



(11) **EP 3 434 802 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
01.07.2020 Bulletin 2020/27

(51) Int Cl.:
C22C 38/00 (2006.01) **C21D 9/46** (2006.01)
C22C 38/38 (2006.01) **C22C 38/58** (2006.01)
C21D 6/00 (2006.01) **C21D 8/02** (2006.01)
C22C 38/18 (2006.01) **C22C 38/42** (2006.01)

(21) Application number: **18188353.9**

(22) Date of filing: **01.08.2008**

(54) **FERRITIC-AUSTENITIC STAINLESS STEEL EXCELLENT IN CORROSION RESISTANCE AND WORKABILITY**

FERRITISCH-AUSTENITISCHER EDELSTAHL MIT HERVORRAGENDER KORROSIONSBESTÄNDIGKEIT UND BEARBEITBARKEIT

ACIER INOXYDABLE FERRITIQUE-AUSTÉNITIQUE PRÉSENTANT UNE EXCELLENTE RÉSISTANCE À LA CORROSION ET UNE EXCELLENTE APTITUDE AU FAÇONNAGE

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR

(30) Priority: **02.08.2007 JP 2007202016**
29.08.2007 JP 2007222259

(43) Date of publication of application:
30.01.2019 Bulletin 2019/05

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:
08792317.3 / 2 172 574

(73) Proprietor: **Nippon Steel & Sumikin Stainless Steel Corporation**
Chiyoda-ku
Tokyo 100-0004 (JP)

(72) Inventors:
• **HATANO, Masaharu**
Chiyoda-ku, Tokyo 100-0004 (JP)
• **TAKAHASHI, Akihiko**
Chiyoda-ku, Tokyo 100-0004 (JP)
• **ISHIMARU, Eiichiro**
Chiyoda-ku, Tokyo 100-0004 (JP)
• **KIMURA, Ken**
Chiyoda-ku, Tokyo 100-8071 (JP)

(74) Representative: **Vossius & Partner**
Patentanwälte Rechtsanwälte mbB
Siebertstrasse 3
81675 München (DE)

(56) References cited:
EP-A1- 0 889 145 **EP-A1- 1 715 073**
JP-A- H02 305 940 **JP-A- 2006 233 308**
JP-A- 2007 154 283

EP 3 434 802 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to ferritic-austenitic stainless steel excellent in corrosion resistance and workability.
[0002] According to the present invention, it is possible to produce ferritic-austenitic stainless steel excellent in corrosion resistance and workability without including a large amount of the expensive and rare element of Ni, so it is believed this can contribute to resource conservation and environmental protection. Herein also disclosed is a method of producing the same.

BACKGROUND ART

10
[0003] Stainless steel may be broadly divided into austenitic stainless steel, ferritic stainless steel, and two-phase (ferritic-austenitic) stainless steel. Austenitic stainless steel contains expensive Ni in 7% mass or more. Many types are excellent in workability. Ferritic stainless steel contains almost no Ni and generally has considerably lower workability than austenitic stainless steel. On the other hand, two-phase (ferritic-austenitic) stainless steel has a comparatively small Ni content. It is considered that many types have an intermediate position in workability, corrosion resistance, etc. between austenitic stainless steel and ferritic stainless steel.

15
[0004] In recent years, improvements in refining technology have enabled a shift to ultra low carbon/nitrogen content. Due to the addition of Ti, Nb, and other stabilizing elements, corrosion resistance and workability are being improved as well in ferritic stainless steel. This is therefore being used in a broader range of fields. A large factor in this is that ferritic stainless steel is economically superior to austenitic stainless steel, which contains a large amount of Ni. However, ferritic stainless steel is very inferior to austenitic stainless steel with respect to workability, particularly in material elongation and uniform elongation.

20
[0005] Therefore, austenitic-ferritic stainless steel, which is positioned between austenitic and ferritic steel, has come under the spotlight in recent years. Conventionally, austenitic-ferritic stainless steel such as SUS 329J4L contains over 5% of Ni. Further, it contains several percent of Mo - which is rarer and more expensive than Ni. Therefore, there is still a problem in terms of spread of use and economy.

25
[0006] To deal with this problem, austenitic-ferritic stainless steel using Mo as an optional additive element and limiting the amount of Ni to more than 0.1% and less than 1% has been disclosed in Japanese Patent Publication (A) No. 11-071643 or to 0.5% to 1.7% has been disclosed in WO/02/27056. These austenitic-ferritic stainless steels are directed at lower Ni content, so contain N in an amount exceeding 0.1% and Mn in an amount substantially exceeding 3.7%.

30
[0007] Japanese Patent Publication (A) No. 2006-169622 and Japanese Patent Publication (A) No. 2006-183129 disclose austenitic-ferritic stainless steels aimed at improvement of total elongation and deep drawability by limiting the Ni amount to substantially 3% or less and adjusting the austenite phase C+N and ingredient balance. Further, Japanese Patent Publication (A) No. 10-219407 discloses ferritic stainless steel excellent in ductility having an amount of N of substantially less than 0.06, having a ferrite phase as the matrix phase, and having a residual austenite phase of less than 20%.

35
[0008] If seen from the viewpoint of workability, these patent citations include findings for improving the ductility of ferritic-austenitic stainless steel, but these are all techniques for improving the tensile elongation at break. Elongation at break comprises uniform elongation and local elongation, so there sometimes increasing the local elongation may result in the elongation at break increasing. However, if the uniform elongation does not increase, the actual workability will not improve. In the above art, there is no mention at all of a technique for improving the uniform elongation which is so important in actual workability.

40
[0009] For example, Japanese Patent Publication (A) No. 10-219407 describes technology that uses stainless steel having a ferrite phase as its principal constituent phase and containing a residual austenite phase to improve the tensile elongation at break by the TRIP phenomenon. Japanese Patent Publication (A) No. 11-071643 describes a method defining the stability of an austenite phase to improve the tensile elongation. Japanese Patent Publication (A) No. 2006-169622 discloses the art of defining the percentage of the austenite phase and amounts of C and N in the austenite phase to improve the total elongation in a tensile test.

45
[0010] However, in Japanese Patent Publication (A) No. 10-219407, as shown in the examples, the values of the tensile elongation at break are 34 to 42%, that is, the elongation at break is not necessarily high. Further, even if steel sheet or plate does not break and "fracture" in actual shaping, it is often judged unworkable when necking occurs. That is, rather than the "elongation at break" in a tensile test, the uniform deformation limit, that is, the "uniform elongation", determines the workability, but what extent of level the uniform elongation is at is unknown. Japanese Patent Publication 11-071643 describes a tensile elongation at break of up to a 46% maximum. Further, Japanese Patent Publication (A) No. 2006-169622 describes an elongation at break of up to a 71% maximum in the examples. However, even these citations do not describe at all the uniform elongation which governs the actual workability.

[0011] Next, let's look at this from the viewpoint of the corrosion resistance. Japanese Patent Publication (A) No. 2006-200035 and Japanese Patent Publication (A) No. 2006-233308 disclose improvements in the crevice corrosion resistance and intergranular corrosion resistance of austenitic-ferritic stainless steels similar to Japanese Patent Publication (A) No. 2006-169622 and Japanese Patent Publication (A) No. 2006-183129. Japanese Patent Publication (A) No. 2006-200035 describes suppression of crevice corrosion in a coastal environment exposure test for an austenitic-ferritic stainless steel in which an amount of Mn is limited to less than 2% and an amount of Ni of over 0.5% is added.

[0012] On the other hand, Japanese Patent Publication (A) No. 2006-233308 describes an austenitic-ferritic stainless steel containing Mn in over 2% and less than 4% and having an amount of Ni of substantially less than 0.6% in which grain boundary cracking after boiling in a sulfuric acid/cupric sulfate solution is suppressed.

[0013] Japanese Patent Publication (A) No. 5-247594 discloses two-phase stainless steel with improved resistance to weather under near coastal conditions. This two-phase stainless steel contains an amount of Mn substantially over 4% or an amount of Mn less than 4% and an amount of Ni over 3%.

[0014] None of the above publications have descriptions suggesting in any way corrosion resistance in a neutral chloride environment such as the pitting potential most generally used at. In other words, it can be said that the ingredients of ferritic-austenitic stainless steel oriented at lower Ni which is provided with a corrosion resistance in a neutral chloride environment equal to or greater than SUS 304 and which is excellent in workability and the method of production of the same have not yet been clarified.

[0015] EP-A-0 889 145 describes an austenoferritic stainless steel with low nickel content and high tensile elongation, having a composition comprising (by wt.):

carbon < 0.04%, 0.4% < silicon < 1.2%, 2% < manganese < 4%, 0.1% < nickel < 1%, 18% < chromium < 22%, 0.05% < copper < 4%, sulfur < 0.03%, phosphorus < 0.1%, 0.1% < nitrogen < 0.3%, and molybdenum < 3%, wherein the steel has a two-phase structure of austenite and ferrite and comprises between 30% and 70% of austenite, and wherein the steel is defined by further conditions.

[0016] EP-A-1 715 073 describes an austenitic-ferritic stainless steel having a metal structure containing ferrite phase and austenite phase, the amount of (C + N) in the austenite phase being in a range from 0.16 to 2% by mass, and the volume percentage of the austenite phase being in a range from 10 to 85%. Furthermore, the stainless steel comprises, beside other elements, 12% or less Mn, and 0.05 to 0.6% N. This document teaches that from the point of austenite-phase formation, the N content is further preferably limited to 0.18% by mass or more. From the point of hot-workability, the N content is further preferably limited to 0.34% by mass or less.

DISCLOSURE OF THE INVENTION

[0017] The present invention was made in view of the current state of the prior art and has as its object to provide ferritic-austenitic stainless steel oriented at lower Ni which is excellent in corrosion resistance, particularly corrosion resistance in a neutral chloride environment, and which has a high "uniform elongation", the factor governing workability, and a method of production of the same.

[0018] The inventors engaged in intensive research to solve the above problems and as a result discovered that by defining the ingredients and metal structure of the steel, particularly the balance of the ferrite phase and austenite phase, and controlling the annealing conditions and other production conditions, ferritic-austenitic stainless steel which has a corrosion resistance in a neutral chloride environment equal to or greater than SUS 304, which has excellent uniform elongation, and which is excellent in corrosion resistance and workability can be obtained and thereby completed the present invention as defined in the claims.

[0019] Herein also disclosed is the following which is not within the claims:

(1) Ferritic-austenitic stainless steel excellent in corrosion resistance and workability characterized by containing, by mass%,

C: 0.001 to 0.1%,
 Cr: 17 to 25%,
 Si: 0.01 to 1%,
 Mn: 0.5 to 3.7%, and
 N: 0.06% to less than 0.15%,

having a pitting indicator (PI value) shown by the following formula (a) of over 18%, having a balance of Fe and unavoidable impurities, and having a ferrite phase as the matrix phase and having a volume fraction of the austenite phase of 15 to 50%.

Pitting indicator (PI value) = Cr + 3Mo + 10N - Mn... (a)

5 (2) Ferritic-austenitic stainless steel excellent in corrosion resistance and workability as set forth in (1), characterized by further containing, by mass%, both Ni: 0.6 to 3% and Cu: 0.1 to 3%.

(3) Ferritic-austenitic stainless steel excellent in corrosion resistance and workability as set forth in (1) or (2), characterized by further containing, by mass%, one or more of

10 Mo: 1% or less,
 Nb: 0.5% or less,
 Ti: 0.5% or less,
 Al: 0.1% or less,
 B: 0.01% or less,
 15 Ca: 0.01% or less, and
 Mg: 0.01% or less

(4) Ferritic-austenitic stainless steel excellent in corrosion resistance and workability as set forth in any of (1) to (3), characterized by having a pitting potential $V_c'100$ in a 30°C, 3.5% NaCl aqueous solution of 0.3V (Vv.s.AGCL) or more.

20 (5) A method of production of ferritic-austenitic stainless steel excellent in corrosion resistance and workability comprising hot forging or hot rolling a stainless steel ingot having steel ingredients as set forth in any of (1) to (3) to obtain a hot rolled steel material, annealing the hot rolled steel material, then repeating cold working and annealing, said method of production of a steel material characterized by performing the final annealing by heating and holding the material at 950 to 1150°C, making an average cooling rate from the heating temperature to 200°C 3°C/sec or more, and making the ferrite phase a matrix phase and making a volume fraction of the austenite phase 15 to 50%.

25 (6) A method of production of ferritic-austenitic stainless steel excellent in corrosion resistance and workability comprising hot forging or hot rolling a stainless steel ingot having steel ingredients as set forth in any of (1) to (3) to obtain a hot rolled steel material, annealing the hot rolled steel material, then repeating cold working and annealing, said method of production of a steel material characterized by performing the final annealing by heating and holding the material at 950 to 1150°C, then making an average cooling rate until 600°C 3°C/sec or more, holding the material at a 200 to 600°C temperature region for 1 minute or more, then making the average cooling rate from the holding temperature to room temperature 3°C/sec or more, and making a ferrite phase the matrix phase and making a volume fraction of the austenite phase 15 to 50%.

30 (7) A method of production of ferritic-austenitic stainless steel excellent in corrosion resistance and workability as set forth in (5) or (6), characterized by making a ferrite phase the matrix phase and making a volume fraction of the austenite phase 15 to 50% and by making a pitting potential $V_c'100$ in a 30°C, 3.5% NaCl aqueous solution 0.3V (Vv.s.AGCL) or more.

