(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 915 894 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
09.09.2015 Bulletin 2015/37

(21) Application number: **13851279.3**

(22) Date of filing: **30.10.2013**

(51) Int Cl.:
C22C 38/00 $^{(2006.01)}$
C21D 9/46 $^{(2006.01)}$
C22C 38/26 $^{(2006.01)}$
C22C 38/60 $^{(2006.01)}$

(86) International application number:
PCT/JP2013/079461

(87) International publication number:
WO 2014/069543 (08.05.2014 Gazette 2014/19)

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

(30) Priority: **30.10.2012 JP 2012239148**

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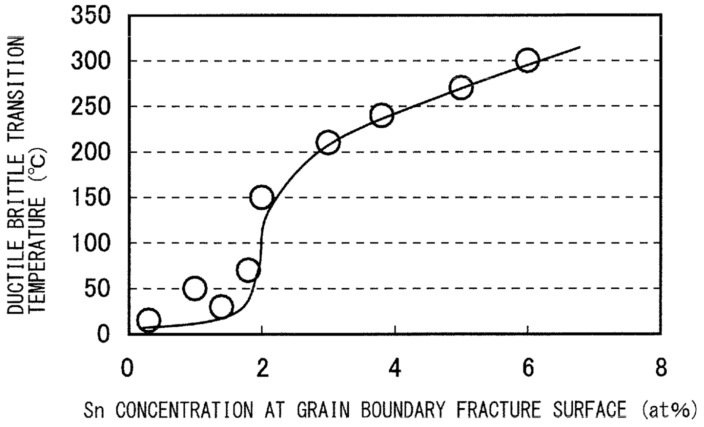
(54) FERRITIC STAINLESS STEEL SHEET HAVING EXCELLENT HEAT RESISTANCE

(57) The present invention provides a Sn-containing ferritic stainless steel sheet having excellent heat resistance. The ferritic stainless steel contains, in terms of mass %, 0.015% or less of C, 1.5% or less of Si, 1.5% or less of Mn, 0.035% or less of P, 0.015% or less of S, 13-21% of Cr, 0.01-0.50% of Sn, 0.05-0.60% of Nb and 0.020% or less of N, with the remainder consisting of Fe and unavoidable impurities. The ferritic stainless steel satisfies formula 1 and formula 2, and has a grain boundary Sn concentration of 2 atom % or less when subjected to a heat treatment at 600-750°C in which the value of L, as shown in formula 3, is 1.91×10^4 or higher. $8 \leq CI = (Ti+0.52Nb) / (C+N) \leq 26$ (formula 1) $GBSV = Sn+Ti-2Nb-0.3Mo-0.2 \leq 0$ (formula 2) $L = (273+T) (\log(t)+20)$ (formula 3) T: Temperature (°C), t: time (h)

FIG. 4



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Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to a material for sheet structure which is used at a high temperature, in particular relates to ferritic stainless steel which exhibits corrosion resistance at ordinary temperature and which is resistant to embrittlement due to use at a high temperature, such as a material for an automobile exhaust system.

Background Art

[0002] Ferritic stainless steel is inferior to austenitic stainless steel in workability, toughness, and high-temperature strength, but does not contain a large amount of Ni, so is inexpensive. Further, it has a small heat expansion, so in recent years has been used for roofing and other building materials or materials for parts of automobile exhaust systems becoming high in temperature and other applications where thermal strain becomes a problem. In particular, when used as material for parts of exhaust systems of automobiles, high-temperature strength, corrosion resistance at ordinary temperature, and high toughness associated with high-temperature use are important. In general, SUH409L, SUS429, SUS430LX, SUS436J1L, SUS432, SUS444, and other steels are used as ferritic stainless steel suitable for these applications.

[0003] In these materials, PLT 1 discloses a material using 0.05 to 2% of Sn to raise the high-temperature strength. Further, PLT 2 discloses the technique of adding 0.005 to 0.10% of Sn to improve the surface quality of stainless steel sheet. Further, in recent years, scrap iron containing surface-treated steel sheet has been used as raw materials, and so large amounts of Sn exceeding 0.05% have come to be included in stainless steel as unavoidable impurities.

Citations List

Patent Literature

[0004]

PLT 1: Japanese Patent Publication No. 2000-169943A
PLT 2: Japanese Patent Publication No. H11-92872A

Summary of Invention

Technical Problem

[0005] If using stainless steel containing Sn described in the background art at a high temperature, it has been learned that the previously unknown grain boundary embrittlement phenomenon occurs and the problem arises that the strength of the parts becomes impaired. An object of the present invention is to provide ferritic stainless steel which does not deteriorate in toughness at ordinary temperature even if exposed to a high temperature over a long period of time like in a material for an automobile exhaust system.

Solution to Problem

[0006] The inventors engaged in various studied on the drop in toughness at ordinary temperature of ferritic stainless steel containing Sn after long term exposure to high temperatures. First, they investigated temperature range at which a drop in toughness is caused when using the SUS430LX containing 0.3% of Sn, and they found that the temperature range was 500 to 800°C. In addition, particularly, the temperature at which a drop in toughness occurred in a short time was 700°C and it was learned that a large drop in toughness occurred in just 1 hour. As shown in FIG. 1, the mode of fracture surface which occurs due to brittle fracture differs from a general cleavage fracture surface and has the characteristic of a grain boundary fracture surface. The inventors cooled a sample to a low temperature in an AES (Auger electron spectroscopy) apparatus, then broke it and analyzed the grain boundary fracture surface, and remarkable Sn segregation was observed at a thickness of about 1 nm. That is, it was believed that the drop in toughness due to long term use at a high temperature occurred due to Sn grain boundary segregation.

[0007] To prevent such grain boundary embrittlement, decreasing the content of Sn is the most effective. However, recycling surface-treated steel sheet is unavoidable for environmental protection, so scrap containing Sn actually has to be used. Further, removing the Sn by refining is difficult for the existing technique. A material which is resistant to grain boundary embrittlement even if containing Sn has been desired.

[0008] Therefore, the inventors investigated in detail the effects of various types of alloy elements so as to prevent embrittlement due to grain boundary segregation of Sn and discovered that to secure corrosion resistance, the stabilizing elements Ti and Nb which are added for immobilizing the C and N in the stainless steel have significant effect. That is, as shown in FIG. 1 and 2, they found that if steel stabilized using Ti contains Sn, the grain boundary embrittlement associated with high-temperature use becomes remarkable and that steel stabilized by Nb is resistant to embrittlement even if containing Sn.

[0009] Based on these discoveries, the inventors investigated the effects on toughness when adding the stabilizing elements Ti and Nb alone and when adding them together and were able to develop steel resistant to the drop in toughness due to high-temperature use.

[0010] The present invention was reached based on these discoveries. The solution to the problem of the present invention, that is, the ferritic stainless steel of the present invention, is as follows:

(1) Ferritic stainless steel containing, by mass %, Cr: 13.0 to 21.0%, Sn: 0.01 to 0.50%, and Nb: 0.05 to 0.60%, restricted to C: 0.015% or less, Si: 1.5% or less, Mn: 1.5% or less, N: 0.020% or less, P: 0.035% or less, and S: 0.015% or less, containing a balance of Fe and unavoidable impurities, satisfying formula 1 and formula 2, and having a grain boundary Sn concentration of 2 at% or less when performing heat treatment at a temperature of 600 to 750°C so that an L-value shown by formula 3 becomes 1.91×10^4 or more:

$$8 \le CI = 0.52Nb/(C+N) \le 26 \cdots \text{(formula 1)}$$

$$GBSV = Sn - 2Nb - 0.2 \le 0 \cdots \text{(formula 2)}$$

$$L = (273+T)(\log(t)+20) \cdots \text{(formula 3)}$$

where, T: temperature (°C), t: time (h)

(2) The ferritic stainless steel according to (1), wherein the heat treatment is performed at a temperature of 700°C for 1 hour.

(3) The ferritic stainless steel according to (1) or (2) further containing, by mass%, one or more of Ti: 0.32% or less, Ni: 1.5% or less, Cu: 1.5% or less, Mo: 2.0% or less, V: 0.3% or less, Al: 0.3% or less, and B: 0.0020% or less:

where formula 1 and formula 2 are replaced by formula 1' and formula 2'.

$$8 \le CI = (Ti + 0.52Nb)/(C+N) \le 26 \cdots \text{formula 1'}$$

$$GBSV = Sn + Ti - 2Nb - 0.3Mo - 0.2 \le 0 \cdots \text{formula 2'}$$

(4) The ferritic stainless steel according to any one of (1) to (3) further containing, by mass%, one or more of W: 0.20% or less, Zr: 0.20% or less, Sb: 0.5% or less, Co: 0.5% or less, Ca: 0.01% or less, Mg: 0.01% or less, and REM: 0.1% or less.

(5) The ferritic stainless steel according to any one of (1) to (4) wherein a grain size number after annealing the cold-rolled sheet is made 5.0 to 9.0.

