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

(11) **EP 2 692 889 A1**

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

(43) Date of publication:
05.02.2014 Bulletin 2014/06

(21) Application number: **12765258.4**

(22) Date of filing: **28.03.2012**

(51) Int Cl.:
C22C 38/00 *(2006.01)* ***C21D 9/46*** *(2006.01)*
C22C 38/32 *(2006.01)* ***C22C 38/54*** *(2006.01)*

(86) International application number:
PCT/JP2012/058218

(87) International publication number:
WO 2012/133573 (04.10.2012 Gazette 2012/40)

(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

(30) Priority: **29.03.2011 JP 2011072270**

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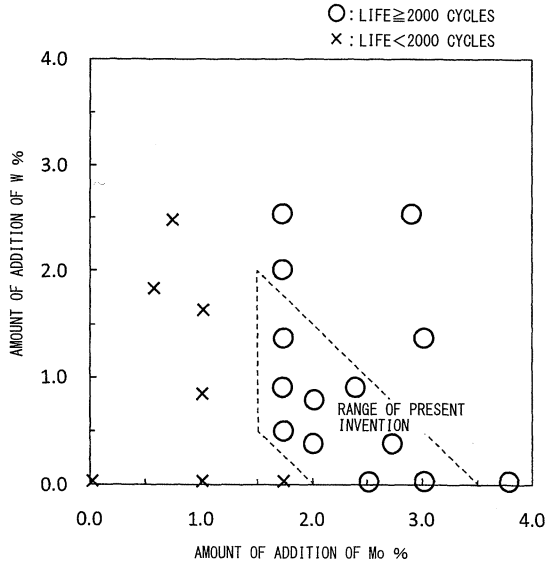
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(54) FERRITIC STAINLESS STEEL SHEET HAVING EXCELLENT HEAT RESISTANCE AND PROCESSABILITY, AND METHOD FOR PRODUCING SAME

(57) The present invention provides ferritic stainless steel sheet which is excellent in heat resistance at 950°C and workability at ordinary temperature, that is, ferritic stainless steel sheet excellent in heat resistance and workability which is characterized by containing, by mass%, C: 0.02% or less, N: 0.02% or less, Si: over 0.1 to 1.0%, Mn: 0.5% or less, P: 0.020 to 0.10%, Cr: 13.0 to 20.0%, Nb: 0.5 to 1.0%, Cu: 1.0 to 3.0%, Mo: 1.5 to 3.5%, W: 2.0% or less, B: 0.0001 to 0.0010%, and Al: 0.01 to 1.0% and having a balance of Fe and unavoidable impurities, where Mo+W is made 2.0 to 3.5%.

Fig.1



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Description

Technical Field

[0001] The present invention relates to ferritic stainless steel sheet excellent in heat resistance which is optimal for use for an exhaust system member etc. which requires high temperature strength and oxidation resistance and a method of production of the same.

Background Art

[0002] Exhaust manifolds, front pipes, center pipes, and other exhaust system members of automobiles carry high temperature exhaust gas which is exhausted from the engine, so the materials forming the exhaust members are required to offer oxidation resistance, high temperature strength, heat fatigue characteristics, and diverse other characteristics.

[0003] In the past, cast iron has generally been used for automobile exhaust members, but from the viewpoint of the toughening of exhaust gas regulations, improvement of engine performance, reduction of the weight of the chassis, etc., stainless steel exhaust manifolds are being used. The temperature of exhaust gas differs depending on the vehicle type and engine structure, but often is 700 to 900°C or so in general gasoline vehicles. In environments of long term use in such a temperature region, materials which have an excellent high temperature strength and oxidation resistance are being demanded.

[0004] Among stainless steels, austenitic stainless steel is excellent in heat resistance and workability, but it has a large heat expansion coefficient, so if used for members which are repeatedly heated and cooled such as exhaust manifolds, heat fatigue fracture easily occurs.

[0005] On the other hand, ferritic stainless steel has a smaller heat expansion coefficient compared with austenitic stainless steel, so is excellent in heat fatigue characteristics and scale spalling resistance. Further, it does not contain Ni, so compared with austenitic stainless steel, the cost of material is low. Therefore, this is being used for general applications. However, ferritic stainless steel is lower in high temperature strength compared with austenitic stainless steel, so art for improving the high temperature strength has been developed. For example, there are SUS430J1 (Nb steel), Nb-Si steel, and SUS444 (Nb-Mo steel) of the Japan Industrial Standard (JIS). These all are predicated on addition of Nb. This uses solution strengthening or precipitation strengthening by Nb so as to raise the high temperature strength.

[0006] As alloys other than Nb contributing to improvement of the high temperature strength, PLTs 1 to 4 disclose the art of composite addition of Cu or Cu-V. In PLT 1, to improve low temperature toughness, addition of 0.5% or less of Cu is being studied. It is not addition from the viewpoint of heat resistance. PLTs 2 to 4 disclose the art which utilizes precipitation strengthening by Cu precipitates to improve the high temperature strength in the 600°C or 700 to 800°C temperature range. PLTs 1 to 2 and PLTs 5 to 7 disclose steel containing B as ferritic stainless steel excellent in high temperature characteristics.

[0007] These prior art can all be applied to cases where the exhaust gas temperature is up to 850°C. SUS 444 with the highest heat resistance could not handle the over 900°C exhaust gas atmospheres in terms of high temperature strength, heat fatigue, and oxidation resistance. From the viewpoint of protection of the global environment in recent years, there has been a movement toward higher temperatures of exhaust gas of automobiles and improved fuel efficiency. Due to this, it is considered that exhaust gas temperatures will rise to 950°C. In this case, in existing steel, use for exhaust manifolds would be difficult.

[0008] As measures for dealing with the higher temperatures of exhaust gas, PLTs 8 to 13 disclose arts relating to ferritic stainless steel containing W. W is known as an element which improves the high temperature strength, but addition of W causes the workability (elongation) to worsen and gives rise to the problem of the difficulty of forming the parts and issues in terms of costs. Further, at a high temperature, it bonds with Fe and precipitates as the later explained Laves phases, so there was the issue that when the Laves phases coarsened, it was not possible to effectively improve the heat resistance. Further, PLTs 14 and 15 disclose to define the sum of the Mo and W added, that is, Mo+W, to secure the high temperature strength of the ferritic stainless steel, but again concern over coarsening of the Laves phases was unavoidable. That is, when, like with exhaust manifolds, being subjected to thermal cycles along with starting and stopping of the engine, at the stage of long term use, the high temperature strength would fall and there would be the danger of heat fatigue breakage. That is, in existing materials, even if the high temperature strength is excellent, there was a concern that with long term use, coarsening of the Laves phases and ε-Cu and other precipitates would cause deterioration of the heat fatigue characteristics. As an example of a precipitate which imparts a detrimental effect, PLT 16 describes that inclusion of P causes FeTiP to precipitate which has a detrimental effect, so the content of P has to be kept low. However, PLT 17 prescribes that in ferritic stainless steel, P is useful for increasing the high temperature strength (solution strengthening) and prescribes that P be included up to 0.1 wt%, but examples including high P contents are not disclosed.

