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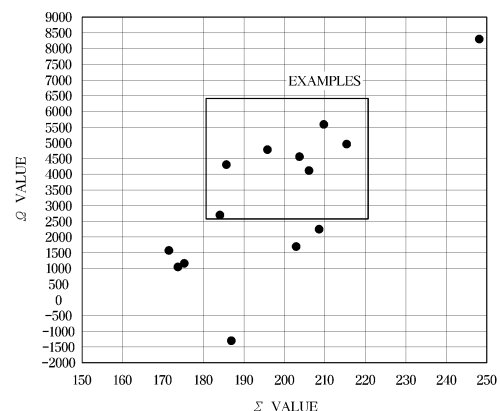
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(57) An austenitic stainless steel according to an embodiment of the present disclosure includes, in percent by weight (wt%), 0.04 to 0.07% of C, 0.3 to 0.6% of Si, 0.5 to 1.5% of Mn, 0.1 to 0.4% of Cu, 0.05 to 0.2% of Mo, 8.0 to 9.0% of Ni, 18.0 to 19.0% of Cr, 0.02 to 0.05% of N, and the remainder of Fe and inevitable impurities, wherein the thickness of the austenitic stainless steel is from 0.4 to 2.0 mm, the average grain size d at a central portion in the thickness direction is at least 3 but not more than 10 μm , the martensite fraction after cold rolling is 60% or more, the fraction of misorientation angles 15° or more is 95% or more after cold annealing, the pitting potential value is 250 mV or more, the surface roughness R_a when stretched by 30% is 0.50 μm or less, the surface roughness R_a when stretched by 20% is 0.36 μm or less, the surface roughness R_a when stretched by 10% is 0.25 μm or less, the aging crack limit drawing ratio during a drawing process is 2.0 or more, the average earring height is 2.2 mm or less, and bending cracks may not occur after a 180° bending test.

[FIG. 1]

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Description

[Technical Field]

[0001] The present disclosure relates to an austenitic stainless steel having excellent hardness, high strength-high ductility, drawability, bending properties, and improved surface properties.

[Background Art]

[0002] In general, austenitic stainless steels have been applied for various uses to manufacture parts for transportation and construction due to excellent formability, work hardenability, and weldability. However, since 304 series stainless steels or 301 series stainless steels have low yield strengths of 200 to 350 MPa, there are limits to apply these stainless steels to structural materials. Thus, a skin pass rolling process is generally conducted to increase yield strength of 300 series stainless steels for common use. However, the skin pass rolling process may cause problems of increasing manufacturing costs and significantly deteriorating elongation of materials.

[0003] Patent Document 0001 discloses a method for manufacturing a 300 series stainless steel for a laser metal mask for photoetching having a small curvature even after half etching, by performing stress relief (SR) heat treatment twice after skin pass rolling a cold-rolled, annealed material. However, Patent Document 0001 relates to a manufacturing method to control etchability and a curvature after etching, but does not include technical content regarding structural parts with a thickness of 0.4 to 2.0 mm. Because an austenitic stability parameter (ASP) calculated by $Md30(^{\circ}C)=497-462*([C]+[N])-9.2*[Si]-8.1*[Mn]-13.7*[Cr]-20*[Ni]+[Cu]-18.7*[Mo]$ is in the range of 30 to 50, strain-induced martensite transformation occurs too quickly during forming, for example, during a tensile test, resulting in deterioration of elongation.

[0004] Patent Document 0002 discloses a method of performing heat treatment for a long time over 48 hours in a temperature range of 600 to 700°C to adjust an average grain size to 10 μm or less. However, according to the method disclosed in Patent Document 2, productivity decreases in the case of being implemented in a real production line, and manufacturing costs increase.

(Related Art Documents)

[0005]

Patent Document 0001: International Patent Application Publication No. 2016-043125 A1 (Date of Publication: March 14, 2016)

Patent Document 0002: Japanese Patent Application Laid-Open No. 2020-050940 A (Date of Publication: April 2, 2020)

[Disclosure]

[Technical Problem]

[0006] The present disclosure has been proposed to solve the above-described problems, and provided is an austenitic stainless steel having excellent surface roughness properties without surface cracks at bent portions by suggesting an ultra-fine grain manufacturing technique realizing hardness, high strength-high ductility, drawability, bending properties, and sound surface properties of bent portions.

[Technical Solution]

[0007] An austenitic stainless steel according to an embodiment of the present disclosure includes, in percent by weight (wt%), 0.04 to 0.07% of C, 0.3 to 0.6% of Si, 0.5 to 1.5% of Mn, 0.1 to 0.4% of Cu, 0.05 to 0.2% of Mo, 8.0 to 9.0% of Ni, 18.0 to 19.0% of Cr, 0.02 to 0.05% of N, and the remainder of Fe and inevitable impurities, wherein a Σ value represented by Equation (1) below is at least 180 but not more than 240:

$$\Sigma = 105 + 146d^{-1/2} + 7.36SPM_El + 102[C] + 154[N] + 51.8[Si] + 1.4[Mo] - 17.7[Cu] \quad \text{Equation (1):}$$

(in Equation (1), [C], [N], [Si], [Mo], and [Cu] represent weight percentages (wt%) of respective elements, d represents an average grain size (μm), and SPM_El represents a difference in elongation (%) before and after skin pass milling).

[0008] In addition, in the austenitic stainless steel, an Ω value represented by Equation (2) below may be 2500 or more:

$$\text{Equation (2): } \Omega = \text{YS} \cdot \text{El} - 500 \cdot ([\text{Ni}] + [\text{Cr}] + [\text{Cu}] + [\text{Mn}])$$

(in Equation (2), [Ni], [Cr], [Cu], and [Mn] represent weight percentages (wt%) of respective elements, YS represents yield strength (MPa), and El represents elongation (%)).

[0009] In addition, in the austenitic stainless steel, an austenitic stability parameter (ASP) value represented by Equation (3) below may be from -5 to 12:

$$\text{ASP} = 551 - 462 \cdot ([\text{C}] + [\text{N}]) - 9.2 \cdot [\text{Si}] - 8.1 \cdot [\text{Mn}] - 13.7 \cdot [\text{Cr}] - 29 \cdot ([\text{Ni}] + [\text{Cu}]) - 18.5 \cdot [\text{Mo}] \quad \text{Equation (3):}$$

(in Equation (3), [C], [N], [Si], [Mn], [Cr], [Ni], [Cu], and [Mo] represent weight percentages (wt%) of respective elements).

[0010] In addition, in the austenitic stainless steel, a Π value represented by Equation (4) below may be 6000 or more:

$$\Pi = 100 \cdot \text{FCRR} \text{ (final cold rolling ratio, \%)} + 100 \cdot \text{ASP} \text{ (austenitic stability parameter)} + \text{CAT} \text{ (cold annealing temperature, } ^\circ\text{C)} \quad \text{Equation (4):}$$

(in Equation (4), FCRR is a reduction ratio by cold rolling before final cold annealing, ASP is a value obtained by Equation (3), and CAT is a value defined by a temperature of a final cold-annealed steel material).

[0011] In addition, in the austenitic stainless steel, an average grain size d at a central portion in the thickness direction of a transverse direction (TD) side may be at least 3 but not more than 10 μm assuming that a total thickness of a steel material is t .

[0012] In addition, in the austenitic stainless steel, the t may be from 0.4 to 2.0 mm.

[0013] In addition, in the austenitic stainless steel, a martensite fraction (%) of a cold-rolled material may be 60% or more when the central portion in the thickness direction of the transverse direction (TD) side is analyzed by electron back scatter diffraction (EBSD).

[0014] In addition, in the austenitic stainless steel, a fraction (%) of misorientation angles 15° or more may be 95% or more when the central portion in the thickness direction of the transverse direction (TD) side is analyzed by electron back scatter diffraction (EBSD).

[0015] In addition, in the austenitic stainless steel, a pitting potential measured by immersing the austenitic stainless steel in a 3.5% NaCl solution at 30°C may be 250 mV or more.

[0016] In addition, in the austenitic stainless steel, a surface roughness R_a when stretched by 30% may be 0.50 μm or less, a surface roughness when stretched by 20% R_a may be 0.36 μm or less, and a surface roughness R_a when stretched by 10% may be 0.25 μm or less.

[0017] In addition, in the austenitic stainless steel, the austenitic stainless steel may have an aging crack limit drawing ratio of 2.0 or more.

[0018] In addition, in the austenitic stainless steel, an average earring height may be 2.2 mm or less after a drawing process of the stainless steel.

[0019] In addition, in the austenitic stainless steel, surface cracks do not occur in a bent portion after a 180° bending test.

[Advantageous Effects]

[0020] According to an embodiment of the present disclosure, a ultra-fine grain 300 series stainless steel having excellent hardness may be provided.

[0021] According to an embodiment of the present disclosure, a ultra-fine grain 300 series stainless steel satisfying both high strength and high ductility may be provided.

[0022] According to an embodiment of the present disclosure, an austenitic stainless steel having excellent surface roughness without surface cracks at bent portions may be provided by a ultra-fine grain manufacturing technique realizing bending formability and sound surface properties of bent portions.

[Description of Drawings]

[0023]

FIG. 1 is a graph showing Σ and S2 values of embodiments and comparative examples.

FIG. 2 is a photograph showing a microstructure of an embodiment satisfying a Π value of 6000 or more.

FIG. 3 is a photograph showing non-annealed bands in a microstructure of Comparative Example 1 in which the Π value is less than 6000.

FIG. 4 is a photograph showing cold-rolled materials according to embodiments in which fractions (%) of martensite

(red color) are 91.5% and 73.5% when phase fractions of a central portion in the thickness direction of the transverse direction (TD) side is analyzed by electron back scatter diffraction (EBSD).

FIG. 5 is a photograph showing a cold-rolled material according to a comparative example in which a fraction (%) of martensite (red color) is 48.5% when a phase fraction of a central portion in the thickness direction of the transverse direction (TD) side is analyzed by electron back scatter diffraction (EBSD).

FIG. 6 is a photograph showing cold-annealed materials according to an embodiment in which fractions (%) of misorientation angles of 15° or more are 96% and 96.5% when a central portion in the thickness direction of the transverse direction (TD) side is analyzed by electron back scatter diffraction (EBSD).

