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

(11) **EP 2 264 202 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
08.10.2014 Bulletin 2014/41

(21) Application number: **09718001.2**

(22) Date of filing: **05.03.2009**

(51) Int Cl.:
C22C 38/00 *(2006.01)* ***C22C 38/28*** *(2006.01)*
C22C 38/54 *(2006.01)*

(86) International application number:
PCT/JP2009/054707

(87) International publication number:
WO 2009/110641 (11.09.2009 Gazette 2009/37)

(54) **FERRITIC STAINLESS STEEL WITH EXCELLENT HEAT RESISTANCE AND TOUGHNESS**

FERRITISCHER NICHTROSTENDER STAHL MIT HERVORRAGENDER WÄRMEBESTÄNDIGKEIT UND ZÄHIGKEIT

ACIER INOXYDABLE FERRITIQUE AYANT D'EXCELLENTES RÉSISTANCE À LA CHALEUR ET TÉNACITÉ

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

(30) Priority: **07.03.2008 JP 2008057613**

(43) Date of publication of application:
22.12.2010 Bulletin 2010/51

(73) Proprietor: **JFE Steel Corporation**
Tokyo 100-0011 (JP)

(72) Inventors:
- **KATO, Yasushi**
  Tokyo 100-0011 (JP)
- **HIRATA, Norimasa**
  Tokyo 100-0011 (JP)
- **NAKAMURA, Tetsuyuki**
  Tokyo 100-0011 (JP)
- **UJIRO, Takumi**
  Tokyo 100-0011 (JP)

(74) Representative: **Grünecker, Kinkeldey,**
Stockmair & Schwanhäusser
Leopoldstrasse 4
80802 München (DE)

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Description

Technical Field

[0001] The present invention relates to a Cr-containing steel and, specifically, relates to a ferritic stainless steel having high heat resistance (thermal fatigue resistance and oxidation resistance) and being excellent in toughness of the base material, which can be suitably applied to exhaust system members that are used under high-temperature environments, such as exhaust pipes of automobiles and motorcycles, exhaust air ducts of converter cases and thermal electric power plants, and so on.

Background Art

[0002] Exhaust system members that are used under exhaust system environments of automobiles, such as exhaust manifolds, exhaust pipes, converter cases, and mufflers, are required to be excellent in thermal fatigue resistance and oxidation resistance (hereinafter, both properties are collectively called "heat resistance"). In such purposes that require high heat resistance, at present, Cr-containing steels including Nb and Si therein, such as Type 429 (14Cr-0.9Si-0.4Nb), are widely used. However, the thermal fatigue resistance of Type 429 has been insufficient, since the exhaust gas temperature is raised to higher than 900°C along with improvement in engine performance.

[0003] Against this problem, for example, a Cr-containing steel that has been improved in high-temperature proof stress by adding Nb and Mo thereto, SUS444 (19Cr-0.5Nb-2Mo) in conformity with JIS G4305, and a ferritic stainless steel including Nb, Mo, and W therein have been developed (for example, see Japanese Unexamined Patent Application Publication No. 2004-018921). However, since prices of rare metal materials such as Mo and W have escalated considerably nowadays, development of materials having heat resistance equivalent to that of those containing Mo, W, or the like, using inexpensive raw materials has been required.

[0004] As raw materials excellent in heat resistance not including expensive elements such as Mo and W, for example, WO2003/004714 discloses a ferritic stainless steel as an automobile exhaust gas path member where Nb: 0.50 mass% or less, Cu: 0.8 to 2.0 mass%, and V: 0.03 to 0.20 mass% are added to a 10 to 20 mass% Cr steel; Japanese Unexamined Patent Application Publication No. 2006-117985 discloses a ferritic stainless steel excellent in thermal fatigue resistance where Ti: 0.05 to 0.30 mass%, Nb: 0.10 to 0.60 mass%, Cu: 0.8 to 2.0 mass%, and B: 0.0005 to 0.02 mass% are added to a 10 to 20 mass% Cr steel; and Japanese Unexamined Patent Application Publication No. 2000-297355 discloses a ferritic stainless steel for automobile exhaust gas system parts where Cu: 1 to 3 mass% is added to a 15 to 25 mass% Cr steel. These steels are all characterized in that thermal fatigue resistance is increased by adding Cu to steels.

[0005] However, according to studies by the present inventors, it has been found that the addition of Cu, as in the techniques of the above-mentioned Patent Documents increases thermal fatigue resistance but decreases the oxidation resistance of steel itself and, as a whole, the heat resistance is deteriorated. Furthermore, SUS444 contains Cr in an amount larger than that of Type 429 and also contains a large amount of Mo. Therefore, it remains a problem that the toughness of the base material is low.

[0006] Accordingly, it is an object of the present invention to provide a ferritic stainless steel that is excellent in thermal fatigue resistance and oxidation resistance and also has toughness being equivalent to or higher than that of Type 429 without containing expensive elements such as Mo and W by developing a technique that can prevent a decrease in oxidation resistance due to addition of Cu. In the present invention, the term "excellent in thermal fatigue resistance and oxidation resistance" means that having characteristics that are equivalent to or higher than those of SUS444 and, specifically, that the oxidation resistance at 950°C and the thermal fatigue resistance in a cyclic thermal load between 100°C to 850°C are equivalent to or higher than those of SUS444. In addition, the term "toughness that is equivalent to that of Type 429" means that the brittle fracture surface ratio of a cold-rolled steel sheet with a thickness of 2 mm is equivalent to that of Type 429 in a Charpy impact test at -40°C.

Disclosure of Invention

[0007] The present invention provides a ferritic stainless steel including C: 0.015 mass% or less, Si: 0.5 mass% or less, Mn: 0.5 mass% or less, P: 0.04 mass% or less, S: 0.006 mass% or less, Cr: 16 to 20 mass%, N: 0.015 mass% or less, Nb: 0.3 to 0.55 mass%, Ti: 0.01 mass% or less, Mo: 0.1 mass% or less, W: 0.1 mass% or less, Cu: 1.0 to 2.5 mass%, Al: 0.2 to 1.2 mass%, and the balance of Fe and inevitable impurities.

[0008] The ferritic stainless steel of the present invention can further include one or more selected from the group consisting of B: 0.003 mass% or less, REM: 0.08 mass% or less, Zr: 0.5 mass% or less, V: 0.5 mass% or less, Co: 0.5 mass% or less, and Ni: 0.5 mass% or less, in addition to the above-mentioned component composition.

[0009] According to the present invention, a ferritic stainless steel that has heat resistance (thermal fatigue resistance and oxidation resistance) being equivalent to or higher than that of SUS444 and also toughness being equivalent to or

higher than that of Type 429 (refer to the steel No. 29 in Table 1 for its representative components) can be obtained inexpensively without containing expensive Mo or W therein. Therefore, the steel of the present invention can be suitably applied to automobile exhaust system members.

Brief Description of Drawings

[0010]

[Fig. 1] Fig. 1 is a view illustrating a thermal fatigue test specimen.
[Fig. 2] Fig. 2 is a diagram illustrating temperature and restraining conditions in a thermal fatigue test.
[Fig. 3] Fig. 3 is a graph showing an effect of Cu content on thermal fatigue resistance.
[Fig. 4] Fig. 4 is a graph showing an effect of Al content on oxidation resistance (weight gain by oxidation).
[Fig. 5] Fig. 5 is a graph showing an effect of Al content on oxidation resistance (spalling amount of scale).
[Fig. 6] Fig. 6 is a graph showing an effect of Si content on oxidation resistance (spalling amount of scale).
[Fig. 7] Fig. 7 is a graph showing an effect of Mn content on toughness (brittle fracture surface ratio).
[Fig. 8] Fig. 8 is a graph showing an effect of Al content on toughness (brittle fracture surface ratio).
[Fig. 9] Fig. 9 is a graph showing an effect of Ti content on toughness (brittle fracture surface ratio).