Citations List

Patent Literature

[0009] PLT 1: Japanese Patent Publication No. 2006-37176A

PLT 2: WO2003/004714A
PLT 3: Japanese Patent No. 3468156B2
PLT 4: Japanese Patent No. 3397167B2
PLT 5: Japanese Patent Publication No. 9-279312A
PLT 6: Japanese Patent Publication No. 2000-169943A
PLT 7: Japanese Patent Publication No. 10-204590A
PLT 8: Japanese Patent Publication No. 2009-215648A
PLT 9: Japanese Patent Publication No. 2009-235555A
PLT 10: Japanese Patent Publication No. 2005-206944A
PLT 11: Japanese Patent Publication No. 2008-189974A
PLT 12: Japanese Patent Publication No. 2009-120893A
PLT 13: Japanese Patent Publication No. 2009-120894A
PLT 14: Japanese Patent Publication No. 2009-197306A
PLT 15: Japanese Patent Publication No. 2009-197307A
PLT 16: Japanese Patent Publication No. 2000-336462A
PLT 17: Japanese Patent No. 3021656B2

Summary of Invention

Technical Problem

[0010] The present invention provides ferritic stainless steel which is used in a hot environment of a maximum temperature of exhaust gas of 950°C and which is excellent heat resistance and workability.

Solution to Problem

[0011] The present invention has as its object to solve the above problem by balancing the various dissolved elements including P and dispersing the various precipitates so as to improve the high temperature characteristics and providing ferritic stainless steel sheet for exhaust manifold use which is excellent in ordinary temperature workability. That is, the present invention provides new ferritic stainless steel sheet which is balanced in precipitate refinement and solution strengthening and a method of production of the same.

[0012] The inventors investigated in detail the expression of high temperature strength at 950°C, the improvement of the heat fatigue life, the suppression of abnormal oxidation, and the ordinary temperature rollability. As a result, they obtained the following discovery. That is, the present invention suppresses Mo and W to suitable amounts while adding Cu in a predetermined amount as a precipitation strengthening element during which it secures the amount of precipitates formed at 950°C and controls the form of precipitation so as to effectively express precipitation strengthening. Further, the present invention combines solution strengthening by Nb, Mo, and W to secure heat resistance while keeping the drop in ductility extremely low. Specifically, intermetallic compounds called "Laves phases" formed by composite addition of Nb, Mo, and W and ε-Cu which is formed by addition of Cu are actively utilized for high temperature precipitation strengthening. When steel materials where these precipitate independently are exposed to high temperature atmospheres for long periods of time, the precipitates coarsen, so the precipitation strengthening ability only acts for an extremely short time. As a result, the steel material is not improved in heat fatigue life and ends up breaking in a short time. Therefore, the inventors discovered that by utilizing compounds of Fe and P as precipitation sites, the above-mentioned Laves phases and ε-Cu uniformly finely precipitate in the grains and as a result the precipitation strengthening becomes stable for a long period of time and the heat fatigue life is improved. Furthermore, the inventors discovered that by utilizing solution strengthening by the dissolved Nb, Mo, and W, the high temperature characteristics are improved much more. In addition, the inventors discovered that by defining Mo+W and the amount of addition of Cu as predetermined ranges, it is possible to improve both the heat fatigue life and the ordinary temperature ductility. Due to this, it was made possible to provide highly reliable ferritic stainless steel sheet which has a high heat resistance and freedom of working of parts at a temperature region of exhaust gas with a maximum temperature of 950°C. Note that, Mo+W is the sum, by mass%, of the amount of addition of Mo and the amount of addition of W.

[0013] That is, the gist of the present invention is as follows:

(1) Ferritic stainless steel sheet excellent in heat resistance and workability characterized by containing, by mass%, C: 0.02% or less, N: 0.02% or less, Si: over 0.1 to 1.0%, Mn: 0.5% or less, P: 0.02 to 0.10%, Cr: 13.0 to 20.0%, Nb: 0.5 to 1.0%, Cu: 1.0 to 3.0%, Mo: 1.5 to 3.5%, W: 2.0% or less, B: 0.0001 to 0.0010%, and Al: 0.01 to 1.0% and having a balance of Fe and unavoidable impurities, where Mo+W is 2.0 to 3.5%.

(2) Ferritic stainless steel sheet excellent in heat resistance and workability of (1) characterized by further containing, by mass%, one or more of Ti: 0.05 to 0.4%, V: 0.05 to 1.0%, Zr: 0.05 to 1.0%, Sn: 0.05 to 0.5%, and Ni: 0.05 to 1.0%.

(3) A method of production of ferritic stainless steel sheet excellent in heat resistance and workability characterized by producing ferritic stainless steel sheet as set forth in the above (1) or (2) during which water cooling a steel sheet within one hour after hot rolling and coiling and cold rolling and annealing the cold rolled steel sheet while omitting annealing of hot rolled steel sheet.

(4) The method of production of ferritic stainless steel sheet excellent in heat resistance and workability characterized by producing ferritic stainless steel sheet as set forth in the above (1) or (2) during which water cooling a steel sheet within one hour after hot rolling and coiling, annealing the hot rolled steel sheet in a 700 to 950°C non-recrystallization region, and cold rolling and annealing the cold rolled steel sheet.

[0014] Here, cases where no lower limit is defined means inclusion up to the level of unavoidable impurities.

Advantageous Effects of Invention

[0015] According to the present invention, ferritic stainless steel sheet excellent in heat resistance and workability is obtained which is suitable for exhaust system parts which are exposed to an atmosphere of 950°C for which use of ferritic stainless steel sheet had been difficult in the past.

Brief Description of Drawings

[0016]

FIG. 1 is a view which shows the effects of Mo+W on the heat fatigue characteristics in the case of a maximum temperature of 950°C.

FIG. 2 is a view which shows the effects of Mo+W on the elongation at break at ordinary temperature.

FIG. 3 is a view which shows the effects of Mo+W on the oxidation resistance in a continuous oxidation test at 950°C.

Description of Embodiments

[0017] Below, the present invention will be explained. In the explanation, "%" means mass% unless otherwise indicated.

[0018] 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. Accordingly, the content of C is made 0.02% or less. However, excessive reduction leads to an increase in the refining costs, so 0.002 to 0.009% is preferable.

[0019] N, in the same way as C, degrades the formability and corrosion resistance and causes a drop in the high temperature strength, so the smaller the content, the better. Accordingly, the amount of N is made 0.02% or less. However, excessive reduction leads to an increase in the refining costs, so 0.003 to 0.015% is preferable.

[0020] Si is an element useful as a deoxidizing agent and is an element which improves the high temperature strength and the oxidation resistance. The high temperature strength and the oxidation resistance are improved along with the increase in the amount of Si. The effect is manifested at over 0.1%. In particular, this effect becomes remarkable when compositely adding Mo and W. However, excessive addition causes the ordinary temperature ductility to fall, so the upper limit is made 1.0%. Further, if considering the manufacturability, 0.2 to 0.5% is preferable.

[0021] Mn is an element which is added as a deoxidizing agent and contributes to the rise in high temperature strength in the 600 to 800°C or so temperature region (medium temperature region). However, by addition of over 0.5%, it forms an Mn-based oxide surface layer at high temperatures and easily causes scale adhesion or abnormal oxidation. In particular, when compositely adding Mo and W, there is a tendency for abnormal oxidation to easily occur for the amount of Mn. Therefore, the upper limit was made 0.5% or less. Further, if considering the pickling ability at the time of production of steel sheet and the ordinary temperature ductility, 0.05 to 0.2% is preferable.