(6) A method of production of ferritic stainless steel according to any one of (1) to (5) comprising annealing stainless steel of a composition of (1) (3), or (4) at a cold-rolled strip annealing temperature of 850°C to 1100°C and then cooling from the cold-rolled strip annealing temperature by a cooling rate of 5°C/s or more in temperature range of 800 to 500°C. Advantageous Effects of Invention

[0011] According to the ferritic stainless steel containing Sn of the present invention, the stabilizing elements Nb and Ti are optimized, and so stainless steel sheet which has little deterioration of the toughness even when used at a high temperature and further is excellent in corrosion resistance is obtained.

Brief Description of Drawings

[0012]

FIG. 1 shows photos of ferritic stainless steels of the present embodiment and comparative steels which are hot rolled annealed sheets of thickness 4.0 mm as is, and shows photos of fractured surfaces of test pieces showing brittle fracture in a Charpy impact test for ferritic stainless steels of the present embodiment and comparative after heat treating at 700°C for 1 hour.

FIG. 2 is a graph which shows ductile brittle transition temperatures measured by conducting V-notch Charpy impact tests on subsize test pieces of thickness 4.0 mm for ferritic stainless steels of the present embodiment and comparative steels which are hot rolled annealed sheets of thickness 4.0 mm as is, and which shows ductile brittle transition temperatures measured by conducting the V-notch Charpy impact tests on the test pieces for ferritic stainless steels of the present embodiment and comparative steels after heat-treating at 700°C for 1 hour.

FIG. 3 is a graph which shows the relationship between a ductile brittle transition temperature (DBTT) measured by conducting V-notch Charpy impact tests on subsize test pieces of thickness 4.0 mm and an indicator (GBSV) showing the tendency of the grain boundary segregation of Sn when using ferritic stainless steels of the present embodiment and comparative steels that are hot rolled annealed sheets of thickness 4.0 mm and further heat-treating the ferritic stainless steels at 700°C for 1 hour.

[0013] FIG. 4 is a graph which shows the relationship between Sn concentration at the grain boundary and ductile brittle transition temperature (DBTT) when measuring the Sn concentration at the grain boundary fracture surface by AES and measuring the DBTT by a Charpy impact test and using ferritic stainless steels of the present embodiment and comparative steels which are hot rolled annealed sheets of thickness 4.0 mm and further heat-treating the ferritic stainless steels at 700°C for 1 hour.

Description of Embodiment

[0014] Below, an embodiment of the present invention will be explained. First, the reasons for limiting the steel composition of the stainless steel sheet of the present embodiment will be explained. Note that, the indications % for the composition mean mass% unless particularly stated otherwise.

C: 0.015% or less

[0015] C causes the formability, corrosion resistance, and hot rolled sheet toughness to deteriorate, so the content is preferably as small as possible. Therefore, the upper limit is made 0.015%. However, excessive reduction causes an increase in the refining cost, so the lower limit may also be 0.001%. Further, if considered from the viewpoint of the corrosion resistance, the lower limit is preferably made 0.002% and the upper limit is preferably made 0.009%.

N: 0.020% or less

[0016] N, like C, causes the formability, corrosion resistance, and toughness of hot rolled sheet to deteriorate, so and the smaller the content, the better. Therefore the content is made 0.02% or less. However, excessive reduction leads to an increase in the refining cost, so the lower limit may be made 0.001%. To more reliably avoid a drop in corrosion resistance and deterioration of toughness, the upper limit is preferably made 0.018%. More preferably, the upper limit may be made 0.015%.

Si: 1.5% or less

[0017] Excessive addition of Si causes a drop in the ordinary temperature ductility, so the upper limit is made 1.5%. However, Si is an element which is useful as a deoxidizing agent and is an element which improves the high-temperature strength and oxidation resistance. The deoxidizing effect is improved along with the increase in the amount of Si. The effect is manifested at 0.01% or more and stabilizes at 0.05% or more, so the lower limit may be made 0.01%. Note that, if considering the oxidation resistance in adding Si, the lower limit is more preferably made 0.1% and the upper limit is more preferably made 0.7%.

Mn: 1.5% or less

[0018] Excessive addition of Mn causes a drop in the toughness of the hot rolled sheet due to precipitation of the y phase (austenite phase) and, in addition, forms MnS to cause a drop in the corrosion resistance, so the upper limit is made 1.5%. On the other hand, Mn is an element which is added as a deoxidizing agent and an element which contributes to the rise in high-temperature strength in the medium temperature region. Further, it is an element whereby during long term use, Mn-based oxides form at the surface and contribute to the effect of suppressing adhesion of scale (oxides) and abnormal oxidation. To cause this effect to be manifested, Mn may be added so that the content of Mn in the stainless steel of the present invention becomes 0.01% or more. Note that, if considering the high-temperature ductility or adhesion property of the scale and suppression of abnormal oxidation, the lower limit is more preferably made 0.1 and the upper limit is more preferably made 1.0%.

P: 0.035% or less

[0019] P is an element with a large solution strengthening ability, but is a ferrite stabilizing element and further is an element harmful to corrosion resistance and toughness, and so the content is preferably as small as possible. P is contained as an impurity in the ferrochrome material of stainless steel. Removal of P from the melt of stainless steel is extremely difficult, so 0.010% or more is acceptable. Further, the content of P is substantially determined by the purity and amount of the ferrochrome material used. The content of P in the ferrochrome material is preferably low, but ferrochrome containing low P is expensive, and so the content is set to a range not causing the quality or corrosion resistance to greatly deteriorate, that is, 0.035% or less. Note that, the content is preferably 0.030% or less.

S: 0.015% or less

[0020] S forms sulfide-based inclusions and cause the general corrosion resistance of the steel material (general corrosion or pitting corrosion) to deteriorate. Therefore, the content of S is preferably as small as possible. Considering a range not affecting the corrosion resistance, the upper limit is made 0.015%. Further, the smaller the content of S, the better the corrosion resistance, but to lower the S, the desulfurization load increases and the manufacturing cost increases, so the lower limit may be 0.001%. Note that, preferably, the lower limit is made 0.001% and the upper limit is made 0.008%.

Cr: 13.0 to 21.0%

[0021] Cr is an essential element for securing oxidation resistance and corrosion resistance in the present invention. If less than 13.0%, these effects are not manifested, while if over 21.0%, a drop in workability or deterioration of toughness is caused, so the lower limit is made 13.0 and the upper limit is made 21.0%. Furthermore, if considering the manufacturability and high temperature ductility, the upper limit is preferably made 18.0%.

Sn: 0.01 to 0.50%

[0022] Sn is an element which is effective for improvement of the corrosion resistance or high-temperature strength. Further, it also has an effect of not causing a great deterioration of the mechanical properties at ordinary temperature. The effect on the corrosion resistance is manifested at 0.01% or more, so the lower limit is made 0.01%. The contribution to high-temperature strength stably manifests with addition of 0.05% or more, and so the preferable lower limit is made 0.05%. On the other hand, if excessively adding it, the manufacturability and weldability remarkably deteriorate, and so the upper limit is made 0.50%. Note that, if considering the oxidation resistance etc., the lower limit is preferably made 0.1%. Further, if considering the weldability etc., the upper limit is preferably made 0.3%. The manifestation of the embrittlement phenomenon at high-temperature use becomes remarkable by inclusion of Sn: 0.05% or more, but by jointly adding Nb as explained below, the embrittlement phenomenon due to inclusion of Sn can be suppressed. Further, to make the DBTT (ductile brittle transition temperature) less than 50°C, the upper limit of content of Sn is more preferably made 0.21%.

Nb: 0.05 to 0.60%

[0023] Nb is an element which forms carbonitrides and thereby has the effect of suppressing sensitization due to precipitation of chrome carbonitrides at the stainless steel and the drop in corrosion resistance. The effect is manifested at 0.05% or more. Furthermore, the inventors found the fact that this also has the effect of suppressing grain boundary embrittlement in the steel containing Sn. The two effects of improvement of corrosion resistance and suppression of grain boundary embrittlement are manifested at 0.05% or more, so the lower limit is made 0.05%. To obtain the effects more reliably, the content is preferably made 0.09% or more. If 0.2% or more, the effects can be substantially reliably obtained. On the other hand, excessive addition causes the problem of a drop in the manufacturability due to the formation of Laves phases. Considering these, the upper limit of Nb was made 0.60%. Furthermore, from the viewpoint of the weldability and workability as a sheet, the lower limit is sometimes made 0.3% and the upper limit is sometimes made 0.5%. Further, the effect of suppression of grain boundary embrittlement in the steel containing Sn can be obtained even by joint addition of Ti and Nb. In this case as well, the effects are obtained with an amount of addition of Nb of 0.05% or more. However, in both sole addition of Nb and joint addition of Ti and Nb, the later explained CI value has to be adjusted to fall in a predetermined range.