Best Modes for Carrying Out the Invention

[0011] The present inventors have intensively investigated to develop a ferritic stainless steel being excellent in thermal fatigue resistance and oxidation resistance and also excellent in toughness, without including expensive elements such as Mo or W therein, while preventing a decrease in oxidation resistance due to addition of Cu, which is a problem in conventional techniques. As a result, it has been found that high high-temperature strength is obtained in a broad temperature range and thermal fatigue resistance is increased by combined addition of Nb in the range of 0.3 to 0.55 mass% and Cu in the range of 1.0 to 2.5 mass%; that the decrease in oxidation resistance due to the addition of Cu can be prevented by addition of Al in the range of 0.2 mass% or more; and that, therefore, heat resistance (thermal fatigue resistance and oxidation resistance) being equivalent to or higher than that of SUS444 can be obtained by controlling the amounts of Nb, Cu, and Al to the appropriate ranges mentioned above. Furthermore, it has been found that scale spalling resistance in a cyclic oxidation test of steels containing Cu and Al can be improved by optimizing the Si addition amount (0.5 mass% or less); and that toughness can be increased to a level being equivalent to or higher than that of Type 429 by optimizing the addition amounts of Mn, Al, and Ti (Mn: 0.5 mass% or less, Al: 1.2 mass% or less, Ti: 0.01 mass% or less). Thus, the present invention has been accomplished.

[0012] First, basic experiments leading to the development of the present invention will be described.

[0013] Steels prepared by adding Cu in different amounts to a base having a component composition consisting of C: 0.005 to 0.007 mass%, N: 0.004 to 0.006 mass%, Si: 0.3 mass%, Mn: 0.2 mass%, Cr: 17 mass%, Nb: 0.45 mass%, and Al: 0.35 mass% were laboratory-ingoted to give 50 kg steel ingots. The steel ingots were heated to 1170°C and then hot-rolled into sheet bars with a thickness of 30 mm and a width of 150 mm. Then, the sheet bars were forged into bars having a cross section of 35x35 mm. The bars were annealed at 1030°C and then machined to produce thermal fatigue test specimens having a size shown in Fig. 1. Then, as shown in Fig. 2, the specimens were applied with cyclic heat treatment in which heating and cooling were repeated between 100°C to 850°C at a restraint ratio of 0.35 and were measured for their thermal fatigue lives. Incidentally, the thermal fatigue life was determined as the smallest number of cycles until a stress, which was calculated by dividing a load detected at 100°C by the cross section of a soaking parallel portion of the test specimen shown in Fig. 1, starts to continuously decrease relative to the stress of a previous cycle. This is equivalent to the number of cycles until cracks occur in the test specimen. For comparison, SUS444 (steel containing Cr: 18 mass%, Mo: 2 mass%, and Nb: 0.5 mass%) was subjected to the same test.

[0014] Fig. 3 shows the results of the thermal fatigue test. From this figure, it is confirmed that by adding Cu in an amount of 1.0 mass% or more, a thermal fatigue life equivalent to or higher than the thermal fatigue life (about 1100 cycles) of SUS444 is obtained, and, therefore, that the addition of Cu in an amount of 1 mass% or more is effective for improving the thermal fatigue resistance.

[0015] Next, steels prepared by adding Al in different amounts to a base having a component composition consisting of C: 0.006 mass%, N: 0.007 mass%, Mn: 0.2 mass%, Si: 0.3 mass%, Cr: 17 mass%, Nb: 0.49 mass%, and Cu: 1.5 mass% were laboratory-ingoted to give 50 kg steel ingots. The steel ingots were subjected to hot-rolling, hot-rolled sheet annealing, cold-rolling, and finishing annealing to be formed into cold-rolled annealed sheets having a thickness of 2 mm. 30x20 mm test specimens were cut out from the thus obtained cold-rolled steal sheets. Then, the test specimens were each provided with a 4 mmφ hole in the upper portion thereof. Then, the front surface and the end surface of each specimen were polished with #320 emery paper, and the specimen was degreased and subjected to the following tests.

<Continuous oxidation test in air>

[0016] The test specimen was held for 300 hours in an atmospheric air furnace heated to 950°C. Then, the difference in mass of the test specimen between before and after the heating test was measured to determine the weight gain by oxidation per unit area (g/m^2).

<Cyclic oxidation test in air>

[0017] The test specimen was subjected to 600 cycles of cyclic heat treatment in which heating at 950°C for 25 minutes and cooling at 100°C for 1 minute were conducted in the air. Then, the scale amount (g/m^2) of spalls detached from the test specimen surface was determined from the difference in mass between before and after the test. Incidentally, the heating rate and the cooling rate in the test were 5°C/sec and 1.5°C/sec, respectively.

[0018] Fig. 4 shows the measurement results of weight gain by oxidation. Fig. 5 shows the measurement results of spalling amount of scale. It is confirmed from these results that oxidation resistance being equivalent to or higher than that of SUS444 (weight gain by oxidation: 27 g/m^2 or less, spalling amount of scale: less than 4 g/m^2) is obtained by adding Al in an amount of 0.2 mass% or more.

[0019] Next, steels prepared by adding Si in different amounts to a base having a component composition consisting of C: 0.006 mass%, N: 0.007 mass%, Mn: 0.2 mass%, Al: 0.45 mass%, Cr: 17 mass%, Nb: 0.49 mass%, and Cu: 1.5 mass% were laboratory-ingoted to give 50 kg steel ingots. Then, cold-rolled annealed sheets having a thickness of 2 mm were prepared as in above and subjected to a cyclic oxidation test as in above and measured for spalling amounts of scale. The results are shown in Fig. 6. It was confirmed from the results that when the amount of Si is higher than 0.5%, even if Al is added in an appropriate amount, scale adhesion is decreased thereby to increase the spalling amount, resulting in that heat resistance equivalent to that of SUS444 cannot be obtained.

[0020] Lastly, steels prepared by adding Mn, Al, and Ti in different amounts to a base having a component composition consisting of C: 0.006 to 0.007 mass%, N: 0.006 to 0.007 mass%, Si: 0.3 mass%, Cr: 17 mass%, Nb: 0.45 mass%, and Cu: 1.5 mass% were laboratory-ingoted to give 50 kg steel ingots. The steel ingots were subjected to hot-rolling, hot-rolled sheet annealing, cold-rolling, and finishing annealing to be formed into cold-rolled annealed sheets having a thickness of 2 mm. Charpy impact test specimens with a sub-size were sampled from the cold-rolled annealed sheets and were subjected to a Charpy impact test at -40°C for measuring brittle fracture surface ratio to evaluate toughness.

[0021] Fig. 7 shows effects of Mn contents on toughness when the amounts of Al and Ti are 0.25 mass% and 0.006 mass%, respectively; Fig. 8 shows effects of Al contents on toughness when the amounts of Mn and Ti are 0.1 mass% and 0.005 mass%, respectively; and Fig. 9 shows effects of Ti contents on toughness when the amounts of Al and Mn are 0.25 mass% and 0.1 mass%, respectively. It was confirmed from these results that in order to obtain toughness being equivalent to or higher than that of Type 429, the amounts of Mn: 0.3 mass% or less, Al: 1.2 mass% or less, and Ti: 0.01 mass% or less are necessary.

[0022] The present invention has been accomplished by further investigation based on the above-described findings.

[0023] Next, the component composition of the ferritic stainless steel of the present invention will be described.

C: 0.015 mass% or less

[0024] C is an element effective for increasing the strength of a steel, but an amount higher than 0.015 mass% significantly decreases toughness and formability. Therefore, in the present invention, the amount of C is 0.015 mass% or less. Incidentally, from the viewpoint of ensuring formability, a lower amount of C is preferred, and an amount of 0.008 mass% or less is desirable. On the other hand, in order to ensure strength required in exhaust system members, the amount of C is preferably 0.001 mass% or more. Therefore, more preferred amount is in the range of 0.002 to 0.008 mass%.

Si: 0.5 mass% or less

[0025] Si is added as a deoxidizing material. It is preferable to add in an amount of 0.05 mass% or more. In addition, Si has an effect improving oxidation resistance, which is the focus of the present invention, but the effect is not high compared to that of Al. On the other hand, as shown in Fig. 6, the addition of Si in an excess amount higher than 0.5 mass% decreases scale spalling resistance thereby not to give oxidation resistance being equivalent to or higher than that of SUS444. Therefore, the upper limit of the Si amount is determined to be 0.5 mass%.

