



(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
28.04.2004 Bulletin 2004/18

(51) Int Cl.7: **C22C 38/00, C22C 38/32**

(21) Application number: **02743819.1**

(86) International application number:
PCT/JP2002/006768

(22) Date of filing: **04.07.2002**

(87) International publication number:
WO 2003/004714 (16.01.2003 Gazette 2003/03)

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SK TR**
Designated Extension States:
AL LT LV MK RO SI

- **FUJIMURA, Yoshitomo,**
Stainless Steel Business Div.
Shin-Nanyo-shi, Yamaguchi 746-8666 (JP)
- **NAGOYA, Toshirou,**
Stainless Steel Business Div.
Shin-Nanyo-shi, Yamaguchi 746-8666 (JP)

(30) Priority: **05.07.2001 JP 2001204444**

(74) Representative: **Müller-Boré & Partner**
Patentanwälte
Grafinger Strasse 2
81671 München (DE)

(71) Applicant: **NISSHIN STEEL CO., LTD.**
Chiyoda-ku Tokyo 100-8366 (JP)

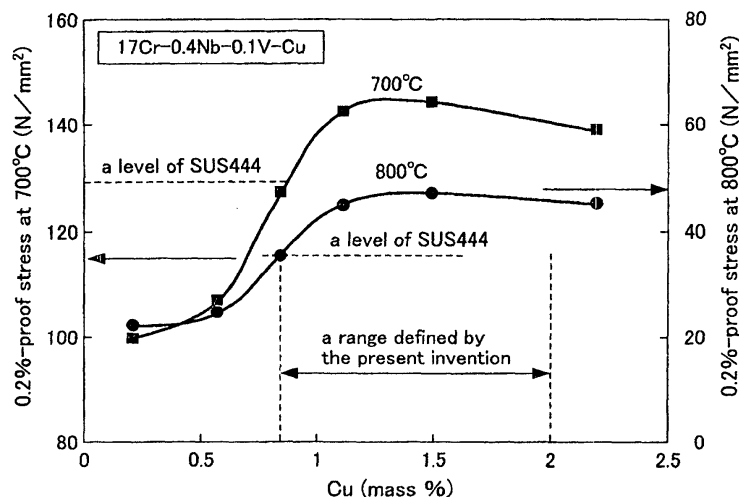
(72) Inventors:
• **OKU, Manabu, c/o Stainless Steel Business Div.**
Shin-Nanyo-shi, Yamaguchi 746-8666 (JP)

(54) **FERRITIC STAINLESS STEEL FOR MEMBER OF EXHAUST GAS FLOW PASSAGE**

(57) A ferritic stainless steel useful as conduit members for emission of automotive exhaust gas consists of C up to 0.03 mass %, Si up to 1.0 mass %, Mn up to 1.5 mass %, Ni up to 0.6 mass %, 10-20 mass % of Cr, Nb up to 0.50 mass %, 0.8-2.0 mass % of Cu, Al up to 0.03 mass %, 0.03-0.20 mass % of V, N up to 0.03 mass %

and the balance being Fe except inevitable impurities with a provision of $Nb \geq 8(C+N)$. The steel may further contain 0.05-0.30 mass % of Ti and/or 0.0005-0.02 mass % of B. Mo as an inevitable impurity is controlled less than 0.10 mass %. The steel has excellent formability, low-temperature toughness and weldability as well as the same heat-resistance as Nb, Mo-alloyed steel.

FIG. 1



Description

INDUSTRIAL FIELD

5 **[0001]** The present invention relates to a ferritic stainless steel, which is excellent in heat-resistance, low-temperature toughness and weldability, useful as conduit members, e.g. exhaust manifolds, front pipes, center pipes and outer casings of catalytic converters in internal combustion engines of automobiles or the like, for emission of exhaust gas.

BACKGROUND OF THE INVENTION

10 **[0002]** Conduit members of automobiles for emission of exhaust gas are directly exposed to a high-temperature atmosphere containing exhaust gas during driving automobiles, and subjected to thermal stress caused by repetition of driving and stopping as well as vibration during driving. Mechanical stress is also applied to conduit members at a low temperature, when automobiles are started in winter in cold districts. Therefore, a material for use as the conduit members shall have durability in severe environments.

15 **[0003]** Since conduit members are fabricated by welding or forming steel sheets or pipes to product shapes, steels necessarily have excellent heat-resistance, weldability and formability for the purpose. Toughness, especially low-temperature toughness, is also an important property, in order to secondarily form a stainless steel sheet or pipe without cracks and to render conduit members resistant to mechanical stress at a low temperature.