[0024] CI=(Ti+0.52Nb)/(C+N) is set to not less than 8 to not more than 26. If not containing Ti, CI=0.52Nb/(C+N) is set to not more than 8 to not less than 26. Ti and Nb form carbonitrides and suppress the drop in corrosion resistance due to formation of chromium carbonitrides and sensitization. That is, an amounts of addition corresponding to the amounts of C and N in the steel are necessary. The CI value is an indicator for causing the C and N in the steel to precipitate as carbonitrides of Ti and Nb and suppressing sensitization. The larger the CI value, the more the sensitization is suppressed. To stably suppress the precipitation of chromium carbonitrides even in a weld heat cycle etc., the CI has to be 8 or more. However, if excessively adding Ti and Nb, they form large inclusions and lower the workability, so CI is made 26 or less. To stably secure corrosion resistance and workability, CI is preferably made 10 to 20.

[0025] Furthermore, in the present invention, GBSV=Sn+Ti-2Nb-0.3Mo-0.2 is set to 0 or less. When not containing Ti and Mo, GBSV=Sn-2Nb-0.2 is set to 0 or less. GBSV is an indicator which shows the tendency of grain boundary segregation of Sn. The larger the value, the more remarkable the grain boundary segregation. The coefficients of the elements which form the GBSV are for evaluating the effects on grain boundary segregation. Sn is an element which is effective for high-temperature strength and corrosion resistance, but grain boundary segregation causes the toughness of the material to fall at 400°C or less. On the other had, Nb and Mo have not only actions of suppressing grain boundary segregation of Sn, but also effects of raising the grain boundary strength and have actions of suppressing embrittlement due to grain boundary segregation of Sn. As shown in FIG. 3, it can be found that along with a drop in the GBSV, the ductile brittle transition temperature becomes lower and that if the GBSV becomes 0 or less, the ductile brittle transition temperature of a hot rolled annealed sheet of thickness 4.0 mm becomes 150°C or less and that the toughness is greatly improved. Therefore, GBSV is set to 0 or less.

[0026] Next, the inventors used the concentration of Sn at the grain boundary fracture surface (at%) as an indicator of Sn grain boundary segregation to investigate the relationship with the ductile brittle transition temperature. As shown in FIG. 4, it was found that if the concentration of Sn at the grain boundaries exceeds 2.0 at%, the ductile brittle transition temperature rapidly increases and grain boundary embrittlement easily occurs. In a high temperature service environment as well, making the concentration of Sn at the grain boundaries 2.0 at% or less is important for suppressing grain boundary embrittlement due to Sn.

[0027] Here, as an indicator which treats the temperature and time in a standardized fashion in the case of using at a high temperature for long time, the L-value, which is usually used as an indicator for evaluation of heat treatment and is shown by the formula 3, was introduced. If performing heat treatment at 600 to 750°C to make an L-value shown by formula 3 become 1.91×10^4 or more, remarkable segregation of Sn at the grain boundaries is observed in the case of addition of Ti. The inventors found the fact that segregation of Sn at the grain boundaries has a detrimental effect on the properties (transition temperature). Further, the inventors confirmed that in the case of the composition of components in the present invention, the grain boundary Sn concentration when performing heat treatment which gives an L-value of 1.91×10^4 or more becomes 2 at% or less. Note that, as a condition further simplifying the provision on the heat treatment conditions by the L-value, the grain boundary Sn concentration after performing heat treatment at 700°C for 1 hour is preferably 2.0 at% or less.

[0028] The concentration of Sn at the grain boundaries is fractured and measured in an AES apparatus in an ultrahigh vacuum. Auger electrons are emitted not only from atoms at the surface, but also at several nm inside from the surface, and so the value does not show just the concentration of Sn at the grain boundaries. Further, the precision of analysis differs with each apparatus. However, in principle, the concentration of Sn at the cleavage fracture surface is the same as the average concentration of Sn of the base material. Therefore, the concentration of Sn at the grain boundaries has been determined by calibrating the measurement values of Sn concentration at the cleavage fracture surface so that the concentration of Sn measured at the cleavage fracture surface becomes the average concentration of Sn of the base material. To stably reduce the grain boundary embrittlement, it is preferable to make the concentration of Sn at the grain boundaries 1.7 at% or less. Further, making the concentration lower than the concentration of Sn at the base material is difficult, so it is preferable to make 0.02 at% the lower limit.

[0029] Further, in the present invention, in addition to the above elements, it is preferable to add one or more of Ti: 0.32% or less, Ni: 1.5% or less, Cu: 1.5% or less, Mo: 2.0% or less, V: 0.3% or less, Al: 0.3% or less, and B: 0.0020% or less.

Ti: 0.32% or less

[0030] Ti, like Nb, is an element which forms carbonitrides and thereby has the effect of suppressing sensitization due to precipitation of chrome carbonitrides in the stainless steel and the drop in corrosion resistance. However, compared with Nb, this has a larger effect in exacerbating grain boundary embrittlement in the steel containing Sn, so in the steel containing Sn, this is an element which should be decreased. The effect on grain boundary segregation of Sn is manifested when the content of Ti exceeds 0.05%. However, when including Nb, it is possible to reduce the detrimental effect due to Ti. When jointly adding it with Nb, it was confirmed that if making the upper limit 0.32%, the grain boundary concentration of Sn becomes 2.0 at% or less even in the above heat treatment. The preferable upper limit which including Nb is 0.15%. Note that, this enters from the starting materials as an unavoidable impurity, so excessive reduction is difficult, so the content of Ti is preferably made 0.001% or more. From the viewpoint of the improvement of the workability by the reduction of inclusions, the lower limit is more preferably made 0.001 and the upper limit is more preferably made 0.03%.

Ni: 1.5% or less

[0031] Ni enters the alloy materials of the ferritic stainless steel as an unavoidable impurity and generally is contained in an amount of 0.03 to 0.10% in range. Further, it is an element which is effective for suppressing the progression of pitting. That effect is stably exhibited by addition of 0.05% or more, so the lower limit is preferably made 0.05%. More preferably, the lower limit is 0.1%.

[0032] On the other hand, addition of a large amount is liable to invite hardening of the material due to solution strengthening, so the upper limit is made 1.5%. Note that, if considering the alloy cost, the upper limit is preferably 1.0%. More preferably, the upper limit is 0.5%. Due to this, Ni is suitably 0.1 to 0.5%.

[0033] In the present invention, Ni is an element which improves the corrosion resistance due to the synergistic effect with Sn. Joint addition with Sn is useful. Furthermore, Ni has the action of reducing the drop in workability (elongation and r-value) which accompanies the addition of Sn. When added together with Sn, the lower limit of Ni is preferably made 0.2 and the upper limit is preferably made 0.4%.

Cu: 1.5% or less

[0034] Cu is effective for improving the corrosion resistance. In particular, it is effective for reducing the rate of progression of crevice corrosion after occurrence the crevice corrosion. To improve the corrosion resistance, inclusion of 0.1% or more is preferable. However, excessive addition causes deterioration of the workability. Therefore, Cu is preferably included with a lower limit of 0.1 and an upper limit of 1.5%. Cu is an element which improves the corrosion resistance by a synergistic effect with Sn. Joint addition with Sn is useful. Furthermore, Cu has the action of reducing the drop in workability (elongation and r-value) which accompanies the addition of Sn. When jointly adding this with Sn, the Cu is preferably included with a lower limit of 0.1 and an upper limit of 0.5%.

[0035] Due to the above, in the present invention, joint addition of Sn and Ni and/or Cu is useful for improving the corrosion resistance.

[0036] Further, Cu is an element which is required for raising the high-temperature strength which is used for use as a member for a high temperature environment such as a high temperature exhaust system of an automobile. Cu mainly exhibits a precipitation strengthening ability at 500 to 750°C and acts to suppress plastic deformation of the material and raise the thermal fatigue-resistance by solution strengthening at temperatures above that. Such a Cu precipitation hardening action or solution strengthening is manifested by addition of 0.2% or more. On the other hand, excessive addition becomes a cause of abnormal oxidation and surface defects at the time of heating for hot rolling, so the upper limit is made 1.5%. To make use of the high-temperature strengthening ability of Cu and stably suppress surface defects, the lower limit is preferably made 0.5 and the upper limit is preferably made 1.0%.

Mo: 2.0% or less

[0037] Mo should be added as needed for improving the high-temperature strength and thermal fatigue-resistance. To exhibit these effects, the lower limit is preferably made 0.01%.

[0038] On the other hand, excessive addition is liable to cause the formation of Laves phases and cause a drop in the toughness of the hot rolled sheet. Considering these, the upper limit of Mo is made 2.0%. Furthermore, from the viewpoint of the productivity and manufacturability, the lower limit is preferably made 0.05% and the upper limit is preferably made 1.5%.

