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

(72) Inventors:
- **HAMADA, Junichi**
  Tokyo 100-0004 (JP)
- **KANNO, Norihiro**
  Tokyo 100-0004 (JP)
- **TAKAHASHI, Akihiko**
  Tokyo 100-0004 (JP)
- **INOUE, Yoshiharu**
  Tokyo 100-8071 (JP)
- **TERAOKA, Shinichi**
  Tokyo 100-8071 (JP)

(74) Representative: **Vossius & Partner**
Siebertstrasse 4
81675 München (DE)

(54) FERRITIC STAINLESS STEEL PLATE HAVING EXCELLENT HEAT RESISTANCE AND EXCELLENT WORKABILITY

(57) Ferritic stainless steel excellent in heat resistance and workability which contains, by mass%, C: 0.02% or less, N: 0.02% or less, Si: 2% or less, Mn: 2% or less, Cr: 10 to 20%, Cu: 0.4 to 3%, Ti: 0.01 to 0.5%, and B: 0.0002 to 0.0030% and has a balance of Fe and unavoidable impurities.

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Description

Technical Field

[0001] The present invention relates to a ferritic stainless steel sheet excellent in heat resistance which is optimal for use in particular for an exhaust system member in which high temperature strength or oxidation resistance is required.

Background Art

[0002] An exhaust manifold, front pipe, center pipe, or other exhaust system member of an automobile carries high temperature exhaust gas which is exhausted from the engine. For this reason, the material forming the exhaust system member requires oxidation resistance, high temperature strength, heat fatigue characteristics, and other various characteristics.

[0003] In the past, cast iron was generally used for automobile exhaust members, but from the viewpoints of meeting tougher exhaust gas restrictions, improving engine performance, reducing the weight of the chassis, etc., exhaust manifolds made of stainless steel are being used.

[0004] The exhaust gas temperature differs depending on the car model or engine structure, but usually is 600 to 800°C or so. A material which has an excellent high temperature strength and oxidation resistance in an environment of long term use in such a temperature region has been demanded.

[0005] Among stainless steels, austenitic stainless steel is excellent in heat resistance and workability. However, austenitic stainless steel has a large coefficient of heat expansion, so when applied to a member like an exhaust manifold which is repeatedly subjected to heating and cooling, thermal fatigue failure easily occurs.

[0006] Ferritic stainless steel is smaller in coefficient of heat expansion compared with austenitic stainless steel, so is better in heat fatigue characteristics and scale peeling resistance. It does not contain Ni, so is also lower in material cost compared with austenitic stainless steel and is being generally used.

[0007] Ferritic stainless steel is lower than high temperature strength compared with austenitic stainless steel. For this reason, the art of improving the high temperature strength has been developed. For example, there are SUS430J1 (Nb steel), Nb-Si steel, and SUS444 (Nb-Mo steel). In each case, Nb is added. These use solution strengthening or precipitation strengthening by Nb for raising the high temperature strength.

[0008] If adding Nb, the recrystallization temperature of stainless steel becomes higher, so when producing steel sheet, it is necessary to raise the annealing temperature.

[0009] Stainless steel becomes harder due to the addition of Nb, so after hot rolling, it is necessary to anneal the hot rolled sheet to soften it, then cold roll it.

[0010] Due to the Nb precipitates formed in the hot rolling process, the toughness falls and cracking or fracture sometimes occurs in the production process.

[0011] In Nb steel, the product sheet easily becomes harder and easily falls in elongation and, furthermore, the r-value, an indicator of deep drawability, is low. This is because due to the presence of the solute Nb and precipitated Nb, the hardening at ordinary temperature and growth of the recrystallized texture are suppressed. For this reason, the press formability when forming exhaust parts falls and the freedom of shape becomes smaller.

[0012] In the above way, Nb steel is inferior in productivity, manufacturability, and workability of the steel sheet. Nb is high in alloy cost, so addition of Nb also results in higher production costs.

[0013] Furthermore, the Mo which is added to SUS444 is high in alloy cost, so the part costs remarkably rises.

[0014] If it were possible to increase the high temperature strength by an additive element other than Nb, it is possible to suppress the amount of addition of Nb, so it becomes possible to provide heat resistant ferritic stainless steel sheet which is low in cost and excellent in workability.

[0015] As an additive element other than Nb and Mo which contributes to improvement of high temperature strength, there is Cu.

[0016] PLT 1 discloses addition of 0.5% or less of Cu for improvement of the low temperature toughness. This is not addition of Cu from the viewpoint of heat resistance.

[0017] PLT 2 discloses the art for utilizing the action of steel in improving the corrosion resistance and weatherability. This is not addition of Cu from the viewpoint of heat resistance.

[0018] PLT's 3 to 6 discloses the art of precipitation hardening by Cu precipitates to improve the high temperature strength in a 600°C or 700 to 800°C temperature region. However, these are all composite addition with Nb, are inferior in manufacturability and workability, and are high in cost.

[0019] The prior art for improvement of the high temperature strength by addition of Cu utilizes Cu precipitates. When Cu precipitates are exposed to a high temperature for a long time, aggregation and combination of the precipitates rapidly occur, so the precipitation strengthening ability remarkably falls.

[0020] When subjected to a heat cycle accompanying startup and stopping of an engine such as like in an exhaust manifold, long term use results in a remarkable drop in high temperature strength and the danger of thermal fatigue failure.

