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# (54) STEEL SHEET FOR CAN, AND PROCESS FOR PRODUCING SAME

(57) The present invention relates to a high-strength high-formability steel sheet for a can and a method for manufacturing the same. The steel sheet is characterized by containing C: 0.070% or more and less than 0.080%, Si: 0.003% or more and 0.10% or less, Mn: 0.51% or more and 0.60% or less, and the like, on a percent by mass basis, wherein in a cross-section in the rolling direction, the average grain size is 5  $\mu m$  or more, the grain elongation rate is 2.0 or less, the difference in hardness determined by subtracting an average Vickers hardness of a cross-section between the surface and a depth of one-eighth of the sheet thickness from an average Vickers hardness of a cross-section between a depth of three-

eighths of the sheet thickness and a depth of four-eighths of the sheet thickness is 10 points or more and/or the difference in hardness determined by subtracting a maximum Vickers hardness of a cross-section between the surface and a depth of one-eighth of the sheet thickness from a maximum Vickers hardness of a cross-section between a depth of three-eighths of the sheet thickness and a depth of four-eighths of the sheet thickness is 20 points or more, the tensile strength is 500 MPa or more, and the elongation after fracture is 10% or more. This high-strength high-formability steel sheet for a can is suitable for a material of an easy open can.

## Description

Technical Field

<sup>5</sup> **[0001]** The present invention relates to a steel sheet for a can having high strength and high formability and a method for manufacturing the same.

**Background Art** 

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10 [0002] Among steel sheets used for beverage cans and food cans, steel sheets referred to as DR (Double Reduce) materials may be used for ends, bottoms, bodies of three-piece cans, drawn cans and the like. Regarding the DR material, cold rolling is performed again (secondary cold rolling) after annealing and, therefore, the sheet thickness can be reduced easily as compared with a SR (Single Reduce) material, where only temper rolling with a small reduction ratio is performed, and it is possible to reduce the can production cost by using a thin steel sheet. The DR material is a thin hard steel sheet because work hardening occurs by applying cold rolling after annealing. However, the DR material has low with the SR material.

**[0003]** Meanwhile, EOE (Easy Open End) has been used widely as ends for beverage cans and food cans. In production of EOE, it is necessary that a rivet to attach a tab is formed through punch stretch forming and draw forming, and the elongation of the material required for this forming corresponds to the ductility of about 10% in a tensile test.

**[0004]** Furthermore, regarding the body material for a three- piece beverage can, after forming into the shape of a tube, flange forming is applied to both ends to perform seaming of a end and a bottom. Therefore, can body end portions are required to have the ductility of about 10% likewise.

**[0005]** Meanwhile, a steel sheet serving as a raw material for producing a can is required to have strength in accordance with the sheet thickness. In the case of the DR material, a tensile strength of about 500 MPa or more is required in order to ensure the can strength because the thickness is reduced.

**[0006]** It is difficult for the previously used DR material to ensure both the above- described elongation and the strength and, therefore, the SR material has been used as the body material for EOE and the beverage can. However, at present, from the viewpoint of cost reduction, demands for application of the DR material to the body material for EOE and the beverage can have also been intensified. Furthermore, this material can also be used as a raw material of the steel sheet for cans, e.g., two- piece can bodies, DI (Drawn and Ironed) cans, DRD (Draw- redraw) cans, aerosol cans, and bottom ends.

[0007] In consideration of them, Patent Literature 1 discloses a method for manufacturing a steel sheet having a high r value and excellent flange formability by producing a DR material from low-carbon steel with a primary cold reduction ratio of 85% or less.

**[0008]** Patent Literature 2 discloses a method for manufacturing a DR material, wherein the compatibility between the hardness and the formability is ensured by applying a nitriding treatment in a low-carbon steel annealing step.

**[0009]** Patent Literature 3 discloses a method for manufacturing a end for an easy open can, wherein scoring is performed in such a way that the ratio of score residual thickness/steel sheet thickness becomes 0.4 or less through the use of a thin steel sheet which has a sheet thickness of less than 0.21 mm and which is produced by subjecting a steel slab containing C: 0.01% to 0.08%, Mn: 0.05% to 0.50%, and Al: 0.01% to 0.15% to hot finish rolling at a temperature lower than or equal to the Ar<sub>3</sub> transformation temperature, then performing cold rolling, subsequently effecting recrystallization annealing through continuous annealing, and thereafter, performing skin pass rolling with a reduction ratio of about 5% to 10%.

**[0010]** Patent Literature 4 discloses a continuous annealing DR steel sheet for a welded can and a manufacturing method, wherein the steel sheet contains C: 0.04% to 0.08%, Si: 0.03% or less, Mn: 0.05% to 0.50%, P: 0.02% or less, S: 0.02% or less, Al: 0.02% to 0.10%, and N: 0.008% to 0.015%, the amount of (N total - N as AIN) in the steel sheet is 0.007% or more, and in the case where the relationship of X  $\geq$  10% and Y  $\geq$  -0.05X + 1.4 are satisfied, where a total ductility value in the rolling direction is represented by X and the average value is represented by Y, the steel sheet has excellent flange formability better than or equal to that of a batch annealing DR steel sheet.

Citation List

Patent Literature

<sup>55</sup> [0011]

PTL 1: Japanese Unexamined Patent Application Publication No. 63-7336

PTL 2: Japanese Unexamined Patent Application Publication No. 2004-323905

- PTL 3: Japanese Unexamined Patent Application Publication No. 62-96618
- PTL 4: Japanese Unexamined Patent Application Publication No. 2007-177315

Summary of Invention

**Technical Problem** 

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[0012] However, all the above- described conventional technologies have problems as described below.

**[0013]** Regarding the manufacturing method described in Patent Literature 1, it is necessary to reduce the primary cold reduction ratio and, therefore, very thin steel sheet cannot be produced because of the limited finish thickness of hot rolling. If the finish thickness of hot rolling is reduced, the finish rolling temperature is lowered, so that it is difficult to keep at a predetermined temperature.

