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(54) **FINE GRAINED AUSTENITIC STAINLESS STEEL SHEET EXHIBITING EXCELLENT STRESS CORROSION CRACKING RESISTANCE AND PROCESSABILITY**

(57) This fine grained austenitic stainless steel sheet exhibiting excellent stress corrosion cracking resistance and formability includes: in terms of percent by mass, C: 0.05% or less; Cr: 14 to 19%; Si: 2% or less; Mn: 4% or less; Ni: 5 to 8%; Cu: 4% or less; and N: 0.1 % or less, with the remainder being Fe and unavoidable impurities, wherein steel components are included in a manner such that the following Md is in a range of -20 to 40, and an average grain size is in a range of 10 μ m or less, an occupancy ratio of high angle grain boundaries having angles of 15° or more is in a range of more than 80%,

$$Md = 551 - 462(C + N) - 9.2Si - 8.1Mn - 13.7Cr - 29(Ni + Cu) - 18.2Mo.$$

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Description

TECHNICAL FIELD

[0001] The present invention relates to an austenitic stainless steel sheet that has a fine grained structure (structure including fine crystal grains) with an average grain size of 10 μm or less and that is excellent in stress corrosion cracking resistance (resistance to stress corrosion cracking) and formability (workability).

The present application claims priority on Japanese Patent Application No. 2009-273868, filed on December 1, 2009, the content of which is incorporated herein by reference.

BACKGROUND ART

[0002] In recent years, with regard to a steel material, it is well known that refinement of crystal grains is the most effective method of increasing strength and toughness without adding an alloy element. With regard to an austenitic stainless steel, Non-Patent Document 1 and Non-Patent Document 2 disclose refinement of crystal grains by utilizing a phase transformation from strain-induced martensite to austenite in SUS304 defined in JIS G4305. According to this method, a fine grained structure with grain sizes of 1 to 5 μm is formed, and as an effect of the refinement, an increase in yield strength (0.2% proof stress) is reported in Non-Patent Document 1, and exhibition of superplasticity in a temperature range of 650 to 750°C is reported in Non-Patent Document 2.

[0003] With regard to the austenitic stainless steel, as a technology using the effect of the refinement of the crystal grains, Patent Document 1 discloses a metallic gasket, a material thereof, and a method of manufacturing the metallic gasket. In Patent Document 1, in SUS301L defined in JIS G4305, a fine grained structure with grain sizes of 5 μm or less is formed by utilizing the phase transformation from strain-induced martensite to austenite and precipitation of chromium nitrides. High strengthening to Hv 500 or more is attempted by a combination of the formation of the fine grained structure and temper rolling.

[0004] In a technology of refining crystal grains of austenitic stainless steel in the related art, as described above, with regard to SUS304 or SUS301L, the grain sizes are adjusted to 1 to 5 μm ; and thereby, an increase in 0.2% proof stress and high strengthening are imparted.

[0005] In the related art, with regard to an austenitic stainless steel sheet, it is well known that stress corrosion cracking occurs in a corrosion environment including chloride ions. In Non-Patent Document 3, as a countermeasure, it is disclosed that changing to a ferritic stainless steel without containing Ni is reliable. In addition, it is also disclosed that in the case where it is difficult to use the ferritic stainless steel from an aspect of formability and weldability, austenitic stainless steels of SUSXM15J1 series are effective which have high Ni contents (11.5 to 15%), increased Si contents, and increased Cu content.

[0006] With regard to improvement in stress corrosion cracking that originates from pitting corrosion and crevice corrosion, the addition of the above-described alloy elements operates in an effective manner. Patent Document 2 discloses an austenitic stainless steel excellent in stress corrosion cracking resistance and pitting corrosion resistance that includes substantially 9% of Ni, more than 1.5% to less than 2.5% of Cu, and small amounts of Mo and N. Patent Document 3 discloses an austenitic alloy excellent in stress corrosion cracking resistance, characterized in that the austenitic alloy includes 18 to 35% of Cr, 25 to 50% of Ni, 8% or less of Mo, 6% or less of Mn, 0.5% or less of N, and 0.03% or less of C, in which large amounts of Cr and Ni are included. Patent Document 4 discloses an austenitic stainless steel excellent in weather resistance, crevice corrosion resistance, and stress corrosion cracking resistance, characterized in that the austenitic stainless steel includes 0.08% or less of C, 0.1 to 3% of Si, 18 to 23% of Cr, 8.5 to 12% of Ni, 0.2 to 2% of Mo, 0.2 to 3.5% of Cu, 0.03 to 0.25% of N, in which a Mn content and a S content are adjusted, Cu and N are added in a combined manner, and small amounts of Co, W, V, and Nb are added.

[0007] In addition, since grain boundary cracking occurs as the stress corrosion cracking, Patent Documents 5 to 7 disclose improvements in grain-boundary-type stress corrosion cracking. Patent Document 5 discloses an austenitic stainless steel excellent in grain boundary corrosion resistance and grain boundary stress corrosion cracking resistance, characterized in that the austenitic stainless steel includes either one or both of Mo and Nb. Patent Documents 6 and 7 disclose austenitic stainless steels excellent in grain boundary stress corrosion cracking resistance and methods of producing the same, characterized in that a C content is restricted to 0.03% or less, 0.15% or less of N is included, and a slab heating temperature and a slab heating time are adjusted; and thereby, a precipitation amount of carbides is reduced, and a Cr depletion amount at or in a vicinity of grain boundaries is reduced.

[0008] All the above-described austenitic stainless steels disclosed in Non-Patent Document 3, and Patent Documents 2 to 7 include more than 8% of Ni, and Cu, Mo, and Si, are added with Nb, Co, W, V, or the like as minor elements; and thereby, the stress corrosion cracking resistance is improved.

An annealing temperature in an industrial production is disclosed in Non-Patent Documents 3 and 4. In addition, a grain size is disclosed in Non-Patent Document 5. It is disclosed that commonly, even when the austenitic stainless steel is

annealed at a temperature of 1000 to 1100°C and components thereof are adjusted, the limit of the grain refining does not reach a grain size of No. 10, that is, the grain sizes become in a range of larger than 10 μm.

[0009] In the technologies of refining crystal grains of an austenitic stainless steel in the related art, an effect of the refinement of the crystal grains with respect to the stress corrosion cracking resistance is not apparently clear yet.

In addition, as described above, commonly, even when the austenitic stainless steel is annealed at a temperature of 1000 to 1100°C and the components thereof are adjusted, the grain sizes become in a range of larger than 10 μm. In Patent Documents 2 to 7, a producing method (annealing temperature) and the grain sizes are not particularly disclosed. Therefore, with regard to the steels disclosed in Patent Documents 2 to 7, as far as a particular producing method different from a normal method is not disclosed, it can be easily assumed that the grain sizes thereof are in a range of larger than 10 μm similarly to the steel of Non-Patent Document 3.

[0010] As described above, with regard to the austenitic stainless steel, an examination is not found which attempts to improve the stress corrosion cracking resistance with a Ni content of 8% or less. Furthermore, there is no disclosure related to a technical idea of attempting compatibility between the stress corrosion cracking resistance and formability by reducing stress corrosion cracking that is a defect of the austenitic stainless steel through refinement of crystal grains with an Ni content of 8% or less and without adding expensive Mo.

PRIOR ART DOCUMENT

Patent Document

[0011]

Patent Document 1: PCT International Publication No. WO 02/088410

Patent Document 2 Japanese Unexamined Patent Application, First Publication No. S61-9557

Patent Document 3 Japanese Unexamined Patent Application, First Publication No. S62-180037

Patent Document 4 Japanese Unexamined Patent Application, First Publication No. S62-247048

Patent Document 5 Japanese Unexamined Patent Application, First Publication No. S62-287051

Patent Document 6 Japanese Unexamined Patent Application, First Publication No. H08-269550

Patent Document 7 Japanese Unexamined Patent Application, First Publication No. H10-317104

Patent Document 8 Japanese Patent Application No. 2008-157717 (Japanese Unexamined Patent Application, First Publication No. 2009-299171)

Non-Patent Document

[0012]

Non-Patent Document 1: Iron and Steel, 78 (1992), 141 to 148

Non-Patent Document 2: Iron and Steel, 80 (1994), 249 to 253

Non-Patent Document 3: Stainless Steel Handbook, Third Edition, 560

Non-Patent Document 4: Nishiyama Memorial Technology Course "Recent Advances in Technology of Producing of Stainless Steel" 115, (Incorporated Association) Iron and Steel Inst. of Japan

Non-Patent Document 5: Nippon Kokan Technical Report, No. 87 (1980), 51 to 60

Non-Patent Document 6: OIM ACADEMY, (Inc.) TSL Solutions

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0013] The present invention aims to overcome stress corrosion cracking that is a defect of an austenitic stainless steel by refining crystal grains with an Ni content of 8% or less and without adding expensive Mo; and thereby, an austenitic stainless steel sheet is provided which has a fine grained structure with an average grain size of 10 μm or less, in which compatibility is ensured between stress corrosion cracking resistance and formability.