Mn: 0.5 mass% or less

[0026] Mn is an element that increases the strength of a steel and also has an effect as a deoxidizing material. It is

preferable that the addition amount be 0.05 mass% or more. However, an excess addition tends to generate a γ phase at high temperature and decreases heat resistance. In addition, as shown in Fig. 7, when the addition amount is higher than 0.5 mass%, toughness being equivalent to or higher than that of Type 429 is not obtained, and the object of the present invention cannot be achieved. Therefore, the amount of Mn in the present invention is determined to be 0.5 mass% or less.

P: 0.04 mass% or less

[0027] P is a harmful element that decreases toughness, and it is desirable that the amount be as low as possible. Therefore, in the present invention, the amount of P is determined to be 0.04 mass% or less and is preferably 0.03 mass% or less.

S: 0.006 mass% or less

[0028] S is a harmful element that decreases elongation and r value and adversely affects formability and also decreases corrosion resistance, which is a basic property of stainless steels. Therefore, it is desirable to reduce the amount as far as possible. Therefore, in the present invention, the amount of S is 0.006 mass% or less and preferably 0.003 mass% or less.

Cr: 16 to 20 mass%

[0029] Cr is an important element effective for improving corrosion resistance and oxidation resistance, which are characteristic properties of stainless steels, but sufficient oxidation resistance cannot be obtained when the amount is less than 16 mass%. On the other hand, Cr is an element providing high hardness and low ductileness to a steel by solid-solution strengthening of the steel at room temperature. In particular, an addition amount of higher than 20 mass% makes the above-mentioned adverse effects significant, resulting in that workability and toughness that are equivalent to or higher than those of Type 429 cannot be obtained. Therefore, in the present invention, the amount of Cr is in the range of 16 to 20 mass%, preferably, in the range 16 to 19 mass%.

N: 0.015 mass% or less

[0030] N is an element that decreases the toughness and the formability of a steel, and an addition amount of higher than 0.015 mass% makes the decreases significant. Therefore, the amount of N is determined to be 0.015 mass% or less. Furthermore, in the case of requiring a higher toughness, the amount of N is further decreased and is preferably lower than 0.010 mass%.

Nb: 0.3 to 0.55 mass%

[0031] Nb is an element having effects of increasing corrosion resistance and formability and intergranular corrosion resistance of a weld zone by forming a carbonitride with C and N to fix them and also improving thermal fatigue resistance by increasing the high-temperature strength. These effects are recognized when the amount is 0.3 mass% or more. On the other hand, when the addition amount is higher than 0.55 mass%, a Laves phase tends to precipitate to decrease the toughness. Therefore, the amount of Nb is determined in the range of 0.3 to 0.55 mass% and is preferably in the range of 0.4 to 0.5 mass%.

Ti: 0.01 mass% or less

[0032] Ti is an element that bonds to N easier than Nb does and tends to form coarse TiN. The coarse TiN act as a notch to significantly decrease the toughness. In particular, as shown in Fig. 9, when the content of Ti is higher than 0.01 mass%, such adverse effects become significant. Therefore, in the present invention, the amount of Ti is limited to 0.01% or less.

Mo: 0.1 mass% or less

[0033] Mo is an expensive element and is not willingly added on the basis of the purpose of the present invention. However, it may be mixed from the raw materials such as a scrap in an amount of 0.1 mass% or less. Therefore, the amount of Mo is determined to be 0.1 mass% or less.

W: 0.1 mass% or less

[0034] W is an expensive element similar to Mo and is not willingly added on the basis of the purpose of the present invention. However, it may be mixed from the raw materials such as a scrap in an amount of 0.1 mass% or less. Therefore, the amount of W is determined to be 0.1 mass% or less.

Cu: 1.0 to 2.5 mass%

[0035] Cu is an element that is very effective for increasing thermal fatigue resistance. As shown in Fig. 3, in order to obtain thermal fatigue resistance that is equivalent to or higher than that of SUS444, a Cu addition amount of 1.0 mass% or more is necessary. However, if the addition amount is larger than 2.5 mass%, ε-Cu is precipitated during the cooling after heat treatment thereby to harden the steel and readily cause embrittlement during hot-working. More importantly, though the thermal fatigue resistance is increased by the addition of Cu, the oxidation resistance of steel itself is rather decreased. Therefore, the overall heat resistance may be decreased. The reason thereof is not sufficiently clear, but it may be because that Cu is concentrated in a de-Cr layer just below the generated scale to prevent Cr, which is an element that increases intrinsic oxidation resistance of stainless steels, from being rediffused. Therefore, the amount of Cu is determined in the range of 1.0 to 2.5 mass%, more preferably in the range of 1.1 to 1.8 mass%.

Al: 0.2 to 1.2 mass%

[0036] Al is, as shown in Figs. 4 and 5, an indispensable element for increasing the oxidation resistance of a Cu-containing steel. In particular, in order to obtain oxidation resistance that is equivalent to or higher than that of SUS444, which is an object of the present invention, an addition amount of 0.2 mass% or more is necessary. On the other hand, as shown in Fig. 8, an addition amount of higher than 1.2 mass% hardens the steel not to obtain toughness equivalent to or higher than that of Type 429. Therefore, the upper limit is determined to be 1.2 mass%, and, preferably, the amount is in the range of 0.3 to 1.0 mass%.

[0037] The ferritic stainless steel of the present invention can include, one or more selected from the group consisting of B, REM, Zr, V, Co, and Ni in the following ranges, in addition to the above-mentioned components as essential elements.

B: 0.003 mass% or less

[0038] B is an element effective for improving workability, in particular, second workability. This noticeable effect can be obtained when the addition amount is 0.0005 mass% or more, but a large amount of higher than 0.003 mass% precipitates BN to reduce workability. Therefore, when B is added, the amount is 0.003 mass% or less, more preferably in the range of 0.0005 to 0.002 mass%.

REM: 0.08 mass% or less, Zr: 0.5 mass% or less

[0039] Rare-earth element (REM) and Zr are each an element increasing oxidation resistance and, in the present invention, can be added according to need. In order to obtain the effect, the addition amount of each is 0.01 mass% or more, 0.05 mass% or more respectively. However, the addition of REM in an amount of higher than 0.08 mass% embrittles the steel, and the addition of Zr in an amount of higher than 0.5 mass% precipitates Zr intermetallics to embrittle the steel. Therefore, when REM is added, the amount is limited to 0.08 mass% or less, and when Zr is added, the amount is limited to 0.5 mass% or less.

V: 0.5 mass% or less

[0040] V is an element effective for increasing workability and oxidation resistance. In particular, the amount for obtaining the effect increasing oxidation resistance is preferably 0.15 mass% or more. However, the addition in an excess amount of higher than 0.5 mass% precipitate coarse V(C, N) to deteriorate surface properties. Therefore, when V is added, the amount is preferably 0.5 mass% or less, preferably in the range of 0.15 to 0.4 mass%.

Co: 0.5 mass% or less

[0041] Co is an element effective for increasing toughness, and the addition amount is preferably 0.02 mass% or more. However, Co is an expensive element, and the effect is saturated when the addition amount is higher than 0.5 mass%. Therefore, when Co is added, the amount is preferably 0.5 mass% or less, more preferably, in the range of 0.02 to 0.2 mass%.

Ni: 0.5 mass% or less

[0042] Ni is an element increasing toughness. In order to obtain the effect, the amount is preferably 0.05 mass% or more. However, Ni is expensive and a strong γ-phase-forming element. Therefore, a γ-phase is formed at high temperature to decrease oxidation resistance. Therefore, when Ni is added, the amount is preferably 0.5 mass% or less and more preferably in the range of 0.05 to 0.4 mass%.

[0043] Next, a method of manufacturing the ferritic stainless steel of the present invention will be described.

