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(54) COLD ROLLED STEEL SHEET AND METHOD FOR MANUFACTURING SAME

(57) A cold rolled steel sheet according to an exemplary embodiment of the present invention comprises, by wt%: C: 0.01 to 0.10%; Mn: 0.1 to 0.4%; Al: 0.01 to 0.10%; P: 0.003 to 0.020%; N: 0.001 to 0.006%; S: 0.015% or less; Cr: 0.1 to 0.4%; B: 0.0005 to 0.0035%; Ni: 0.04 to 0.10%; and the balance Fe and other unavoidable impurities, and comprises a (Cr-B)(C-N)-based composite precipitate having a size of 0.01 to 0.1 μm, wherein a [I 222+I 554]/I 200 texture ratio is 5.0 to 10.0, an earing rate is less than 3.0%, and an alloying rate of an alloy layer may be 5 to 15%.

Description

[Technical Field]

[0001] The present invention relates to a steel sheet, and more particularly, to a cold rolled steel sheet and a method for manufacturing the same.

[Background Art]

[0002] In the case of a round can used in a battery case of a primary battery, generally, nickel (Ni) plating is performed on a steel sheet as corrosion resistance is fundamentally required to withstand an alkaline property entering the battery contents. Recently, a cylindrical battery case material has been widely used as battery case materials not only for primary batteries, but also for secondary batteries for mobile devices such as cell phones, power tools, and electric vehicles.

[0003] As the use environments for battery case materials become diverse, the demand for improving the characteristics and lifespan of battery cases is increasing. In addition, in order to improve battery performance by increasing the capacity of a charger, technology development has been promoted to ensure safety while reducing the thickness of the case body.

[0004] As the application of battery cases using steel expands to the automobile industry, the demand for improved properties, especially high-temperature properties, to ensure the safety of the can is also increasing. In the field of electric vehicles and hybrid vehicles, research is ongoing to apply a round can-shaped steel sheet in terms of cost reduction and productivity improvement of battery cases that have been used with materials such as aluminum. As such, battery case products may be momentarily exposed to a high temperature of hundreds of °C in a use environment to secure heat resistance capable of withstanding high temperature conditions.

[0005] The heat resistance may be evaluated in various methods, and for example, as the method is applied with a method for evaluating the stability of a cell by charging a battery in an electric vehicle battery case and then heating the battery to a temperature of around 600°C, heat resistance at a certain temperature is emerging as an important management factor. In addition, since a battery cell portion is degraded due to local temperature rise when the vehicle is driven, which may affect the driving of the vehicle, deformation characteristics at a high temperature need to be strictly managed to prevent the degradation.

[0006] In addition, sag resistance, which prevents a sagging phenomenon that occurs due to changes in mechanical property repeatedly exposed to the high temperature, is considered as one of the important factors. When the sagging phenomenon occurs, it is difficult to maintain the shape of a forming portion, and when thermal stress is concentrated in a specific region, the high-temperature resistance decreases and thus, the shape of the product may be deformed, or the fracture may occur in a severe case. In order to ensure the stability of parts by ensuring the shape fixability of processed products, a cold rolled steel sheet with high yield strength at the high temperature and low material sagging is required in the management temperature of parts and battery case applications for electric vehicles.

[0007] In the related art, a stainless steel sheet has been mainly used for heat-resistant use, but as the stainless steel sheet is added with a large amount of expensive alloy elements such as chromium (Cr) and nickel (Ni), not only the manufacturing cost is high, but when applied at a high temperature, chromium at the grain boundaries is bound with carbon (C) to be precipitated in the form of chromium-carbide at the grain boundary, resulting in intergranular corrosion at a formed chromium depleted zone to deteriorate corrosion resistance.

[0008] In the case of battery cases used in vehicles, the same processed products are mounted in a limited space in a stacked form, and multi-stage machining processes such as drawing and stretching are required during forming, so that in addition to the high-temperature characteristics, processability at room temperature is also one of the important factors. Steel case materials are attracting attention to exhibit superior characteristics compared to other materials in terms of productivity and stability, and since most cases are formed in a cylindrical shape, a desired case shape is obtained through D&I forming, which is mainly subjected to drawing and ironing steps.

[0009] As a processing method of the cold rolled steel sheet, there are stretching closely related to ductility, deep drawing related to Lankford values, and bending closely related to a ratio of yield strength to tensile strength. Most cold rolled steel sheets are formed using complex processing modes, and among them, the deep drawing method is a processing mode similar to a processing method for generally producing the shape of a cup and has a relation with the Lankford value (hereinafter referred to as a r value) expressed as the strain in a width direction relative to the strain in a thickness direction among mechanical properties of the material. The △r value measured from the r value measured in each direction with respect to a rolling direction is a representative value for simply evaluating the earing in a shaped cup and calculated as shown in Equation 1 below.

[Equation 1]

$$\triangle r = (r_0 + r_{90} - 2r_{45})/2$$

[0010] In Equation 1 above, r_i represents a r value measured from a specimen taken in an i° direction from a rolling direction. The △r value is closer to 0, the strain in all directions is constant to show an isotropic property, and earing is reduced during cup processing, thereby minimizing a loss due to cutting of the material after processing.

[0011] The earing is due to a difference in cup height at each processing region due to anisotropy of a formed cup. In addition, planar anisotropy refers to the degree to which the physical and/or mechanical properties of a material are directional. Factors causing the planar anisotropy include a combination of two-phase textures such as carbides and/or inclusions, a surface friction effect, a local steel sheet thickness, or a difference in properties. The planar anisotropy may be fundamentally due to the fact that respective ferrite grains that have undergone plastic deformation exhibit strong directionality.