FIG. 7 is a photograph showing a cold-annealed material according to a comparative example in which a fraction (%) of misorientation angles of 15° or more is 92.9% when a central portion in the thickness direction of the transverse direction (TD) side is analyzed by electron back scatter diffraction (EBSD). Here, a misorientation angle less than 15° corresponds to red color.

FIG. 8 is a photograph showing an average grain size at a central portion in the thickness direction of the transverse direction (TD) side of a steel material with a thickness of 0.4 to 2.0 mm manufactured according to an embodiment.

FIG. 9 is a photograph showing an average grain size at a central portion in the thickness direction of the transverse direction (TD) side of a steel material with a thickness of 0.4 to 2.0 mm manufactured according to a comparative example.

FIG. 10 shows surface roughness Ra (μm) values of an embodiment and Comparative Example 2 according to tensile strain.

FIG. 11 is a photograph showing shapes of surface roughness Ra (μm) according to tensile strain in an embodiment and a comparative example.

FIG. 12 is a photograph showing earring heights after a drawing process in an embodiment and a comparative example.

[Best Mode]

[0024] An austenitic stainless steel according to an embodiment of the present disclosure includes, in percent by weight (wt%), 0.04 to 0.07% of C, 0.3 to 0.6% of Si, 0.5 to 1.5% of Mn, 0.1 to 0.4% of Cu, 0.05 to 0.2% of Mo, 8.0 to 9.0% of Ni, 18.0 to 19.0% of Cr, 0.02 to 0.05% of N, and the remainder of Fe and inevitable impurities, wherein a Σ value represented by Equation (1) below may be at least 180 but not more than 240.

$$\Sigma = 105 + 146d^{-1/2} + 7.36\text{SPM_EI} + 102[\text{C}] + 154[\text{N}] + 51.8[\text{Si}] + 1.4[\text{Mo}] - 17.7[\text{Cu}] \quad \text{Equation (1):}$$

[0025] In Equation (1) above, [C], [N], [Si], [Mo], and [Cu] represent weight percentages (wt%) of respective elements, d represents an average grain size (μm), and SPM_EI represents a difference in elongation (%) before and after skin pass milling.

[Modes of the Invention]

[0026] Hereinafter, embodiments of the present disclosure will be described in detail with reference to the accompanying drawings. The embodiments of the present disclosure may, however, be embodied in many different forms and should not be construed as being limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the concept of the invention to those skilled in the art.

[0027] The terms used herein are merely used to describe particular embodiments. An expression used in the singular encompasses the expression of the plural, unless otherwise indicated. Throughout the specification, the terms such as "including" or "having" are intended to indicate the existence of features, operations, functions, components, or combinations thereof disclosed in the specification, and are not intended to preclude the possibility that one or more other features, operations, functions, components, or combinations thereof may exist or may be added.

[0028] Meanwhile, unless otherwise defined, all terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Thus, these terms should not be interpreted in an idealized or overly formal sense unless expressly so defined herein. As used herein, the singular forms are intended to include the plural forms as well, unless the context clearly indicates otherwise.

[0029] The terms "about", "substantially", etc. used throughout the specification means that when a natural manufacturing and a substance allowable error are suggested, such an allowable error corresponds the value or is similar to the value, and such values are intended for the sake of clear understanding of the present invention or to prevent an unconscious infringer from illegally using the disclosure of the present invention.

[0030] An austenitic stainless steel according to an embodiment of the present disclosure may include, in percent by

weight (wt%), 0.04 to 0.07% of C, 0.3 to 0.6% of Si, 0.5 to 1.5% of Mn, 0.1 to 0.4% of Cu, 0.05 to 0.2% of Mo, 8.0 to 9.0% of Ni, 18.0 to 19.0% of Cr, 0.02 to 0.05% of N, and the remainder of Fe and inevitable impurities.

[0031] Hereinafter, reasons for numerical limitations on the contents of alloying elements in the embodiment of the present disclosure will be described.

[0032] The content of carbon (C) may be from 0.04% to 0.07%.

[0033] C is an austenite phase-stabilizing element. In consideration thereof, C may be added in an amount of 0.04% or more. However, since an excess of C causes a problem of deteriorating grain boundary corrosion resistance by forming a chromium carbide during low-temperature annealing. In consideration thereof, the upper limit of the C content may be controlled to 0.07%.

[0034] The content of silicon (Si) may be from 0.3 to 0.6%.

[0035] Si is an element added as a deoxidizer during a steel-making process and has an effect on improving corrosion resistance of a steel by forming an Si oxide in a passivated layer in the case of performing a bright annealing process. In consideration thereof, Si may be added in an amount of 0.3 wt% or more. However, an excess of Si may cause a problem of deteriorating ductility. In consideration thereof, the upper limit of the Si content may be controlled to 0.6%.

[0036] The content of manganese (Mn) may be from 0.5 to 1.5%.

[0037] Mn is an austenite phase-stabilizing element. In consideration thereof, Mn may be added in an amount of 0.5 wt% or more. However, an excess of Mn may cause a problem of deteriorating corrosion resistance. In consideration thereof, the upper limit of the Mn content may be controlled to 1.5%.

[0038] The content of nickel (Ni) may be from 8.0 to 9.0%.

[0039] Ni is an austenite phase-stabilizing element and has an effect on softening a steel material. In consideration thereof, Ni may be added in an amount of 8.0 wt% or more. However, an excess of Ni may cause a problem of increasing costs. In consideration thereof, the upper limit of the Ni content may be controlled to 9.0 wt%.

[0040] The content of chromium (Cr) may be from 18.0 to 19.0%.

[0041] Cr is a major element for improving corrosion resistance of a stainless steel. In consideration thereof, Cr may be added in an amount of 18.0 wt% or more. However, an excess of Cr causes problems of hardening of a steel material and inhibiting strain-induced martensite transformation during cold rolling. In consideration thereof, the upper limit of the Cr content may be controlled to 19.0 wt%.

[0042] The content of copper (Cu) may be from 0.1 to 0.4%.

[0043] Cu is an austenite phase-stabilizing element. In consideration thereof, Cu may be added in an amount of 0.1% or more. However, an excess of Cu may cause problems of deteriorating corrosion resistance of a steel material and increasing costs. In consideration thereof, the upper limit of the Cu content may be controlled to 0.4%.

[0044] The content of nitrogen (N) may be from 0.02 to 0.05%.

[0045] N is an austenite phase-stabilizing element and improves strength of a steel material. In consideration thereof, N may be added in an amount of 0.02% or more. However, an excess of N causes problems of hardening a steel material and deteriorating hot workability. In consideration thereof, the upper limit of the N content may be controlled to 0.05 wt%.

[0046] The content of molybdenum (Mo) may be from 0.05 to 0.2%.

[0047] Mo has an effect on improving corrosion resistance and workability. In consideration thereof, Mo may be added in an amount of 0.05% or more. However, an excess of Mo may cause a problem of increasing costs. In consideration thereof, the upper limit of the Mo content may be controlled to 0.2 wt%.

[0048] The remaining component of the composition of the present disclosure is iron (Fe). However, the composition may include unintended impurities inevitably incorporated from raw materials or surrounding environments, and thus addition of other alloying elements is not excluded. These impurities are known to any person skilled in the art of manufacturing and details thereof are not specifically mentioned in the present disclosure.

[0049] As well as limiting the contents of the alloying elements of the stainless steel according to the present disclosure as described above, the relationships therebetween may further be limited as follows.

[0050] In an embodiment of the present disclosure, a Σ value represented by Equation (1) below may be at least 180 but not more than 240.

$$\Sigma = 105 + 146d^{-1/2} + 7.36\text{SPM_EI} + 102[\text{C}] + 154[\text{N}] + 51.8[\text{Si}] + 1.4[\text{Mo}] - 17.7[\text{Cu}] \quad \text{Equation (1):}$$

[0051] Σ is an indicator representing hardness of a material, and a higher Σ value indicates a greater hardness.

[0052] In Equation (1) above, [C], [N], [Si], [Mo], and [Cu] represent weight percentages (wt%) of respective elements, d represents an average grain size (μm), and SPM_EI represents a difference in elongation (%) before and after skin pass milling.

[0053] The SPM_EI according to an embodiment of the present disclosure may be from 0.01 to 1.2.

[0054] The skin pass milling may be performed to improve gloss of a steel material and to ensure the shape of a coil.

[0055] In an embodiment of the present disclosure, an Ω value represented by Equation (2) below may be 2500 or more.

$$\text{Equation (2): } \Omega = \text{YS} \cdot \text{EI} - 500 \cdot ([\text{Ni}] + [\text{Cr}] + [\text{Cu}] + [\text{Mn}])$$

[0056] Ω is an indicator representing high strength and high ductility, and a higher Ω value indicates a higher product of strength and ductility.

[0057] In Equation (2) above, [Ni], [Cr], [Cu], and [Mn] represent weight percentages (wt%) of respective elements, YS represents yield strength (MPa), and EI represents elongation (%).

[0058] The YS and EI values refer to values obtained after a tensile test is conducted on a sample according to JIS13B standards at room temperature in a crosshead range of 10 mm/min to 20 mm/min.

[0059] In an embodiment of the present disclosure, an austenitic stability parameter (ASP) value represented by Equation (3) below may be from -5 to 12.

$$\text{ASP} = 551 - 462 \cdot ([\text{C}] + [\text{N}]) - 9.2 \cdot [\text{Si}] - 8.1 \cdot [\text{Mn}] - 13.7 \cdot [\text{Cr}] - 29 \cdot ([\text{Ni}] + [\text{Cu}]) - 18.5 \cdot [\text{Mo}]$$

Equation (3):

[0060] In Equation (3) above, [C], [N], [Si], [Mn], [Cr], [Ni], [Cu], and [Mo] represent weight percentages (wt%) of respective elements.

[0061] If the ASP value is out of the range of -5 to 12, transformation of a material excessively occurs, failing to satisfy a desired elongation in the present disclosure.

[0062] In an embodiment of the present disclosure, a Π value represented by Equation (4) below may be 6000 or more.

$$\Pi = 100 \cdot \text{FCRR} (\text{final cold rolling ratio, \%}) + 100 \cdot \text{ASP} (\text{austenitic stability parameter}) + \text{CAT} (\text{cold annealing temperature, } ^\circ\text{C})$$

Equation (4):

[0063] Π is an indicator that represents the degree of completion of recrystallization, and a higher Π value indicates a higher degree of recrystallization.