[0044] The method of manufacturing the stainless steel of the present invention may be any known method of manufacturing a ferritic stainless steel and is not particularly limited. Preferably, for example, a sheet is ingoted in a known melting furnace such as a converter furnace or an electric furnace or is further subjected to secondary refining such as ladle refining or vacuum refining so as to have the above-described component composition of the present invention. Then, the molten steel is formed into a billet (slab) by continuous-casting or ingot-casting-blooming. The slab is hot-rolled to a hot-rolled sheet, and, according to need, the sheet is subjected to hot-rolled sheet annealing. The hot-rolled sheet is further subjected to a process such as pickling, cold-rolling, finishing annealing, and pickling to give a cold-rolled annealed sheet. The cold-rolling may be performed once or twice having middle annealing therebetween, and each step of the cold-rolling, the finishing annealing, and the pickling may be performed repeatedly. Furthermore, in some cases, the hot-rolled sheet annealing may be omitted. When the steel sheet is required to have surface gloss, skin pass may be conducted after the cold-rolling or the finishing annealing. In addition, it is preferable that the slab-heating temperature before the hot-rolling be in the range of 1000 to 1250°C, the hot-rolled sheet annealing temperature be in the range of 900 to 1100°C, and the finishing annealing temperature is in the range of 900 to 1120°C.

[0045] The thus obtained ferritic stainless steel of the present invention is then subjected to processing such as cutting, bending work, or press work, according to the respective purposes, to obtain various types of exhaust system members that are used under high temperature environments, such as exhaust pipes of automobiles and motorcycles and exhaust air ducts of converter cases and thermal electric power plants. Furthermore, the stainless steel of the present invention used in the above-mentioned members is not limited to cold-rolled annealed sheets and may be used as a hot-rolled sheet or a hot-rolled annealed sheet and, further, may be used after descale treatment according to need. In addition, the welding method for assembling the above-mentioned members is not particularly limited, and, for example, common arc welding such as metal inert gas (MIG), metal active gas (MAG), or tungsten inert gas (TIG) welding, electric resistance welding such as spot welding or seam welding, and a method used in electric resistance welding, such as high-frequency resistance welding, high-frequency induction welding, or laser welding, can be used.

Example 1

[0046] Steels Nos. 1 to 27 having component compositions shown in Table 1 were ingoted in a vacuum melting furnace to give 50 kg steel ingots. Each steel ingot was divided into two steel ingots by forging. Then, one steel ingot of the two was heated to 1170°C and then hot-rolled into a hot-rolled sheet having a thickness of 5 mm. The sheet was subjected to hot-rolled sheet annealing at 1020°C, pickling, cold-rolling at a draft of 60%, finishing annealing at 1030°C, cooling at an average cooling rate of 20°C/sec, and pickling to be formed into a cold-rolled annealed sheet having a thickness of 2 mm. The resulting sheet was subjected to the following oxidation resistance test and impact test. Incidentally, as reference, cold-rolled annealed sheets were produced as in above from SUS444, Type 429, and steels disclosed in WO2003/004714 and Japanese Unexamined Patent Application Publication Nos. 2006-117985 and 2000-297355, shown as Nos. 28 to 32 of Table 1, and were subjected to the same evaluation tests.

<Continuous oxidation test in air>

[0047] Test specimens of 30x20 mm were cut out from the thus obtained different cold-rolled annealed sheets and were each provided with a 4 mmφ hole in the upper portion thereof. Then, the front surface and the end surface of each specimen were polished with #320 emery paper, and the specimen was degreased and then suspended in an atmospheric air furnace heated to 950°C and held for 300 hours. After the test, the mass of the specimen was measured, and the difference from the mass previously measured before the test was determined to calculate the weight gain by oxidation (g/m^2). Incidentally, the test was performed twice, and the average value was used for evaluating the continuous oxidation resistance.

<Cyclic oxidation test in air>

[0048] Test specimens of 30×20 mm were cut out from the different cold-rolled annealed sheets and were each provided with a 4 mmφ hole in the upper portion thereof. Then, the front surface and the end surface of each specimen were polished with #320 emery paper, and the specimen was degreased and then subjected to an oxidation test in which

heating and cooling were repeated between 100°C and 950°C in the air. The heating rate and the cooling rate were 5°C/sec and 1.5°C/sec, respectively, and the holding times were 1 minute at 100°C and 25 minutes at 950°C, and this was repeated 600 cycles. In the evaluation of cyclic oxidation resistance, the mass of the specimen after the test was measured, and the difference from the mass previously measured before the test was determined to calculate the spalling amount of scale (g/m^2). Incidentally, the test was performed twice, and the average value was used for evaluating the cyclic oxidation resistance.

<Charpy impact test>

[0049] Three Charpy impact test specimens each provided with a V-notch perpendicular to the rolling direction were sampled from each of the different cold-rolled annealed sheets and were subjected to a Charpy impact test at -40°C. The brittle fracture surface ratios of the three were measured, and the average value thereof was determined for evaluating the toughness.

Example 2

[0050] The remaining steel ingot of the two that was obtained by dividing the 50 kg steel ingot in Example 1 was heated to 1170°C and then hot-rolled to a sheet bar having a thickness of 30 mm and a width of 150 mm. Then, the sheet bar was forged into a bar of 35 mm square. The bar was annealed at 1030°C and then machined to produce a thermal fatigue test specimen having a size shown in Fig. 1. Then, the specimen was subjected to the following thermal fatigue test. As in Example 1, specimens were produced similarly from SUS444, Type 429, and steels disclosed in WO2003/004714 and Japanese Unexamined Patent Application Publication Nos. 2006-117985 and 2000-297355, as reference, and were subjected to the thermal fatigue test.

<Thermal fatigue test>

[0051] In a thermal fatigue test, heating and cooling were repeated between 100°C and 850°C at a restraint ratio of 0.35, and the thermal fatigue life was measured. In this test, the heating rate and the cooling rate were each 10°C/sec, and the holding times were 2 minutes at 100°C and 5 minutes at 850°C. Incidentally, the thermal fatigue life was determined as the smallest number of cycles until a stress, which was calculated by dividing a load detected at 100°C by the cross section of a soaking parallel portion of the test specimen, started to continuously decrease relative to the stress of a previous cycle.

[0052] The results of the continuance oxidation test in air, the cyclic oxidation test in air, and the Charpy impact test in Example 1 and the results of the thermal fatigue test in Example 2 are shown together in Table 2. As obvious from Table 2, all the steels adapted to the present invention have oxidation resistance properties and thermal fatigue resistance properties being equivalent to or higher than those of SUS444 and toughness being equivalent to or higher than that of Type 429 and therefore satisfy the purpose of the present invention. On the other hand, any of the steels of comparative examples that are out of the scope of the present invention and the steels of reference examples according to known technology is not simultaneously excellent in all the oxidation resistance properties, the thermal fatigue resistance properties, and the toughness of the base material and is not provided with properties that are the purpose of the present invention.

Industrial Applicability

[0053] The steel of the present invention can be suitably used in not only exhaust system members of, for example, automobiles but also exhaust system members of thermal electric power systems and fuel cell members of solid-oxide fuel cells, which are required to have similar properties.