**[0014]** Regarding the manufacturing method described in Patent Literature 2, it is necessary to apply the nitriding treatment after recrystallization is completed. Therefore, even in the case where the nitriding treatment is applied in the continuous annealing step, cost increases, e.g., a reduction in line speed and an increase in furnace length, are not avoided.

**[0015]** Regarding the manufacturing methods described in Patent Literature 3 and Patent Literature 4, the amount of Mn is controlled to a low level of 0.05 to 0.50 percent by weight. Consequently, it is not possible to respond to an increase in strength to ensure pressure-resistant strength against thickness reduction.

**[0016]** The present invention has been made in consideration of such circumstances, and it is an object to provide a high-strength high-formability steel sheet for a can and a method for manufacturing the same, wherein the steel sheet can be applied to ends, bottoms, three-piece can bodies, two-piece can bodies, DI cans, DRD cans, aerosol cans, and bottom ends and, in particular, is suitable for a material of EOE. Solution to Problem

[0017] The gist of the present invention is as described below.

[0018] A first invention is a high-strength high-formability steel sheet for a can, characterized by containing C: 0.070% or more and less than 0.080%, Si: 0.003% or more and 0.10% or less, Mn: 0.51% or more and 0.60% or less, P: 0.001% or more and 0.100% or less, S: 0.001% or more and 0.020% or less, Al: 0.005% or more and 0.100% or less, N: 0.010% or less, and the remainder composed of Fe and incidental impurities, on a percent by mass basis, wherein in a cross-section in the rolling direction, the average grain size is 5  $\mu m$  or more, the grain elongation rate is 2.0 or less, the difference in hardness determined by subtracting an average Vickers hardness of a cross-section between the surface and a depth of one-eighth of the sheet thickness from an average Vickers hardness of a cross-section between a depth of three-eighths of the sheet thickness and a depth of four-eighths of the sheet thickness of a cross-section between the surface and a depth of one-eighth of the sheet thickness from a maximum Vickers hardness of a cross-section between the surface and a depth of one-eighth of the sheet thickness from a maximum Vickers hardness of a cross-section between a depth of three-eighths of the sheet thickness and a depth of four-eighths of the sheet thickness is 20 points or more, the tensile strength is 500 MPa or more, and the elongation after fracture is 10% or more.

[0019] A second invention is the high-strength high-formability steel sheet for a can, according to the first invention, characterized in that regarding the above-described grain size, the difference in average grain size determined by subtracting an average grain size between a depth of three-eighths of the sheet thickness and a depth of four-eighths of the sheet thickness from an average grain size between the surface and a depth of one-eighth of the sheet thickness is 1  $\mu$ m or more.

**[0020]** A third invention is the high-strength high-formability steel sheet for a can, according to the first invention or the second invention, characterized in that regarding the above-described amount of nitrogen, the difference in average amount of N determined by subtracting an average amount of N between the surface and a depth of one-eighth of the sheet thickness from an average amount of N between a depth of three-eighths of the sheet thickness and a depth of four-eighths of the sheet thickness is 10 ppm or more.

**[0021]** A fourth invention is the high-strength high-formability steel sheet for a can, according to any one of the first invention to the third invention, characterized in that regarding nitrides having a diameter of 1  $\mu$ m or less and 0.02  $\mu$ m or more, the average nitride number density between the surface and a depth of one-quarter of the sheet thickness is larger than the average nitride number density between the surface and a depth of one-eighth of the sheet thickness.

[0022] A fifth invention is the high-strength high-formability steel sheet for a can, according to any one of the first invention to the fourth invention, characterized in that regarding the above-described nitrides having a diameter of 1  $\mu$ m or less and 0.02  $\mu$ m or more, the value obtained by dividing the average nitride number density between the surface and a depth of one-twentieth of the sheet thickness by the average nitride number density between the surface and a depth of one-quarter of the sheet thickness is less than 1.5.

**[0023]** A sixth invention is the high-strength high-formability steel sheet for a can, according to any one of the first invention to the fifth invention, characterized in that regarding the above-described amount of carbon, the amount of solid solution C in the steel is 51 ppm or more.

**[0024]** A seventh invention is a method for manufacturing a high-strength high-formability steel sheet for a can, characterized by including the steps of slabbing a steel containing C: 0.070% or more and less than 0.080%, Si: 0.003% or more and 0.10% or less, Mn: 0.51% or more and 0.60% or less, P: 0.001% or more and 0.100% or less, S: 0.001% or more and 0.020% or less, Al: 0.005% or more and 0.100% or less, N: 0.010% or less, and the remainder composed of Fe and incidental impurities, on a percent by mass basis, through continuous casting, performing hot rolling so as to coil at a temperature lower than 620°C, performing rolling with a primary cold reduction ratio of 86% or more in total and a cold reduction ratio of a final stand in primary cold rolling of 30% or more, performing annealing in an atmosphere containing less than 0.020 percent by volume of ammonia gas, and performing secondary cold rolling with a reduction ratio of 20% or less. Advantageous Effects of Invention

**[0025]** According to the present invention, the high-strength high-formability steel sheet for a can having a tensile strength of 500 MPa or more and an elongation after fracture of 10% or more can be obtained. As a result, the formability of the steel sheet is improved and, thereby, cracking does not occur during rivet forming of EOE and flange formability of the three-piece can, it becomes possible to produce a can from the DR material having a small thickness, and significant thickness reduction of the steel sheet for a can is achieved.

Description of Embodiments

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[0026] In order to solve the above-described problems, the inventors conducted intensive research and obtained the following findings.