[0022] P controls the precipitation of the Laves phases and ε-Cu, so is an important element. Usually, it is considered that P should be reduced as much as possible from the viewpoint of the workability. However, in the present invention, compounds of Fe and P are formed and these compounds are used as nuclei for fine dispersion and precipitation of Laves phases and ε-Cu at 950°C. Even if held at a high temperature for a long period of time, coarsening of these precipitates is prevented. If the Laves phases and ε-Cu independently precipitate in the ferrite grains and at the grain boundaries in the matrix, they will coarsen early and the precipitation strengthening ability will fall. In addition, in the

process of heat fatigue, they will form starting points of cracks and will end up accelerating crack propagation. However, by fine dispersion and precipitation using the compounds of Fe and P as nuclei, the drop in high temperature strength is suppressed and the heat fatigue life is improved. PLTs 14 and 15 and other numerous literature consider P to be an element which lowers the toughness, so consider that the content should be as low as possible. However, if, like in the present invention, P is copresent with the precipitates of the Laves phases and ε-Cu, the P will interact with these precipitates and the precipitates will be refined. Further, by refining these precipitates, the high temperature fatigue characteristics will be improved. In the past, P had been treated as an unavoidable impurity, so the effects of P on high temperature fatigue had never been investigated in detail. The refining of the precipitates by P is manifested from 0.02%, so the lower limit of P was made 0.02%. Further, by addition of over 0.10%, the ordinary temperature ductility dropped sharply, so the upper limit was made 0.10%. Further, if considering the pickling ability at the time of production of steel sheet, 0.028 to 0.080% is preferable.

[0023] Cr is an element which is essential for securing oxidation resistance and corrosion resistance. If less than 13%, the oxidation resistance cannot be secured, while if over 20%, a drop in workability and deterioration of the toughness are caused, so the content was made 13 to 20%. Further, if considering the manufacturability and high temperature ductility, 16 to 18% is preferable.

[0024] Nb is an element necessary for improving the high temperature strength by solution strengthening and precipitate refining strengthening. Further, it also has the role of fixing the C and N as carbonitrides and contributing to the growth of a recrystallized structure having an effect on the corrosion resistance and r value of the product sheet. The strength at 950°C is mainly solution strengthening, but when compositely adding Mo and W, they also have the effect of contributing to fine precipitation of Laves phases and promoting formation of compounds of Fe and P acting as sites for precipitation of Laves phases. This is believed to be because FeNbP precipitates in the grains at the product stage which serve as nuclei for fine precipitation of the Laves phases and suppresses coarsening of the Laves phases. Fine Laves phases are effective for improvement of the high temperature strength and heat fatigue life. The effects are manifested with addition of 0.5% or more. On the other hand, excessive addition causes a drop in uniform elongation, so the content was made 0.5 to 1.0%. Furthermore, if considering the intergranular corrosion and weld cracking at the weld zone and the manufacturability and production costs, 0.5 to 0.6% is preferable.

[0025] Cu contributes to precipitation strengthening by precipitation of ε-Cu, but to secure the amount of precipitation which contributes to high temperature strength at 950°C, addition of 1.0% or more is necessary, so the lower limit was made 1.0%. Furthermore, ε-Cu precipitates, as explained above, interact with Fe-P-based precipitates and finely disperse with each other. This point is greatly different from PLT 16. On the other hand, Cu is an element which remarkably lowers the ordinary temperature ductility. If adding over 3.0%, the total elongation of the steel sheet does not reach the 30% required for ordinary press-forming, so the upper limit was made 3.0%. Furthermore, if considering the manufacturability and oxidation resistance, 1.2 to 2.0% is preferable.

[0026] Mo is an element which is effective for solution strengthening at 950°C and forms Laves phases (Fe_2Mo) to give rise to a precipitation strengthening action. These effects are manifested at 1.5% or more, but excessive addition raises the alloy cost. With addition of over 3.5%, the ordinary temperature ductility and the oxidation resistance are remarkably degraded, so the content was made 1.5 to 3.5%. Furthermore, if considering the manufacturability, 1.5 to 2.7% is preferable.

[0027] W, like Mo, is an element which is effective for solution strengthening at 950°C and forms Laves phases (Fe_2W) to give rise to a precipitation strengthening action. In particular, when compositely adding Nb and Mo, Laves phases of $Fe_2(Nb,Mo,W)$ precipitate, but if adding W, coarsening of the Laves phases is suppressed and the precipitation strengthening ability is improved. The reason is believed to be dispersion of W and the interaction between the FeP compounds which form precipitation sites for $Fe_2(Nb,Mo,W)$ and W. Furthermore, as explained above, due to the copresence with Fe-P-based precipitates, these Laves phases tend to become finer. That is, the three Cu precipitates, Laves phases, and Fe-P-based precipitates affect each other and finely disperse and precipitate whereby coarsening is inhibited and improvement of the high temperature fatigue characteristics is contributed to. That is, the composite addition of Mo, W, and P is also a great difference from PLT 16.

[0028] FIG. 1 shows the influence of the addition of Mo and W on the heat fatigue life of a steel material which has a chemical composition of 17.3%Cr-0.005%C-0.010%N-0.03%P-0.55%Nb-1.5%Cu-0.0004%B-0.03%Al. Here, the heat fatigue life was measured using a welded pipe of $\phi 38.1 \times 2$ mm thickness which was prepared from 2 mm thick steel sheet as a test piece. The test conditions were made a constraining rate (ratio of amount of deformation to free heat expansion) held at 20% while giving a thermal cycle (minimum temperature 200°C, maximum temperature 950°C, holding time at maximum temperature 2 minutes). Further, the number of cycles when the cracks passed through the test piece was measured. In this test, the life was illustrated assuming 2000 cycles or more as passing (in figure, ○) and less than 2000 cycles as failing (in figure, x).

[0029] Further, as the ordinary temperature workability, a JIS No. 13B test piece was fabricated and subjected to a tensile test in a direction parallel to the rolling direction to measure the elongation at break. FIG. 2 shows the influence of the addition of Mo and W on the total elongation at ordinary temperature of the same system of chemical compositions.

When producing an exhaust part by press forming, usually the elongation at break has to be 30% or more. Therefore, the case giving an elongation at break of 30% or more was shown as "○" and the case of less than 30% was shown as "x".

[0030] Further, as a test of the oxidation resistance, a continuous oxidation test was run in the atmosphere at 950°C for 200 hours. The presence of any abnormal oxidation or scale spalling was evaluated (based on JIS Z 2281). FIG. 3 shows the effects of the addition of Mo and W on the oxidation resistance at 950°C for the same system of chemical compositions. The case where no abnormal oxidation and scale spalling occurred was shown as "○", while the case where they occurred was shown as "x".

[0031] From FIGS. 1 to 3, it is learned that to satisfy the heat fatigue life, ordinary temperature ductility, and oxidation resistance, it is effective to make the range of Mo+W 2.0 to 3.5% and make Mo 1.5% or more. Further, excessive addition of W raises the cost and lowers the ordinary temperature ductility, so the upper limit of W was made 2.0%. Furthermore, if considering the manufacturability, low temperature toughness, and oxidation resistance, the amount of addition of W is preferably 1.5% or less and the amount of Mo+W is preferably 2.1 to 2.9%.

