Cold-rolled steel sheet, method of producing the same, battery, and method of producing the same

Provided are a cold-rolled steel sheet having a composition containing, by mass percent, 0.0040% or less of C, 0.02% or less of Si, 0.14% to 0.25% of Mn, 0.020% or less of P, 0.015% or less of S, 0.0040% or less of N, 0.020% to 0.070% of Al, 0.005% to 0.030% of Nb, 0.005% to 0.030% of Ti, (0.0003% to 0.0010% of the equivalent amount of solid solution B (from which the amount of B forming BN has been subtracted)), and the balance composed of Fe and inevitable impurities, wherein even when the rolling reduction of cold rolling is 85% or less, the average grain size of a ferrite structure is reliably 12.0 μm or less, and the relationship -0.20 ≤ Δr ≤ 0.20 can be reliably satisfied and which has an excellent earing property, and a method of producing the same.
The present invention relates to a cold-rolled steel sheet particularly suitable for a battery case, and a method of producing the same.

Technical Field

In working a battery case, it is desired to suppress the generation of ears (called "earing"), more specifically, to prevent the height of the can after the working from being uneven in the circumferential direction thereof. It is generally known that the height of such an ear significantly correlates with planar anisotropy of the steel sheet for a battery case, and that as the earing property of the steel sheet for a battery case is controlled to be close to zero.

In order to suppress earing, desirably, the rolling reduction in cold rolling is controlled to be close to zero. Therefore, it is desired that a cold-rolled steel sheet be produced at a rolling reduction of at least 90% or less, and more preferably, 85% or less.

In order to prevent degradation of a can shape due to wrinkles called "stretcher strain" generated during deep drawing, it is desired that a steel sheet for a battery case have excellent strain aging resistance. In addition, in order to suppress surface roughening during working, it is also desired that a steel sheet for a battery case have fine crystal grains.

As such a steel sheet for a battery case, hitherto, interstitial free steels (IF steels), which are suitable for deep drawing and to which Nb and/or Ti is added, have been studied. For example, Japanese Unexamined Patent Application Publication No. 9-310150 discloses a steel sheet for a two-piece can having excellent earing property and surface roughening resistance. In the method, a steel slab containing at least one type of element selected from, by mass percent, 0.0005% to 0.0150% of C, 0.10% or less of Si, 0.1% to 0.6% of Mn, 0.02% or less of P, 0.02% or less of S, 0.015% to 0.15% of Al, 0.02% or less of N, 0.020% or less of Nb, 0.020% or less of Ti, and 0.0001% to 0.0030% of B, and the balance composed of Fe and inevitable impurities is hot-rolled, cold-rolled, and annealed to form recrystallized grains having an ASTM grain size number of 10 or more and a crystal grain axial ratio of 1.2 or less. Subsequently, a secondary cold rolling is performed at a rolling reduction in the range of 0.5% to 40%.

In addition, Japanese Unexamined Patent Application Publication No. 10-81919 discloses a method of producing a steel sheet for a two-piece can having excellent workability, earing property, and surface roughening resistance. The steel sheet for a can contains at least one type of element selected from, by mass percent, 0.0005% to 0.0150% of C, 0.10% or less of Si, 0.1% to 0.6% of Mn, 0.02% or less of P, 0.02% or less of S, 0.015% to 0.15% of Al, 0.02% or less of N, 0.020% or less of Nb, and 0.020% or less of Ti, and the balance composed of Fe and inevitable impurities, wherein crystal grains in a surface layer region from the surface of the steel sheet to 1/10 of the sheet thickness are composed of fine equiaxed crystal grain structure having an ASTM grain size number of 10 or more and a crystal grain axial ratio of 1.5 or less, and crystal grains in the inner layer of the steel sheet except for this surface layer are composed of coarse equiaxed crystal grain structure having an ASTM grain size number of 9 or less and a crystal grain axial ratio of 1.5 or less.

Furthermore, Japanese Unexamined Patent Application Publication No. 63-310924 discloses a method of producing an ultra-thin steel sheet having small planar anisotropy. In this method, a steel sheet having a composition containing, by mass percent, 0.004% or less of C, 0.1% or less of Si, 0.5% or less of Mn, 0.025% or less of P, 0.025% or less of S, 0.006% or less of N, 0.001% to 0.100% of Al, 0.01% to 0.10% of Ti wherein the relationship Ti ≥ (48/12)C + (48/14)N is satisfied, 0.003% to 0.03% of Nb, and 0.001% to 0.0010% of B, and the balance substantially composed of Fe except for inevitable impurities is hot-rolled under the conditions of a hot-rolling finishing temperature in the range of 850°C to 900°C and a winding temperature in the range of 300°C to 600°C, cold-rolled, and then undergoes continuous annealing, followed by skin-pass rolling to reduce the thickness thereof in the range of 0.15 to 0.60 mm, wherein the cold-rolling reduction is controlled to be in the range of 85% to 95%, and the continuous annealing temperature is controlled to be in the range of 650°C to 750°C.
Disclosure of Invention

[Problems to be Solved by the Invention]

However, in the steel sheets described in Japanese Unexamined Patent Application Publication Nos. 10-81919, 9-310150, and 63-310924, when the rolling reduction of cold rolling is 85% or less, which is a preferable value, the average grain size of a ferrite structure does not always stably become small (specifically, 12.0 μm or less), and Δr that is sufficiently close to zero (specifically, -0.20 ≤ Δr ≤ 0.20) is not always obtained.