[0021] In particular, in the case of a composition of ingredients in which a large amount of Nb is added, at the time of high temperature heating, Cu precipitates form at the interface of the coarse precipitates (Fe_2Nb) called "Laves phases" and the base phase, so the effect of precipitation strengthening by the Cu precipitates cannot be obtained.

[0022] PLT 6 discloses the art of using composite addition of Nb-Cu-B to cause precipitation of fine Cu. However, even with this method, composite precipitation with the Laves phases cannot be avoided. Further, it adds a fine amount of Mo, so the workability becomes inferior and the cost becomes high.

[0023] In the above way, there are examples of causing the precipitation of Cu for improving the high temperature strength, but in the prior art, fine precipitation of Cu has not yet been achieved. The results were insufficient from the viewpoints of workability and cost as well.

[0024] Further, as steel containing B, PLT's 7 to 9 disclose ferritic stainless steel excellent in high temperature characteristics. These all add B for improving the workability and do not disclose addition from the viewpoint of the heat resistance.

Citation List

Patent Literature

[0025]

PLT 1: Japanese Patent Publication (A) No. 2006-37176
PLT 2: Japanese Patent No. 3446667
PLT 3: WO2003/004714
PLT 4: Japanese Patent No. 3468156
PLT 5: Japanese Patent No. 3397167
PLT 6: Japanese Parent Publication (A) No. 2008-240143
PLT 7: Japanese Patent Publication (A) No. 9-279312
PLT 8: Japanese Patent Publication (A) No. 2000-169943
PLT 9: Japanese Patent Publication (A) No. 10-204590

Summary of Invention

Technical Problem

[0026] The present invention has as its object the inexpensive provision of ferritic stainless steel excellent in heat resistance and workability which may be used in particular under a heat environment of a maximum temperature of the exhaust gas of 600 to 800°C.

Solution to Problem

[0027] In the present invention, the object is to improve the high temperature characteristics of ferritic stainless steel sheet by adding Cu in steel ingredients not including Nb and causing the fine dispersion of Cu precipitates.

[0028] Therefore, the inventors focused on the use of composite addition of Ti-Cu-B and resultant increased fineness of precipitates.

[0029] The inventors investigated in detail the strength at 500°C to 800°C or so and the ordinary temperature ductility of steel to which no Nb is added (or a small amount is added) and obtained the following discoveries.

[0030] In the case of Cu steel, in the range of 500°C to 800°C or so, a large amount of Cu precipitate forms, so the method of controlling the form of the precipitates is effective for improving the high temperature strength.

[0031] Specifically, by composite addition of Ti and Cu and, furthermore, addition of B, the Cu precipitates uniformly finely form and it becomes possible to utilize precipitation strengthening and suppress a drop in strength due to aging heat treatment. This is effective for the durable stability of parts such as exhaust members which are repeatedly subjected to a heat cycle and are used over long periods of time.

[0032] Even when adding Cu to Nb steel, the Cu precipitates form and act to strengthen the steel, but simultaneously precipitates of Fe and Nb called the Laves phases (Fe_2Nb) are formed. In Mo steel as well, precipitates of Fe and Mo (Fe_2Mo) are similarly formed.

[0033] In this case, Cu compositely precipitates at the interface between the coarse Laves phases and base phase, so the result does not become fine precipitation. Further, depending on the temperature conditions, the Cu precipitates rapidly coarsen along with the elapse of time.

[0034] In the case of such a mode of precipitation, the effect of the precipitation strengthening falls, so sufficient high temperature strength cannot be obtained and the durability becomes lower.

[0035] Based on the above discovery, the inventors caused the sole formation of fine Cu precipitates so as to obtain the effect of precipitation strengthening and suppressed the coarsening of Cu precipitates by using the art of fine precipitation where composite precipitation of the Laves phases and Cu does not occur so as to provide ferritic stainless steel which is inexpensive and exhibits heat resistance.

[0036] The gist of the present invention is as follow:

(1) Ferritic stainless steel excellent in heat resistance and workability which contains, by mass%,
C: 0.02% or less,
N: 0.02% or less,
Si: 2% or less,
Mn: 2% or less,
Cr: 10 to 20%,
Cu: 0.4 to 3%,
Ti: 0.01 to 0.5%, and
B: 0.0002 to 0.0030% and
has a balance of Fe and unavoidable impurities.

(2) Ferritic stainless steel excellent in heat resistance and workability as set forth in (1) which, further contains, by mass%, one or more of:

Nb: 0.01 to 0.3%,
Mo: 0.01 to 0.3%,
Al: 2.5% or less,
V: 1% or less,
Zr: 1% or less, and
Sn: 1% or less.

(3) Method of production of ferritic stainless steel excellent in heat resistance and workability characterized by hot rolling ferritic stainless steel which has a composition of ingredients of (1) or (2) so as to obtain a hot rolled sheet, then, omitting annealing of the hot rolled sheet, pickling the hot rolled sheet, cold rolling it by rolling rolls of a diameter of 400 mm or more, then performing final annealing.

Advantageous Effect of Invention

[0037] According to the present invention, even if not adding a large amount of Nb, ferritic stainless steel sheet excellent in high temperature strength and workability is obtained. The ferritic stainless steel sheet of the present invention gives a large effect in environmental protection and lowering cost of parts upon application in particular to an exhaust system member of an automobile etc.

Brief Description of Drawings

[0038] FIG. 1 is a view showing the 0.2% yield strength in a high temperature tensile test of invention steel and comparative steel.

Description of Embodiments

[0039] Below, the reason for limitation of the composition of ingredients of the ferritic stainless steel sheet of the present invention will be explained. Steel with no provision of a lower limit is included in the scope of the present invention down to the level of unavoidable impurities.