35 **[0020]** The present invention relates to the following:

40 (8) Ferritic-austenitic stainless steel excellent in workability, characterized by consisting of, by mass%,

C: 0.002 to 0.1%,
 Si: 0.05 to 2%,
 45 Mn: 0.05 to 3.00%,
 P: less than 0.05%,
 S: less than 0.01%,
 Cr: 17 to 25%,
 N: 0.03 to 0.13%, and
 50 a balance of iron and unavoidable impurities, and

optionally one or more of, by mass%,

55 Ni: 0.1 to 5%,
 Cu: 0.1 to 5%,
 Mo: 0.1 to 5%,
 Nb: 0.03 to 0.5%,
 Ti: 0.03 to 0.5%,

EP 3 434 802 B1

Ca: 0.0002 to 0.003%, and

Mg: 0.0002 to 0.003%;

having a volume fraction of an austenite phase of 10% to less than 50%,

having an Md value calculated from the chemical composition in the austenite phase that satisfies the following formula (b),

having a ratio of austenite grains in a cross-section vertical to a rolling transverse direction with a grain size of 15 μm or less and a shape aspect ratio of less than 3 accounting for 90% or more of the total number of austenite grains, and further having at the same cross-section an average distance between nearest austenite grains of 12 μm or less:

$$-10 \leq \text{Md} \leq 110 \quad (\text{b})$$

wherein

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

[] is the composition (mass%) in the austenite phase, and

{ } is the average composition (mass%).

(9) Ferritic-austenitic stainless steel excellent in workability as set forth in (8) characterized by further containing, by mass%, one or more of

Ni: 0.1 to 5%,

Cu: 0.1 to 5%, and

Mo: 0.1 to 5%.

(10) Ferritic-austenitic stainless steel excellent in workability as set forth in any of (8) or (9) characterized by further containing, by mass%, one or both of

Nb: 0.03 to 0.5% and

Ti: 0.03 to 0.5%.

(11) Ferritic-austenitic stainless steel excellent in workability as set forth in any of (8) to (10) characterized by further containing, by mass%, one or both of

Ca: 0.0002 to 0.003% and

Mg: 0.0002 to 0.003%.

(12) A method of production of ferritic-austenitic stainless steel excellent in workability characterized by continuously casting steel of ingredients as set forth in any of (8) to (11), heating the obtained steel slab before hot rolling at a heating temperature T1 ($^{\circ}\text{C}$) of 1150 $^{\circ}\text{C}$ to less than 1250 $^{\circ}\text{C}$, then rolling at 1000 $^{\circ}\text{C}$ or more with reduction of a 30% or higher reduction rate then holding for 30 sec or more for one pass or more so as to obtain a hot rolled plate with a total rolling rate of hot rolling of 96% or more, annealing this at a temperature of T1-100 $^{\circ}\text{C}$ to T1 $^{\circ}\text{C}$, suitably thereafter cold rolling, performing process annealing or not performing it, then performing final annealing at 1000 $^{\circ}\text{C}$ to 1100 $^{\circ}\text{C}$ (method not within the claims).

BRIEF DESCRIPTION OF THE DRAWINGS

[0021]

FIG. 1 is a view showing the relationship of the cooling rate of final annealing and the pitting potential of Steel No. 1.

FIG. 2 is a view showing the EBSD measurement results classified into a BCC phase and FCC phase, where (a) shows the BCC phase, and (b) the FCC source by a white color.

FIG. 3 is a view showing the relationship of a γ fraction and uniform elongation (u-EL).

FIG. 4 is a view showing the relationship of an Md value and uniform elongation (u-EL).

EP 3 434 802 B1

FIG. 5 is a view showing the relationship of the ratio (X1) of austenite grains with a grain size of 15 μm or less and a shape aspect ratio of less than 3 in all austenite grains and uniform elongation (u-EL).

FIG. 6 is a view showing the relationship of the average value (X2) of distance of each austenite grain to the nearest grain and uniform elongation (u-EL).

5

BEST MODE FOR CARRYING OUT THE INVENTION

[0022] The inventors engaged in research on the effects of the ingredients, phase balance, and final annealing condition on the corrosion resistance and workability of ferritic-austenitic stainless steel oriented toward lower Ni.

10 **[0023]** As a first findings (not within the claims), they discovered that, from the viewpoint of corrosion resistance, it is possible to obtain ferritic-austenitic stainless steel excellent in corrosion resistance and workability provided with a corrosion resistance in a neutral chloride environment equal to or greater than SUS 304, that is, of a pitting potential Vc'100 in a 30°C, 3.5% NaCl aqueous solution of 0.3V (Vv.s.AGCL) or more, and provided with an excellent material elongation, particularly an excellent uniform elongation of a uniform elongation in a tensile test of 30% or more.

15 **[0024]** Further, as a second finding, they discovered that, from the viewpoint of workability, it is possible to obtain ferritic-austenitic stainless steel excellent in corrosion resistance and workability by making the conditions which the austenite grains should be provided with: (1) a grain size which is small and a shape which is close to spherical (is not flattened in the rolling direction), (2) a distance between nearest austenite grains which is narrow, and, further, (3) an austenite stability (Md value) calculated from the chemical composition in the austenite phase which is within an appropriate range, and thereby completed the present invention as defined in the claims.

20 **[0025]** First, the inventors will explain the first findings (not within the claims).

[0026] The inventors engaged in intensive research on the effects of the ingredients and phase balance on the corrosion resistance and the workability of ferritic-austenitic stainless steel oriented to lower Ni and the effects of the final annealing conditions on the corrosion resistance.

25 **[0027]** Below, they will explain representative test results.

[0028] The inventors hot rolled a stainless steel ingot obtained by vacuum melting ferritic-austenitic stainless steel having the ingredients shown in Table 1 to produce 5 mm thick hot rolled plate. They annealed the hot rolled plate at 1000°C, pickled it, then cold rolled it to prepare 1 mm thick cold rolled sheet. They annealed the cold rolled sheet at 1000°C, then cooled it by forced air cooling from 1000°C to 200°C at an average cooling rate in a range of 35 to 40°C/secs. The cold rolled annealed sheet was used for measurement of the volume fraction of the austenite (γ) phase, measurement of the pitting potential, and a JIS 13B tensile test. As comparative materials, 1 mm thick SUS 304 and ultralow C and N SUS 430LX were used. Note that, the pitting indicator (PI value) of steel containing a comparatively large amount of Mn was calculated from Cr+3Mo+10N-Mn(%).

30 **[0029]** The volume fraction of the γ phase (hereinafter described as the "γ fraction") was found by measurement of a phase map that identifies the crystal structure of fcc and bcc by using the EBSD method at the sheet cross-section. For the pitting potential, the Vc'100 (Vv.s.AGCL) was measured on a #500 polished surface in a 30°C, 3.5% NaCl aqueous solution. The measurement value of the pitting potential was made the average of n3. For the JIS 13B tensile test, a tensile test piece was taken from the rolling direction, and the uniform elongation until necking occurred was measured at a tension rate of 20 mm/min (range of tension rate defined in JIS Z 2241).

35 **[0030]** Table 1 shows, in addition to the steel ingredients, the measurement results of the γ fraction, Vc'100, and uniform elongation. As clear from Table 1, Steel No. 1 has a pitting potential of 0.38V, a uniform elongation of 35%, and corrosion resistance in a neutral chloride environment equal to or greater than SUS 304. Compared with SUS 430LX with workability improved through a shift to ultra low C and N, the uniform elongation was greatly improved.

40 **[0031]** On the other hand, Steel Nos. 2 to 6 have uniform elongations sufficiently higher than SUS 430LX, but have pitting potentials equal to or less than SUS 430LX or greatly inferior compared to SUS 304. The ingredients of steels with inferior pitting potentials are characterized by having (i) an amount of Si which is a high over 1% (Steel No. 2), (ii) an amount of Mn which is a high 3.8% (Steel No. 3), (iii) an amount of N which is a high 0.15% (Steel No. 4), (iv) a pitting indicator (PI value) which is less than 18% (Steel No. 5), and (v) an amount of N which is a high 0.16% and a γ fraction which is over 50% (Steel No. 6).

50

[Table 1]

Steel No.	Chemical ingredients (mass%)								γ fraction	Vc' 100	Uniform elongation
	C	Si	Mn	Cr	N	Ni	Cu	Pi			
1	0.03	0.1	3.2	21.2	0.09	1.0	0.4	19.0	30%	0.38	35%
2	0.03	1.1	3.2	21.3	0.10	1.0	0.5	19.2	25%	0.16	31%

55

(continued)

Steel No.	Chemical ingredients (mass%)								γ fraction	Vc' 100	Uniform elongation
	C	Si	Mn	Cr	N	Ni	Cu	Pi			
3	0.03	0.1	3.8	22.0	0.12	0.9	0.6	19.4	35%	0.22	36%
4	0.02	0.1	3.1	21.0	0.15	0.8	0.4	19.5	35%	0.18	37%
5	0.03	0.1	3.2	20.0	0.09	1.0	0.5	17.7	20%	0.23	30%
6	0.02	0.1	3.0	21.2	0.16	1.6	0.4	19.8	55%	0.12	40%
SUS 304	0.05	0.5	1.0	18.1	0.03	8.3	0.2	17.4	100%	0.33	42%
SUS 430LX	0.003	0.1	0.1	16.3	0.01	-	-	16.3	0%	0.20	19%
Vv.s.AGCL -: No addition SUS430LX: 0.3% Ti content											

[0032] FIG. 1 shows the relationship of the cooling rate in the final annealing and the pitting potential of the Steel No. 1. To obtain a pitting potential equal to or greater than SUS 304 (0.3V or more), it is necessary to restrict the cooling rate to 3°C/sec or more. Further, as shown by the black dot in the drawing, steel cooled by the method of holding at 500°C for 1 minute has the feature of having a pitting potential higher than when continuously cooling by a cooling rate of 5°C/sec without holding.

[0033] To explain the test results, the inventors analyzed the structure in detail using an optical microscope, SEM (scan electron microscope), and TEM (transmission electron microscope).

[0034] First, they buried the cross-section of the sheet in resin and polished it, then etched it with a potassium ferricyanide solution (product name: Murakami's Reagent) and further electrolytically etched it by oxalic acid for use for observation by an optical microscope. If etching by a potassium ferricyanide solution, the ferrite phase can be discerned by its gray color and the austenite phase by its white color. Further, if electrolytically etching by oxalic acid, when sensitized, intergranular corrosion can be confirmed. Next, the inventors analyzed the same test piece by SEM-EDS so as to analyze the metal elements in the ferrite phase and austenite phase. Finally, they identified the precipitate of the same test piece by the extraction replica TEM method.

[0035] For the volume fraction of the γ phase, the inventors engaged in a detailed structural analysis by the method of measurement of a phase map identifying the fcc and bcc crystal structures at the sheet cross-section by the EBSD method, measured the pitting potential by the method of measuring the Vc'100 (Vv.s.AGCL) on a #500 polished surface as an evaluation surface in a 30°C, 3.5% NaCl aqueous solution (note that the measurement value of the pitting potential was made the average of n3), and, according to a JIS 13B tensile test, obtained a tensile test piece from the rolling direction and measured the uniform elongation until necking occurred by a tension rate of 20 mm/min (range of tension rate defined in JIS Z 2241). As a result, the inventors arrived at the following findings explaining the test results of Table 1 and FIG. 1.

(a) At the ferrite grain boundaries and ferritic-austenitic grain boundaries of Steel Nos. 2, 4, and 6, intergranular corrosion due to sensitization was confirmed. Further, at the crystal grain boundaries, precipitation of Cr nitrides was observed. Therefore, the reduction in the pitting potential can be interpreted as being due to the sensitization accompanying precipitation of Cr nitrides. That is, by increasing the amount of Si (over 1%) or the amount of (0.15% or more), the precipitation sensitivity of Cr nitrides at the crystal grain boundaries rises, and the pitting potential falls in inverse proportion to the PI value of the pitting indicator.

(b) The amount of Cr and the amount of Mn relating to the PI value differ in distribution in the ferrite phase and austenite phase. For example, in the case of Steel Nos. 1, 2, 4, and 6, the amount of Cr is 22 to 23% at the ferrite phase and 18 to 19% at the austenite phase, while the amount of Mn amount is approximately 3% at the ferrite phase and approximately 4% at the austenite phase. Despite Steel Nos. 4 and 6 having the same degrees of amount of N, the pitting potential of No. 6 is low. It is believed that the drop in the pitting potential, in addition to the sensitization mentioned in (a), is also due to the γ fraction with the low amount of Cr and high amount of Mn being a large rate of over 50%. That is, the possibility is suggested that if allowing the formation of a large amount of an austenite phase with a low amount of Cr and a high amount of Mn, the corrosion resistance will become inferior.

(c) Steel No. 3, in comparison with the other steels, has large Mn-based sulfides exceeding 5 μ m in long sides scattered in it. Due to this, the drop in pitting potential is believed to be due to the comparatively large Mn-based sulfides formed due to the high amount of Mn (3.8%) acting starting points of pitting.

(d) Steel Nos. 1 and 5 did not exhibit either the above-mentioned sensitization or comparatively large Mn-based

sulfides. Therefore, the drop in the pitting potential in Steel No. 5 is believed to be largely due to the low PI value (<18%).

(e) The pitting potential of Steel No. 1 falls as the cooling rate drops as shown in FIG. 1. When cooling rate is 5°C/sec or less, while clear intergranular corrosion could not be confirmed with electrolytic etching by oxalic acid, the presence of some Cr nitrides at the crystal grain boundaries was found by TEM observation. Due to this, the drop in pitting potential is believed to be related to precipitation of Cr nitrides.

(f) The pitting potential of Steel No. 1, as shown by the black dot in FIG. 1, improves if temporarily holding the steel at 500°C instead of being continuously cooling it. When held at 500°C, the presence of Cr nitrides explained in the above (e) was not seen. It is thought that the N present in an oversaturated state near the ferritic-austenitic grain boundaries diffuses to austenite grains with large solid solubility limits when holding the steel at 500°C and thereby suppresses precipitation of Cr nitrides.

(g) The uniform elongation of a material, the indicator of workability, tends to increase as the γ fraction rises as is clear from Table 1. However, while a high uniform elongation comparable to SUS 304 is obtained when the γ fraction is over 50%, the drop in corrosion resistance is remarkable as explained in the above (b). When the γ fraction is 20 to 35%, the metal structure becomes one where the ferrite phase is the matrix phase and elliptic to circular austenite phases are equally dispersed in it. Such a metal structure with the austenite phase dispersed in it has a uniform elongation higher compared with the ferritic-austenitic phase layer structure seen in normal SUS 329J4L and other two-phase stainless steels.

