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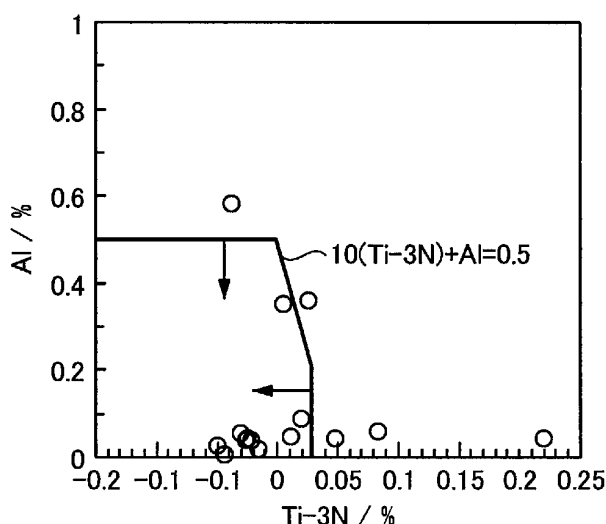
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(54) **FERRITIC STAINLESS STEEL SHEET FOR EGR COOLERS**

(57) A ferritic stainless steel sheet for EGR coolers includes at least, by mass% C: 0.03% or less, N: 0.05% or less, Si: 0.1% to 1%, Mn: 0.02% to 2%, Cu: 0.2% to 1.5%, Cr: 15% to 25%, Nb: 8 (C + N) % to 1%, Al: 0.5% or less, and Fe and inevitable impurities as the balance,

wherein the steel sheet further includes, by mass%, Ti at an amount fulfilling the following formulae (1) and (2), and Cr and Cu are included at amounts fulfilling the following formula (3), $Ti - 3N \leq 0.03 \cdots (1)$, $10(Ti - 3N) + Al \leq 0.5 \cdots (2)$, and $Cr + 2.3Cu \geq 18 \cdots (3)$.

FIG. 1



Description

TECHNICAL FIELD

[0001] The present invention relates to a ferritic stainless steel sheet for EGR coolers that cool exhaust gas with an engine coolant, air or the like in an exhaust gas recirculation (hereinafter, referred to as EGR) system used in, for example, a diesel engine, a gasoline engine or the like of a vehicle.

BACKGROUND ART

[0002] In recent years, as a result of increased concern about environmental issues, exhaust gas emission regulations have become stricter, and efforts are being made to suppress carbon dioxide emission in the automotive industry. Also, in addition to efforts made in relation to fuels such as bio-ethanol or biodiesel fuel, efforts are being made to improve gas mileage by reducing weight or installing a heat exchanger that recovers exhaust heat or to install an exhaust gas treatment device, such as EGR, Diesel Particulate Filter (DPF) and urea Selective Catalytic Reduction (SCR) system.

[0003] Among the above, in the EGR system, for the purpose of reducing NO_x which is a toxic gas, exhaust gas of the engine is cooled, and then the cooled exhaust gas is brought to the air intake side and re-combusting it; and thereby, the combustion temperature is decreased. As a result, NO_x is reduced. In addition, an EGR cooler is an apparatus that cools exhaust gas with an engine coolant or air, and is desired to have a good thermal conductivity in order to have the good thermal efficiency demanded at the heat exchanging unit.

[0004] As disclosed in Patent Documents 1, 2 or the like below, in the past, an austenitic stainless steel, such as SUS304 or SUS316, was generally used for EGR coolers. However, in recent years, there has been a demand to lower the temperature at the outlet of an EGR cooler in order to further reduce NO_x . Therefore, in such an austenitic stainless steel, there are ongoing concerns about degradation of thermal fatigue properties due to the enlarged difference of temperature between the inlet and outlet. In view of these, a ferritic stainless steel which has a higher thermal conductivity and a smaller thermal expansion coefficient than those of an austenitic stainless steel and is cheap is gaining attention.

[0005] In addition, thus far, the EGR cooler has been installed generally for diesel engines; however, studies have been carried out regarding the application thereof to gasoline engines in order to meet both of the improvement of gas mileage through achieving direct injection and the reduction of NO_x . In general, it is said that, in gasoline engines, the temperature of exhaust gas is higher than that in diesel engines and the temperature at the inlet of the EGR cooler reaches 500 °C to 600 °C. This temperature range is a range in which there are concerns about intergranular corrosion due to the sensitization of the austenitic stainless steel such as SUS304 or SUS316, and this is another reason why the ferritic stainless steel is drawing attention.

[0006] In general, an EGR cooler, particularly the heat exchanging unit thereof is assembled by a brazing joint in the manufacture thereof. In addition, in the exhaust gas emission side of an EGR cooler, the components of exhaust gas can be condensed during cooling. As a result, there is a demand for brazability and corrosion resistance against the condensed water of exhaust gas.

[0007] Patent Document 3 below discloses a precoated brazing filler metal-coated metal sheet manufactured by suspending a Ni-based brazing filler metal with an organic binder, spray-coating the suspension on the surface of a stainless steel, and heating the coat.

[0008] Patent Document 4 below discloses a method for manufacturing a stainless steel sheet coated with a Ni-based brazing filler metal excellent in self-brazability in which a Ni-based brazing filler metal is coated on a stainless steel sheet with a controlled surface roughness by plasma spraying. In any of the above cases, the stainless steels of the embodiments are austenitic stainless steels.

[0009] Patent Document 5 below discloses an exhaust gas recirculation part substantially made of an austenitic stainless cast steel which includes C: 0.5% or less, Si: 2% or less, Mn: 3% or less, S: 0.2% or less, Ni: 8% to 18%, Cr: 12% to 25%, Mo: 0% to 4%, W: 0% to 2%, (Ni/Cu): 2 or more, and Nb: 0% to 2.5%.

[0010] Patent Document 6 below discloses a heat exchanger in which fins are inserted into a pipe or between a plurality of pipes to form a high-heat fluid passage and a low-heat fluid is formed adjacent to the high-heat fluid, wherein the fins are made of an austenitic stainless steel and the pipes are made of a ferritic stainless steel. SUS304 is exemplified as the austenitic stainless steel, and SUS430 is exemplified as the ferritic stainless steel. The heat exchanger has a structure in which the difference in thermal expansion coefficient between an austenitic stainless steel and a ferritic stainless steel is utilized, and this invention is characterized in that the heat exchanger can be manufactured within a short time at a low cost by removing brazing joints. Therefore, Patent Document 6 does not include any description regarding the brazability and also does not mention about corrosion resistance against condensed water.