[0040] C causes deterioration of the formability and corrosion resistance and causes a drop in the high temperature strength, so the smaller the content, the better. For this reason, the content of C is made 0.02% or less, more preferably 0.009% or less. The lower limit of the content of C is not particularly provided, but excessive reduction leads to an increase in the refining cost, so the content is preferably made 0.001% or more.

[0041] N, like C, causes deterioration of the formability and corrosion resistance and causes a drop in the high temperature strength, so the smaller the content, the better. For this reason, the content of N is made 0.02% or less, more preferably 0.015% or less. The lower limit of the content of N is not particularly provided, but excessive reduction leads to an increase in the refining cost, so the content is preferably made 0.003% or more.

[0042] Si is an element which is useful as a deoxidizing agent and an element which improves the high temperature strength and oxidation resistance. The high temperature strength up to 800°C or so is improved along with an increase in the amount of Si. To obtain this effect, the content of Si is preferably made 0.1% or more. Excessive addition of Si lowers the ordinary temperature ductility, so the upper limit of the content of Si is made 2%. If considering the oxidation resistance, 0.2 to 1.0% is preferable.

[0043] Mn is an element which is added as a deoxidizing agent and contributes to the rise in the high temperature strength in the medium temperature region of 600 to 800°C or so. Further, during long term use, it forms Mn-based oxides at the surface layer and thereby contributes to improvement of scale adhesion and suppression of abnormal oxidation. If the content of Mn is over 2%, the ordinary temperature ductility falls and, furthermore, MnS is formed and thereby the corrosion resistance falls, so the upper limit of content of Mn is made 2%. If considering the high temperature ductility and scale adhesion, the content of Mn is preferably 0.1 to 1.0%.

[0044] Cr is an element essential in the present invention for securing oxidation resistance and corrosion resistance. If the content of Cr is less than 10%, that effect cannot be obtained. If the content of Cr is over 20%, a drop in workability and deterioration of the toughness are caused. For this reason, the content of Cr is made 10 to 20%. If considering the manufacturability and the high temperature ductility, 10 to 18% is preferable.

[0045] Cu in particular is an element which is effective for improvement of the high temperature strength in the medium temperature region of 600 to 800°C or so. This is due to the precipitation strengthening due to the Cu precipitates in the medium temperature region.

[0046] FIG. 1 shows the 0.2% yield strength in a high temperature tensile test of steels of the present invention (steel A, steel B, and steel C) and comparative steels (SUH409L and Nb-Si steel).

[0047] The composition of ingredients of the steel A is 0.005%C-0.007%N-0.41%Si-0.45%Mn-10.5%Cr-1.25%Cu-0.15%Ti-0.0009%B.

[0048] The composition of ingredients of the steel B is 0.006%C-0.009%N-0.88%Si-0.31%Mn-13.9%Cr-1.42%Cu-0.11%Ti-0.0005%B.

[0049] The composition of ingredients of the steel C is 0.004%C-0.011%N-0.11%Si-0.13%Mn-17.5%Cr-1.36%Cu-0.19%Ti-0.0004%B.

[0050] The comparative steels are steels which are used for general purposes.

[0051] The composition of ingredients of the SUH409L is 0.005%C-0.007%N-0.35%Si-0.50%Mn-10.5%Cr-0.15%Ti.

[0052] The composition of ingredients of the Nb-Si steel is 0.006%C-0.009%N-0.90%Si-0.35%Mn-13.8%Cr-0.45%Nb.

[0053] The high temperature tensile test was performed based on JISG0567 by running a tensile test in the rolling direction and measuring the 0.2% yield strength.

[0054] From the results of the test, it is learned that the steel A, steel B, and steel C, regardless as to the fact that Nb is not added, have high temperature strengths higher than SUH409L and Nb-Si steel in all temperature regions.

[0055] The steel of the present invention is high in strength in the 600°C or so temperature region and is particularly effective when used in an environment with a low exhaust gas temperature. The steel of the present invention can be applied even in an environment less than 600°C.

[0056] In the present invention, considering the high temperature yield strength of the Nb-Si steel being used for general purposes, a 600°C yield strength of 150 MPa or more and a 800°C yield strength of 30 MPa or more are made the required properties of the high temperature strength.

[0057] In the above way, high temperature strength becomes higher due to the precipitation strengthening due to the formation of Cu precipitate.

[0058] To obtain this effect, it is necessary to make the content of Cu 0.4% or more.

[0059] In the present invention, coarsening of the Cu precipitate due to the composition precipitation with the Laves phases is suppressed. Due to the composite addition with Ti or B, fine Cu precipitate is formed.

[0060] If the content of Cu exceeds 3%, the ordinary temperature ductility and oxidation resistance deteriorate. Further, the edge cracking in the hot rolling process becomes remarkable and the manufacturability deteriorates. For this reason, the upper limit of the content of Cu is made 3%. If considering the manufacturability, scale adhesion, weldability, etc., the content of Cu is preferably 0.5 to 2.5%.

[0061] Ti is an element which bonds with C, N, and S and improves the corrosion resistance, grain boundary corrosion resistance, ordinary temperature ductility, and deep drawability. Further, by addition of a suitable quantity in composition addition with Cu, it gives rise to uniform formation of the Cu precipitates and improves the high temperature strength and heat fatigue characteristics.