V: 0.3% or less

[0039] V enters the alloy material of the ferritic stainless steel as an unavoidable impurity and is difficult to remove in the refining process, so generally is contained in 0.01 to 0.1% in range. Further, it forms fine carbonitrides and has the effect of giving rise to a precipitation strengthening action and contributing improvement of the high-temperature strength, and so it is an element which is deliberately added as needed. This effect is stably manifested by addition of 0.03% or more, so the lower limit is preferably made 0.03%.

[0040] On the other hand, if excessively added, coarsening of the precipitates is liable to be invited. As a result, the high-temperature strength falls and the thermal fatigue life ends up falling, so the upper limit is made 0.3%. Note that, if considering the manufacturing cost and the manufacturability, the lower limit is preferably made 0.03% and the upper limit is preferably made 0.1%.

Al: 0.3% or less

[0041] Al is an element which is added as a deoxidizing element and also improves the oxidation resistance. Further, it is useful as a solution strengthening element in improving the strength at 600 to 700°C. This action is stably manifested from 0.01%, so the lower limit is preferably made 0.01%.

[0042] On the other hand, excessive addition causes hardening and causes the uniform elongation to remarkably fall. In addition, it causes the toughness to remarkably fall. Therefore, the upper limit is made 0.3%. Furthermore, if considering the formation of surface defects and the weldability and manufacturability, the lower limit is preferably made 0.01% and the upper limit is preferably made 0.07%.

B: 0.0020% or less

[0043] B is effective for immobilizing the N which is harmful to the workability and for improving the secondary workability. It is added as needed in 0.0003% or more. Further, even if added in over 0.0020%, the effect becomes saturated. The B causes a deterioration in the workability and a drop in the corrosion resistance, so this is added in 0.0003 to 0.002%. If considering the workability and the manufacturing cost, the lower limit is preferably made 0.0005% and the upper limit is preferably made 0.0015%.

W: 0.20% or less

[0044] W is effective for improvement of the high-temperature strength and is added as needed in 0.01% or more. Further, if added in over 0.20%, the solution strengthening becomes too great and the mechanical properties fall, so 0.01 to 0.20% is added. If considering the manufacturing cost and the toughness of hot rolled sheet, the lower limit is preferably made 0.02% and the upper limit is preferably made 0.15%.

Zr: 0.20% or less

[0045] Zr, like Nb, Ti, etc., forms carbonitrides to suppress the formation of Cr carbonitrides and improve the corrosion resistance, so is added as needed in 0.01% or more. Further, even if added in over 0.20%, the effect becomes saturated and formation of large oxides causes surface defects, so and it is added in 0.01 to 0.20%. Compared with Ti and Nb, this is an expensive element, so if considering the manufacturing cost, the lower limit is preferably made 0.02% and the upper limit is preferably made 0.05%.

Sb: 0.5% or less

[0046] Sb is effective for improvement of the resistance to sulfuric acid and is added as needed in 0.001% or more. Further, even if added in over 0.5%, the effect becomes saturated and embrittlement occurs due to grain boundary segregation of Sb, so 0.001 to 0.20% is added. If considering the workability and manufacturing cost, the lower limit is preferably made 0.002% and the upper limit is preferably made 0.05%.

Co: 0.5% or less

[0047] Co is effective for improvement of the wear resistance and improvement of the high-temperature strength and is added as needed in 0.01% or more. Further, even if added over 0.5%, the effect becomes saturated and the mechanical properties are degraded due to solution strengthening, so 0.01 to 0.5% is added. From the manufacturing cost and stability of high-temperature strength, the lower limit is preferably made 0.05% and the upper limit is preferably made 0.20%.

Ca: 0.01% or less

[0048] Ca is an important desulfurizing element in the steelmaking process and also has a deoxidizing effect, so is added as needed in 0.0003% or more. Further, even if added over 0.01%, the effect becomes saturated and a drop in corrosion resistance due to Ca granules or deterioration of workability due to oxides occurs, so this is added in 0.0003 to 0.01%. If considering the slag treatment and other aspects of manufacturability, the lower limit is preferably made 0.0005% and the upper limit is preferably made 0.0015%.

Mg: 0.01% or less

[0049] Mg is an element which is effective for refining the solidified structure in the steelmaking process and is added as needed in 0.0003% or more. Further, even if added in over 0.01%, the effect becomes saturated and a drop in corrosion resistance due to the sulfides or oxides of Mg easily occurs, so this is added in 0.0003 to 0.01%. Addition of Mg in the steelmaking process results in violent combustion by oxidation of Mg and lower yield. If considering the large increase in cost, the lower limit is preferably made 0.0005% and the upper limit is preferably made 0.0015%.

REM: 0.1% or less

[0050] A REM is effective for improvement of the oxidation resistance and is added as needed in 0.001% or more. Further, even if added in over 0.1%, the effect becomes saturated and granules of REM cause a drop in corrosion resistance, so 0.001 to 0.1% is added. If considering the workability of the products and the manufacturing cost, the lower limit is preferably made 0.002% and the upper limit is preferably made 0.05%.

[0051] The grain size number after cold rolling and annealing is made 5.0 to 9.0.

[0052] If exposing Sn adding steel to a high temperature environment, even if controlling the components by the GBSV value, the drop in toughness will not be totally eliminated. In this case, it is possible to increase the area of the grain boundaries at which the Sn segregates so as to ease the grain boundary embrittlement. For that reason, the grain size number has to be made 5 or more. However, if the grain size number is made too large, grain refinement will cause the mechanical properties to change to a low ductility and high strength, so the size is made 5.0 to 9.0. If considering optimization of the Lankford value, which governs improvement of deep drawability, and reduction of the skin roughness at the time of working, the size is preferably made 6.0 to 8.5.

[0053] Further, even if not using Sn adding steel in a high temperature environment, in the manufacturing process, if Sn segregates at the grain boundaries, it becomes a cause of a drop in toughness of the sheet product, so after annealing the cold-rolled sheet, it becomes necessary to raise the cooling rate so as to suppress grain boundary segregation. The cold-rolled strip annealing temperature is made 850°C or more where grain boundary segregation of Sn will not easily occur and is made 1100°C or less where the grain size number will not easily coarsen. At the time of cooling, it is preferable to make the cooling rate 5°C/s or more in the 800 to 600°C temperature range where grain boundary segregation of Sn proceeds in a short time.

(Example 1)

[0054] Below, examples will be used to explain the effects of the present invention, but the present invention is not limited to the conditions used in the following examples.

[0055] In this example, first, steel of each of the compositions of components which are shown in Table 1-1 and Table 1-2 was smelted and cast into a slab. This slab was heated to 1190°C, then given a final temperature in range of 800 to 950°C and hot rolled down to a thickness of 4 mm to obtain a hot rolled sheet. Note that, in Table 1-1 and Table 1-2, numerical values which are outside the scope of the present invention are underlined. The hot rolled steel sheet was cooled by aerated water cooling down to 500°C, then was wound up in a coil.

[0056] In Table 1-1 and Table 1-2, the invention examples and comparative examples not containing Ti or Mo have contents of Ti and Mo shown by the symbols "-". Further, in Table 1-1 and Table 1-2, the values of CI and GBSV of the invention examples and comparative examples not containing Ti or Mo were calculated based on the above-mentioned formula 1 and formula 2. Further, the values of CI and GBSV of the invention examples and comparative examples containing Ti and Mo were calculated based on the above-mentioned formula 1' and formula 2'.

[0057] After this, the hot rolled coil was annealed at 900 to 1100°C and was cooled down to ordinary temperature. At this time, the average cooling rate in the range of 800 to 550°C was made 20°C/s or more. Next, the hot rolled annealed sheet was pickled and cold-rolled to obtain sheet thickness 1.5 mm sheet, then the cold-rolled sheet was annealed and pickled to obtain a sheet product. Nos. 1 to 34 in Table 1-1 are invention examples, while Nos. 35 to 56 in Table 1-2 are comparative examples.

[0058] The thus obtained hot rolled annealed sheet was heat treated at 700°C for 1 hour (L-value: 19460), then was subjected to a Charpy impact test according to JIS Z 2242 and was measured for ductile brittle transition temperature (DBTT). The measurement results are shown in Table 2-1 and Table 2-2. Further, the test piece in this embodiment is a subsize test piece of the thickness of the hot rolled annealed sheet as is, and so the absorption energy was divided by the cross-sectional area (units: cm^2) to compare and evaluate the toughnesses of the hot rolled annealed sheets in the examples. Note that, the criteria for evaluation of toughness was a ductility-brittleness transition temperature (DBTT) of 150°C or less as being "good".

[0059] Further, from the hot rolled annealed sheet, 14x4x4 mm test pieces for Auger electron spectroscopy (AES) were prepared. At the center parts of the test pieces in the longitudinal direction, notches of a depth of 1 mm and a width of 0.2 mm were formed. The test pieces were cooled by liquid nitrogen in the AES apparatus under super-high vacuum and struck to make them break, then measured for concentration of Sn at the grain boundary fracture surfaces. The measurement results are shown as "Grain boundary Sn concentration (at%)" in Tables 2-1 and 2-2. For the AES apparatus, a SAM-670 (made by PHI, Model FE) was used. The beam size was made 0.05 μm. The concentration was calibrated so that the analysis value at the cleavage fracture surface becomes the same as the concentration of the base material. Auger electrons are emitted not only from the most superficial surface of the grain boundary fracture surface, but also from several nm deep. Therefore, with this method, while not the accurate concentration of Sn at the grain boundaries, as a general measurement value, using this technique, 2 at% or less was deemed as good.