[0011] Patent Document 7 below discloses an inner fin for an exhaust gas heat exchanger made of a ferritic stainless steel, which is built in a flat tube incorporated in the exhaust gas heat exchanger so as to divide the wide direction of an exhaust gas passage formed by the flat tube into small compartments, thereby forming multiple long and slender exhaust

gas passages. This invention is characterized in that the inner fin has a shape in consideration of the formability of the ferritic stainless steel; and thereby, the heat resistance is improved. SUS 405 and SUS 446 are exemplified. Patent Document 7 mentions only good heat resistance and foldability as the necessary characteristics; however, brazability and corrosion resistance against condensed water are not mentioned.

[0012] Patent Document 8 below discloses a ferritic stainless steel for a heat exchanger including C: 0.025% or less, Si: 0.10% or less, Mn: 1.0% or less, Cr: 17.0% to 25.0%, Ni: 0.50% or less, Mo: 0.50% to 2.00%, Al: 0.025% or less, N: 0.025% or less, and either one or both of Nb and Ti at an amount within a range of 10(C+N) % to 1.0%. This invention limits the amounts of Si and Al from the viewpoint of brazability and has large amounts of Cr and Mo from the viewpoint of corrosion resistance and oxidation resistance. In particular, it is mentioned that Mo is an extremely effective element for the corrosion resistance against the condensed water of exhaust gas. In the case where corrosive environment is severer, it is necessary to increase the amount of Mo; however, there is a concern regarding poor cost performance since Mo is an expensive element.

[0013] Patent Document 9 below discloses ferritic stainless steel for an ammonia-water based absorption type cycle heat exchanger excellent in terms of a brazing property C: 0.08% or less, Si: 0.01% to 2.0%, Mn: 0.05% to 1.5%, P: 0.05% or less, S: 0.01% or less, Cr: 13% to 32%, Mo: 3.0% or less, Al: 0.005% to 0.1%, Ni: 1.0% or less, Cu: 1.0% or less, and Ti: 0.05% or less. This invention is characterized in that the amount of Ti is limited to be within a range of 0.05% or less from the viewpoint of a brazing property (brazability), and Cr is included at an amount within a range of 13% or more from the viewpoint of corrosion resistance in a high-temperature and high-pressure ammonia water environment. Patent Document 9 describes Mo, Ni and Cu as effective elements for corrosion resistance; however, the necessary amounts thereof are not described.

[0014] Patent Document 10 below discloses a ferritic stainless cast steel having excellent acid resistance which includes Cr: 18.0% to 27.0%, Cu: 0.8% to 3.5%, Si: 0.5% to 2.0%, Mo: 0.5% to 1.5%, Nb: 2.5% or less, Ni: 0.6% or less, C: 0.12% or less, Mn: 1.0% or less, Al: 0.10% or less, P: 0.15% or less, S: 0.15% or less, N: 0.10% or less and (Cu + Si): more than 2.0%. This invention is characterized in that the cast steel is made of a ferritic stainless steel from the viewpoint of machinability and the amounts of Cr, Cu, Si and (Cu + Si) are defined from the viewpoint of acid resistance. Since this cast steel requires large amounts of Cu and Si from the viewpoint of acid resistance, the cast steel becomes hard and, in the case of being used as a steel sheet, there is a concern about formability.

PRIOR ART DOCUMENTS

Patent Documents

[0015]

Patent Document 1: Japanese Unexamined Patent Application, First Publication No. 2007-64515

Patent Document 2: Japanese Unexamined Patent Application, First Publication No. 2007-224786

Patent Document 3: Japanese Unexamined Patent Application, First Publication No. H01-249294

Patent Document 4: Japanese Unexamined Patent Application, First Publication No. 2001-26855

Patent Document 5: Japanese Unexamined Patent Application, First Publication No. 2003-193205

Patent Document 6: Japanese Unexamined Patent Application, First Publication No. 2005-55153

Patent Document 7: Japanese Unexamined Patent Application, First Publication No. 2008-96048

Patent Document 8: Japanese Unexamined Patent Application, First Publication No. H07-292446

Patent Document 9: Japanese Unexamined Patent Application, First Publication No. H11-236654

Patent Document 10: Japanese Unexamined Patent Application, First Publication No. 2008-195985

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

5 **[0016]** The present invention has been suggested in consideration of the above situation, and the object of the present invention is to provide a ferritic stainless steel sheet for EGR coolers having both excellent brazability and corrosion resistance against the condensed water of exhaust gas.

Means for Solving the Problems

10 **[0017]** The features of the present invention having an object of solving the above-described problems are as follows:

15 [1] A ferritic stainless steel sheet for EGR coolers includes: at least, by mass%, C: 0.03% or less; N: 0.05% or less; Si: 0.1% to 1%; Mn: 0.02% to 2%; Cu: 0.2% to 1.5%; Cr: 15% to 25%; Nb: 8(C + N) % to 1%; Al: 0.5% or less; and Fe and inevitable impurities as the balance, wherein the steel sheet further includes, by mass%, Ti at an amount fulfilling the following formulae (1) and (2), and Cr and Cu are included at amounts fulfilling the following formula (3).

$$20 \quad Ti - 3N \leq 0.03 \quad \dots (1)$$

$$25 \quad 10(Ti - 3N) + Al \leq 0.5 \quad \dots (2)$$

$$30 \quad Cr + 2.3Cu \geq 18 \quad \dots (3)$$

[2] The ferritic stainless steel sheet for EGR coolers according to the above [1], wherein the steel sheet further includes, by mass%, either one or both of Mo: 3% or less, and Ni: 3% or less at amounts fulfilling the following formula (4).

$$35 \quad Cr + 1.9Mo + 1.6Ni + 2.3Cu \geq 18 \quad \dots (4)$$

40 [3] The ferritic stainless steel sheet for EGR coolers according to the above [1] or [2], wherein the steel sheet further includes, by mass%, either one or both of V: 3% or less, and W: 5% or less.

[4] The ferritic stainless steel sheet for EGR coolers according to any one of the above [1] to [3], wherein the steel sheet further includes, by mass%, one or more selected from the group consisting of Ca: 0.002% or less, Mg: 0.002% or less, and B: 0.005% or less.

45 [5] The ferritic stainless steel sheet for EGR coolers according to any one of the above [1] to [4], wherein the steel sheet fulfills C + N: 0.015% or more.

Effects of the Invention

50 **[0018]** As described above, according to the present invention, since a ferritic stainless steel sheet for EGR coolers having both excellent brazability and corrosion resistance against the condensed water of exhaust gas can be provided, it is possible to preferably use the ferritic stainless steel sheet for an EGR cooler, particularly for the heat exchanging unit in the EGR cooler.

BRIEF DESCRIPTION OF THE DRAWINGS

55 **[0019]**

FIG. 1 is a characteristic view showing the relationship between the wetting property of a brazing filler metal and

the amounts of Ti and Al.

FIG. 2 is a characteristic view showing the relationship between the corrosion rate in the simulated condensed water of exhaust gas and $\text{Cr} + 2.3\text{Cu} \geq 18$ (at a pH of 1.5).