[0032] B is an element which improves the secondary workability at the time of press-forming a product. Further, in the present invention, addition of B suppresses coarsening of the Cu precipitates, Laves phases, and FeP compounds and raises the stability of strength at the time of use in a high temperature environment. This is believed to be because the B segregates at the crystal grain boundaries at the time of recrystallization treatment in the cold rolled sheet annealing step whereby it becomes harder for the above precipitates which precipitate when exposed to a high temperature environment after that to precipitate at the crystal grain boundaries and fine precipitation in the grains is promoted. Due to this, long term stability of precipitation strengthening is expressed, the drop in strength is suppressed, and the heat fatigue life is improved. This effect is manifested at 0.0001% or more, but excessive addition invites hardening and causes deterioration of the intergranular corrosion resistance and oxidation resistance. In addition, weld cracks occur, so the content was made 0.0001 to 0.0010%. Furthermore, if considering the corrosion resistance and the production costs, 0.0001 to 0.0004% is preferable.

[0033] Al is an element which is added as a deoxidizing element and also improves the oxidation resistance. Further, it is useful for improvement of strength at 600 to 700°C as a solution strengthening element. Its action is stably expressed from 0.01%, but excessive addition causes the steel to harden, uniform elongation to be remarkably degraded, and, furthermore, the toughness to remarkably fall, so the upper limit was made 1.0%. If considering the occurrence of surface defects and the weldability and manufacturability, 0.01 to 0.2% is preferable.

[0034] Furthermore, the following elements may be included in accordance with need.

[0035] Ti is an element which bonds with C, N, and S to improve the corrosion resistance, intergranular corrosion resistance, ordinary temperature ductility, and deep drawability and is added in accordance with need. These effects are manifested at 0.05% or more, but addition of over 0.4% causes the amount of dissolved Ti to increase and the ordinary temperature ductility to fall and further causes coarse Ti-based precipitates to form and act as starting points of cracking at the time of hole enlargement and thereby degrades the press formability. Further, the oxidation resistance is also degraded, so the amount of addition of Ti was made 0.4% or less. Furthermore, if considering the formation of surface flaws and the toughness, 0.05 to 0.2% is preferable.

[0036] V is an element which improves the corrosion resistance and is added in accordance with need. This effect is stably manifested by addition of 0.05% or more, but if adding over 1%, the precipitates coarsen and the high temperature strength falls and, in addition, the oxidation resistance deteriorates, so the upper limit was made 1%. Furthermore, if considering the manufacturing cost and manufacturability, 0.08 to 0.5% is preferable.

[0037] Zr is a carbonitride-forming element in the same way as Ti and Nb and is an element which improves the corrosion resistance and deep drawability, so is added in accordance with need. These effects are manifested at 0.05% or more, but adding over 1.0% causes the manufacturability to remarkably deteriorate, so the content was made 0.05 to 1.0%. Furthermore, if considering the cost and surface quality, 0.1 to 0.6% is preferable.

[0038] Sn is an element which improves the corrosion resistance. It improves the high temperature strength in the medium temperature region, so is added in accordance with need. These effects are manifested at 0.05% or more, but if adding over 0.5%, the manufacturability remarkably falls, so the content was made 0.05 to 0.5%. Furthermore, if considering the oxidation resistance and production costs, 0.1 to 0.5% is preferable.

[0039] Ni is an element which improves the oxidation resistance and toughness and is added in accordance with need. These effects are manifested at 0.05% or more, but if adding over 1.0%, the cost becomes high, so the content was made 0.05 to 1.0%. Furthermore, if considering the manufacturability, 0.1 to 0.5% is preferable.

[0040] Next, the method of production will be explained. The method of production of steel sheet of the present invention has the steps of steelmaking, hot rolling, pickling, cold rolling, annealing, and pickling. In steelmaking, the method of melting steel which contains the above essential elements and optional elements which are added in accordance with need in a converter, then performing secondary refining is preferable. The melted steel is made into a slab in accordance with a known casting method (continuous casting). The slab is heated by an ordinary method to a predetermined temperature and is hot rolled to a predetermined sheet thickness by continuous rolling. The hot rolling is performed by a hot rolling mill comprised of a plurality of stands, then the sheet is coiled.

[0041] In the present invention, preferably, to improve the hot rolled sheet toughness, the coil is water cooled after coiling. The steel of the present invention has various alloy elements added to it, so the hot rolled sheet easily falls in toughness and the steel sheet sometimes breaks in the next step or other trouble occurs. As the causes, coarsening of the crystal grains, formation of Cu clusters, and two-phase separation of Cr may be mentioned. Therefore, to reliably eliminate these causes, the coil is immersed as is into a pool for water cooling. However, if the time from coiling to water cooling is over 1 hour, there is no effect of improvement of the toughness, so the time from coiling to water cooling is made within 1 hour. This time is preferably within 20 minutes. Further, the coiling temperature is not particularly defined, but is preferably 400 to 750°C from the viewpoint of refinement of the structure.

[0042] Usually, the hot rolled sheet is annealed by heating until the recrystallization temperature from the viewpoint of homogenizing and softening the structure. However, the recrystallized structure becomes coarse in crystal grains, so sometimes the toughness of the hot rolled annealed sheet becomes an issue. Therefore, in the present invention, preferably, the annealing of the hot rolled sheet is omitted or heat treatment is performed at a temperature not causing recrystallization so as to refine the structure and thereby secure toughness. The recrystallization temperature of the present invention is 1000°C or more, but when obtaining a recrystallized structure, the crystal grains end up coarsening, the toughness falls, and the steel sheet sometimes breaks when running the coil. If omitting the annealing of the hot rolled sheet, the sheet is cold rolled while having nonuniformity of the structure, but in such a case as well, a regular grain structure is obtained after the annealing of the cold rolled sheet. Further, even if the cold rolled material is hard, cold rolling is possible. Finely worked grains can be obtained at the hot rolling stage, so the toughness is not a problem. Further, in the present invention, sub grains are formed, so it is possible to remove the working strain and obtain a sub grain structure to prevent a drop in toughness due to formation of deformed twin crystals. This effect is obtained by heat treatment at 700 to 950°C in temperature region, so the hot rolled sheet annealing temperature is preferably 700 to 950°C. Furthermore, from the viewpoint of the pickling ability, heat treatment at 750 to 900°C is preferable. In the present invention, the holding time and the cooling rate are not particularly prescribed, but from the viewpoint of productivity, the holding time is within 20 seconds and the cooling rate is preferably 10°C/sec or more.

[0043] The annealing after cold rolling was performed for obtaining a recrystallized structure. The recrystallization temperature of the steel having the chemical composition of the present invention is 1000 to 1100°C, so the sheet was heated to this temperature range, then cooled. Cu, Nb, Mo, and W form ε-Cu and Laves phases in the cooling process, but if the cooling rate is slow, the ε-Cu and Laves phases are sometimes made to excessively precipitate and a drop is caused in the high temperature strength and ordinary temperature ductility, so the solid solution state is preferably held as much as possible. For this reason, the cooling rate until 400°C where a salt treatment or neutral salt electrolysis treatment is performed is preferably made 10°C/sec or more. If considering the productivity and the pickling ability, the cooling rate is preferably 20 to 100°C/sec. Further, as the cooling method, mist cooling, water cooling, etc. may be suitably selected.