**[0027]** In order to ensure the elongation with respect to a high-strength material, it is possible to ensure compatibility between the strength and the elongation by adding an appropriate amount of C so as to give strength, introducing a strain into a surface layer while the reduction ratio of the final stand in primary cold rolling is improved, allowing ferrite grains in the surface layer to become coarse through annealing while an ammonia gas in the annealing atmosphere is limited to less than 0.020 percent by volume to suppress nitridation of the surface layer, and allowing the surface of the steel sheet to become mild while the secondary cold reduction ratio is limited in an appropriate range.

**[0028]** Furthermore, if the coiling temperature after hot rolling is high, precipitated cementite becomes coarse and a local ductility is reduced. Therefore, it is also necessary to limit the coiling temperature to an appropriate temperature range.

[0029] In this regard, in the present specification, all components of steel indicated in % are on a percent by mass basis. Meanwhile, a depth of three-eighths of the sheet thickness refers to a position at a distance of three-eighths of the sheet thickness from the surface in the direction of the center of the film thickness. The same goes for the others, that is, a depth of four-eighths of the sheet thickness, a depth of one-eighth of the sheet thickness, a depth of one-quarter of the sheet thickness, and a depth of one-twentieth of the sheet thickness.

**[0030]** The present invention will be described below in detail. The steel sheet for a can according to the present invention is a high-strength high-formability steel sheet for a can having a tensile strength of 500 MPa or more and an elongation after fracture of 10% or more. Then, such a steel sheet can be produced by using a steel containing 0.070% or more and less than 0.080% of C and specifying the coiling temperature after hot rolling and the secondary cold reduction ratio to be appropriate conditions.

[0031] The component composition of the steel sheet for a can according to the present invention will be described. [0032] C: 0.070% or more and less than 0.080%

Regarding the steel sheet for a can according to the present invention, the ductility is ensured by reducing the secondary cold reduction ratio, while high strength is exerted by specifying the amount of C to be somewhat high. If the amount of C is less than 0.070%, the tensile strength of 500 MPa required for obtaining significant economic effect based on a thickness reduction of the steel sheet is not obtained. Therefore, the amount of C is specified to be 0.070% or more.

Meanwhile, if the amount of C is 0.080% or more, the steel sheet becomes too hard, and it becomes impossible to produce a thin steel sheet through secondary cold rolling while the formability is held ensured. Therefore, the upper limit of the amount of C is specified to be less than 0.080%.

[0033] Si: 0.003% or more and 0.10% or less

If the amount of Si exceeds 0.10%, problems, e.g., reduction in surface-treatability and degradation of corrosion resistance, are brought about. Therefore, the upper limit is specified to be 0.10%. Meanwhile, a smelting cost becomes too high to achieve less than 0.003%. Therefore, the lower limit is specified to be 0.003%.

**[0034]** Mn: 0.51% or more and 0.60% or less

Manganese has functions of preventing hot shortness due to S during hot rolling and making crystal grains finer and is an element necessary for ensuring desirable material properties. Furthermore, in order to satisfy the can strength with a material having a reduced thickness, it is necessary to increase the strength of the material. In order to respond to this increase in strength, a required amount of addition of Mn is 0.51% or more. On the other hand, if Mn is added too much, the corrosion resistance is degraded and the steel sheet becomes hard excessively. Therefore, the upper limit is specified to be 0.60%.

[0035] P: 0.001% or more and 0.100% or less

Phosphorus is a harmful element which makes the steel hard, which degrades the formability and, at the same time, which degrades even the corrosion resistance. Therefore, the upper limit is specified to be 0.100%. Meanwhile, if P is specified to be less than 0.001%, a dephosphorization cost is too large. Therefore, the lower limit is specified to be 0.001%.

[0036] S: 0.001% or more and 0.020% or less

Sulfur is a harmful element which is present as an inclusion in the steel and which causes reduction in the elongation and degradation of the corrosion resistance. Therefore, the upper limit is specified to be 0.020%. Meanwhile, if S is specified to be less than 0.001%, a desulfurization cost is too large. Therefore, the lower limit is specified to be 0.001%. [0037] Al: 0.005% or more and 0.100% or less

Aluminum is an element necessary as a deoxidizer in steel making. If the amount of addition is small, deoxidation becomes insufficient, inclusions increase, and the formability is degraded. In the case where the content is 0.005% or more, it is assumed that deoxidation is performed sufficiently. Meanwhile, if the content exceeds 0.100%, the frequency of occurrence of surface defects resulting from alumina clusters and the like increases. Therefore, the amount of Al is specified to be 0.005% or more and 0.100% or less.

15 [0038] N: 0.010% or less

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If large amounts of N is added, hot elongation is degraded and cracking of slab occurs in continuous casting. Therefore, the upper limit is specified to be 0.010%. Meanwhile, if the amount of N is specified to be less than 0.001%, a smelting cost is too large. Therefore, it is preferable that the amount of N is specified to be 0.001% or more. In this regard, the remainder is specified to be Fe and incidental impurities.

[0039] Next, the mechanical properties of the steel sheet for a can according to the present invention will be described. [0040] The tensile strength is specified to be 500 MPa or more. If the tensile strength is less than 500 MPa, the thickness of the steel sheet cannot be reduced to the extent that a significant economic effect is obtained because the strength of the steel sheet serving as a raw material for can production is ensured. Therefore, the tensile strength is specified to be 500 MPa or more.

[0041] The elongation after fracture is specified to be 10% or more. If the elongation after fracture is less than 10%, cracking occurs in rivet forming in the case of application to EOE. Moreover, in the case of application to a three-piece can body as well, cracking occurs in flange forming. Therefore, the elongation after fracture is specified to be 10% or more.

[0042] In this regard, the above-described tensile strength and the above-described elongation after fracture can be measured by the method of tensile test for metallic materials shown in "JIS Z 2241".

[0043] Next, crystal grains of the steel sheet for a can according to the present invention will be described.