[0060] Furthermore, the hot rolled annealed sheet was cold-rolled down to 1.5 mm, was annealed at 840 to 980°C for 100 seconds, then was pickled. The cold-rolled annealed sheet was welded by MIG bead-on-plate welding and was subjected to a sulfuric acid-copper sulfate corrosion test of stainless steel prescribed in JIS G 0575 to investigate the presence of any sensitization of the weld HAZ. However, the sulfuric acid concentration was made 0.5% and the test time was made 24 hours. Sheets exhibiting grain boundary corrosion were deemed as failed in corrosion resistance. The results of evaluation are shown as "Improved Strauss test" in Tables 2-1 and 2-2.

[0061] Further, the surfaces of the cold-rolled, annealed, and pickled sheets were polished by #600 paper, then treated by the salt spray test method prescribed in JIS Z 2371 for 24 hours and checked for any rust. Sheets exhibiting rust were deemed as failed. The results of evaluation are shown as "Salt spray test" in Table 2-1 and Table 2-2.

[0062] Further, the heat treatment conditions of the hot rolled annealed sheets were changed and similar tests were run as the items described in Table 2-1 and Table 2-2. The results are shown in Table 3. Part of the steels which are shown in Table 3 were evaluated by a repeated dry/wet test. The test solution was made one containing nitrate ions NO_3^-: 100 ppm, sulfate ions SO_4^{2-} : 10 ppm, and chloride ions Cl^-: 10 ppm and having a pH=2.5. A test tube of an outside diameter of 15 mm, a height of 100 mm, and a thickness of 0.8 mm was filled with the test solution to 10 ml. Into this, the different types of stainless steels obtained by cutting into 1 "t" ×15×100 mm pieces and wet-polishing the entire surface by #600 emery paper were half-immersed. This test tube was inserted in an 80°C warm bath. The sample, which was completely dried after the elapse of 24 hours, was lightly washed by distilled water, then a newly washed test tube was again filled with the test solution to half-immerse the sample again and was held at 80°C for 24 hours. This was performed for 14 cycles.

[0063] Further, the annealing conditions of the cold-rolled annealed sheet were changed to obtain 1.5 mm sheet products. These were subjected to aging treatment at 600°C for 1 week, then were subjected to a V-notch Charpy impact test in that thickness as is. The results are shown in Table 4. At this time, the ductile brittle transition temperature becoming -20°C or less was made the passing condition.

Table 1-1

	No.	C	Si	Mn	P	S	Cr	Sn	Nb	N	Ti	Mo	Others	CI	GBSV
Inv. ex.	1	0.006	0.15	0.20	0.027	0.001	17.2	0.20	0.40	0.0070	-	-		16.0	-0.8
	2	0.006	0.10	0.11	0.028	0.001	16.8	0.50	0.17	0.0046	-	-		8.3	0.0
	2-2.	0.005	0.07	0.06	0.019	0.001	16.6	0.32	0.12	0.0098	0.10	-		11.0	0.0
	3	0.015	0.14	0.21	0.017	0.001	17.1	0.21	0.60	0.0104	-	-	-	12.3	-1.2
	4	0.006	0.25	0.25	0.025	0.001	17.5	0.21	0.40	0.0072	-	-	-	15.8	-0.8
	5	0.005	1.50	0.21	0.026	0.001	17.2	0.15	0.28	0.0078	-	-	-	11.4	-0.6
	6	0.003	0.45	0.28	0.027	0.002	17.1	0.21	0.13	0.0048	0.1	-	Cu: 0.25%, Ni: 0.25%	21.5	-0.2
	7	0.010	0.35	1.50	0.026	0.001	17.6	0.22	0.40	0.0084	-	-	-	11.3	-0.8
	8	0.005	0.32	0.23	0.029	0.001	17.5	0.28	0.41	0.0085	-	-	Cu: 0.6%	15.8	-0.7
	9	0.003	0.25	0.21	0.035	0.001	17.4	0.20	0.40	0.0092	-	-	-	17.0	-0.8
	10	0.006	0.10	0.18	0.027	0.015	18.1	0.21	0.40	0.0089	-	-	-	14.0	-0.8
	11	0.008	0.18	0.13	0.027	0.001	13.0	0.12	0.41	0.0058	-	-	-	15.4	-0.9
	12	0.011	0.18	0.12	0.027	0.001	21.0	0.32	0.42	0.0069	-	-	-	12.2	-0.7
	13	0.010	0.21	0.11	0.025	0.002	17.5	0.01	0.40	0.0111	-	-	-	9.9	-1.0
	14	0.008	0.20	0.10	0.027	0.001	17.5	0.50	0.39	0.0086	-	-	-	12.2	-0.5
	15	0.002	0.23	0.08	0.019	0.001	17.4	0.01	0.05	0.0044	0.1	-	-	19.7	-0.2
	16	0.015	0.25	0.15	0.027	0.003	17.1	0.23	0.60	0.0054	-	-	-	15.3	-1.2
	17	0.012	0.30	0.21	0.021	0.001	17.6	0.28	0.41	0.0117	-	-	Ni: 0.5%	9.0	-0.7
	18	0.014	0.31	0.18	0.027	0.001	17.3	0.25	0.38	0.0092	0.32	-	-	22.3	-0.4
	19	0.006	0.32	0.21	0.026	0.001	17.2	0.25	0.41	0.0060	-	-	-	17.8	-0.8
	20	0.011	0.18	0.21	0.027	0.001	17.5	0.23	0.60	0.0200	-	-	-	10.1	-1.2
	21	0.012	0.21	0.30	0.028	0.002	17.4	0.21	0.40	0.0059	-	-	-	11.6	-0.8
	22	0.005	0.29	0.31	0.027	0.001	17.2	0.20	0.40	0.0087	-	2.0	-	15.2	-1.4
	23	0.008	0.21	0.21	0.027	0.001	17.2	0.21	0.40	0.0135	-	-	v: 0.3%	9.7	-0.8
	24	0.003	0.22	0.15	0.026	0.001	17.2	0.25	0.41	0.0052	-	-	Ni: 1.5%	26.0	-0.8

(continued)

	No.	C	Si	Mn	P	S	Cr	Sn	Nb	N	Ti	Mo	Others	CI	GBSV
	25	0.008	0.20	0.18	0.027	0.003	17.3	0.21	0.41	0.0185	-	-	Cu: 1.5%	8.0	-0.8
	26	0.010	0.21	0.19	0.025	0.001	17.5	0.21	0.38	0.0110	-	-	B: 0.0020%	9.4	-0.8
	27	0.010	0.18	0.21	0.028	0.001	16.9	0.22	0.41	0.0097	-	-	Al: 3.0%	10.8	-0.8
	28	0.010	0.15	0.17	0.027	0.001	16.8	0.22	0.40	0.0053	-	-	W: 0.2%	13.6	-0.8
	29	0.014	0.16	0.10	0.024	0.001	16.5	0.28	0.42	0.0064	-	-	Sb: 0.5%	10.7	-0.8
	30	0.015	0.17	0.11	0.027	0.001	17.1	0.30	0.41	0.0038	-	-	Zr: 0.2%	11.3	-0.7
	31	0.007	0.21	0.18	0.025	0.005	17.5	0.31	0.41	0.0082	-	-	Co: 0.5%	14.0	-0.7
	32	0.003	0.22	0.21	0.027	0.001	17.4	0.21	0.15	0.0060	0.10	-	Mg: 0.01%, Cu: 0.25%, Ni: 0.25%	19.8	-0.2
	33	0.004	0.23	0.32	0.026	0.005	14.1	0.10	0.15	0.0063	0.10	-	Ca: 0.01%	17.3	-0.3
	33-2.	0.003	0.12	0.10	0.024	0.001	14.4	0.11	0.15	0.0101	0.10	-	B: 0.0005%	13.6	-0.3
	34	0.005	0.35	0.28	0.027	0.001	17.9	0.31	0.42	0.0070	-	-	REM: 0.1%	18.2	-0.7