20 **[0004]** A ferritic stainless steel is often used as a material for such conduit members, due to its small thermal expansion coefficient, thermal fatigue strength and scale spalling resistance in comparison with an austenitic stainless steel. A low price is also an advantage of the ferritic stainless steel.

25 **[0005]** Various improvements have been proposed so far in order to improve a high-temperature strength of a ferritic stainless steel, which is intrinsically lower than an austenitic stainless steel. For instance, JP3-274245A discloses Nb-alloyed steel and Nb, Si-alloyed steel as new SUS430J1 stainless steels, and JP5-125491A discloses Nb, Mo-alloyed steel. Especially, the Nb, Mo-alloyed steel is useful as parts or members exposed to severe high-temperature atmosphere due to its excellent high-temperature strength and thermal fatigue-resistance. However, poor formability and inferior low-temperature toughness are disadvantages of the Nb, Mo-alloyed steel. Although a few reports are published on improvement of formability and low-temperature toughness, the improvement is still insufficient for the purpose.

30 Consumption of expensive Mo at a high ratio is also an disadvantage of the Nb, Mo-alloyed steel.
[0006] By the way, high-temperature strength (e.g. resistance to thermal fatigue failure) and high-temperature oxidation-resistance (evaluated as a critical temperature of abnormal oxidation) are not necessarily balanced at high level for some parts or members. In the case of a part or member, which has a complicate profile but does not come in contact with high-temperature exhaust gas, high-temperature strength is more important than high-temperature oxidation-resistance, and formability and low-temperature toughness are also important factors so as to form a stainless steel sheet or pipe to the complicate profile. However, the Nb, Mo-alloyed steel is necessarily used for such a part or member with emphasis on heat-resistance regardless poor formability, inferior low-temperature toughness and expensiveness.

SUMMARY OF THE INVENTION

40 **[0007]** The present invention aims at provision of a ferritic stainless steel useful as conduit members for emission of exhaust gas. An object of the present invention is to bestow a ferritic stainless steel, which does not contain expensive Mo, with heat-resistance similar to that of Nb, Mo-alloyed steel in addition to excellent formability, low-temperature toughness and weldability.

45 **[0008]** The present invention proposes a ferritic stainless steel, which consists of C up to 0.03 mass %, Si up to 1.0 mass %, Mn up to 1.5 mass %, Ni up to 0.6 mass %, 10-20 mass % of Cr, Nb up to 0.50 mass %, 0.8-2.0 mass % of Cu, Al up to 0.03 mass %, 0.03-0.20 mass % of V, N up to 0.03 mass % and the balance being Fe except inevitable impurities with a provision of $Nb \geq 8(C+N)$.

50 **[0009]** The ferritic stainless steel does not contain Mo as an alloying element, but optionally contains 0.05-0.30 mass % of Ti for further improvement of formability and/or 0.0005-0.02 mass % of B for further improvement of secondary formability.

BRIEF DESCRIPTION OF THE DRAWING

55 **[0010]**

Fig. 1 is a graph, which shows an effect of Cu on 0.2%-proof stress of a ferritic stainless steel at an elevated

temperature.

BEST MODES OF THE INVENTION

5 **[0011]** Such stainless steels as SUH409, SUS430J11 and SUS429 have been used as materials good of heat-resistance in an atmosphere, to which conduit members are exposed. Some parts or members, which are heated up to 800-900°C at highest, need high-temperature strength fairly higher than conventional steels. Such a part or member ordinarily has a complicate profile, so that it shall be made of a stainless steel good of formability and low-temperature toughness, which are never estimated from Mo-alloyed steel. Moreover, the part or member is likely to break down
10 due to thermal fatigue, since thermal stress is repeatedly applied to the complicate profile.

[0012] The inventors have researched and examined effects of various alloying elements on properties of such a part or member, and discovered that a ferritic stainless steel is improved in all of high-temperature strength below 900°C, formability and low-temperature toughness by addition of both V and Cu to the same level of Nb, Mo-alloyed steel.

15 **[0013]** Several Nb-alloyed ferritic stainless steels, which contained V at a small ratio and Cu at various ratios, were examined by high-temperature tensile test at 700°C and 800°C for measurement of 0.2%-proof stress. Test results prove that high-temperature strength below 900°C is remarkably raised to a level similar to Nb, Mo-alloyed steel by addition of V at a small ratio and Cu at a controlled ratio.

[0014] Fig. 1 shows test results of ferritic stainless steels with a basic composition of 17Cr-0.4Nb-0.1V, to which Cu
20 is added at various ratios. Fig. 1 also shows strength of SUS444 steel with basic composition of 18Cr-2Mo-0.4Nb as a comparative example of Nb, Mo-alloyed steel.