[0044] The average grain size in a cross-section in the rolling direction is specified to be 5  $\mu$ m or more. The state of crystal grains has a large influence on the final mechanical properties of the steel sheet for a can according to the present invention. If the average grain size in a cross-section in the rolling direction is less than 5  $\mu$ m, the ductility of the steel sheet is insufficient and the formability is impaired.

**[0045]** Furthermore, the grain elongation rate in a cross- section in the rolling direction is specified to be 2.0 or less. The elongation rate refers to a value representing the degree of elongation of ferrite grain due to forming, as shown in "JIS G 0202". If the grain elongation rate in a cross- section in the rolling direction is more than 2.0, the ductility in the direction perpendicular to the rolling direction, which is important for the flange formability and the neck formability, is insufficient. Although the elongation rate increases along with secondary cold reduction ratio, it is necessary that the steel contains 0.070% or more of C in order to control to the above- described elongation rate while the secondary cold reduction ratio is up to about 20%. That is, if the C is less than 0.070%, the number of cementite grains precipitated after hot rolling is reduced and, as a result, much of solid solution C remains. The solid solution C suppresses growth of grains during annealing and, thereby, the shapes of crystal grains flattened through primary cold rolling remain and the elongation rate increases.

In this regard, the above- described average grain size in a cross- section in the rolling direction and the above- described grain elongation rate in a cross- section in the rolling direction can be measured by micrographic determination of the apparent grain size shown in "JIS G 0551".

**[0046]** By the way, in the case where there is no remark, the surface and the back of the steel sheet are not specifically distinguished.

[0047] The Vickers hardness can be measured by the test method for hardness shown in "JIS Z 2244". The Vickers hardness test with a load of 10 gf is performed in such a way that the hardness distribution in a steel sheet cross-section in the sheet thickness direction can be evaluated appropriately. The measurement is performed at 10 places each, and an average value of the measured values is specified to be the average hardness of each cross-section. In this regard, a maximum of the Vickers hardness measurement is specified to be a cross-section Vickers maximum hardness.

**[0048]** Regarding difference in hardness: 10 points or more and 20 points or more In the case where a surface layer is made hard, the strength increases. However, a mild center layer is sandwiched between hard surface layers and, thereby, the whole sheet is constrained, the ductility is reduced, constriction occurs easily, and the formability is degraded. In the case where the surface layer is mild and the center layer is hard, only the

center layer of the sheet is constrained and, therefore, a high-strength high-formability steel sheet is obtained, wherein the strength is high, and reduction of ductility and constriction do not occur. If a difference in cross-section average hardness is less than 10 points and/or the cross-section maximum hardness is less than 20 points, the whole sheet has a uniform hardness and, therefore, there is no difference from a current material and a high-strength high-formability steel sheet cannot be obtained. The tensile strength of 500 MPa or more and the elongation after fracture of 10% can be achieved by specifying the difference in cross-section average hardness to be 10 points or more and/or the cross-section maximum hardness to be 20% or more.

[0049] Difference in average grain size: 1  $\mu$ m or more

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Regarding the above-described grain size of the high-strength high-formability steel sheet for a can according to the present invention, it is preferable that a difference in average grain size determined by subtracting an average grain size between a depth of three-eighths of the sheet thickness and a depth of four-eighths of the sheet thickness from an average grain size between the surface and a depth of one-eighth of the sheet thickness is 1  $\mu$ m or more. This is because in the case where the difference in average grain size is 1 µm or more, a steel sheet having excellent characteristics ensuring the compatibility between the strength and the elongation can be obtained. In this regard, the ductility is improved because of enhance of mildness due to the large grain size at a depth of one-eighth of the sheet thickness, and the small grain size between a depth of three-eighths of the sheet thickness and a depth of four-eighths of the sheet thickness contributes to hardness and high strength. Consequently, the compatibility between the high strength and the elongation is ensured, and the tensile strength of 500 MPa or more and the elongation after fracture of 10% can be achieved easily. [0050] Regarding the average amount of N between a depth of three-eighths of the sheet thickness and a depth of four-eighths of the sheet thickness, the amount of N of a sample which had been subjected to electrolytic polishing up to the depth of three-eighths of the sheet thickness was measured by using a combustion method. Regarding the average amount of N between the surface and a depth of one-eighth of the sheet thickness, after one surface of a sample was sealed with a tape, chemical polishing was performed from the surface up to the depth of one-eighth of the sheet thickness with oxalic acid, and the amount of N of the remaining sample was measured by using a combustion method.

[0051] Regarding difference in average amount of N: 10 ppm or more

If the difference in average amount of N is less than 10 ppm, the whole sheet has a uniform amount of N and, therefore, a significant enhancement of mildness due to reduction in the amount of N of the surface layer cannot be expected. However, in the case where the difference in average amount of N is specified to be 10 ppm or more, the mildness of the surface layer is enhanced because the amount of N is small and, thereby, solid solution N contributing to solution strengthening is small, whereas the center layer has a large amount of N and is hard, so that the compatibility between the high strength and the elongation is ensured and the tensile strength of 500 MPa or more and the elongation after fracture of 10% or more can be achieved easily. Consequently, a high-strength high-formability steel sheet is obtained easily.

[0052] Regarding the nitride number density, after chemical polishing with oxalic acid or the like was performed up to a predetermined position, electrolysis of 10  $\mu$ m was performed by using a SPEED method to produce an extraction replica, and the number of nitrides per unit field of view 1  $\mu$ m square was measured with TEM. The nitrides were analyzed with EDX, so as to be identified.