[0062] This action is believed to be because the clusters of Ti in the crystal grains or the fine precipitates of Ti form sites for formation of Cu precipitates and suppress coarse formation of Cu at the grain boundaries.

[0063] Furthermore, if adding Ti, a recrystallized texture easily grows at the time of recrystallization annealing after cold rolling, so the r-value is improved and the press formability is remarkably improved.

[0064] TO obtain these effects, the content of Ti is made 0.01% or more. If the content of Ti is over 0.5%, the amount of solute Ti increases, the ordinary temperature ductility falls, further, coarse Ti-based precipitates are formed and become starting points of cracking at the time of hole enlargement, and the press formability deteriorates. Furthermore, the oxidation resistance deteriorates. For this reason, the content of Ti is made 0.5% or less. If considering the formation of surface flaws or toughness, the content of Ti is preferably 0.05 to 0.3%.

[0065] B is an element which improves the secondary workability at the time of press-forming a product. In the present invention, by composite addition with Ti-Cu, Cu precipitates finely form and the high temperature strength is improved.

[0066] In general, B easily forms $(Fe,Cr)_{23}(C,B)_6$ or Cr_2B at a high temperature. However, in Ti-Cu composite steel, it is learned that these precipitates do not form and Cu precipitates can be made to finely form.

[0067] Cu precipitates usually form extremely finely at the initial stage of precipitation. The effect of improvement of strength is large, but coarsening occurs due to aging heat treatment and the strength greatly falls after aging. However, by adding B, coarsening of the Cu precipitates is suppressed and the stability of strength becomes higher at the time of use.

[0068] The mechanism of the effect of addition of B on increasing the fineness of Cu precipitates and suppressing coarsening is not clear, but it is believed that B precipitates at the grain boundaries and thereby suppresses the grain boundary formation and coarsening of the Cu precipitates and causes fine precipitation of Cu in the grains.

[0069] To obtain these effects, the content of B is made 0.0002% or more. If the content of B is over 0.0030%, the steel hardens, the grain boundary corrosion and oxidation resistance deteriorate, and, furthermore, weld cracking easily occurs. For this reason, the content of B is made 0.0002 to 0.0030%. If considering the corrosion resistance and production costs, 0.0003 to 0.0015% is preferable.

[0070] In addition to the above elements, in accordance with need, Nb, Mo, Al, V, and Zr may be added.

[0071] Nb may be added in accordance with need so as to improve the high temperature strength or heat fatigue characteristics. If the content of Nb is less than 0.01%, the effect of addition cannot be obtained. If adding Nb, formation of Laves phases occurs and the effect of precipitation of Cu on precipitation strengthening is suppressed, so addition of a large amount is not preferred. Further, the workability is inhibited and the elongation at break at ordinary temperature deteriorates. Therefore, the upper limit of the content of Nb is made 0.3%. From the viewpoint of productivity and manufacturability, the content of Nb is preferably 0.01 to 0.2%.

[0072] Mo is an element which further improves the high temperature strength and heat fatigue characteristics. If the content of Mo is less than 0.01%, the effect of addition cannot be obtained. If adding Mo, formation of the Laves phases occurs, the effect of precipitation of Cu on precipitation strengthening is suppressed, and, further, the ordinary temperature ductility falls, so addition of a large amount is not preferred. For this reason, the content of Mo is made 0.3% or less. The more preferable content of Mo is 0.01% to 0.2%.

[0073] When simultaneously adding Nb and Mo, the workability sometimes falls. For this reason, the total of the contents of Nb and Mo is preferably less than 0.2%.

[0074] Al is an element which is added in accordance with need as a deoxidizing element or for improving the oxidation resistance. Furthermore, it is useful for improving the strength at 600 to 700°C as a solution strengthening element. To stably obtain this effect, the content of Al is preferably made 0.01% or more. If excessively adding Al, the steel hardens, uniform elongation remarkably falls, and, furthermore, the toughness remarkably falls. For this reason, the upper limit of the content of Al is made 2.5%. If considering the occurrence of surface flaws and weldability and manufacturability, the content of Al is preferably 0.01 to 2.0%.

[0075] V forms fine carbonitrides and contributes to the improvement of the high temperature strength by the precipitation strengthening action, so is an element which is added in accordance with need. To stably obtain this effect, the content of V is preferably made 0.01% or more. If the content of V is over 1%, the precipitates coarsen, the high temperature strength falls, and the heat fatigue life falls. For this reason, the upper limit of content of V is made 1%. If considering the production cost and manufacturability, the content of V is preferably 0.08 to 0.5%.

[0076] Zr is carbonitride-forming element. It contributes to the improvement of the high temperature strength and improvement of the oxidation resistance by the increase of the amounts of solute Ti and Nb. To stably obtain this effect, the content of Zr is preferably made 0.2% or more. If the content of Zr is over 1%, the manufacturability remarkably deteriorates. For this reason, the upper limit of the content of Zr is made 1%. If considering the cost and surface quality, 0.2 to 0.6% is preferable.

[0077] Sn is an element which is large in atomic radius and which is effective for solution strengthening. It does not cause major deterioration of the mechanical properties at ordinary temperature, so is an element which is added according to need. To stably obtain this effect, the content of Sn is preferably made 0.1% or more. If the content of Sn is over 1%, the manufacturability and the weldability remarkably deteriorate. For this reason, the upper limit of the content of Sn is made 1%. If considering the oxidation resistance etc., the content of Sn is preferably 0.2 to 0.5%.

[0078] The steel of the present invention either does not have any Nb and Mo added or contains them in low concentrations and thereby secures high temperature strength. As a result, it is possible to realize improvement of the ordinary temperature elongation.