[0015] Values of 0.2%-proof stress at 700°C and 800°C are remarkably raised in response to increase of a Cu content, as noted in Fig. 1. The value of 0.2%-proof stress at 0.8 mass % or more of Cu is similar or superior to that of SUS444 steel, which contains approximately 2 mass % of Mo. The inventors have already confirmed from another
25 test results that a value of 0.2%-proof stress at 900°C is not raised to a level of SUS444 but higher than Nb-containing ferritic stainless steel by increase of V and Cu contents. In short, addition of both V and Cu is effective for improvement of high-temperature strength in a hot zone below 900°C without significant troubles at a temperature higher than 900°C.

[0016] Improvement of high-temperature strength by addition of both V and Cu to Nb-alloyed steel is probably explained as follows: When a metallurgical structure of the inventive stainless steel is observed after heating a short or
30 long while, distribution of fine particles of Nb and Cu compounds is detected. The observation result means that particles of V compounds are preferentially precipitated at the beginning of heating so as to keep Nb and Cu in a dissolved state and that Nb and Cu compounds are finally precipitated as fine particles effective for precipitation-hardening. The precipitates, which are uniformly distributed as fine particles in a steel matrix at the beginning of heating, do not aggregate together during long-term heating, so that precipitation-hardening is maintained effective a long while.

[0017] A ratio of dissolved Nb for improvement of high-temperature strength is also kept at a higher value by presence
35 of V, which converts free C and N to carbonitrides, than V-free steels containing Nb at the same ratio. Increase of dissolved Nb assures that high-temperature strength necessary for the purpose is attained by saved consumption of Nb in comparison with the V-free steels, resulting in improvement of formability and low-temperature toughness.

[0018] Carbonitrides of Nb and V increase in an annealed matrix of the inventive ferritic stainless steel. Increase of
40 the carbonitrides suppresses crystal growth to coarse grains at a weld heat-affected zone, resulting in improvement of toughness. Formation of chromium carbide, which is harmful on intergranular corrosion-resistance, is also suppressed by increase of the carbonitrides.

[0019] Individual effects of alloying elements in the inventive ferritic stainless steel will become apparent from the following explanation.

45 C up to 0.03 mass %, N up to 0.03 mass %

[0020] C and N are generally regarded as elements effective for high-temperature strength, e.g. creep strength, but excess C and N unfavorably degrade oxidation-resistance, formability, low-temperature toughness and weldability. In the inventive alloy system, which contains V and Nb for fixation of C and N as carbonitrides, V and Nb are necessarily added at ratios corresponding to concentrations of C and N. Therefore, each of C and N contents is controlled to 0.03
50 mass % or less (preferably 0.015 mass % or less), in order to avoid increase of V and Nb, which causes a rise of material expense.

Si up to 1.0 mass %

[0021] Si is an element effective for high-temperature oxidation-resistance, but not so effective on high-temperature strength below 900°C. Excess Si hardens a ferritic stainless steel, resulting in degradation of formability and low-
55 temperature toughness. In this sense, a Si content is determined at 1.0 mass % or less (preferably 0.1-0.5 mass %).

Mn up to 1.5 mass %

[0022] Mn is an alloying element, which improves high-temperature oxidation-resistance, especially scale spalling resistance property, of a ferritic stainless steel, but excess Mn degrades formability and weldability. Excess addition

of Mn to a steel containing Cr at a relatively small ratio causes formation of a martensitic phase harmful on thermal fatigue strength and formability, since Mn is an austenite-stabilizing element. Therefore, a Mn content is determined at 1.5 mass % or less (preferably 0.5 mass % or less).

Ni up to 0.6 mass %

[0023] Ni is an austenite-stabilizing element. Excess addition of Ni to a steel containing Cr at a relatively small ratio promotes formation of a martensitic phase harmful on thermal fatigue strength and formability, as the same as Mn. Excess Ni also raises a steel cost. Therefore, a Ni content is determined at 0.6 mass % or less (preferably 0.5 mass % or less).

10-20 mass% of Cr

[0024] Cr is an essential element for stabilization of a ferritic phase and improvement of oxidation-resistance as an important property for high-temperature use. Oxidation-resistance becomes better as increase of a Cr content, but excess Cr causes embrittlement of a stainless steel, resulting in increase of hardness and degradation of formability. In this sense, a Cr content is determined within a range of 10-20 mass %. Cr is preferably controlled to a proper value in response to a temperature on use. For instance, 16-19 mass % of Cr is favorable for oxidation-resistance at a temperature not higher than 950°C, and 12-16 mass % of Cr is favorable for oxidation-resistance at a temperature not higher than 900°C.