It is an object of the present invention to provide a cold-rolled steel sheet in which even when the rolling reduction of cold rolling is 85% or less, the average grain size of a ferrite structure can be reliably controlled to be 12.0 μm or less and the relationship -0.20 ≤ Δr ≤ 0.20 can be reliably satisfied and which has an excellent earing property, and a method of producing the same.

[Means for Solving the Problems]

The present inventors have been studied a cold-rolled steel sheet in which even when the rolling reduction of cold rolling is 85% or less, the relationship -0.20 ≤ Δr ≤ 0.20 can be reliably satisfied, using an IF steel to which Nb and/or Ti is added. As a result, the present inventors have found that it is effective that boron (B) is added so that an appropriately amount of B is present in the form of a solid solution (i.e., solid solution B) before cold rolling. Note that even when the rolling reduction is more than 85%, in the case where the rolling reduction is 90% or less, Δr can be within ± 0.20.

The present invention has been made on the basis of the above finding and provides a cold-rolled steel sheet having an excellent earing property and including, by mass percent, 0.0040% or less of C, 0.02% or less of Si, 0.14% to 0.25% of Mn, 0.020% or less of P, 0.015% or less of S, 0.0040% or less of N, 0.020% to 0.070% of Al, 0.020% to 0.030% of Nb, 0.005% to 0.030% of Ti, B in a content satisfying formula (1) or formula (2) below, and the balance composed of Fe and inevitable impurities, wherein the average grain size of a ferrite structure is 12.0 μm or less, and the relationship -0.20 ≤ Δr ≤ 0.20 is satisfied.

In the case of N - (14/48)Ti > 0,

\[ 0.0003 \leq B - (11/14)\{ N - (14/48) Ti \} \leq 0.0010 \cdots (1) \]

In the case of N - (14/48)Ti ≤ 0,

\[ 0.0003 \leq B \leq 0.0010 \cdots (2) \]

Here, each of the symbols of elements in formulae (1) and (2) represents the content (mass percent) of the element.

The above cold-rolled steel sheet can be produced by, for example, a method of producing a cold-rolled steel sheet having an average grain size of a ferrite structure of 12.0 μm or less, satisfying the relationship -0.20 ≤ Δr ≤ 0.20, and having an excellent earing property, the method including the steps of hot-rolling a steel slab having the above component composition at a rolling finishing temperature of the Ar3 transformation point or higher, cold-rolling the resulting steel sheet at a rolling reduction in the range of 70% to 90%, and then annealing the steel sheet in a continuous annealing line at an annealing temperature in the range of 750°C to 800°C.

In addition, the present invention provides a cold-rolled steel sheet having an excellent earing property and including, by mass percent, 0.0040% or less of C, 0.02% or less of Si, 0.14% to 0.25% of Mn, 0.020% or less of P, 0.015% or less of S, 0.0040% or less of N, 0.020% to 0.070% of Al, 0.005% or more and less than 0.020% of Nb, Ti in a content satisfying formula (3) or formula (4) below, B in a content satisfying formula (1) or formula (2) above, and the balance composed of Fe and inevitable impurities, wherein the average grain size of a ferrite structure is 12.0 μm or less, and the relationship -0.20 ≤ Δr ≤ 0.20 is satisfied.

In the case of C/12 - Nb/93 ≤ 0,

\[ 0.005 \leq Ti \leq 0.020 \cdots (3) \]

In the case of C/12 - Nb/93 > 0,
Here, each of the symbols of elements in formulae (3) and (4) represents the content (mass percent) of the element.

The above cold-rolled steel sheet can be produced by, for example, a method of producing a cold-rolled steel sheet having an average grain size of a ferrite structure of 12.0 μm or less, satisfying the relationship -0.20 \leq \Delta r \leq 0.20, and having an excellent earing property, the method including the steps of hot-rolling a steel slab having the above component composition at a rolling finishing temperature of the Ar₃ transformation point or higher, cold-rolling the resulting steel sheet at a rolling reduction in the range of 70% to 90%, and then annealing the steel sheet in a continuous annealing line at an annealing temperature in the range of 700°C to 800°C.

The present invention also provides a battery including a battery can produced by forming the above-described cold-rolled steel sheet and a method of producing a battery including a step of deep-drawing the above-described cold-rolled steel sheet to form a battery can.