Table 1-1

Steel No	Chemical Component (mass%)														Notes
	C	Si	Mn	Al	P	S	Cr	Cu	Nb	Ti	Mo	W	N	Others	
1	0.006	0.19	0.13	0.37	0.032	0.004	17.5	1.35	0.43	0.006	0.02	0.04	0.008	-	Example
2	0.005	0.35	0.28	0.51	0.026	0.002	17.3	1.56	0.41	0.002	0.03	0.01	0.007	-	Example
3	0.005	0.27	0.33	0.48	0.022	0.001	17.7	1.46	0.48	0.006	0.02	0.01	0.011	-	Example
4	0.008	0.28	0.11	0.44	0.032	0.001	17.4	1.92	0.49	0.001	0.03	0.02	0.005	-	Example
5	0.005	0.07	0.42	0.84	0.022	0.002	16.3	1.32	0.41	0.003	0.01	0.04	0.006	-	Example
6	0.003	0.38	0.28	0.61	0.029	0.004	17.8	1.55	0.37	0.004	0.02	0.03	0.007	-	Example
7	0.006	0.22	0.44	0.47	0.022	0.002	18.2	1.91	0.46	0.007	0.02	0.02	0.007	-	Example
8	0.007	0.17	0.23	0.47	0.029	0.003	17.2	1.39	0.45	0.004	0.01	0.01	0.008	B/0.0009 V/0.051	Example
9	0.008	0.39	0.18	0.35	0.026	0.002	17.9	1.42	0.44	0.001	0.03	0.01	0.004	Co/0.13 B/0.0011	Example
10	0.004	0.27	0.26	0.55	0.031	0.002	17.7	1.39	0.43	0.003	0.02	0.03	0.006	Zr/0.08	Example
11	0.006	0.29	0.39	0.31	0.027	0.005	18.9	1.46	0.46	0.002	0.04	0.02	0.003	Ni/0.21 Zr/0.10	Example
12	0.008	0.17	0.08	0.41	0.021	0.002	17.4	1.38	0.41	0.003	0.02	0.03	0.004	Co/0.09 REM/0.031	Example
13	0.006	0.31	0.35	0.14	0.030	0.002	17.1	1.46	0.44	0.006	0.01	0.02	0.009	-	Comparative Example
14	0.008	0.23	0.66	1.62	0.028	0.004	17.7	1.61	0.49	0.004	0.05	0.01	0.008	-	Comparative Example
15	0.006	0.32	0.55	0.69	0.028	0.003	17.4	0.87	0.51	0.004	0.02	0.01	0.009	-	Comparative Example
16	0.011	0.82	0.41	0.72	0.020	0.002	17.1	1.21	0.44	0.009	0.04	0.02	0.004	-	Comparative Example
17	0.007	0.34	0.15	1.19	0.029	0.003	17.4	1.58	0.42	0.095	0.03	0.02	0.005	-	Comparative Example
18	0.005	0.21	0.37	1.24	0.031	0.002	17.3	1.45	0.44	0.002	0.02	0.04	0.007	-	Comparative Example

Table 1-2

Steel No	Chemical Component (mass%)														Notes
	C	Si	Mn	Al	P	S	Cr	Cu	Nb	Ti	Mo	W	N	Others	
19	0.007	0.71	0.11	0.38	0.027	0.001	17.5	1.28	0.48	0.007	0.04	0.02	0.006	-	Comparative Example
20	0.008	0.14	0.71	0.47	0.031	0.003	17.1	1.66	0.39	0.003	0.01	0.02	0.007	-	Comparative Example
21	0.006	0.33	0.22	0.57	0.025	0.001	18.1	0.72	0.41	0.002	0.05	0.02	0.005	-	Comparative Example
22	0.005	0.29	0.28	0.44	0.030	0.002	17.9	1.54	0.44	0.11	0.03	0.03	0.008	-	Comparative Example
23	0.007	0.23	0.25	0.47	0.027	0.002	17.6	1.18	0.44	0.003	0.06	0.02	0.008	V:0.18	Example
24	0.003	0.09	0.12	0.46	0.025	0.003	17.5	1.26	0.42	0.008	0.05	0.03	0.007	V:0.22	Example
25	0.006	0.32	0.34	0.46	0.024	0.002	17.7	1.22	0.46	0.005	0.06	0.02	0.005	V:0.38	Example
26	0.007	0.27	0.15	0.53	0.027	0.003	19.1	1.28	0.45	0.004	0.05	0.02	0.007	V:0.20	Example
27	0.005	0.03	0.11	0.51	0.024	0.002	18.2	1.19	0.45	0.006	0.05	0.03	0.006	V:0.23	Example
28	0.008	0.31	0.42	0.019	0.031	0.003	18.7	0.02	0.52	0.003	1.87	0.02	0.008	-	SUS444
29	0.007	0.87	0.33	0,028	0.029	0.004	14.5	0.03	0.45	0.007	0.03	0.02	0.008	-	Type429
30	0.008	0.32	0.05	0.01	0.028	0.002	17.02	1.93	0.33	0.002	0.01	0.02	0.010	Ni/0.10 V/0.10	Reference Example 1
31	0.009	0.46	0.54	0.002	0.029	0.003	18.90	1.36	0.35	0.08	0.01	0.02	0.007	Ni/0.10 V/0.03 B/0.0030	Reference Example 2
32	0.006	0.22	0.05	0.052	0.005	0.0052	18.8	1.65	0.42	0.09	0.02	0.02	0.006	Ni/0.15	Reference Example3

Notes Reference Example 1: Steel No. 3 of WO2003/004714
Reference Example 2: Steel No. 7 of Japanese Unexamined Patent Application Publication No. 2006-117985
Reference Example 3: Steel No. 5 of Japanese Unexamined Patent Application Publication No. 2000-297355

Table 2

Steel No	Heat Resistance		Thermal fatigue life (cycle)	Brittle fracture surface ratio at -40°C (%)	Notes
	Weight gain by oxidation (g/m^2)	Spalling amount of scale (g/m^3)			
1	21	3	1230	<5	Example
2	20	2	1330	<5	Example
3	21	2	1300	<5	Example
4	21	2	1500	<5	Example
5	17	<0.1	1230	<5	Example
6	20	1	1320	<5	Example
7	21	2	1510	<5	Example
8	21	2	1260	<5	Example
9	22	3	1280	<5	Example
10	20	1	1250	<5	Example
11	22	3	1290	<5	Example
12	21	2	1250	<5	Example
13	80	10	1290	<5	Comparative Example
14	11	<0.1	1400	50	Comparative Example
15	14	1	820	<5	Comparative Example
16	18	5	1210	<5	Comparative Example
17	15	<0.1	1350	15	Comparative Example
18	15	<0.1	1300	15	Comparative Example
19	21	10	1210	<5	Comparative Example
20	21	2	1380	15	Comparative Example
21	20	1	700	<5	Comparative Example
22	21	2	1320	20	Comparative Example
23	15	1	1200	<5	Example
24	15	1	1230	<5	Example
25	14	0.9	1210	<5	Example
26	15	1	1240	<5	Example
27	15	1	1210	<5	Example
28	27	4	1120	10	SUS444
29	51	25	500	<5	Type429

(continued)

Steel No	Heat Resistance		Thermal fatigue life (cycle)	Brittle fracture surface ratio at -40°C (%)	Notes
	Weight gain by oxidation (g/m^2)	Spalling amount of scale (g/m^3)			
30	>100	>100	1480	<5	Reference Example 1
31	>100	>100	1240	<10	Reference Example 2
32	>100	>100	1400	<10	Reference Example 3
Notes Reference Example 1: Steel No. 3 of WO2003/004714 Reference Example 2: Steel No. 7 of Japanese Unexamined Patent Application Publication No. 2006-117985 Reference Example 3: Steel No. 5 of Japanese Unexamined Patent Application Publication No. 2000-297355					

Claims

1. A ferritic stainless steel comprising C: 0.015 mass% or less, Si: 0.5 mass% or less, Mn: 0.5 mass% or less, P: 0.04 mass% or less, S: 0.006 mass% or less, Cr: 16 to 20 mass%, N: 0.015 mass% or less, Nb: 0.3 to 0.55 mass%, Ti: 0.01 mass% or less, Mo: 0.1 mass% or less, W: 0.1 mass% or less, Cu: 1.0 to 2.5 mass%, Al: 0.2 to 1.2 mass%, and the balance of Fe and inevitable impurities.

2. The ferritic stainless steel according to Claim 1, further comprising one or more selected from the group consisting of B: 0.003 mass% or less, REM: 0.08 mass% or less, Zr: 0.5 mass% or less, V: 0.5 mass% or less, Co: 0.5 mass% or less, and Ni: 0.5 mass% or less, in addition to the component composition.

Patentansprüche

1. Ein ferritischer Edelstahl enthaltend C: 0,015 Massen% oder weniger, Si: 0,5 Massen% oder weniger, Mn: 0,5 Massen% oder weniger, P: 0,04 Massen% oder weniger, S: 0,006 Massen% oder weniger, Cr: 16 bis 20 Massen%, N: 0,015 Massen% oder weniger, Nb: 0,3 bis 0,55 Massen%, Ti: 0,01 Massen% oder weniger, Mo: 0,1 Massen% oder weniger, W: 0,1 Massen% oder weniger, Cu: 1,0 bis 2,5 Massen%, Al: 0,2 bis 1,2 Massen%, und als Rest Fe und unvermeidbare Verunreinigungen.