[0044] The conditions of the other steps are not particularly defined, but the thickness of the hot rolled sheet, the annealing atmosphere of the cold rolled sheet, etc. may be suitably selected. Further, after cold rolling and annealing, at least one of temper rolling and a tension leveler may be applied. Furthermore, the thickness of the product sheet may be selected in accordance with the required thickness of the member. Examples

[0045] Steel of each of the chemical compositions shown in Table 1 was smelted, cast into a slab, and hot rolled to obtain a 5 mm thick hot rolled coil. At this time, the slab heating temperature was made 1250°C, the finishing temperature was made 850 to 950°C, and the coiling temperature was made 450 to 750°C. Within 1 hour after hot rolling and coiling, the sheet was water cooled. The annealing of the hot rolled sheet was omitted or heat treatment was performed at 700 to 900°C. After that, the coil was pickled, cold rolled down to 2 mm thickness, and annealed and pickled to obtain the product sheet. At this time, the annealing temperature of the cold rolled sheet was made 1000 to 1100°C to make the crystal granularity number 5 to 7 or so. To suppress the drop in ordinary temperature ductility due to formation of ε-Cu and Laves phases after heating to that temperature, the sheet was cooled by a cooling rate until 400°C of 20 to 100°C/sec to obtain the product sheet. From the thus obtained product sheet, the above-mentioned methods were used to run heat fatigue tests and measure the ordinary temperature elongation at break and continuous oxidation test. The results were judged in the same way as FIGS. 1 to 3. In Table 1, for "good" and "poor", judgment criteria similar to those of FIG. 1 to 3 are shown for "○" and "x". Namely, "good" is corresponding to "○", and "poor" is corresponding to "x". Note that the crystal grain size numbers are the austenite crystal granularity defined in JIS G 0551.

Table 1

	Steel no.	Chemical compositions (mass%)																		Results of evaluation of quality		
		C	N	Si	Mn	P	Cr	Nb	Cu	Mo	W	B	Al	Ti	V	Zr	Sn	Ni	Mo+W	Heat fatigue characteristics	Ordinary temperature elongation	Oxidation resistance
Inv. ex.	1	0.006	0.013	0.2	0.08	0.03	17.5	0.51	1.51	1.8	1.1	0.0003	0.03	–	–	–	–	–	2.9	Good	Good	Good
	2	0.009	0.015	0.3	0.12	0.03	17.1	0.55	1.56	1.5	1.3	0.0004	0.05	0.12	–	–	–	–	2.8	Good	Good	Good
	3	0.002	0.004	0.5	0.15	0.05	16.8	0.60	1.48	1.5	2.0	0.0002	0.04	0.08	–	–	–	–	3.5	Good	Good	Good
	4	0.005	0.011	0.4	0.18	0.02	16.5	0.50	1.35	1.7	1.5	0.0005	0.01	–	–	–	–	–	3.2	Good	Good	Good
	5	0.003	0.010	0.2	0.40	0.06	17.9	0.52	1.55	2.7	0.02	0.0001	0.15	0.19	–	–	–	–	2.7	Good	Good	Good
	6	0.004	0.009	0.3	0.13	0.08	14.2	0.55	1.22	1.8	1.5	0.0002	0.05	–	–	–	–	–	3.3	Good	Good	Good
	7	0.005	0.008	0.9	0.09	0.06	17.6	0.51	1.56	1.5	1.5	0.0003	0.88	0.19	0.11	–	–	–	3.0	Good	Good	Good
	8	0.013	0.005	0.3	0.10	0.05	17.0	0.53	1.49	1.6	0.5	0.0004	0.07	–	–	0.50	–	–	2.1	Good	Good	Good
	9	0.007	0.014	0.2	0.11	0.03	16.8	0.72	1.55	1.8	0.5	0.0007	0.07	0.19	–		–	0.50	2.3	Good	Good	Good
	10	0.006	0.015	0.5	0.15	0.03	17.5	0.51	1.59	1.9	1.6	0.0008	0.04	–	–	–	0.20	–	3.5	Good	Good	Good
Comp. ex.	11	0.035	0.015	0.2	0.10	0.03	17.3	0.52	1.49	1.5	0.5	0.0003	0.02	–	–	–	–	–	2.0	Poor	Poor	Poor
	12	0.005	0.026	0.3	0.15	0.04	15.5	0.56	1.25	1.6	1.9	0.0005	0.11	–	–	–	–	–	3.5	Poor	Poor	Poor
	13	0.003	0.019	0.08	0.50	0.02	14.5	0.50	1.33	1.5	0.5	0.0002	0.09	–	–	–	–	–	2.0	Poor	Poor	Poor
	14	0.011	0.012	0.5	1.10	0.02	16.5	0.62	1.10	1.1	0.01	0.0005	0.01	–	–	–	–	–	1.1	Poor	Poor	Poor
	15	0.013	0.019	0.9	0.30	0.01	17.3	0.72	1.36	1.5	1.5	0.0005	0.19	–	–	–	–	–	3.0	Poor	Good	Good
	16	0.009	0.009	0.8	0.20	0.15	17.5	0.55	1.51	1.7	1.0	0.0002	0.02	–	–	–	–	–	2.7	Poor	Poor	Good
	17	0.008	0.006	0.3	0.22	0.05	12.5	0.89	2.20	2.6	1.8	0.0008	0.55	–	–	–	–	–	4.4	Poor	Good	Poor
	18	0.012	0.007	0.2	0.45	0.09	14.5	0.35	1.90	2.5	2.0	0.0003	0.03	–	–	–	–	–	4.5	Poor	Good	Good
	19	0.010	0.008	0.3	0.08	0.03	14.5	1.20	1.70	2.3	2.0	0.0003	0.04	–	–	–	–	–	4.3	Poor	Poor	Good
	20	0.005	0.008	0.8	0.15	0.04	19.9	0.52	0.80	1.6	0.6	0.0009	0.01	–	–	–	–	–	2.2	Poor	Good	Good
	21	0.005	0.008	0.7	0.17	0.03	19.5	0.51	3.50	1.6	0.6	0.0005	0.02	–	–	–	–	–	2.2	Good	Poor	Poor
	22	0.005	0.009	0.9	0.03	0.06	18.5	0.55	1.32	0.5	0.8	0.0005	0.06	–	–	–	–	–	1.3	Poor	Good	Poor
	23	0.003	0.011	0.2	0.13	0.05	18.5	0.52	1.33	3.8	0.8	0.0005	0.05	–	–	–	–	–	4.6	Good	Poor	Poor
	24	0.008	0.013	0.7	0.13	0.07	17.3	0.60	1.25	1.8	2.5	0.0002	0.06	–	–	–	–	–	4.3	Good	Poor	Poor
	25	0.012	0.006	0.2	0.50	0.03	16.5	0.53	1.19	1.9	0.4	0.0035	0.07	–	–	–	–	–	2.3	Poor	Poor	Poor
	26	0.010	0.013	0.3	0.41	0.02	14.5	0.55	1.65	3.2	1.0	0.0006	1.50	–	–	–	–	–	4.2	Good	Poor	Poor
	27	0.005	0.009	0.5	0.39	0.08	16.3	0.55	1.55	2.5	1.5	0.0003	0.12	0.45	–	–	–	–	4.0	Good	Poor	Good
	28	0.008	0.015	0.6	0.15	0.06	16.9	0.92	1.43	2.3	0.2	0.0013	0.05	–	1.5	–	–	–	2.5	Good	Poor	Poor
	29	0.004	0.019	0.9	0.22	0.07	15.5	0.88	1.22	2.1	0.6	0.0008	0.03	–	–	1.1	–	–	2.7	Good	Poor	Good
	30	0.004	0.019	0.8	0.07	0.05	15.9	0.73	1.67	1.6	1.9	0.0008	0.03	–	–	–	0.6	–	3.5	Good	Poor	Poor
	31	0.004	0.019	0.5	0.20	0.04	14.2	0.50	1.53	1.6	1.9	0.0008	0.03	–	–	–	–	1.5	3.5	Good	Poor	Good