Brief Description of Drawing

Fig. 1 is a graph showing the effect of the rolling reduction (horizontal axis) in cold rolling on the \( \Delta r \) value (vertical axis) of steel sheets in accordance with the steel sheet compositions.

Best Modes for Carrying Out the Invention

(1) Component composition (the symbol "%" below represents "mass percent")

C: As the carbon (C) content is decreased, the steel becomes soft and exhibits satisfactory elongation, and thus the steel is advantageous in terms of press workability. In addition, when carbon (C) contained in the form of a solid solution (solid solution C) is precipitated as a carbide, deep drawability can be improved without causing strain age hardening. If the C content exceeds 0.0040%, it is difficult to precipitate all the carbon as carbides of Nb and Ti. Consequently, hardening and degradation of elongation due to the solid solution C occur. Accordingly, the C content is 0.0040% or less, and preferably 0.0030% or less.

Si: A silicon (Si) content more than 0.02% causes hardening and degradation of a plating property. Accordingly, the Si content is 0.02% or less. Note that the lower limit of the Si content that can be industrially realized is about 0.001%.

Mn: Manganese (Mn) is an element effective to prevent red shortness during hot rolling caused by sulfur (S), and thus, it is necessary to control the Mn content to be 0.14% or more. More preferably, the Mn content is 0.15% or more. On the other hand, if the Mn content exceeds 0.25%, MnS is precipitated during continuous casting, thereby causing hot shortness and resulting in steel slab cracking (also referred to as "cast slab cracking"), and in addition, the amount of solid solution Mn increases in the steel, thereby causing hardening and degradation of elongation. Also, at a high Mn content, the recrystallization temperature during annealing increases. Such an increase in the recrystallization temperature may cause a problem particularly in the case where the rolling reduction is 85% or less at which the driving force of recrystallization is low. Accordingly, the upper limit of the Mn content is 0.25%.

P: A phosphorus (P) content more than 0.020% degrades the workability, and thus, the upper limit of the P content is 0.020%. Note that the lower limit of the P content that can be industrially realized is about 0.001%.

S: If the sulfur (S) content exceeds 0.015%, red shortness may be caused during hot rolling, and MnS is precipitated during continuous casting, thereby causing hot shortness and resulting in cast slab cracking. Accordingly, the upper limit of the S content is 0.015%, but preferably, the S content should be minimized. Note that the lower limit of the S content that can be industrially realized is about 0.001%.

N: If the nitrogen (N) content exceeds 0.0040%, the workability is degraded by solid solution N. Accordingly, the upper limit of the N content is 0.0040%. More preferably, the N content is preferably 0.0030% or less. Note that the lower limit of the N content that can be industrially realized is about 0.001%.

Al: Aluminum (Al) is an element required for deoxidation of a steel, and thus, it is necessary to control the Al content to be 0.020% or more. On the other hand, if the Al content exceeds 0.070%, the amount of inclusion increases, and thus, surface defects are easily generated. Accordingly, the upper limit of the Al content is 0.070%.

Nb: Niobium (Nb) is an important element in the present invention. As in Ti, Nb allows solid solution C in the
steel to precipitate as a carbide to suppress degradation of deep drawability due to the solid solution C. In addition, even a trace amount of addition of Nb is also effective to decrease the grain size of a hot-rolled sheet and to suppress the crystal grain growth during annealing. From this point of view, the Nb content is 0.005% or more. In particular, from the standpoint of the effects of decreasing the grain size and the suppressing crystal grain growth during annealing, the Nb content is preferably 0.020% or more. However, excessive addition of Nb increases the recrystallization temperature. Therefore, the upper limit of the Nb content is 0.030%.

[0034] Ti: Titanium (Ti) allows solid solution C in the steel to precipitate as a carbide to suppress degradation of deep drawability due to the solid solution C, as in Nb. Furthermore, since Ti precipitates as TiN at a high temperature, the formation of BN is suppressed, and thus solid solution B can be reliably ensured. On the other hand, excessive addition of Ti increases the recrystallization temperature, coarsens crystal grains during hot-rolling or annealing, thereby degrading the earing property, and causes surface roughening during working.

[0035] The present inventors have found that, in the steel sheet of the present invention, such effects of Ti are also dependent on Nb content, and optimum Ti content is dependent on Nb content.

(I) In the case where the Nb content is 0.020% or more and 0.030% or less (this case is referred to as "high-Nb composition"):  

[0036] In this case, the effects of decreasing the grain size of a hot-rolled sheet and suppressing the crystal grain growth during annealing achieved by Nb is significant. Accordingly, even when Ti is added in a relatively large amount, the above-mentioned adverse effects of Ti do not occur. Therefore, the upper limit of the Ti content is 0.030%. If Ti is contained in a large amount of more than 0.030%, as described above, the recrystallization temperature increases, crystal grains are coarsened during hot-rolling or annealing, thereby degrading the earing property, and surface roughening during working is caused. Furthermore, in this case, in order to achieve the above-described effects of Ti, it is necessary to control the lower limit of the Ti content to be 0.005%.