2. Der ferritische Edelstahl gemäß Anspruch 1, weiter enthaltend ein oder mehrere, ausgewählt aus der Gruppe von B: 0,003 Massen% oder weniger, REM: 0,08 Massen% oder weniger, Zr: 0,5 Massen% oder weniger, V: 0,5 Massen% oder weniger, Co: 0,5 Massen% oder weniger, und Ni: 0,5 Massen% oder weniger zusätzlich zu der Zusammensetzung der Komponenten.

Revendications

1. Acier inoxydable ferritique comprenant : C : 0,015 % en masse ou moins, Si : 0,5 % en masse ou moins, Mn : 0,5 % en masse ou moins, P : 0,04 % en masse ou moins, S : 0,006 % en masse ou moins, Cr : de 16 à 20 % en masse, N : 0,015 % en masse ou moins, Nb : de 0,3 % à 0,55 % en masse, Ti : 0,01 % en masse ou moins, Mo : 0,1 % en masse ou moins, W : 0,1 % en masse ou moins, Cu : 1,0 à 2,5 % en masse, Al : 0,2 à 1,2 % en masse, le reste étant constitué de Fe et d'impuretés inévitables.

2. Acier inoxydable ferritique selon la revendication 1, comprenant en outre un ou plusieurs éléments choisis dans le groupe constitué de B : 0,003 % en masse ou moins, REM : 0,08 % en masse ou moins, Zr : 0,5 % en masse ou moins, V : 0,5 % en masse ou moins, Co : 0,5 % en masse ou moins, et Ni : 0,5 % en masse ou moins, s'ajoutant à la composition du composant.

FIG.1

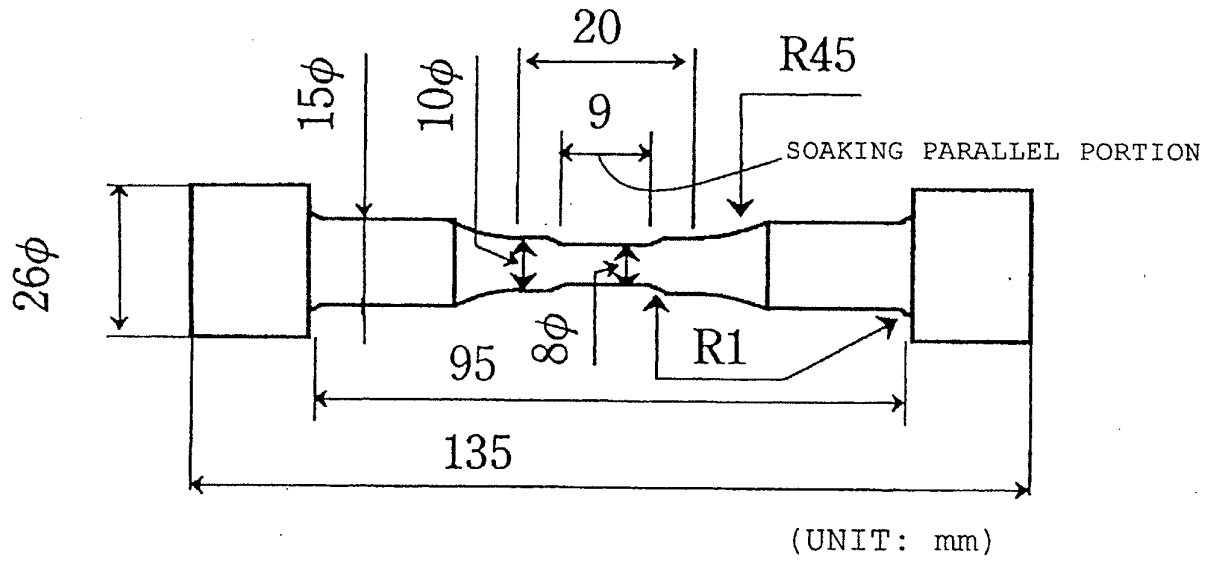

20
R45
15φ
10φ
9
SOAKING PARALLEL PORTION
26φ
8φ
R1
95
135
(UNIT: mm)

FIG.2

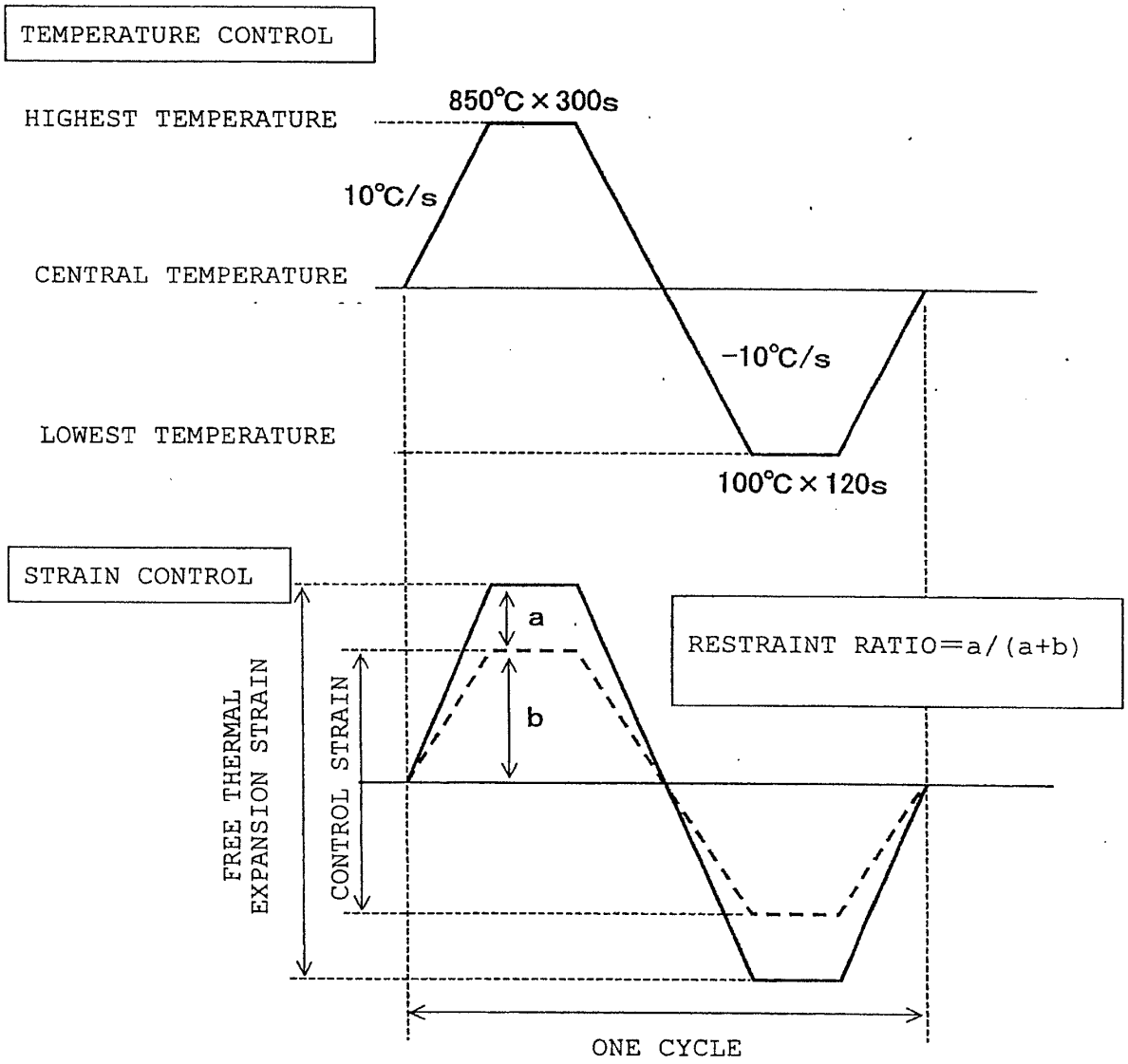

TEMPERATURE CONTROL
HIGHEST TEMPERATURE
850℃×300s
10℃/s
CENTRAL TEMPERATURE
-10℃/s
LOWEST TEMPERATURE
100℃×120s
STRAIN CONTROL
a
b
RESTRAINT RATIO=a/(a+b)
FREE THERMAL EXPANSION STRAIN
CONTROL STRAIN
ONE CYCLE