FIG. 3 is a characteristic view showing the relationship between the corrosion rate in the simulated condensed water of exhaust gas and $\text{Cr} + 1.9\text{Mo} + 1.6\text{Ni} + 2.3\text{Cu}$ (at a pH of 1.5).

FIG. 4 is a characteristic view showing the effect of Cu (at a pH of 1) which affects the corrosion rate in the simulated condensed water of exhaust gas.

FIG. 5 is a characteristic view showing the effect of Mo (at a pH of 1) which affects the corrosion rate in the simulated condensed water of exhaust gas.

FIG. 6 is a characteristic view showing the effect of Ni (at a pH of 0.5) which affects the corrosion rate in the simulated condensed water of exhaust gas.

BEST MODE FOR CARRYING OUT THE INVENTION

[0020] Hereinafter, the embodiment of the present invention will be described with reference to the accompanying drawings.

EGR coolers demand brazability due to Ni or Cu. Therefore, the inventors of the present invention have conducted thorough studies on the effect of alloy elements on brazability. As a result, the inventors of the present invention have found that, as shown in the following formulae (1) and (2), in a ferritic stainless steel sheet, there are upper limits for an amount of Ti which is often added to improve formability or intergranular corrosion resistance and an amount of Al which is added for deoxidization, for the purpose of ensuring good brazability.

$$\text{Ti} - 3\text{N} \leq 0.03 \quad \dots (1)$$

$$10(\text{Ti} - 3\text{N}) + \text{Al} \leq 0.5 \quad \dots (2)$$

[0021] In order to obtain good brazability, a melted brazing filler metal needs to wet and flow over the surface of a stainless steel sheet; however, the wetting property is affected by a surface film formed on the stainless steel sheet in a brazing atmosphere. In addition, in a brazing atmosphere, even in the case where conditions can be maintained under which the oxides of Fe and Cr are reduced, Ti and Al which are more liable to be oxidized than Fe and Cr form oxides which inhibit the wetting of a brazing filler metal; and thereby, brazability is degraded. Solid-soluted Ti and Al are elements that contribute to the formation of such a film, but in a case in which Ti and Al are present as relatively stable nitrides even at the brazing temperature, they do not contribute to the formation of the film and they do not inhibit the wetting of a brazing filler metal.

[0022] From such a standpoint, the relationship between the amounts of Ti and Al and the wetting of a brazing filler metal was evaluated under the same test conditions as the below-described examples using ferritic stainless steel sheets including Cr: 16 mass% to 21 mass% described in Table 1. In Table 1, the balance consists of Fe and inevitable impurities. The results are shown in FIG. 1.

[0023]

Table 1

No.	Chemical composition (mass%)										
	Cr	Si	Mn	P	S	Cr	Ti	Nb	Al	N	Others
1	0.012	0.42	0.15	0.028	0.0015	19.42	0.004	0.39	0.025	0.018	0.42Cu, 0.32Ni, 0.0010Ca
2	0.013	0.55	0.45	0.029	0.0008	16.58	0.002	0.55	0.004	0.015	0.32Ni, 0.35Cu
3	0.006	0.12	0.19	0.022	0.0010	18.84	0.004	0.42	0.036	0.010	1.86Mo, 0.0003B
4	0.016	0.25	0.18	0.029	0.0011	18.23	0.021	0.36	0.036	0.014	0.52Cu, 1.02Mo
5	0.007	0.16	0.15	0.022	0.0008	20.25	0.012	0.22	0.015	0.009	1.03Ni, 1.08Mo

(continued)

No.	Chemical composition (mass%)										
	Cr	Si	Mn	P	S	Cr	Ti	Nb	Al	N	Others
6	0.014	0.33	0.45	0.030	0.0014	18.15	0.015	0.36	0.055	0.015	2.15W, 0.35V
7	0.015	0.40	0.32	0.025	0.0019	20.88	0.042	0.40	0.046	0.010	0.34Ni
8	0.016	0.41	0.29	0.024	0.0016	19.19	0.066	0.42	0.086	0.015	1.88W, 0.0005Mg
9	0.018	0.39	0.33	0.023	0.0015	19.34	0.032	0.39	0.35	0.009	0.56Ni, 0.38V, 0.0004Ca
10	0.008	0.18	0.15	0.026	0.0011	17.25	0.25	0.002	0.042	0.010	1.12Mo, 0.0005B
11	0.007	0.11	0.12	0.025	0.0012	18.85	0.12	0.22	0.056	0.012	1.80Mo, 0.0004B
12	0.012	0.33	0.25	0.025	0.0012	18.22	0.004	0.35	0.58	0.014	0.29Ni
13	0.010	0.42	0.36	0.026	0.0007	16.89	0.062	0.003	0.36	0.012	
14	0.011	0.15	0.22	0.028	0.0009	19.12	0.073	0.25	0.041	0.008	1.90Mo

[0024] From the results shown in Table 1, it has been clarified that the wetting property of a brazing filler metal is good in steels fulfilling the above-described formulae (1) and (2). In addition, with regard to the steels of which the amounts of Ti and Al did not fulfill the above-described conditions, the surface films after a brazing thermal treatment were analyzed. As a result, it was found that a Ti or Al-concentrated oxide film was uniformly formed with a thickness within a range of several tens of nanometers to several hundreds of nanometers. Therefore, such film formation is considered to inhibit the wetting of a brazing filler metal.

[0025] EGR coolers, for which the present invention is to be used, also demand strength; and therefore, it is desirable that a decrease in strength after brazing be small. In the case where brazing is conducted at high temperatures within a range of 1000 °C to 1150°C, such as Ni brazing or Cu brazing, it is considered important to suppress a decrease of strength due to grain coarsening. Pinning by precipitates is useful to suppress the coarsening of grains. In the present invention, it has been found that the precipitation amount and stability of carbonitrides of Nb, which are useful to suppress the coarsening of grains, are ensured by using the carbonitrides of Nb as the precipitates and including 0.015% or more of C + N (refer to Japanese Patent Application No. 2007-339732).

[0026] In EGR coolers, SO_x, NO_x and HC included in exhaust gas generate acidic condensed water including sulfuric acid, nitric acid and organic acid. Unlike downstream members such as mufflers, EGR coolers are provided just below the engine and in front of a catalyst; and thus, the EGR coolers have to deal with unpurified exhaust gas. Therefore, the acid concentration in the condensed water to be generated becomes high.