[0079] Next, the method of production of the steel of the present invention sheet will be explained. The process of production of the steel of the present invention is comprised of the steps of steelmaking, hot rolling, pickling, cold rolling, annealing, and pickling.

[0080] In steelmaking, the method of smelting steel containing the above essential ingredients and ingredients which are added in accordance with need in a converter, then performing secondary refining is preferable. The smelted molten steel is made into a slab by continuous casting or another known casting method.

[0081] The slab is heated to a predetermined temperature and is hot rolled to a predetermined sheet thickness by continuous rolling. The cold rolling of stainless steel sheet is usually reverse rolling by a Sendimir rolling mill with a roll diameter of 60 to 100 mm or so or one-directional rolling by a tandem rolling mill with a roll diameter of 400 mm or more. In each case, the slab is rolled by several passes.

[0082] In the present invention, to raise the r-value indicator of the workability, the slab is preferably cold rolled by a tandem rolling mill with roll diameters of 400 mm or more. If the roll diameters are 100 mm or less, a large amount of shear strain is introduced near the surface layer at the time of cold rolling, <111> and <554> crystal orientation growth is suppressed at the time of recrystallization annealing, and improvement of the r-value becomes difficult. By cold rolling by large size rolls, shear strain is suppressed, the above crystal orientation remarkably grows, and improvement of the r-value is contributed to.

[0083] Tandem rolling is one-directional rolling and has fewer rolling passes compared with Sendimir rolling, so is also better in productivity. If the reduction rate in the cold rolling process is low, after annealing, a recrystallized microstructure will not be obtained or excessive grain coarsening will occur causing degraded mechanical properties, so the reduction rate at the cold rolling process is preferably 30% or more.

[0084] It is possible to anneal the hot rolled sheet as is normally performed in the production of ferritic stainless steel sheet, but from the viewpoint of the improvement of the productivity, it is preferable not to anneal the hot rolled sheet.

[0085] Ordinary Nb steel gives a hard hot rolled sheet, so is annealed before cold rolling. However, the present invention steel has no Nb added or has only a small amount added, so the annealing of the hot rolled sheet can be omitted. As a result, the production costs can be reduced. Furthermore, by omitting the annealing of the hot rolled sheet, the texture after cold rolling and annealing develops and the press formability is improved by improvement of the r-value and reduction of the anisotropy.

[0086] The other steps of the method of production are not particularly limited. The hot rolling conditions, hot rolled sheet thickness, cold rolled sheet annealing temperature, atmosphere, etc. may be suitably selected. It is also possible to impart temper rolling and a tension leveler after cold rolling and annealing. Furthermore, the product sheet thickness may also be selected in accordance with the required member thickness.

[0087] The steel of the present invention has no Nb added or is low in Nb content, so the annealing temperature after cold rolling can be made a low temperature of 850 to 970°C. Due to this, the high temperature yield strength is improved compared to when the annealing temperature is over 970°C.

EXAMPLES

[0088] Steel of each of the compositions of ingredients shown in Tables 1 and 2 was smelted and cast into a slab. The slab was hot rolled to obtain a 5 mm thick hot rolled coil. After that, the hot rolled coil was pickled without annealing, then was cold rolled down to a 2 mm thickness and was annealed and pickled to obtain the product sheet.

[0089] In cold rolling, a rolling mill having large sized rolls (diameter 450 mm) was used for one-directional multipass rolling. For comparison, a rolling mill having small sized rolls (diameter 100 mm) was used for reverse type multipass rolling.

[0090] The annealing temperature of the cold rolled sheet was made 850 to 970°C so as to make the crystal grain size number 6 to 8 or so. For the comparative examples in which the Nb content is over the upper limit of the present invention, the annealing temperature of the cold rolled sheet was made 1000 to 1050°C.

[0091] In the tables, Nos. 1 to 17 and 37 are invention steels, while Nos. 18 to 36 are comparative steels. Comparative Steel No. 18 is SUH409L, while Nos. 19 and 20 are steels with goods records of use as Nb-Si steels.

[0092] From the thus obtained product sheets, test pieces for high temperature tensile tests were obtained, tensile tests were run at 600°C and 800°C, and the 0.2% yield strength was measured (based on JISG0567). The tensile tests which gave a 600°C yield strength of 150 MPa or more and a 800°C yield strength of 30 MPa or more were judged passing.

[0093] Further, as tests for the oxidation resistance, a continuous oxidation test was performed in the atmosphere at 900°C for 200 hours to evaluate the occurrence of abnormal oxidation (based on JISZ2281). As a result of the tests, test pieces with no abnormal oxidation were judged passing.

[0094] For ordinary temperature workability, a JIS No. 13B test piece was prepared and a tensile test was performed in a direction parallel to the rolling direction and the elongation at break measured. If the elongation at break at ordinary temperature is 35% or more, working into complicated parts becomes possible, so an elongation at break of 35% or more was judged passing.

[0095] The average r-value was calculated by obtaining a JIS No. 13B tensile test piece, giving 15% strain in the rolling direction, direction 45° from the rolling direction, and direction 90° from the rolling direction, then using formula (1) and formula (2).

$$r = \ln(W_0/W)/\ln(t_0/t) \quad (1)$$

where, W_0 is the sheet width before tension, W is the sheet width after tension, t_0 is the sheet thickness before tension, and "t" is the sheet thickness after tension.

$$\text{Average r-value} = (r_0 + 2r_{45} + r_{90})/4 \quad (2)$$

where, r_0 is the r-value in the rolling direction, r_{45} is the r-value in the direction 45° from the rolling direction, and r_{90} is the r-value in the direction 90° from the rolling direction. If the average r-value is 1.3 or more, working into complicated parts becomes possible, so an average r-value of 1.3 or more is preferable.