[0064] In Equation (4) above, FCRR refers to a reduction ratio by cold rolling before final cold annealing, ASP refers to a value obtained by Equation (3), and CAT refers to a value defined by a temperature of a final cold-rolled, annealed steel material.

[0065] The average grain size d according to an embodiment of the present disclosure may be at least 3 but not more than 10 μm .

[0066] The average grain size refers to an average grain size at a central portion in the thickness direction of the transverse direction (TD) side assuming that a total thickness of a steel material is t , and the average refers to an average of values measured at 5 random positions, and the central portion refers to a position located from $1/4t$ to $3/4t$ assuming that the total thickness of the steel material is t .

[0067] The total thickness t according to an embodiment of the present disclosure may be from 0.4 to 2.0 mm. Materials with a thickness of 0.4 to 2.0 mm are widely used for parts of kitchen and building materials, and stainless steel having excellent hardness, high strength, and high ductility may be provided within the thickness range described above according to the present disclosure.

[0068] In an embodiment of the present disclosure, when the central portion in the thickness direction of the transverse direction (TD) side is analyzed by electron back scatter diffraction (EBSD), a martensite phase fraction (%) of a cold-rolled material may be 60% or more, and a fraction (%) of misorientation angles of 15° or more may be 95% or more after cold annealing.

[0069] A misorientation angle is 15° or more indicates that recrystallization occurs after cold annealing, and a misorientation angle less than 15° indicates that recrystallization does not occur due to a small difference in orientations.

[0070] The average grain size d , the martensite fraction (%) of the cold-rolled material, and the fraction (%) of misorientation angles of 15° or more after cold annealing of the present disclosure were measured by analyzing orientations of the central portion in the thickness direction by electron back scatter diffraction (EBSD) with Model No. e-Flash FS.

[0071] Pitting potential refers to a critical potential causing corrosion in the form of holes in a passivated metal material. The austenitic stainless steel according to an embodiment of the present disclosure may have a pitting potential of 250 mV or more when measured by immersing the austenitic stainless steel in a NaCl solution and applying a potential causing pitting thereto. In this regard, a temperature of the NaCl solution may be 30°C and a concentration thereof may be 3.5%.

[0072] The austenitic stainless steel according to an embodiment of the present disclosure may have a surface roughness R_a of 0.50 μm or less when stretched by 30%, a surface roughness R_a of 0.36 μm or less when stretched by 20%, and a surface roughness R_a of 0.25 μm when stretched by 10%.

[0073] In the case of performing a drawing process with a punch size of $\Phi 50$ mm and a disc size of $\Phi 100$ mm according to an embodiment of the present disclosure, an aging crack limit drawing ratio may be 2.0 or more. In addition, an average earring height may be 2.2 mm or less.

[0074] The aging crack limit drawing ratio, as a limit drawing ratio not causing aging cracks, refers to a ratio of maximum diameter of a material to punch diameter during a drawing process.

[0075] The average earring height refers to an average of a value obtained by subtracting a sum of minimum heights h of earrings from a sum of maximum heights H of earrings from the bottom after the drawing process.

[0076] Surface cracks may not occur at bent portions after a 180° bending test according to an embodiment of the present disclosure.

[0077] Hereinafter, a method of manufacturing an austenitic stainless steel according to an embodiment of the present disclosure will be described in more detail.

[0078] A method of manufacturing an austenitic stainless steel according to an embodiment of the present disclosure may include: manufacturing a slab including, in percent by weight (wt%), 0.04 to 0.07% of C, 0.3 to 0.6% of Si, 0.5 to 1.5% of Mn, 0.1 to 0.4% of Cu, 0.05 to 0.2% of Mo, 8.0 to 9.0% of Ni, 18.0 to 19.0% of Cr, 0.02 to 0.05% of N, and the remainder of Fe and inevitable impurities;

hot rolling and hot annealing the slab into a hot-rolled steel sheet; and

cold rolling and cold annealing the hot-rolled steel sheet into a cold-rolled steel sheet.

[0079] Reasons for limitations on the composition of alloying elements are as described above, and hereinafter, processes of the manufacturing method will be described in more detail.

[0080] The hot annealing may be performed at a temperature of 1000 to 1150°C.

[0081] When a hot annealing temperature is below 1000°C, elongation may deteriorate due to a high fraction of remaining martensite. On the contrary, when the hot annealing temperature exceeds 1150°C, strength may decrease due to coarsening of crystal grains. In consideration thereof, the hot annealing is performed at a temperature of 1000 to 1150°C.

[0082] A reduction ratio of the cold rolling may be 60% or more.

[0083] When the reduction ratio is less than 60%, the martensite fraction of the cold-rolled material decreases and the fraction of retained austenite phase increases due to a too low amount of TRIP transformation. As the amount of the strain-induced martensite decreases, the ratio of the reverted austenite phase during the subsequent low-temperature annealing decreases, and the fraction of retained austenite phase without being transformed into martensite increases, making it difficult to obtain ultra-fine grains.

[0084] The cold annealing may be performed at a temperature of 800 to 950°C.

[0085] When the temperature of the cold annealing is below 800°C, recrystallization does not sufficiently occur, resulting in a decrease in elongation. On the contrary, when the temperature of the cold annealing exceeds 950°C, grains coarsen making formation of ultra-fine grains with a size of 3 to 10 μm difficult, so that there may be problems such as surface cracks occurring at bent portions of the austenitic stainless steel and worsening of surface roughness. In consideration thereof, the cold annealing is performed at a temperature of 800 to 950°C.

[0086] In addition, the manufacturing method may be a method of manufacturing an austenitic stainless steel including skin pass milling the cold-rolled steel sheet.

[0087] The SPM_EI, as a difference in elongation (%) before and after skin pass milling, may be from 0.01 to 1.2.

[0088] Hereinafter, the present disclosure will be described in more detail through following examples. However, it is necessary to note that the following examples are only intended to illustrate the present disclosure in more detail and are not intended to limit the scope of the present disclosure. This is because the scope of the present disclosure is determined by matters described in the claims and able to be reasonably inferred therefrom.

Examples

[0089] Slabs having the compositions of alloying elements shown in Table 1 below were hot-rolled and hot-annealed at a temperature of 1000 to 1150°C, and then cold-rolled at room temperature with a reduction ratio of 60% or more. Subsequently, the resultant was cold-annealed at a temperature of 800 to 950°C into a cold annealed material.

[Table 1]

Category	C	Si	Mn	Cr	Ni	Cu	Mo	N
Example 1	0.05	0.3	1.1	18.1	8.1	0.25	0.1	0.03
Example 2	0.05	0.3	1.1	18.1	8.1	0.25	0.1	0.03
Example 3	0.06	0.3	1.1	18.1	8.1	0.25	0.1	0.04
Example 4	0.06	0.5	1.1	18.1	8.1	0.22	0.1	0.05
Example 5	0.04	0.4	0.8	18.1	8.1	0.24	0.1	0.05

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(continued)

Category	C	Si	Mn	Cr	Ni	Cu	Mo	N
Example 6	0.04	0.3	0.8	18.1	8.2	0.35	0.1	0.05
Comparative Example 1	0.05	<u>0.2</u>	1.1	18.1	8.05	0.28	0.1	0.04
Comparative Example 2	0.06	0.5	1.1	18.1	8.1	0.22	0.1	0.05
Comparative Example 3	<u>0.02</u>	0.3	1.4	18.5	8.7	0.35	0.1	0.04
Comparative Example 4	0.05	0.4	1.1	<u>19.1</u>	<u>9.5</u>	0.35	0.1	0.04
Comparative Example 5	<u>0.10</u>	0.3	1.1	<u>17.1</u>	<u>6.8</u>	0.25	0.1	0.03
Comparative Example 6	<u>0.02</u>	0.3	<u>2.5</u>	<u>17.2</u>	<u>2.5</u>	0.25	0.1	<u>0.12</u>
Comparative Example 7	0.05	<u>0.2</u>	<u>5.5</u>	18.1	<u>3.5</u>	<u>1.50</u>	0.1	0.04
Comparative Example 8	<u>0.10</u>	<u>0.2</u>	<u>6.5</u>	18.1	<u>2.5</u>	0.25	0.1	<u>0.20</u>

[0090] Table 2 below shows output values of Equations (1) to (4) based on the contents of the elements of Table 1, skin pass mill elongations (SPM EI, %), final cold rolling ratios (FCRR, %), cold annealing temperatures (CAT, °C), and YS(MPa)*EI (%) values.

[Table 2]

Category	SPM_EI (%)	FCRR (%)	CAT (°C)	YS(MPa)*EI (%)	Equation (1): Σ	Equation (2): Ω	Equation (3): ASP	Equation (4): Π
Example 1	0.5	72	950	16464	184	2689	10.4	9190
Example 2	0.7	65	850	18576	196	4801	10.4	8390
Example 3	0.7	82	800	18758	215	4983	1.2	9116
Example 4	1.0	67	900	17889	206	4129	-4.4	7157
Example 5	1.0	75	820	19228	210	5608	7.6	9078
Example 6	0.4	67	925	18040	186	4315	2.4	7866
Comparative Example 1	0.5	<u>35</u>	<u>750</u>	18336	204	4571	7.3	<u>4978</u>
Comparative Example 2	0.5	82	<u>1100</u>	14824	<u>174</u>	<u>1064</u>	-4.4	8857
Comparative Example 3	0.5	62	<u>980</u>	16065	<u>171</u>	<u>1590</u>	<u>-8.6</u>	6323
Comparative Example 4	0.4	70	950	16203	<u>175</u>	<u>1178</u>	<u>-52.3</u>	<u>2716</u>
Comparative Example 5	0.4	68	800	14331	203	<u>1706</u>	<u>38.7</u>	11470
Comparative Example 6	0.4	70	800	13568	209	<u>2343</u>	<u>146.1</u>	22407
Comparative Example 7	0.5	68	800	13003	187	<u>-1297</u>	<u>68.2</u>	14421
Comparative Example 8	0.5	64	<u>780</u>	22000	248	8325	<u>28.3</u>	10014

[0091] The YS and EI values refer to values obtained after conducting a tensile test on the manufactured samples according to the JIS13B standards at room temperature within a crosshead range of 10 mm/min to 20mm/min.