[0012] If the grains that have undergone processing such as plastic deformation are non-directionally, for example, randomly present, these grains will not have directionality, and a problem of earing, which is closely related to planer anisotropy, will not occur. However, ferrite grains that go through hot rolling, soddus, and alc recrystallization annealing processes exhibit strong directionality, and accordingly, anisotropy of plastic behavior appears during the D&I processing.

[0013] The ear of the cup generates peaks based on 0° and 90°. As the reduction ratio increases, the peak of the cup transition to 0°, 60°, and 45°, and this phenomenon may occur repeatedly. In addition, it is necessary to manage the earing rate during cup forming to less than 3%.

[0014] In addition, a steel sheet used as a material for alkaline manganese battery or lithium battery cases is manufactured into a two-piece circular can in which a lower part and a body part of the can processed into the cylindrical shape are integrally processed by press forming. In this case, the D&I processing is performed by a process of punching the material into a circular blank and simultaneously deep-drawing and forming the material into a cylindrical shape, and an ironing process of passing the deep-drawn material through a plurality of ironing molds to reduce the thickness and increasing the height of the can. As such, the two-piece round can is able to be made thinner than the original sheet by ironing the case body during the manufacturing process, and through this, the body thickness of the final case is about 20 to 40% thinner than the original sheet.

[0015] In addition, Japanese Patent Publication No. 11-189841 proposed a method of improving the sealability of a battery can by increasing the material strength through secondary rolling using medium and low carbon steel. However, in the case of the method, it was not possible to solve the problems related to securing strength at high temperatures, for example, 600°C, and suppressing dynamic strain aging required for battery cases for electric vehicles, and even in terms of the manufacturing process of the original sheet, there is a problem that the secondary rolling process is added to act as a separate factor in increasing manufacturing costs.

[Disclosure]

[Technical Problem]

[0016] The present disclosure attempts to provide a cold rolled steel sheet capable of securing room temperature and high temperature D&I processability applicable to applications such as battery cases.

[0017] The present disclosure also attempts to provide a method for manufacturing a cold rolled steel sheet having the advantage.

[Technical Solution]

[0018] According to an exemplary embodiment of the present invention, a cold rolled steel sheet includes, by wt%: C: 0.01 to 0.10%; Mn: 0.1 to 0.4%; Al: 0.01 to 0.10%; P: 0.003 to 0.020%; N: 0.001 to 0.006%; S: 0.015% or less; Cr: 0.1 to 0.4%; B: 0.0005 to 0.0035%; Ni: 0.04 to 0.10%; and the balance Fe and other unavoidable impurities, and comprises a (Cr-B)(C-N)-based composite precipitate having a size of 0.01 to 0.1 μm, wherein a [I(222)+I(554)]/I(200) texture ratio is 5.0 to 10.0, an earing rate is less than 3.0%, and an alloying rate of an alloy layer may be 5 to 15%. In an exemplary embodiment, the cold rolled steel sheet may satisfy Equation 1 below.

<Equation 1>

$$0.0002 \le ([Cr]/52) \times 1.6([B]/11)) / (([C]/12) + ([N]/14)) \le 0.0006$$

(in Equation 1 above, [Cr], [B], [C], and [N] refer to the weights of Cr, B, C, and N, respectively)

[0019] In an exemplary embodiment, during drawing processing, fracture may not occur during cupping under the condition that a blank diameter/drawing die diameter is 1.85. In an exemplary embodiment, through a salt spray test, red rust may not occur within 12 hours.

[0020] In an exemplary embodiment, after the cold rolled steel sheet is heated at 600°C for 100 hours, the degree of sagging of the steel sheet may be less than 3 mm. In an exemplary embodiment, the cold rolled steel sheet may have yield strength at 600°C of 95 MPa or more.

[0021] According to another exemplary embodiment of the present invention, a method for manufacturing a cold rolled steel sheet includes heating a steel slab including, by wt%: C: 0.01 to 0.10%; Mn: 0.1 to 0.4%; Al: 0.01 to 0.10%; P: 0.003 to 0.020%; N: 0.001 to 0.006%; S: 0.015% or less; Cr: 0.1 to 0.4%; B: 0.0005 to 0.0035%; Ni: 0.04 to 0.10%; and the balance Fe and other unavoidable impurities, finish hot-rolling the heated steel slab at 860 to 930°C, winding the finish hot rolled steel sheet at 580 to 700°C, cold-rolling the wound hot rolled steel sheet at a reduction ratio of 78 to 92%, annealing the cold rolled steel sheet at 650 to 750°C, cooling the annealed cold rolled steel sheet at a cooling rate of 30 to 70°C/sec, and electroplating the cold rolled steel sheet and then alloying and heating the cold rolled steel sheet at 650 to 750°C. In an exemplary embodiment, the cold rolled steel sheet may satisfy Equation 1 below.

<Equation 1>

$$0.0002 \leq ([Cr]/52) \times 1.6([B]/11)) / (([C]/12) + ([N]/14)) \leq 0.0006$$

(in Equation 1 above, [Cr], [B], [C], and [N] refer to the weights of Cr, B, C, and N, respectively)

[0022] According to an exemplary embodiment of the present invention, it is possible to secure shape fixability at high temperatures with excellent room temperature processability even in a D&I process which is a processing process such as ironing and drawing, and excellent high-temperature strength and high-temperature deformation characteristics even at high temperatures by controlling the contents of chromium (Cr), boron (B), carbon (C), and nitrogen (N) among essential components, and to manufacture a cold rolled steel sheet with excellent heat resistance having high heat resistance with high product safety and D&I processability.

[0023] According to another exemplary embodiment of the present invention, it is possible to provide a method for manufacturing a cold rolled steel sheet using the cold rolled steel sheet having the aforementioned advantage.