Means for Solving the Problems

[0014] According to an aspect of the present invention, there is provided a fine grained austenitic stainless steel sheet exhibiting excellent stress corrosion cracking resistance and formability, the steel sheet includes: in terms of percent by mass, C: 0.05% or less; Cr: 14 to 19%; Si: 2% or less; Mn: 4% or less; Ni: 5 to 8%; Cu: 4% or less; and N: 0.1% or less,

with the remainder being Fe and unavoidable impurities, wherein steel components are included in a manner such that the following Md is in a range of -20 to 40, and an average grain size is in a range of 10 μm or less, an occupancy ratio of high angle grain boundaries having angles of 15° or more is in a range of more than 80%,

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$$\text{Md} = 551 - 462(\text{C} + \text{N}) - 9.2\text{Si} - 8.1\text{Mn} - 13.7\text{Cr} - 29(\text{Ni} + \text{Cu}) - 18.2\text{Mo}.$$

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[0015] In the fine grained austenitic stainless steel sheet exhibiting excellent stress corrosion cracking resistance and formability according to the aspect of the present invention, the steel components may further include, in terms of percent by mass, one or more selected from a group consisting of Mo: 1% or less, V: 1% or less, B: 0.010% or less, Nb: 0.5% or less, Ti: 0.5% or less, rare earth elements: 0.5% or less, Al: 0.5% or less, Mg: 0.005% or less, and Ca: 0.005% or less. In the fine grained austenitic stainless steel sheet exhibiting excellent stress corrosion cracking resistance and formability according to the aspect of the present invention, cracking may not occur in a stress cracking test in which the steel sheet is subjected to cylindrical deep drawing at a drawing ratio of 1.5 to 2.0 to obtain a molded product, the molded product is immersed into a boiling aqueous solution of 42% magnesium chloride for four hours, and occurrence of cracking in the molded product is checked..

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Here, the drawing ratio is a value obtained by dividing a blank diameter by a punch diameter.

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In the fine grained austenitic stainless steel sheet exhibiting excellent stress corrosion cracking resistance and formability according to the aspect of the present invention, 0.2% proof stress may be in a range of less than 400 MPa, and uniform elongation may be in a range of more than 30% which are obtained from a tensile test.

Effects of the Invention

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[0016] According to the austenitic stainless steel sheet having a fine grained structure according to the aspect of the present invention, stress corrosion cracking that is a defect of the austenitic stainless steel is overcome with an Ni content of 8% or less and without adding expensive Mo; and thereby, compatibility can be ensured between stress corrosion cracking resistance and formability.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

FIG. 1 shows a graph illustrating a relationship between an average grain size and Md.

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FIG. 2 shows photographs illustrating exterior appearances of molded products after being immersed in a boiling aqueous solution of 42% magnesium chloride for four hours.

FIG. 3 shows photographs illustrating microstructures of steels shown in (i) and (ii) of FIG. 2.

FIG. 4 shows a graph illustrating a relationship between a cracking initiation time in a boiling aqueous solution of 42% magnesium chloride, an average grain size, and Md.

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FIG. 5 shows a graph illustrating a relationship between a cracking initiation time of a fine grained material (steel sheet in which crystal grains are fine) in a boiling aqueous solution of 42% magnesium chloride, and a ratio of high angle grain boundaries.

BEST MODE FOR CARRYING OUT THE INVENTION

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[0018] To solve the above-described problems, the present inventors targeted at an austenitic stainless steel having a Ni content of 8% or less, and they made a thorough investigation on optimal component balance for forming a fine grained structure, and compatibility between formability and an operation of improving stress corrosion cracking due to the refinement; and as a result, they accomplished the invention. Representative experimental results will be described below.

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Here, in the present embodiment, the fine grained structure represents a structure having an average grain size of 10 μm or less.

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[0019] Austenitic stainless steels having steel components shown in Table 1 were melted, and hot-rolling was conducted to produce hot-rolled steel sheets having the thickness of 3.0mm. The hot-rolled sheets were annealed at 1150°C, and acid-pickling and cold rolling were conducted to produce cold-rolled sheets having the thickness of 0.5 mm. Then, the cold-rolled steel sheets were annealed.

In the cold-rolling, a temperature of the steel sheet was held at 10°C while performing water cooling to suppress generation of heat during processing. Thereby, generation of strain-induced martensite was promoted.

In the annealing of the cold-rolled steel sheet (final annealing), a temperature was adjusted in a range of 600 to 1050°C, and a holding time was adjusted in a range of one minute to 24 hours in order to form a fine grained structure by utilizing a phase transformation from the strain-induced martensite to austenite.

The steel sheets that were obtained by performing the final annealing after the cold rolling were acid-pickled. Next, with regard to the obtained the steel sheets, average grain sizes, occupancy ratios of high angle grain boundaries, and cracking initiation times were measured.

[0020]

Table 1

	(mass%)							
	C	Si	Mn	Cr	Ni	Cu	N	Md
A	0.029	0.29	1.2	14.3	7.0	2.5	0.020	43.0
B	0.024	0.90	1.8	15.9	7.1	2.0	0.010	29.5
C	0.040	0.60	1.5	16.1	6.4	2.2	0.060	15.3
D	0.043	0.41	1.0	17.2	6.5	2.3	0.058	-0.3
E	0.013	0.33	2.3	16.8	7.1	3.2	0.014	-13.4
F	0.021	0.28	2.0	15.6	8.4	2.9	0.009	-25.0
SUS304	0.055	0.60	1.1	18.2	8.3	0.1	0.035	0.6

[0021] In the measurement of the average grain size, a cross-section surface of the steel sheet was buried in a resin, the cross-section surface was polished, and then the cross-section surface was subjected to nitric acid electrolytic etching. Next, the average grain size was measured by a microscope test method of steel-grain size defined in JIS G0551. The occupancy ratio of the high angle grain boundaries was measured by a grain boundary map with an EBSP method. In the EBSP method, low angle grain boundaries having angles of less than 15° and high angle grain boundaries having angles of 15° or more can be discriminated by the grain boundary mapping, and the occupancy ratio of the high angle grain boundaries in the entirety of grain boundaries can be calculated. Here, in Non-Patent Document 6, it is reported that a result of measuring 3000 or more crystal grains statistically reflects a bulk property. Therefore, a measurement magnification was adjusted to include 3000 or more crystal grains.

[0022] In the measurement of the cracking initiation time, the steel sheet was subjected to a cylindrical deep drawing processing under conditions where a blank diameter was 67.5 mmφ, a punch diameter was 35 mmφ, a die diameter was 37 mmφ, a blank hold force was 1 ton, and a drawing ratio (a value obtained by dividing the blank diameter by the punch diameter) was 1.9. The obtained molded product was left as it was for 48 hours, and it was confirmed that aging cracking did not occur. Then, the molded product was immersed into a boiling aqueous solution of 42% magnesium chloride that is defined in JIS G0576, and the cracking initiation time was measured.

[0023] (a) FIG. 1 illustrates a relationship between the average grain size and a component balance (Md) of a steel sheet that was obtained by annealing the cold-rolled sheet at 800°C for four hours.

Md is a value defined in the following Equation (1). Here, each element symbol in Equation (1) represents a content (mass%) of the element.

[0024]

$$Md = 551 - 462(C + N) - 9.2Si - 8.1Mn - 13.7Cr - 29(Ni + Cu) - 18.2Mo \cdots (1)$$

[0025] From FIG. 1, it can be understood that as Md increases, the average grain size becomes small. Due to the increase in Md, an amount of strain-induced martensite that is generated by the cold rolling increases. Therefore, it is considered that due to the increase in Md, as described in Non-Patent Document 1 and Non-Patent Document 2, the refinement by utilizing the phase transformation from the strain-induced martensite to austenite is promoted during the annealing after the cold rolling. From this examination, it is effective that Md be set to be in a range of -20 or more for refining the average grain size to 10 μm or less that is a target value.

In addition, when the result of SUS304 (a diamond-shaped symbol in FIG. 1) was compared to the result of steel D in which Md is substantially the same, it was confirmed that steel components (steel D) in which a Cr content and a Ni content are reduced and Cu is added are effective for the refinement.

[0026] (b) Similarly to the measurement of the cracking initiation time, steel B(i) and steel B(ii) in which the average

grain sizes (d) were different, and SUS316L(iii) were subjected to the cylindrical deep drawing processing to produce molded products (cylindrically deep drawn materials). These molded products were immersed into a boiling aqueous solution of 42% magnesium chloride for four hours. FIG. 2 illustrates exterior appearances of the molded products after the immersing. Furthermore, FIG. 3 illustrates photographs of microstructures of the steel B(i) and the steel B(ii) provided for an experiment in FIG. 2.