(II) In the case where the Nb content is 0.005% or more and less than 0.020% (this case is referred to as "low-Nb composition"):  

[0037] In the case where the Nb content is relatively low, the effect of decreasing the grain size of a hot-rolled sheet and suppressing the crystal grain growth during annealing achieved by Nb is smaller than the case of (I) where 0.020% of more of Nb is added. Accordingly, even when the Ti content is lower than that in the case of (I), more specifically, when the Ti content exceeds 0.020%, the above-described adverse effects caused by excessive addition of Ti, namely, the phenomenon in which crystal grains are coarsened during hot-rolling or annealing, thereby degrading the earing property and the phenomenon in which surface roughening during working is caused, easily occur. Therefore, when the Nb content is 0.005% or more and less than 0.020%, it is necessary to control the upper limit of the Ti content to be 0.020%.

[0038] Furthermore, when the Nb content is relatively small as described above, namely, 0.005% or more and less than 0.020%, the lower limit of the Ti content required for achieving the above effects is different in accordance with the Nb content.

(a) In the case of C/12 - Nb/93 ≤ 0, that is, in the case where the equivalent of the Nb content is equal to or higher than the equivalent of the C content (this case is referred to as "low-Nb(NbC) composition"), the lower limit of the Ti content required for achieving the above-described effects of Ti is 0.005%.

(b) In the case of C/12 - Nb/93 > 0, that is, in the case where the equivalent of the Nb content is less than the equivalent of the C content, solid solution C that is not fixed (precipitated) by Nb must be more reliably fixed by Ti (this case is referred to as "low-Nb(NbC + C) composition"). As described above, it is believed that Ti first precipitates as TiN at a high temperature, and then allows solid solution C to precipitate as a carbide (TiC). Therefore, it is necessary to control the Ti content (equivalent) to be equal to or higher than the residual total content (equivalent) of C and N obtained after subtracting the amount of C and N precipitated by Nb from the total content of C and N. More specifically, in the case of C/12 - Nb/93 > 0, it is necessary to control the lower limit of the Ti content to be 48 × ((C/12 + N/14) - Nb/93). In the case where the value represented by 48 × ((C/12 + N/14) - Nb/93) is less than 0.005%, though such a case rarely occurs, preferably, 0.005% of more of Ti is added.

[0039] The Ti content is summarized as follows on the basis of the above description. In the case of the low-Nb(NbC) composition, it is necessary to satisfy formula (3):

\[
0.005 \leq Ti \leq 0.020 \quad \cdots (3)
\]
In the case of the low-Nb(NbC + C) composition, it is necessary to satisfy formula (4):

$$48 \times \{ (C/12 + N/14) - Nb/93 \} \leq Ti \leq 0.020 \cdots (4)$$

(Each of the symbols of elements in the formulae represents the content (mass percent) of the element.)

In the case where the Nb content is 0.005% or more and less than 0.020% (low-Nb composition) and the Ti content satisfies formula (3) or formula (4), the recrystallization temperature during annealing can be further decreased, and thus, the object of the present invention can be achieved even at an annealing temperature in the range of 700°C to 800°C. In particular, since the object of the present invention can be achieved even at an annealing temperature in the range of 700°C to 750°C, this is advantageous in terms of the energy cost and productivity.

B: By controlling the solid solution boron (B) content to be 0.0003% or more before cold rolling, even when the rolling reduction of the cold rolling is 85% or less, the relationship $$-0.20 \leq \Delta r \leq 0.20$$ can reliably be satisfied. However, if this solid solution B content exceeds 0.0010%, the recrystallization temperature increases. Therefore, the upper limit of the solid solution B content is 0.0010% or less. Here, the solid solution B content is determined as follows. That is, solid solution B precipitates a nitride with solid solution nitrogen (N) in the steel, but solid solution N forms a precipitate more easily with Ti than with B. Accordingly,

(B) In the case where Ti is present in the steel in an amount with which solid solution N can be fixed by precipitation, that is, in the case where Ti is present in the steel in an equivalent equal to or larger than the equivalent of N (in the case of N \(\leq (14/48)Ti\)) (this case is referred to as "(TiN) composition"), the solid solution B content is equal to the B content in the steel. On the other hand, (A) In the case where the equivalent of Ti is less than the equivalent of N (in the case of N > (14/48)Ti) (this case is referred to as "(TiN + N) composition"), N that is not fixed by precipitation with Ti in the steel forms a precipitate with B, and the solid solution B content is decreased accordingly, as compared with the B content in the steel. Accordingly, it is necessary that the solid solution B content obtained after subtracting this amount of decrease be in the range of 0.0003% to 0.0010%.