Table 1

	No	Composition of ingredients (mass%)														Rolls in cold rolling	0.2% yield strength at 600°C MPa	0.2% yield strength at 800°C MPa	Abnormal oxidation after 200 hr continuous oxidation test at 900°C	Ordinary temp. elongation at break %	Average r-value
		C	N	Si	Mn	Cr	Cu	Ti	Mo	Nb	B	Al	V	Zr	Sn						
Inv. ex.	1	0.005	0.007	0.41	0.45	10.5	1.25	0.15	-	-	0.0009	-	-	-	-	Large sized rolls	202	34	No	40	1.5
	2	0.006	0.009	0.88	0.31	13.9	1.42	0.11	-	-	0.0005	-	-	-	-	Large sized rolls	220	40	No	38	1.3
	3	0.004	0.011	0.11	0.13	17.5	1.36	0.19	-	-	0.0004	-	-	-	-	Large sized rolls	202	36	No	39	1.4
	4	0.008	0.015	0.22	0.16	11.1	1.56	0.12	-	-	0.0005	0.05	-	-	-	Large sized rolls	205	37	No	39	1.6
	5	0.003	0.013	0.33	0.15	14.5	1.95	0.08	-	-	0.0003	0.04	-	-	-	Large sized rolls	245	43	No	37	1.4
	6	0.002	0.005	0.25	0.09	18.5	1.63	0.21	-	-	0.0013	0.06	-	-	-	Large sized rolls	216	44	No	38	1.5
	7	0.008	0.006	0.25	0.95	11.5	1.15	0.12	-	-	0.0006	1.90	-	-	-	Large sized rolls	213	45	No	36	1.3
	8	0.006	0.015	0.16	0.53	17.6	2.50	0.08	-	-	0.0007	-	0.20	-	-	Large sized rolls	263	50	No	37	1.3
	9	0.009	0.006	1.50	0.13	14.6	1.31	0.05	-	-	0.0006	-	-	0.58	-	Large sized rolls	226	41	No	38	1.4
	10	0.003	0.005	1.20	0.25	18.2	0.96	0.13	-	-	0.0013	-	-	-	0.41	Large sized rolls	223	44	No	37	1.3
	11	0.004	0.009	0.11	1.00	17.6	0.52	0.11	-	-	0.0025	1.50	0.50	-	-	Large sized rolls	235	47	No	35	1.3
	12	0.007	0.012	0.33	0.28	11.3	1.13	0.09	-	0.08	0.0006	0.03	-	-	-	Large sized rolls	215	35	No	39	1.5
	13	0.008	0.015	0.92	0.21	14.2	1.65	0.16	-	0.11	0.0004	0.05	0.11	-	-	Large sized rolls	236	41	No	37	1.4
	14	0.002	0.014	0.13	0.15	17.9	1.35	0.07	-	0.17	0.0009	0.07	0.09	-	-	Large sized rolls	222	37	No	38	1.4
	15	0.003	0.012	0.25	0.30	15.2	1.31	0.18	0.18	-	0.0011	-	-	-	-	Large sized rolls	228	40	No	37	1.4
	16	0.003	0.008	0.20	0.35	14.6	1.21	0.21	0.07	0.12	0.0009	-	-	-	-	Large sized rolls	230	42	No	36	1.4
	17	0.003	0.010	0.27	0.15	14.3	1.15	0.22	0.11	0.08	0.0007	0.04	-	-	-	Large sized rolls	232	45	No	35	1.4

Table 2 (Continuation of Table 1)