From 8(C+N) to 0.50 mass % of Nb

[0025] Nb fixes C and N as carbonitrides, and also improves high-temperature strength in a state dissolved in a steel matrix. However, excess Nb is unfavorable for formability, low-temperature toughness and to welding hot crack-resistance. Nb not less than 8(C+N) is necessary for fixation of C and N, but an upper limit of Nb is determined at 0.5 mass % in order to maintain proper formability, low-temperature toughness and tensile type hot-cracking resistance. A Nb content is preferably controlled within a range of from 8(C+N)+0.10 to 0.45 mass %.

0.8-2.0 mass % of Cu

[0026] Cu is the most important element in the inventive alloy system. Within a temperature range which the inventors have researched and examined, most of Cu is dissolved in an annealed steel matrix and precipitated during heat-treatment. Cu precipitates exhibits the same strengthening effect as Mo at the beginning of heating, but the strengthening effect gradually becomes weaker as the lapse of heating time. At least 0.8 mass % of Cu is necessary in order to gain high-temperature strength suitable for the purpose, as noted in Fig. 1. However, formability, low-temperature toughness and weldability are degraded as increase of a Cu content. The unfavorable effect of Cu on formability, low-temperature toughness and weldability is suppressed by controlling an upper limit of the Cu content at 2.0 mass %. The Cu content is preferably determined within a range of 1.0-1.7 mass %.

Al up to 0.03 mass %

[0027] Al is added as a deoxidizing element in a steel making process. But, excess Al degrades an external appearance of a stainless steel sheet and also puts harmful effects on formability, low-temperature toughness and weldability. In this sense, an Al content is preferably controlled at a lowest possible level, so that its upper limit is determined at 0.03 mass %.

0.03-0.20 mass % of V

[0028] The additive V improves high-temperature strength of a ferritic stainless steel in co-presence of Nb and Cu. Addition of V together with Nb is also effective for formability, low-temperature toughness, intergranular corrosion-resistance and toughness at a weld heat affected-zone. These effects are noted at 0.03 mass % or more of V, but excess V above 0.20 mass % is rather unfavorable for formability and low-temperature toughness. In this sense, a V content is determined within a range of 0.03-0.20 mass % (preferably 0.04-0.15 mass %).

0.05-0.30 mass % of Ti

[0029] Ti is an optional element, which raises Lankford value (r) and improves formability of a ferritic stainless steel, and its effect is noted at 0.05 mass % or more of Ti. However, excess Ti promotes formation of TiN harmful on external appearance of a stainless steel and also degrades formability and low-temperature toughness. In this regard, Ti shall be held at a smallest possible ratio, even when Ti is added for improvement of formability. Therefore, an upper limit of a Ti content is determined at 0.30 mass % (preferably 0.20 mass %).

0.0005-0.02 mass % of B

[0030] B is another optional element for improving secondary formability of a stainless steel and suppressing cracking during multi-stepped forming. The effect on formability is noted at 0.0005 mass % or more of B, but excess B causes degradation of productivity and weldability. In this sense, a B content is determined within a range of 0.0005-0.02 mass % (preferably 0.001-0.01 mass %).

0-0.10 mass % of Mo

[0031] The inventive alloy system is designed on the assumption that expensive Mo is not added as an alloying element, but Mo is likely to be included as an impurity during steel making. Since inclusion of Mo at a relatively high ratio is harmful on formability, low-temperature toughness and weldability, it shall be controlled at a ratio less than 0.10 mass %.

EP 1 413 640 A1

5 [0032] There are no restrictions on elements other than the above, but ordinary impurities such as P, S and O are preferably controlled at lowest possible levels. Accounting hot-workability, oxidation-resistance and so on, upper limits of P, S and O are preferably determined at 0.04 mass %, 0.03 mass % and 0.02 mass %, respectively. At least one of W, Zr, Y and REM (rare earth metals) may be added for heat-resistance, or at least one of Ca, Mg and Co may be added for hot-workability.

10 [0033] There are not special restrictions on manufacturing conditions, as far as Cu is dissolved in a steel matrix beforehand in order to gain excellent heat-resistance as an annealed state after hot-rolling. In the case where a ferritic stainless steel can not be hot-rolled to predetermined thickness, a steel sheet bestowed with the same heat-resistance as an annealed hot-rolled steel sheet is manufactured by repetition of cold-rolling and annealing. High-temperature strength is further improved by dispersion of Cu as fine particles at any stage of a manufacturing process. The excellent properties are maintained as such, even after the annealed hot-rolled or cold-rolled steel sheet is formed or welded to a certain profile (involving production of a steel pipe).

[0034] The other features of the present invention will be apparent from the following examples.