[Mode for Invention]

[0024] Terms such as first, second and third are used to describe various parts, components, regions, layers and/or sections, but are not limited thereto. These terms are only used to distinguish one part, component, region, layer or section from another part, component, region, layer, or section. Accordingly, a first part, component, region, layer, or section to be described below may be referred to as a second part, component, region, layer or section without departing from the scope of the present invention.

[0025] The terms used herein is for the purpose of describing specific exemplary embodiments only and are not intended to be limiting of the present invention. The singular forms used herein include plural forms as well, if the phrases do not clearly have the opposite meaning. The "comprising" used in the specification means that a specific feature, region, integer, step, operation, element and/or component is embodied and other specific features, regions, integers, steps, operations, elements, components, and/or groups are not excluded.

[0026] When a part is referred to as being "above" or "on" the other part, the part may be directly above or on the other part or may be followed by another part therebetween. In contrast, when a part is referred to as being "directly on" the other part, there is no intervening part therebetween.

[0027] Unless defined otherwise, all terms including technical and scientific terms used herein have the same meaning as commonly understood by those skilled in the art to which the present invention belongs. Commonly used predefined terms are further interpreted as having a meaning consistent with the relevant technical literature and the present invention and are not to be construed as ideal or very formal meanings unless defined otherwise.

[0028] In addition, unless otherwise specified, % means weight%, and 1 ppm is 0.0001 weight%.

[0029] In an exemplary embodiment of the present invention, the meaning of further including an additional element means replacing and including iron (Fe), which is the remainder by an additional amount of an additional element.

[0030] The present invention will be described more fully hereinafter with reference to the accompanying drawings, in which exemplary embodiments of the invention are shown. As those skilled in the art would realize, the described embodiments may be modified in various different ways, all without departing from the spirit or scope of the present invention.

[0031] According to an exemplary embodiment of the present invention, a cold rolled steel sheet includes, by wt%: C:

0.01 to 0.10%; Mn: 0.1 to 0.4%; Al: 0.01 to 0.10%; P: 0.003 to 0.020%; N: 0.001 to 0.006%; S: 0.015% or less; Cr: 0.1 to 0.4%; B: 0.0005 to 0.0035%; Ni: 0.04 to 0.10%; and the balance Fe and other unavoidable impurities.

[0032] The reason for limiting the alloy components will be described below (hereinafter, wt% is represented by %).

Carbon (C): 0.01 to 0.10%

[0033] Carbon is an element added to improve the strength of the steel sheet and used for a reaction with chromium (Cr) to form a carbide-based precipitate. The carbon content may be 0.01 to 0.10%, specifically 0.01 to 0.10%, and more specifically 0.015 to 0.09%.

[0034] As the carbon content increases, tensile and yield strengths increase. If the carbon content is excessively high, processability decreases, and if the carbon content is excessively small, a strengthening effect at a high temperature due to a (Cr-B)(C-N)-based composite precipitate cannot be sufficiently obtained, and the grain size increases, resulting in processing defects such as orange peel during forming.

Manganese (Mn): 0.1 to 0.4%

[0035] Manganese is an austenite stabilizing element and a solid solution strengthening element that increases the strength of steel and prevents hot tearing of the slab by precipitating sulfur (S) in the form of MnS. The manganese content may be 0.1 to 0.4%, specifically, 0.12 to 0.29%.

[0036] If the manganese content is excessively high, not only ductility may be reduced and central segregation may occur, but also the corrosion resistance of the steel sheet and plating adhesion during nickel (Ni) plating may be reduced. If the manganese content is excessively low, there is a problem of causing hot tearing in the slab.

Aluminum (Al): 0.01 to 0.10%

[0037] Aluminum is an element added to prevent mechanical-property degradation due to aging by promoting deoxidation of molten steel and binding with solid nitrogen in steel. The aluminum content may be 0.01 to 0.10%, specifically, 0.015 to 0.085%.

[0038] If the aluminum content is excessively high, the deoxidation effect may be saturated, while inclusions in the steel may increase, thereby causing surface defects. If the aluminum content is excessively small, there is a problem that mechanical-property deterioration may occur due to aging.

Phosphorus (P): 0.003 to 0.020%

[0039] Phosphorus is an element added to improve the strength and corrosion resistance of steel. The phosphorus content may be 0.003 to 0.020%, specifically, 0.004 to 0.019%.

[0040] If the phosphorus content is excessively high, the phosphorus may segregate at grain boundaries, causing grain boundary embrittlement, lowering processability, and lowering adhesion during nickel (Ni) plating. If the phosphorus content is excessively small, it is difficult to secure the strength and corrosion resistance of the steel.

Nitrogen (N): 0.001 to 0.006%

[0041] Nitrogen is an element added to strengthen the mechanical property and form nitrides while existing in a solid solution state inside the steel to form an annealed texture and secure physical properties at high temperatures. The nitrogen content may be 0.001 to 0.006%, specifically 0.0014 to 0.0056%.

[0042] If the nitrogen content is excessively high, excessive solid solution elements cause aging, which causes deterioration of formability, and if the nitrogen content is excessively small, it is difficult to form an annealed texture and secure high-temperature properties.

Sulfur (S): 0.015% or less

[0043] Sulfur is bound with iron (Fe) in steel to form non-metallic inclusions that serve as a starting point of corrosion and is a factor of red shortness, so that it is preferred to reduce the content. The sulfur content may be 0.015%, specifically 0.014% or less.

Chromium (Cr): 0.1 to 0.4%

[0044] Chromium is an element added to control the texture by strengthening a solid solution and refining grains and secure the mechanical property of a product. The chromium content may be 0.1 to 0.4%, specifically 0.13 to 0.39%.