Underlines show outside range of the present invention.

[0046] As clear from Table 1, when producing steel which has the chemical composition which is prescribed in the present invention by the above ordinary method, it is learned that compared with the comparative steels, the heat fatigue characteristics, ordinary temperature elongation, and oxidation resistance characteristics are excellent. That is, in a heat fatigue test with a maximum temperature of 950°C, characteristics of 2000 cycles or more are shown and the elongation at break at ordinary temperature was a high 30% or more. Therefore, it was confirmed that, in the ferritic stainless steel sheet of the present invention, the press formability was excellent and no abnormal oxidation or scale spalling occurred in a 950°C continuous oxidation test. In Nos. 11 and 12 of the comparative steels, C and N are off from the upper limit, so all of the heat fatigue, elongation, and oxidation resistance are inferior. In No. 13, Si is off from the lower limit, so all of the heat fatigue, elongation, and oxidation resistance are inferior. In No. 14, Mn is off from the upper limit, so all of the heat fatigue, elongation, and oxidation resistance are inferior. In No. 15, P is off from the lower limit, so the heat fatigue characteristics are inferior. In No. 16, P is off from the upper limit, so the heat fatigue characteristics and the ordinary temperature workability are inferior. In No. 17, Cr is off from the lower limit, so the oxidation resistance is inferior and heat fatigue breakage occurs early starting from the parts with abnormal oxidation. In No. 18, Nb is off from the lower limit, so the high temperature strength is insufficient and the heat fatigue life is short. In No. 19, Nb is off from the upper limit, so the Laves phases coarsely precipitate and therefore the heat fatigue characteristics and workability are inferior. In No. 20, Cu is off from the lower limit, so the high temperature strength is insufficient and the heat fatigue life is short. In No. 21, Cu is excessively added. The heat fatigue characteristics are good, but the ordinary temperature ductility and oxidation resistance are inferior. In No. 22, Mo is off from the lower limit, so the high temperature strength is insufficient and the heat fatigue life is short and the oxidation resistance is also inferior. In No. 23, Mo is excessively added, so the workability and oxidation resistance are inferior. In No. 24, W is off from the upper limit, so the elongation is insufficient and the oxidation resistance is also inferior. In No. 25, B is off from the upper limit, so all characteristics are inferior. In Nos. 26 and 27, Al and Ti are off from the upper limit, so the workability is inferior. In Nos. 28 and 30, V and Sn are off from the upper limit, so the workability and oxidation resistance are inferior. In Nos. 29 and 31, Zr and Ni are off from the upper limit, so the workability is inferior.

[0047] In the steels of the chemical compositions which are shown in Table 1, Steel Nos. 1 to 6 were produced by changing the time after coiling in hot rolling until water cooling of the coil, the hot rolled sheet annealing temperature, and the cooling rate until 400°C at the time of annealing the cold rolled sheet. The hot rolled sheet or hot rolled sheet toughness was evaluated and the cold rolled annealed sheet was measured for ordinary temperature elongation. Here, the heating temperature in the hot rolling was made 1250°C, the finishing temperature was made 900°C, and the time after coiling to water cooling of the coil was changed in the range of 400 to 750°C. Further, the annealing temperature of the hot rolled sheet was changed, then the sheet was cold rolled to a 2 mm thickness and the cold rolled sheet was annealed. At this time, at the time of cooling, the cooling rate was changed from the maximum temperature to 400°C. The hot rolled sheet or the hot rolled annealed sheet was evaluated for toughness by preparing a V-notch Charpy test piece notched in the width direction, running a Charpy impact test at ordinary temperature, judging the case where an impact value or 20J/cm2 or more as passing (in figure, A), and judging the case where it less than this as somewhat unpreferable (in figure, B). Further, the ordinary temperature elongation of the cold rolled annealed sheet was evaluated by the above-mentioned method. The results are shown in Table 2, Nos. 41 to 50.

Table 2

	No.	Steel No.	Time from hot rolling coiling to water cooling	Hot rolled sheet annealing temp. °C	Cooling sped in hot rolled steel hardening °C/sec	Toughness of hot rolled sheet and hot rolled annealed sheet	Ordinary temp. elongation
	41	1	15	900	20	A	A
	42	2	30	800	75	A	A
	43	3	60	700	30	A	A
	44	4	40	No	25	A	A
	45	5	10	No	100	A	A
	46	6	5	950	15	A	A
	47	1	No water cooling	900	20	B	A

(continued)

	No.	Steel No.	Time from hot rolling coiling to water cooling	Hot rolled sheet annealing temp. °C	Cooling sped in hot rolled steel hardening °C/sec	Toughness of hot rolled sheet and hot rolled annealed sheet	Ordinary temp. elongation
	48	2	No water cooling	800	75	B	A
	49	3	60	1050	30	B	A
	50	4	40	600	25	B	A

[0048] Underlines show outside preferable range of present invention.

[0049] As clear from Table 2, it is learned that in Nos. 41 to 46 which were produced under the preferable manufacturing conditions of the present invention, product sheet is obtained which is high in toughness in the manufacturing process and excellent in workability. On the other hand, in Nos. 47 and 48 which are off from the preferred conditions of the present invention, the hot rolled sheets are not water cooled in the coil state, so the hot rolled sheets are low in toughness. Further, in Nos. 49 and 50, the hot rolled sheet annealing temperatures are outside the preferred range and the hot rolled annealed sheets are low in toughness. Sometimes the steel sheets break at the time of production of the sheets.

[0050] Note that, what was explained above only illustrates embodiments of the present invention. The present invention can be changed in various ways within the scope of the claims.

Industrial Applicability

[0051] As explained above, according to the present invention, it is possible to provide ferritic stainless steel sheet excellent in heat resistance and workability which is suitable for exhaust gas system parts which are exposed to an atmosphere of 950°C. Therefore, the present invention is useful for environmental measures, reducing the cost of exhaust gas system parts, etc. and is therefore industrially useful.