15 [0035] Each ferritic stainless steel with chemical composition shown in Table 1 or 2 was melted in a vacuum furnace and cast to a 30 kg ingot. The ingot was forged, hot-rolled, annealed, cold-rolled to thickness of 2.0 mm or 1.2 mm, and finish-annealed. Table 1 shows compositions according to the present invention, while Table 2 shows comparative compositions.

20 [0036] In Table 2, a steel No. 11 corresponds to SUS430J11, a steel No. 15 corresponds to SUH409L, a steel No. 16 corresponds to a 14Cr-Si-Nb steel, and a steel No. 17 corresponds to SUS444. Any of these steels has been used so far as a material for an exhaust manifold.

25

30

35

40

45

50

55

Table 1: Chemical Compositions of Inventive Ferritic Stainless Steels

| No. | Alloying elements (mass %) | | | | | | | | | | | | | [Nb] |
|-----|----------------------------|------|------|------|-------|------|------|------|------|------|-----|------|-------|------|
| | C | Si | Mn | Ni | Cr | Nb | Ti | Mo | Cu | Al | B | V | N | |
| 1 | 0.015 | 0.31 | 0.15 | 0.10 | 17.09 | 0.35 | - | 0.01 | 0.85 | 0.01 | - | 0.10 | 0.009 | 0.16 |
| 2 | 0.010 | 0.28 | 0.17 | 0.11 | 17.13 | 0.36 | - | 0.01 | 1.50 | 0.01 | - | 0.11 | 0.008 | 0.22 |
| 3 | 0.008 | 0.32 | 0.05 | 0.10 | 17.02 | 0.33 | - | 0.01 | 1.93 | 0.01 | - | 0.10 | 0.010 | 0.19 |
| 4 | 0.012 | 0.33 | 0.22 | 0.09 | 10.71 | 0.35 | - | - | 1.42 | 0.01 | - | 0.12 | 0.011 | 0.17 |
| 5 | 0.011 | 0.39 | 0.50 | 0.09 | 14.01 | 0.38 | - | - | 1.45 | 0.01 | 30 | 0.12 | 0.006 | 0.24 |
| 6 | 0.007 | 0.21 | 0.16 | 0.21 | 19.52 | 0.33 | - | - | 1.51 | 0.01 | 20 | 0.11 | 0.008 | 0.21 |
| 7 | 0.007 | 0.81 | 0.18 | 0.12 | 12.03 | 0.31 | 0.15 | 0.04 | 1.50 | 0.03 | 10 | 0.06 | 0.006 | 0.21 |
| 8 | 0.011 | 0.30 | 1.21 | 0.10 | 17.44 | 0.36 | 0.20 | 0.03 | 1.53 | 0.03 | 50 | 0.03 | 0.009 | 0.20 |
| 9 | 0.011 | 0.36 | 0.12 | 0.11 | 17.42 | 0.21 | 0.11 | 0.09 | 1.51 | 0.02 | 150 | 0.04 | 0.007 | 0.07 |
| 10 | 0.028 | 0.33 | 0.31 | 0.11 | 17.40 | 0.45 | 0.07 | 0.02 | 1.48 | 0.01 | 20 | 0.04 | 0.021 | 0.06 |

The B content is represented by ppm unit.

[Nb] is calculated as $Nb - 8[C + N]$.

The mark (-) means a value below detection limit.

Table 2: Chemical Compositions of Comparative Ferritic Stainless Steels

| No. | Alloying elements (mass %) | | | | | | | | | | | | | |
|-----|----------------------------|-------------|------|------|-------|-------------|-------------|-------------|-------------|-------------|-----------|-------------|-------|--------------|
| | C | Si | Mn | Ni | Cr | Nb | Ti | Mo | Cu | Al | B | V | N | [Nb] |
| 11 | 0.008 | 0.30 | 0.28 | 0.14 | 17.00 | 0.37 | - | 0.02 | 0.60 | 0.03 | - | - | 0.011 | 0.22 |
| 12 | 0.010 | 0.36 | 0.28 | 0.17 | 16.99 | 0.38 | - | 0.01 | <u>4.08</u> | 0.01 | - | 0.04 | 0.012 | 0.20 |
| 13 | 0.008 | <u>1.38</u> | 0.26 | 0.17 | 17.06 | 0.41 | 0.01 | 0.01 | 1.48 | - | - | - | 0.013 | 0.24 |
| 14 | 0.009 | 0.35 | 0.32 | 0.31 | 17.24 | <u>0.74</u> | - | 0.01 | 2.48 | 0.02 | - | <u>0.01</u> | 0.013 | 0.56 |
| 15 | 0.020 | 0.42 | 0.39 | 0.10 | 12.16 | <u>0.01</u> | <u>0.23</u> | <u>0.02</u> | - | 0.02 | - | - | 0.014 | <u>-0.26</u> |
| 16 | 0.011 | <u>1.10</u> | 0.98 | 0.10 | 14.75 | 0.50 | - | <u>0.01</u> | <u>0.03</u> | - | - | - | 0.012 | 0.31 |
| 17 | 0.012 | 0.40 | 0.70 | 0.22 | 18.28 | 0.50 | - | <u>1.94</u> | <u>0.24</u> | 0.01 | 20 | 0.04 | 0.011 | 0.32 |
| 18 | 0.011 | 0.82 | 0.25 | 0.11 | 17.42 | 0.45 | 0.01 | 0.02 | 1.69 | <u>0.34</u> | <u>20</u> | <u>0.01</u> | 0.021 | 0.19 |
| 19 | 0.012 | 0.31 | 0.29 | 0.11 | 19.55 | 0.20 | 0.01 | - | 0.82 | - | - | <u>0.02</u> | 0.008 | 0.04 |