[0027] As shown in FIG. 2, in the steel (FIG. 2(i)) in which the average grain size was refined to 3 μm , it could be seen that cracking did not occur from the result of experiment of immersing the molded product (the cylindrical deep drawn material) into the boiling aqueous solution of 42% magnesium chloride, as compared to the steel (FIG. 2(ii)) having the average grain size of 28 μm which was produced with normal annealing (holding at 1050°C for one minute).

SUS316L (17Cr-12Ni-2Mo)(FIG. 2(iii)) is expensive austenitic stainless steel that contains Ni and Mo at high contents and is superior in stress corrosion cracking resistance compared to general purpose SUS304 (18Cr-8Ni). However, as shown in FIG. 2(iii), a plurality of cracking occurred in an opening end portion of the molded product.

From this results, it was newly found that the stress corrosion cracking resistance (whether or not cracking occurs) is greatly improved by refining the crystal grains.

[0028] (c) FIG. 4 illustrates a relationship between a cracking initiation time in the boiling aqueous solution of 42% magnesium chloride, an average grain size, and Md. Here, an arrow (T) in FIG. 4 represents that the cracking initiation time is longer than a value at a plotted point.

In a steel sheet (steel B) having steel components that fulfill Md = 29.5, due to an effect of refinement of crystal grains (average grain size of 10 μm or less), it can be seen that the cracking initiation time greatly increases. This reason is not clear; however, it is assumed to be as follows. The stress corrosion cracking is basically transgranular cracking. Due to the refinement of the crystal grains, an area ratio of starting points of cracking in grains decreases greatly. Furthermore, it is known that fracture toughness in a steel material is greatly improved due to the refinement of crystal grains. It is considered that these factors exert an effect with respect to the stress corrosion cracking resistance.

In the SUS316L as a comparative example, cracking occurred during being immersed for 2 to 3 hours under the same test conditions. In the present embodiment, a property in which cracking does not occur during being immersed for 4 hours under the test conditions is set as a target property. This target property represents that the cracking initiation time is longer than 4 hours, and is clearly superior to the stress corrosion cracking resistance (cracking initiation time) of the SUS316L.

[0029] Here, in FIG. 4, the steel sheets (steel sheets having steel components of steel B) in which the stress corrosion cracking resistances are improved due to the refinement of crystal grains are steel sheets that were produced by subjecting cold-rolled sheets after cold rolling to final annealing at 800°C for 4 hours or 24 hours.

In addition, in FIG. 4, the steel sheets in which the cracking initiation times are shorter than 4 hours and the average grain sizes are larger than 10 μm are steel sheets that were produced by subjecting cold-rolled sheets after cold rolling to final annealing in a temperature range of 900 to 1050°C for one minute to four hours. The steel sheet in which the cracking initiation time is shorter than 4 hours and the average grain size is 10 μm or smaller is a steel sheet that was produced by subjecting a cold-rolled sheet after cold rolling to final annealing at 800°C for 4 hours.

[0030] (d) An exhibition of an effect due to the refinement with respect to the stress corrosion cracking resistance is affected by a component balance (Md). For the exhibition of the effect of suppressing the stress corrosion cracking due to the refinement, it is necessary for Md to be set to be in a range of -20 to 40.

In FIG. 4, in the steel sheets (steel A) having steel components that fulfill Md = 43, the cracking initiation times do not increase largely even when crystal grains are refined. This reason is assumed to be as follows. That is, it is considered that a material itself is hardened due to the refinement. Thereby, it is assumed that a large amount of strain-induced martensite is generated in the cylindrical deep drawing, and the effect of suppressing the stress corrosion cracking is not exerted (exhibited) due to an increase in residual stress in a side wall of a cup. From this examination, it is effective to set Md to be in a range of 40 or less for exerting (exhibiting) the effect of suppressing the stress corrosion cracking due to the refinement.

[0031] (e) In the steel sheets (steel G) having steel components that fulfill Md = -25 that is a low Md value, it becomes difficult to form the fine grained structure as described in the item (a). Therefore, in FIG. 4, it is difficult to suppress the stress corrosion cracking by setting the average grain size to be in a range of 10 μm or less (an effect due to the refinement). From this result, it is effective to set Md to be in a range of -20 or more for exerting (exhibiting) the effect of suppressing the stress corrosion cracking due to the refinement.

[0032] (f) An occupancy ratio of high angle grain boundaries in grain boundaries also has an effect on the stress corrosion cracking resistance of a fine grained material (a steel sheet in which crystal grains are fine) in addition to Md. FIG. 5 shows a graph illustrating a relationship between a cracking initiation time and a ratio of the high angle grain boundaries having angles of 15° or more in a steel sheet having steel components of steel B. Here, an arrow (T) in FIG. 5 represents that the cracking initiation time is longer than a value at a plotted point. As shown in FIG. 5, with regard to a steel sheet which has steel components of steel B and in which crystal grains are fine, the stress corrosion cracking resistance described in the items (b) and (c) is greatly improved in the case where a ratio of the high angle grain

boundaries having angles of 15° or more is higher than 80%. The reason for this is considered to be as follows. A fine grained material is produced according to a method in which a large amount of strain-induced martensite is generated by cold rolling, and then annealing is conducted at a lower temperature than normal annealing so as to utilize an inverse transformation from the strain-induced martensite to austenite. An accumulated amount of strains during the cold rolling is large, and the annealing is conducted at a low temperature; and thereby, an amount of residual strains after the annealing is apt to be large. In the case where a steel sheet is produced under these conditions, recrystallization of austenitic grains is stopped during progressing, and a large amount of low angle grain boundaries having angles of less than 15° are present which are not recognized as the high angle grain boundaries. Therefore, a decrease in the occupancy ratio of the high angle grain boundaries means that an amount of the residual strains in a steel is large, and it is assumed that the residual strains in the steel deteriorate the stress corrosion cracking resistance.

[0033] In FIG. 5, the steel sheets having steel components of steel B are steel sheets that were produced by subjecting cold-rolled sheets after cold rolling to final annealing at 800°C for 10 minutes to 24 hours. Heating times of the final annealing were adjusted; and thereby, the steel sheets were produced in which the ratios of the high angle grain boundaries were different. The steel sheets shown in FIG. 5 in which the ratios of the high angle grain boundaries are higher than 80% are steel sheets that were produced by subjecting cold-rolled sheets after cold rolling to final annealing at 800°C for longer than one hour.

[0034] (g) The refinement of crystal grains is affected by manufacturing conditions with the steel components. In order to utilize the phase transformation from strain-induced martensite to austenite, it is effective to promote a strain-induced martensite transformation during cold rolling. To achieve this, it is preferable that a rolling reduction rate is set to be large in the cold rolling and generation of heat during processing is suppressed. Furthermore, in the fine grained material, in order to increase the ratio of the high angle grain boundaries to exert an effect of improving the stress corrosion cracking resistance, it is preferable to conduct the final annealing after the cold rolling at a temperature as low as possible for a long time. Specifically, it is effective to conduct the final annealing in a temperature range of 700 to 900°C for longer than one hour. In addition, the increase in the ratio of the high angle grain boundaries having angles of 15° or more is effective for a decrease in 0.2% proof stress and an increase in elongation, which contributes to improvement of formability.

[0035] In Patent Document 8, the present inventors have already proposed an austenitic stainless steel sheet for press molding which has a fine grained structure with an average grain size of 10 μm or less, and a method of producing the same. Patent Document 8 aims to improve "aging cracking", that is, delayed fracture, after the deep drawing processing; and therefore, a technology of Patent Document 8 relates to a technical problem different from "stress corrosion cracking" that is improved in the present embodiment, and the stress corrosion cracking is a phenomenon in which corrosion and dissolution are involved. In Patent Document 8, any examination was not made with respect to the ratio of the high angle grain boundaries having angles of 15° or more which has an effect on the above-described stress corrosion cracking. In addition, the final annealing time was substantially one hour or less.

In the present embodiment, with regard to a fine grained steel that was proposed in Patent Document 8, the present inventors found a requisite range of the ratio of the high angle grain boundaries having angles of 15° or more which is an influencing factor, so as to improve the stress corrosion cracking resistance. In addition, the present inventors also found that it is effective to control the final annealing time to be in a range of longer than one hour.

[0036] The present embodiment was accomplished on the basis of the findings of (a) to (g).

Hereinafter, respective requirements of the present embodiment will be described in detail. In addition, an expression of "%" in each element content represents "mass%".

[0037] (A) The reasons why steel components of a steel sheet are restricted in the present embodiment will be described below.

In the present embodiment, a fine grained structure with an average grain size of 10 μm or less is formed, and stress corrosion cracking resistance is improved due to an effect of the refinement. Therefore, in an austenitic stainless steel sheet of the present embodiment, components and a component balance (Md) are defined.

[0038] C is an element of generating austenite, and C is added for the purpose of securing stability of austenite. In the case where C is added at a large amount, this leads to hardening; and thereby, formability is deteriorated. In addition, precipitation of carbides is promoted; and thereby, the stress corrosion cracking resistance that is an object of the present embodiment is deteriorated. Therefore, the upper limit of a C content is set to 0.05%. This upper limit is preferably 0.03%. The lower limit of the C content is preferably set to 0.005% from a relationship with manufacturability.