[0045] If the chromium content is excessively high, there is a problem that the manufacturing cost increases due to excessive addition of expensive elements, which is uneconomical, and a recrystallization temperature increases. If the chromium content is excessively low, there is a problem that it is difficult to strengthen the solid solution, control the texture by refining the grains, and secure the mechanical property of the product.

Boron (B): 0.0005 to 0.0035%

[0046] Boron is an element that forms high-temperature nitrides, improves hardenability, and improves high-temperature characteristics by suppressing grain growth at high temperatures. The boron content may be 0.005 to 0.0035%, specifically 0.0005 to 0.0035, and more specifically, 0.0007 to 0.0032%.

[0047] If the boron content is excessively high, there is a problem that recrystallization is delayed to reduce annealing passability and worsen processability. If the boron content is excessively small, there is a problem that grain growth at high temperatures is not suppressed and high temperature characteristics are deteriorated.

Nickel (Ni): 0.04 to 0.10%

[0048] Nickel is an element added to improve high-temperature properties and corrosion resistance. The nickel content may be 0.04 to 0.10%, specifically, 0.042 to 0.095%.

[0049] If the nickel content is excessively high, there is a problem of deteriorating workability such as rollability. If the nickel content is excessively small, there is a problem of deteriorating high-temperature properties and corrosion resistance.

[0050] According to the present invention, it is possible to secure excellent press processability by excluding expensive elements such as Nb, Ti, P, and Mn, and optimizing the content of alloys such as C, N, and S, which are relatively inexpensive elements to lower the yield strength and increase the ductility of steel materials used in press forming. Specifically, the cold rolled steel sheet may contain 0.002% or less of Nb, 0.002% or less of Ti, 0.03% or less of Ni, and 0.03% or less of Cu.

[0051] The cold rolled steel sheet includes the balance of iron (Fe). In addition, the cold rolled steel sheet may include unavoidable impurities. The unavoidable impurities refer to impurities that are inevitably mixed during steel-making and the manufacturing process of the cold-rolled steel sheet. Since the unavoidable impurities are widely known, detailed descriptions are omitted. In an exemplary embodiment of the present invention, the addition of elements other than the above-described alloy components is not excluded, and various elements may be included within the scope that does not impair the technical spirit of the present invention. If additional elements are included, the additional elements are included by replacing the balance Fe.

[0052] In an exemplary embodiment, the cold rolled steel sheet of the present invention may include a (Cr-B)(C-N)-based composite precipitate. The size of the (Cr-B)(C-N)-based composite precipitate may be in the range of 0.01 to 0.10 μm.

[0053] If the size of the (Cr-B)(C-N)-based composite precipitate is out of the upper limit of the range, there is a problem in that high-temperature properties cannot be secured. If the size of the (Cr-B)(C-N)-based composite precipitate is out of the lower limit of the range, grain growth may be suppressed, but there is a problem that annealing workability is deteriorated.

[0054] In an exemplary embodiment, the cold rolled steel sheet may have a $[I_{222}+I_{554}]/I_{200}$ texture ratio of 5.0 to 10.0. In the texture ratio, I_{222} means the strength of (222) plane, I_{554} means the strength of (554) plane, and I_{200} means the strength of (200) plane in the plane strength. The texture ratio may be in the range of 5.0 to 10.0, specifically 5.2 to 9.9. D&I characteristics may be secured when the texture ratio satisfies the range.

[0055] If the texture ratio is out of the upper limit of the range, it is suitable for improving the depth of a forming cup, but there is a problem that the plastic strain ratio in a direction forming 45° with the rolling direction increases to increase the earing rate of the forming cup, resulting in short-can, or the amount of trimming of the material increases to increase a material loss. If the texture ratio is out of the lower limit of the range, there is a problem of deteriorating processability due to the development of a (200) component that is disadvantageous to formability.

[0056] In an exemplary embodiment, the cold rolled steel sheet may have an earing rate of less than 3.0%. The earing rate is a value obtained by measuring the height of each part of the forming cup and calculating {(maximum cup height) - (minimum cup height)} $\times$ 100/(maximum cup height). The earing rate of the cold rolled steel sheet may be less than 3.0%, specifically less than 2.8%. When the ear occurrence rate is 3.0% or more, there is a problem that as the height deviation of the forming cup increases, the amount of trimming to cut off unnecessary forming parts increases, leading to an increase in material loss.

[0057] In an exemplary embodiment, the cold rolled steel sheet includes an alloy layer, and an alloying rate of the alloy layer may be in the range of 5 to 15%. The alloying rate of the alloy layer is a percentage of a coexistence area of iron (Fe) and nickel (Ni), and may be a percentage of the area where the iron and nickel coexist, and the alloying rate may have a close relation between corrosion resistance and surface hardness of the material.

[0058] When the alloying rate of the alloy layer exceeds the upper limit, it is advantageous in terms of improving mold life, but there is a problem that the corrosion resistance of the surface layer is deteriorated. When the alloying rate of the alloy layer exceeds the lower limit, there is a problem that the surface property of a plating material is hardened due to a low alloying degree to degrade the life of the processing mold.

[0059] According to an exemplary embodiment of the present invention, the cold rolled steel sheet satisfies Equation 1 below.

<Equation 1>

$$0.0002 \leq ([Cr]/52 \times 1.6([B]/11)) / (([C]/12) + ([N]/14)) \leq 0.0006$$

(in Equation 1, [Cr], [B], [C], and [N] refer to the weights of Cr, B, C, and N, respectively.)