The B content is represented by ppm unit.

[Nb] is calculated as $Nb-8[C+N]$

The mark (-) means a value below detection limit.

The underlined figures are out of the ranges defined by the present invention.

[0037] Each annealed cold-rolled steel sheet of 2.0 mm in thickness was examined by a high-temperature tensile test, a high-temperature oxidation test, a room-temperature tensile test and Charpy impact test. Each annealed cold-

rolled steel sheet of 1.2 mm in thickness was examined by a tensile type hot-cracking test.

[0038] In the high-temperature tensile test, a test piece was stretched at 800°C under conditions regulated in JIS G0567, so as to measure its 0.2%-proof stress.

[0039] In the high-temperature oxidation test, a test piece was heated at each temperature of 850°C, 900°C, 950°C, 1000°C and 1100°C for 200 hours under conditions regulated in JIS Z2281. The heated test piece was observed by naked eyes to detect occurrence of abnormal oxidation (i.e. growth of knobby thick oxide through a steel sheet). A critical temperature, at which the test piece was heated without abnormal oxidation, was determined from the observation results.

[0040] In the room-temperature tensile test, each annealed cold-rolled steel sheet of 2.0 mm in thickness was shaped to a test piece No. 13B and stretched under conditions regulated in JIS Z2241 to measure its elongation after fracture.

[0041] In Charpy impact test, an impact was applied to a sub-sized test piece of 2.0 mm in thickness at each temperature of -75°C, -50°C, -25°C, 0°C and 25°C under conditions of JIS Z2242, to detect a ductile-brittle transition temperature.

[0042] In the tensile type hot-cracking test, a test piece of 40 mm in length and 20 mm in width was clamped at its both ends and TIG-welded under the condition that a tensile stress was applied to the test piece along its longitudinal direction, so as to detect a minimum strain at which the test piece began to crack. Tensile type hot-cracking resistance was evaluated by the critical strain detected in this way.

[0043] Test results are shown in Table 3.

[0044] It is noted from Table 3 that any of the inventive steels Nos. 1-10 has 0.2%-proof stress at 800°C, fairly higher than the Nb, Si-alloyed steel No. 16 and similar or superior to the Nb, Mo-alloyed steel No. 17. Values of elongation by the room-temperature tensile test, a ductile-brittle transition temperature by Charpy impact test and a critical strain by the tensile type hot-cracking test were also similar or superior to the Nb, Mo-alloyed steel No. 17. These results prove that objective performance is attained without necessity of Mo as an alloying element. When results of the steels Nos. 4, 5 and 12 are compared with each other, it is understood that a critical temperature for occurrence of abnormal oxidation becomes lower as decrease of a Cr content. Due to the effect of Cr on abnormal oxidation, the Cr content shall be determined at a proper value in response to a temperature at which a steel member or part will be exposed.

[0045] The comparative steels Nos. 11, 15, 16 and 19, which lacked of V and Cu, had formability, low-temperature toughness and weldability at levels required for the purpose but poor high-temperature strength at 800°C. The comparative steel No. 12, which contained excess Cu, was good of high-temperature strength but inferior in formability and weldability to the Nb, Mo-alloyed steel No. 17, so that it was hardly formed or welded to a product shape.

[0046] The comparative steel No. 13, which contained Cu within a range defined by the present invention but excess Si, and the comparative steel No. 14, which contained excess Nb, were good of high-temperature strength but inferior in formability, low-temperature toughness and weldability to the inventive steels Nos. 1-10.

[0047] The comparative steel No. 18, which contained less V and excess Al, had the same heat-resistance and formability as the inventive steels Nos. 1-10 but poor low-temperature toughness, which led to occurrence of troubles during manufacturing or on use. The comparative steel No. 19 was poor of high-temperature strength due to shortage of V.