[0039] It is necessary to include 14% or more of Cr so as to obtain sufficient corrosion resistance; and therefore, the lower limit of a Cr content is set to 14%. This lower limit is preferably 15%, and more preferably 16%. On the other hand, in the case where Cr is added at a large amount, this leads to hardening and δ-ferrite is formed; and thereby, formability is deteriorated. Furthermore, the refinement of crystal grains that is an object of the present embodiment is prevented. Therefore, the upper limit of the Cr content is set to 19%. This upper limit is preferably 18%.

[0040] Si is effective as a strong deoxidizing agent. However, in the case where Si is added at a large amount, this leads to hardening and deterioration of manufacturability. Therefore, the upper limit of a Si content is set to 2%. This upper limit is preferably 1.5%. On the other hand, Si has an operation of improving the stress corrosion cracking resistance

that is an object of the present embodiment. In order to obtain this operation, it is preferable to include 0.5% or more of Si. The lower limit of the Si content is preferably set to 0.1% from a relationship with manufacturability.

[0041] Mn is an element of generating austenite, and Mn is added for the purpose of securing stability of austenite and improving formability. In the case where Mn is added at a large amount, MnS is generated; and thereby, corrosion resistance is deteriorated. Therefore, the stress corrosion cracking resistance that is an object of the present embodiment is deteriorated. As a result, the upper limit of Mn content is set to 4%. This upper limit is preferably 3%. The lower limit of a Mn content is preferably set to 0.5% for the above-described object.

[0042] Ni is a requisite element in an austenitic stainless steel, and the lower limit of a Ni content is set to 5% for the purpose of securing austenite stability and formability. This lower limit is preferably 6%. On the other hand, Ni is an expensive and rare element, and Ni also has an operation of inhibiting the refinement of crystal grains that is an object of the present embodiment. Therefore, the upper limit of a Ni content is set to 8%. This upper limit is preferably 7.5% or less.

[0043] Similarly to Ni, Cu is added for the purpose of securing stability of austenite and softening. Furthermore, Cu is a preferable element to reduce the Ni content and to promote the improvement in the stress corrosion cracking resistance and the refinement of crystal grains. However, in the case where Cu is added at a large amount, hot workability is deteriorated. Furthermore, the addition of Cu has an adverse effect on qualities of a molten steel and a discharged slag in which Cu is not necessary, and an effective usage of thereof; and therefore, a problem may be caused. Therefore, the upper limit of a Cu content is set to 4%. This upper limit is preferably 3%. In order to obtain the above-described effect, the lower limit of the Cu content is preferably 1%, and more preferably 1.5%.

[0044] Similarly to C, N is an element of generating austenite, and N is added for the purpose of securing stability of austenite. However, in the case where N is added at a large amount, this leads to hardening; and thereby, formability is deteriorated. Therefore, the upper limit of a N content is set to 0.1 %. This upper limit is preferably in a range of 0.06% or less. The lower limit of the N content is preferably 0.005%, and more preferably 0.01% from a relationship with manufacturability.

[0045] Mo is not a requisite element in the present embodiment; however, Mo may be added as necessary to improve corrosion resistance and the stress corrosion cracking resistance that is an object of the present embodiment. However, Mo is a very expensive and a rare element; and therefore, in the case of adding Mo, the upper limit of a Mo content is set to 1%. This upper limit is preferably 0.5%. In order to obtain the above-described effect, the lower limit of the Mo content is preferably 0.1%.

[0046] V is not a requisite element in the present embodiment; however, V may be added as necessary to improve the corrosion resistance and the stress corrosion cracking resistance that is an object of the present embodiment even though the effect obtained by V is smaller than the effect obtained by Mo. However, V is an expensive element, and V is a solid-solution strengthening element; and thereby, V deteriorates formability. Therefore, in the case of adding V, the upper limit of a V content is set to 1 %. This upper limit is preferably 0.5%. In order to obtain the above-described effect, the lower limit of the V content is preferably 0.1 %.

[0047] B and a rare earth element (REM) may be added as necessary to improve hot workability. However, in the case where a B content is in a range of more than 0.010%, manufacturability and the corrosion resistance may be greatly deteriorated. Therefore, in the case of adding B, the upper limit of the B content is set to 0.010%. This upper limit is preferably 0.005%. In the case of adding B, the lower limit of the B content is preferably 0.0005%.

On the other hand, in the case where a content of the rare earth element is more than 0.5%, manufacturability may be deteriorated and economical efficiency may be lowered. Therefore, the upper limit of the content of the rare earth element is preferably set to 0.5%. This upper limit is more preferably 0.2%. In the case of adding the rare earth element, the lower limit of the content of the rare earth element is preferably 0.005%.

Here, the rare earth element (REM) is one or more selected from a group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

[0048] Nb and Ti generate carbonitrides; and thereby, the generation of Cr carbides is suppressed. Due to this, Nb and Ti contribute to improvement in the stress corrosion cracking resistance. Therefore, Nb and Ti may be added as necessary. However, in the case where Nb or Ti is added at a large amount, formability and manufacturability are deteriorated. Therefore, each upper limit of a Nb content and a Ti content is set to 0.5%. Each upper limit of the Nb content and the Ti content is preferably 0.3%. In the case of adding Nb or Ti, each lower limit of the Nb content and the Ti content is preferably 0.005%, and more preferably 0.01%.

[0049] Al is an effective element as a deoxidizing element; and therefore, Al may be added as necessary. However, in the case where Al is added excessively, this leads to deterioration of formability and weldability; and therefore, the upper limit of an Al content is set to 0.5%. This upper limit is preferably 0.3%, and more preferably 0.1%. In the case of adding Al, the lower limit of the Al content is preferably 0.01 %.

[0050] Mg and Ca form oxides in a molten steel together with Al; and therefore, Mg and Ca operate as deoxidizing agents. Therefore, Mg and Ca may be added as necessary.

Ca fixes S to improve hot workability. However, in the case where Mg and Ca are added excessively, this leads to deterioration of corrosion resistance and weldability; and therefore, each upper limit of a Mg content and a Ca content

is set to 0.005%. Each upper limit of the Mg content and the Ca content is preferably 0.002%. In the case of adding Mg or Ca, each lower limit of the Mg content and the Ca content is 0.0001%, and more preferably 0.0003%.

[0051] In addition to the above-described components, the austenitic stainless steel according to the present embodiment may contain P and S as a part of unavoidable impurities within a range described below. P and S are elements that are harmful to hot workability and corrosion resistance. A P content is preferably set to be in a range of 0.1% or less. The P content is more preferably in a range of 0.05% or less. A S content is preferably set to be in a range of 0.01% or less. The S content is more preferably in a range of 0.005% or less.

[0052] In the present embodiment, in addition to the above-described component ranges, a component balance that is optimal to the formation of a fine grained structure is defined by Md which is expressed by Equation (1).

$$Md = 551 - 462(C + N) - 9.2Si - 8.1Mn - 13.7Cr - 29(Ni + Cu) - 18.2Mo \cdots (1)$$

[0053] In a metastable austenitic stainless steel, a martensite transformation is caused by a plastic processing even in a temperature range of an Ms point (martensite transformation initiation temperature) or higher. The upper limit temperature at which transformation is caused by processing is called an Md point. That is, the Md point is an index indicating stability of austenite.

In the case where components are adjusted such that the Md expressed by Equation (1) becomes in a range of -20 to 40, an operation of improving the stress corrosion cracking resistance, which is an object of the present embodiment, can be obtained due to the formation of the fine grained structure and the refinement. In the case where the Md is less than -20, as described in the items (d) and (e), it is difficult to form the fine grained structure and to improve the stress corrosion cracking resistance. On the other hand, in the case where the Md is more than 40, as described in the items (d) and (e), this is effective for the formation of the fine grained structure; however, the improvement of the stress corrosion cracking resistance is inhibited. A preferable range of the Md is -5 to 35.

[0054] (B) A method of producing a steel sheet according to the present embodiment will be described below.

In the case of producing a fine grained austenitic stainless steel sheet according to the present embodiment, it is preferable that steel components described in (A) are contained. In addition, it is also preferable that the following production conditions are applied in order to make an average grain size be in a range of 10 μm or less, and to make an occupancy ratio of high angle grain boundaries having angles of 15° or more be in a range of more than 80% so as to effectively improve the stress corrosion cracking resistance.

The method of producing a steel sheet according to the present embodiment includes: a process of subjecting a slab having the steel components in the item (A) to hot rolling so as to produce a hot-rolled steel sheet; a process of annealing the hot-rolled steel sheet (annealing of hot-rolled steel sheet); a process of subjecting the annealed hot-rolled steel sheet to cold rolling so as to produce a cold-rolled steel sheet; and a process of annealing the cold-rolled steel sheet (referred to as annealing of cold-rolled steel sheet or final annealing).