Table 1-2

	No.	C	Si	Mn	P	S	Cr	Sn	Nb	N	Ti	Mo	Others	Cl	GBSV
Comp. ex.	35	0.016	0.21	0.21	0.028	0.003	17.5	0.41	0.00	0.0082	0.25	-	-	10.3	0.5
	36	0.008	1. 60	0.22	0.025	0.001	17.2	0.35	0.41	0.0074	-	-	-	13.8	-0.7
	37	0.007	0.15	1.60	0.025	0.001	17.2	0.36	0.40	0.0065	-	-	-	15.4	-0.6
	38	0.005	0.12	0.20	0.040	0.002	17.5	0.41	0.40	0.0078	-	-	-	16.3	-0.6
	39	0.001	0.13	0.20	0.028	0.020	16.8	0.41	0.01	0.0074	0.21		-	25.6	0.4
	40	0.012	0.14	0.31	0.028	0.002	12.5	0.42	0.04	0.0071	0.15	-	-	8.9	0.3
	41	0.008	0.15	0.28	0.027	0.002	22.0	0.40	0.01	0.0082	0.21	-	-	13.3	0.4
	42	0.007	0.12	0.25	0.028	0.001	17.5	0.005	0.00	0.0085	0.15	-	-	9.7	0.0
	43	0.006	0.21	0.25	0.026	0.003	17.2	0.60	0.20	0.0087	0.1	-	-	13.9	0.1
	44	0.005	0.21	0.25	0.027	0.001	17.2	0.40	0.01	0.0074	-	-	-	0.4	0.2
	45	0.003	0.22	0.24	0.027	0.002	17.1	0.21	0.80	0.0065	-	-	-	43.8	-1.6
	46	0.004	0.25	0.21	0.024	0.001	17.2	0.40	0.25	0.0062	0.21	-	-	23.1	0.3
	47	0.007	0.21	0.25	0.018	0.002	17.1	0.30	0.40	0.0058	0.33	-	-	42.0	-0.4
	48	0.004	0.18	0.21	0.026	0.002	17.3	0.31	0.41	0.0250	-	-	-	7.4	-0.7
	49	0.005	0.21	0.21	0.027	0.001	17.5	0.30	0.05	0.0087	0.40	-	-	31.1	0.4
	50	0.006	0.21	0.26	0.027	0.002	17.2	0.35	0.05	0.0091	0.35	-	-	24.9	0.4
	51	0.007	0.21	0.25	0.028	0.002	17.1	0.36	0.42	0.0082	-	2.5	-	14.4	-1.4
	52	0.005	0.25	0.21	0.025	0.003	17.2	0.37	0.41	0.0058	-	-	Ni: 2.2	19.7	-0.7
	53	0.006	0.24	0.25	0.026	0.001	17.1	0.39	0.40	0.0097	-	-	Cu: 1.8	13.2	-0.6
	54	0.006	0.24	0.25	0.027	0.002	17.3	0.41	0.40	0.0079	-	-	V: 0.5	15.0	-0.6
	55	0.006	0.15	0.21	0.024	0.002	17.0	0.42	0.41	0.0082	-	-	B: 0.003	15.0	-0.6
	56	0.007	0.18	0.21	0.027	0.001	17.1	0.43	0.48	0.0081	-	-	Al: 3.5%	16.5	-0.7

Table 2-1

	No.	Grain boundary Sn concentration (at%)	Ductile brittle transition temperature (°C)	Improved Strauss test	Salt spray test	Other properties
Inv. ex.	1	1.4	28	Pass	Pass	
	2	1.1	30	Pass	Pass	
	2-2.	1.5	110	Pass	Pass	
	3	1.2	90	Pass	Pass	
	4	0.9	25	Pass	Pass	
	5	1.0	35	Pass	Pass	
	6	0.9	32	Pass	Pass	
	7	1.0	30	Pass	Pass	
	8	1.2	28	Pass	Pass	
	9	0.9	35	Pass	Pass	
	10	1.8	30	Pass	Pass	
	11	1.9	40	Pass	Pass	
	12	0.8	62	Pass	Pass	
	13	1.2	-10	Pass	Pass	
	14	1.3	140	Pass	Pass	
	15	1.4	27	Pass	Pass	
	16	1.6	110	Pass	Pass	
	17	1.7	85	Pass	Pass	
	18	1.4	145	Pass	Pass	
	19	1.3	36	Pass	Pass	
	20	1.1	32	Pass	Pass	
	21	1.2	30	Pass	Pass	
	22	1.7	40	Pass	Pass	
	23	1.5	36	Pass	Pass	
	24	1.1	29	Pass	Pass	
	25	0.8	10	Pass	Pass	
	26	0.8	28	Pass	Pass	
	27	1.5	25	Pass	Pass	
	28	1.1	26	Pass	Pass	
	29	0.9	20	Pass	Pass	
	30	0.7	10	Pass	Pass	
	31	0.6	16	Pass	Pass	
	32	1.5	10	Pass	Pass	
	33	1.5	20	Pass	Pass	
	33-2.	1.3	30	Pass	Pass	

(continued)

	No.	Grain boundary Sn concentration (at%)	Ductile brittle transition temperature (°C)	Improved Strauss test	Salt spray test	Other properties
	34	1.4	24	Pass	Pass	

Table 2-2

	No.	Grain boundary Sn concentration (at%)	Ductile brittle transition temperature (°C)	Improved Strauss test	Salt spray test	Other properties
Comp. ex.	35	3.5	270	Pass	Pass	
	36	1.8	80	Pass	Pass	Poor mechanical properties
	37	1.5	25	Pass	Pass	Poor mechanical properties
	38	1.9	45	Pass	Pass	Poor mechanical properties
	39	5.0	270	Pass	Fail	
	40	2.8	230	Pass	Fail	
	41	3.9	205	Pass	Pass	surface defects
	42	0.5	15	Pass	Fail	
	43	7.1	350	Pass	Pass	
	44	3.5	240	Fail	Fail	
	45	1.7	90	Fail	Fail	Defects due to large inclusions
	46	3.4	210	Pass	Pass	
	47	2.4	18	Fail	Fail	Defects due to large inclusions
	48	1.8	40	Fail	Fail	
	49	1.7	35	Pass	Pass	Defects due to large inclusions
	50	1.7	170	Pass	Pass	Defects due to large inclusions
	51	1.6	38	Pass	Pass	Poor mechanical properties
	52	1.0	40	Pass	Pass	Poor mechanical properties
	53	0.9	50	Pass	Fail	Poor mechanical properties
	54	1.6	68	Pass	Pass	Poor mechanical properties
	55	1.9	20	Fail	Fail	
	56	1.7	60	Pass	Pass	surface defects

Table 3

	Code	Steel No.	Heat treatment		L-value	Grain boundary Sn concentration (at%)	Ductile-brittle transition temperature (°C)	Improved Strauss test	Salt spray test	Other properties Maximum depth of corrosion of repeated dry/wet test
			Temp. (°C)	Time (h)						
Inv. ex.	A1	6	600	168	19403	1.5	51	Pass	Pass	20 μm or less
	A2	4	650	300	20746	1.7	42	Pass	Pass	50 μm or less
	A3	4	700	0.5	19167	0.9	28	Pass	Pass	50 μm or less
	A4	4	700	1	19460	1.4	52	Pass	Pass	50 μm or less
	A5	4	750	0.3	19925	0.8	32	Pass	Pass	50 μm or less
	A7	6	650	300	20746	1.2	41	Pass	Pass	20 μm or less
	A8	6	700	0.5	19167	0.7	21	Pass	Pass	20 μm or less
	A9	6	700	1	19460	0.9	32	Pass	Pass	20 μm or less
	A10	6	750	0.3	19925	0.7	23	Pass	Pass	20 μm or less
	A11	1	700	1	19460	1.4	28	Pass	Pass	50 μm or less
	A12	8	650	300	20746	1.6	55	Pass	Pass	20 μm or less
	A13	8	700	1	19460	1.2	28	Pass	Pass	20 μm or less
	A14	8	750	0.3	19925	0.7	24	Pass	Pass	20 μm or less
	A15	17	650	300	20746	1.9	80	Pass	Pass	20 μm or less
	A16	17	700	1	19460	1.7	85	Pass	Pass	20 μm or less
	A17	17	750	0.3	19925	0.9	50	Pass	Pass	20 μm or less
	A18	18	700	1	19460	1.4	145	Pass	Pass	50 μm or less
Comp. ex.	a1	43	650	300	20746	2.4	270	Pass	Pass	50 μm or less
	a2	43	700	1	19460	3.2	330	Pass	Pass	50 μm or less
	a3	43	750	0.5	20152	3.0	300	Pass	Pass	50 μm or less
	a4	43	700	0.1	18487	1.5	80	Pass	Pass	50 μm or less

Table 4

	Code	Steel No.	Cold-rolled sheet annealing temperature	grain size number	Cooling rate	Ductile brittle transition temperature		Other properties
			Temperature (°C)		800 to 500°C			
Inv. ex.	B1	4	850	9.0	20	-50	Pass	
	B2	4	920	8.1	50	-30	Pass	
	B3	4	940	6.3	25	-30	Pass	
	34	4	880	7.2	5	-50	Pass	
	B5	4	1100	5.0	100	-20	Pass	
Comp. ex.	b1	4	1150	4.8	5	0	Fail	
	b2	4	840	8.8	5	-20	Pass	Poor mechanical properties
	b3	4	880	7.8	2	5	Fail	
	b4	39	900	7.5	20	15	Fail	
	b5	43	900	7.6	20	10	Fail	
	b6	4	850	7.9	4	25	Fail	

[0064] As clear from Table 1-1, Table 1-2, Table 2-1, Table 2-2, and Table 3, in steels with compositions of components and grain boundary Sn concentrations according to the present invention, the ductility-brittleness transition temperatures (DBTT) evaluated by the hot rolled annealed sheets were low, the corrosion resistances evaluated by the cold-rolled annealed sheets were good, and the total elongations evaluated by a tensile test were also good ones of 30% or more. Further, surface defects also could not be observed. On the other hand, the comparative examples outside the present invention failed in at least one of the Charpy impact value (absorption energy), corrosion resistance, material quality, and surface defects. Due to this, it is learned that the heat resistance and corrosion resistance of the ferritic stainless steels in the comparative examples are inferior.