The B content is summarized as follows on the basis of the above description. In order to control the solid solution B content in the steel to be in the range of 0.0003% to 0.0010%, in the case of the (TiN + N) composition, it is necessary to satisfy formula (1):

$$0.0003 \leq B - (11/14)(N - (14/48)Ti) \leq 0.0010 \cdots (1)$$

In the case of the (TiN) composition, it is necessary to satisfy formula (2):

$$0.0003 \leq B \leq 0.0010 \cdots (2)$$

(Each of the symbols of elements in the formulae represents the content (mass percent) of the element.)

That is, in the present invention, five types of component designs, namely,

- high-Nb-(TiN + N) composition (wherein formula (1) is applied),
- high-Nb-(TiN) composition (wherein formula (2) is applied),
- low-Nb(NbC)-(TiN + N) composition (wherein formulae (1) and (3) are applied),
- low-Nb(NbC)-(TiN) composition (wherein formulae (2) and (3) are applied), and
- low-Nb(NbC + C)-(TiN) composition (wherein formulae (2) and (4) are applied)

are performed in accordance with the fixing states of C and N. In addition, the content of B for ensuring the solid solution B content is determined by formula (1) or formula (2) in accordance with the fixing state of N. Note that, in the case of the low-Nb(NbC + C) composition, the combination with the (TiN + N) composition is not present because, in addition to Ti used for fixing N, an excessive amount of Ti for fixing C is necessary, as described above.

The balance is composed of iron (Fe) and inevitable impurities. Various types of elements such as Sn, Pb, Cu, Mo, V, Zr, Ca, Sb, Te, As, Mg, Na, Ni, Cr, and rare-earth elements (REM) may be mixed as impurities in a total amount
of about 0.5% or less in the production process, but these impurities also do not particularly affect the advantages of the present invention.

(2) Characteristics of steel sheet

- Average grain size of ferrite structure is 12.0 μm or less:

[0047] The steel sheet of the present invention is mainly composed of a polygonal ferrite structure (80% or more in terms of the cross-sectional area ratio), and the average grain size of the ferrite structure is 12.0 μm or less. That is, a steel sheet for a battery case requires a fine grain size in order to suppress surface roughening during working. Specifically, if the average grain size of the ferrite structure exceeds 12.0 μm, surface roughening occurs. Therefore, the average grain size is limited to 12.0 μm or less.

[0048] Note that, as the average grain size, the value measured in accordance with the cutting method described in JIS G 0552 (1998) is used, and the L-cross section (the cross section which penetrates in the steel sheet thickness direction and which is along the rolling direction) is used as the observation surface.

-0.20 ≤ Δr ≤ 0.20

[0049] As described above, in order to suppress earing, it is necessary to control the absolute value of Δr of the steel sheet to be close to zero. When the relationship -0.20 ≤ Δr ≤ 0.20 is satisfied, ear to be formed is small, and thus an excellent earing property is exhibited. Therefore, Δr is limited to this range.

[0050] Note that Δr is determined by the following formula:

\[
\Delta r = \frac{r_0 + r_{90} - 2 \times r_{45}}{2}
\]

wherein \( r_0 \) is the r value in the rolling direction, \( r_{45} \) is the r value in a direction at 45° with respect to the rolling direction, and \( r_{90} \) is the r value in a direction at 90° with respect to the rolling direction.

[0051] In addition to the above characteristics, the steel sheet of the present invention preferably has a strain-aging index AI of 4.9 MPa or less. Satisfying the relationship AI ≤ 4.9 MPa is effective to prevent stretcher strain.

[0052] The above-described ferrite structure, the grain size thereof, and the values of Δr and AI are achieved by the combination of the component ranges described above and production conditions described below.

[0053] The present invention is advantageous in that the relationship -0.20 ≤ Δr ≤ 0.20 can be stably satisfied at a cold-rolling reduction in the range of 70% to 90%, and in particular, in the range of 70% to 85%, in which variation in Δr is significant in the related art. Thus, the present invention has the above advantage, which cannot be achieved in the related art.

(3) Production conditions

[0054] The cold-rolled steel sheet of the present invention can be formed by, for example, hot-rolling a steel slab having the above-described component composition at a rolling finishing temperature of the Ar3 transformation point or higher, optionally pickling the resulting steel sheet, cold-rolling the steel sheet at a rolling reduction in the range of 70% to 90%, and then annealing the steel sheet in a continuous annealing line at an annealing temperature in the range of 750°C to 800°C or 700°C to 800°C, and optionally skin-pass-rolling the steel sheet as needed.

[0055] The steel slab used as a material of the hot rolling is preferably produced by continuous casting. After the continuous casting, the steel slab may be hot-rolled directly or after the steel slab is somewhat heated. Alternatively, after the continuous casting, the steel slab may be cooled and then reheated to perform hot rolling. In the case where the steel slab is reheated, the heating temperature is preferably in the range of 1,050°C to 1,300°C. The reason for this is as follows. If the heating temperature during the reheating is lower than 1,050°C, in general, it tends to be difficult to control the rolling finishing temperature of the subsequent hot rolling to be the Ar3 transformation point or higher, though it depends on the equipment. If the heating temperature during the reheating is higher than 1,300°C, the amount of oxide formed on the surface of the steel slab increases, and surface defects tend to be generated.