[0055] Production methods of the processes until the hot rolling are not particularly limited, and well known conditions are applied.

In order to form the fine grained structure by the final annealing after the cold rolling, as described in the item (g), it is effective to promote strain-induced martensite transformation in the cold rolling. In order to make the average grain size be in a range of 10 μm or less, which is an object of the present embodiment, it is effective to set a volume ratio of the strain-induced martensite to be in a range of 50% or more after the cold rolling. The volume ratio of the strain-induced martensite is preferably in a range of more than 60%. Conditions of the final annealing after the cold rolling are adjusted so as to refine crystal grains and increase the ratio of the high angle grain boundaries having angles of 15° or more. It is also preferable to adjust conditions of the cold rolling, and furthermore, it is also preferable to adjust conditions of the annealing of hot-rolled steel sheet.

Conditions of respective processes will be described below.

[0056] In the annealing of hot-rolled steel sheet, it is preferable to set a temperature of the annealing of hot-rolled steel sheet to be in a range of 1050 to 1200°C in order to coarsen austenite grains, which are to be subjected to the cold rolling, to be in a range of 20 μm or more; and thereby, the strain-induced martensite transformation is promoted in the cold rolling. In the case where the temperature of the annealing of hot-rolled steel sheet is lower than 1050°C, grain sizes of austenite may be smaller than 20 μm . In the case where the temperature of the annealing of hot-rolled steel sheet is higher than 1200°C, an acid pickling property after annealing may be deteriorated; and thereby, a surface quality may be deteriorated. In addition, the annealing at a temperature of higher than 1200°C causes large load to a facility. The temperature of the annealing of hot-rolled steel sheet is more preferably in a range of 1080 to 1180°C.

[0057] In the cold rolling, it is preferable that a rolling reduction ratio is set to be in a range of 70% or more and a rolling temperature is set to be in a range of 50°C or lower in order to promote the strain-induced martensite transformation. In the case where the rolling reduction ratio is less than 70%, a volume ratio of the strain-induced martensite becomes

less than 50%; and thereby, it is difficult to form the fine grain structure as described above. The rolling reduction ratio is more preferably in a range of 80% or more. The upper limit of the rolling reduction ratio is not particularly limited; however, the upper limit of the rolling reduction ratio is preferably in a range of 90% or less in consideration of a production of a hot-rolled steel sheet and a cold rolling facility capability.

In the case where the rolling temperature is higher than 50°C, the volume ratio of the strain-induced martensite becomes less than 50%; and thereby, it is difficult to form the fine grain structure as described above. The lower limit of the rolling temperature is not particularly limited; however, it is preferable that the lower limit is in a range of 10°C or more which is a temperature reached by industrial water cooling. In the case of producing the steel sheet with a small-sized rolling facility, the rolling temperature is not limited to the temperature of 10°C or higher, and may be set to a low temperature (for example, -200°C) that is reached through cooling by liquid nitrogen or the like.

[0058] In the final annealing after the cold rolling, a temperature of the final annealing is set to be in a range of 700 to 1050°C in order to make the average grain size be in a range of 10 μm or less and to make the ratio of the high angle grain boundaries be in a range of larger than 80%. In the case where the temperature of the final annealing is lower than 700°C, a state is maintained in which strains during the cold rolling are accumulated, and recrystallization of austenite grains becomes insufficient; and thereby, formability is deteriorated greatly. In addition, the ratio of the high angle grain boundaries having angles of 15° or more is small; and thereby, the stress corrosion cracking resistance that is an object of the present embodiment is deteriorated. It is preferable to set the lower limit of the temperature of the final annealing to be in a range of 750°C or higher. In the case where the temperature of the final annealing is higher than 1050°C, grain growth of austenite is progressed; and thereby, the average grain size becomes larger than 10 μm . It is preferable to set the temperature of the final annealing to be in a range of 900°C or lower. In order to obtain a fine grained structure in which the ratio of the high angle grain boundaries is higher than 80%, which is a target of the present embodiment, it is more preferable to set the temperature of the final annealing to be in a range of 750 to 850°C.

[0059] In the case where the temperature of the final annealing is within a range of 700 to 900°C, it is preferable to set an annealing time of the final annealing to be in a range of longer than one hour in order to promote the recrystallization of austenite; and thereby, the ratio of the high angle grain boundaries having angles of 15° or more is increased. The annealing time of the final annealing is more preferably in a range of two hours or more. The upper limit of the annealing time (holding time) of the final annealing is not limited; however, it is preferable to set the annealing time to be in a range of 24 hours or less on the assumption that industrially well-known box annealing of chromium-based stainless steel is used. In order to obtain a fine grained structure in which the ratio of the high angle grain boundaries is higher than 80% which is a target of the present embodiment, it is more preferable to set the annealing time of the final annealing to be in a range of 4 to 24 hours. In the case of producing the steel sheet with a small-scaled annealing facility, the annealing time of the final annealing is not limited to 24 hours or less, and may be set to be in a range of longer than 24 hours. In the case where the temperature of the final annealing is in a range of higher than 900°C to 1050°C, it is preferable to set the annealing time to be in a range of 10 minutes or less (a short holding time) in consideration of grain growth. More preferably, the annealing time (holding time) of the final annealing may be in a range of one minute or less.

[0060] (C) The reason why the metal structure of the steel sheet according to the present embodiment is restricted will be described below.

In the fine grained austenitic stainless steel sheet according to the present embodiment, the average grain size is in a range of 10 μm or less, and the ratio of the high angle grain boundaries having angles of 15° or more is in a range of higher than 80%. This metal structure may be obtained by subjecting a slab having the steel components in the item (A) to processes under preferred production conditions in the item (B).

[0061] In the case where the average grain size is larger than 10 μm , it is difficult to obtain excellent stress corrosion cracking resistance due to the refinement which is an object of the present embodiment. Furthermore, even when the average grain size is in a range of 10 μm or less, in the case where the ratio of the high angle grain boundaries having angles of 15° or more is less than 80%, the improvement of the stress corrosion cracking resistance due to the refinement is lowered as described in the item (f).

In order to effectively improve the stress corrosion cracking resistance that is an object of the present embodiment, it is preferable that the average grain size is in a range of 5 μm or less and the ratio of the high angle grain boundaries having angles of 15° or more is in a range of higher than 85%. The lower limit of the average grain size is not particularly limited; however, from Non-Patent Documents 1 and 2 and Patent Document 1, it can be understood that it is difficult for the average grain size to be less than 1 μm . Therefore, in consideration of a practical aspect, it is preferable to set the average grain size to be in a range of 1 to 5 μm .

[0062] The ratio of the high angle grain boundaries having angles of 15° or more is set to be in a range of higher than 80% as described above, and preferably in a range of higher than 85%. The increasing of the ratio of the high angle grain boundaries is effective for a decrease in 0.2% proof stress and an increase in elongation in a fine grained material (steel sheet in which crystal grains are fine), and the increasing of the ratio of the high angle grain boundaries contributes to improvement of formability.

From the above-described background, it is preferable that the formability, which is a target of the present embodiment,

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is superior to formability of a ferritic stainless steel and is close to formability of an austenitic stainless steel represented by SUS304 or the like. Therefore, it is preferable that 0.2% proof stress is in a range of lower than 400 MPa, and uniform elongation is in a range of higher than 30%.

In order to fulfill both of the stress corrosion cracking resistance and the formability, the ratio of the high angle grain boundaries having angles of 15° or more is preferably in a range of higher than 85%, and more preferably in a range of higher than 90%.

Here, in the present embodiment, mechanical properties of 0.2% proof stress and the uniform elongation are evaluated by a JIS 13 No. B tensile test.

EXAMPLES

[0063] Hereinafter, examples of the present embodiment will be described.

Austenitic stainless slabs having steel components shown in Table 2 were melted, and hot rolling was performed to produce a hot-rolled steel sheet having a sheet thickness of 4 mm. Steel Nos. 1 to 23 fulfill the steel component conditions defined in the present embodiment. Steel Nos. 24 to 28 do not fulfill the steel component conditions defined in the present embodiment.

