	250	10							0.1
7	10	860	60	None		20	350	350	250	10							0.1
8	10	880	60	None		20					500	500	20	460	500	10	0.1
9	10	880	60	None		20	350	350	250	10							0.1
10	10	860	60	None		25	280	280	250	10							0.1
11	10	880	60	None		20	280	280	250	10							0.1
12	10	840	60	None		20	360	360	250	10							0.1
13	10	840	60	None		20					500	500	20	460	500	10	0.1
14	10	860	60	None		20	250	250	250	10							0.1
15	10	860	60	None		20					500	500	20	460	500	10	0.1
16	10	900	60	None		20					500	500	20	460	500	10	0.1
17	10	820	120	None		≥500	20	*300	200	10							0.1
18	10	860	120	None		≥500	20	*400	200	10							0.1
19	10	860	120	None		≥500	20	*400	200	10							0.1
20	10	860	120	3	670	≥500	20	*340	200	10							0.1
21	10	900	120	None		≥500	20	*200	200	10							0.1
22	10	775	120	None		≥500	20	*450	200	10							0.1
23	10	850	120	3	720	≥500	20	*300	200	10							0.1
24	10	820	120	None		≥500	20	*300	200	10							0.1
25	10	840	120	3	720	≥500	20	*420	200	10							0.1
26	10	850	30	None		20					500	500	40	460	500	10	0.1
27	10	850	30	None		20					500	500	40	460	500	10	0.1
28	10	780	30	None		10					500	500	40	460	500	10	0.1
29	10	820	30	4	700	20					500	500	40	460	500	10	0.1
30	10	820	30	None	700	10					500	500	40	460	500	10	0.1
31	10	820	30	None		10					500	500	40	460	500	10	0.1
32	10	820	30	None		10					500	500	40	460	500	10	0.1
33	10	810	30	None		10					500	500	40	460	500	10	0.1
34	10	810	30	None		10					500	500	40	460	500	10	0.1
35	10	790	30	4	700	25					500	500	40	460	500	10	0.1
36	10	850	30	None		30					500	500	40	460	500	10	0.1
37	10	850	60	6	700	50	260	260	350	10							0.1
38	10	850	60	3	700	50	360	360	300	10							0.1
39	10	850	60	None		50	220	220	300	10							0.1
40	10	820	60	3	700	50	400	400	400	10							0.1
41	10	850	60	3	700	50	230	230	500	10							0.1
42	10	800	60	3	700	50	340	340	350	10							0.1

\* After cooling was stopped, reheating to the holding temperature was carried out.

[0074] The Mn distribution in the resulting cold-rolled steel sheets for testing obtained under various manufacturing conditions (those which underwent heat treatment under the conditions shown in Table 3) was analyzed using an EPMA. A tensile test and a bending test in which the axis for bending was the rolling direction were performed on the cold-rolled

steel sheets for testing to evaluate mechanical properties.

# Test Methods

## 5 [Average Solidification Rate]

10 **[0075]** A cross section of each of the resulting slabs was etched with a pickling acid, and the secondary dendrite arm spacing  $\lambda$  (micrometers) at a depth of 10 mm from the surface skin of the slab was measured at 5 locations. Using the following equation, the cooling rate A from the liquidus temperature to the solidus temperature of the slab (°C per minute) was calculated from those values.

$$\lambda = 710 \times A^{-0.39}$$

## 15 [EPMA Analysis]

20 **[0076]** A sample for analysis was prepared from each cold-rolled steel sheet for testing by grinding and buffing the rolled surface of the steel sheet so as to expose a surface to be analyzed located at a depth of 1/20 of the sheet thickness from the rolled surface, and the Mn distribution was examined using an EPMA. A region which did not include MnS was selected, and using a beam diameter of 10 micrometers, the Mn concentration distribution was analyzed in an area which measured 500 micrometers in the rolling direction and a total of 4 mm in the direction perpendicular to the rolling direction and which was divided into sections with a width of 500 micrometers each in the direction perpendicular to the rolling direction by finding the average Mn concentration of each section. Using the resulting data of Mn concentration distribution, the Mn segregation ratio ( $Mn_{max}/n_{av}$ ) was calculated from the average Mn concentration ( $Mn_{av}$ ) and the maximum Mn concentration ( $Mn_{max}$ ).

## 25 [Tensile Test]

30 **[0077]** A ns No. 5 tensile test piece was taken from each cold-rolled steel sheet for testing in a direction perpendicular to the rolling direction and the tensile strength (TS) was measured.