[0060] Equation 1 above refers to an effective atomic ratio of carbon (C) and nitrogen (N) to chromium (Cr) and boron (B), and it is possible to secure aging resistance, processability, and high temperature deformation behavior can be secured at the same time by controlling the precipitation conditions of the (Cr-B)(C-N)-based composite precipitate.

[0061] In an exemplary embodiment, the range of Equation 1 may be 0.0002 to 0.0006, specifically 0.00021 to 0.00058. When the range of Equation 1 is out of the upper limit, it is advantageous to secure strength, but there is a problem that the recrystallization temperature rises, so that annealing passability and surface properties are deteriorated to reduce post-process workability. When the range of Equation 1 is out of the lower limit, there is a problem of deteriorating aging resistance and workability due to an increase in the amount of solid solution elements in steel, and as the precipitation amount of the (Cr-B)(C-N)-based composite precipitate decreases, it may be difficult to secure the high temperature strength.

[0062] In an exemplary embodiment, the cold rolled steel sheet may not generate work cracks. In an exemplary embodiment, the cold rolled steel sheet may have excellent corrosion resistance. The corrosion resistance may be evaluated through a salt spray test (SST) and may be evaluated based on whether red rust occurs within 12 hours. Accordingly, it can be confirmed that red rust does not occur in the cold rolled steel sheet within 12 hours when subjected to the salt spray test.

[0063] In an exemplary embodiment, after heating the cold rolled steel sheet at 600°C for 100 hours, the degree of sagging may be less than 3 mm. The degree of sagging of the cold rolled steel sheet may mean sag resistance, and the sag resistance is measured by measuring the sagging of the steel sheet after heating at 600°C for 100 hours. When the degree of sagging is less than 3 mm, the sag resistance of the cold rolled steel sheet may be excellent.

[0064] In an exemplary embodiment, the cold rolled steel sheet may have yield strength of 95 MPa or more at 600°C. Measuring the yield strength after heating the cold rolled steel sheet at 600°C for 100 hours refers to high-temperature yield strength and is used to evaluate safety at high temperatures.

[0065] The high temperature yield strength may be 95 MPa or more, specifically 100 MPa. When the high-temperature yield strength is 95 MPa or less, there is a problem that safety at high temperatures is reduced, and the possibility of fire or explosion increases when applying the cold rolled steel sheet to a battery.

[0066] According to another exemplary embodiment of the present invention, a method for manufacturing a cold rolled steel sheet may include heating a steel slab including, by wt%: C: 0.01 to 0.10%; Mn: 0.1 to 0.4%; Al: 0.01 to 0.10%; P: 0.003 to 0.020%; N: 0.001 to 0.006%; S: 0.015% or less; Cr: 0.1 to 0.4%; B: 0.0005 to 0.0035%; Ni: 0.04 to 0.10%; and the balance Fe and other unavoidable impurities, finish hot-rolling the heated steel slab at 860 to 930°C, winding the finish hot rolled steel sheet at 580 to 700°C, cold-rolling the wound hot rolled steel sheet at a reduction ratio of 78 to 92%, annealing the cold rolled steel sheet at 650 to 750°C, cooling the annealed cold rolled steel sheet at a cooling rate of 30 to 70°C/sec, and electroplating the cold rolled steel sheet and then alloying and heating the cold rolled steel sheet at 650 to 750°C. Since the alloy composition of the slab is the same as that of the cold rolled steel sheet described above, duplicated description will be omitted. Since the alloy composition does not change during the manufacturing process of the cold rolled steel sheet, the alloy compositions of the slab and the cold rolled steel sheet are substantially the same.

[0067] In the heating of the steel slab containing the alloy composition, the steel slab is heated at a low temperature at which the (Cr-B)(C-N)-based composite precipitate is not re-dissolved. In an exemplary embodiment, the reheating of the slab may be performed at a temperature range of 1180 to 1280°C. By performing the heating within the temperature range, it is possible to secure a sufficient temperature during hot rolling to be described below.

[0068] The finish hot rolling of the heated steel slab at 860 to 930°C is reheating the steel slab and then hot rolling the steel slab in the temperature range of 860 to 930°C. The finish hot rolling step may be performed in the temperature range of 860 to 930°C, specifically 870 to 920°C.

[0069] If the temperature exceeds the upper limit of the temperature range, there is a problem that impact toughness is reduced due to grain coarsening. If the temperature exceeds the lower limit of the temperature range, there is a problem that as the hot rolling is completed in a relatively low-temperature region, the finally formed grains are mixed to deteriorate processability and rolling properties.

[0070] The winding of the finish hot-rolled hot rolled steel sheet at 580 to 700°C includes cooling the finish hot-rolled hot rolled steel sheet on a run-out table and winding the cooled hot rolled steel sheet. The winding step may be performed in a temperature range of 580 to 700°C, specifically 590 to 695°C.

[0071] If the temperature exceeds the upper limit of the temperature range, there is a problem that the grains of the product become coarse, thereby deteriorating high-temperature strength and corrosion resistance. If the temperature exceeds the lower limit of the temperature range, there is a problem that the mechanical property of a hot-rolled material is hardened, so that the rolling load in the cold rolling step to be described below increases and the temperature unevenness in the width direction increases, thereby deteriorating mechanical-property deviation and workability.

[0072] The cold rolling of the wound hot rolled steel sheet at a reduction ratio of 78 to 92% is for manufacturing a cold rolled steel sheet by cold rolling the hot rolled steel sheet. The cold rolling may be performed at a reduction ratio in the range of 78 to 92%, specifically 80 to 90%.

[0073] If the reduction ratio is out of the upper limit of the range, there is a problem that the load of a cold roller increases and workability deteriorates. If the reduction ratio is out of the lower limit of the range, it is difficult to form a texture suitable for planar anisotropy.