[0064]

Table 2

(mass%)									
Steel No.	C	Si	Mn	Cr	Ni	Cu	N	Others	Md
1	0.023	0.88	1.8	16.0	7.1	2.1	0.011		25.3
2	0.047	0.89	1.7	16.1	6.9	2.0	0.010		22.2
3	0.007	0.90	1.8	16.1	7.1	2.1	0.011		30.9
4	0.040	0.88	1.8	14.2	7.2	2.1	0.011		38.9
5	0.023	0.88	1.8	18.8	6.9	2.0	0.011		-4.6
6	0.020	0.20	1.8	16.0	7.1	2.1	0.011		33.0
7	0.023	1.60	1.8	16.0	7.1	2.5	0.011	-	7.1
8	0.023	0.88	3.6	16.0	7.1	1.9	0.011		16.3
9	0.023	0.88	0.5	16.0	7.1	2.2	0.011		32.7
10	0.023	0.88	1.8	16.0	7.8	2.0	0.011		7.4
11	0.045	0.90	2.0	16.5	5.6	2.5	0.011		37.9
12	0.025	1.20	2.0	16.0	7.5	1.0	0.015		37.8
13	0.020	0.80	1.7	16.0	7.0	3.5	0.012		-10.4
14	0.023	0.90	1.8	16.0	7.1	1.6	0.090		2.9
15	0.023	0.90	1.9	16.0	7.0	2.0	0.007		31.5
16	0.025	0.90	1.8	16.1	7.0	2.0	0.010	Mo:0.8	15.8
17	0.023	0.88	1.8	16.0	7.0	2.1	0.011	B:0.0015	27.9
18	0.023	0.88	1.8	16.0	7.1	2.0	0.011	REM:0.12	28.2
19	0.025	0.90	2.0	16.0	7.1	2.1	0.011	Ti:0.05	22.4
20	0.023	0.88	2.0	15.8	7.1	2.1	0.011	Nb:0.2,Ti:0.01	26.2
21	0.023	0.90	2.0	15.9	7.1	2.1	0.011	Mg,Ca:0.0007	24.7
22	0.025	0.90	2.0	15.8	7.1	2.1	0.011	Al:0.2	25.1
23	0.025	1.00	1.8	16.0	7.2	1.8	0.013	V:0.4	27.6
24	0.040	0.60	1.0	18.2	8.4	0.8	0.035		-15.2

(continued)

(mass%)									
Steel No.	C	Si	Mn	Cr	Ni	Cu	N	Others	Md
25	0.011	0.50	0.6	18.1	<u>8.2</u>	0.1	0.01		<u>41.8</u>
26	<u>0.060</u>	0.55	0.9	16.8	<u>10.0</u>	0.2	0.015	<u>Mo:2</u>	<u>-58.9</u>
27	0.013	0.31	2.1	16.8	7.6	3.5	0.025		<u>-39.9</u>
28	0.010	0.55	1.0	16.2	7.0	2.0	0.01		<u>43.8</u>

[0065] The hot-rolled sheets were annealed, and then cold rolling and final annealing were performed. The cold rolling and the final annealing were performed under preferred conditions of the present embodiment and other conditions. Particularly, the cold rolling was performed under either of a condition in which a rolling temperature was lower than 30°C (<30°C) while being cooled with water at room temperature, or a condition in which the rolling temperature was higher than 50°C (>50°C) during cold rolling due to heat generated during processing without performing cooling with water or the like.

The steel sheets produced by the cold rolling and the final annealing were acid-pickled, and then measurement of the average grain size, measurement of the ratio of the high angle grain boundaries having angles of 15° or more according to an EBSP method, measurement of the stress corrosion cracking resistance (cracking initiation time), and measurement of mechanical properties (0.2% proof stress and uniform elongation) were conducted.

[0066] Various evaluation methods were performed under the above-described conditions.

Specifically, in the measurement of the average grain size, a cross section surface of the steel sheet was buried in a resin and the cross section surface was polished, and then the cross section surface was subjected to nitric acid electrolytic etching. Next, the average grain size was measured by a microscope test method of steel-grain size defined in JIS G0551. In the measurement of the ratio of the high angle grain boundaries, a measurement magnification was adjusted to include 3000 or more crystal grains, and a grain boundary map of a microstructure of the steel sheet was measured by the EBSP method. The low angle grain boundaries having angles of less than 15° and the high angle grain boundaries having angles of 15° or more were discriminated by the grain boundary map, and then the occupancy ratio of the high angle grain boundaries in the entirety of grain boundaries was calculated.

In the measurement of the cracking initiation time, similarly to the above-described measurement method, the steel sheet was subjected to a cylindrical deep drawing processing under conditions where a blank diameter was 67.5 mmφ, a punch diameter was 35 mmφ, a die diameter was 37 mmφ, a blank hold force was 1 ton, and a drawing ratio (a value obtained by dividing the blank diameter by the punch diameter) was 1.9. The obtained molded product was left as it was for 48 hours, and it was confirmed that aging cracking did not occur. Then, the molded product was immersed into a boiling aqueous solution of 42% magnesium chloride that is defined in JIS G0576, and the cracking (stress corrosion cracking) initiation time was measured. Whether or not the cracking occurred was determined by visual observation. The mechanical properties were evaluated by a JIS No. 13 B tensile test.

[0067] A relationship between production conditions and properties are shown in Table 3.

In Table 3, "HA" represents annealing of hot-rolled steel sheet, and "FA" represents final annealing. "Grain size" represents an average grain size, and "high angle ratio" represents an occupancy ratio (%) of the high angle grain boundaries (large angle grain boundaries) (ratio of high angle grain boundaries). "SCC initiation time" represents a time at which the stress corrosion cracking occurs. In "SCC initiation time", "↑" represents that the time is longer than a value described on the left side thereof. In addition, a symbol "*" represents a value out of requisite conditions or preferred conditions defined in the present embodiment.

[0068]

Table 3

Test Steel No.	HA No.	FA		Cold Rolling		Grain Size μm (Ratio of High Angle Grain Boundaries)	SCC Initiation time (hr)	0.2% Proof Stress (MPa)	Uniform Elongation (%)	Remark
		Temperature (°C)	Time	Rolling Reduction	Temperature (°C)					
1	1	1150	4 hr	85%	<30	3.5(88)	12↑	330	41	Present Example
2	1	1150	2 hr	85%	>50	7(82)	8	350	39	Present Example
3	1	1150	1 min	85%	<30	9(90)	8	310	43	Present Example
4	1	1150	12 hr	68%	>50	7.5(95)	8	310	43	Present Example
5	1	1150	1 hr	85%	>50	6(75*)	3*	320	42	Comparative Example
6	1	1150	24 hr	85%	<30	1(70*)	0.5*	460*	28*	Comparative Example
7	1	1080	1 min	85%	>50	30*(98)	3*	260	49	Comparative Example
8	2	1150	4 hr	85%	<30	2(85)	8	370	38	Present Example
9	3	1150	4 hr	85%	<30	4.5(90)	12↑	290	43	Present Example
10	4	1150	4 hr	85%	<30	3(90)	10	310	40	Present Example
11	5	1150	4 hr	85%	<30	5.5(88)	12↑	350	37	Present Example
12	6	1150	4 hr	85%	<30	3(90)	10	320	44	Present Example
13	7	1150	4 hr	85%	<30	6.5(88)	12↑	370	37	Present Example

(Notes) HA: annealing of hot-rolled steel sheet, FA: final annealing, Grain Size: average grain size

Ratio of High Angle Grain Boundaries: occupancy ratio of high angle grain boundaries (%), SCC: stress corrosion cracking

A value of the occupancy ratio of the high angle grain boundaries (%) is described in parentheses in parallel with the grain size.

In SCC initiation time, "↑" represents that the time is longer than a number range.

"*" represents a value out of conditions defined in the present embodiment.

Table 3 (Continued)

Test Steel No.	HA No.	FA		Cold Rolling		Grain Size μm (Ratio of High Angle Grain Boundaries)	SCC Initiation time (hr)	0.2% Proof Stress (MPa)	Uniform Elongation (%)	Remark
		Temperature (°C)	Time	Rolling Reduction	Temperature (°C)					
14	8	1150	4 hr	85%	<30	6.5(88)	9	340	40	Present Example
15	9	1150	4 hr	85%	<30	4(90)	12↑	320	41	Present Example
16	10	1150	4 hr	85%	<30	6.5(85)	9	340	40	Present Example
17	11	1150	4 hr	85%	<30	3(90)	8	320	37	Present Example
18	12	1150	4 hr	85%	<30	3.5(90)	8	320	36	Present Example
19	13	1150	4 hr	85%	<30	6(85)	12↑	350	36	Present Example
20	14	1150	4 hr	85%	<30	7(85)	12↑	380	33	Present Example
21	15	1150	4 hr	85%	<30	3.5(90)	10	300	42	Present Example
22	16	1150	4 hr	85%	<30	6(85)	12↑	340	37	Present Example
23	17	1150	4 hr	85%	<30	3.5(85)	12↑	300	43	Present Example
24	18	1150	4 hr	85%	<30	3.5(85)	12↑	320	39	Present Example
25	19	1150	4 hr	85%	<30	3(85)	12↑	280	44	Present Example
26	20	1150	4 hr	85%	<30	3(83)	12↑	350	39	Present Example

(Notes) HA: annealing of hot-rolled steel sheet, FA: final annealing, Grain Size: average grain size

Ratio of High Angle Grain Boundaries: occupancy ratio of high angle grain boundaries (%), SCC: stress corrosion cracking

A value of the occupancy ratio of the high angle grain boundaries (%) is described in parentheses in parallel with the grain size.

In SCC initiation time, "↑" represents that the time is longer than a number range.

"*" represents a value out of conditions defined in the present embodiment.