[0053] Furthermore, regarding nitrides having a diameter of 1  $\mu$ m or less and 0.02  $\mu$ m or more, it is preferable that the average nitride number density between the surface and a depth of one- quarter of the sheet thickness is larger than the average nitride number density between the surface and a depth of one- eighth of the sheet thickness. This is because if the the average nitride number density between the surface and a depth of one- eighth of the sheet thickness is small, fine precipitates are low in number, so as to enhance the mildness, and if the average nitride number density between the surface and a depth of one- quarter of the sheet thickness is large, fine precipitates are high in number, so as to become hard on the basis of precipitation strengthening, so that the compatibility between the high strength and the elongation is ensured and the tensile strength of 500 MPa or more and the elongation after fracture of 10% or more can be achieved easily.

[0054] Regarding average nitride number density ratio: 1.5 or less

If the average nitride number density ratio is 1.5 or more, the nitride number density of the surface layer increases and precipitation strengthening due to nitrides occurs, so that significant enhancement of mildness is not expected. However, the tensile strength of 500 MPa or more and the elongation after fracture of 10% or more can be achieved easily by specifying the average nitride number density ratio to be less than 1.5. Consequently, a high-strength high-formability steel sheet is obtained easily.

[0055] The amount of solid solution C was calculated from a peak of internal friction. The internal friction was measured with a torsional vibration type internal friction measuring apparatus produced by Vibran, where the shape of a test piece was 1 mm  $\times$  1 mm  $\times$  80 mm, the measurement frequency was 0.001 to 10 Hz, and the temperature was 0°C, background of the measured data was removed and, thereafter, Q-1 of the peak value was read. Calculation was performed from Q-1 and a calibration curve. If the amount of solid solution C in the steel is large, the strength increases on the basis of strengthening due to solid solution C, and the ductility increases because the amount of carbide serving as a start point

of fracture is reduced.

[0056] Next, a method for manufacturing a steel sheet for a can according to the present invention will be described. The high- strength high- formability steel sheet for a can, according to the present invention, is produced by using a steel slab which is produced through continuous casting and which has the above- described composition, performing hot rolling so as to coil at a temperature lower than 620°C, performing rolling with a primary cold reduction ratio of 86% or more and a cold reduction ratio of a final stand in primary cold rolling of 30% or more, performing annealing in an atmosphere containing less than 0.020 percent by volume of ammonia gas, and performing secondary cold rolling with a reduction ratio of 20% or less.

[0057] It is usually difficult to obtain a small sheet thickness, which exerts a significant economic effect, by only one time of cold rolling. That is, to obtain a small sheet thickness by one time of cold rolling applies an excessive load to a rolling mill, and is impossible depending on the equipment capacity. For example, in the case where the final sheet thickness is specified to be 0.15 mm, if the sheet thickness after hot rolling is specified to be 2.0 mm, a large primary cold reduction ratio of 92.5% is required.

[0058] Meanwhile, in order to reduce the sheet thickness after the cold rolling, it is considered to perform rolling at the stage of hot rolling in such a way as to have a thickness smaller than usual. However, if the reduction ratio in the hot rolling increases, the temperature of the steel sheet during the rolling decreases significantly, so that a predetermined finish rolling temperature is not obtained. Furthermore, if the sheet thickness before the annealing is reduced, in the case where continuous annealing is applied, the possibility of an occurrence of a trouble, e.g., fracture or deformation, of a steel sheet during the annealing increases. For these reasons, in the present invention, a secondary cold rolling is applied after the annealing, so as to obtain a very thin steel sheet.

Coiling temperature after hot rolling: lower than 620°C

If the coiling temperature after the hot rolling is 620°C or higher, formed pearlite microstructures become coarse, and these serve as start points of brittle fracture. Therefore, local ductility is reduced and the elongation after fracture of 10% or more is not obtained. Therefore, the coiling temperature after the hot rolling is specified to be lower than 620°C. More preferably, the coiling temperature is 560°C to 620°C.

[0060] Primary cold reduction ratio: 86% or more

In the case where the primary cold reduction ratio is small, in order to obtain a very thin steel sheet finally, it is necessary to increase the reduction ratios in hot rolling and cold rolling. It is not preferable to increase the hot reduction ratio because of the above-described reason, and it is necessary that the secondary cold reduction ratio is limited for the reason described below. For the above-described reasons, if the primary cold reduction ratio is specified to be less than 86%, production is difficult. Therefore, the primary cold reduction ratio is specified to be 86% or more. More preferably, 90% to 92% is employed.

[0061] Reduction ratio of final stand in primary cold rolling: 30% or more

In order to make the surface layer of the steel sheet coarse grains so as to enhance mildness, it is necessary to increase the reduction ratio of a final stand to introduce a strain into the steel sheet surface layer and, thereby, facilitate growth of ferrite grains during annealing. In order to make the grain size of the surface layer coarse by 1 µm as compared with that of the center layer, it is necessary that the reduction ratio of a final stand in primary cold rolling is specified to be 30% or more.

# [0062] Annealing

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40 Regarding annealing, in order to suppress nitridation of the surface layer, it is necessary to specify the ammonia gas concentration in the atmosphere to be less than 0.020 percent by volume. Preferably, 0.018 percent by volume or less is employed, and more preferably 0.016 percent by volume or less is employed. Furthermore, it is necessary that recrystallization is completed through annealing. It is preferable that the soaking temperature is specified to be 600°C to 750°C from the viewpoint of the operation efficiency and prevention of fracture of the thin steel sheet during annealing. 45

[0063] Secondary cold reduction ratio: 20% or less

The secondary cold reduction ratio is specified to be 20% or less. If the secondary cold reduction ratio is more than 20%, work hardening due to secondary cold rolling becomes excessive, and the elongation after fracture of 10% or more is not obtained. Therefore, the secondary cold reduction ratio is specified to be 20% or less. Preferably, 15% or less is employed, and more preferably, 10% or less is employed.

50 [0064] After the secondary cold rolling, steps of coating and the like are performed in the usual manner, so as to complete a steel sheet for a can.