FIG.3

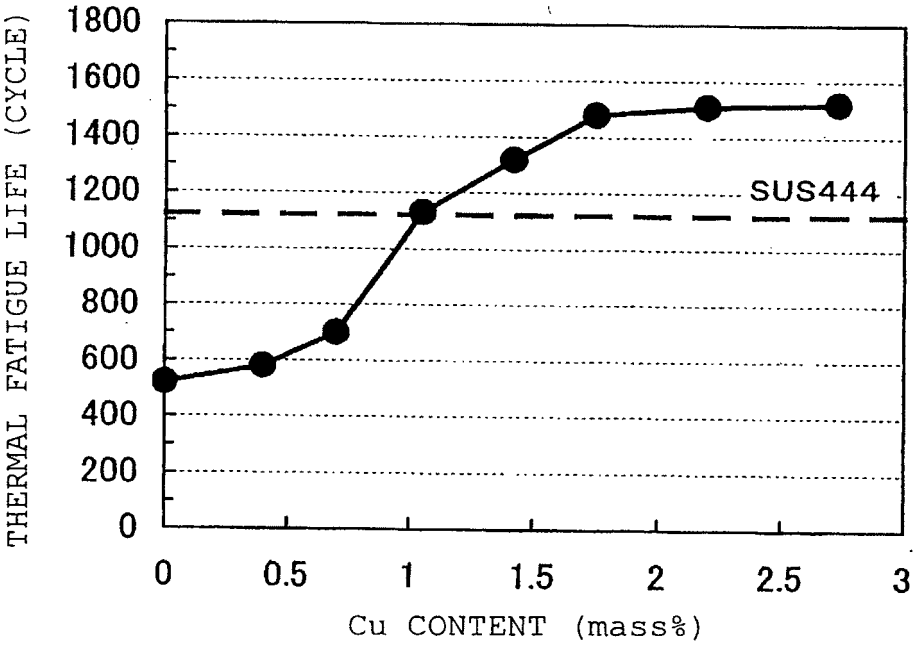

THERMAL FATIGUE LIFE (CYCLE)
1800
1600
1400
1200
1000
800
600
400
200
0
SUS444
0
0.5
1
1.5
2
2.5
3
Cu CONTENT (mass%)

FIG.4

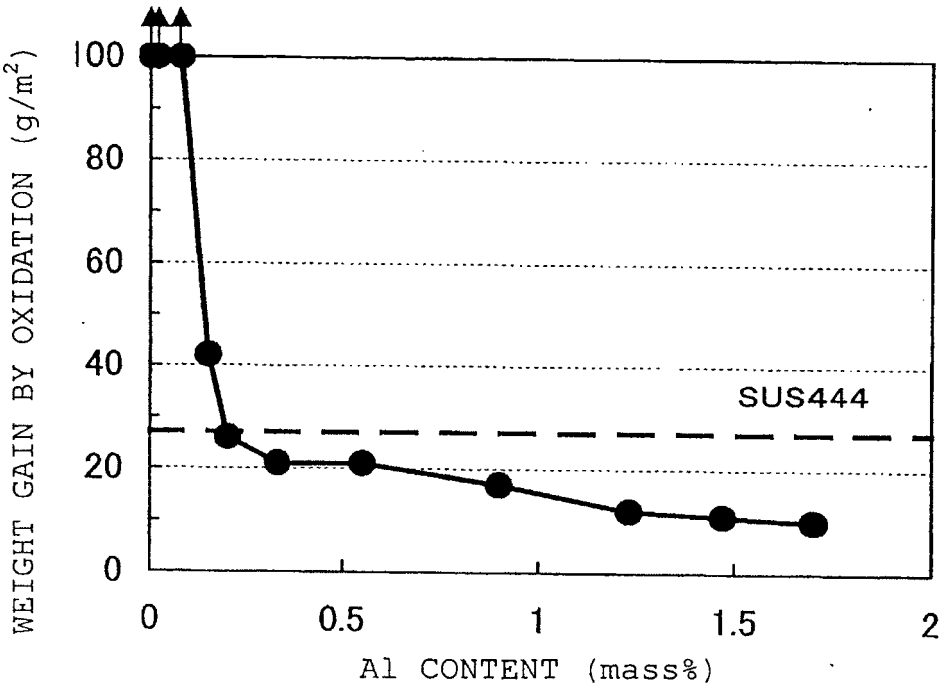

WEIGHT GAIN BY OXIDATION (g/m²)
100
80
60
40
20
0
SUS444
0
0.5
1
1.5
2
Al CONTENT (mass%)

FIG.5

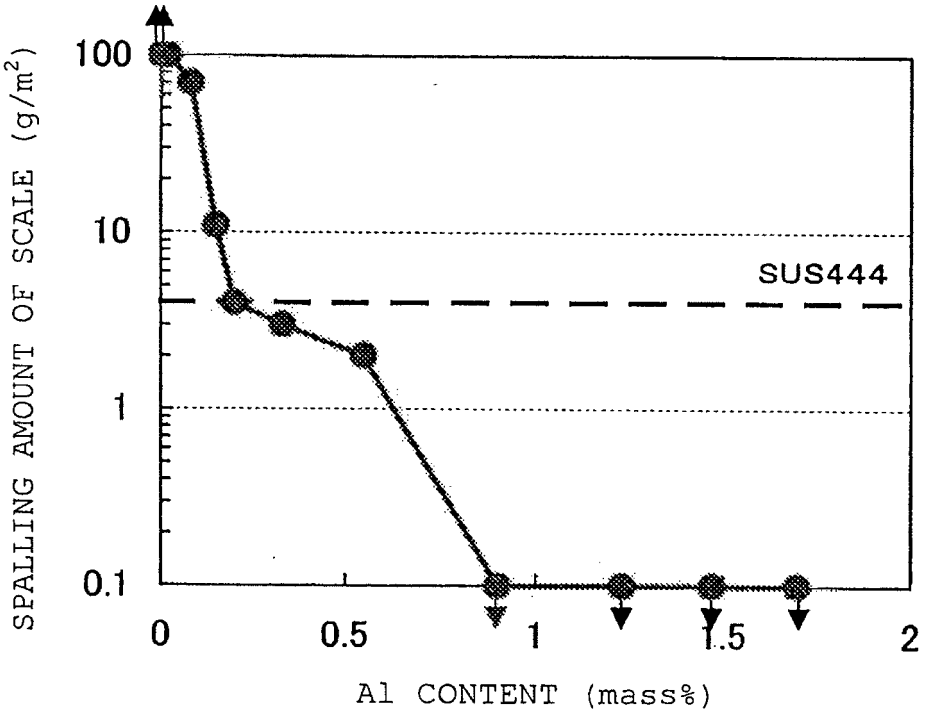

SPALLING AMOUNT OF SCALE (g/m²)
100
10
1
0.1
SUS444
0
0.5
1
1.5
2
Al CONTENT (mass%)