[0036] The disclosure as set forth in the above (1) to (7) were completed based on the first findings, that is, the findings of (a) to (g).

[0037] Next, the inventors will explain the second findings. The second findings include the invention as defined in the claims.

[0038] The inventors investigated the factors of metal structure governing uniform elongation in relation to the above problems by producing various ferritic-austenitic stainless steels in the laboratory, hot rolling them, then annealing and cold rolling them to produce thin-gauge steel sheet. They investigated the relationship of the metal structures of the obtained thin-gauge steel sheet and the uniform elongation after the tensile tests and as a result obtained the following findings concerning the characteristics of austenite grain in steels with high uniform elongation.

(h) The grain size was small and shape was close to spherical (not flattened in the rolling direction).

(i) The distance between nearest austenite grains was narrow.

(j) There was a suitable value for the austenite stability calculated from the chemical composition in the austenite phase.

[0039] The inventors will explain details of these next.

[0040] First, the inventors produced 10 types of steel having compositions of 0.006 to 0.030% C, 0.10 to 0.85% Si, 1.0 to 3.0% Mn, 0.022 to 0.039% P, 0.0002 to 0.0035% S, 20.1 to 21.0% Cr, and 0.08 to 0.12% N, then hot rolled them, then annealed and cold rolled them to produce thin-gauge steel sheets. During this, they changed the hot rolling conditions, annealing temperatures, and other production conditions. They obtained JIS 13B tensile test pieces from the obtained 1 mm thick thin-gauge steel sheets parallel to the rolling direction and measured their uniform elongations by a method based on JIS Z 2241. The tension rate was made 10 mm/min. Further, they investigated the metal structure at a cross-section vertical to the rolling transverse direction (L-section) at the center position of the rolling transverse direction of each of the thin-gauge steel sheets by EBSP and identified the phases. They classified the data obtained by EBSP for each crystal grain into ferrite grains (BCC phase) and austenite grains (FCC phase) and first measured the austenite fraction. Further, places where the crystal orientation difference was 15° or more at adjacent measurement points were deemed crystal grain boundaries and shown by black lines. Measurement examples are shown in FIG. 2. FIG. 2(a) shows the BCC phase, and FIG. 2(b) the FCC phase, each shown by the white color.

[0041] Further, the inventors measured the grain sizes and aspect ratios of the grains of the austenite grains (FCC phase) and measured the distance between nearest grains for the austenite grains. For the distance between nearest grains, they used the smallest value of the distance between the center positions of austenite grains as the distance between nearest grains of those grains. For the center position of each crystal grain, they made the position of 1/2L and 1/2H, where the rolling direction length of the grain is L and the thickness direction length of the sheet is H, the center position. They measured the distance between nearest grains for each of 100 austenite grains and found their average value.

[0042] Further, the inventors used EPMA to investigate the chemical composition in the austenite grains. From the obtained chemical composition, they calculated an Md value as an indicator of the stability of the austenite phase. Here, Md is an indicator expressing the austenite stability calculated by the following formula (2). The coefficients in the formula were based on the formula of Nohara et al. (see Journal of the ISIJ 63 (1977) p. 772). The [] in the formula indicates a

EP 3 434 802 B1

composition measured by EPMA for each element. However, for C, quantification in the austenite phase is difficult by EPMA, so the average composition { } is shown. The "average composition" referred to here expresses the average composition contained in the steel irrespective of the phase and is found by the combustion-infrared absorption method described in JIS G 1211:

$$\begin{aligned} \text{Md} = & 551 - 462 (\{C\} + [N]) - 9.2 [Si] - 8.1 [Mn] \\ & - 13.7 [Cr] - 29 [Ni] - 29 [Cu] - 18.5 [Mo] \cdots \cdots (2) \end{aligned}$$

[0043] The Md value is determined by the chemical composition in the austenite grains. Therefore, by changing the chemical composition in the austenite grains by, for example, the annealing temperature, annealing time, or the like, the Md value can be adjusted.

[0044] N, Cu, Ni, and Mn concentrate at the austenite phase, that is, are elements which have higher concentrations in the austenite phase than concentrations in the ferrite phase, so by increasing the amounts of addition of these, the Md value can be lowered. Further, normally, the composition of the austenite phase is not an equilibrium composition determined by the annealing temperature. This is because time is needed for diffusion for the elements to be distributed to the austenite phase and ferrite phase at a certain annealing temperature. Therefore, increasing the holding time at the final annealing process will enable the equilibrium composition to be approached (the concentration in the austenite phase of N, Cu, Ni, and Mn rising), so making the holding time longer is also an effective method of lowering the Md value. However, with a holding time of 30 minutes, the equilibrium composition will substantially be reached.

[0045] C is an element lowering the Md value. By increasing the amount of addition, the Md value can be lowered. Further, C is also an element that concentrates in the austenite phase, however, measurement of the concentration in the austenite phase is difficult. In the present invention, in the formula for calculation of the Md value, the average composition of C is used. Therefore, the holding time of the annealing has no effect on the Md value of the present invention.

[0046] The effects of Si and Cr on the Md value cannot be said to be clear. That is, these elements act as minus coefficients on the Md value, so when these elements are viewed alone, addition of larger amounts will lower the Md value. However, when the amounts of Si and Cr are high, the concentrations of Mn, Ni, Cu, and the like in the austenite phase drop, so sometimes, conversely, the Md value increases. Depending on the concentrations of Mn, Ni, Cu, and other elements and the annealing conditions, the degrees of the effects of Cr and Si change.

[0047] As explained above, the Md value is determined by the chemical composition in the austenite grains. The chemical composition in the austenite grains also changes depending on the austenite fraction. That is, when the austenite fraction is low, the concentration of austenite forming elements in the austenite phase becomes higher, so the Md value tends to fall. On the other hand, when the austenite fraction is low, the concentration of austenite forming elements in the austenite phase becomes lower, so the Md value rises. Further, the austenite fraction changes depending on the temperature. In the ingredients set forth in the present invention, the austenite fraction is the highest at 1000°C to 1150°C. At temperatures higher or lower than that, the austenite fraction decreases.

[0048] Further, the higher the absolute value of the uniform elongation, the higher the workability, however, if the uniform elongation is 30% or more, the level becomes higher compared to ferritic stainless steel, while if 40% or more, it is possible to work the steel into nearly the same shape as with austenitic stainless steel with good workability.

[0049] First, the inventors investigated the relationship between the volume fraction (austenite fraction) of the austenite phase and the uniform elongation for all data. The relationship between the austenite phase and the uniform elongation during a tensile test is shown in FIG. 3.

[0050] There is a range of suitability of the austenite fraction with respect to the uniform elongation. If too high or too low, the uniform elongation will drop. To secure a uniform elongation of 30% or more, it is necessary to make the austenite fraction 10% to less than 50%. The range is preferably 15 to 40%.

[0051] Next, the relationship between the Md value and the uniform elongation for data where the austenite fraction is 10% to less than 50% is shown in FIG. 4. To obtain a good uniform elongation, there is also a suitable range of the Md value similar to the austenite fraction. At a -10 to +110 Md value range, the uniform elongation is a high value of 34 to 44%. Such a high uniform elongation cannot be obtained outside this range. However, with just the Md value alone, the variation in uniform elongation is too large. There may also be other structural factors that affect the uniform elongation.

[0052] The grain size and shape of the austenite grains may also affect the uniform elongation, so the inventors measured, for the -10 to +110 Md value data in FIG. 4, the "ratio of austenite grains with a grain size of 15 μm or less and a shape aspect ratio of less than 3 in the total number of austenite grains" X1(%) was measured and investigated its relationship to the uniform elongation u-EL(%). The results are shown in FIG. 5. As shown in FIG. 5, the higher this ratio, the higher the uniform elongation tends to be. When the ratio is 90% or more, even better uniform elongation can be obtained.

[0053] Further, the relationship between the average distance X2 (μm) with the nearest grains of the austenite grains,

measured as explained above extracting data where the uniform elongation is 37% or more in FIG. 5, and the uniform elongation $u\text{-EL}(\%)$ is shown in FIG. 6. The shorter the average value of the distance with the nearest grains, the higher the uniform elongation. When $12\ \mu\text{m}$ or less, the uniform elongation becomes extremely high.

[0054] The aspects of the invention set forth in (8) to (11) were completed based on the above explained second findings, that is, the findings of (h) to (j).

[0055] Below, the requirements of the first findings and second findings will be explained in detail. Note that, the "%" indications of the contents of the elements mean "mass%".

[0056] First, the reasons for limiting the ingredients, metal structure, and production conditions according to the first findings (not within the claims) will be explained below.

[0057] C is an element raising the volume fraction of the austenite phase and concentrating in the austenite phase to raise the austenite phase stability. To obtain the above effects, it is included in 0.001% or more. However, if over 0.1%, the heat treatment temperature for making C form a solid solution becomes remarkably high and the steel will become susceptible to sensitization due to carbide grain boundary precipitation. Therefore, the content is made 0.1% or less, preferably 0.05% or less.

[0058] Cr is an element necessary to secure the corrosion resistance. To achieve the object of the first findings of corrosion resistance, its lower limit is made 17%. However, if over 25%, a drop in toughness and drop in elongation occur and formation of an austenite phase in the steel becomes difficult. For this reason, the content is made 25% or less. From the viewpoints of the corrosion resistance, workability, and production, the content is preferably 19 to 23%, more preferably 20 to 22%.

[0059] Si is sometimes added as a deoxidizing element. To obtain the above effect, it is included in 0.01% or more. However, if over 1%, it becomes difficult to secure the object of the first findings of corrosion resistance. Therefore, the content is made 1% or less. Excessive addition leads to an increase in refining costs as well. From the viewpoint of corrosion resistance and production, the content is preferably 0.02 to 0.6%, more preferably 0.05 to 0.2%.

[0060] Mn is an element raising the volume fraction of the austenite phase and concentrating in the austenite phase to raise the austenite phase stability. Further, it is also an element effective as a deoxidizing agent. To obtain the above effect, it is included in 0.5% or more. However, if over 3.7%, it becomes difficult to secure the object of the first findings of corrosion resistance. Therefore, the content is made 3.7% or less. From the viewpoints of corrosion resistance, workability, and production, the content is preferably 2 to 3.5%, more preferably 2.5 to 3.3%.

[0061] N, like C, is an element raising the volume fraction of the austenite phase and concentrating in the austenite phase to stabilize the austenite phase. Further, it is an element forming a solid solution with the austenite phase and raising pitting resistance. To obtain the above effects, its lower limit is made 0.06%. However, if 0.15% or more is added, the chromium nitride contained in the steel material will exceed 0.1 mass% and most of the chromium nitride will precipitate at the crystal grain boundaries, so this will become a factor forming a chrome-depleted layer. Therefore, securing the object of the first findings of corrosion resistance, will become difficult.

[0062] Therefore, the content is made less than 0.15%. Further, adding N causes the occurrence of blowholes during melting and causes the hot workability to drop. From the viewpoints of corrosion resistance, workability, and production, the content is preferably 0.07 to 0.14%, more preferably 0.08 to 0.12%.

[0063] The pitting indicator (PI value) at a neutral chloride environment is calculated by the following formula (a):

$$\text{Pitting indicator (PI value)} = \text{Cr} + 3\text{Mo} + 10\text{N} - \text{Mn}(\%) \dots \text{(a)}$$

[0064] Note that the Cr, Mo, N, and Mn in the above formula mean the mass% of the elements. Elements that are not contained are treated as 0.

[0065] As described in for example "Stainless Steel Handbook 3rd edition", p. 622, Japan Stainless Steel Association, a coefficient of Mo to Cr of 3 and a coefficient of N to Cr of 10 were employed.

[0066] A coefficient of Mn to Cr of for example -1 described in for Current Advances in Materials and Processes, vol. 18 (2005), 607 was used. To obtain a corrosion resistance equal to or greater than SUS 304 in a neutral chloride environment as targeted by the first findings, $\text{Cr} + 3\text{Mo} + 10\text{N} - \text{Mn} > 18(\%)$, more preferably 19% or more.

[0067] Ni is an austenite forming element and is effective in securing the objects of the first findings of corrosion resistance and workability. When adding it, the content is made 0.6% or more to achieve the above effects. A content exceeding 3% leads to a rise in material costs and makes it difficult to achieve effects that match the costs. Therefore, when adding it, its content is 3% or less. From the viewpoints of corrosion resistance, workability, and economy, the content is preferably 0.7 to 2.8%, more preferably 0.9 to 2.0%.

[0068] Cu, like Mn and Ni, is an austenite forming element and is effective in securing mainly the objects of the first findings of corrosion resistance and workability. Particularly, it is an element effective in improving corrosion resistance added in combination with Ni. When adding it, it is made 0.1% or more to obtain the above effect added in combination with Ni. A content exceeding 3% leads to a rise in material costs and makes it difficult to achieve effects that match the

costs. Therefore, when adding it, the content is made 3% or less. From the viewpoints of corrosion resistance, workability, and economy, the content is preferably 0.3 to 1%, more preferably 0.4 to 0.6%.

[0069] Mo can be appropriately added to improve the corrosion resistance. To obtain the above effect, addition of 0.2% or more is preferable. However, a content exceeding 1% sometimes detracts from the economy. Therefore, when adding it, the content is made 1% or less. From the viewpoints of corrosion resistance and economy, the content is preferably 0.2 to 0.8%.

[0070] Ti and Nb can be appropriately added to suppress sensitization due to C and N and thereby improve the corrosion resistance. To obtain the above effect, addition of 0.01% or more for each is preferable.

[0071] However, contents exceeding 0.5% sometimes detract from the economy and also lower the austenite fraction and harden the ferrite phase to thereby detract from the workability. Therefore, when adding these, the content of each is respectively made 0.5% or less. From the viewpoints of corrosion resistance and workability, the content of each is more preferably 0.03 to 0.3%, further preferably 0.05 to 0.1%.