Table 3 (Continued)

Test Steel No.	HA No.	FA		Cold Rolling		Grain Size μm (Ratio of High Angle Grain Boundaries)	SCC Initiation time (hr)	0.2% Proof Stress (MPa)	Uniform Elongation (%)	Remark
		Temperature (°C)	Time	Rolling Reduction	Temperature (°C)					
27	21	1150	4 hr	85%	<30	3.5(90)	12↑	300	43	Present Example
28	22	1150	4 hr	85%	<30	3.5(85)	12↑	310	42	Present Example
29	23	1100	1 min	85%	<30	7.5(85)	12↑	340	39	Present Example
30	24	1150	4 hr	85%	<30	6(78*)	1*	450*	37	Comparative Example
31	24	1080	1 min	85%	<30	28*(98)	1*	270	47	Comparative Example
32	25	1150	4 hr	85%	<30	3.5(75*)	1*	430*	35	Comparative Example
33	25	1080	1 min	85%	<30	30*(98)	2*	240	50	Comparative Example
34	26	1150	4 hr	85%	<30	15*(75*)	2*	410*	28*	Comparative Example
35	27	1150	4 hr	85%	<30	12*(90)	3*	260	45	Comparative Example
36	27	1080	1 min	85%	<30	30*(98)	3*	240	47	Comparative Example
37	28	1150	4 hr	85%	<30	3(90)	2*	300	43	Comparative Example

(Notes) HA: annealing of hot-rolled steel sheet, FA: final annealing, Grain Size: average grain size

Ratio of High Angle Grain Boundaries: occupancy ratio of high angle grain boundaries (%), SCC: stress corrosion cracking

A value of the occupancy ratio of the high angle grain boundaries (%) is described in parentheses in parallel with the grain size.

In SCC initiation time, "↑" represents that the time is longer than a number range.

"*" represents a value out of conditions defined in the present embodiment.

[0069] Test Nos. 1, 3, 8 to 29 had steel components of the present embodiment, and were produced under preferred production conditions of the present embodiment. In these steel sheets, evaluation results described below were obtained. The average grain sizes were in a range of 10 μm or less, the ratios of the high angle grain boundaries having angles of 15° or more were in a range of higher than 80%, and the stress corrosion cracking initiation times were largely longer than four hours that is a target value. Furthermore, these steel sheets had mechanical properties in which 0.2% proof stresses were in a range of lower than 400 MPa, and the uniform elongations were in a range of more than 30%. Therefore, preferred formability was accomplished together with excellent stress corrosion cracking resistance. From this, in the austenitic stainless steel sheet that had steel components of the present embodiment and was produced under the preferred production conditions of the present embodiment, the excellent stress corrosion cracking resistance was exhibited due to the refinement of crystal grains; and thereby, the compatibility between the stress corrosion cracking resistance and the formability was accomplished.

[0070] Test No. 5 had the steel component of the present embodiment; however, the annealing time of the final annealing was one hour which was short. Therefore, the recrystallization of austenite was not sufficiently promoted, and the ratio of the high angle grain boundaries having angles of 15° or more was 75% and did not reach 80%. As a result, the average grain size was 6 μm which was small; however, the stress corrosion cracking initiation time was three hours. Therefore, the target stress corrosion cracking resistance was not obtained.

[0071] Test No. 6 had the steel components of the present embodiment; however, Test No. 6 was produced under conditions out of the preferred production conditions of the present embodiment. Since the temperature of the final annealing was lower than 700°C, a state was maintained in which strains were accumulated during the cold rolling, and recrystallization of austenite grains was insufficient. As a result, the ratio of the high angle grain boundaries having angles of 15° or more did not reach 80%. In addition, the average grain size was 1 μm which was small; however, the stress corrosion cracking resistance was not improved due to the residual strains during the cold rolling, and the stress corrosion cracking initiation time was 0.5 hours. Furthermore, 0.2% proof stress was 400 MPa or more, and the steel sheet was hardened; and thereby, the formability was deteriorated.

[0072] Test No. 7 had the steel components of the present embodiment; however, Test No. 7 was produced by annealing at a known annealing temperature, and the temperature of the final annealing was higher than 1050°C. Therefore, the average grain size was 30 μm . The ratio of the high angle grain boundaries having angles of 15° or more was 98%; however, a cracking initiation time was three hours, and the improvement in the stress corrosion cracking resistance due to the refinement of crystal grains was not found.

[0073] Test Nos. 30, 32, 34, 35, and 37 had steel components out of the conditions of the present embodiment; however, these test steels were produced under the preferred production conditions of the present embodiment. In Test Nos. 30, 32, and 37, crystal grains were refined; and thereby, the average grain sizes were in a range of 10 μm or less. However, the stress corrosion cracking initiation times were shorter than four hours, and improvement in the stress corrosion cracking resistance, which is a target of the present embodiment, was not found. Particularly, in test No. 37, since Md was more than 40, it was considered that the exhibition of the stress corrosion cracking resistance was inhibited. In test Nos. 34 and 35, since Md was less than -20, it became difficult to form the fine grained structure; and thereby, the average grain sizes were larger than 10 μm . Therefore, the stress corrosion cracking initiation times became shorter than four hours, and improvement in the stress corrosion cracking resistance, which is a target of the present embodiment, was not found.

[0074] Test Nos. 31, 33, and 36 had steel components out of the conditions of the present embodiment, and these test steels were produced under conditions out of the preferred production conditions of the present embodiment. The average grain sizes of these steel sheets were 28 μm or 30 μm , and the stress corrosion cracking resistances did not reach the target value of the present embodiment, and these results were expected from the components which were known from the related art.

Industrial Applicability

[0075] According to the present embodiment, crystal grains are refined under conditions where a Ni content is in a range of 8% or less and expensive Mo is not included; and thereby, it is possible to obtain an austenitic stainless steel sheet in which stress corrosion cracking that is a defect of austenitic stainless steel is overcome, and compatibility between stress corrosion cracking resistance and formability is promoted. Therefore, the austenitic steel sheet according to the present embodiment can be suitably applied to members that are used under a corrosion environment including chloride ions, or the like.

Claims

1. A fine grained austenitic stainless steel sheet exhibiting excellent stress corrosion cracking resistance and formability,

the steel sheet comprising: in terms of percent by mass,

C: 0.05% or less;

Cr: 14 to 19%;

Si: 2% or less;

Mn: 4% or less;

Ni: 5 to 8%;

Cu: 4% or less; and

N: 0.1% or less,

with the remainder being Fe and unavoidable impurities,

wherein steel components are included in a manner such that the following Md is in a range of -20 to 40, and an average grain size is in a range of 10 μm or less, an occupancy ratio of high angle grain boundaries having angles of 15° or more is in a range of more than 80%,

$$\text{Md} = 551 - 462(\text{C} + \text{N}) - 9.2\text{Si} - 8.1\text{Mn} - 13.7\text{Cr} - 29(\text{Ni} + \text{Cu}) - 18.2\text{Mo}.$$

2. The fine grained austenitic stainless steel sheet exhibiting excellent stress corrosion cracking resistance and formability according to Claim 1, wherein the steel components further comprise, in terms of percent by mass, one or more selected from a group consisting of Mo: 1% or less, V: 1% or less, B: 0.010% or less, Nb: 0.5% or less, Ti: 0.5% or less, rare earth elements: 0.5% or less, Al: 0.5% or less, Mg: 0.005% or less, and Ca: 0.005% or less.
3. The fine grained austenitic stainless steel sheet exhibiting excellent stress corrosion cracking resistance and formability according to Claim 1 or 2, wherein cracking does not occur in a stress cracking test in which the steel sheet is subjected to cylindrical deep drawing at a drawing ratio of 1.5 to 2.0 to obtain a molded product, the molded product is immersed into a boiling aqueous solution of 42% magnesium chloride for four hours, and occurrence of cracking in the molded product is checked.
4. The fine grained austenitic stainless steel sheet exhibiting excellent stress corrosion cracking resistance and formability according to any one of Claims 1 to 3, wherein 0.2% proof stress is in a range of less than 400 MPa, and uniform elongation is in a range of more than 30% which are obtained from a tensile test.