[0092] The cold annealed material was manufactured into a sample having a thickness of 0.4 to 2.0 mm. Then, average grain sizes d at central portions in the thickness direction of the samples, pitting potentials (mV), occurrence of surface cracks in bent portions after a 180° bending test (radius of curvature R of the bent portion is the same as the thickness of the

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material), and surface roughnesses at different tensile strains in a uniaxial tensile test were measured, and results are shown in Table 3 below.

[Table 3]

Category	d (μm)	Pitting potential (mV)	Surface roughness at 10% tensile strain (Ra, μm)	Surface roughness at 20% tensile strain (Ra, μm)	Surface roughness at 30% tensile strain (Ra, μm)	Bending cracks (Y/N)
Example 1	7.2	341	0.22	0.36	0.49	N
Example 2	5.1	283	0.18	0.28	0.39	N
Example 3	3.2	254	0.15	0.17	0.19	N
Example 4	6.4	313	0.20	0.38	0.45	N
Example 5	4.5	289	0.17	0.24	0.32	N
Example 6	6.7	305	0.21	0.35	0.48	N
Comparative Example 1	3.5	<u>240</u>	0.15	0.18	0.25	<u>Y</u>
Comparative Example 2	<u>25.2</u>	312	<u>0.38</u>	<u>0.66</u>	<u>0.80</u>	N
Comparative Example 3	<u>10.5</u>	345	<u>0.28</u>	<u>0.45</u>	<u>0.55</u>	N
Comparative Example 4	<u>12.5</u>	322	<u>0.32</u>	<u>0.49</u>	<u>0.61</u>	N
Comparative Example 5	4.5	255	0.15	0.24	0.32	<u>Y</u>
Comparative Example 6	4.5	295	0.15	0.25	0.32	<u>Y</u>
Comparative Example 7	3.1	<u>150</u>	0.14	0.18	0.25	<u>Y</u>
Comparative Example 8	<u>2.5</u>	<u>190</u>	0.11	0.16	0.11	<u>Y</u>

[0093] The average grain size d of the central portion in the thickness direction refers to an average grain size d of the central portion in the thickness direction of the transverse direction (TD) side of each sample having a thickness of 0.4 to 2.0 mm.

[0094] The average grain size d of the present disclosure was measured by analyzing orientations at the central portion in the thickness direction by electron back scatter diffraction (EBSD) with Model No. e-Flash FS.

[0095] The pitting potential refers to a potential at which pitting occurs measured by immersing each sample in a 3.5% NaCl solution at 30°C, and applying potentials thereto.

[0096] The tensile strain refers to a value measured by a uniaxial tensile test conducted on each sample according to JIS13B standards with a crosshead speed of 10 to 20 mm/min.

[0097] Occurrence of bending cracks was measured by a 180° bending test conducted by adjusting the radius of curvature R of the bent portion to be equal to the thickness of the material and bending once.

[0098] Table 4 below shows average earring heights according to an embodiment of the present disclosure.

[Table 4]

	Earring 1	Earring 2	Earring 3	Earring 4	Average earring height
Comparative Example maximum height (H)	43.54	42.87	43.67	44.00	2.87
Comparative Example minimum height (h)	40.96	39.87	40.82	40.96	
Example maximum height (H)	41.59	42.40	42.87	42.62	1.88
Example minimum height (h)	40.05	39.86	40.96	41.07	

[0099] The average earring height refers to an average of a value obtained by subtracting a sum of minimum heights h of earrings from a sum of maximum heights H of earrings from the bottom after a drawing process. H refers to a maximum height, h refers to a minimum height, and Earrings 1 to Earring 4 are random orders of the earrings.

[0100] LDR value and average earring height refer to aging crack limit drawing ratio and average earring height in the case of conducting a drawing process with a punch size of $\Phi 50$ mm and a disc size of $\Phi 100$ mm, respectively.

[0101] Referring to Tables 1 and 2, all of Examples 1 to 6 satisfied the Σ value (Equation (1)) range of at least -180 but not more than 240 and the S2 value (Equation (2)) range of 2500 or more, and may realize excellent hardness, high strength, and high ductility.

[0102] Referring to Tables 1 to 3, all of Examples 1 to 6 satisfied the ASP value (Equation (3)) range of -5 to 12 and the Π value (Equation (4)) of 6000 or more, so that surface cracks did not occur after the 180° bending test.

[0103] Referring to Table 3, in the case of Examples 1 to 6, the average grain sizes d of the central portions in the thickness direction satisfied the range of at least 3 but not more than 10 μm in the material having a thickness of 0.4 to 2.0 mm, and after the uniaxial tensile test, the surface roughnesses R_a when stretched by 30% were not more than 0.50 μm , the surface roughnesses R_a when stretched by 20% were not more than 0.36 μm , and the surface roughnesses R_a when stretched by 10% were not more than 0.25 μm . In addition, the pitting potentials satisfied the range of 250 mV or more.

[0104] On the contrary, the Σ values of Comparative Examples 2 to 4 were less than 180 failing to satisfy the hardness of the present disclosure. This may be confirmed in Table 2.

[0105] In addition, the S2 values of Comparative Examples 2 to 7 were less than 2500 failing to satisfy the high strength-high ductility of the present disclosure. This may be confirmed in Table 2.

[0106] In addition, the ASP values of Comparative Examples 3 to 8 were out of the ASP range disclosed in the present disclosure. According to Comparative Examples 5 to 8 in which the ASP values exceeded 12, elongation was low due to too fast transformation rates. According to Comparative Examples 2 to 4 in which the ASP values were less than -5, ultra-fine grains could not be obtained due to high fractions of the remaining austenite phase. This may be confirmed in Tables 2 and 3.

[0107] In addition, non-annealed bands are shown in Comparative Example 1 because the Π value is smaller than 6000, and bending cracks occur after the 180° bending test in the steel material including the same. This may be confirmed in Tables 2 and 3 and FIG. 3. On the contrary, FIG. 2 shows a microstructure of an embodiment in which a non-annealed band is not observed and bending cracks do not occur after the 180° bending test.

[0108] In addition, Comparative Examples 6 to 8 exhibited low pitting potentials because the Mn contents were excessive due to the low Ni contents, resulting in deterioration of corrosion resistance.

[0109] Also, because the average grain size d of Comparative Example 2 was 25.2, which was greater than that of the present disclosure, the surface roughness was greater in accordance with the tensile strain. This may be confirmed in Table 3 and FIG. 6.

[0110] FIG. 1 shows ranges of Σ values and Ω values of Examples 1 to 6 and Comparative Examples 1 to 8. Comparative Examples 2 to 8 did not simultaneously satisfy the Σ value and the S2 value. That is, both of hardness and high strength-high ductility cannot be satisfied thereby.

[0111] FIGS. 2 and 3 are photographs showing microstructures of central portions in the thickness direction obtained by EBSD. Non-annealed bands were observed in the microstructure in a comparative example (FIG. 3). On the contrary, non-annealed bands were not observed in the microstructure of an embodiment (FIG. 2). In comparison, the austenitic stainless steel according to an embodiment of the present disclosure was confirmed to have ultra-fine grains without non-annealed portions in the form of band.

[0112] FIGS. 4 and 5 show fractions (%) of martensite (red color) in cold-rolled materials of an embodiment and a comparative example when the phase fraction of the central portion in the thickness direction of the transverse direction (TD) side was analyzed by electron back scatter diffraction (EBSD) after cold rolling. The martensite fraction of 60% or more in the embodiment (FIG. 4) may be compared with the martensite fraction less than 60% in the comparative example (FIG. 5).

[0113] FIGS. 6 and 7 show fractions (%) of misorientation angles of 15° or more in the cold-annealed materials of an embodiment and a comparative example when the central portion in the thickness direction of the transverse direction (TD) side was analyzed by electron back scatter diffraction (EBSD). The fraction (%) of misorientation angles $\geq 15^\circ$ of 95% or more in the embodiment (FIG. 6) may be compared with the fraction (%) of misorientation angles $< 15^\circ$ of 95% in the comparative example (FIG. 7). The misorientation angle less than 15° corresponds to red color.

[0114] FIGS. 8 and 9 are photographs showing average grain sizes of central portions in the thickness direction of the transverse direction (TD) side in a steel material with a thickness of 0.4 to 2.0 mm according to an embodiment and a comparative example. It was confirmed that the average grain size of the comparative example (FIG. 9) was greater than that of the embodiment (FIG. 8).

[0115] FIG. 10 shows surface roughnesses R_a (μm) values of Comparative Example 2 having a greater average grain size of a central portion on the surface of the manufactured steel material than that of the embodiment after conducting a uniaxial tensile test at different tensile strains with a crosshead speed of 10 to 20 mm/min. It was confirmed that the surface

roughness Ra values at the tensile strains did not satisfy the range of the present disclosure when the average grain size is out of the range of the present disclosure.

[0116] FIG. 11 is a photograph showing shapes of surface roughness Ra (μm) after a uniaxial tensile test was performed at different tensile strains with a crosshead speed of 10 to 20 mm/min. Units of the x-axis and y-axis were mm and the unit of the height corresponds to μm . Because the height increases as the strains increases, it was confirmed surface roughness was high. On the contrary, it may be confirmed that the embodiment exhibited lower surface roughness than that of comparative example although strains are applied thereto.

[0117] FIG. 12 is a photograph showing earring heights after a drawing process (punch size of $\Phi 50$ mm and disc size of $\Phi 100$ mm). The average earring height is an average of a value obtained by subtracting a sum of minimum heights h of earrings from a sum of maximum heights H of earrings from the bottom after a drawing process. It was confirmed that the average earring height of the embodiment was smaller than that of the comparative example.

[0118] While the present disclosure has been particularly described with reference to exemplary embodiments, it should be understood by those of skilled in the art that the scope of the present disclosure is not limited thereby and various changes in form and details may be made without departing from the spirit and scope of the present disclosure.

[Industrial Applicability]

[0119] According to the present disclosure, an ultra-fine grain 300 series stainless steel satisfying both high strength and high ductility may be provided. In addition, by the ultra-fine grain manufacturing technique realizing bending formability and sound surface properties of bent portions, an austenitic stainless steel without surface cracks in bent portions and having excellent surface roughness properties may be provided. Therefore, industrial applicability of the present disclosure is apparent from the above description.