[0056] It is necessary to control the rolling finishing temperature of the hot rolling to be the Ar3 transformation point or higher in order to obtain a uniform grain size after the rolling and to decrease planar anisotropy after the hot rolling. Here, the Ar3 transformation point may be determined by a known method. For example, the Ar3 transformation point can be determined by heating a test piece with a Formaster tester, and then examining the change in the coefficient of thermal expansion during cooling.
After the hot rolling, scale formed on the surfaces of the resulting steel sheet is removed, and the steel sheet is then cold-rolled at a rolling reduction in the range of 70% to 90%. The scale is generally removed by pickling. The pickling can be performed in accordance with a known method.

It is necessary to control the rolling reduction of the cold rolling to be 70% or more because a rolling reduction of less than 70% coarsens the grain size, thus causing surface roughening during working. As described above, from the standpoint of production, the upper limit of the rolling reduction is preferably 85% or less. In addition, a feature of the present invention lies in that satisfactory Δr and a satisfactory grain size can be obtained in this range. However, in the steel of the present invention, the relationship $-0.20 \leq \Delta r \leq 0.20$ can be ensured when the rolling reduction is up to 90%. Therefore, the upper limit of the rolling reduction is 90%.

The steel sheet after the cold rolling is annealed in a continuous annealing line at an annealing temperature in the range of 750°C to 800°C in the case where the Nb content is in the range of 0.020% to 0.030% (high-Nb composition) or at an annealing temperature in the range of 700°C to 800°C in the case where the Nb content is 0.005% or more and less than 0.020% (low-Nb composition). The reason why the lower limit of the annealing temperature is 750°C or 700°C is that the steel sheet cannot be completely recrystallized in some cases at a temperature lower than the above temperature. The reason why the upper limit thereof is 800°C is that the grain size is coarsened and surface roughening may easily occur during working at a temperature higher than this temperature. The reason why the annealing is performed by continuous annealing is that the production with high productivity can be realized.

After the annealing, skin-pass rolling is preferably performed in order to tailor the shape of the steel sheet and the surface roughness thereof.

The elongation (elongation percentage) of the skin-pass rolling is not limited as long as the above object can be achieved, but is preferably in the range of 0.3% to 2.0%, in which such skin-pass rolling is generally performed. If the elongation percentage becomes excessive, the steel sheet becomes hardened, and degradation of elongation occurs, and thus a problem tends to occur in forming. Accordingly, it is desirable that an elongation percentage does not exceed 5%.

Applications of steel sheet

The steel sheet of the present invention is produced as described above, but Ni plating, Sn plating, Cr plating, or plating of an alloy of these metals may be performed, as needed. Alternatively, diffusion annealing may be performed after plating to form a diffusion alloy plating film. Alternatively, any other surface coating film, such as a resin coating, may be formed in accordance with the use. In general, the steel sheet of the present invention is subjected to a forming process. Such a forming process may be performed after the above-mentioned surface treatment, the resin coating, or the like is performed. Alternatively, after such a forming process is performed, the surface treatment, the resin coating, or the like may be performed.

The steel sheet of the present invention is particularly suitable for application to a battery can, which is used as a component of a battery, and battery cans can be produced with high yield of the steel sheet. The type of the battery (chemical cell) to which the steel sheet of the present invention can be applied is not particularly limited. The steel sheet of the present invention can be used for, for example, batteries and secondary batteries (such as a lithium-ion battery, a nickel-metal hydride battery, and a nickel-cadmium battery). In particular, the steel sheet of the present invention can be suitably used for batteries produced by forming the steel sheet into a cylindrical shape having a diameter in the range of about 10 to 30 mm (or batteries produced by further forming such a cylindrical steel sheet into a rectangular tube).

In producing a battery can, various types of working methods such as the above-mentioned DI forming can be employed. In producing a battery, other necessary materials and components, such as a positive electrode material, a negative electrode material, a separator, and terminals, are charged and installed in the battery can.

[EXAMPLE]

(EXAMPLE 1)

Steels No. 1 to 18 having the component compositions shown in Table 1 were smelted and steel slabs (cast slabs) were produced by continuous casting. Table 2 shows the values of formulae (1) to (4) described above and the classification of each of the compositions. These steel slabs were heated to 1,250°C, and hot rolling was finished at 900°C, which is higher than the Ar3 transformation point of these steels, namely, 880°C. After the hot-rolled steel sheets were pickled, the steel sheets were cold-rolled at the rolling reductions shown in Table 3. The cold-rolled steel sheets were then annealed in a continuous annealing line at annealing temperatures shown in Table 3, and skin-pass rolling was then performed at an elongation percentage of 0.5%. Thus, samples of steel sheet Nos. 1 to 33 were prepared. The Ar values, the grain sizes, and the strain-aging index (AI) of the prepared samples were examined by the following methods. However, for samples which were not recrystallized at 800°C or lower or at a predetermined temperature, the
characteristics of the steel sheets were not evaluated.