	No	Composition of ingredients (mass%)														Rolls in cold rolling	0.2% yield strength at 600°C MPa	0.2% yield strength at 800°C MPa	Abnormal oxidation after 200 hr continuous oxidation test at 900°C	Ordinary temp. elongation at break %	Average r-value
		C	N	Si	Mn	Cr	Cu	Ti	Mo	Nb	B	Al	V	Zr	Sn						
Comp. ex.	18	0.005	0.007	0.35	0.50	10.5	-	0.15	-	-	0.0003	-	-	-	-	Large sized rolls	128	20	No	39	1.4
	19	0.006	0.009	0.90	0.35	13.8	-	-	-	0.45	0.0005	-	-	-	-	Large sized rolls	142	25	No	36	1.0
	20	0.003	0.008	0.50	0.50	14.5	-	0.12	-	0.32	0.0012	-	-	-	-	Large sized rolls	145	27	No	34	1.2
	21	0.025	0.012	0.18	1.10	11.5	0.90	0.16	-	-	0.0015	-	-	-	-	Large sized rolls	174	25	Yes	33	0.9
	22	0.005	0.029	0.32	0.98	18.5	1.10	0.08	-	-	0.0005	-	-	-	-	Large sized rolls	186	25	Yes	32	0.9
	23	0.003	0.006	2.50	1.00	13.2	1.80	0.07	-	-	0.0008	-	-	-	-	Large sized rolls	230	40	No	30	1.2
	24	0.008	0.007	0.11	2.50	17.3	0.62	0.11	-	-	0.0009	-	-	-	-	Large sized rolls	216	33	Yes	34	1.2
	25	0.004	0.009	0.15	0.90	9.1	1.53	0.26	-	-	0.0002	-	-	-	-	Large sized rolls	119	29	Yes	40	1.4
	26	0.004	0.005	0.13	0.95	16.8	0.20	0.36	-	-	0.0011	-	-	-	-	Large sized rolls	130	25	No	37	1.5
	27	0.006	0.013	0.82	0.80	13.5	1.33	0.70	-	-	0.0010	-	-	-	-	Large sized rolls	216	36	Yes	33	1.2
	28	0.005	0.008	0.85	0.25	13.5	1.15	0.005	-	0.35	0.0006	-	-	-	-	Large sized rolls	219	40	No	32	1.4
	29	0.007	0.013	0.55	0.45	17.1	1.22	0.10	-	0.38	0.0004	-	-	-	-	Large sized rolls	245	39	No	31	1.2
	30	0.003	0.011	0.31	1.20	16.2	1.68	0.42	-	-	0.0045	-	-	-	-	Large sized rolls	216	39	Yes	33	1.2
	31	0.006	0.014	0.89	0.35	14.2	1.35	0.09			0.0001	-	-	-	-	Large sized rolls	190	25	No	28	1.3
	32	0.008	0.016	0.21	0.80	17.8	1.25	0.36	-	-	0.0025	2.8	-	-	-	Large sized rolls	236	43	No	32	1.4
	33	0.004	0.017	0.15	1.03	17.9	1.33	0.27	-	-	0.0009	-	1.6	-	-	Large sized rolls	223	41	No	33	1.4
	34	0.005	0.020	0.18	1.50	17.9	1.50	0.25	0.50	-	0.0015	-	-	-	-	Large sized rolls	240	43	No	30	1.2
	35	0.004	0.003	0.13	0.75	17.9	2.35	0.16	-	-	0.0006	-	-	1.7	-	Large sized rolls	238	38	No	34	1.4
	36	0.006	0.002	0.81	1.03	14.1	1.96	0.14	-	-	0.0005	-	-	-	1.5	Large sized rolls	256	42	No	30	1.3
Inv. ex.	37	0.004	0.005	0.11	0.22	17.3	1.35	0.12	-	-	0.0007	-	-	-	-	Small sized rolls	213	38	No	38	0.9

[0096] The underlines in the compositions of ingredients in Tables 1 and 2 mean outside the scope of the present invention. The underlines in the results of evaluation of quality mean the tests were not passed.

[0097] From Tables 1 and 2, it is learned that the Steel Nos. 1 to 17 having the compositions of ingredients prescribed in the present invention had high temperature yield strengths at 600°C and 800°C which are higher than the comparative examples and are excellent in oxidation resistance as well without abnormal oxidation at 900°C in the case of production by an ordinary method as explained above.

[0098] Further, it is learned that the Steel Nos. 1 to 17 have high elongations at break of 35% or more and workabilities better than the comparative steels in mechanical properties at ordinary temperature.

[0099] Comparative Steel Nos. 18, 19, and 20 are existing steels, but have high temperature strengths lower than the requested values. Comparative Steel Nos. 19 and 20 to which Nb is added in excess also have low r-values.

[0100] Nos. 21 and 22 have C and N which are over the upper limits and are inferior in high temperature strength, oxidation resistance, and workability.

[0101] No. 23 has excessively added Si and is inferior in workability.

[0102] No. 24 has excessively added Mn and is inferior in oxidation resistance and workability.

[0103] No. 25 has a small amount of Cr, so is low in high temperature strength and is also inferior in oxidation resistance.

[0104] No. 26 has a small amount of Cu, so is low in 0.2% yield strengths at 600°C and 8C0°C.

[0105] No. 27 has an amount of Ti which is over the upper limit, so is inferior in oxidation resistance and workability.

[0106] No. 28 has an amount of Ti which is less than the lower limit and has excessively added Nb, so is low in ductility.

[0107] No. 29 has excessively added Nb, so is low in ductility and r-value.

[0108] No. 30 has B which is over the upper limit, so is low in oxidation resistance and workability.

[0109] No. 31 has an amount of addition of B of 0.0001% or less than the lower limit, so at 800°C the Cu precipitate coarsens, the effect of the precipitation strengthening falls, and the yield strength is low.

[0110] Nos. 32 to 36 has Mo, Al, V, Zr, and Sn which are over the upper limit, the ordinary temperature ductility is low, and working into a part is hindered.

[0111] In the invention examples, Nos. 1 to 17 which use large sized rolls for cold rolling exhibited average r-values of 1.3 or more, that is, good values.

[0112] The Invention Steel No. 37 is excellent in high temperature yield strength and ordinary temperature elongation at break. However, the cold rolling roll size is small, so the r-value is a value lower than the preferable range.

Industrial Applicability

[0113] According to the present invention, it is possible to provide a stainless steel sheet excellent in high temperature characteristics and workability without addition of large amounts of expensive alloy elements such as Nb and Mo. In particular, by using this for an exhaust member, the reduction of the parts costs, reduction of weight, and resultant contributions to environment protection and social contributions are remarkably great.

Claims

1. Ferritic stainless steel excellent in heat resistance and workability which contains, by mass%,
C: 0.02% or less,
N: 0.02% or less,
Si: 2% or less,
Mn: 2% or less,
Cr: 10 to 20%,
Cu: 0.4 to 3%,
Ti: 0.01 to 0.5%, and
B: 0.0002 to 0.0030% and
has a balance of Fe and unavoidable impurities.