Claims

1. An austenitic stainless steel including, in percent by weight (wt%), 0.04 to 0.07% of C, 0.3 to 0.6% of Si, 0.5 to 1.5% of Mn, 0.1 to 0.4% of Cu, 0.05 to 0.2% of Mo, 8.0 to 9.0% of Ni, 18.0 to 19.0% of Cr, 0.02 to 0.05% of N, and the remainder of Fe and inevitable impurities, wherein a Σ value represented by Equation (1) below is at least 180 but not more than 240:

$$\Sigma = 105 + 146d^{-1/2} + 7.36\text{SPM_El} + 102[\text{C}] + 154[\text{N}] + 51.8[\text{Si}] + 1.4[\text{Mo}] - 17.7[\text{Cu}] \quad \text{Equation (1):}$$

(in Equation (1), [C], [N], [Si], [Mo], and [Cu] represent weight percentages (wt%) of respective elements, d represents an average grain size (μm), and SPM_El represents a difference in elongation (%) before and after skin pass milling).

2. The austenitic stainless steel according to claim 1, wherein an Ω value represented by Equation (2) below is 2500 or more:

$$\text{Equation (2): } \Omega = \text{YS} \cdot \text{El} - 500 \cdot ([\text{Ni}] + [\text{Cr}] + [\text{Cu}] + [\text{Mn}])$$

(in Equation (2), [Ni], [Cr], [Cu], and [Mn] represent weight percentages (wt%) of respective elements, YS represents yield strength (MPa), and El represents elongation (%)).

3. The austenitic stainless steel according to claim 1, wherein an austenitic stability parameter (ASP) value represented by Equation (3) below is from -5 to 12:

$$\text{ASP} = 551 - 462 \cdot ([\text{C}] + [\text{N}]) - 9.2 \cdot [\text{Si}] - 8.1 \cdot [\text{Mn}] - 13.7 \cdot [\text{Cr}] - 29 \cdot ([\text{Ni}] + [\text{Cu}]) - 18.5 \cdot [\text{Mo}] \quad \text{Equation (3):}$$

(in Equation (3), [C], [N], [Si], [Mn], [Cr], [Ni], [Cu], and [Mo] represent weight percentages (wt%) of respective elements).

4. The austenitic stainless steel according to claim 1, wherein a Π value represented by Equation (4) below is 6000 or more:

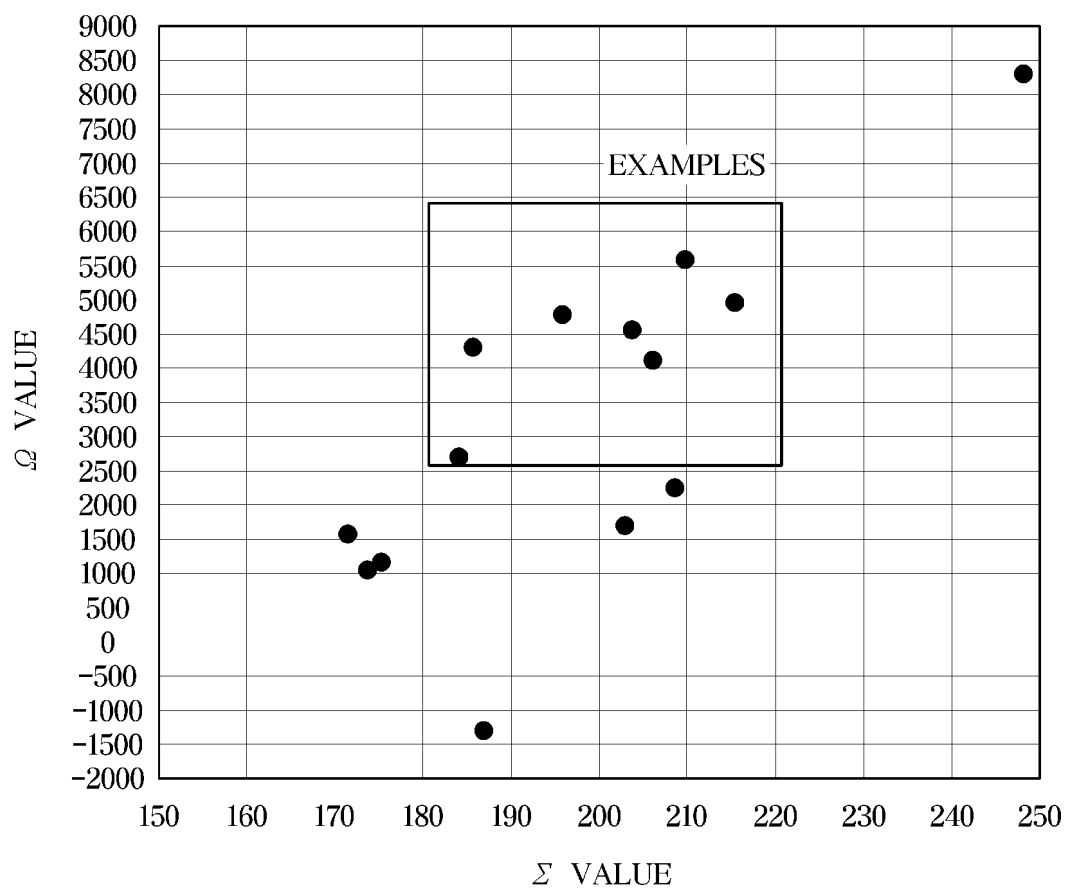
$$\Pi = 100 \cdot \text{FCRR} (\text{final cold rolling ratio, \%}) + 100 \cdot \text{ASP} (\text{austenitic stability parameter}) + \text{CAT} (\text{cold annealing temperature, } ^\circ\text{C}) \quad \text{Equation (4):}$$

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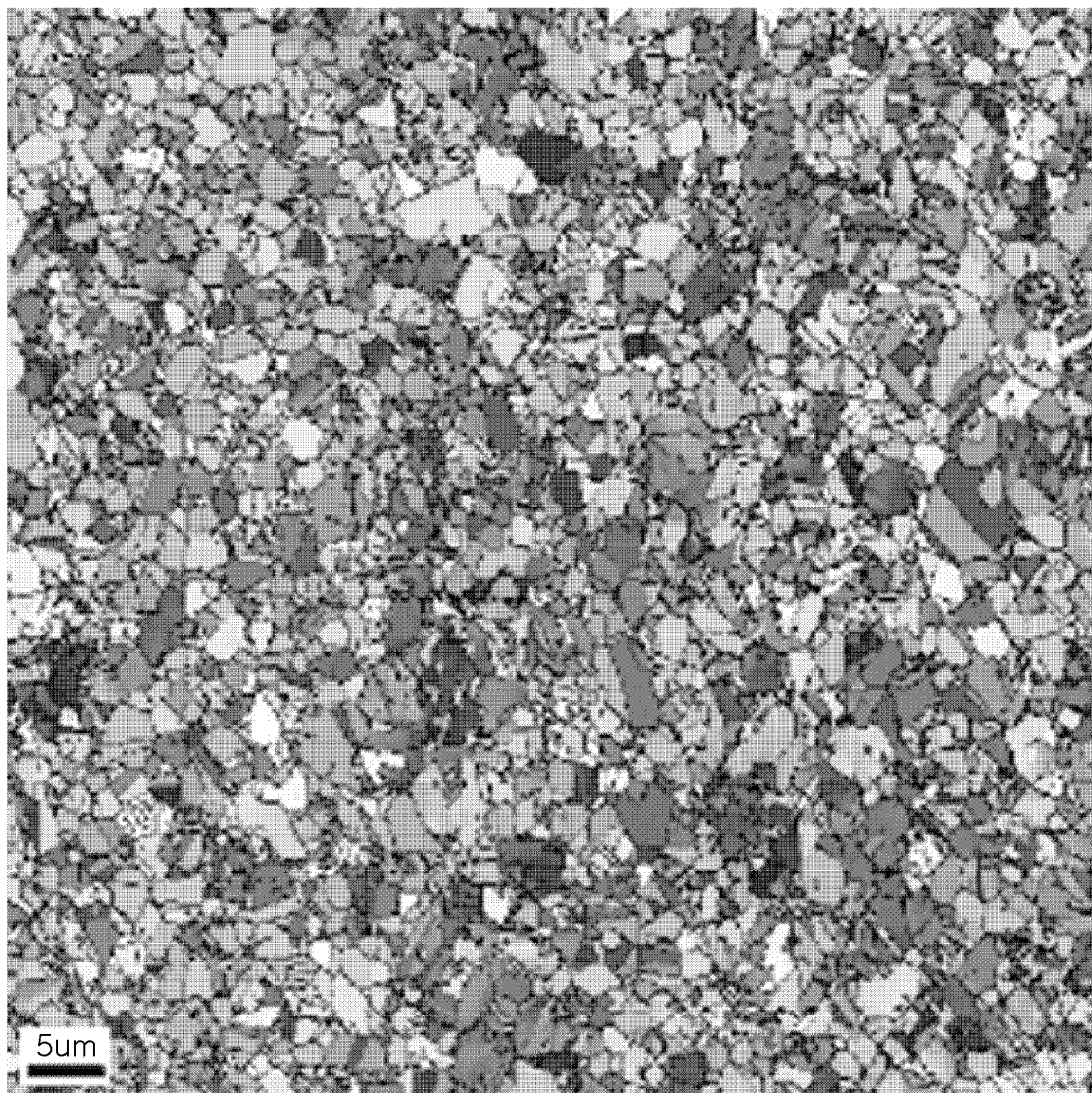
(in Equation (4), FCRR is a reduction ratio by cold rolling before final cold annealing, ASP is a value obtained by Equation (3), and CAT is a value defined by a temperature of a finally cold-annealed steel material).