[0027] In addition, recently, there have been cases in which low-grade fuels with a high concentration of S have been used as vehicle fuels due to globalization. In these cases, the concentration of sulfuric acid in condensed water also increases. Such an increase in acid concentration results in a decrease in pH, and the pH of the condensed water in EGR coolers is said to reach about 1.5. Generally, since a sheet thickness of the heat exchanging unit in an EGR cooler is thin, which is within a range of 0.1 mm to 0.5 mm, excellent corrosion resistance against such condensed water including sulfuric acid, nitric acid and organic acid with a pH of about 1.5 is required.

[0028] Therefore, the inventors of the present invention studied the effect of Cr and Cu which affect corrosion resistance against condensed water using ferritic stainless steels including Cr: 16 to 19% and Cu: 0 to 0.5% through corrosion testing under the same conditions as the examples. The results are shown in FIG. 2. Here, since NO₃⁻ ions serve as corrosion suppression ions, NO₃⁻ ions were evaluated as safe, without adding it.

[0029] FIG. 2 shows the test results in a solution with a pH of 1.5, and it can be understood that by fulfilling Cr + 2.3Cu ≥ 18, excellent corrosion resistance is obtained.

[0030] Next, the effect of Cr, Ni, Mo and Cu which affect corrosion resistance against condensed water was studied using ferritic stainless steels including, in addition to Ni and Mo, Cr: 13 to 21%, Mo: 0 to 2%, Ni: 0 to 3% and Cu: 0 to 1% through corrosion testing under the same conditions as the examples. The results are shown in FIG. 3. Meanwhile, in this test as well, NO₃⁻ ions were not added.

[0031] FIG. 3 shows the test results in a solution with a pH of 1.5, and it can be understood that any elements of Cr, Ni, Mo and Cu are effective for the improvement of corrosion resistance; however, among them, Cu is most effective for the improvement of corrosion resistance, and it can be understood that by fulfilling Cr + 1.9Mo + 1.6Ni + 2.3Cu ≥ 18, excellent corrosion resistance is obtained.

[0032] Here, the coefficient of each alloy element is obtained by multiple linear regression analysis of the degree of contribution of alloy elements to a critical pH. Meanwhile, the critical pH is the upper limit of pH at which the corrosion rate becomes $0.1 \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ or less. FIG. 4 shows the effect of Cu which affects corrosion rate in a solution with a pH of 1; FIG. 5 shows the effect of Mo which affects corrosion rate in a solution with a pH of 1; and FIG. 6 shows the effect of Ni which affects corrosion rate in a solution with a pH of 0.5.

[0033] From the results of FIGS. 4 to 6, it can be understood that, compared with Mo and Ni, Cu remarkably lowers the corrosion rate with a smaller added amount; and therefore, Cu is an extremely effective element for the improvement of corrosion resistance. In addition, although Cu is known as an element that improves acid resistance, the effect of Cu was studied by electrochemical measurement. As a result, a phenomenon in which the addition of Cu leads to the ennoblement of corrosion potential was confirmed. This shows that Cu exhibits an operation that accelerates passivation as well as an operation that suppresses active dissolution, and it is considered that these two effects makes the contribution to the improvement of corrosion resistance larger.

[0034] The present invention has been made based on the above finding, and the object of the present invention is to provide a ferritic stainless steel sheet for EGR coolers having both excellent brazability and corrosion resistance against the condensed water of exhaust gas, and the features of the present invention is as contained in the scope of the claims.

[0035] Hereinafter, the reason why each composition of the ferritic stainless steel sheet for EGR coolers is limited will be described. Meanwhile, in the description below, unless otherwise described, % in each component refers to mass %.

(C: 0.03% or less)

[0036] Since C degrades intergranular corrosion resistance and formability, it is necessary to suppress the content of C at a low level. Therefore, the content of C is set to be within a range of 0.03% or less. However, an excessive lowering of the C content leads to grain coarsening during brazing and increasing of refining costs. Therefore, the content of C is preferably set to be within a range of 0.002% or more, and more preferably within a range of 0.005% to 0.025%.

(N: 0.05% or less)

[0037] N is a useful element for pitting corrosion resistance; however, N degrades intergranular corrosion resistance and formability. Therefore, it is necessary to suppress the content of C at a low level. As a result, the content of N is set to be within a range of 0.05% or less. However, since an excessive lowering of the N content leads to grain coarsening during brazing, and increasing of refining costs. Therefore, the content of N is preferably set to be within a range of 0.002% or more, and more preferably within a range of 0.005% to 0.03%.

(Si: 0.1% to 1%)

[0038] Since the contents of Ti and Al, which are useful as deoxidizing elements, are restricted, Si is required as a deoxidizing element. In addition, since the concentration of Cr in the surface is lowered by a brazing thermal treatment, Si is an effective element for the improvement of oxidation resistance after the brazing. Therefore, it is necessary to include at least 0.1% or more of Si. However, an excessive addition of Si degrades formability. Therefore, the content of Si is preferably set to be within a range of 1% or less, and more preferably within a range of 0.1 % to 0.5%.

(Mn: 0.02% to 2%)

[0039] Mn is a useful element as a deoxidizing element; and therefore, it is necessary to include at least 0.02% or more of Mn. However, since an excessive inclusion of Mn degrades corrosion resistance, the content of Mn is preferably set to be within a range of 2% or less, and more preferably within a range of 0.1 % to 1%.

(Cu: 0.2% to 1.5%)

[0040] Cu is an element as important as Cr for ensuring the corrosion resistance against the condensed water of exhaust gas; and therefore, it is necessary to include at least 0.2% or more of Cu. Meanwhile, as the content of Cu increases, corrosion resistance can be further improved. However, an excessive addition of Cu degrades formability. Therefore, the content of Cu is preferably set to be within a range of 1.5% or less, and more preferably within a range of 0.2% to 1.0%.

(Cr: 15% to 25%)

[0041] Cr is a fundamental element for ensuring corrosion resistance against the condensed water of exhaust gas and oxidation resistance; and therefore, it is necessary to include at least 15% or more of Cr. Meanwhile, as the content of Cr increases, corrosion resistance and oxidation resistance can be further improved. However, an excessive addition of Cr degrades formability and manufacturability. Therefore, the content of Cr is preferably set to be within a range of 25% or less, and more preferably within a range of 17% to 23%.

(Nb: $8(C + N)$ % to 1%)

[0042] Since Nb is a useful element for fixing C and N, and improving the intergranular corrosion resistance of welded portions, it is necessary to include Nb at an amount of 8 or more times the amount of (C + N). In addition, Nb is also useful for improving strength at high temperatures; and therefore, Nb is required for members used at high temperatures, such as EGR coolers. Furthermore, the carbonitride of Nb is useful for suppressing the coarsening of crystal grains during brazing. However, an excessive addition of Nb degrades formability and manufacturability. Therefore, the content of Nb is preferably set to be within a range of 1.0% or less, and more preferably within a range of $10(C + N)$ % to 0.6%.