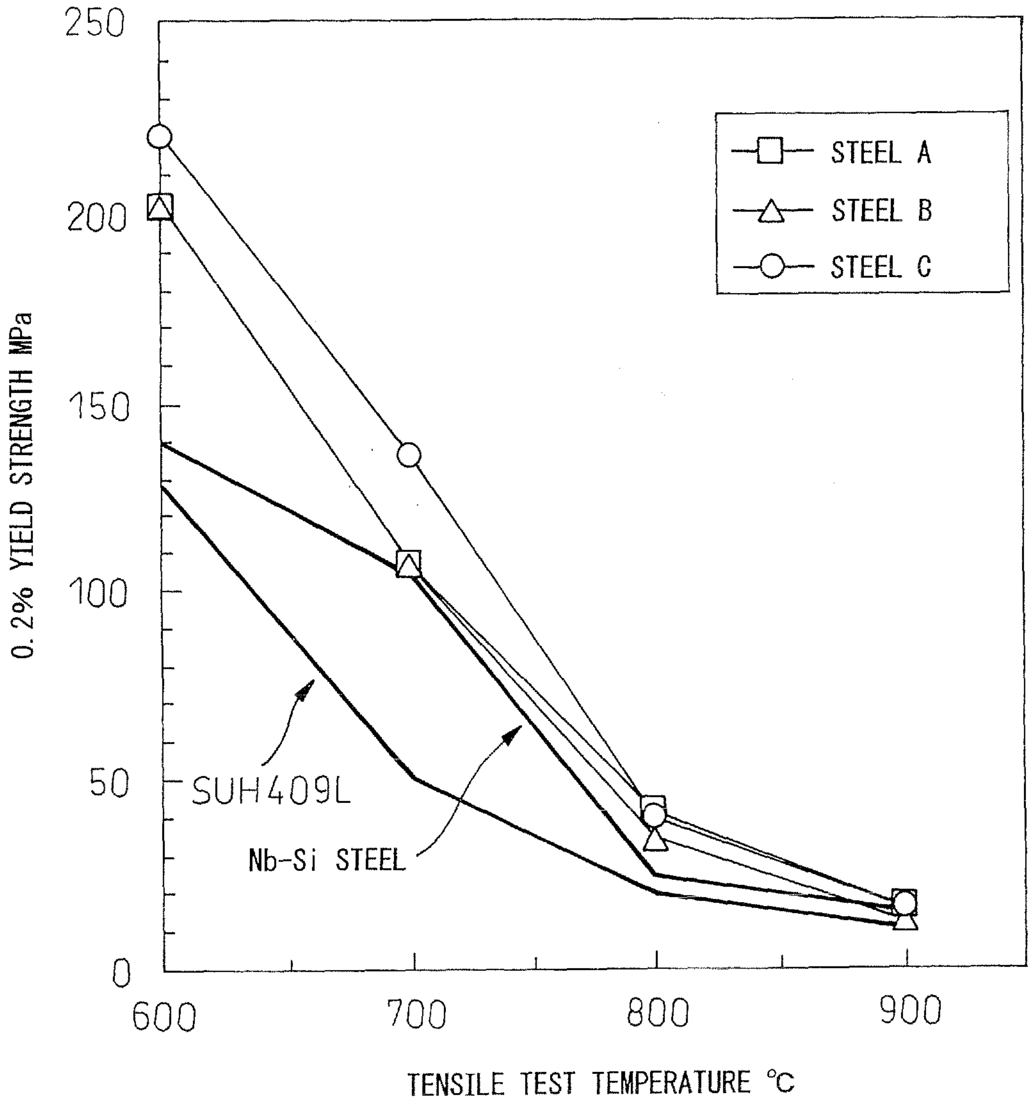
2. Ferritic stainless steel excellent in heat resistance and workability as set forth in claim 1 which, further contains, by mass%, one or more of:

Nb: 0.01 to 0.3%,
Mo: 0.01 to 0.3%,
Al: 2.5% or less,
V: 1% or less,
Zr: 1% or less, and

Sn: 1% or less.

3. Method of production of ferritic stainless steel excellent in heat resistance and workability **characterized by** hot rolling ferritic stainless steel which has a composition of ingredients of claim 1 or 2 so as to obtain a hot rolled sheet, then, omitting annealing of the hot rolled sheet, pickling the hot rolled sheet, cold rolling it by rolling rolls of a diameter of 400 mm or more, then performing final annealing.

Fig.1


250
200
150
100
50
0
0.2% YIELD STRENGTH MPa
600
700
800
900
TENSILE TEST TEMPERATURE ℃
STEEL A
STEEL B
STEEL C
SUH409L
Nb-Si STEEL

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/055488

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21D9/46*(2006.01)i, *C22C38/38*(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, C22C38/38

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 9-143614 A (Kawasaki Steel Corp.), 03 June 1997 (03.06.1997), claims; paragraph [0001]; examples; table 1 (particularly, steel 5) (Family: none)	1,2 3
X Y	JP 2006-117985 A (Nisshin Steel Co., Ltd.), 11 May 2006 (11.05.2006), claims; examples; table 1 (particularly, steel 1, 5, 6) (Family: none)	2 3
Y	JP 2006-193771 A (Nippon Steel & Sumikin Stainless Steel Corp.), 27 July 2006 (27.07.2006), claims; paragraph [0034] (Family: none)	3

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

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Date of the actual completion of the international search 07 June, 2010 (07.06.10)	Date of mailing of the international search report 15 June, 2010 (15.06.10)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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