[0065] Specifically, Nos. 35, 39 to 41, 43, 44, 46, 49, and 50 had GBSV's larger than 0 and had amounts of grain boundary segregation of Sn after performing heat treatment at 700°C for 1 hour larger than 2 at% by measurement by AES. The toughnesses were low as shown by the ductile brittle transition temperatures being over 150°C. Nos. 43 to 45, and 47 to 49 had CI values of less than 8, so the grain boundary corrosion resistance evaluated by the improved Strauss test and the rust resistance evaluated by the salt spray test were inferior. Nos. 36, 37, 38, 52, 53, and 51 were respectively high in Si, Mn, P, Ni, Cu, and Mo and were low in elongation due to solution strengthening, so were poor in mechanical properties. While No. 39 was high in S and No. 40 was low in Cr, No. 42 was low in Sn, and No. 55 was high in B, so were poor in corrosion resistances evaluated by the salt spray test. Further, No. 42 was low in Sn, so was good in toughness even if GBSV was larger than 0. No. 45 was high in Nb, while Nos. 47, 45, and 50 were high in Ti and No. 54 was high in V, so defects occurred due to large inclusions and these were judged poor in quality. No. 41 was high in Cr, while No. 56 was high in Al and had surface defect, so were judged poor in quality.

[0066] In Table 3, references a1 to a3 all had grain boundary Sn concentrations of 2 at% or more after performing heat treatment giving L-values of 1.91×10^4 or more, and so all of a1 to a3 had DBTTs over 150°C and had poor toughnesses. Further, as with a4, if the L-value is less than 1.91×10^4, Sn does not segregate at the grain boundaries, so the DBTT is a low 80°C, but if the L-value becomes large, Sn segregates at the grain boundaries and the DBTT rises, so it was confirmed that it is necessary to evaluate the segregation of Sn at grain boundaries by an L-value of 1.91×10^4 or more.

[0067] Further, steels in the range of the present invention all had maximum depths of corrosion of 50 μm or less. Note that, in the case of steel containing Ni or Cu in the range of the present invention, the maximum depth of corrosion was 20 μm or less or an extremely good result for corrosion resistance.

[0068] Further, as will be clear from Table 4, sheets having compositions of components, grain size numbers after cold-rolling and annealing, cold-rolled strip annealing temperatures, and cooling rates according to the present invention exhibited low ductile brittle transition temperatures and good toughness.

[0069] On the other hand, b1 had a cold-rolled strip annealing temperature of 1100°C or more, and a grain size number which is defined by the Microscope Type Test Method of Crystal Granularity of Steel set down in JIS G 0551 was less than 5.0. Therefore, the cooling rate at 800 to 500°C was 20°C/s. However, the ductile brittle transition temperature was high. The reference b2 had a cold-rolled strip annealing temperature of less than 850°C and a grain size number of over 9.0, so the mechanical properties were poor. Further, b3 and b6 had cooling rates of less than 5°C/s at 800 to 500, and so the annealing temperature was suitable and the grain size number was also a suitable 8.0. However, the ductile brittle transition temperature was high. Furthermore, b4 and b5 were compositions of the comparative examples, and so the cold-rolled strip annealing temperatures, cooling rates, and grain size numbers were in suitable ranges, but the ductile brittle transition temperatures were high.

[0070] From these results, it was possible to confirm the above findings. Further, it was possible to verify the grounds for limiting the compositions and constitutions of the steels explained above.

Industrial Applicability

[0071] As clear from the above explanation, according to the ferritic stainless steel containing Sn of the present invention, the stabilizing elements Nb and Ti are optimized, so it becomes possible to produce stainless steel sheet which has little deterioration in toughness even if used at a high temperature and further is excellent in corrosion resistance of the sheet. Further, by applying the material according to the present invention to particularly the exhaust system parts of automobiles and motorcycles, it becomes possible to extend the service life of the parts and thereby raise the degree of contribution to society in general. That is, the present invention has sufficient applicability in industry.

Claims

1. Ferritic stainless steel containing, by mass %,
   Cr: 13.0 to 21.0%,
   Sn: 0.01 to 0.50%, and
   Nb: 0.05 to 0.60%,
   restricted to:

   C: 0.015% or less,
   Si: 1.5% or less,
   Mn: 1.5% or less,
   N: 0.020% or less,
   P: 0.035% or less, and
   S: 0.015% or less,

   containing a balance of Fe and unavoidable impurities,
   satisfying formula 1 and formula 2, and
   having a grain boundary Sn concentration of 2 at% or less when performing heat treatment at a temperature of 600 to 750°C so that an L value shown by formula 3 becomes 1.91×10^4 or more:

$$8\leq CI=0.52Nb/(C+N)\leq 26 \cdots (\text{formula } 1)$$

$$GBSV=Sn-2Nb-0.2\leq 0 \cdots (\text{formula } 2)$$

$$L=(273+T)(\log(t)+20) \cdots (\text{formula } 3)$$

   where, T: temperature (°C), t: time (h)

2. The ferritic stainless steel according to claim 1, wherein said heat treatment is performed at a temperature of 700°C for 1 hour.

3. The ferritic stainless steel according to claim 1 or 2 further containing, by mass%, one or more of
Ti: 0.32% or less,
Ni: 1.5% or less,
Cu: 1.5% or less,
Mo: 2.0% or less,
V: 0.3% or less,
Al: 0.3% or less, and
B: 0.0020% or less:

where formula 1 and formula 2 are replaced by formula 1' and formula 2'.

$$8 \leq CI = (Ti + 0.52Nb)/(C + N) \leq 26 \cdots \text{formula 1'}$$

$$GBSV = Sn + Ti - 2Nb - 0.3Mo - 0.2 \leq 0 \cdots \text{formula 2'}$$

4. The ferritic stainless steel according to any one of claims 1 to 3 further containing, by mass%, one or more of
W: 0.20% or less,
Zr: 0.20% or less,
Sb: 0.5% or less,
Co: 0.5% or less,
Ca: 0.01% or less,
Mg: 0.01% or less, and
REM: 0.1% or less.

5. The ferritic stainless steel according to any one of claims 1 to 4 wherein a crystal grain size after annealing the cold-rolled sheet is made 5.0 to 9.0.

6. A method of production of ferritic stainless steel according to any one of claims 1 to 5 comprising annealing stainless steel of a composition of claim 1, 3, or 4 at a cold-rolled strip annealing temperature of 850°C to 1100°C and then cooling from cold-rolled strip annealing temperature by a cooling rate of 5°C/s or more in the temperature range of 800 to 500°C.