#### **EXAMPLES**

55 [0065] A steel having the component composition as shown in Table 1, where the remainder was Fe and incidental impurities, was prototyped, and a steel slab was obtained through casting. The resulting steel slab was reheated at 1,250°C and, thereafter, hot rolling and primary cold rolling were applied under the condition shown in Table 2. The finish rolling temperature of the hot rolling was specified to be 890°C, and pickling was applied after the rolling. Subse-

quently, after the primary cold rolling, continuous annealing at a soaking temperature of 630°C and a soaking time of 25 seconds and secondary cold rolling under the condition shown in Table 2 were applied. Both surfaces of the steel sheet obtained as described above was subjected to Sn coating continuously, so as to obtain a tin plate with an amount of adhesion of Sn of 2.8 g/m² per one surface. The test results are shown in Table 2 and Table 3. In this regard, in Table 3, the grain size, the amount of N, and the nitride number density refers to the average grain size, the average amount of N, and the average nitride number density, respectively. [0066]

Table 1

No		Com	ponent co	mposition	(percent n	nass)		
NO	С	Si	Mn	Р	S	Al	N	Remarks
Α	0.069	0.01	0.51	0.010	0.010	0.040	0.0070	Conparative steel
В	0.080	0.01	0.51	0.010	0.010	0.040	0.0070	Conparative steel
С	0.070	0.01	0.50	0.010	0.010	0.040	0.0070	Conparative steel
D	0.070	0.01	<u>0.61</u>	0.010	0.010	0.040	0.0070	Conparative steel
E	0.070	0.01	0.51	0.010	0.010	0.040	0.011	Conparative steel
F	0.070	0.01	0.51	0.010	0.010	0.040	0.0070	Invention steel
G	0.070	0.01	0.51	0.010	0.010	0.040	0.0095	Invention steel
Note: Ur	nderlined o	data indica	te data wh	nich are ou	ut of the so	cope of the	invention	

5		Grain elongation rate		1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.70	2.10	1.80	1.80	1.80
40		Average grain size	ш <sup>т</sup>	5.5	5.7	5.5	2.7	5.8	5.9	5.7	2.7	5.7	2.7	5.7	5.7	6.5	6.2	4.9	5.9	6.1	5.5
10		Total ductility	%	11	6	11	6	6	11	11	12	12	12	12	11	13	12	6	6	8	11
15		Tensile	МРа	495	501	496	205	202	205	205	205	502	205	502	504	490	495	203	203	503	514
20		Ammonia gas concentration	%IoA	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.020	0.021	0.018
25	-	Final sheet thickness	mm	0.213	0.213	0.213	0.213	0.213	0.213	0.213	0.211	0.213	0.213	0.213	0.213	0.213	0.213	0.205	0.213	0.213	0.213
30	Table 2	Secondary cold reduction ratio	%	18	18	18	18	18	18	18	19	18	18	18	18	18	18	21	18	18	18
35		Reduction ratio of final stand in primary cold rolling	%	30	30	30	30	30	30	30	30	30	30	30	30	30	27	30	30	30	30
40		Primary cold reduction ratio	%	06	06	06	06	06	06	06	06	06	06	06	06	06	90	06	06	06	06
45		Sheet thickness after hot rolling	шш	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
50		Coiling temperature	၁့	610	610	610	610	610	610	610	610	610	610	610	610	640	610	610	610	610	610
55		Steel		А	В	С	D	Е	F	F	F	Ь	F	Н	Ь	F	F	F	F	Ь	G
	[0067]	o Z		-	2	3	4	9	9	2	8	6	10	7	12	13	14	15	16	17	18

## [0068]

Table 3

	(	Grain si	ze	Ar	nount o	of N		rage Vi ness of section	cross-		mum V ness of section	cross-	Nit	ride num	ber dens	ity	Solid solution C	Pressure- resitant strength	Form- ability	Remarks
No.	Layer 1*	Layer 2 **	Layer 2 - layer 1	Layer 1*	Layer 2 **	Layer 1 - layer 2	Layer 1*	Layer 2 **	Layer 1 - layer 2	Layer 1*	Layer 2 **	Layer 1 - layer 2	1/20 surface layer ***	1/8 surface layer ****	1/4 surface layer	(1/20)/ (1/4)				
		μm			ppm			Hv			Hv			/µr	n <sup>3</sup>		ppm			
1	5.5	6.4	0.9	70	60	10	165	145	20	170	150	20	9	0.1	11	0.8	53	×	0	Comparative example
2	5.7	6.6	0.9	70	60	10	167	147	20	172	152	20	9	0.1	11	0.8	52	0	×	Comparative example
3	5.5	6.4	0.9	70	60	10	165	145	20	170	150	20	9	0.1	11	0.8	51	×	0	Comparative example
4	5.7	6.6	0.9	70	60	10	167	147	20	172	152	20	9	0.1	11	0.8	53	0	×	Comparative example
5	5.8	6.7	0.9	70	60	10	168	148	20	173	153	20	9	0.1	11	0.8	50	0	×	Comparative example
6	5.9	6.9	1.0	70	60	10	167	147	20	172	152	20	9	0.1	11	0.8	51	0	0	Invention example
7	5.7	6.6	0.9	72	63	9	167	147	20	172	152	20	20	6	5	4.0	46	0	0	Invention example
8	5.9	6.9	1.0	72	63	9	167	147	20	172	152	20	20	6	5	4.0	46	0	0	Invention example
9	5.7	6.6	0.9	72	62	10	168	147	21	173	152	21	20	6	5	4.0	46	0	0	Invention example
10	5.7	6.6	0.9	72	63	9	169	147	22	172	152	20	18	0.5	11	1.6	46	0	0	Invention example
11	5.8	6.7	0.9	72	63	9	167	147	20	172	152	20	1	3.0	2	0.5	46	0	0	Invention example
12	5.7	6.6	0.9	72	63	9	167	147	20	172	152	20	20	6	5	4.0	53	0	0	Invention example
13	6.5	7.4	0.9	70	60	10	163	144	19	168	149	19	9	0.1	11	0.8	52	×	0	Comparative example
14	6.0	6.2	0.2	70	60	10	165	160	5	175	172	3	9	0.1	11	0.8	51	×	0	Comparative example
15	4.8	5.5	0.7	70	60	10	168	149	19	173	154	19	9	0.1	11	0.8	53	0	×	Comparative example
16	6.0	6.3	0.3	70	60	10	168	160	8	174	166	8	10	2.0	8	1.3	51	0	×	Comparative example
17	6.0	6.1	0.1	70	60	10	168	190	-22	178	198	-20	20	3.0	5	4.0	51	0	×	Comparative example
18	6.0	6.1	0.1	100	90	10	168	190	-22	178	198	-20	20	3.0	5	4.0	51	0	0	Invention example