## [Bending Test]

35 **[0078]** A bending test piece (40 mm wide x 100 mm long x 1.2 mm thick) in which the lengthwise direction was in the direction perpendicular to the rolling direction was taken from each cold-rolled steel sheet for testing so that the axis about which bending took place coincided with the rolling direction. The test piece was subjected to a 180° bending test with a steel sheet having a thickness of 2.4 mm being disposed on the inside of the bend (to make a bend with a radius of 1.0t), and it was visually ascertained whether cracking occurred. Cold-rolled steel sheets which did not undergo cracking were subjected to a 180° bending test with a steel sheet having a thickness of 1.2 mm being disposed on the inside of the bend (to make a bend with a radius of 0.5t) using a test piece which was taken in the same manner as described above, and visual observation for the occurrence of cracking was performed in the same manner. Cold-rolled steel sheets which did not undergo cracking in this test were subjected to a 180° bending test without disposing a steel sheet on the inside of the bend (a bending test with intimate contact and a bending radius of 0t), and it was ascertained in the same manner whether cracking took place.

45 **[0079]** The bending radius expressed as a function of the sheet thickness (t) was found by dividing the sheet thickness of the steel sheet disposed on the inside of the bend by two times the thickness of the bending test piece (2.4 mm), and the smallest bending radius ( $R_{min}$  shown in Table 4) for the cases in which cracking was not ascertained after the test was determined. When cracking was observed with a bending radius of 1.0t, the minimum bending radius was determined to be greater than 1.0t

## 50 [Surface Condition After Bending Deformation]

55 **[0080]** A bending test piece (40 mm wide x 60 mm long x 1.2 mm thick) in which the lengthwise direction was in the direction perpendicular to the rolling direction was taken from each cold-rolled steel sheet for testing from each cold-rolled steel sheet for which the minimum bending radius in the above-described bending test was at most 1.0t so that the axis for bending coincided with the rolling direction. Each test piece was subjected to a 90° V bending test by pressing a 90° punch having a radius of 1.2 mm at its end (to make a bend with a radius of 1.0t) against the test piece, and it was

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visually ascertained whether there were irregularities in the surface. The surface condition was evaluated as poor for samples having surface irregularities and good for samples with no surface irregularities. Cold-rolled steel sheets having a good surface condition and a minimum bending radius in the above-described bending test of at most 0.5t were further subjected to a 90° V bending test by pressing a 90° punch having a radius at its end of 0.6 mm (to make a bend with a radius of 0.5t) against a test piece taken in the same manner as described above, and it was visually observed whether there were irregularities in the surface. The surface condition was evaluated in the same manner as described above.

### Explanation of Test Results

**[0081]** The results of these tests are shown in Table 4.

Table 4

Test steel No.	Mn segregation ratio	TS (MPa)	R <sub>min</sub> in bending test	Surface condition after bending (bending radius = 1.0t)	Surface condition after bending (bending radius = 0.5t)	Category
1	1.14	876	0t	Good	Good	Inventive
2	1.27	853	0.5t	Good	Poor	Inventive
3	1.22	982	1.0t	Good	N.D.	Inventive
4	<u>1.39</u>	864	0.5t	<u>Poor</u>	N.D.	Comparative
5	1.19	<u>553</u>	0t	Good	Good	Comparative
6	<u>1.35</u>	982	0.5t	<u>Poor</u>	N.D.	Comparative
7	1.15	883	0t	Good	Good	Inventive
8	1.10	927	0.5t	Good	Good	Inventive
9	1.16	<u>565</u>	0t	Good	Good	Comparative
10	1.11	774	0t	Good	Good	Inventive
11	1.08	1035	0.5t	Good	Good	Inventive
12	1.08	984	0.5t	Good	Good	Inventive
13	1-12	1001	0.5t	Good	Good	Inventive
14	1.14	1022	0.5t	Good	Good	Inventive
15	1.15	983	0.5t	Good	Good	Inventive
16	1.06	987	0.5t	Good	Good	Inventive
17	1.12	1010	0.5t	Good	Good	Inventive
18	<u>1.32</u>	1032	1.0t	<u>Poor</u>	N.D.	Comparative
19	<u>1.30</u>	1021	<u>&gt;1.0t</u>	N.D.	N.D.	Comparative
20	1.14	1012	0.5t	Good	Good	Inventive
21	1.15	794	0t	Good	Good	Inventive
22	1.17	1009	0.5t	Good	Good	Inventive
23	1.12	983	0.5t	Good	Good	Inventive
24	1.12	986	0.5t	Good	Good	Inventive
25	1.23	1032	0.5t	Good	Poor	Inventive
26	1.12	725	0.5t	Good	Good	Inventive
27	1.14	751	0.5t	Good	Good	Inventive
28	1.17	<u>502</u>	0t	Good	Good	Comparative