[0072] Al is a powerful deoxidizing agent and can be appropriately added. To obtain the above effect, addition of 0.001% or more is preferable. However, a content exceeding 0.2% sometimes is a factor in forming nitrides and causing surface damage and a drop in corrosion resistance. Therefore, when adding it, the content is made 0.2% or less. From the viewpoint of production and corrosion resistance, the content is more preferably 0.005 to 0.1%.

[0073] B, Ca, and Mg can be appropriately added to improve the hot workability. To obtain the above effect, addition for each of 0.0002% or more is preferable. However, a content for each exceeding 0.01% sometimes causes the corrosion resistance to drop remarkably. Therefore, when adding these, the content for each is made 0.01% or less. From the viewpoints of hot workability and corrosion resistance, the content for each is more preferably 0.0005 to 0.005%.

[0074] Further, the stainless steel according to the first findings may contain, other than the above ingredients, P and S as part of the unavoidable impurities in the ranges below. P and S are elements harmful to hot workability and corrosion resistance. The content of P is preferably 0.1% or less, more preferably 0.05% or less. Excessive reduction leads to an increase in refining and material costs, so the lower limit is preferably 0.005%. The content of S is preferably 0.01% or less, more preferably 0.005% or less. Excessive reduction leads to an increase in refining and material costs, so the lower limit is preferably 0.0005%.

[0075] Next, the reasons for limitation of the metal structure will be explained. The ferritic-austenitic stainless steel according to the first findings has the above ingredients and is improved in corrosion resistance and workability by having a defined volume fraction of the austenite phase (hereinafter, " γ fraction").

[0076] The γ fraction, as mentioned above, can be found by the EBSP method. The EBSP method, as for example described in Microscopy; Seiichi Suzuki, Vol. 39, No. 2, 121 to 124, designates the crystal system data of the austenite phase (fcc) and ferrite phase (bcc) and displays a phase distribution map in which a color is given to each phase. Due to this, the state of dispersion of the austenite phase can be understood and the γ fraction found. The test piece is a sheet cross-section, and measurement is at a magnification of 500X and step size of 10 μm .

[0077] The upper limit of the γ fraction is made 50% or less to secure the object of the first findings mentioned above of corrosion resistance. To improve the uniform elongation of the material, the lower limit of the γ fraction is made 15% or more, more preferably 20% or more. From the viewpoints of the corrosion resistance and elongation, the content is more preferably 30 to 40% in range.

[0078] The state of dispersion of the austenite phase is not particularly defined, but from the viewpoint of improving the uniform elongation of the material, it is preferable that, rather than have a ferritic-austenitic phase layer-type structure, the ferrite phase be made the matrix phase and 100 μm elliptical to circular austenite phases be dispersed, more preferably austenite phases less than 50 μm be dispersed.

[0079] The ferritic-austenitic stainless steel having the ingredients of the first findings and the above metal structure can have a pitting potential, an indicator of the corrosion resistance, of 0.3V or more and a uniform elongation, an indicator of the workability, increased from 30% to 50% and can give a corrosion resistance in a neutral chloride environment equal to or greater than SUS 304 and a workability significantly higher than SUS 430LX and close to SUS 304. The measurement conditions of the pitting potential and uniform elongation are similar to those mentioned above and are as follows. For the pitting potential, Vc'100 (Vv.s.AGCL) was measured on a #500 polished surface as the evaluation surface in a 30°C, 3.5% NaCl aqueous solution. The measurement value of the pitting potential was made the average value of n3. For the uniform elongation, according to the JIS 13 B tensile test, a tensile test piece was taken from the rolling direction and the uniform elongation until necking occurred was measured at a tension rate of 20 mm/min (range of tension rate specified in JIS Z 2241).

[0080] To achieve the objects of the first findings of corrosion resistance and workability, in ferritic-austenitic stainless steels having the ingredients and metal structure explained above, the following production conditions are preferable.

[0081] The hot rolled steel material used for production is not particularly limited so long as it has the above ingredients. The final annealing following the cold working preferably comprises heating and holding at 950 to 1150°C. When less than 950°C, recrystallization of the worked structure sometimes is insufficient. When over 1150°C, the grain size becomes larger and sometimes the structure becomes not a ferritic-austenitic phase layer-type structure, but one greatly deviating

from the preferred one where the ferrite phase is the matrix phase and elliptical to circular austenite phases less than 100 μm are dispersed. Further, sometimes the γ fraction decreases and good elongation is not able to be obtained. To obtain a preferable structure for achieving corrosion resistance and workability, the range is more preferably 980 to 1100°C, further preferably 980 to 1050°C.

[0082] The cooling following the final annealing preferably is performed at an average cooling rate from the heating temperature to 200°C of 3°C/sec or more. When less than 3°C/sec, the corrosion resistance drops due to the sensitization based on grain boundary precipitation of Cr nitrides. The upper limit of the cooling rate is not particularly defined, but in the case of gas cooling, it is approximately 50°C/sec. In the case of water cooling, it is 300 to 500°C/sec. When using an industrial continuous annealing facility, the rate is preferably 10 to 40°C/sec, more preferably 25 to 35°C/sec.

[0083] In the cooling process of the final annealing, it is preferable that the steel material be held at a 200 to 600°C temperature region for 1 minute or more. By the N present in an oversaturated state near the crystal grain boundaries diffusing into the austenite phase with its large solid solubility limit and forming a solid solution at the time of holding at that temperature region, the grain boundary precipitation of Cr nitrides leading to a drop in pitting potential is suppressed. That is, the drop in the corrosion resistance caused by sensitization can be suppressed.

[0084] The higher the holding temperature, the more effective for diffusing N, however, a temperature over 600°C accelerates grain boundary precipitation of Cr carbon nitrides. Therefore, the upper limit is made 600°C. If less than 200°C, N diffusion will take a long time, making achievement of the above effect difficult. Therefore, the lower limit is made 200°C, more preferably in the range of 300 to 550°C, further preferably 400 to 550°C.

[0085] The holding time is preferably made 1 minute or more in order to obtain above effect. The upper limit is not particularly defined, but when using an industrial continuous annealing facility, a long holding time leads to a drop in productivity, so the time is preferably 5 minutes or less, more preferably 3 minutes or less.

[0086] According to the above method of production, it is possible to produce ferritic-austenitic stainless steel excellent in corrosion resistance and workability having a ferrite phase as the matrix phase, having a volume fraction of an austenite phase of 15 to 50%, having a pitting potential $V_c'100$ of 0.3V (Vv.s.AGCL) or more in a 30°C, 3.5% NaCl aqueous solution, and having a uniform elongation in a tensile test of 30% or more.

[0087] Next, the reasons for limiting the ingredients, metal structure, and production conditions according to the second findings will be explained below.

[0088] C is an element having a large effect on the stability of the austenite phase. When adding over 0.100%, sometimes the uniform elongation drops. Further, it promotes precipitation of the Cr carbides, so causes granular corrosion. Therefore, the upper limit was made 0.100%. Further, from the viewpoint of corrosion resistance, the lower the C, the more preferable, however, if taking the ability of current facilities into consideration, lowering the amount of C to less than 0.002% would lead to a large increase in costs, so the lower limit is this value, preferably 0.002 to 0.8%.

[0089] Si is used as a deoxidizing element and sometimes is added to improve the oxidation resistance. However, adding over 2.00% will lead to hardening of the material and cause a drop in uniform elongation, so the upper limit is this value, preferably 1.6% or less. Further, extreme reduction of Si would lead to an increase in costs at the time of refining, so the lower limit was made 0.05, preferably 0.08%.

[0090] Mn concentrates at the austenite phase and has an important role in changing the stability of the austenite phase. However, large addition will not only lower the uniform elongation, but also lower the corrosion resistance and hot workability, so the upper limit was made 5.00%. Less than 0.05% causes an increase in costs in the refining process, so this value was made the lower limit. From the viewpoint of corrosion resistance, a lower value is preferable, so the upper limit in the present invention is 3.00%, preferably 2.60%.

[0091] P is an element which is unavoidably included. Further, it is contained in Cr and other materials. Therefore, reducing it is difficult, however, if a large amount is contained, it causes the workability to drop, so the upper limit was made less than 0.050%. However, the lower it is, the more preferable, so making it 0.035% or less is preferable.

[0092] S is an element which is unavoidably included. It bonds with Mn to form inclusions and sometimes becomes the starting point of rust, therefore the upper limit was made less than 0.010%. The lower it is, the more preferable from the viewpoint of corrosion resistance, so making it 0.0020% or less is preferable.

[0093] Cr is an element necessary for securing the corrosion resistance. An addition of 17% or more is necessary. However, large addition causes hot working cracks and leads to an increase in refining process costs, so the upper limit was made 25%, preferably 17 to 22%.

[0094] N, like C, is an element having a large effect on the stability of the austenite phase. Further, if existing in a solid solution, it has the effect of improving corrosion resistance, so 0.010 or more is added. However, if over 0.150% is added, sometimes the uniform elongation will drop. Also, Cr nitrides will precipitate easily and cause the corrosion resistance to conversely drop. Therefore, in the present invention N is contained in a range of 0.03 to 0.13%.

[0095] Further, the following elements may be selectively added.

[0096] Ni is an austenite stabilizing element and is important for adjusting the stability of the austenite phase. Further, it has the effect of suppressing hot working cracks, so when wishing to obtain these effects, 0.10% or more may be added. Addition over 5.00% causes an increase in material costs and, further, sometimes makes achievement of an

austenitic-ferritic two-phase structure difficult, so the upper limit was made this value, preferably 3.00% or less.

[0097] Cu, like Ni, is an austenite stabilizing element and is important for adjusting the stability of the austenite phase. Further, it has the effect of improving corrosion resistance, so 0.10% or more may be added. However, addition over 5.00% promotes cracks during hot working and, further, lowers the corrosion resistance, so the upper limit was made this value.

[0098] Mo is an element improving corrosion resistance, so may be selectively added. Addition of 0.10% or more enables the effect of improving corrosion resistance to be obtained, so addition of this value or more is preferable. However, addition over 5.00% lowers the uniform elongation and greatly increases the material costs, so the upper limit was made this value.

[0099] Nb has the effect of preventing coarsening of the weld heat affected zone, so to obtain good effects even when added, addition of 0.03% or more is required. This therefore may be added with the lower limit as this value. However, addition over 0.50% lowers the uniform elongation, so the upper limit was made this value.

[0100] Ti, like Nb, may be added in 0.03% or more so as to prevent coarsening of the weld heat affected zone and further make the solidified structure finer equiaxial crystalline. However, addition over 0.50% lowers the uniform elongation, so the upper limit was made this value.

[0101] Some amount of Ca is sometimes added for desulfurization and deoxidation. The effects are demonstrated with addition of 0.0002% or more, so this may be added with the lower limit as this value. However, addition over 0.0030% makes the steel susceptible to hot working cracks and, further, lowers the corrosion resistance, so the upper limit was made this value.

[0102] Mg has an effect of not only deoxidation, but also making the solidified structure finer and therefore is sometimes added. To obtain these effects, addition of 0.0002% or more is necessary, so this may be added with the lower limit as this value. Further, addition over 0.0030% causes an increase in costs in the steelmaking process, so the upper limit was made this value.

[0103] Next, the reasons for limiting the metal structure will be explained.

[0104] Volume fraction of austenite phase of 10% to less than 50%: As shown by the results of the study above, to obtain a good uniform elongation, a ratio of austenite phase of 10% or more is required, so the lower limit was made this value. Further, the uniform elongation does not necessarily become higher the higher the austenite fraction. If over 50%, the uniform elongation conversely drops, so the upper limit was made this value. It is preferable to measure the austenite fraction with a method classifying phases using EBSD, extracting only the austenite grains, then measuring the area ratio. The measurement range at this time is 200 μm×200 μm or more. In the present invention, the austenite fraction is important as an indicator of workability (uniform elongation). The reasons for this are thought to be as follows. The austenite phase causes work-induced martensite transformation during work and contributes to an increase in the uniform elongation. If the amount transformed at this time is small, the uniform elongation becomes smaller. Further, the reason why the uniform elongation is low when the austenite fraction is over 50% is not currently clear, but it is believed that it is because deformation concentrates in the ferrite phase which is softer in comparison to the austenite phase.

[0105] Md value calculated from chemical composition in austenite phase of -10 to 110: In the present invention, the properties of the austenite phase are also defined. That is, the steel is characterized in that the Md value calculated from the chemical composition in the austenite phase satisfies the following formula (b):

$$-10 \leq Md \leq 110 \dots (b)$$

(where, $Md = 551 - 462\{C\} + [N] - 9.2[Si] - 8.1[Mn] - 13.7[Cr] - 29[Ni] - 29[Cu] - 18.5[Mo]$, [] is composition (mass%) in the austenite phase, and { } is the average composition (mass%))

[0106] The chemical composition in the austenite phase forming the basis of the calculation of the Md is measured by EPMA. [] in the above Md formula shows the composition (mass%) in the austenite phase measured by EPMA for each element. However, for C, measurement by the EPMA is difficult, so instead of the composition in the austenite phase, the average composition (mass%) is shown. When the Md value is less than -10 or over +110, a good uniform elongation cannot be obtained, so the lower limit and upper limit were made these values. The reason why the Md value affects the uniform elongation is thought to be as follows: The Md value is an indicator representing the stability of the austenite phase, that is, it can be said to represent the amount of strain needed to cause work-induced martensite transformation. If the amount of strain is too small, work-induced martensite transformation finishes at the initial steps of working and sufficient ductility cannot be maintained at the later steps of working important for determining success of working. Further, if the amount of strain is too large, uniform deformation finishes before reaching that amount of strain and work-induced martensite transformation cannot be applied effectively. Therefore, there is a suitable range of Md value for generating work-induced martensite transformation during work.