Layer 1\*: from depth of three-eighths to depth of four-eighths of sheet thickness

Layer 2\*\* : from surface to depth of one-eighth of sheet thickness

1/20 surface layer\*\*\* : from surface to depth of one-twentieth of sheet thickness 1/8 surface layer\*\*\*\* : from surface to depth of one-eighth of sheet thickness

1/4 surface layer\*\*\*\*\* : from surface to depth of one-quarter of sheet thickness

[0069] The coated steel sheet (tin plate) obtained as described above was subjected to a heat treatment corresponding to painting and baking at 210°C for 10 minutes and, thereafter, a tensile test was performed. Regarding the tensile test, a tensile test piece of JIS No. 5 size was used and the tensile strength (strength after fracture) and the elongation after fracture was measured at a cross head speed of 10 mm/min.

Furthermore, a sample of the coated steel sheet was taken, and the average grain size and the grain elongation rate in a cross-section in the rolling direction were measured. The average grain size and the grain elongation rate in a crosssection in the rolling direction were measured by a cutting method with a straight test line described in "JIS G 0551" after the vertical cross-section of the steel sheet was polished and grain boundaries were revealed through nital etching.

[0070] Regarding measurement of the pressure-resistant strength, a sample having a sheet thickness of 0.21 mm was formed into a lid of 63 mm $\Phi$  and was attached to a welded can body of 63 mm $\Phi$  through seaming. Compressed air was introduced into the can, and a pressure at which the can lid was deformed was measured. The case where the can lid was not deformed even when the pressure of the inside was 0.20 MPa was indicated by a symbol  $\odot$ , the case where the can lid was not deformed when the pressure of the inside was increased up to 0.19 MPa and the can lid was deformed when the pressure of the inside was 0.20 MPa was indicated by a symbol O, and the case where the can lid was deformed at 0.19 MPa or less was indicated by a symbol x.

[0071] Regarding the formability, the tester specified in JIS B 7729 was used, and a test was performed by a method specified in JIS Z 2247.

The case where the Erichsen value (forming height when penetration cracking occurred) was 6.5 mm or more was indicated by a symbol ⊙, the case of less than 6.5 mm and 6.0 mm or more was indicated by a symbol ⊙, and the case of less than 6.0 mm was indicated by a symbol x.

[0072] As shown in Table 1 to Table 3, No. 6 to No. 12 and No. 18, which are invention examples, have excellent strength and achieve the tensile strength of 500 MPa or more required of a very thin steel sheet for a can. Furthermore, excellent formability is exhibited and the ductility of 10% or more required for forming a lid and a three-piece can body is provided.

Meanwhile, regarding No. 1, which is a comparative example, the C content is too small, so that the tensile strength is insufficient. Moreover, regarding No. 2, which is a comparative example, the C content is too large, so that the elongation is impaired through secondary cold rolling and the elongation after fracture (in Table 2, expressed as "total ductility") is insufficient. Regarding No. 3, which is a comparative example, the Mn content is too small, so that the tensile strength is insufficient. Regarding No. 4, which is a comparative example, the Mn content is too large, so that the elongation is impaired through secondary cold rolling and the elongation after fracture is insufficient. Meanwhile,

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regarding No. 5, which is a comparative example, the N content is too large, so that the elongation is impaired through secondary cold rolling and the elongation after fracture is insufficient.

**[0074]** Regarding No. 13, which is a comparative example, the coiling temperature is too high, so that crystal grains become coarse and the strength is insufficient. Regarding No. 14, which is a comparative example, the secondary cold reduction ratio of a final stand is too small, so that the average grain size is large, the average grain size of the center layer is large, and the strength is insufficient. Regarding No. 15, which is a comparative example, the secondary cold reduction ratio is too large, so that the elongation is impaired through secondary cold rolling and the elongation after fracture is insufficient. Regarding No. 16 and No. 17, which are comparative examples, the ammonia gas concentration in the annealing atmosphere is too high, so that the elongation is impaired because of the surface layer becoming hard and the elongation after fracture is insufficient.

#### Industrial Applicability

**[0075]** According to the present invention, a steel sheet for a can having high strength and high formability in combination, that is, a tensile strength of 500 MPa or more and an elongation after fracture of 10% or more, can be obtained. As a result, the formability of the steel sheet is improved and, thereby, cracking does not occur even during rivet forming of the EOE and during flange forming of the three-piece can. Consequently, can production from the DR material having a small sheet thickness becomes possible, so that it is possible to contribute to development of the industry to a great extent, for example, significant thickness reduction of the steel sheet for a can is achieved.