[0066] \( \Delta r \): JIS No. 13 B tensile test pieces were prepared using the prepared steel sheet samples in directions at 0°, 45°, and 90° with respect to the rolling direction, and \( r_0 \), \( r_{45} \), and \( r_{90} \), which are the r values in directions at 0°, 45°, and 90°, were measured in accordance with JIS Z 2254. The value of \( \Delta r \) was determined from the formula \( \Delta r = (r_0 + r_{90} - 2r_{45})/2 \).

[0067] Grain size: The average grain sizes of a ferrite structure of the prepared steel sheet samples were measured in accordance with the cutting method described in JIS G 0552 (1998). As described above, in order that surface roughening does not occur when the steel sheets are worked into a battery case, it is necessary to control the grain size to be 12.0 \( \mu \)m or less.

[0068] AI: JIS No. 13 B tensile test pieces were prepared using the steel sheet samples in a direction at 0° with respect to the rolling direction. Mobile dislocations were introduced into the samples by introducing 8.0% of tensile strain, and an isothermal treatment was then performed at 100°C for one hour. The AI was calculated by the following formula. When the AI was 4.9 MPa or less, the steel sheet sample was evaluated that the sample had excellent strain aging resistance.

\[
AI = \left( \frac{\text{yield load after isothermal treatment} - \text{yield load before isothermal treatment}}{\text{cross-sectional area of parallel portion of test piece before introduction of strain}} \right)
\]

[0069] The results are shown in Table 3. The relationship between the rolling reduction in the cold rolling and \( \Delta r \) is shown in Fig. 1. The results showed that, in the steel sheets Nos. 7 to 16, 18, 19, 22 to 25, 27, 30, and 33, which are steel sheets of the present invention, \( \Delta r \) was within \( \pm 0.20 \) and had an excellent earing property, and the grain size was 12.0 \( \mu \)m or less, and thus, surface roughening did not occur during working. In addition, among the examples of the present invention, steel sheet Nos. 13 to 16, 22 to 24, and 30, whose Nb content is 0.005% or more and less than 0.020%, had excellent characteristics even at an annealing temperature of 700°C or higher and lower than 750°C. Furthermore, the results of steel sheet Nos. 21 to 31 showed that appropriate amounts of, for example, Ti and B should not be determined in fixed ranges but should be controlled in consideration of the relationship with the contents of other elements. Note that, in all the examples of the present invention, the AI was 4.9 MPa or less and had excellent strain aging resistance.

[0070] Regarding Nos. 3, 6, 17, and 14, each of which had a \( \Delta r \) of within \( \pm 0.20 \) but has a grain size of more than 12.0 \( \mu \)m, when deep drawing was performed at a drawing ratio of 2.0, surface roughening was observed. In contrast, regarding the steels of the present invention, when deep drawing was performed under the same condition, surface roughening was not observed.

[0071] Furthermore, the AI of No. 31 was 15.5 MPa, and stretcher strain was generated by working (deep drawing under the same condition as that described above). In contrast, the AI of each of the steels of the present invention was 4.9 MPa or less, and no stretcher strain was generated.

[0072] Fig. 1 shows an example of the relationship between the rolling reduction in the cold rolling (horizontal axis) and \( \Delta r \) (vertical axis) of steel sheet Nos. 1 to 4. The results showed that, in the cold-rolled steel sheets having component compositions of the present invention, \( \Delta r \) can be controlled within the range of \( \pm 0.20 \) at a rolling reduction in the cold rolling of 90% or less. In addition, in comparative examples (Nos. 1 and 2), when the rolling reduction decreased from 85% to 70%, \( \Delta r \) significantly increased. On the other hand, in the steels of the present invention (Nos. 3 and 4), variations in \( \Delta r \) could be suppressed in this range. In the case where the rolling reduction increased from 85% to 90%, variations in \( \Delta r \) in the steels of the present invention somewhat increased. However, as described above, \( \Delta r \) could be maintained within the range of \( \pm 0.20 \).