[0048] The Mo-containing comparative steel No. 17 had the same properties as the inventive steels Nos. 1-10, but its low-temperature toughness was relatively inferior. A cost of the steel No. 17 is inevitably higher than the inventive steels Nos. 1-10, due to consumption of Mo at approximately 2 mass %.

Table 3: Evaluation of Test Results

| No. | 0.2%-proof stress at 800°C (N/mm ²) | A critical temperature (°C) of abnormal oxidation | Elongation after fracture (%) | A transition temperature (°C) | Inventive Examples | |
|-----|--|--|----------------------------------|----------------------------------|--------------------|----------------------|
| | | | | | A critical strain | Comparative Examples |
| 1 | 35 | 1000 | 34 | -50 | ○ | ○ |
| 2 | 45 | 1000 | 32 | -50 | ○ | ○ |
| 3 | 47 | 1000 | 31 | -50 | ○ | ○ |
| 4 | 43 | 850 | 34 | -50 | ○ | ○ |
| 5 | 44 | 900 | 33 | -50 | ○ | ○ |
| 6 | 44 | 1000 | 32 | -50 | ○ | ○ |
| 7 | 45 | 950 | 32 | -50 | ○ | ○ |
| 8 | 43 | 1000 | 34 | -50 | ○ | ○ |
| 9 | 36 | 1000 | 35 | -50 | ○ | ○ |
| 10 | 35 | 1000 | 32 | -50 | ○ | ○ |
| 11 | <u>24</u> | 1000 | 34 | -50 | ○ | ○ |
| 12 | 50 | 950 | <u>29</u> | -25 | × | × |
| 13 | 45 | 1100 | <u>28</u> | <u>0</u> | × | × |
| 14 | 47 | 1000 | 30 | <u>0</u> | × | × |
| 15 | <u>18</u> | 850 | 37 | -75 | ○ | ○ |
| 16 | <u>25</u> | 950 | 35 | -50 | ○ | ○ |
| 17 | 35 | 1000 | 32 | -25 | ○ | ○ |
| 18 | 40 | 1000 | 31 | <u>0</u> | ○ | ○ |
| 19 | <u>30</u> | 1000 | 32 | -25 | ○ | ○ |

A critical strain of 3% or more is evaluated as the mark ○, and less than 3% is evaluated as the mark ×.
The underlined figures do not meet with objective property.