[0107] Ratio of austenite grains with a grain size of 15 μm or less and a shape aspect ratio of less than 3 accounting

for 90% or more of the total number of austenite grains: As metal structural features of the austenite grains when good uniform elongation is obtained, the grains are fine and not flattened in the rolling direction. Specifically, the ratio of austenite grains with a grain size of 15 μm or less and a shape aspect ratio of less than 3 account for 90% or more of the total number of austenite grains. When there are many crystal grains with a grain size over 15 μm , the uniform elongation drops, so the upper limit was made this value. Further, it is not particularly necessary to define the lower limit, however, making it 1 μm or less greatly increases costs in the production process, so the lower limit is preferably made 1 μm .

[0108] Further, the shape of crystal grains is also an important factor. In the present invention, through observation from the L cross-section (surface parallel to the rolling direction observed from the sheet width direction), the aspect ratio of each grain was measured. The ratio of crystal grains with an aspect ratio of less than 3 becomes important. At this time, when the aspect ratio is 3 or more, the uniform elongation tends to drop, so the condition of the aspect ratio defined as a structural factor was made less than 3. The aspect ratio is measured by dividing the length of the longest side of each grain by the length orthogonal to it. Therefore, the lower limit of the aspect ratio is 1. The number of crystal grains for measuring the grain size and aspect ratio is 100 or more. In the present invention, it was first discovered that the austenite grain size and grain shape affect the uniform elongation, but the reasons for this are currently unknown. However, it is believed that there have an effect on the mode of deformation in the austenite grains (dislocation density, deformation zone, twinning presence, etc.) and that this changes the work-induced martensite transformation behavior.

[0109] Average distance between nearest austenite grains of 12 μm or less: The distance between nearest austenite grains also affects the uniform elongation, so the average distance was made 12 μm or less. If over 12 μm , the uniform elongation drops, so the upper limit was made this value. Further, the lower limit is not particularly defined. The distance between nearest grains is determined by defining the point where the center line of the rolling direction length of each austenite grain intersects the center line of the sheet thickness direction length as the center position of a crystal grain and defining the smallest value of the distances between center positions of grains as the distance between nearest grains of that grain. The average of the results of measurements for 100 crystal grains or more is defined as the "average distance between nearest austenite grains". The reason why the average distance between nearest austenite grains affects the uniform elongation is thought to be as follows: In the deformation process, when strain is introduced in a certain austenite grain, work-induced martensite transformation occurs, and a certain degree of strain is reached, if considering the process by which deformation spreads, a smaller distance between austenite grains enables work-induced martensite transformation to propagate to several crystal grains and occurs continuously allowing extremely high uniform elongation to be obtained. This is clear from the fact that, in comparison to the uniform elongation of 30% or more secured in the first findings, an even higher 40% or more can be secured in the second findings.

[0110] Note that the uniform elongation is an important indicator representing the workability in the present invention. The uniform elongation is measured by taking a JIS 13 B tensile test piece parallel to the rolling direction and following the method based on JIS Z 2241. Note that, the state of the ferrite grains is not particularly defined in the second findings, however, when the ferrite phase is coarse in grain size, the above distance between austenite grains becomes larger, so the grain size is preferably at average of 25 μm or less. Further, when the shape aspect ratio is large as well, the distance between austenite grains becomes large, so the ratio is preferably less than 3.

[0111] As mentioned above, to obtain an extremely good uniform elongation, it is necessary to control the metal structure, but such a metal structure is not obtained only by the chemical composition. To achieve the object of the second discovery of workability, particularly uniform elongation and corrosion resistance, the following production conditions are preferable.

[0112] As hot rolling material, a steel slab obtained by continuous casting is used. The heating temperature T1 before hot rolling is made 1150°C to less than 1250°C. When less than 1150°C, edge cracking occurs in hot rolling, so the lower limit was made this value. Further, when the heating temperature is made over 1250°C, it is easy for the austenite grain size after final annealing to become larger, the steel slab deforms inside the heating furnace, and defects are likely to occur during hot rolling, so the upper limit was made this value.

[0113] Further, during hot rolling, rolling at 1000°C or more with reduction of a 30% or higher reduction rate then holding for 30 sec or more for one pass or more is performed. To make a metal structure for obtaining a good uniform elongation, a grain refining process in which recrystallization is applied during hot rolling is necessary. To cause hot recrystallization in ferritic-austenitic stainless steel, this reduction process is necessary. When the rolling temperature is less than 1000°C, even if holding for 30 sec or more after 1 pass of 30% or more rolling, the austenite grain size in the metal structure after cold rolling and annealing becomes coarser and the uniform elongation during the tensile test becomes insufficient. Further, the reduction rate and time between passes both greatly affect the recrystallization behavior, but to obtain austenite grains that are fine and have small aspect ratios after cold rolling and annealing, it is necessary for the reduction rate during hot rolling to be 30% or more and the holding time following it to be 30 sec or more.

[0114] Further, the total rolling rate of hot rolling was made 96% or more. When less than 96%, the crystal grains after cold rolling and annealing become coarser. Further, the distance between austenite grains becomes larger, so the uniform elongation becomes insufficient. The annealing temperature of the hot rolled sheet is between the heating

EP 3 434 802 B1

temperature T1-100°C before hot rolling and T1°C. When lower than T1-100°C, the aspect ratio of the crystal grains after cold rolling and annealing becomes larger. Further, when T1°C or more, the grain size after cold rolling and annealing becomes coarser, the metal structure of the object is not obtained, and the uniform elongation during the tensile test drops.

[0115] Further, the cold rolling and annealing may be repeatedly performed, i.e., so called two-time cold rolling may be performed. It is necessary to make the process annealing temperature at this time T1-100°C to T1°C in the same way as hot rolled sheet annealing.

[0116] Further, the final annealing temperature is 1000°C to 1100°C. This is because when less than 1000°C, the shape aspect ratios of the austenite and ferrite grain become bigger, the Md value deviates from the appropriate range, and the uniform elongation drops. Further, when over 1100°C, the γ fraction drops, the Md value deviates from the appropriate range, or the grain size becomes too large

[0117] Below, examples according to the first findings (not within the claims) will be explained.

[Example 1] (not within the claims)

[0118] Ferritic-austenitic stainless steel 250 mm thick cast slabs if the ingredients shown in Table 2 were produced and hot rolled into hot rolled steel plates with 5.0 mm plate thicknesses. Steel No. 1 to Steel No. 20 have ingredients defined in the above first findings. Steel No. 21 to 26 have ingredients deviating from the definitions in the above first findings. These hot rolled steel plates were annealed and pickled, then cold rolled to 1 mm thicknesses and final annealed. The final annealing was also performed under conditions deviating from the definitions of the first findings for comparison.

[0119] Various test pieces were taken from each of the obtained cold rolled and annealed sheets and evaluated for the γ phase volume fraction (γ fraction), pitting potential, and uniform elongation. The γ fraction was found by the EBSD method described in paragraph 0046. For the pitting potential, the V'c100 (Vv.s.AGCL) was measured for a #500 polished surface in a 30°C, 3.5% NaCl aqueous solution. The measurement value of the pitting potential was made the average value of n3. For the uniform elongation, a JIS 13 B test piece was taken from the rolling direction and the value was measured at a tension rate of 20 mm/min (range of the tension rate defined in JIS Z 2241).

[Table 2]

Steel No	Chemical ingredients (mass%)									Remarks
	C	Si	Mn	Cr	N	Ni	Cu	Other	PI	
1	0.06	0.1	2.9	20.8	0.14	-	-	-	19.3	Example
2	0.03	0.1	3.2	21.2	0.09	1.0	0.47		18.9	Example
3	0.01	0.1	3.1	21.0	0.11	0.9	0.45		19.0	Example
4	0.06	0.1	3.0	20.8	0.10	1.0	0.50		18.8	Example
5	0.03	0.8	3.0	21.2	0.10	1.0	0.48		19.2	Example
6	0.03	0.1	0.5	21.0	0.11	1.0	0.47		21.6	Example
7	0.03	0.1	1.5	21.0	0.11	1.0	0.48		20.6	Example
8	0.03	0.1	3.7	21.0	0.11	1.0	0.48		18.4	Example
9	0.03	0.1	3.0	21.0	0.06	1.0	0.47		18.6	Example
10	0.03	0.1	3.1	21.0	0.14	1.0	0.47		19.3	Example
11	0.03	0.1	0.8	17.5	0.14	1.0	0.45		18.1	Example
12	0.03	0.1	3.7	24.0	0.11	1.5	0.70		21.4	Example
13	0.03	0.1	3.2	21.0	0.11	0.6	0.45		18.9	Example
14	0.03	0.1	3.2	21.0	0.10	2.7	0.45		18.8	Example
15	0.03	0.1	3.1	21.0	0.10	1.0	0.10		18.9	Example
16	0.03	0.1	3.1	21.0	0.10	1.0	2.80		18.9	Example
17	0.03	0.1	3.2	21.0	0.10	1.1	0.45	Mo:0.7	20.9	Example
18	0.03	0.1	3.2	21.0	0.10	1.1	0.45	Nb:0.1	18.8	Example
19	0.03	0.1	3.1	21.0	0.10	1.0	0.46	Mo:0.3, Nb:0.05	19.8	Example

EP 3 434 802 B1

(continued)

Steel No	Chemical ingredients (mass%)									Remarks
	C	Si	Mn	Cr	N	Ni	Cu	Other	PI	
20	0.03	0.1	3.1	21.0	0.10	1.0	0.48	Ti:0.1	18.9	Example
21	0.03	0.1	3.1	21.0	0.10	1.0	0.48	Al:0.05	18.9	Example
22	0.03	0.1	3.1	21.0	0.10	1.0	0.48	Al:0.03, B:0.001	18.9	Example
23	0.03	0.1	3.1	21.0	0.10	1.0	0.48	Ca:0.002, Mg:0.001	18.9	Example
24	0.01	0.3	0.9	20.0	0.20	0.5	0.53		21.1	Comp. ex.
25	0.01	0.3	5.0	20.0	0.26	0.5	0.50		17.6	Comp. ex.
26	0.01	0.3	5.2	21.5	0.10	0.5	0.55		17.3	Comp. ex.
27	0.11	0.5	1.3	21.2	0.15	1.2	-		21.4	Comp. ex.
28	0.04	1.1	3.1	21.3	0.10	1.0	0.48		19.2	Comp. ex.
29	0.01	0.3	0.3	16.5	0.13	1.0	0.55		17.5	Comp. ex.
-: means not added. Underlines mean deviation from the definition of the first findings										

[0120] The relationship of the production conditions and the γ fraction and characteristics of the final annealed sheet are shown in Table 3. Here, the "Cooling rate 1" shows the average cooling rate from the annealing temperature to 200°C. However, when held during cooling, the average cooling rate from the annealing temperature to the holding temperature is shown. Further, the "Cooling rate 2" shows the average cooling rate from the holding temperature to ordinary temperature when holding during cooling.

[0121] Nos. 1 to 11 and 15 to 35 have the ingredients of the first findings and final annealed as defined in the first findings. These examples satisfy the γ fraction 15 to 50% defined in the first findings and have 0.3V or more pitting potentials and 30% or more uniform elongations. Due to this, by subjecting the ferritic-austenitic stainless steels having the ingredients defined in the first findings to the final annealing defined in the first findings, a corrosion resistance equal to or greater than SUS 304 in a neutral chloride environment is provided and a ductility sufficiently high compared to SUS 430LX and comparable to SUS 304 is obtained. Particularly, Nos. 9 to 11 are examples in which, as the final annealing condition, the steels are held for approximately two minutes at a specified temperature of the 200 to 600°C temperature region with final annealing, then cooled from the holding temperature to room temperature. In these examples, the pitting potential $V_c'100$ shows good values.

[0122] Nos. 12 to 14 have the ingredients defined in the first findings, but deviate from the final annealing conditions defined in the first findings. They did not give the pitting potential and uniform elongation of the objects of the first findings.

[0123] Nos. 36 to 41 have ingredients deviating from the definition of the first findings. Even if subjected to final annealing defined in the first findings, they did not give the pitting potential and uniform elongation of the objects of the first findings.

[Table 3]

No.	Steel No.	Final annealing conditions				γ phase volume fraction %	Characteristics		Remarks
		Temp. (°C)	Cooling rate 1 (°C/sec)	Holding (°C)	Cooling rate 2 (°C/sec)		Pitting potential $V_c'100$ (V)	Uniform elongation (%)	
1	1	1000	33	-	-	30	0.34	32.5	Example
2	2	1000	32	-	-	30	0.37	33.5	Example
3	2	1000	5	-	-	30	0.33	33.0	Example
4	2	1000	400 (Water cooling)	-	-	30	0.40	32.0	Example
5	2	960	35	-	-	20	0.35	31.0	Example

EP 3 434 802 B1

(continued)

No.	Steel No.	Final annealing conditions				γ phase volume fraction %	Characteristics		Remarks
		Temp. (°C)	Cooling rate 1 (°C/sec)	Holding (°C)	Cooling rate 2 (°C/sec)		Pitting potential Vc'100 (V)	Uniform elongation (%)	
6	2	1050	30	-	-	35	0.36	38.0	Example
7	2	1100	25	-	-	35	0.35	35.0	Example
8	2	1130	25	-	-	30	0.33	33.0	Example
9	2	1000	25	300	20	30	0.40	34.0	Example
10	2	1000	25	400	20	33	0.42	35.0	Example
11	2	1000	25	450	20	33	0.38	34.5	Example
12	2	900	30	-	-	10	0.35	21.5	Comp. ex.
13	2	1180	30	-	-	12	0.35	25.0	Comp. ex.
14	2	1000	2	-	-	25	0.20	30.0	Comp. ex.
15	3	1000	32	-	-	27	0.37	32.5	Example
16	4	1000	33	-	-	35	0.36	33.5	Example
17	5	1000	30	-	-	17	0.31	30.0	Example
18	6	1000	32	-	-	20	0.45	31.0	Example
19	7	1000	32	-	-	25	0.40	32.0	Example
20	8	1000	30	-	-	45	0.35	40.0	Example
21	9	1000	30	-	-	16	0.30	30.0	Example
22	10	1000	32	-	-	35	0.38	35.0	Example
23	11	1000	32	-	-	20	0.32	30.0	Example
24	12	1000	33	-	-	30	0.37	32.0	Example
25	13	1000	33	-	-	18	0.33	31.0	Example
26	14	1000	33	-	-	45	0.38	40.0	Example
27	15	1000	32	-	-	25	0.32	31.0	Example
28	16	1000	33	-	-	35	0.37	31.0	Example
29	17	1000	32	-	-	25	0.50	31.0	Example
30	18	1000	32	-	-	30	0.40	33.0	Example
31	19	1000	33	-	-	27	0.45	31.0	Example
32	20	1000	32	-	-	25	0.39	31.0	Example
33	21	1000	30	-	-	28	0.33	32.0	Example
34	22	1000	31	-	-	28	0.34	31.5	Example
35	23	1000	32	-	-	30	0.32	32.5	Example
36	24	1050	33	-	-	45	0.20	43.0	Comp. ex.
37	25	1050	32	-	-	60	0.15	50.0	Comp. ex.