(C + N: 0.015% or more)

[0043] Furthermore, from the viewpoints of suppressing strength degradation accompanied by the coarsening of crystal grains during brazing, the sum of C + N is preferably set to be within a range of 0.015% or more. The content of C + N is more preferably set to be within a range of 0.02% or more. Since an excessive addition of C and N degrades intergranular corrosion resistance and formability, the sum of C + N is still more preferably set to be within a range of 0.04% or less.

(Al: 0.5% or less)

[0044] Since Al has deoxidizing effect or the like, Al is an effective element for refinement. Al also has an effect of improving formability. However, Al inhibits brazability which is the most important characteristic in the present invention; and therefore, the content of Al is set to be within a range of 0.5% or less. The content of Al is preferably within a range of 0.001% to 0.1%, and more preferably within a range of 0.001% to 0.05%.

(Ti: within a range fulfilling Formulae (1) and (2))

[0045] In the present invention, regarding brazability which is the most important characteristic, it is necessary to fulfill both of the above-described formulae (1) and (2) so as to obtain a good wetting property of a brazing filler metal. In order to satisfy the wetting property, based on the above-described finding, the content of Ti is set to be within a range fulfilling the above-described formulae (1) and (2). The value of $Ti - 3N$ is preferably within a range of 0.02% or less. However, if the content of Ti is excessively lowered, formability is degraded; and therefore, it is preferable to adjust the content of Ti so as to make the value of $Ti - 3N$ to be within a range of -0.08% or more. In the case where formability or the like is not particularly demanded, Ti may not be added.

(Cr and Cu: within a range fulfilling Formula (3))

[0046] In the present invention, in order to develop good corrosion resistance in the condensed water of exhaust gas with a pH of about 1.5 which includes sulfuric acid, nitric acid and organic acid, it is necessary to fulfill the following formula (3) with regard to the contents of Cr and Cu.

$$Cr + 2.3 Cu \geq 18 \quad \dots (3)$$

[0047] In addition, in the present invention, either one or both of Mo and Ni may be further included.

(Mo: 3% or less)

[0048] Mo may be included at a content within a range of 3% or less as necessary to improve corrosion resistance. In order to obtain the effect stably, the content of Mo should be within a range of 0.3% or more. However, an excessive

addition of Mo degrades formability and leads to an increase in costs due to the high price. Therefore, the content of Mo is preferably within a range of 0.3% to 3%.

(Ni: 3% or less)

[0049] Ni may be included at a content within a range of 3% or less as necessary to improve corrosion resistance. In order to obtain the effect stably, the content of Ni should be within a range of 0.2% or more. However, an excessive addition of Ni degrades formability and leads to an increase in costs due to the high price. Therefore, the content of Ni is preferably within a range of 0.2% to 3%.

[0050] Furthermore, in the case of adding either one or both of Mo and Ni, in order to develop good corrosion resistance in the condensed water of exhaust gas with a pH of about 1.5 which includes sulfuric acid, nitric acid and organic acid, it is necessary to fulfill the following formula (4).

$$\text{Cr} + 1.9\text{Mo} + 1.6\text{Ni} + 2.3\text{Cu} \geq 18 \quad \cdots (4)$$

[0051] In addition, in the present invention, either one or both of V and W may be further included.

(V: 3% or less)

[0052] V may be included at a content within a range of 3% or less as necessary to improve corrosion resistance. In order to obtain the effect stably, the content of V should be within a range of 0.2% or more. However, an excessive addition of V degrades formability and leads to an increase in costs due to the high price. Therefore, the content of V is preferably within a range of 0.2% to 3%.

(W: 5% or less)

[0053] W may be included at a content within a range of 3% or less as necessary to improve corrosion resistance. In order to obtain the effect stably, the content of W should be within a range of 0.5% or more. However, an excessive addition of W degrades formability and leads to an increase in costs due to the high price. Therefore, the content of W is preferably within a range of 0.5% to 5%.

[0054] In addition, the present invention may further include one or more selected from the group consisting of Ca, Mg and B.

(Ca: 0.002% or less)

[0055] Since Ca has a deoxidization effect or the like, Ca is a useful element for refinement. Therefore, Ca may be included as necessary at a content within a range of 0.002% or less. In the case of including Ca, the content of Ca is preferably set to be within a range of 0.0002% or more at which the effect can be obtained stably.

(Mg: 0.002% or less)

[0056] Since Mg has a deoxidization effect or the like, Mg is a useful element for refinement. In addition, Mg also refines the microstructure and is useful for the improvement of formability and toughness. Therefore, Mg may be included as necessary at a content within a range of 0.002% or less. In the case of including Mg, the content of Mg is preferably set to be within a range of 0.0002% or more at which the effect can be obtained stably.

(B: 0.005% or less)

[0057] B is a useful element for improving secondary formability, and B may be included as necessary at a content within a range of 0.005% or less. In the case of including B, the content of B is preferably set to be within a range of 0.0002% or more at which the effect can be obtained stably.

[0058] Here, among the inevitable impurities, the content of P is preferably set to be within a range of 0.04% or less from the viewpoint of weldability. In addition, the content of S is preferably set to be within a range of 0.01 % or less from the viewpoint of corrosion resistance.

[0059] In the method for manufacturing the stainless steel according to the present invention, general processes that manufacture ferritic stainless steels may be applied. In general, stainless steels are manufactured by producing molten

steel with a converter furnace or an electric furnace, refining the steel with an AOD furnace, a VOD furnace or the like, producing a slab by a continuous casting method or an ingot-making method, and then subjecting the slab to a process of hot rolling - annealing of a hot-rolled sheet - acid washing - cold rolling - final annealing - acid washing. As necessary, the annealing of the hot-rolled sheet may be omitted, and the process of cold rolling - final annealing - acid washing may be repeated.

EXAMPLES

[0060] Hereinafter, the effects of the present invention will be made more evident by examples. Here, the present invention is not limited to the following examples and can be appropriately modified and carried out within a range not altering the features of the present invention.

[0061] In the present examples, steels having the chemical compositions shown in Table 2 below were manufactured, and cold-rolled steel sheets with a sheet thickness of 0.4 mm were manufactured by conducting the processes of hot rolling, cold rolling and annealing. Then, brazability and corrosion resistance in a simulated condensed water of exhaust gas were evaluated.