## **Claims**

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- 1. A high-strength high-formability steel sheet for a can, characterized by comprising C: 0.070% or more and less than 0.080%, Si: 0.003% or more and 0.10% or less, Mn: 0.51% or more and 0.60% or less, P: 0.001% or more and 0.100% or less, S: 0.001% or more and 0.020% or less, Al: 0.005% or more and 0.100% or less, N: 0.010% or less, and the remainder composed of Fe and incidental impurities, on a percent by mass basis, wherein in a cross-section in the rolling direction, the average grain size is 5 μm or more, the grain elongation rate is 2.0 or less, the difference in hardness determined by subtracting an average Vickers hardness of a cross-section between the surface and a depth of one-eighth of the sheet thickness from an average Vickers hardness of a cross-section between a depth of three-eighths of the sheet thickness and a depth of four-eighths of the sheet thickness of a cross-section between the surface and a depth of one-eighth of the sheet thickness from a maximum Vickers hardness of a cross-section between the surface and a depth of one-eighth of the sheet thickness from a maximum Vickers hardness of a cross-section between a depth of three-eighths of the sheet thickness and a depth of four-eighths of the sheet thickness is 20 points or more, the tensile strength is 500 MPa or more, and the elongation after fracture is 10% or more.
- 2. The high-strength high-formability steel sheet for a can, according to Claim 1, **characterized in that** regarding the grain size, the difference in average grain size determined by subtracting an average grain size between a depth of three-eighths of the sheet thickness and a depth of four-eighths of the sheet thickness from an average grain size between the surface and a depth of one-eighth of the sheet thickness is 1 µm or more.
- 3. The high-strength high-formability steel sheet for a can, according to Claim 1 or Claim 2, **characterized in that** regarding the amount of nitrogen, the difference in average amount of N determined by subtracting an average amount of N between the surface and a depth of one-eighth of the sheet thickness from an average amount of N between a depth of three-eighths of the sheet thickness and a depth of four-eighths of the sheet thickness is 10 ppm or more.
- 4. The high-strength high-formability steel sheet for a can, according to any one of Claims 1 to 3, characterized in that regarding nitrides having a diameter of 1 μm or less and 0.02 μm or more, the average nitride number density between the surface and a depth of one-quarter of the sheet thickness is larger than the average nitride number density between the surface and a depth of one-eighth of the sheet thickness.
- 5. The high-strength high-formability steel sheet for a can, according to any one of Claims 1 to 4, characterized in that regarding nitrides having a diameter of 1 μm or less and 0.02 μm or more, the value obtained by dividing the average nitride number density between the surface and a depth of one-twentieth of the sheet thickness by the average nitride number density between the surface and a depth of one-quarter of the sheet thickness is less than 1.5.

- **6.** The high-strength high-formability steel sheet for a can, according to any one of Claims 1 to 5, **characterized in that** regarding the amount of carbon, the amount of solid solution C in the steel is 51 ppm or more.
- 7. A method for manufacturing a high-strength high-formability steel sheet for a can, **characterized by** comprising the steps of slabbing a steel containing C: 0.070% or more and less than 0.080%, Si: 0.003% or more and 0.10% or less, Mn: 0.51% or more and 0.60% or less, P: 0.001% or more and 0.100% or less, S: 0.001% or more and 0.020% or less, Al: 0.005% or more and 0.100% or less, N: 0.010% or less, and the remainder composed of Fe and incidental impurities, on a percent by mass basis, through continuous casting, performing hot rolling so as to coil at a temperature lower than 620°C, performing rolling with a primary cold reduction ratio of 86% or more in total and a cold reduction ratio of a final stand in primary cold rolling of 30% or more, performing annealing in an atmosphere containing less than 0.020 percent by volume of ammonia gas, and performing secondary cold rolling with a reduction ratio of 20% or less.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/077446

		101/012	011/0/110				
	CATION OF SUBJECT MATTER (2006.01)i, <i>C21D1/76</i> (2006.01)i,	C21D9/46(2006.01)i					
According to Inte	ernational Patent Classification (IPC) or to both nationa	l classification and IPC					
B. FIELDS SE	ARCHED						
	nentation searched (classification system followed by classification syste						
Ti + 011110		nt that such documents are included in the tsuyo Shinan Toroku Koho roku Jitsuyo Shinan Koho	e fields searched 1996-2012 1994-2012				
Electronic data b	ase consulted during the international search (name of o	lata base and, where practicable, search te	rms used)				
C. DOCUMEN	ITS CONSIDERED TO BE RELEVANT						
Category*	Citation of document, with indication, where ap	propriate, of the relevant passages	Relevant to claim No.				
Р,Х	JP 2011-137223 A (JFE Steel 14 July 2011 (14.07.2011), entire text & WO 2011/068231 A1	Corp.),	1-7				
Р,А	JP 2011-001609 A (JFE Steel 06 January 2011 (06.01.2011), claims (Family: none)		1-7				
А	JP 2009-263788 A (JFE Steel 12 November 2009 (12.11.2009) claims; tables 1 to 3 & US 2011/0076177 A1 & WO	,	1-7				
× Further do	cuments are listed in the continuation of Box C.	See patent family annex.					
"A" document do to be of part "E" earlier applie filing date "L" document we cited to este special reaso: "O" document re "P" document ye the priority of	gories of cited documents: efining the general state of the art which is not considered icular relevance cation or patent but published on or after the international thich may throw doubts on priority claim(s) or which is ablish the publication date of another citation or other on (as specified) ferring to an oral disclosure, use, exhibition or other means ablished prior to the international filing date but later than 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 mailing of the international search report					
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Form PCT/ISA/210 (second sheet) (July 2009)

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/077446

C		D.1 1
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
А	JP 2006-009069 A (Nippon Steel Corp.), 12 January 2006 (12.01.2006), claims (Family: none)	1-7
A	(Family: none)  JP 2004-323905 A (Nippon Steel Corp.), 18 November 2004 (18.11.2004), claims (Family: none)	1-7

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

## REFERENCES CITED IN THE DESCRIPTION

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# Patent documents cited in the description

- JP 63007336 A [0011]
- JP 2004323905 A **[0011]**

- JP 62096618 A **[0011]**
- JP 2007177315 A **[0011]**