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<th>Steel No</th>
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<th>Mn</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Al</th>
<th>Nb</th>
<th>Ti</th>
<th>B</th>
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<td>0.01</td>
<td>0.19</td>
<td>0.010</td>
<td>0.011</td>
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<td>0.013</td>
<td>0.032</td>
<td>0.0002</td>
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<tr>
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<td>0.0009</td>
<td>0.01</td>
<td>0.20</td>
<td>0.010</td>
<td>0.012</td>
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<td>0.051</td>
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<td>0.0009</td>
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<td>3</td>
<td>0.0019</td>
<td>tr.*</td>
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<td>0.0012</td>
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<th>Steel No</th>
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<th>Remarks</th>
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<td>0.0006</td>
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<th>Steel No.</th>
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<th>Annealing temperature (°C)</th>
<th>$\Delta r$</th>
<th>Grain size (µm)</th>
<th>Remarks</th>
<th>Classification</th>
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(continued)

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<th>C/12-Nb/93</th>
<th>48x(C/12+N/14-Nb/93)</th>
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<th>Remarks</th>
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<td>Steel No</td>
<td>Rolling reduction of cold rolling (%)</td>
<td>Annealing temperature (°C)</td>
<td>$\Delta r$</td>
<td>Grain size ($\mu$m)</td>
<td>Remarks</td>
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<td>-----------------</td>
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</tr>
<tr>
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<td>12 4</td>
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<td>800</td>
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<td></td>
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<td>730</td>
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<td>Comparative example</td>
<td></td>
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<td>750</td>
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Industrial Applicability

[0073] According to the present invention, a cold-rolled steel sheet in which even when the rolling reduction of cold rolling is 85% or less, an average grain size of a ferrite structure can be reliably 12.0 µm or less and the relationship 
\[-0.20 \leq \Delta r \leq 0.20\]
can be reliably satisfied, and which has an excellent earing property can be produced. Furthermore, the cold-rolled steel sheet of the present invention has an AI of 4.9 MPa or less and has excellent strain aging resistance.

Claims

1. A cold-rolled steel sheet comprising:

   by mass percent,
0.0040% or less of C, 0.02% or less of Si,
0.14% to 0.25% of Mn, 0.020% or less of P,
0.015% or less of S, 0.0040% or less of N,
0.020% to 0.070% of Al,
0.005% or more and less than 0.020% of Nb,

Ti in a content satisfying formula (3) or formula (4),
B in a content satisfying formula (1) or formula (2), and the balance composed of Fe and inevitable impurities,
wherein the average grain size of a ferrite structure is 12.0 µm or less,
and
planar anisotropy $\Delta r$ of the $r$ value satisfies the relationship $-0.20 \leq \Delta r \leq 0.20$;

(A) in the case of $N - (14/48)Ti > 0$,

$$0.0003 \leq B - (11/14)\{N - (14/48)Ti\} \leq 0.0010 \cdots (1)$$

(B) in the case of $N - (14/48)Ti \leq 0$,

$$0.0003 \leq B \leq 0.0010 \cdots (2)$$

(a) in the case of $C/12 - Nb/93 \leq 0$,

$$0.005 \leq Ti \leq 0.020 \cdots (3)$$

(b) in the case of $C/12 - Nb/93 > 0$,

$$48 \times \{(C/12 + N/14) - Nb/93\} \leq Ti \leq 0.020 \cdots (4)$$

wherein each of the symbols of elements in formulae (1) to (4) represents the content (mass percent) of the element.

2. A method of producing a cold-rolled steel sheet having an average grain size of a ferrite structure of 12.0 µm or less and satisfying the relationship $-0.20 \leq \Delta r \leq 0.20$, the method comprising the steps of:

- hot-rolling a steel slab having the component composition according to claim 1 at a rolling finishing temperature of the $Ar_3$ transformation point or higher;
- cold-rolling the resulting steel sheet at a rolling reduction in the range of 70% to 90%; and then annealing the steel sheet in a continuous annealing line at an annealing temperature in the range of 700°C to 800°C.

3. A battery comprising a battery can produced by forming the steel sheet according to claim 1.

4. A method of producing a battery comprising a step of deep-drawing the steel sheet according to claim 1 to form a battery can.
FIG. 1

![Graph showing rolling reduction of cold rolling (%)]
<table>
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<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (IPC)</th>
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<td>X</td>
<td>JP H10 46288 A (NIPPON STEEL CORP) 17 February 1998 (1998-02-17) * abstract; figure 1; example A; tables 1,2 *</td>
<td>1-4</td>
<td>INV. C22C38/00 B21B1/22 B21B3/00 C21D9/48</td>
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<td>A</td>
<td>RALF J A ET AL: &quot;Microstructural evolution during thermomechanical processing of a Ti-Nb interstitial-free steel just below the Ar 3 temperature&quot;, METALLURGICAL AND MATERIALS TRANSACTIONS A, SPRINGER-VERLAG, NEW YORK, vol. 28, no. 7, 1 July 1997 (1997-07-01), pages 1437-1443, X019692353, ISSN: 1543-1940 * abstract *</td>
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The present search report has been drawn up for all claims.

Place of search: Munich
Date of completion of the search: 15 October 2014
Examiner: Catana, Cosmin
This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on 15-10-2014. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

For more details about this annex: see Official Journal of the European Patent Office, No. 12/82.
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- JP 10081919 A [0006] [0009]
- JP 9310150 A [0007] [0009]
- JP 63310924 A [0008] [0009]