[0062]

Table 2

	Examples	Chemical composition (mass%)																	
		C	N	Si	Mn	P	S	Cu	Cr	Nb	Al	Ti	Mo	Ni	V	W	Ca	Mg	B
Inventive Example	1	0.009	0.008	0.26	0.26	0.024	0.0006	0.32	17.64	0.35	-	-	-	-	-	-	-	-	-
Inventive Example	2	0.012	0.018	0.42	0.15	0.028	0.0015	0.42	19.42	0.39	0.025	-	-	0.32	-	-	0.001	-	-
Inventive Example	3	0.006	0.010	0.12	0.19	0.022	0.0010	0.22	18.84	0.42	0.036	-	1.86	-	-	-	-	-	0.0003
Inventive Example	4	0.016	0.014	0.25	0.18	0.029	0.0011	0.52	18.23	0.36	0.036	-	1.02	-	-	-	-	-	-
Inventive Example	5	0.008	0.008	0.22	0.21	0.024	0.0008	0.31	18.25	0.22	0.015	-	-	0.43	-	-	-	-	-
Inventive Example	6	0.012	0.013	0.86	0.36	0.022	0.0007	0.65	15.23	0.36	0.009	-	2.02	0.22	-	-	-	0.0006	-
Inventive Example	7	0.011	0.014	0.21	0.22	0.024	0.0011	0.88	22.21	0.34	0.006	-	1.52	0.47	-	-	-	-	-
Inventive Example	8	0.024	0.008	0.32	0.97	0.028	0.0016	0.34	18.12	0.38	0.042	-	-	-	0.67	1.23	-	0.0008	-
Inventive Example	9	0.010	0.010	0.26	0.20	0.026	0.0011	1.25	18.23	0.56	0.012	0.04	-	-	-	-	0.0004	-	-
Inventive Example	10	0.011	0.011	0.25	0.19	0.025	0.0009	0.45	21.34	0.32	-	-	-	1.98	-	-	-	-	-
Inventive Example	11	0.009	0.013	0.19	0.21	0.022	0.0009	0.50	19.35	0.51	0.004	-	1.91	-	-	-	0.0003	-	-
Inventive Example	12	0.005	0.016	0.25	0.24	0.028	0.0010	0.28	17.45	0.41	0.012	-	-	-	0.32	-	-	-	-
Inventive Example	13	0.006	0.014	0.32	0.28	0.025	0.0011	0.24	17.05	0.38	0.021	-	0.42	-	-	0.82	-	-	-
Comparative Example	14	0.012	0.014	0.33	0.25	0.025	0.0012	-	18.22	0.35	0.58	-	-	0.29	-	-	-	-	-
Comparative Example	15	0.011	0.008	0.15	0.22	0.028	0.0009	-	19.12	0.25	0.041	0.07	1.90	-	-	-	-	-	-
Comparative Example	16	0.004	0.012	0.25	0.22	0.027	0.0017	-	17.72	-	0.046	0.18	-	-	-	-	-	-	-
Comparative Example	17	0.005	0.008	0.96	0.30	0.021	0.0003	-	13.50	0.45	0.035	-	-	-	-	-	0.001	-	-

(Note) The underlines indicate values outside the range of the present invention.

Table 2 (Continued)

Examples	Formula (1)*1 (mass%)	Formula (2)*2 (mass%)	Formula (3)*3 or Formula (4)*4 (mass%)	C+N (mass%)
Inventive Example 1	-0.02	-0.24	18.4	0.017
Inventive Example 2	-0.05	-0.52	20.9	0.030
Inventive Example 3	-0.03	-0.26	22.9	0.016
Inventive Example 4	-0.04	-0.38	21.4	0.030
Inventive Example 5	-0.02	-0.23	19.7	0.016
Inventive Example 6	-0.04	-0.38	20.9	0.025
Inventive Example 7	-0.04	-0.41	27.9	0.025
Inventive Example 8	-0.02	-0.20	18.9	0.032
Inventive Example 9	0.01	-0.29	21.1	0.020
Inventive Example 10	-0.03	-0.33	25.5	0.022
Inventive Example 11	-0.04	-0.39	24.1	0.022
Inventive Example 12	-0.05	-0.47	18.1	0.021
Inventive Example 13	-0.04	-0.40	18.4	0.020
Comparative Example 14	-0.04	0.16	18.7	0.026
Comparative Example 15	0.05	0.53	22.7	0.019
Comparative Example 16	0.15	1.53	17.7	0.016
Comparative Example 17	-0.02	-0.19	13.5	0.013

*1 Formula (1): Ti - 3N

*2 Formula (2): 10(Ti - 3N) + Al

*3 Formula (3): Cr + 2.3Cu

*4 Formula (4): Cr + 1.9Mo + 1.6Ni + 2.3Cu

(Note) The underlines indicate values outside the ranges of the present invention.

(Brazability)

[0063] Test specimens with a width of 50 mm and a length of 70 mm were cut off from the cold-rolled steel sheets, and then wet polishing was conducted on one surface with emery papers up to #400-grit. Thereafter, 0.1 g of Ni brazing filler metal was placed on the polished surface and was heated at a temperature of 1100 °C for 10 minutes in a vacuum atmosphere of 5×10^{-3} Torr. After cooling to a room temperature, the area of the brazing filler metal after the heating

was measured. The measurement results are shown in Table 3.

[0064] Here, regarding brazability shown in Table 3, wetting property was evaluated as "Good" in the case where the area of the brazing filler metal after the heating was two or more times the area of the brazing filler metal before the heating, and the wetting property was evaluated as "Bad" in the case where the area of the brazing filler metal after the heating was less than two times the area of the brazing filler metal before the heating. In addition, after that, the microstructures on the cross-sections were observed. Then, the number of crystal grains present in the sheet thickness direction was measured in a region having a length of 20 mm parallel to the rolling direction. Based on the results, microstructures were evaluated as "Good" in the case where two or more crystal grains were present in the sheet thickness direction, and microstructures were evaluated as "Bad" in the case where only one crystal grain was present.

(Corrosion test)

[0065] 25 W × 40L test specimens were cut off from the cold-rolled steel sheets, and the entire surfaces were wet-polished with emery papers up to #320-grit. A solution including 50 ppm Cl⁻ + 5000 ppm SO₄²⁻ + 5000 ppm HCOO⁻ + 3000 ppm CH₃COO⁻ was prepared using ammonium chloride, sulfuric acid, formic acid and acetic acid as reagents. After that, the pH of the solution was adjusted to be within a range of 1.5 and 1.0 using sulfuric acid or ammonia water. The solution was heated to a temperature of 60°C, and the test specimens were immersed in the solution for 3 hours. The corrosion rate was obtained from the variation of mass before and after the immersion. The measurement results are shown in Table 3.

Here, regarding the corrosion test shown in Table 3, evaluation was given as "Good" in the case where the corrosion rate was 0.1 g·m⁻²·h⁻¹ or less and evaluation was given as "Bad" in the case where the corrosion rate was more than 0.1 g·m⁻²·h⁻¹.