FIG. 1

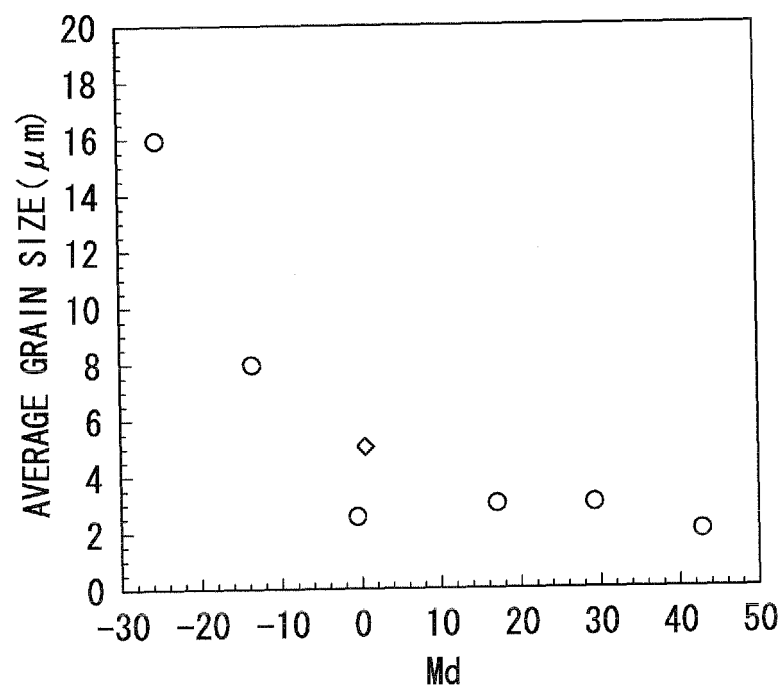
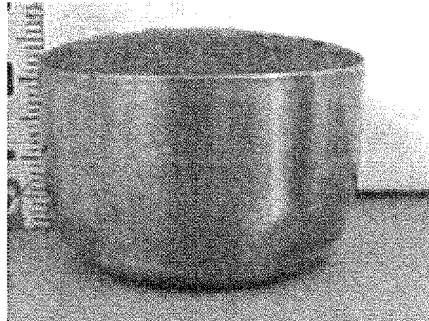
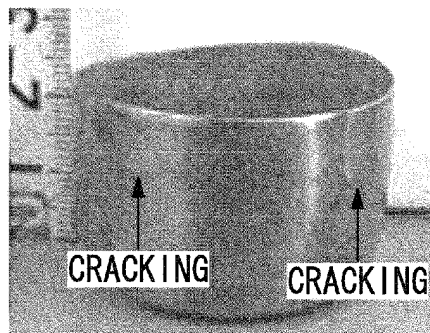


FIG. 2

(i) STEEL B: $d = 3 \mu\text{m}$



(ii) STEEL B: $d = 28 \mu\text{m}$



(iii) SUS316L: $d = 30 \mu\text{m}$

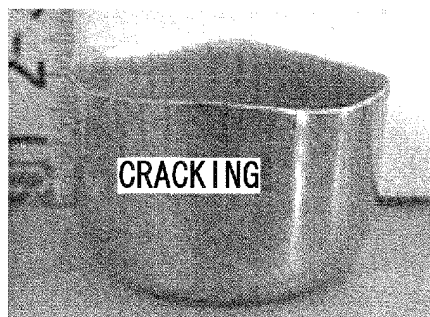


FIG. 3

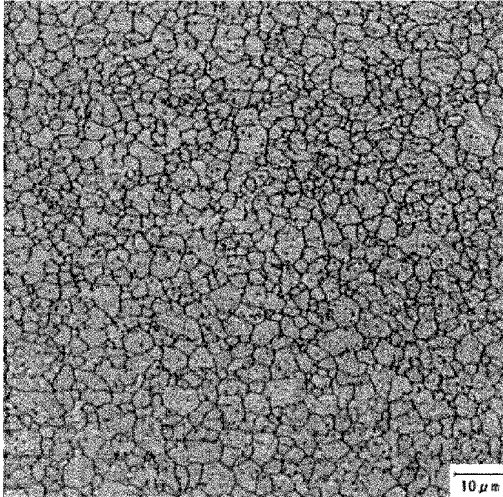
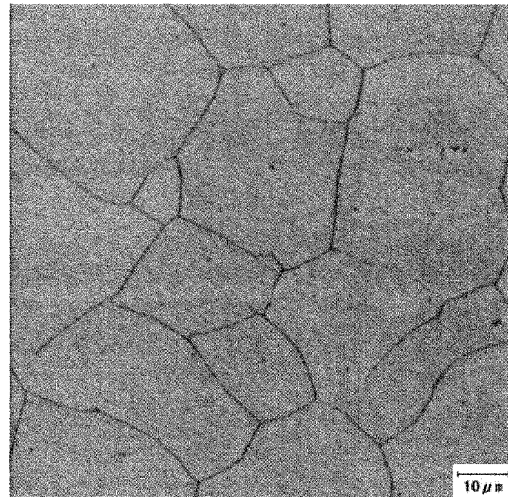
(i) STEEL B: $d = 3 \mu\text{m}$ (ii) STEEL B: $d = 28 \mu\text{m}$ 

FIG. 4

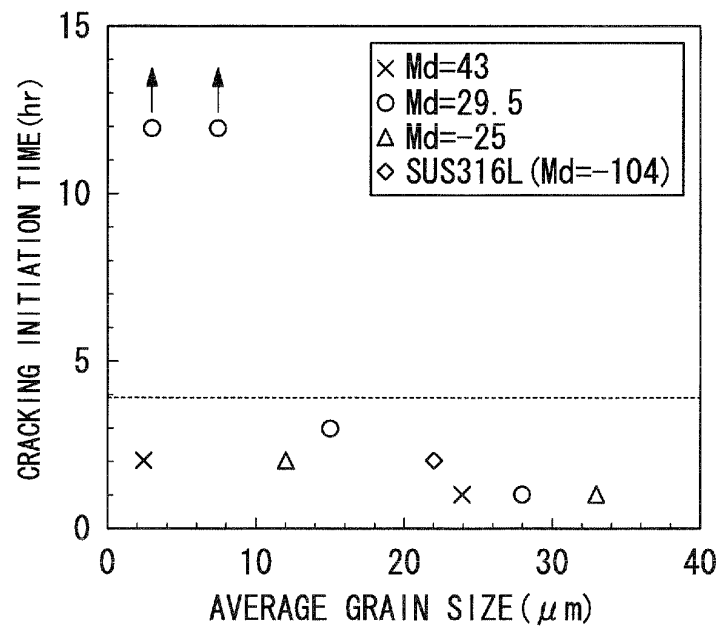
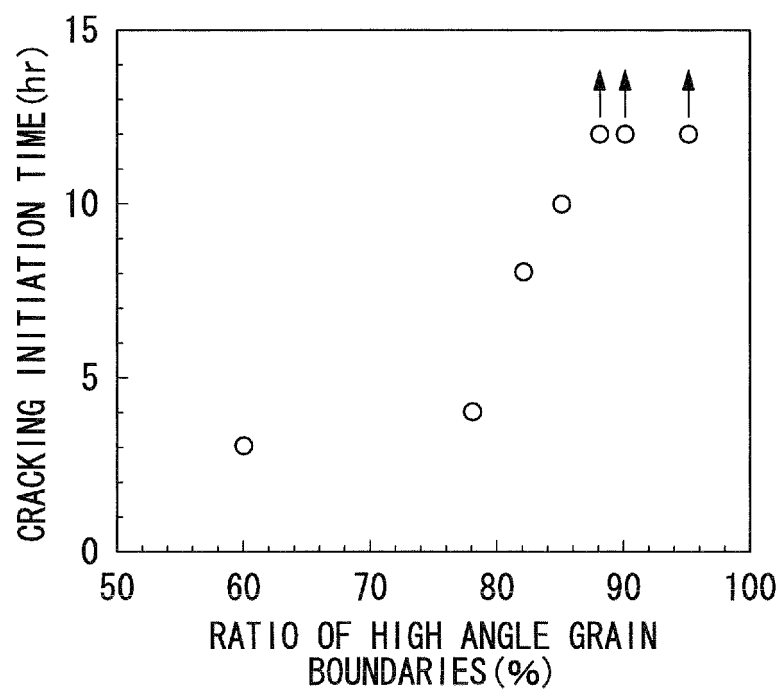


FIG. 5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/066968

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00 (2006.01) i, C22C38/58 (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)

C22C38/00-38/60

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 4-214841 A (Nisshin Steel Co., Ltd.), 05 August 1992 (05.08.1992), claims 1 to 7; paragraph [0019]; examples (Family: none)	1-4
A	JP 2005-105412 A (Nippon Steel & Sumikin Stainless Steel Corp.), 21 April 2005 (21.04.2005), claims 1, 2; examples (Family: none)	1-4
A	JP 2000-79405 A (Sumitomo Metal Industries, Ltd.), 21 March 2000 (21.03.2000), paragraph [0040]; examples (Family: none)	1-4

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

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search
24 November, 2010 (24.11.10)

Date of mailing of the international search report
07 December, 2010 (07.12.10)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/066968

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Yoichi TOKUNAGA, "Austenitic stainless steels having ultra-fine crystal grains", The Japan Society for Heart Treatment Koen Taikai Koen Gaiyoshu, vol.26, 1988.05, pages 71 to 74	1-4
P, X	JP 2009-299171 A (Nippon Steel & Sumikin Stainless Steel Corp.), 24 December 2009 (24.12.2009), entire text (Family: none)	1-4

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

REFERENCES CITED IN THE DESCRIPTION

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- *Nippon Kokan Technical Report*, No. 87, 1980, 51-60 [0012]