(continued)

Test steel No.	Mn segregation ratio	TS (MPa)	$R_{\min}$ in bending test	Surface condition after bending (bending radius = 1.0t)	Surface condition after bending (bending radius = 0.5t)	Category
29	1.24	594	0.5t	Good	Poor	Inventive
30	1.15	621	0.5t	Good	Good	Inventive
31	1.16	632	0.5t	Good	Good	Inventive
32	1.12	<u>542</u>	0t	Good	Good	Comparative
33	1.17	793	0t	Good	Good	Inventive
34	1.23	804	0.5t	Good	Poor	Inventive
35	1.12	631	0.5t	Good	Good	Inventive
36	1.09	995	$\leq 0.5t$	Good	Good	Inventive
37	1.12	994	0.5t	Good	Good	Inventive
38	1.15	846	0t	Good	Good	Inventive
39	1.16	873	0t	Good	Good	Inventive
40	1.15	652	0t	Good	Good	Inventive
41	<u>1.31</u>	787	1.0t	Poor	N.D.	Comparative
42	1.24	702	0.5t	Good	Poor	Inventive
N.D.: Not determined.						

**[0082]** Test steels Nos. 1-3, 7, 8, 10 - 17, 20 - 27, 29 - 31, 33 - 40, and 42 in Table 4 are examples of the present invention which satisfy all the conditions of the present invention.

**[0083]** In contrast, test steels Nos. 4 and 18 had a solidification rate at a depth of 10 mm from the surface in the continuous annealing step which was below the lower limit prescribed by the present invention, so the Mn segregation ratio was greater than 1.30, and bending properties were poor or the surface condition after bending deformation was poor.

**[0084]** Test steels Nos. 6, 19, and 41 did not contain Bi, so the Mn segregation ratio was greater than 1.30, and bending properties were poor or the surface condition after bending deformation was poor.

**[0085]** Test steels Nos. 5, 9, 28, and 32 had a C content or an Mn content which was below the lower limit prescribed by the present invention, so a desired tensile strength was not obtained.

**[0086]** The steel sheets of the examples according to the present invention all had a tensile strength of at least 590 MPa, and the bending properties and the surface condition after bending deformation were good. In particular, for steel sheets of test steels Nos. 1, 7, 8, 10 - 17, 20 - 24, 26, 27, 30, 31, 33, and 35 - 40, the Bi content was in the above-described preferred range of at least 0.0010 % to at most 0.05 %, the homogenization temperature and the duration of homogenization were in the above-described preferred ranges of at least 1200° C to at most 1350° C and at least 1.0 hours to at most 3 hours, respectively, and the Mn segregation ratio was less than 1.20, so the tensile strength was at least 590 MPa and the bending properties were further improved.