[0066]

Table 3

	Examples	Brazability		Corrosion test	
		Wetting	Microstructure	pH 1.5	pH 1.0
Invention example	1	Good	Good	Good	Bad
Invention example	2	Good	Good	Good	Good
Invention example	3	Good	Good	Good	Good
Invention example	4	Good	Good	Good	Good
Invention example	5	Good	Good	Good	Bad
Invention example	6	Good	Good	Good	Good
Invention example	7	Good	Good	Good	Good
Invention example	8	Good	Good	Good	Bad
Invention example	9	Good	Good	Good	Good
Invention example	10	Good	Good	Good	Good
Invention example	11	Good	Good	Good	Good
Invention example	12	Good	Good	Good	Bad
Invention example	13	Good	Good	Good	Bad
Comparative example	14	Bad	Good	Good	Bad
Comparative example	15	Bad	Good	Good	Good
Comparative example	16	Bad	Good	Bad	Bad
Comparative example	17	Good	Bad	Bad	Bad

[0067] From the test results shown in Table 3, it can be understood that the steels of Example Nos. 1 to 13 which fulfill the features of the present invention have a good wetting property of the brazing filler metal, suppress the coarsening of crystal grains after brazing, and have a good corrosion resistance in the simulated condensed water of exhaust gas with a pH of 1.5. Among them, the steels of Example Nos. 2, 3, 4, 6, 7, 9, 10 and 11 exhibit a good corrosion resistance

in the simulated condensed water of exhaust gas with a pH of 1.0; and therefore, the steels of Example Nos. 2, 3, 4, 6, 7, 9, 10 and 11 are preferable as a material for EGR coolers which can deal with the case where a corrosion environment becomes more severe.

[0068] On the other hand, it can be understood that Example No. 14 of which the Al content is outside the range of the present invention and Example No. 15 which does not fulfill the above-described formula (2) are poor in terms of the wetting property of the brazing filler metal. In addition, it can be understood that Example No. 16 of which the values of all the above-described formulae (1) to (3) were not in the ranges of the present invention is poor in terms of both the wetting property of the brazing filler metal and corrosion resistance in the simulated condensed water of exhaust gas. Furthermore, it can be understood that Example No. 17 of which the Cr content and the value of the above-described formula (3) were not in the ranges of the present invention and the sum of (C + N) is less than 0.015% is poor in terms of corrosion resistance in the simulated condensed water of exhaust gas and has remarkably coarsened crystal grains.

INDUSTRIAL APPLICABILITY

[0069] The ferritic stainless steel sheet according to the present invention having both excellent brazability and corrosion resistance against the condensed water of exhaust gas is suitable for EGR cooler members, particularly for heat exchanging members in EGR coolers. In addition, the ferritic stainless steel according to the present invention is also suitable for exhaust gas passage members which are exposed to the condensed water of exhaust gas and are joined by brazing.

Claims

1. A ferritic stainless steel sheet for EGR coolers, comprising: at least, by mass%,

C: 0.03% or less;

N: 0.05% or less;

Si: 0.1% to 1%;

Mn: 0.02% to 2%;

Cu: 0.2% to 1.5%;

Cr: 15% to 25%;

Nb: 8(C + N) % to 1%;

Al: 0.5% or less; and

Fe and inevitable impurities as the balance,

wherein the steel sheet further comprises, by mass%, Ti at an amount fulfilling the following formulae (1) and (2), and

Cr and Cu are included at amounts fulfilling the following formula (3),

$$\text{Ti} - 3\text{N} \leq 0.03 \quad \cdots (1)$$

$$10(\text{Ti} - 3\text{N}) + \text{Al} \leq 0.5 \quad \cdots (2)$$

$$\text{Cr} + 2.3\text{Cu} \geq 18 \quad \cdots (3).$$

2. The ferritic stainless steel sheet for EGR coolers according to Claim 1, wherein the steel sheet further comprises, by mass%, either one or both of Mo: 3% or less, and Ni: 3% or less at amounts fulfilling the following formula (4),

$$\text{Cr} + 1.9\text{Mo} + 1.6\text{Ni} + 2.3\text{Cu} \geq 18 \quad \cdots (4).$$

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3. The ferritic stainless steel sheet for EGR coolers according to Claim 1 or 2,
wherein the steel sheet further comprises, by mass%, either one or both of V: 3% or less, and W: 5% or less.
4. The ferritic stainless steel sheet for EGR coolers according to any one of Claims 1 to 3,
wherein the steel sheet further comprises, by mass%, one or more selected from the group consisting of Ca: 0.002%
or less, Mg: 0.002% or less, and B: 0.005% or less.
5. The ferritic stainless steel sheet for EGR coolers according to any one of Claims 1 to 4,
wherein the steel sheet fulfills C + N: 0.015% or more.