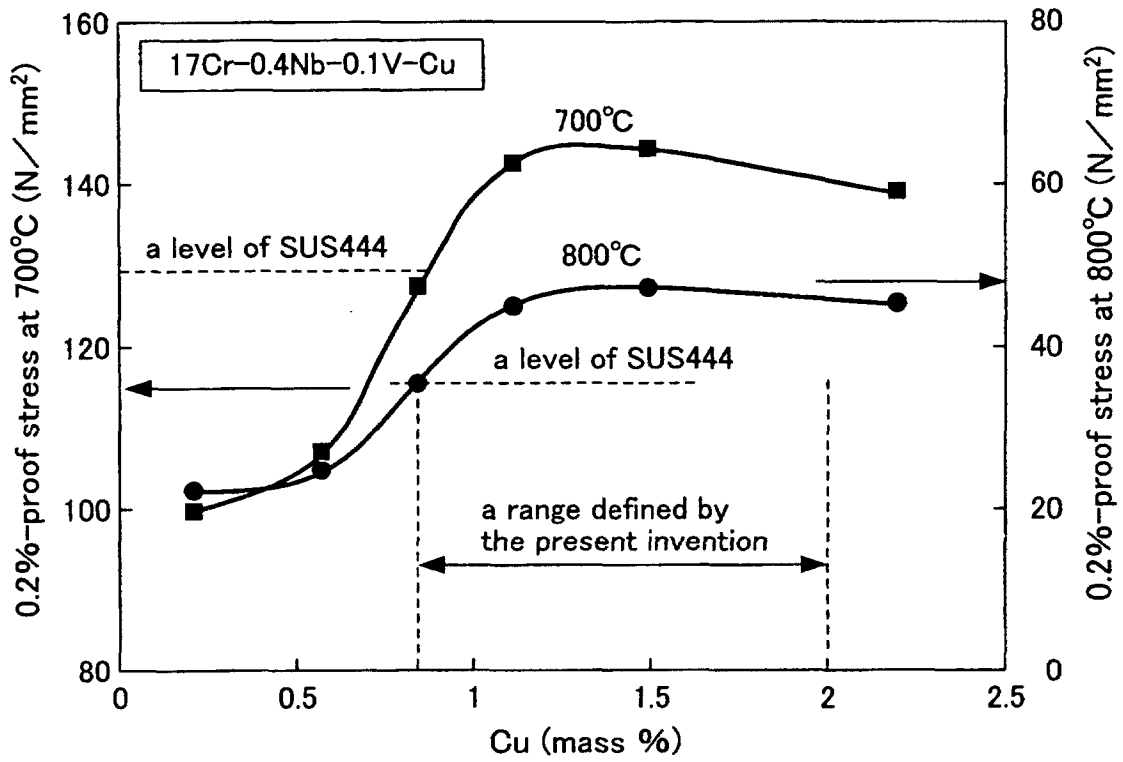
INDUSTRIAL APPLICABILITY

5 [0049] According to the present invention as the above, a ferritic stainless steel is improved in formability, low-temperature toughness and weldability without degradation of heat-resistant by specified alloying design, especially control of V and Cu contents, without necessity of expensive Mo. The newly proposed stainless steel is useful as members or parts for automotive engines or conduit members, e.g. exhaust manifolds, front pipes, center pipes, outer casings of catalytic converters for emission of exhaust gas.

10 **Claims**

- 15 1. A ferritic stainless steel for use as a conduit member for emission of automotive exhaust gas, which consists of C up to 0.03 mass %, Si up to 1.0 mass %, Mn up to 1.5 mass %, Ni up to 0.6 mass %, 10-20 mass % of Cr, Nb up to 0.50 mass %, 0.8-2.0 mass % of Cu, Al up to 0.03 mass %, 0.03-0.20 mass % of V, N up to 0.03 mass % and the balance being Fe except inevitable impurities with a provision of $Nb \geq 8(C+N)$.
- 20 2. The ferritic stainless steel defined by Claim 1, wherein Mo as an inevitable impurity is controlled less than 0.10 mass %.
3. The ferritic stainless steel defined by Claim 1 or 2, which further contains 0.05-3.0 mass % of Ti.
4. The ferritic stainless steel defined by either one of Claims 1 to 3, which further contains 0.0005-0.02 mass % of B.

FIG. 1



INTERNATIONAL SEARCH REPORT

| |
|---|
| International application No. PCT/JP02/06768 |
|---|

| A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ C22C38/00, 38/32 | | | | | | | | | | | | |
|---|--|-----------------------|--|---|--|--|---|--|--|---|--|--|
| 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) Int.Cl. ⁷ C22C38/00-32 | | | | | | | | | | | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2002 Kokai Jitsuyo Shinan Koho 1971-2002 Jitsuyo Shinan Toroku Koho 1996-2002 | | | | | | | | | | | | |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) | | | | | | | | | | | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | | | | | | | | | | | |
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. | | | | | | | | | | |
| Y | EP 0478790 A1 (Nisshin Steel Co., Ltd.), 08 April, 1992 (08.04.92), Claims & JP 3-274245 A | 1-4 | | | | | | | | | | |
| Y | JP 10-204590 A (Kawasaki Steel Corp.), 04 August, 1998 (04.08.98), Claims (Family: none) | 1-4 | | | | | | | | | | |
| Y | JP 10-204591 A (Kawasaki Steel Corp.), 04 August, 1998 (04.08.98), Claims (Family: none) | 1-4 | | | | | | | | | | |
| A | JP 6-279950 A (Nisshin Steel Co., Ltd.), 04 October, 1994 (04.10.94), Claims (Family: none) | 1-4 | | | | | | | | | | |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex. | | | | | | | | | | | | |
| <p>* Special categories of cited documents:</p> <table border="0"> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E" earlier document but published on or after the international filing date</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table> | | | "A" document defining the general state of the art which is not considered to be of particular relevance | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention | "E" earlier document but published on or after the international filing date | "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone | "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art | "O" document referring to an oral disclosure, use, exhibition or other means | "&" document member of the same patent family | "P" document published prior to the international filing date but later than the priority date claimed | |
| "A" document defining the general state of the art which is not considered to be of particular relevance | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention | | | | | | | | | | | |
| "E" earlier document but published on or after the international filing date | "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone | | | | | | | | | | | |
| "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art | | | | | | | | | | | |
| "O" document referring to an oral disclosure, use, exhibition or other means | "&" document member of the same patent family | | | | | | | | | | | |
| "P" document published prior to the international filing date but later than the priority date claimed | | | | | | | | | | | | |
| Date of the actual completion of the international search 25 September, 2002 (25.09.02) | Date of mailing of the international search report 08 October, 2002 (08.10.02) | | | | | | | | | | | |
| Name and mailing address of the ISA/ Japanese Patent Office | Authorized officer | | | | | | | | | | | |
| Facsimile No. | Telephone No. | | | | | | | | | | | |

Form PCT/ISA/210 (second sheet) (July 1998)