Claims

1. Ferritic stainless steel sheet excellent in heat resistance and workability **characterized by** containing, by mass%, C: 0.02% or less, N: 0.02% or less, Si: over 0.1 to 1.0%, Mn: 0.5% or less, P: 0.020 to 0.10%, Cr: 13.0 to 20.0%, Nb: 0.5 to 1.0%, Cu: 1.0 to 3.0%, Mo: 1.5 to 3.5%, W: 2.0% or less, B: 0.0001 to 0.0010%, and Al: 0.01 to 1.0% and having a balance of Fe and unavoidable impurities, where Mo+W is 2.0 to 3.5%.

2. Ferritic stainless steel sheet excellent in heat resistance and workability of claim 1 **characterized by** further containing, by mass%, one or more of Ti: 0.05 to 0.4%, V: 0.05 to 1.0%, Zr: 0.05 to 1.0%, Sn: 0.05 to 0.5%, and Ni: 0.05 to 1.0%.

3. Method of production of ferritic stainless steel sheet excellent in heat resistance and workability **characterized by** producing ferritic stainless steel sheet as set forth in Claim 1 or 2 during which water cooling a steel sheet within one hour after hot rolling and coiling and cold rolling and annealing the cold rolled steel sheet while omitting annealing of hot rolled steel sheet.

4. Method of production of ferritic stainless steel sheet excellent in heat resistance and workability **characterized by** producing ferritic stainless steel sheet as set forth in Claim 1 or 2 during which water cooling a steel sheet within one hour after hot rolling and
coiling, annealing the hot rolled steel sheet in a 700 to 950°C non-recrystallization region, and cold rolling and annealing the cold rolled steel sheet.

Fig.1

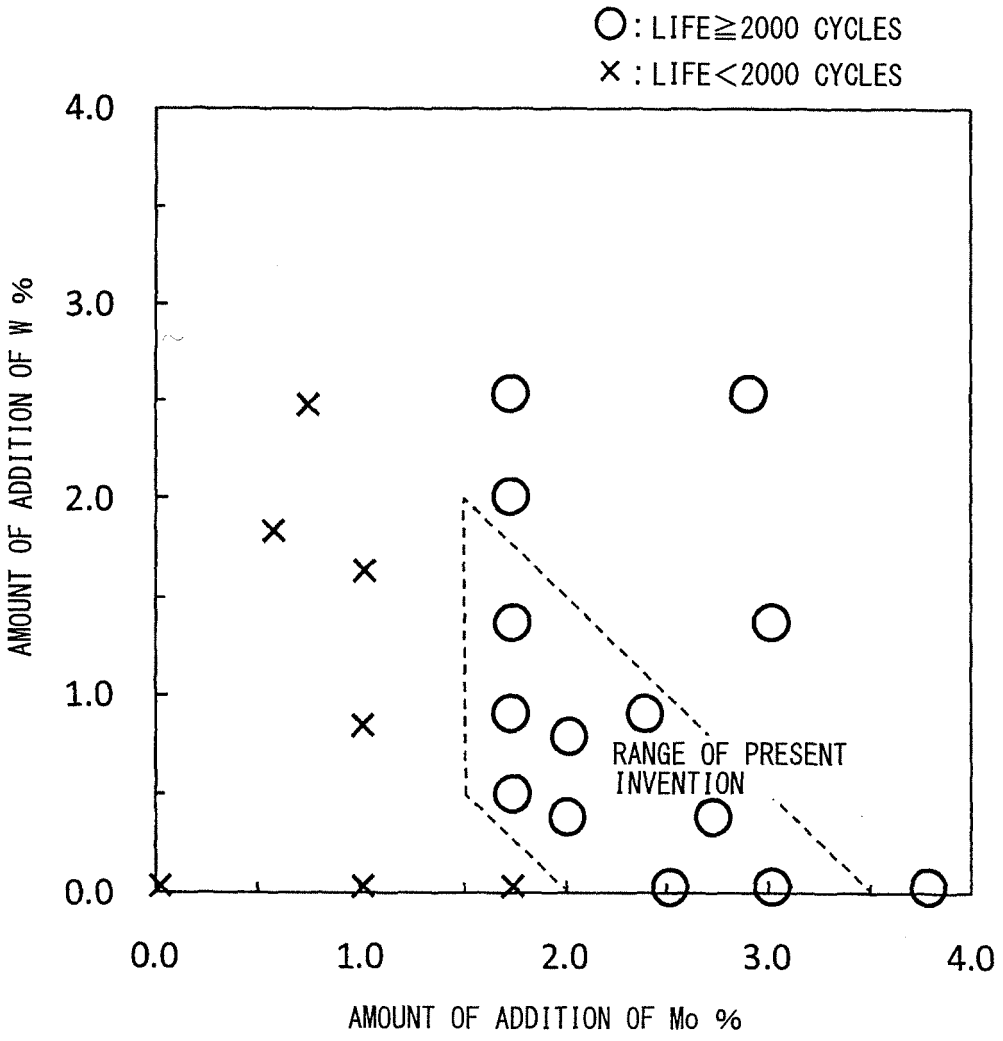

○: LIFE≧2000 CYCLES
×: LIFE<2000 CYCLES
4.0
3.0
2.0
1.0
0.0
AMOUNT OF ADDITION OF W %
RANGE OF PRESENT INVENTION
0.0
1.0
2.0
3.0
4.0
AMOUNT OF ADDITION OF Mo %