FIG. 1

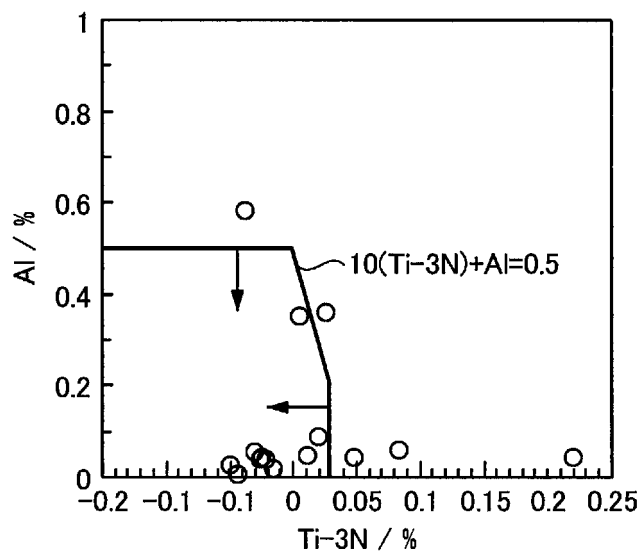


FIG. 2

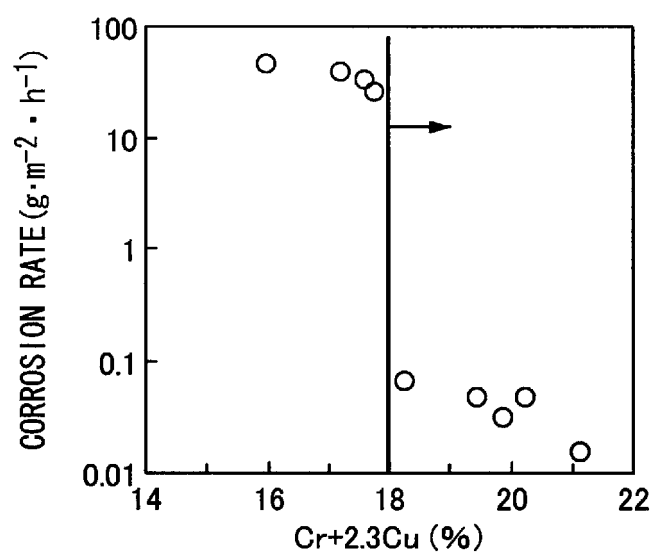


FIG. 3

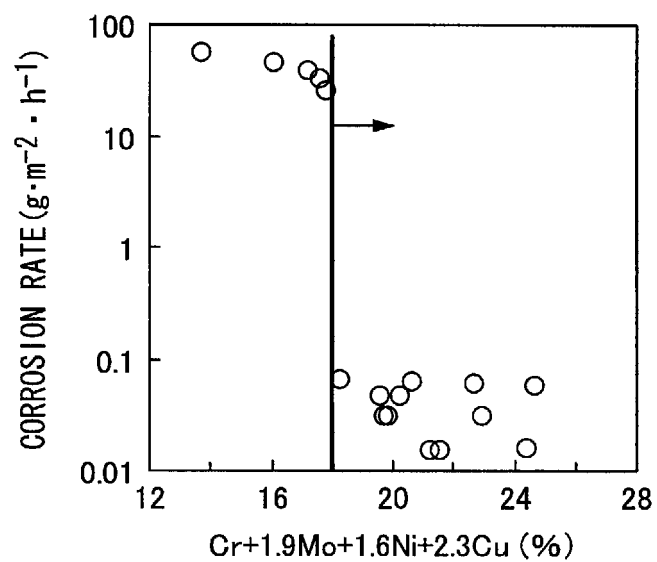


FIG. 4

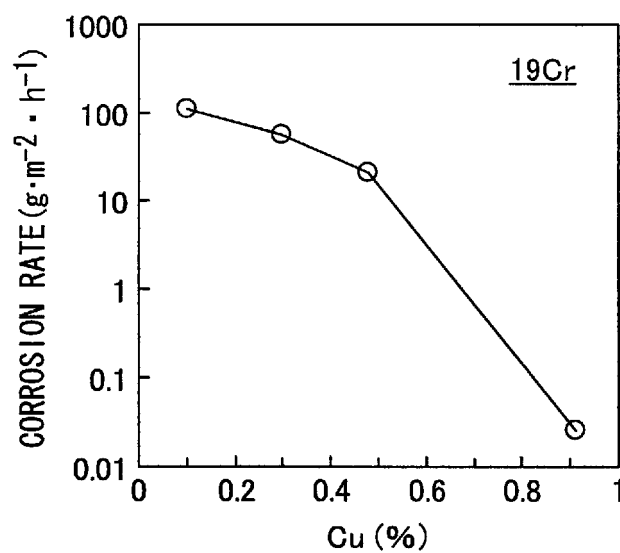


FIG. 5

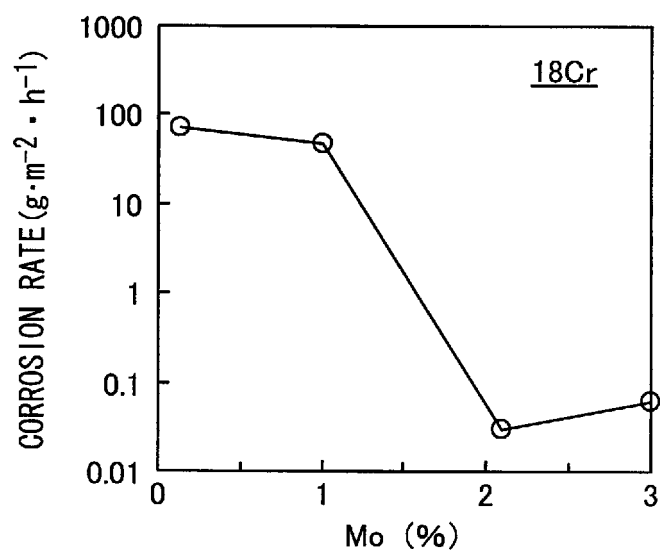
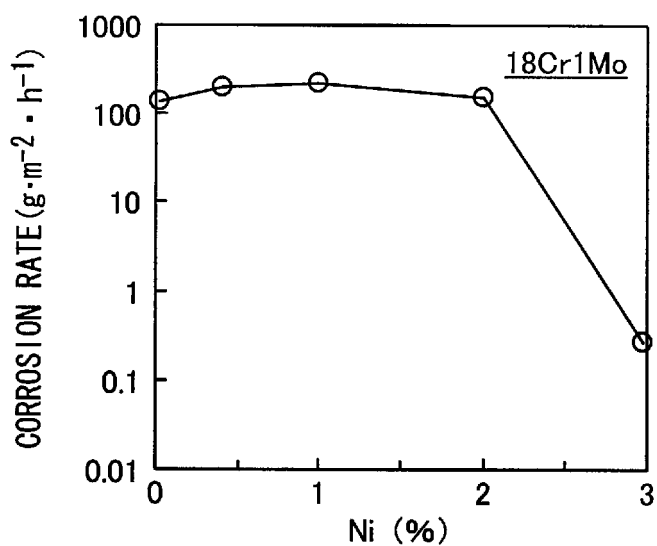


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/005607

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/38(2006.01) i, C22C38/58(2006.01) i, F02M25/07(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, F02M25/07

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 57-060056 A (Allegheny Ludlum Steel Corp.), 10 April 1982 (10.04.1982), claims; table 1 & US 4461811 A & EP 49033 A1	1-5
A	JP 7-292446 A (Nippon Yakin Kogyo Co., Ltd., Tokyo Radiator Mfg. Co., Ltd., Nissan Motor Co., Ltd.), 07 November 1995 (07.11.1995), claims; paragraph [0007]; table 2 (Family: none)	1-5
A	JP 2000-073147 A (Kawasaki Steel Corp.), 07 March 2000 (07.03.2000), claims; paragraph [0001]; table 1 (Family: none)	1-5

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

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search
14 January, 2010 (14.01.10)Date of mailing of the international search report
26 January, 2010 (26.01.10)Name and mailing address of the ISA/
Japanese Patent Office

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/005607

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	JP 2009-174046 A (Nippon Steel & Sumikin Stainless Steel Corp.), 06 August 2009 (06.08.2009), claims; paragraphs [0001], [0009] to [0015], [0030] to [0039] & WO 2009/084526 A1	1-5
P, X	JP 2009-174040 A (Nisshin Steel Co., Ltd.), 06 August 2009 (06.08.2009), claims; paragraphs [0016] to [0020]; tables 1, 2 (Family: none)	1-5

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2007064515 A [0015]
- JP 2007224786 A [0015]
- JP H01249294 B [0015]
- JP 2001026855 A [0015]
- JP 2003193205 A [0015]
- JP 2005055153 A [0015]
- JP 2008096048 A [0015]
- JP H07292446 B [0015]
- JP H11236654 B [0015]
- JP 2008195985 A [0015]
- JP 2007339732 A [0025]