[0074] The annealing of the cold-rolled cold rolled steel sheet at a temperature of 650 to 750°C is for controlling recrystallization and microstructure and is crack annealing. The annealing step may be performed in a temperature range of 650 to 750°C, specifically 660 to 740°C.

[0075] If the temperature exceeds the upper limit of the temperature range, recrystallization is completed and the transformation driving force of a needle-shaped ferrite structure may be secured, but defects such as heat buckles caused by high-temperature heating are caused, resulting in a decrease in annealing passability. If the temperature exceeds the lower limit of the temperature range, there is a problem that the fraction of recrystallized grains is low and the strength is high, but ductility is reduced, so that processability cannot be secured.

[0076] The cooling of the annealed cold rolled steel sheet at a cooling rate of 30 to 70 °C/sec is cooling the crack-annealed steel sheet to a temperature of 30 to 70°C per second. The cooling rate per second may be in the range of 30 to 70 °C/sec, specifically 35 to 65 °C/sec.

[0077] If the cooling rate is out of the upper limit of the range, there is a problem of causing shape and mechanical-property deviation due to uneven cooling in the width direction together with deterioration of processability due to an increase in mechanical property. If the cooling rate is out of the lower limit of the range, the fraction of acicular ferrite grains is lowered and grain growth occurs at high temperatures, thereby making it difficult to secure high temperature characteristics.

[0078] The alloying and heating of the cold rolled steel sheet at 650 to 750°C after electroplating is to form an alloy layer of 5 to 15% by electroplating and alloying and heating the heated steel sheet. The alloying and heating may be performed at a short cracking time of 3 seconds or less. The alloying and heating may be performed in a temperature range of 650 to 750°C, specifically 660 to 745°C.

[0079] If the temperature exceeds the upper limit of the temperature range, it is advantageous in terms of securing the alloying rate of the alloy layer of a plating layer, but there is a problem in that surface grains of the plating material grow abnormally, which may act as a factor in deteriorating processability and corrosion resistance. If the temperature exceeds the lower limit of the temperature range, the target alloying rate of the alloy layer cannot be secured, and thus there is a problem of deteriorating workability when applying the cold rolled steel sheet to a battery case.

[0080] Hereinafter, specific Examples of the present invention will be described. However, the following Examples are only a specific embodiment of the present invention and the present invention is not limited to the following Examples.

Examples

[Tables 1-3]

[0081] Slab steels having compositions shown in Table 1 below and including the balance Fe and unavoidable impurities were manufactured and the components were indicated by actual values. Equation 1 in Table 1 below means a value of $0.0002 < (\text{Cr wt\%}/52)*1.6(\text{B wt\%}/11)/\{(\text{C wt\%}/12) + (\text{N wt\%}/14) < 0.0006$.

(Table 1)

Classific ation	Alloy component (wt%)									**Equatio n 1**
Compon ent	C	Mn	P	S	Al	N	Cr	B	Ni	
Inventive Steel 1	0.028	0.16	0.009	0.005	0.032	0.0031	0.16	0.0018	0.051	0.00031 5
Inventive Steel 2	0.046	0.37	0.007	0.011	0.025	0.0021	0.31	0.0024	0.047	0.00052 2
Inventive Steel 3	0.052	0.28	0.016	0.010	0.049	0.0042	0.24	0.0028	0.091	0.00040 6
Inventive Steel 4	0.068	0.13	0.013	0.008	0.076	0.0048	0.38	0.0014	0.072	0.00024 8
Compar ative Steel 1	0.008	0.22	0.006	0.006	0.034	0.0017	0.03	0.0016	0.015	0.00017 0
Compar ative Steel 2	0.034	0.29	0.011	0.014	0.125	0.0032	0.67	0.0003	0.056	0.00018 4
Compar ative Steel 3	0.062	0.84	0.042	0.011	0.028	0.0024	0.74	0.0023	0.045	0.00089 2
Compar ative Steel 4	0.047	0.07	0.009	0.009	0.0004	0.0042	0.02	0.0017	0.347	0.00002
Compar ative Steel 5	0.155	0.32	0.007	0.008	0.029	0.0084	0.26	0.0002	0.021	0.00001 1

[0082] It can be seen that Inventive Steels 1 to 4 having the compositions in Table 1 above may all have the values of Equation 1 in the range of 0.0002 to 0.0006, and Comparative Steels 1 to 5 are not included in the range of Equation 1 above. Tables 2 and 3 below show the characteristics according to a difference for each manufacturing process in Table 1 above. Inventive Steels 1 to 4 and Comparative Steels 1 to 9 were manufactured by performing steels of Inventive Steels 1 to 4 and Comparative Steels 1 to 5 under process conditions such as controlling a finish rolling temperature, a winding temperature, a cold reduction rate, an annealing temperature, a cooling rate, and an alloying temperature, and then the characteristics of each steel sheet of a $[I_{222}+I_{554}]/I_{200}$ texture ratio, an earing rate, presence of work cracks, processability, a precipitate size, an alloying rate of an alloy layer, corrosion resistance, sag resistance, and high-temperature yield strength were evaluated and shown in Table 3 below.

[0083] The $[I_{222}+I_{554}]/I_{200}$ texture ratio represents a value obtained according a relational formula after calculating the strength of (222) plane, the strength of (554) plane, and the strength of (200) plane in each planer strength through X-ray of the cold rolled steel sheet. The earing rate is a value calculated as {(maximum cup height) - (minimum cup height)} × 100/(maximum cup height) by measuring the height of each part of the cup formed after cupping under a condition that a material blank diameter/drawing die diameter, which was a drawing ratio during drawing processing, was 1.85.