Fig.2

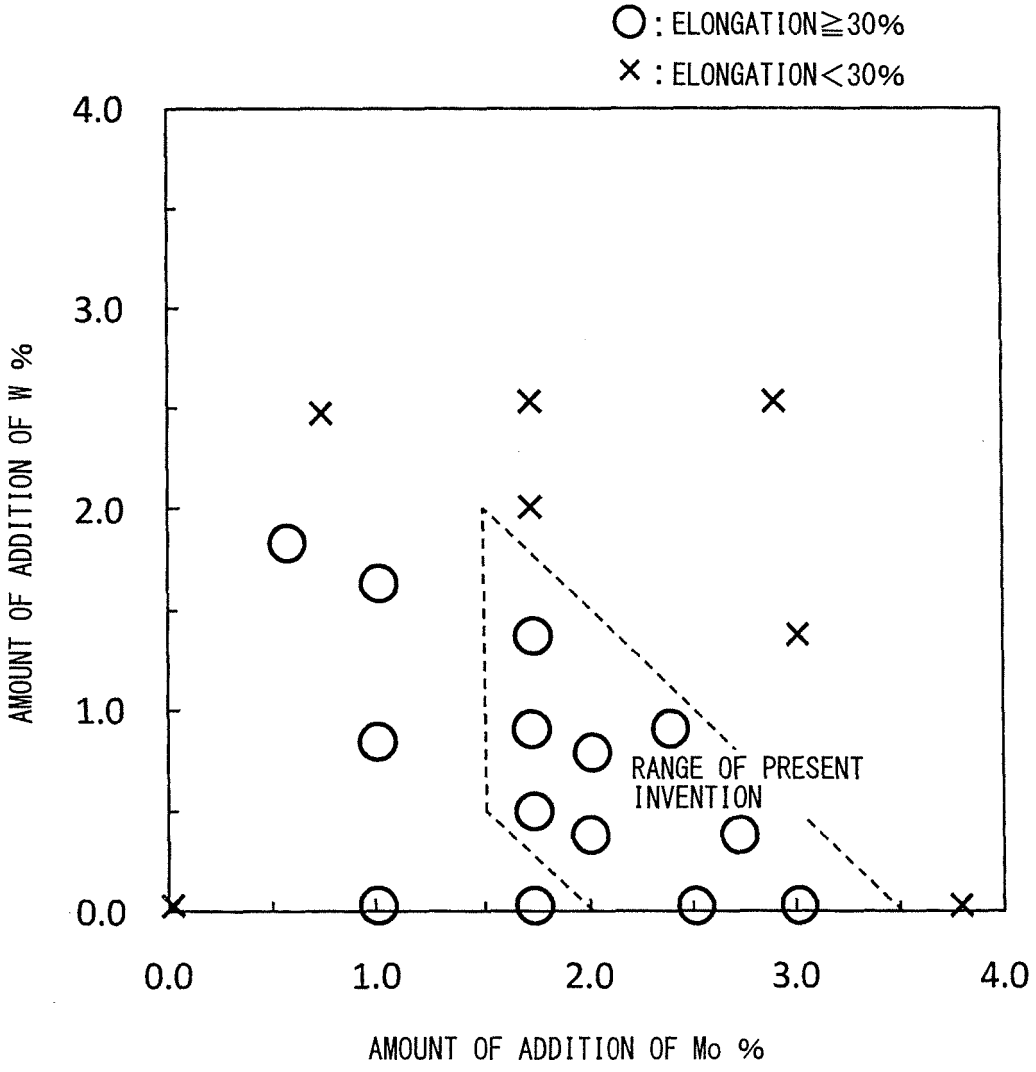
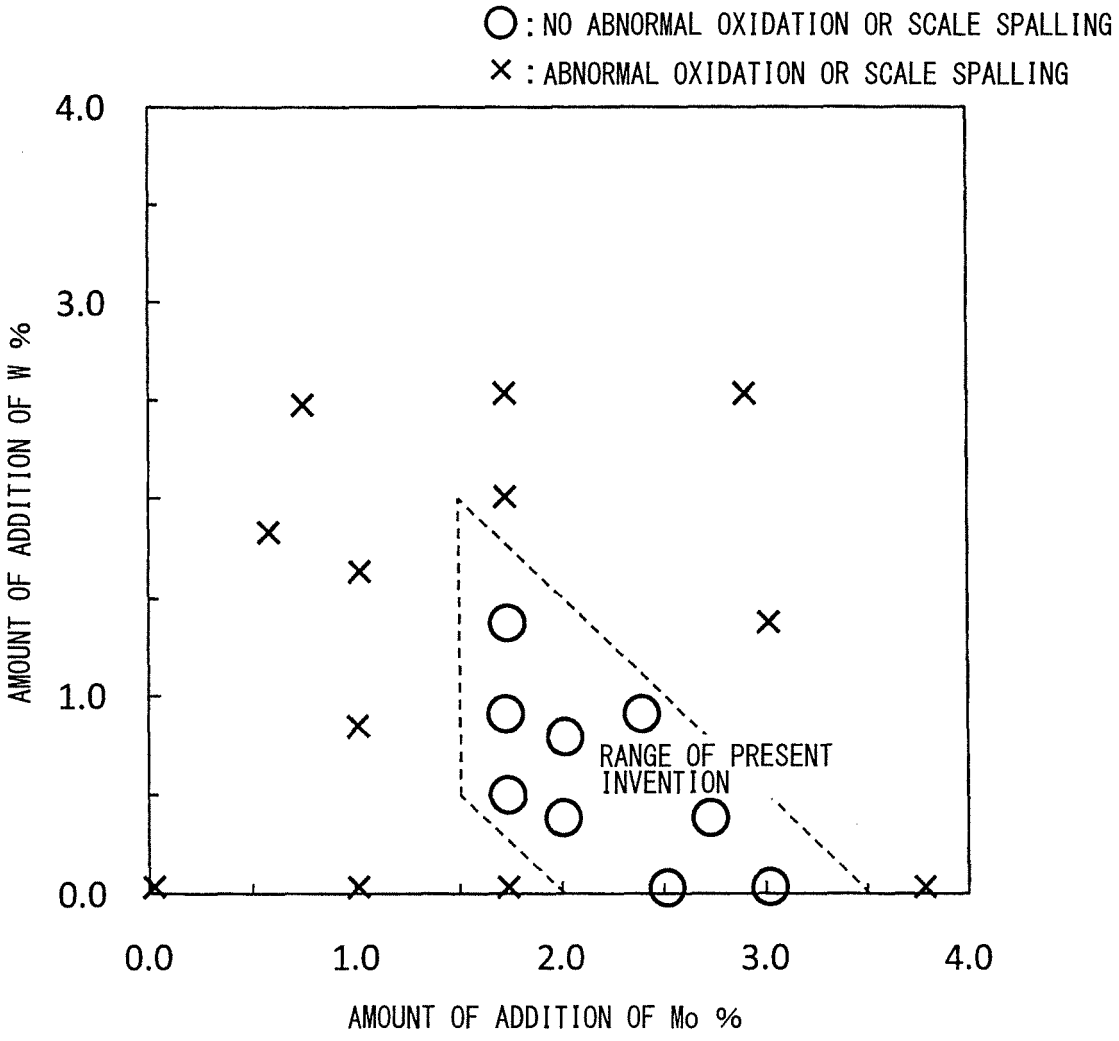

○ : ELONGATION≧30%
× : ELONGATION<30%
4.0
3.0
2.0
1.0
0.0
AMOUNT OF ADDITION OF W %
0.0
1.0
2.0
3.0
4.0
AMOUNT OF ADDITION OF Mo %
RANGE OF PRESENT INVENTION

Fig.3


○ : NO ABNORMAL OXIDATION OR SCALE SPALLING
× : ABNORMAL OXIDATION OR SCALE SPALLING
4.0
3.0
1.0
0.0
AMOUNT OF ADDITION OF W %
RANGE OF PRESENT INVENTION
0.0
1.0
2.0
3.0
4.0
AMOUNT OF ADDITION OF Mo %

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/058218

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21D9/46*(2006.01)i, *C22C38/32*(2006.01)i, *C22C38/54*(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00-38/60, C21D9/46

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 1996-2012
Kokai Jitsuyo Shinan Koho 1971-2012 Toroku Jitsuyo Shinan Koho 1994-2012

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	JP 2006-233278 A (Nippon Steel & Sumikin Stainless Steel Corp.), 07 September 2006 (07.09.2006), entire text; all drawings (Family: none)	1-4
A	JP 2009-102728 A (JFE Steel Corp.), 14 May 2009 (14.05.2009), entire text; all drawings (Family: none)	1-4

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 June, 2012 (13.06.12)	03 July, 2012 (03.07.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/058218

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2010-236001 A (Nisshin Steel Co., Ltd.), 21 October 2010 (21.10.2010), entire text; all drawings (Family: none)	1-2
A	JP 2009-1834 A (JFE Steel Corp.), 08 January 2009 (08.01.2009), entire text; all drawings (Family: none)	1-2
A	JP 2000-336462 A (Nippon Steel Corp.), 05 December 2000 (05.12.2000), entire text; all drawings (Family: none)	1-2

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REFERENCES CITED IN THE DESCRIPTION

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