- 5 **5.** The austenitic stainless steel according to claim 1, wherein an average grain size d at a central portion in the thickness direction of a transverse direction (TD) side is at least 3 but not more than 10 μm assuming that a total thickness of a steel material is t .
- 6.** The austenitic stainless steel according to claim 1, wherein the t is from 0.4 to 2.0 mm.
- 10 **7.** The austenitic stainless steel according to claim 1, wherein a martensite fraction (%) at the central portion in the thickness direction of the transverse direction (TD) side is 60% or more after cold rolling.
- 8.** The austenitic stainless steel according to claim 1, wherein a fraction (%) of misorientation angles of 15° or more is 95% or more at the central portion in the thickness direction of the transverse direction (TD) side after cold annealing.
- 15 **9.** The austenitic stainless steel according to claim 1, wherein a pitting potential measured by immersing the austenitic stainless steel in a 3.5% NaCl solution at 30°C is 250 mV or more.
- 10.** The austenitic stainless steel according to claim 1, wherein a surface roughness R_a when stretched by 30% is 0.50 μm or less, a surface roughness R_a when stretched by 20% is 0.36 μm or less, and a surface roughness R_a when stretched by 10% is 0.25 μm or less.
- 20 **11.** The austenitic stainless steel according to claim 1, wherein the austenitic stainless steel has an aging crack limit drawing ratio of 2.0 or more.
- 25 **12.** The austenitic stainless steel according to claim 1, wherein an average earring height is 2.2 mm or less after a drawing process of the stainless steel, wherein the average earring height is an average of a value obtained by subtracting a sum of minimum heights h of earrings from a sum of maximum heights H of earrings from the bottom after a drawing process.
- 30 **13.** The austenitic stainless steel according to claim 1, wherein surface cracks do not occur in a bent portion after a 180° bending test.

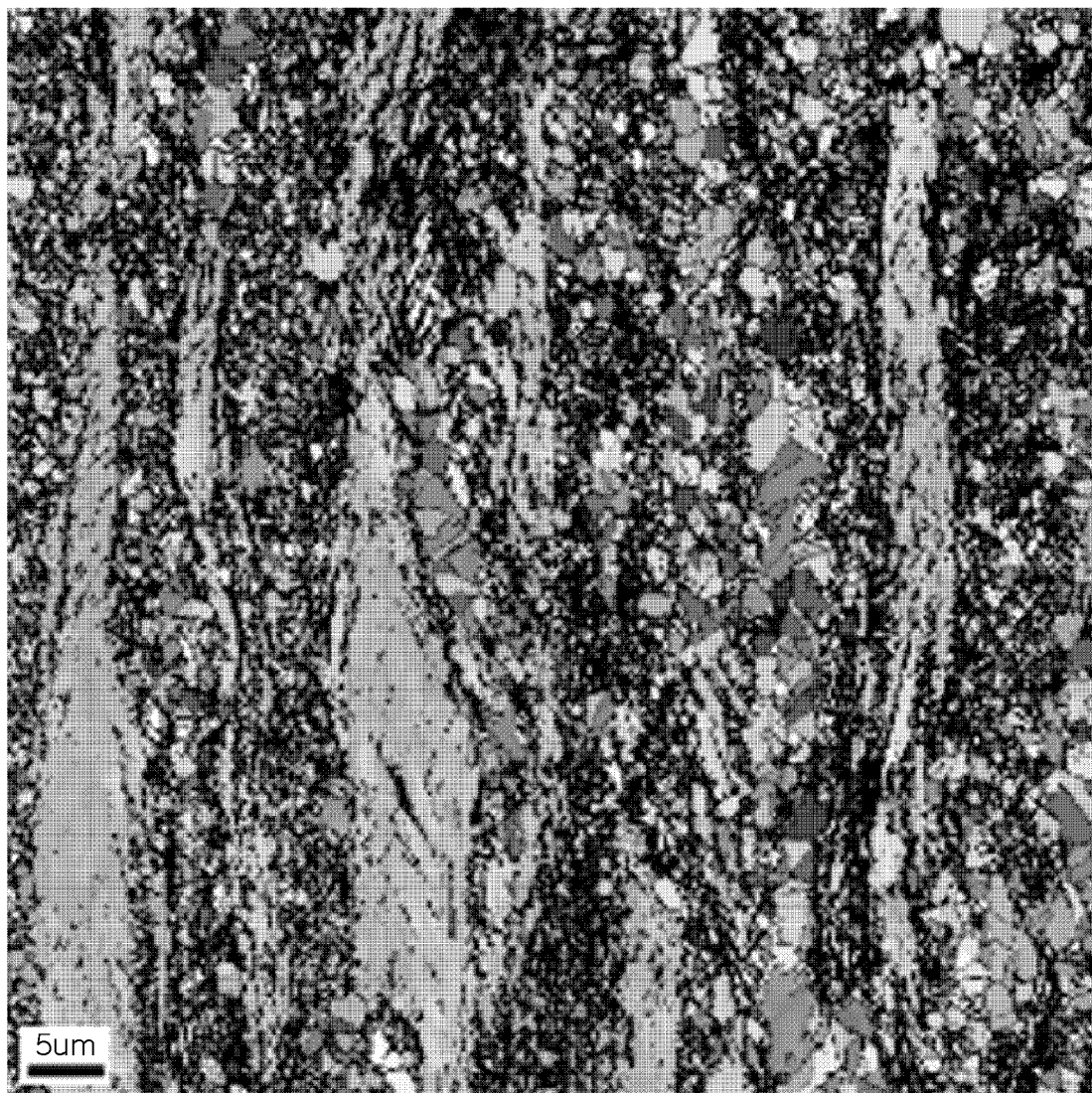
[FIG. 1]



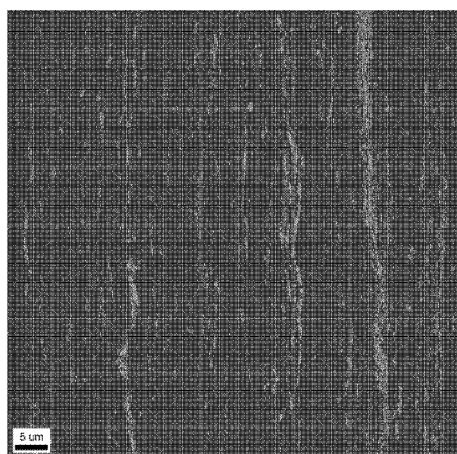
[FIG. 2]



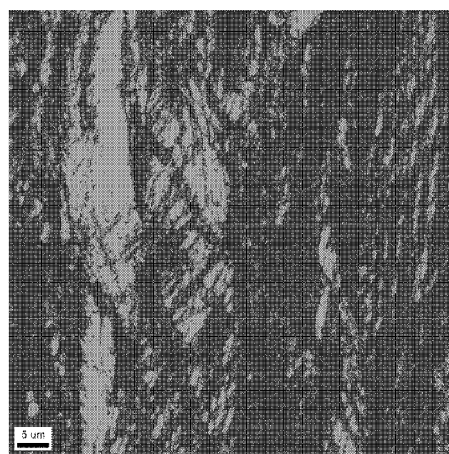
[FIG. 3]



[FIG. 4]

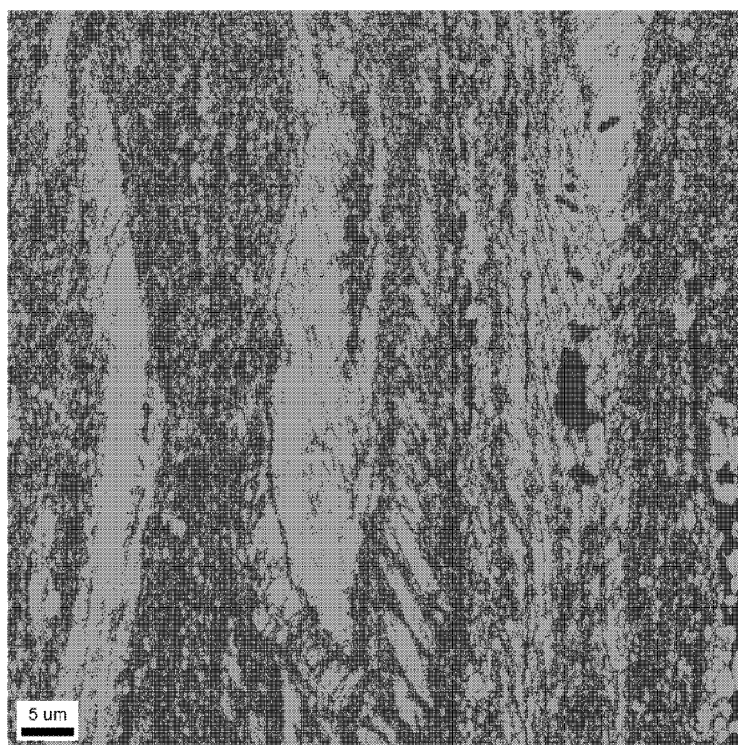


(Fraction(%) of Martensite phase
after cold rolling : 91.5%)



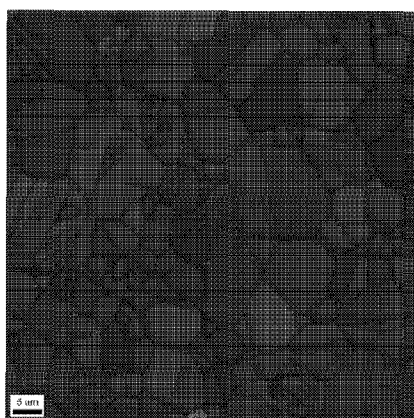
(Fraction(%) of Martensite phase
after cold rolling : 73.5%)

[FIG. 5]

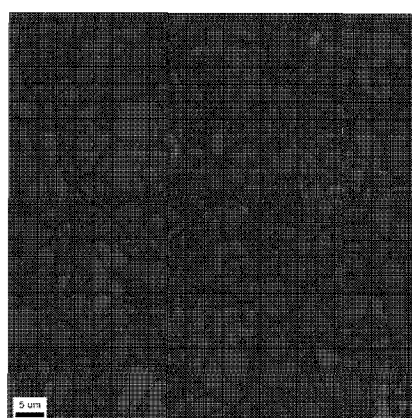


(Fraction(%) of Martensite phase after cold rolling : 48.5%)

[FIG. 6]