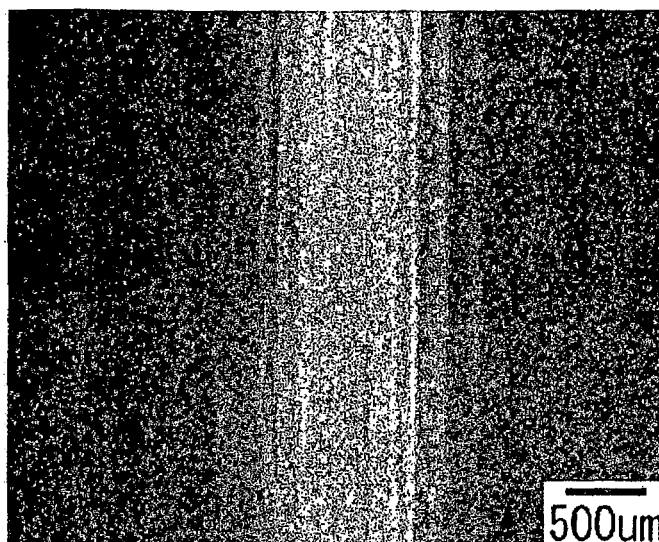
## Claims

1. A steel sheet **characterized by** having a chemical composition in which the content in mass percent of C, Si, Mn, P, S, sol. Al, N, Bi, Ti, Nb, V, Cr, Mo, Cu, Ni, Ca, Mg, REM, Zr, and B is C: 0.03 - 0.20 %, Si: 0.005 - 2.0 %, Mn: 1.2 - 3.5 %,  $P \leq 0.1$  %,  $S \leq 0.01$  %, sol. Al: 0.001 - 1.0 %,  $N \leq 0.01$  %, Bi: 0.0001 - 0.05 %, Ti: 0 - 0.3 %, Nb: 0 - 0.3 %, V: 0 - 0.3 %, Cr: 0 - 1 %, Mo: 0 - 1 %, Cu: 0 - 1 %, Ni: 0 - 1 %, Ca: 0-0.01 %, Mg: 0-0.01 %, REM: 0-0.01 %, Zr: 0-0.01 %, and B: 0-0.01 %, and by the Mn segregation ratio ( $Mn_{\max}/Mn_{av}$ ) calculated from the average Mn concentration ( $Mn_{av}$ ) and the maximum Mn concentration ( $Mn_{\max}$ ) at a depth of 1/20 of the sheet thickness from the surface of the steel sheet being less than 1.30.

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2. A steel sheet as set forth in claim 1 wherein the chemical composition contains, in mass percent, at least one of Ti: 0.003 - 0.3 %, Nb: 0.003 - 0.3 %, and V: 0.003 - 0.3 %.
3. A steel sheet as set forth in claim 1 or claim 2 wherein the chemical composition contains, in mass percent, at least one of Cr: 0.01 - 1 %, Mo: 0.01 - 1 %, Cu: 0.01 - 1 %, and Ni: 0.01 - 1 %.
4. A steel sheet as set forth in any one of claims 1 - 3 wherein the chemical composition contains, in mass percent, at least one of Ca: 0.0001 - 0.01 %, Mg: 0.0001 - 0.01 %, REM: 0.0001 - 0.01 %, and Zr: 0.0001 - 0.01 %.
5. A steel sheet as set forth in any one of claims 1 - 4 wherein the chemical composition contains, in mass percent, B: 0.0003 - 0.01 %.
6. A surface-treated steel sheet **characterized by** having a plating layer formed on the surface of at least one side of a steel sheet as set forth in any one of claims 1 - 5.
7. A method of manufacturing a steel sheet **characterized by** including the following steps (A) - (C):
  - (A) a continuous casting step in which a molten steel having a chemical composition as set forth in any one of claims 1 - 5 is cast to form a slab with a thickness of 200 - 300 mm under conditions such that the rate of solidification at a depth of 10 mm from the surface is of 100 - 1000° C per minute;
  - (B) a rolling step including hot rolling and cold rolling in which the slab obtained in the above-described continuous casting step is hot rolled to obtain a hot-rolled steel sheet and the hot-rolled steel sheet is then cold rolled to obtain a cold-rolled steel sheet; and
  - (C) a continuous annealing step in which the cold-rolled steel sheet obtained in the rolling step is subjected to recrystallization annealing in a temperature range of 750 - 950° C.
8. A method of manufacturing a surface-treated steel sheet in that the steel sheet obtained by the manufacturing method set forth in claim 7 is subjected to plating which forms a plating layer on the surface of at least one side of the steel sheet.

Fig. 1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/069464

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> C22C38/00(2006.01)i, B21B3/00(2006.01)i, B22D11/00(2006.01)i, C21D9/46 (2006.01)i, C22C38/06(2006.01)i, C22C38/58(2006.01)i  According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>  Minimum documentation searched (classification system followed by classification symbols) C22C38/00, B21B3/00, B22D11/00, C21D9/46, C22C38/06, C22C38/58  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 1996-2010 Kokai Jitsuyo Shinan Koho 1971-2010 Toroku Jitsuyo Shinan Koho 1994-2010  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2008-274379 A (Kobe Steel, Ltd.), 13 November 2008 (13.11.2008), (Family: none)	1-8
A	JP 2007-197763 A (Kobe Steel, Ltd.), 09 August 2007 (09.08.2007), (Family: none)	1-8
A	JP 2007-70649 A (Nippon Steel Corp.), 22 March 2007 (22.03.2007), (Family: none)	1-8
A	JP 2007-70659 A (Nippon Steel Corp.), 22 March 2007 (22.03.2007), (Family: none)	1-8
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 18 February, 2010 (18.02.10)		Date of mailing of the international search report 02 March, 2010 (02.03.10)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- JP 62013533 A [0012]
- JP 2004211126 A [0012]
- JP 2004250774 A [0012]
- JP 2002161336 A [0012]
- JP 2002322539 A [0012]
- JP 4191322 A [0012]
- JP 2007070649 A [0012]
- JP 2007070659 A [0012]