[0084] In the case of work cracks, it was determined whether one or more of cups formed after cupping were fractured through drawing processing on three specimens under the condition that the blank diameter/drawing die diameter was 1.85, and when one or more fractures occurred, it was indicated as fracture. In the case of processability, when the earing rate was 3.0% or more or work cracks occurred during drawing processing, it was classified as poor (X), and when the earing rate was less than 3.0 and no work cracks occurred, it was classified as good (O).

[0085] The alloying rate represents a percentage of an area of a region where iron (Fe) and nickel (Ni) coexist measured by energy dispersive X-ray spectroscopy (EDS) for the alloying heat-treated material. The corrosion resistance was evaluated through a salt spray test (SST), and as a result, if red rust occurred within 12 hours, it was classified as poor (X), and if the red rust did not occur, it was classified as good (O).

[0086] The sag resistance was obtained by measuring the sagging of the steel sheet after heating a material with a full-length of 250 mm and a width of 30 mm at 600°C for 100 hours using heating equipment. If the sagging of the steel sheet was less than 3 mm, it was classified as good (O), and if the sagging of the steel sheet was 3 mm or more, it was classified as poor (X). The high-temperature yield strength was obtained by holding the cold rolled steel sheet at 600°C for 15 minutes and then performing a high-temperature tensile test. If the yield strength was 95 MPa or more, it was classified as good (O), and if the yield strength was less than 95 MPa, it was classified as poor (X).

(Table 2)

Steel type	Classification	Finish rolling temperature [°C]	Winding temperature [°C]	Cold reduction rate [%]	Annealing temperature [°C]	Cooling rate [°C/sec]	Alloying temperature [°C]
Inventive Steel 1	Comparative Example 1	840	680	70	680	113	680
	Example 1	910	680	85	680	47	700
	Example 2	910	680	88	720	58	730
Inventive Steel 2	Example 3	880	620	88	670	41	690
	Example 4	880	620	88	730	62	735
	Comparative Example 2	880	450	88	780	48	600
Inventive Steel 3	Example 5	900	640	87	700	47	690
	Example 6	900	640	85	740	56	720
	Comparative Example 3	960	640	96	580	23	700
Inventive Steel 4	Example 7	890	660	84	720	52	740
	Comparative Example 4	890	750	68	680	38	790
Comparative Steel 1	Comparative Example 5	920	680	86	730	41	700
Comparative Steel 2	Comparative Example 6	890	620	86	700	43	700
Comparative Steel 3	Comparative Example 7	890	620	86	700	42	700
Comparative Steel 4	Comparative Example 8	890	620	86	700	40	700
Comparative Steel 5	Comparative Example 9	890	620	86	700	38	700

(Table 3)

Classification	$[I_{222}+I_{554}]/I_{200}$ texture ratio	Earing rate [%]	Presence of work cracks	Processability	Precipitate size [μm]	Alloying rate of alloying layer [%]	Corrosion resistance	Sag resistance	High-temperature yield strength
Comparative Example 1	1.20	5.23	Fracture	X	0.005	6.2	O	X	X
Example 1	7.33	2.21	Good	O	0.034	11.4	O	O	O
Example 2	8.00	1.96	Good	O	0.032	13.9	O	O	O
Example 3	8.00	1.94	Good	O	0.057	7.3	O	O	O
Example 4	9.67	1.73	Good	O	0.071	14.2	O	O	O
Comparative Example 2	2.29	3.68	Fracture	X	0.042	2.5	X	O	X
Example 5	9.33	1.49	Good	O	0.046	6.9	O	O	O
Example 6	5.50	2,04	Good	O	0.049	12.4	O	O	O
Comparative Example 3	3.00	4.23	Fracture	X	0.009	3.4	X	X	X
Example 7	7.33	1.84	Good	O	0.086	13.7	O	O	O
Comparative Example 4	4.25	5.37	Good	X	0.004	20.3	X	X	X
Comparative Example 5	3.40	3.83	Good	X	0.001	3.2	X	X	X
Comparative Example 6	2.67	4.83	Fracture	X	0.164	4.7	X	X	O
Comparative Example 7	2.14	3.62	Good	X	0.208	3.1	X	O	X
Comparative Example 8	1.67	5.27	Fracture	X	0.002	7.2	O	X	X
Comparative Example 9	1.63	5.28	Fracture	X	0.003	3.9	X	X	X

[0087] When describing Tables 2 and 3, in Examples 1 to 7 that satisfy the range of steel components in Table 1, it can be seen that a $[I_{222}+I_{554}]/I_{200}$ texture ratio, an earing rate, presence of work cracks, processability, a (Cr-B)(C-N)-based composite precipitate size, an alloying rate, corrosion resistance, sag resistance, and high-temperature yield strength satisfy the target ranges of the present invention. Accordingly, it can be confirmed that Examples 1 to 7 secured excellent quality characteristics at room temperature and high temperature. On the other hand, in Comparative Examples 1 to 4, in which the ranges of the steel components were satisfied, but the process conditions were out of the manufacturing range of the present invention, it can be seen that the size of the ((Cr-B)(C-N)-based composite precipitate is out of the conditions of the present invention, and the $[I_{222}+I_{554}]/I_{200}$ texture ratio is out of range so that high-temperature heat resistance and D&I processability are not satisfied.

[0088] In the case of Comparative Examples 5 to 9 out of the ranges of the steel components, it can be seen that since the (Cr-B)(C-N)-based composite precipitate size, the texture ratio, the alloying rate, the work cracks, the corrosion resistance, the sag resistance, and the high-temperature yield strength do not satisfy the ranges of the present invention, heat resistance and D&I processability are not satisfied.