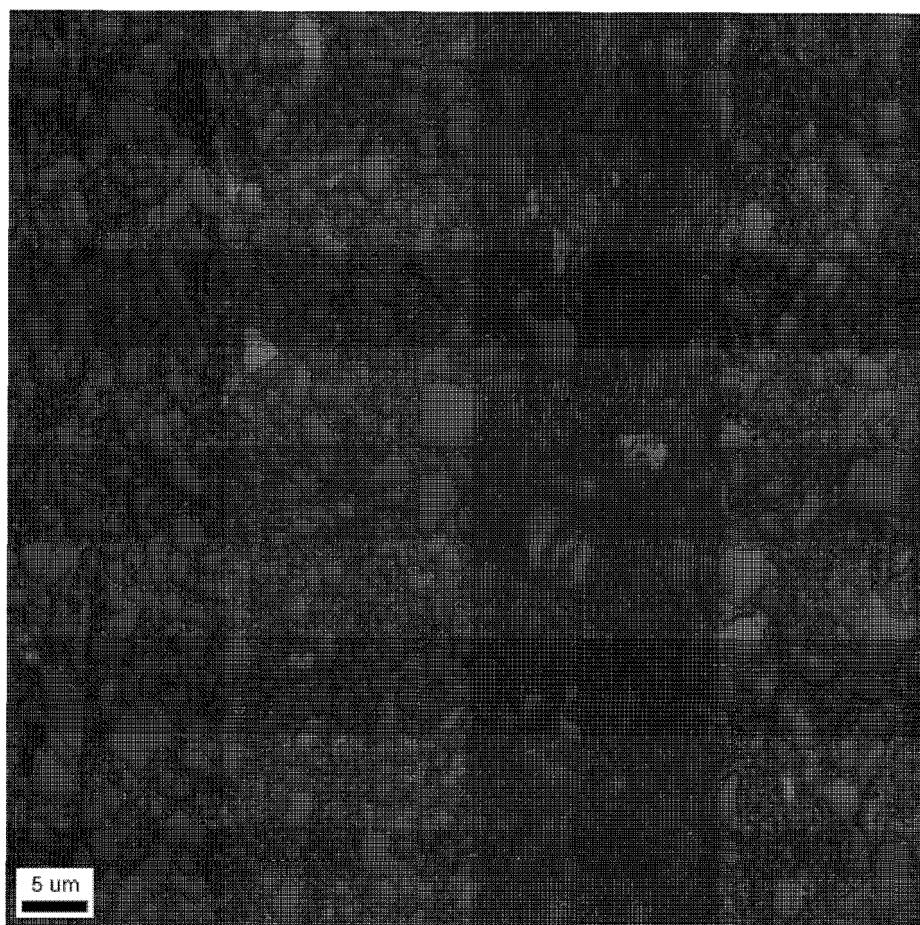


(Fraction(%) of Misorientation
Angle $\geq 15^\circ$: 96%)



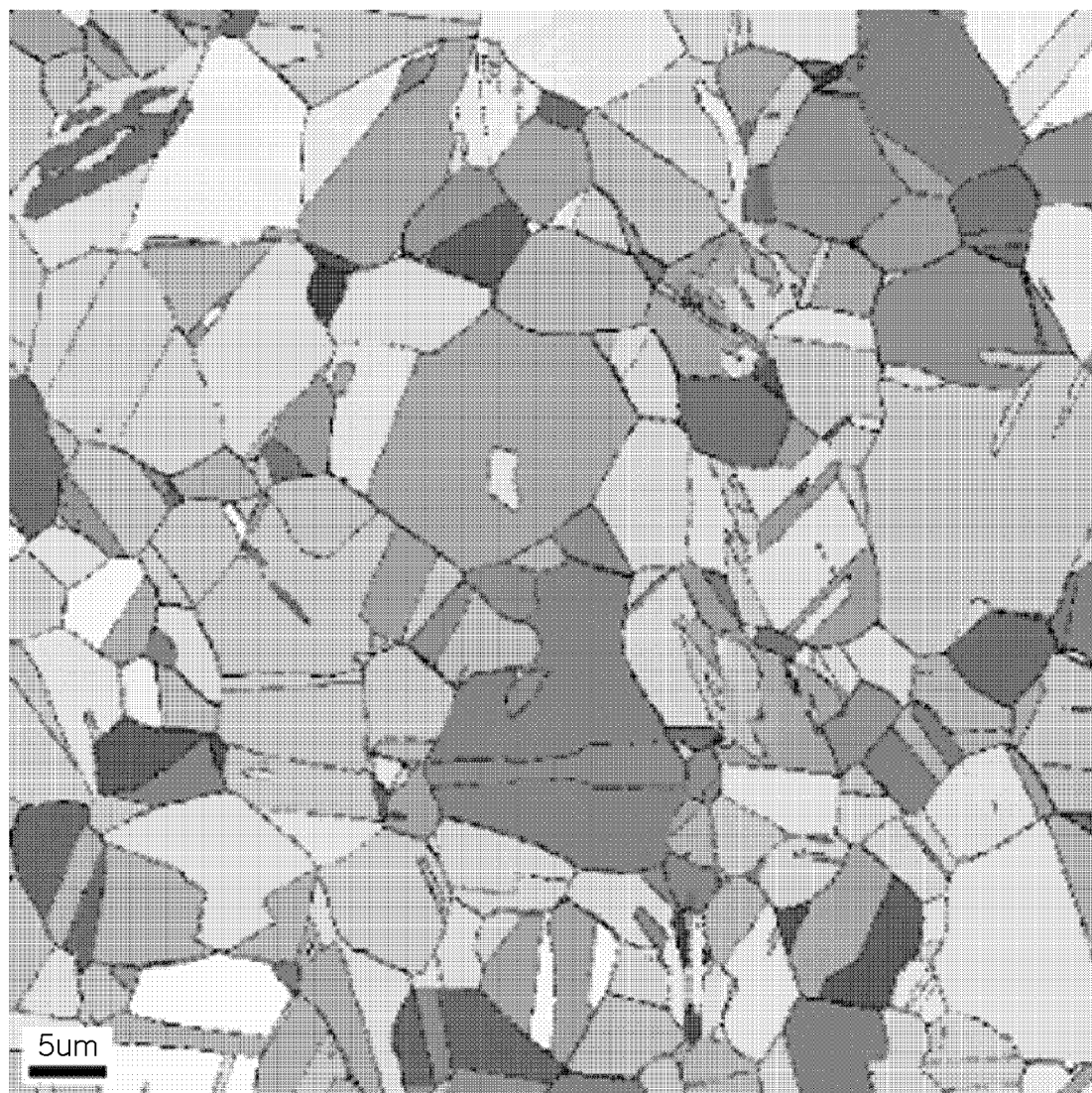
(Fraction(%) of Misorientation
Angle $\geq 15^\circ$: 96.5%)

[FIG. 7]

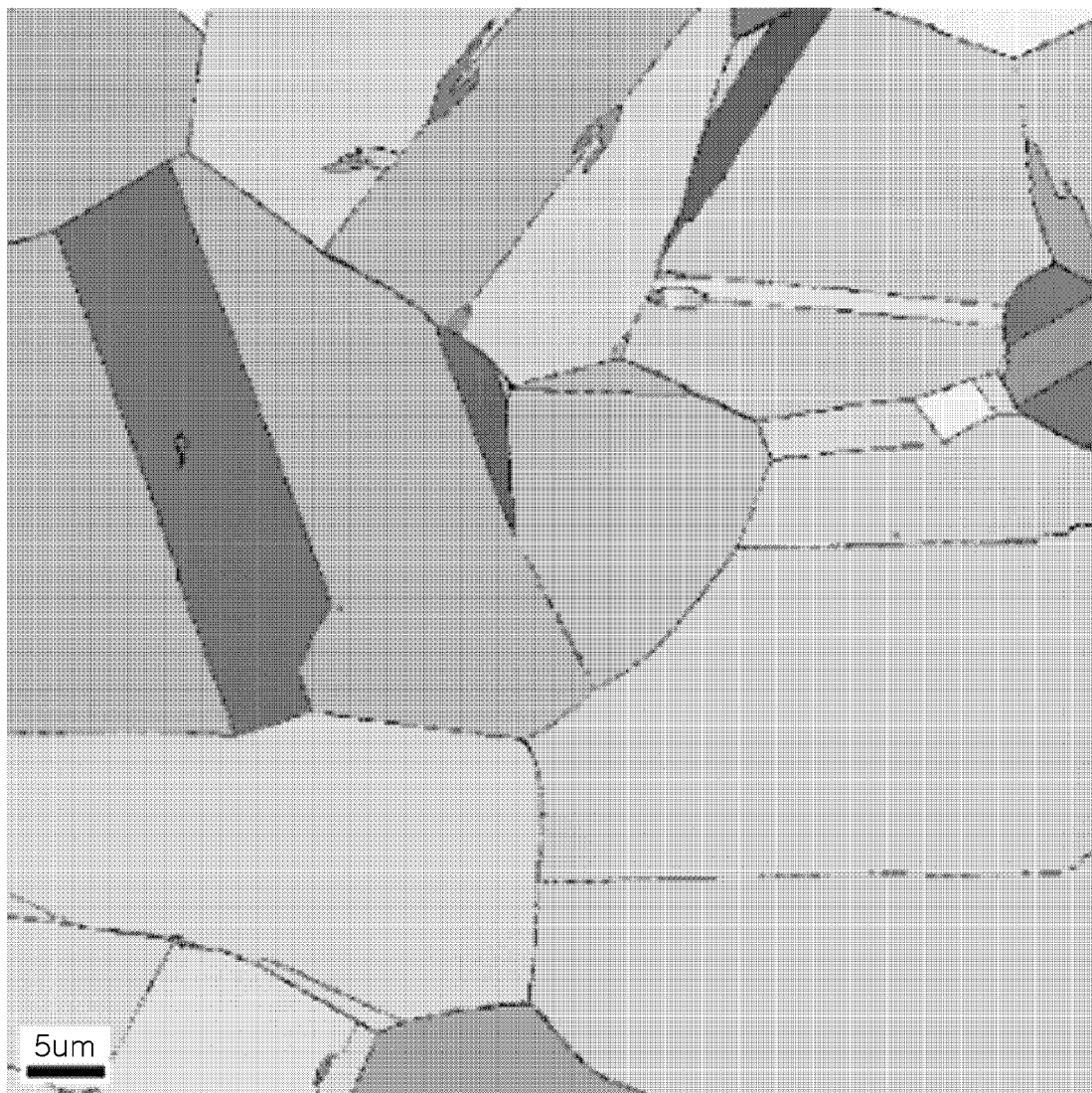


(Fraction(%) of Misorientation
Angle $\geq 15^\circ$: 92.9%)