FIG. 1

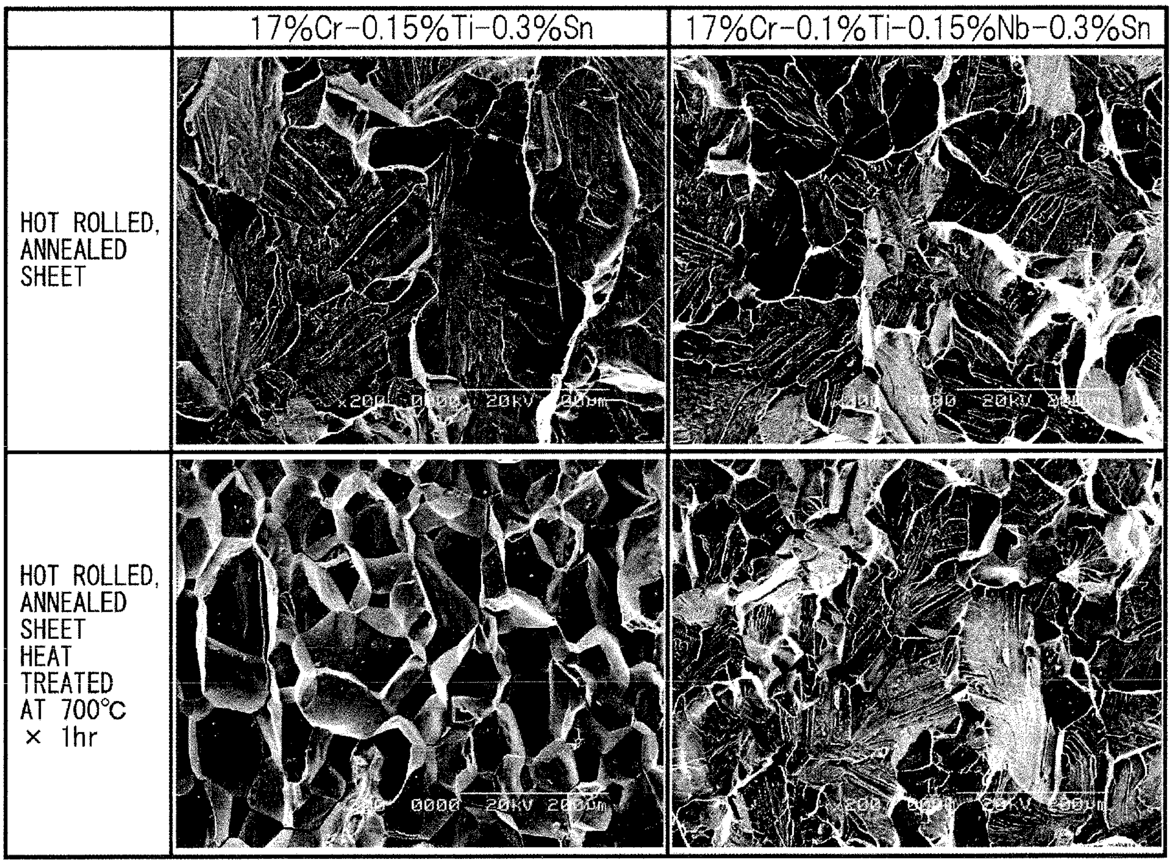

17%Cr-0.15%Ti-0.3%Sn
17%Cr-0.1%Ti-0.15%Nb-0.3%Sn
HOT ROLLED, ANNEALED SHEET
HOT ROLLED, ANNEALED SHEET HEAT TREATED AT 700°C × 1hr
×200 0000 20kV 200μm

FIG. 2

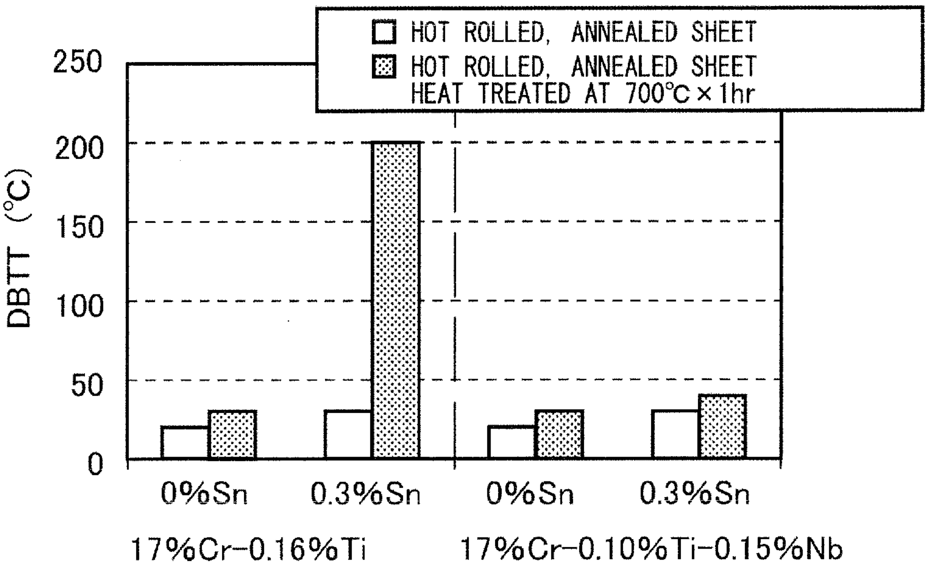

□ HOT ROLLED, ANNEALED SHEET
▨ HOT ROLLED, ANNEALED SHEET HEAT TREATED AT 700°C × 1hr
DBTT (°C)
250
200
150
100
50
0
0%Sn
0.3%Sn
0%Sn
0.3%Sn
17%Cr-0.16%Ti
17%Cr-0.10%Ti-0.15%Nb

FIG. 3

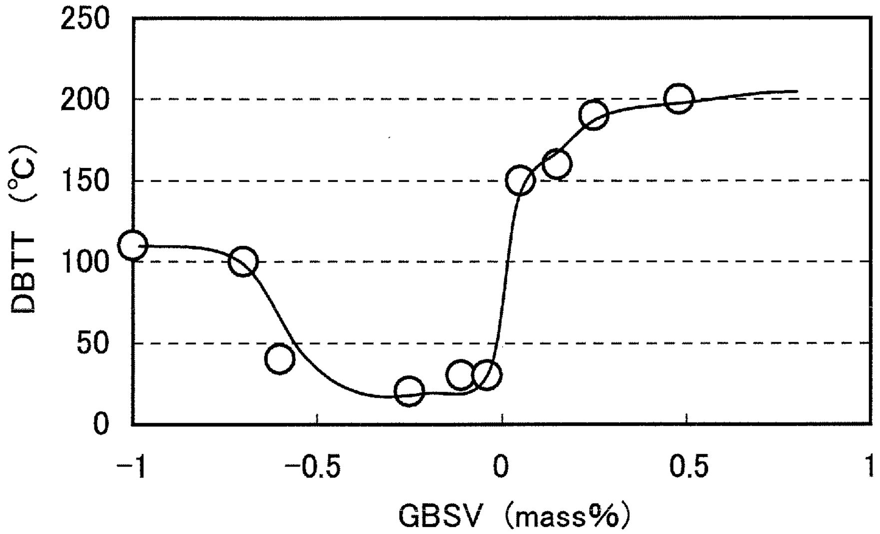
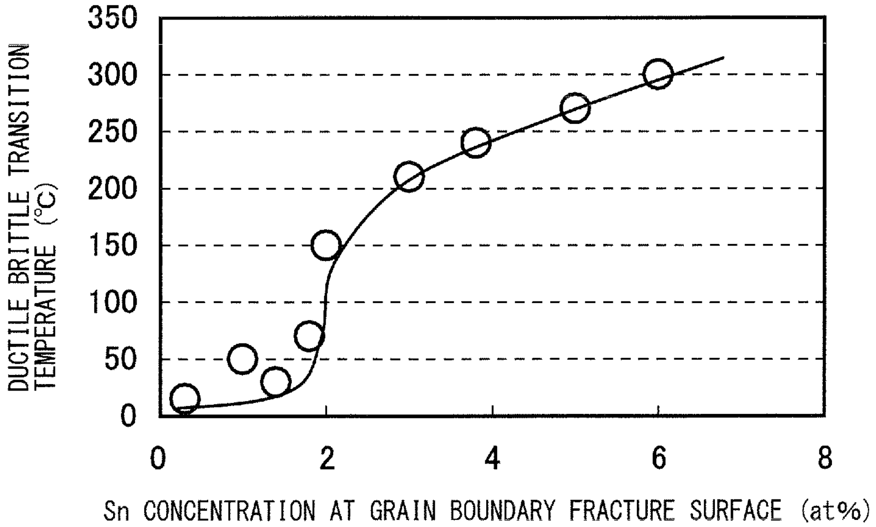

250
200
150
100
50
0
DBTT (°C)
−1
−0.5
0
0.5
1
GBSV (mass%)

FIG. 4


350
300
250
200
150
100
50
0
DUCTILE BRITTLE TRANSITION TEMPERATURE (°C)
0
2
4
6
8
Sn CONCENTRATION AT GRAIN BOUNDARY FRACTURE SURFACE (at%)

INTERNATIONAL SEARCH REPORT	International application No. PCT/JP2013/079461

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21D9/46*(2006.01)i, *C22C38/26*(2006.01)i, *C22C38/60*(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00, C21D9/46, C22C38/26, C22C38/60

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2013
Kokai Jitsuyo Shinan Koho	1971-2013	Toroku Jitsuyo Shinan Koho	1994-2013

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2012-197071 A (Nippon Steel & Sumikin Stainless Steel Corp.), 18 October 2012 (18.10.2012), paragraphs [0031], [0033] to [0036]; tables 1-1, 1-2 & WO 2012/086706 A1	1-4 5,6
X Y	JP 2012-193392 A (Nippon Steel & Sumikin Stainless Steel Corp.), 11 October 2012 (11.10.2012), paragraphs [0040] to [0044]; table 1 & WO 2012/124528 A1 & TW 201245467 A	1-4 5,6

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 25 November, 2013 (25.11.13)	Date of mailing of the international search report 03 December, 2013 (03.12.13)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/079461

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2012-207298 A (Nippon Steel & Sumikin Stainless Steel Corp.), 25 October 2012 (25.10.2012), paragraph [0009] (Family: none)	5,6

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2000169943 A **[0004]**
- JP H1192872 A **[0004]**