[0089] Accordingly, it is possible to manufacture a cold rolled steel sheet with excellent heat resistance and D&I processability that satisfy high-temperature properties, corrosion resistance, and processability at low cost by satisfying the steel composition ranges disclosed in Table 1 of Examples 1 to 7 and satisfying the manufacturing process disclosed in Table 2 to secure characteristics such as a size of the (Cr-B)(C-N)-based composite precipitate, a texture ratio, and an alloying rate targeted by the present invention.

[0090] The present invention can be manufactured in various different forms, not limited to the above embodiments, and it will be appreciated to those skilled in the present invention that the present invention may be implemented in other specific forms without changing the technical idea or essential features of the present invention. Therefore, it should be appreciated that the aforementioned exemplary embodiments are illustrative in all aspects and are not restricted.

Claims

1. A cold rolled steel sheet comprising:

   bywt%: C: 0.01 to 0.10%; Mn: 0.1 to 0.4%; Al: 0.01 to 0.10%; P: 0.003 to 0.020%; N: 0.001 to 0.006%; S: 0.015% or less; Cr: 0.1 to 0.4%; B: 0.0005 to 0.0035%; Ni: 0.04 to 0.10%; and the balance Fe and other unavoidable impurities, and
   a (Cr-B)(C-N)-based composite precipitate having a size of 0.01 to 0.1 μm,
   wherein a $[I_{222}+I_{554}]/I_{200}$ texture ratio is 5.0 to 10.0,
   an earing rate is less than 3.0%, and
   an alloying rate of an alloy layer may be 5 to 15%.

2. The cold rolled steel sheet of claim 1, wherein:

   the cold rolled steel sheet satisfies Equation 1 below:

   <Equation 1>

   $$0.0002 \le ([Cr]/52) \times 1.6([B]/11)) / (([C]/12) + ([N]/14)) \le 0.0006$$

   (in Equation 1 above, [Cr], [B], [C], and [N] refer to the weights of Cr, B, C, and N, respectively)

3. The cold rolled steel sheet of claim 1, wherein:
   during drawing processing, fracture does not occur during cupping under a condition that a blank diameter/drawing die diameter is 1.85.

4. The cold rolled steel sheet of claim 1, wherein:
   through a salt spray test, red rust does not occur within 12 hours.

5. The cold rolled steel sheet of claim 1, wherein:
   after the cold rolled steel sheet is heated at 600°C for 100 hours, the degree of sagging of the steel sheet is less than 3 mm.

6. The cold rolled steel sheet of claim 1, wherein:
   the yield strength at 600°C is 95 MPa or more.

7. A method for manufacturing a cold rolled steel sheet comprising:

   heating a steel slab including, by wt%: C: 0.01 to 0.10%; Mn: 0.1 to 0.4%; Al: 0.01 to 0.10%; P: 0.003 to 0.020%; N: 0.001 to 0.006%; S: 0.015% or less; Cr: 0.1 to 0.4%; B: 0.0005 to 0.0035%; Ni: 0.04 to 0.10%; and the balance Fe and other unavoidable impurities;
   finish hot-rolling the heated steel slab at 860 to 930°C;
   winding the finish hot-rolled hot rolled steel sheet at 580 to 700°C;
   cold-rolling the wound hot rolled steel sheet at a reduction ratio of 78 to 92%;
   annealing the cold-rolled cold rolled steel sheet at 650 to 750°C;
   cooling the annealed cold rolled steel sheet at a cooling rate of 30 to 70°C/sec; and
   electroplating the cold rolled steel sheet and then alloying and heating the cold rolled steel sheet at 650 to 750°C.

8. The method for manufacturing the cold rolled steel sheet of claim 7, wherein:

the cold rolled steel sheet satisfies Equation 1 below:

<Equation 1>

$$0.0002 \leq ([Cr]/52) \times 1.6([B]/11)) / (([C]/12) + ([N]/14)) \leq 0.0006$$

(in Equation 1 above, [Cr], [B], [C], and [N] refer to the weights of Cr, B, C, and N, respectively)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2022/020630

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/54(2006.01)i; **C21D 8/02**(2006.01)i; **C21D 9/46**(2006.01)i; **C25D 3/00**(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C 38/54(2006.01); B21B 1/24(2006.01); C21D 8/02(2006.01); C21D 9/46(2006.01); C22C 38/00(2006.01); C22C 38/14(2006.01); C22C 38/38(2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS (KIPO internal) & keywords: 냉연강판(cold rolled steel plate), 가열(heating), 열간압연(hot rolling), 권취(winding), 냉간압연(cold rolling), 소둔(annealing), 합금화 열처리(alloying heat treatment), 가공성(workability)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-2010-0001334 A (HYUNDAI STEEL COMPANY) 06 January 2010 (2010-01-06) See claim 1.	1-8
Y	KR 10-2018-0073407 A (POSCO) 02 July 2018 (2018-07-02) See paragraphs [0103] and [0118]-[0123]; and claim 7.	1-8
A	JP 2007-070659 A (NIPPON STEEL CORP.) 22 March 2007 (2007-03-22) See paragraphs [0005]-[0010].	1-8
A	KR 10-2021-0079720 A (HYUNDAI STEEL COMPANY) 30 June 2021 (2021-06-30) See claims 1-5.	1-8
A	JP 2015-206086 A (NIPPON STEEL & SUMITOMO METAL) 19 November 2015 (2015-11-19) See paragraph [0029].	1-8

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

* Special categories of cited documents:
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 March 2023	**24 March 2023**

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2022/020630

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JP 2007-070659 A	22 March 2007	JP 4959161 B2	20 June 2012
KR 10-2021-0079720 A	30 June 2021	None	
JP 2015-206086 A	19 November 2015	JP 6248782 B2	20 December 2017

Form PCT/ISA/210 (patent family annex) (July 2022)

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