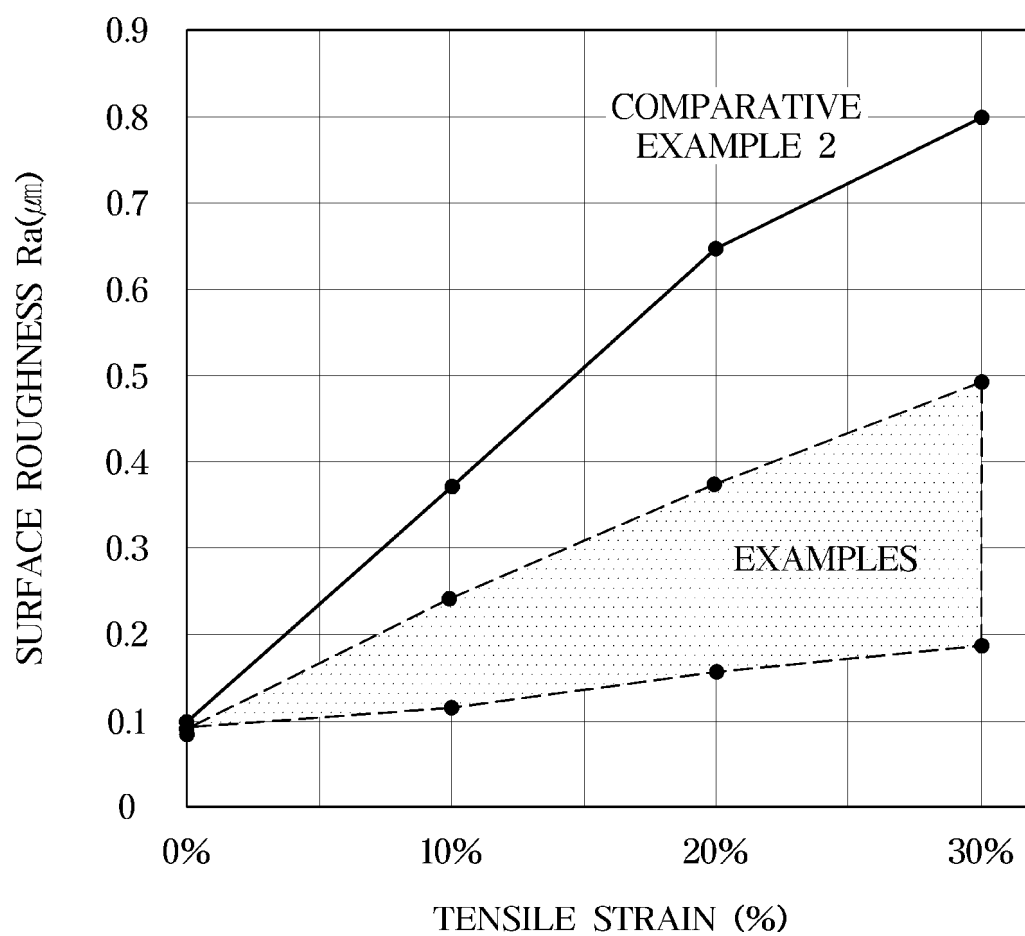
[FIG. 8]



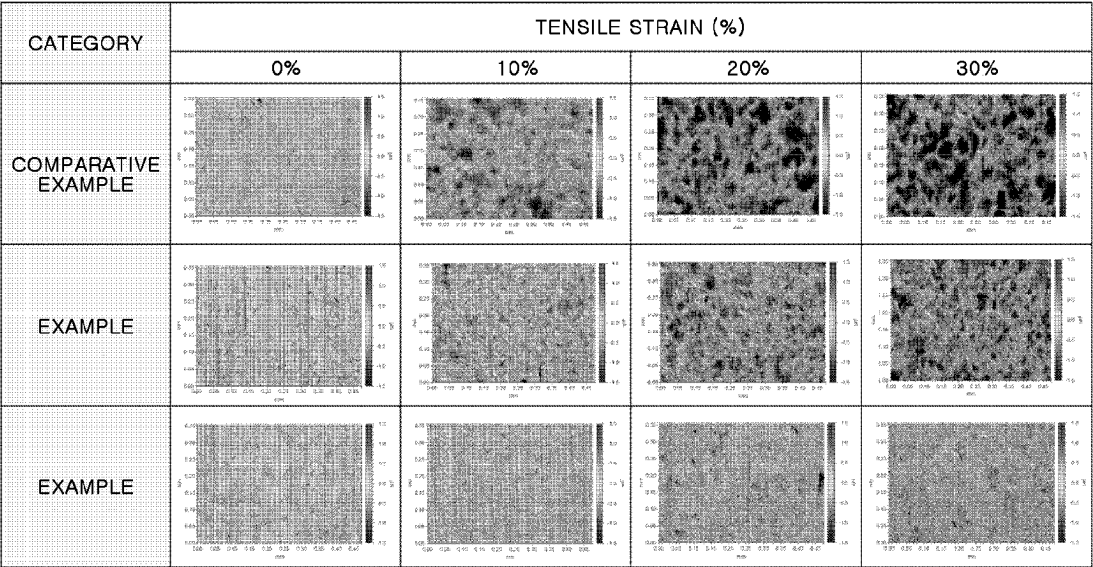
[FIG. 9]



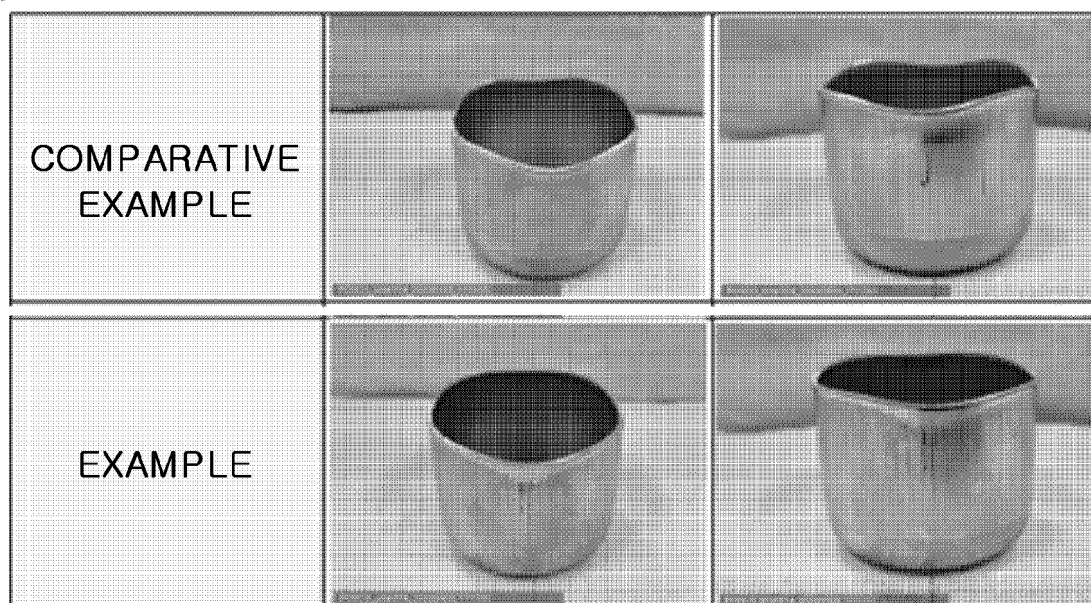
[FIG. 10]



[FIG. 11]



[FIG. 12]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2023/003278

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/44(2006.01)i; C22C 38/00(2006.01)i; C21D 8/02(2006.01)i; C21D 9/46(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 38/44(2006.01); C21D 8/00(2006.01); C21D 8/02(2006.01); C21D 9/46(2006.01); C22C 38/00(2006.01);
C22C 38/18(2006.01); C22C 38/40(2006.01); C22C 38/58(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: 오스테나이트계 스테인레스강(austenitic stainless steel), 결정립 크기(grain size),
조질압연(skin pass rolling)**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2021-0052502 A (NIPPON STEEL CORPORATION) 10 May 2021 (2021-05-10) See paragraphs [0085] and [0139]-[0144] and claims 1-2 and 4.	1-13
X	JP 2021-188081 A (NIPPON STEEL STAINLESS STEEL CORP.) 13 December 2021 (2021-12-13) See paragraph [0061] and claims 1-2 and 5-6.	1-13
A	KR 10-2022-0030722 A (POSCO) 11 March 2022 (2022-03-11) See claims 1 and 3-8.	1-13
A	KR 10-2010-0058850 A (POSCO) 04 June 2010 (2010-06-04) See claims 1-2 and 7.	1-13
A	US 5571343 A (RYOO et al.) 05 November 1996 (1996-11-05) See claims 1-5.	1-13

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

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

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“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

12 June 2023

Date of mailing of the international search report

13 June 2023

Name and mailing address of the ISA/KR

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Authorized officer

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Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2023/003278

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
KR 10-2021-0052502 A	10 May 2021	CN 112789362 A	11 May 2021
		CN 112789362 B	16 August 2022
		EP 3862452 A1	11 August 2021
		JP 2021-071534 A1	02 September 2021
		JP 7165202 B2	02 November 2022
		WO 2020-071534 A1	09 April 2020
JP 2021-188081 A	13 December 2021	None	
KR 10-2022-0030722 A	11 March 2022	EP 4177369 A1	10 May 2023
		KR 10-2448735 B1	30 September 2022
		WO 2022-050635 A1	10 March 2022
KR 10-2010-0058850 A	04 June 2010	KR 10-1056235 B1	11 August 2011
US 5571343 A	05 November 1996	CN 1040669 C	11 November 1998
		CN 1113661 A	20 December 1995
		JP 08-501352 A	13 February 1996
		JP 2693274 B2	24 December 1997
		KR 10-1995-0006015 A	20 March 1995
		KR 10-1995-0009223 B1	18 August 1995
		WO 95-06142 A1	02 March 1995

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

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2016043125 A1 [0005]
- JP 2020050940 A [0005]