EP 3 434 802 B1

(continued)

No.	Steel No.	Final annealing conditions				γ phase volume fraction %	Characteristics		Remarks
		Temp. (°C)	Cooling rate 1 (°C/sec)	Holding (°C)	Cooling rate 2 (°C/sec)		Pitting potential Vc'100 (V)	Uniform elongation (%)	
38	26	1050	33	-	-	20	0.20	38.0	Comp. ex.
39	27	1050	32	-	-	55	0.20	35.0	Comp. ex.
40	28	1000	32	-	-	20	0.20	28.0	Comp. ex.
41	29	1000	32	-	-	10	0.25	20.0	Comp. ex.
Cooling rate 1: Average cooling rate from annealing temperature to 200°C and, when holding during cooling, average cooling rate from annealing temperature to holding temperature Cooling rate 2: When holding during cooling, the average cooling rate from the holding temperature to ordinary temperature -: means continuous cooling with no holding during cooling Underlines mean deviation from the definition of the first findings									

[Example 2]

[0124] Next, examples according to the second findings will be shown.

[0125] The steels shown in Table 4 were produced, then were hot rolled, then the hot rolled plates were annealed, cold rolled, and final annealed to produce 1.0 mm thick thin-gauge steel sheets. In producing the steel sheets, the metal structure can be changed by changing the material thickness, heating temperature of hot rolling, rolling pass schedule, rolling pass time, hot rolled sheet annealing temperature, and final annealing temperature and time. However, this time, the final annealing temperature was changed, and the annealing time was made 60 seconds. The obtained product sheets were subjected to tensile tests and the uniform elongation was measured. Further, from the metal structure of the thin-gauge steel sheet/L cross-section, the phases were identified by EBSP, the grain size and shape aspect ratio were investigated, and the distance between nearest grains of the austenite grains was measured. The conditions were as mentioned above. The γ fraction, Md value, X1, and X2 were measured for the obtained metal structure. The relationship with the uniform elongation was shown in Table 5 together with the production conditions.

[Table 4]

Steel No.	Chemical ingredients (mass%)													Remarks	
	C	Si	Mn	P	S	Cr	N	Ni	Cu	Mo	Nb	Ti	Ca		Mg
101	0.030	0.13	3.10	0.031	0.004	21.0	0.102	0.99	0.48			0.38			Example
102	0.029	0.10	0.51	0.033	0.002	21.1	0.111	1.01	0.47						Inv. ex.
103	0.085	0.95	4.30	0.03	0.001	20.0	0.086								Example
104	0.004	1.85	4.22	0.019	0.001	20.0	0.134	0.54	0.22	0.43					Example
105	0.018	0.35	3.10	0.039	0.002	17.6	0.144				0.04				Example
106	0.065	0.56	1.11	0.035	0.001	24.2	0.089	2.64					0.0006	0.0020	Inv. ex.
107	0.045	0.06	0.09	0.022	0.002	24.6	0.095	2.65				0.05		0.0004	Inv. ex.
108	0.089	1.45	4.01	0.032	0.002	19.3	0.142			2.01	0.40				Example
109	0.078	0.98	4.75	0.03	0.001	20.8	0.085						0.0028		Example
110	0.011	0.35	2.88	0.038	0.001	21.0	0.098		3.40						Inv. ex.
111	0.004	1.58	1.95	0.016	0.001	19.9	0.035	4.30							Inv. ex.
112	0.028	1.11	2.55	0.029	0.002	18.6	0.123			0.50	0.12	0.12			Inv. ex.
113	0.098	0.19	2.87	0.042	0.003	21.5	0.088	1.06	0.55		0.05				Inv. ex.
114	0.028	0.08	2.98	0.034	0.001	21.3	0.110	1.02	0.55						Inv. ex.
115	0.025	0.95	5.65	0.034	0.001	20.1	0.118	0.11							Comp. ex.
<p>Underlines mean deviation from the definition or the present invention Steel Nos. 101, 103 to 105, 108 and 109 are not within the claims</p>															

[Table 5]

Condition	Steel No.	T ₁ (°C)	N(X)	R (%)	T ₂ (°C)	T ₃ (°C)	γ fraction (%)	Md	X ₁ (%)	X ₂ (μm)	Uniform elongation (%)	
1a	101	1240	1	98	1150	1050	34	49	92	9	42	Example
1b		1200	2	97	1220	1020	36	44	89	18	36	Comp. ex.
1c		1260	1	98	1200	1100	19	42	80	11	35	Comp. ex.
2a	102	1200	1	90	1150	1080	38	89	90	21	36	Comp. ex.
2b		1190	1	96	1180	1080	35	72	95	8	43	Inv. ex.
2c		1200	2	97	1180	1140	9	44	92	18	35	Comp. ex.
3a	103	1160	1	97	1160	980	45	78	82	5	32	Comp. ex.
3b		1200	2	98	1100	1080	40	71	98	7	42	Example
3c		1200	0	97	1200	1020	43	82	78	9	36	Comp. ex.
4a	104	1120	1	94	1100	1000	35	21	77	12	37	Comp. ex.
4b		1150	1	96	1140	1100	27	15	100	11	43	Example.
4c		1150	2	97	1200	1100	40	32	91	13	37	Comp. ex.
5a	105	1200	1	98	1180	1080	48	82	94	7	43	Example
5b		1240	1	98	1000	1120	59	100	68	12	35	Example
5c		1120	1	76	1120	1050	40	78	72	10	34	Comp. ex.
6a	106	1250	1	95	1160	1100	25	-9	90	21	36	Comp. ex.
6b		1250	2	96	1170	1100	21	-5	95	8	43	Inv. ex.
6c		1250	1	97	1260	1120	10	-19	92	14	31	Comp. ex.
7a	107	1160	1	98	1160	900	28	13	80	6	30	Comp. ex.
7b		1160	1	96	1140	1100	12	-9	100	8	43	Inv. ex.
7c		1160	0	96	1100	1050	20	-2	78	6	35	Comp. ex.
8a	108	1100	0	94	1100	1150	2	-11	100	35	27	Comp. ex.
8b		1200	1	96	1150	1100	36	-5	98	6	44	Example
8c		1200	1	96	1250	1100	4	5	73	19	35	Comp. ex.

5
10
15
20
25
30
35
40
45
50
55

(continued)

Condition	Steel No.	T ₁ (°C)	N(X)	R(%)	T ₂ (°C)	T ₃ (°C)	γ fraction (%)	Md	X ₁ (%)	X ₂ (μm)	Uniform elongation (%)	
9a	109	1250	2	98	1180	1080	34	78	91	8	42	Example
9b		1250	2	98	950	1050	33	80	81	6	34	Comp. ex.
9c		1270	2	98	1200	1100	25	90	89	15	35	Comp. ex.
10a	110	1200	1	93	1160	1100	34	0	88	9	36	Comp. ex.
10b		1200	1	98	1100	1000	48	10	95	5	42	Inv. ex.
10c		1150	1	96	1100	1110	21	-15	91	13	34	Comp. ex.
11a	111	1150	1	97	1150	900	52	89	40	5	31	Comp. ex.
11b		1200	1	97	1150	1100	24	70	97	9	42	Inv. ex.
11c		1200	0	97	1150	1050	35	60	72	12	35	Comp. ex.
12a	112	1100	0	96	1100	1000	24	64	62	5	30	Comp. ex.
12b		1180	1	97	1160	1050	30	68	98	8	43	Inv. ex.
12c		1160	1	97	1180	1080	21	78	88	13	35	Comp. ex.
13a	113	1220	1	97	1190	1080	46	38	90	8	42	Inv. ex.
13b		1200	1	97	1250	1080	45	37	80	14	35	Comp. ex.
13c		1260	0	96	1200	1100	37	25	64	9	35	Comp. ex.
14a	114	1230	1	97	1200	1080	27	52	95	10	42	Inv. ex.
14b		1220	1	97	1250	1000	34	43	87	16	35	Comp. ex.
14c		1280	2	96	1190	1070	30	40	68	10	34	Comp. ex.
15a	115	1150	1	97	1150	1050	40	56	100	11	34	Comp. ex.
15b		1170	1	98	1100	1050	41	55	90	11	32	Comp. ex.
15c		1150	1	97	1200	1080	32	34	91	13	31	Comp. ex.

Steels Nos. 101, 103 to 105, 108 and 109 are not within the claims

[0126] The notations in Table 5 are as shown below.

T1: Heating temperature (°C) before hot rolling

N: Number of times of rolling in the hot rolling process comprising rolling at 1000°C or more with a 30% or higher reduction rate then holding for 30 sec or more

R: Hot rolling total reduction rate (%)

T2: Hot rolled sheet annealing temperature (°C)

T3: Final annealing temperature (°C)

X1: Ratio of austenite grains with a grain size of 15 μm or less and a shape aspect ratio of less than 3 in total austenite grains

X2: Average value of distance of each austenite grain from nearest grain

Md: Value calculated by the formula below from the composition (average composition only for C) in the austenite phase

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

where [] is composition (mass%) in the austenite phase, and { } is average composition (mass%).

[0127] Condition 1a is **an example outside the claims** where extremely good uniform elongation is obtained. In condition 1b, T2 does not satisfy the present invention range, so X1 and X2 deviate from the present invention. Further, in condition 1c, T1 does not satisfy the present invention range, so X1 deviates from the present invention.

[0128] In condition 2a, R does not satisfy the present invention range, so X2 deviates from the present invention. Condition 2b is an invention example where extremely good uniform elongation is obtained. In condition 2c, T3 does not satisfy the present invention range, so the γ fraction and X2 deviate from the present invention.

[0129] In condition 3a, T3 does not satisfy the present invention range, so X1 deviates from the present invention. Condition 3b is **an example outside the claims** where extremely good uniform elongation is obtained. In condition 3c, N does not satisfy the present invention range, so X1 deviates from the present invention.

[0130] In condition 4a, T1 and R do not satisfy the present invention range, so X1 deviates from the present invention. Condition 4b is **an example outside the claims** where extremely good uniform elongation is obtained. In condition 4c, T2 does not satisfy the present invention range, so X2 deviates from the present invention.

[0131] Condition 5a is **an example outside the claims** where extremely good uniform elongation is obtained. In condition 5b, T2 and T3 do not satisfy the present invention range, so the γ fraction and X1 deviate from the present invention. In condition 5c, T1 does not satisfy the present invention range, so X1 deviates from the present invention.

[0132] In condition 6a, R does not satisfy the present invention range, so X2 deviates from the present invention. Condition 6b is an invention example where extremely good uniform elongation is obtained. In condition 6c, T2 and T3 do not satisfy the present invention range, so Md and X2 deviate from the present invention.

[0133] In condition 7a, T3 does not satisfy the present invention range, so X1 deviates from the present invention. Condition 7b is an invention example where extremely good uniform elongation is obtained. In condition 7c, N does not satisfy the present invention range, so X1 deviates from the present invention.

[0134] In condition 8a, T1, N, R, and T3 do not satisfy the present invention range, so the γ fraction, Md, and X2 deviate from the present invention. Condition 8b is **an example outside the claims** where extremely good uniform elongation is obtained. In condition 8c, T2 does not satisfy the present invention range, so X1 and X2 deviate from the present invention.

[0135] Condition 9a is **an example outside the claims** where extremely good uniform elongation is obtained. In condition 9b, T2 does not satisfy the present invention range, so X1 deviates from the present invention. In condition 9c, T1 does not satisfy the present invention range, so X1 and X2 deviate from the present invention.

[0136] In condition 10a, R does not satisfy the present invention range, so X1 deviates from the present invention. Condition 10b is an invention example where extremely good uniform elongation is obtained. In condition 10c, T3 does not satisfy the present invention range, so Md and X2 deviate from the present invention.

[0137] In condition 11a, T3 does not satisfy the present invention range, so γ fraction and X1 deviate from the present invention. Condition 11b is an invention example where extremely good uniform elongation is obtained. In condition 11c, N does not satisfy the present invention range, so X1 deviates from the present invention.

[0138] In condition 12a, T1 and N do not satisfy the present invention range, so X1 deviates from the present invention. Condition 12b is an invention example where extremely good uniform elongation is obtained. In condition 12c, T2 does not satisfy the present invention range, so X1 and X2 deviate from the present invention.

[0139] Condition 13a is an invention example where extremely good uniform elongation is obtained. In condition 13b,

T2 does not satisfy the present invention range, so X1 and X2 deviate from the present invention. In condition 13c, T1 and N do not satisfy the present invention range, so X1 deviates from the present invention.

[0140] Condition 14a is an invention example where extremely good uniform elongation is obtained. In condition 14b, T2 does not satisfy the present invention range, so X1 and X2 deviate from the present invention. In condition 14c, T1 does not satisfy the present invention range, so X1 deviates from the present invention.

[0141] In each of the conditions 15a, 15b, and 15c, the ingredient systems do not satisfy the present invention range, so extremely good uniform elongation is not obtained.