FIG.6

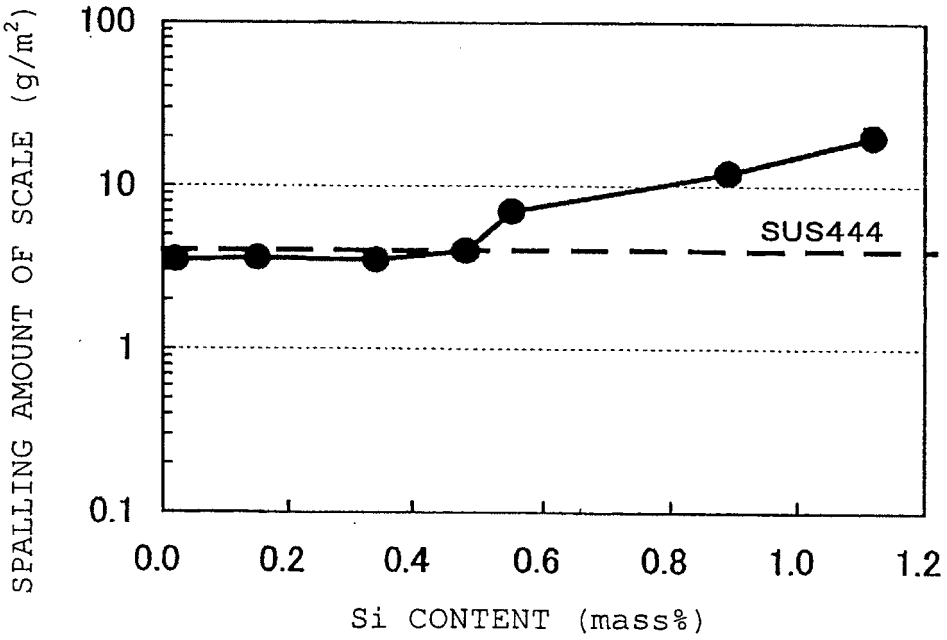

SPALLING AMOUNT OF SCALE (g/m²)
100
10
1
0.1
SUS444
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Si CONTENT (mass%)

FIG. 7

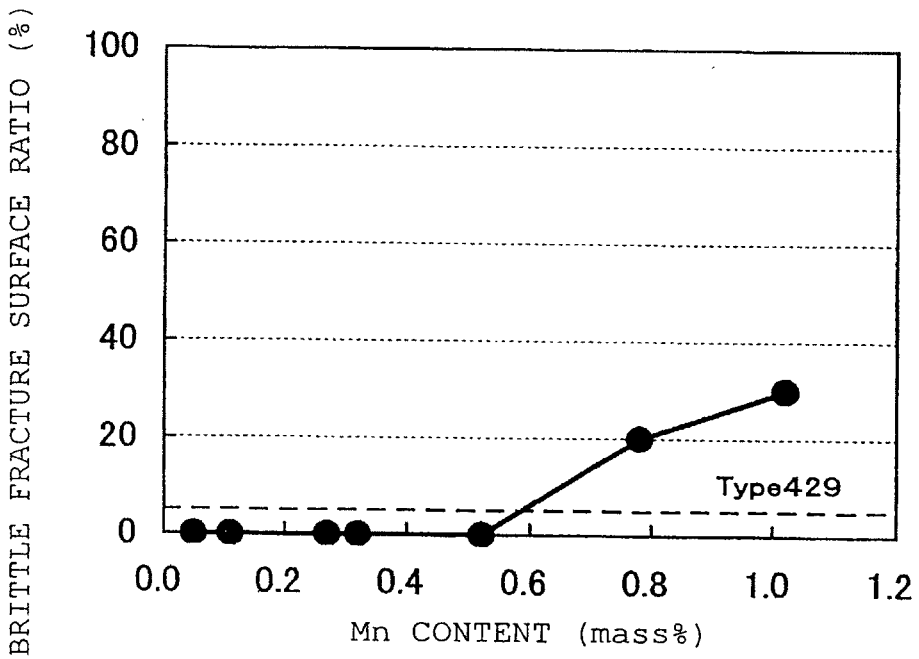

BRITTLE FRACTURE SURFACE RATIO (%)
100
80
60
40
20
0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Type429
Mn CONTENT (mass%)

FIG. 8

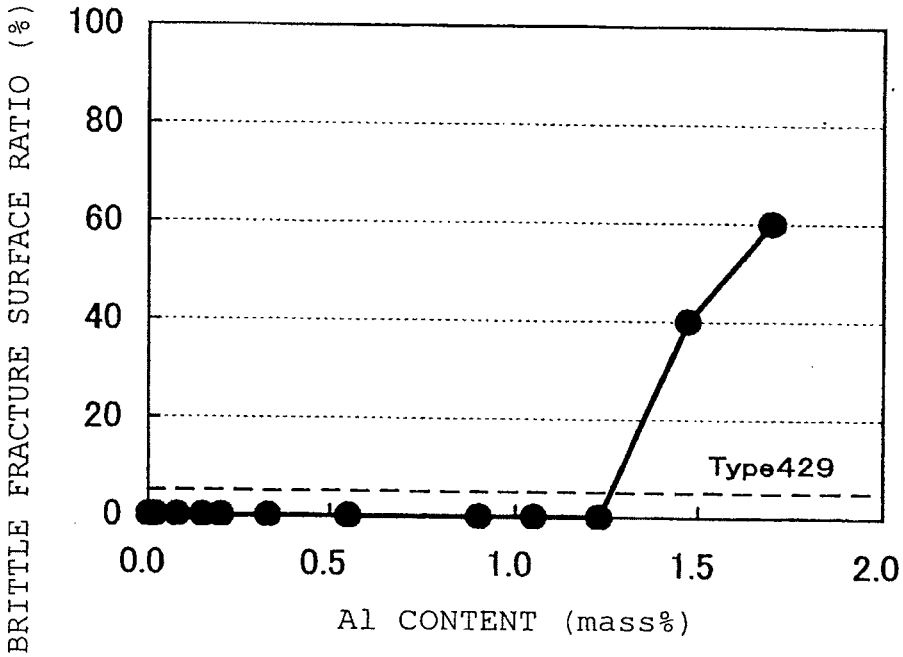
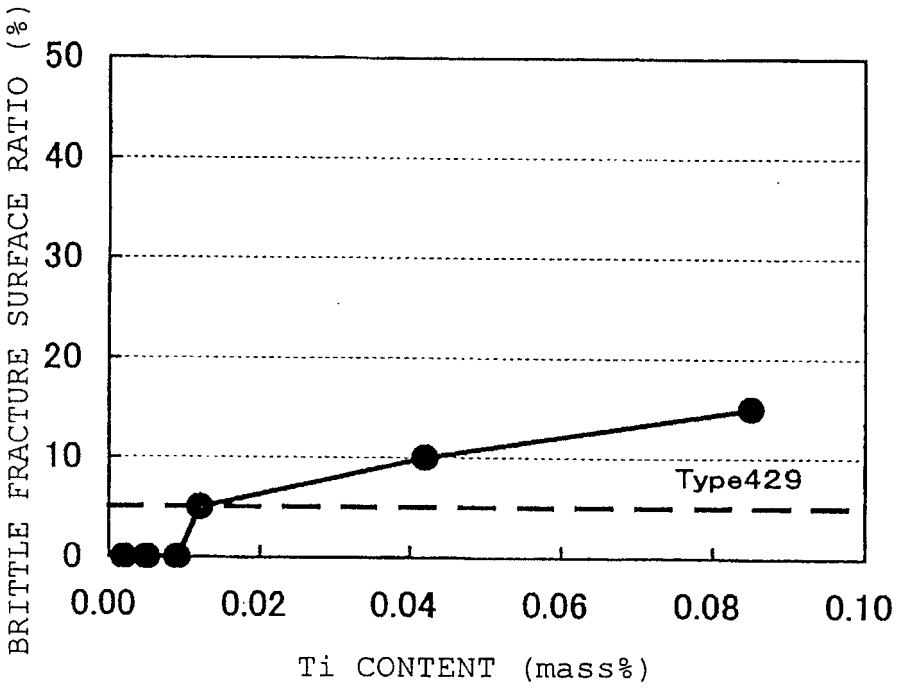

BRITTLE FRACTURE SURFACE RATIO (%)
100
80
60
40
20
0
0.0
0.5
1.0
1.5
2.0
Type429
Al CONTENT (mass%)

FIG.9


BRITTLE FRACTURE SURFACE RATIO (%)
50
40
30
20
10
0
0.00
0.02
0.04
0.06
0.08
0.10
Type429
Ti CONTENT (mass%)

REFERENCES CITED IN THE DESCRIPTION

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