[0142] As explained above, in the invention examples, extremely good uniform elongation is obtained. In the comparative examples, either of the γ fraction, Md value, X1, or X2 does not satisfy the conditions, so the uniform elongation is low.

INDUSTRIAL APPLICABILITY

[0143] According to the first findings **described herein**, by defining the steel ingredients and γ fraction and controlling the final annealing conditions, ferritic-austenitic stainless steel excellent in corrosion resistance and workability having a corrosion resistance equal to or greater than SUS 304 in a neutral chloride environment can be produced.

[0144] Further, according to the second findings of the present invention, ferritic-austenitic-based stainless thin-gauge steel sheet excellent in workability, particularly in uniform elongation, can be obtained without having to include a large amount of Ni.

[0145] The present invention can be applied to parts where conventionally austenitic stainless steel sheets containing large amounts of Ni have been used, for example, kitchen appliances, home electric appliances, electronic equipment, etc. used in a neutral chloride environment, and other broad fields, so from the viewpoint of Ni resource conservation, it greatly contributes to the environment.

[0146] Some embodiments of the present disclosure are summarized in the following items:

1. Ferritic-austenitic stainless steel excellent in corrosion resistance and workability characterized by containing, by mass%,

C: 0.001 to 0.1%,
 Cr: 17 to 25%,
 Si: 0.01 to 1%,
 Mn: 0.5 to 3.7%, and
 N: 0.06% to less than 0.15%,

having a pitting indicator (PI value) shown by the following formula (a) of over 18%, having a balance of Fe and unavoidable impurities, and having a ferrite phase as the matrix phase and having a volume fraction of the austenite phase of 15 to 50%.

$$\text{Pitting indicator (PI value)} = \text{Cr} + 3\text{Mo} + 10\text{N} - \text{Mn} \dots (a)$$

2. Ferritic-austenitic stainless steel excellent in corrosion resistance and workability as set forth in item 1, characterized by further containing, by mass%, both

Ni: 0.6 to 3% and
 Cu: 0.1 to 3%.

3. Ferritic-austenitic stainless steel excellent in corrosion resistance and workability as set forth in item 1 or 2, characterized by further containing, by mass%, one or more of

Mo: 1% or less,
 Nb: 0.5% or less,
 Ti: 0.5% or less,
 Al: 0.1% or less,
 B: 0.01% or less,
 Ca: 0.01% or less, and
 Mg: 0.01% or less.

EP 3 434 802 B1

4. Ferritic-austenitic stainless steel excellent in corrosion resistance and workability as set forth in any of items 1 to 3, characterized by having a pitting potential $V_c'100$ in a 30°C, 3.5% NaCl aqueous solution of 0.3V (Vv.s.AGCL) or more.

5. A method of production of ferritic-austenitic stainless steel excellent in corrosion resistance and workability comprising hot forging or hot rolling a stainless steel ingot having steel ingredients as set forth in any of items 1 to 3 to obtain a hot rolled steel material, annealing the hot rolled steel material, then repeating cold working and annealing, said method of production of a steel material characterized by performing the final annealing by heating and holding the material at 950 to 1150°C, making an average cooling rate from the heating temperature to 200°C 3°C/sec or more, and making a ferrite phase the matrix phase and making a volume fraction of the austenite phase 15 to 50%.

6. A method of production of ferritic-austenitic stainless steel excellent in corrosion resistance and workability comprising hot forging or hot rolling a stainless steel ingot having steel ingredients as set forth in any of items 1 to 3 to obtain a hot rolled steel material, annealing the hot rolled steel material, then repeating cold working and annealing, said method of production of a steel material characterized by performing the final annealing by heating and holding the material at 950 to 1150°C, then making an average cooling rate until 600°C 3°C/sec or more, holding the material at a 200 to 600°C temperature region for 1 minute or more, then making the average cooling rate from the holding temperature to room temperature 3°C/sec or more, and making a ferrite phase the matrix phase and making a volume fraction of the austenite phase 15 to 50%.

7. A method of production of ferritic-austenitic stainless steel excellent in corrosion resistance and workability as set forth in item 5 or 6, characterized by making the ferrite phase the matrix phase and making a volume fraction of the austenite phase 15 to 50% and by making a pitting potential $V_c'100$ in a 30°C, 3.5% NaCl aqueous solution 0.3V (Vv.s.AGCL) or more.

8. Ferritic-austenitic stainless steel excellent in workability characterized by having a volume fraction of an austenite phase of 10% to less than 50%, having an M_d value calculated from the chemical composition in the austenite phase that satisfies the following formula (b), having a ratio of austenite grains in a cross-section vertical to a rolling transverse direction with a grain size of 15 μm or less and a shape aspect ratio of less than 3 accounting for 90% or more of the total number of austenite grains, and further having at the same cross-section an average distance between nearest austenite grains of 12 μm or less:

$$-10 \leq M_d \leq 110 \dots (b)$$

(where, $M_d = 551 - 462(\{C\} + [N]) - 9.2[S_i] - 8.1[Mn] - 13.7[Cr] - 29[Ni] - 29[Cu] - 18.5[Mo]$,
[] is the composition (mass%) in the austenite phase, and { } is the average composition (mass%))

9. Ferritic-austenitic stainless steel excellent in workability as set forth in item 8 characterized by further containing, by mass%,

C: 0.002 to 0.1%,
Si: 0.05 to 2%,
Mn: 0.05 to 5%,
P: less than 0.05%,
S: less than 0.01%,
Cr: 17 to 25%, and
N: 0.01 to 0.15% and

having a balance of iron and unavoidable impurities.

10. Ferritic-austenitic stainless steel excellent in workability as set forth in item 8 or 9 characterized by further containing, by mass%, one or more of

Ni: 5% or less,
Cu: 5% or less, and
Mo: 5% or less.

11. Ferritic-austenitic stainless steel excellent in workability as set forth in any of items 8 to 10 characterized by further containing, by mass%, one or both of

Nb: 0.5% or less and
Ti: 0.5% or less.

12. Ferritic-austenitic stainless steel excellent in workability as set forth in any of items 8 to 11 characterized by further containing, by mass%, one or both of

Ca: 0.003% or less and
Mg: 0.003% or less.

13. A method of production of ferritic-austenitic stainless steel excellent in workability characterized by continuously casting steel of ingredients as set forth in any of items 8 to 12, heating the obtained steel slab before hot rolling at a heating temperature T1 (°C) of 1150°C to less than 1250°C, then rolling at 1000°C or more with reduction of a 30% or higher reduction rate then holding for 30 sec or more for one pass or more so as to obtain a hot rolled plate with a total rolling rate of hot rolling of 96% or more, annealing this at a temperature of T1-100°C to T1°C, suitably thereafter cold rolling, performing process annealing or not performing it, then performing final annealing at 1000°C to 1100°C.

Claims

1. A ferritic-austenitic stainless steel excellent in workability, **characterized by** consisting of, by mass%,

C: 0.002 to 0.1%,
Si: 0.05 to 2%,
Mn: 0.05 to 3.00%,
P: less than 0.05%,
S: less than 0.01%,
Cr: 17 to 25%,
N: 0.03 to 0.13%, and

a balance of iron and unavoidable impurities, and optionally one or more of, by mass%,

Ni: 0.1 to 5%,
Cu: 0.1 to 5%,
Mo: 0.1 to 5%,
Nb: 0.03 to 0.5%,
Ti: 0.03 to 0.5%,
Ca: 0.0002 to 0.003%, and
Mg: 0.0002 to 0.003%;

having a volume fraction of an austenite phase of 10% to less than 50%, having an Md value calculated from the chemical composition in the austenite phase that satisfies the following formula (b),

having a ratio of austenite grains in a cross-section vertical to a rolling transverse direction with a grain size of 15 μm or less and a shape aspect ratio of less than 3 accounting for 90% or more of the total number of austenite grains, and further

having at the same cross-section an average distance between nearest austenite grains of 12 μm or less:

$$-10 \leq Md \leq 110 \quad (b)$$

wherein

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

[] is the composition (mass%) in the austenite phase, and
{ } is the average composition (mass%).

2. The ferritic-austenitic stainless steel excellent in workability as set forth in claim 1, **characterized by** further containing, by mass%, one or more of

EP 3 434 802 B1

Ni: 0.1 to 5%,
Cu: 0.1 to 5%, and
Mo: 0.1 to 5%.

- 5 3. The ferritic-austenitic stainless steel excellent in workability as set forth in claim 1 or 2, **characterized by** further containing, by mass%, one or both of

Nb: 0.03 to 0.5% and
Ti: 0.03 to 0.5%.

- 10 4. The ferritic-austenitic stainless steel excellent in workability as set forth in any of claims 1 to 3, **characterized by** further containing, by mass%, one or both of

15 Ca: 0.0002 to 0.003% and
Mg: 0.0002 to 0.003%.

Patentansprüche

- 20 1. Ein ferritisch-austenitischer Edelstahl mit hervorragender Bearbeitbarkeit, **dadurch gekennzeichnet, dass** dieser, in Massen-%, besteht aus

25 C: 0,002 bis 0,1%,
Si: 0,05 bis 2%,
Mn: 0,05 bis 3,00%,
P: weniger als 0,05%,
S: weniger als 0,01%,
Cr: 17 bis 25%,
N: 0,03 bis 0,13% und

30 einem Rest aus Eisen und unvermeidbaren Verunreinigungen, und gegebenenfalls einem oder mehreren von, in Massen-%,

35 Ni: 0,1 bis 5%,
Cu: 0,1 bis 5%,
Mo: 0,1 bis 5%,
Nb: 0,03 bis 0,5%,
Ti: 0,03 bis 0,5%,
Ca: 0,0002 bis 0,003% und
40 Mg: 0,0002 bis 0,003%;

mit einem Volumenanteil einer austenitischen Phase von 10% bis weniger als 50%,
mit einem aus der chemischen Zusammensetzung in der Austenitphase berechneten Md-Wert, der die nachstehende Formel (b) erfüllt,

45 mit einem Verhältnis von Austenitkörnern in einem Querschnitt senkrecht zu einer transversalen Walzrichtung mit einer Korngröße von 15 μm oder weniger und einem Form-Seitenverhältnis von weniger als 3, das 90% oder mehr der Gesamtanzahl der Austenitkörner beträgt, und ferner mit, an dem gleichen Querschnitt, einer mittleren Entfernung zwischen den nächstgelegenen Austenitkörnern von 12 μm oder weniger:

50

$$-10 \leq \text{Md} \leq 110 \quad (\text{b})$$

wobei

55

$$\text{Md} = 551 - 462(\{\text{C}\} + [\text{N}]) - 9,2[\text{Si}] - 8,1[\text{Mn}] - 13,7[\text{Cr}] - 29[\text{Ni}] - 29[\text{Cu}] - 18,5[\text{Mo}],$$

EP 3 434 802 B1

wobei

[] die Zusammensetzung (Massen-%) in der Austenitphase ist und
{ } die mittlere Zusammensetzung (Massen-%) ist.

5

2. Der ferritisch-austenitische Edelstahl mit hervorragender Bearbeitbarkeit nach Anspruch 1, **dadurch gekennzeichnet, dass** dieser ferner, in Massen-%, eines oder mehrere von

10

Ni: 0,1 bis 5%,
Cu: 0,1 bis 5% und
Mo: 0,1 bis 5% enthält.

3. Der ferritisch-austenitische Edelstahl mit hervorragender Bearbeitbarkeit nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** dieser ferner, in Massen-%, eines oder beide von

15

Nb: 0,03 bis 0,5% und
Ti: 0,03 bis 0,5% enthält.

4. Der ferritisch-austenitische Edelstahl mit hervorragender Bearbeitbarkeit nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** dieser ferner, in Massen-%, eines oder beide von

20

Ca: 0,0002 bis 0,003% und
Mg: 0,0002 bis 0,003% enthält.

25

Revendications

1. Acier inoxydable austéno-ferritique d'excellente aptitude au façonnage, **caractérisé en ce qu'il** consiste en, en % en poids,

30

C : de 0,002 à 0,1 %,
Si : de 0,05 à 2 %,
Mn : de 0,05 à 3,00 %,
P : moins de 0,05 %,
S : moins de 0,01 %,
Cr : de 17 à 25 %,
N : de 0,03 à 0,13 %, et

35

un reste de fer et d'impuretés inévitables, et éventuellement un ou plusieurs des suivants, en % en poids,

40

Ni : de 0,1 à 5 %,
Cu : de 0,1 à 5 %,
Mo : de 0,1 à 5 %,
Nb : de 0,03 à 0,5 %,
Ti : de 0,03 à 0,5 %,
Ca : de 0,0002 à 0,003 %, et
Mg : de 0,0002 à 0,003 % ;

45

présentant une fraction de volume d'une phase d'austénite de 10 % à moins de 50 %, présentant une valeur Md calculée à partir de la composition chimique dans la phase d'austénite qui satisfait la formule (b) suivante,

50

présentant un rapport de grains d'austénite dans une verticale transversale à une direction transversale de laminage avec une taille de grain de 15 μm ou inférieure et un rapport des dimensions de forme inférieur à 3 comptant pour 90 % ou plus du nombre total de grains d'austénite, et de plus

55

présentant sur la même section transversale une distance moyenne entre les grains d'austénite les plus proches de 12 μm ou inférieure :

$$-10 \leq Md \leq 110 \quad (b)$$

dans lequel

5

$$Md = 551 - 462(\{C\} + [N]) - 9,2[Si] - 8,1[Mn] - 13,7[Cr] - 29[Ni] - 29[Cu] - 18,5[Mo],$$

10

[] est la composition (% en poids) dans la phase d'austénite, et

{ } est la composition moyenne (% en poids).

2. Acier inoxydable austéno-ferritique d'excellente aptitude au façonnage selon la revendication 1, **caractérisé en ce qu'il** contient de plus, en % en poids, un ou plusieurs de

15

Ni : de 0,1 à 5 %,

Cu : de 0,1 à 5 %, et

Mo : de 0,1 à 5 %.

20

3. Acier inoxydable austéno-ferritique d'excellente aptitude au façonnage selon la revendication 1 ou 2, **caractérisé en ce qu'il** contient de plus, en % en masse, un ou les deux de

Nb : de 0,03 à 0,5 % et

Ti : de 0,03 à 0,5 %.

25

4. Acier inoxydable austéno-ferritique d'excellente aptitude au façonnage selon l'une quelconque des revendications 1 à 3, **caractérisé en ce qu'il** contient de plus, en % en poids, un ou les deux de

Ca : 0,0002 à 0,003 % et

Mg : 0,0002 à 0,003 %.

30

35

40

45

50

55

Fig.1

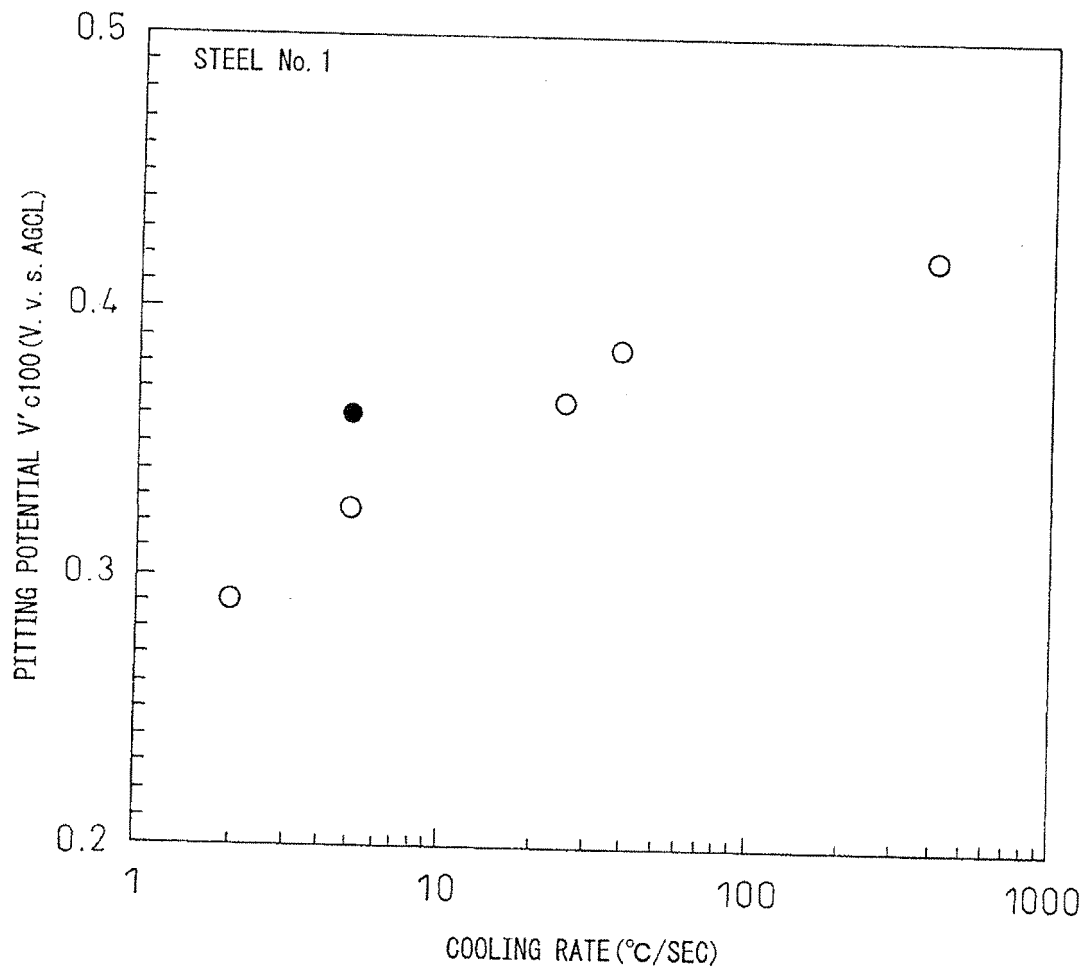
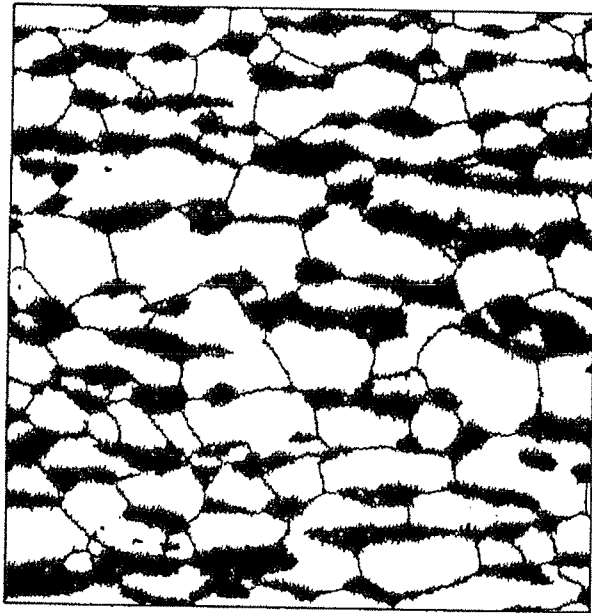
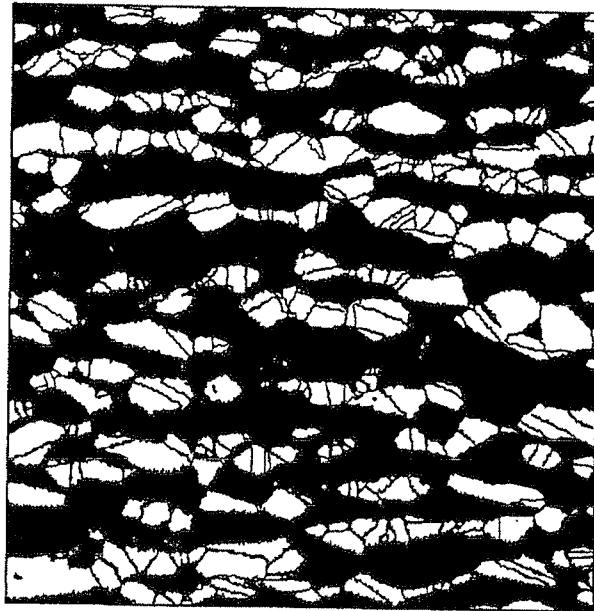


Fig. 2



(a) BCC PHASE SHOWN BY WHITE



20 μ m

(b) FCC PHASE SHOWN BY WHITE

Fig.3

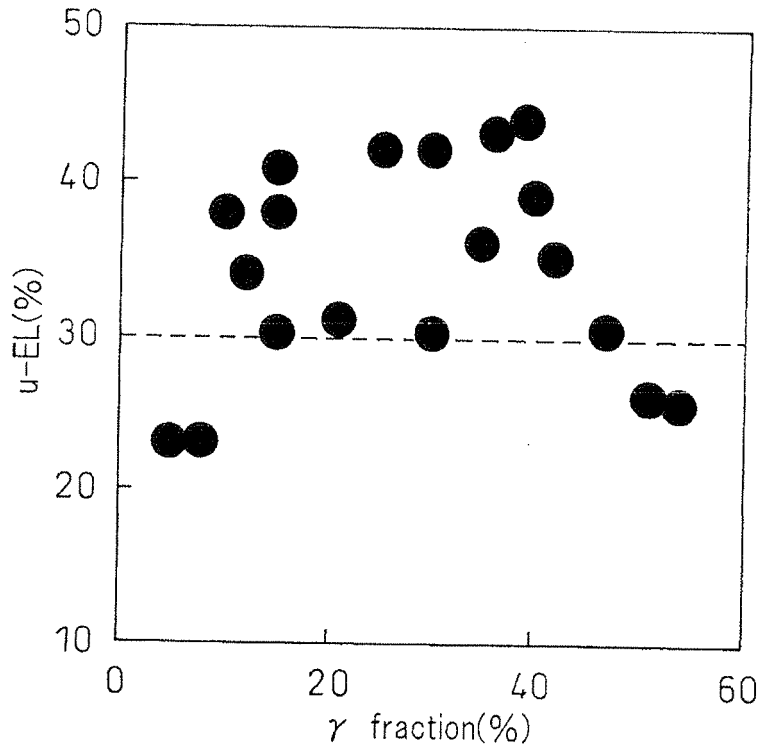


Fig.4

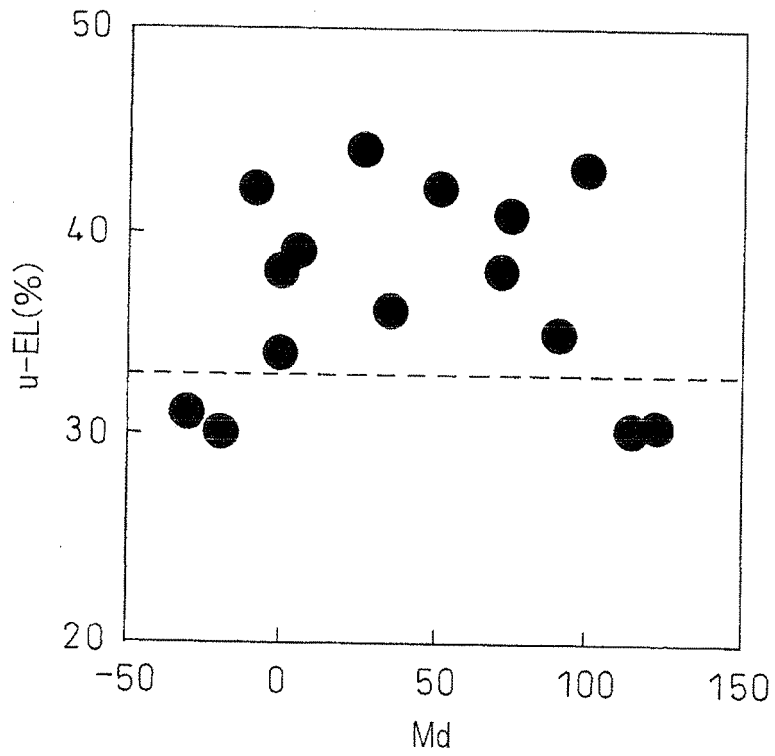


Fig.5

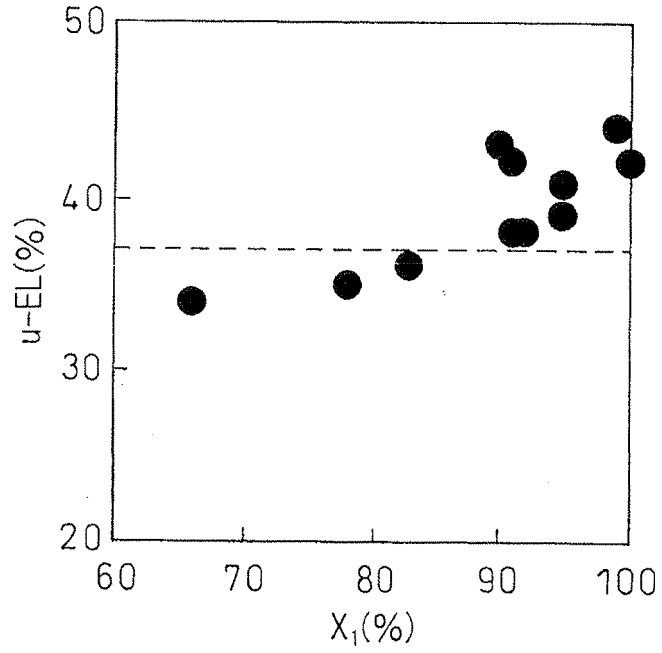
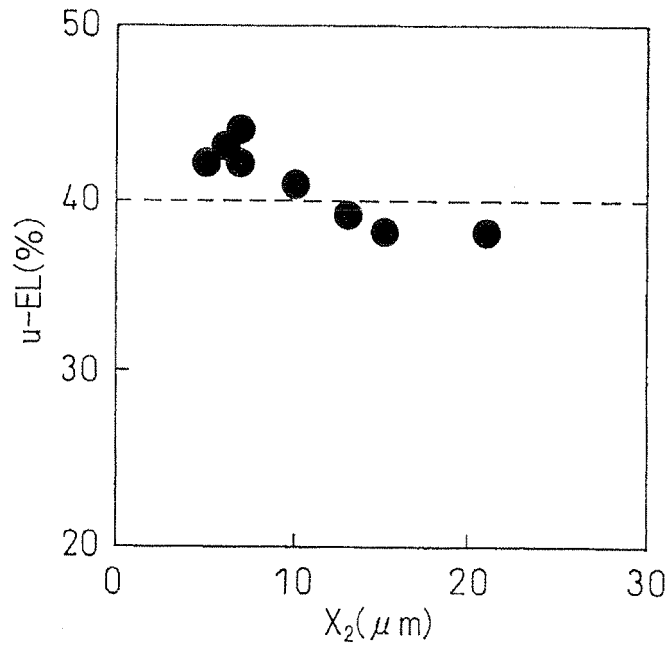


Fig.6



REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 11071643 A [0006] [0009] [0010]
- WO 0227056 A [0006]
- JP 2006169622 A [0007] [0009] [0010] [0011]
- JP 2006183129 A [0007] [0011]
- JP 10219407 A [0007] [0009] [0010]
- JP 2006200035 A [0011]
- JP 2006233308 A [0011] [0012]
- JP 5247594 A [0013]
- EP 0889145 A [0015]
- EP 1715073 A [0016]

Non-patent literature cited in the description

- **NOHARA et al.** *Journal of the ISIJ*, 1977, vol. 63, 772 [0042]
- *Stainless Steel Handbook*. Japan Stainless Steel Association, 622 [0065]
- *Current Advances in Materials and Processes*, 2005, vol. 18, 607 [0066]
- *Microscopy*; *Seichi Suzuki*, vol. 39 (2), 121-124 [0076]