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(54) **HEAT-RESISTANT FERRITE-TYPE STAINLESS STEEL PLATE HAVING EXCELLENT OXIDATION RESISTANCE**

(57) A heat-resistant ferritic stainless steel sheet having excellent oxidation resistance while being low in cost and optimal for use in exhaust system components, wherein mass% falls within the following ranges: C: 0.015% or less, N: 0.020% or less, P: 0.04% or less, S: 0.001% or less, Si: 0.3-1.5% or less, Mn: 0.3-0.7% or less, Cr: 11.0-17.0%, Cu: 0.8-1.5%, Ni: 0.05-1.0%, V: 0.5% or less, Al: over 0.01 up to 0.1%, Ti: 10(C+N) to 0.3%. Also, the element content of the elements in the ferritic stainless steel sheet having excellent oxidation and thermal resistance has been mutually adjusted in a manner such that the value of γ defined in formula (1) is 35 or less.

$$(1)\ \gamma = 23[\%Ni]+9[\%Cu]+7[\%Mn]-11.5[\%Cr]-11.5[\%Si]-52[\%Al]-49[[Ti\%]-4([\%C]+[\%N])]-23[\%V]-12[\%Mo]-47[\%Nb]+189$$

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Description

Technical Field

[0001] The present invention relates to a heat-resistant ferritic stainless steel sheet having excellent oxidation resistance which is optimal in particular for use for exhaust system members which require high temperature strength or oxidation resistance.

Background Art

[0002] Exhaust manifolds, front pipes, center pipers, and other exhaust system members of automobiles carry high temperature exhaust gas which is exhausted from the engines, so the materials forming the exhaust members are required to have various properties such as oxidation resistance, high temperature strength, and heat fatigue characteristics.

[0003] In the past, in automobile exhaust members, exhaust manifolds have generally been made using cast iron, but from the viewpoints of stronger exhaust gas controls, improving engine performance, lightening the car body, etc., exhaust manifolds made of a stainless steel have come into use. Exhaust gas temperatures differ depending on the car model or engine structure, but 600 to 800°C or so is prevalent. A material which has an excellent high temperature strength and oxidation resistance in an environment where it is used for a long period of time in such a temperature region is demanded.

[0004] In the stainless steel, an austenitic stainless steel has excellent heat resistance and workability, but has a large heat expansion coefficient, so when applied to a member like an exhaust manifold which is repeatedly subjected to heating and cooling, thermal fatigue breakage easily occurs.

[0005] On the other hand, a ferritic stainless steel has a smaller heat expansion coefficient compared with the austenitic stainless steel, excellent heat fatigue characteristics, and scale spalling resistance. Further, compared with the austenitic stainless steel, since Ni is not contained, and the material cost is not expensive, therefore this is used for general applications. However, the ferritic stainless steel has lower high temperature strength compared with the austenitic stainless steel, so the art has been developed for improving the high temperature strength. For example, there are SUS430J1L (Nb steel), Nb-Si steel, and SUS444 (Nb-Mo steel). Each of these is predicated on addition of Nb. They used solution strengthening or precipitation strengthening by Nb to raise the high temperature strength.

[0006] In this regard, Nb steel also has problems such as the hardening of the finished sheets, the drop in elongation, and the low r-value which is an indicator of deep drawability. This is because the presence of solute Nb or precipitated Nb enables the hardening at room temperature or the growth of a recrystallized texture to be suppressed, but obstructs the press formability and shape freedom when shaping exhaust parts. Further, Nb is high material cost and raises the manufacturing cost as well. If the steel sheet would secure the high temperature characteristics by added elements other than Nb, it would be possible to keep down the amount of addition of Nb and provide the heat-resistant ferritic stainless steel sheet which has low cost and excellent workability. The Mo which is added to SUS444 results in a high alloy cost, so the problem of a remarkable rise in the part costs also arises.

[0007] PLTs 1 to 6 disclose the art relating to addition of Cu. PLT 1 studies the addition of Cu in an amount of 0.5% or less so as to improve the low temperature toughness, but does not add it from the viewpoint of the heat resistance. PLT 2 is the art which utilizes its action in improving the corrosion resistance and weathering resistance of steel, but does not add it from the viewpoint of the heat resistance. PLTs 3 to 6 disclose the arts which utilize the precipitation hardening by Cu precipitates to improve the high temperature strength at the 600°C or 700 to 800°C temperature region.

Citation List

Patent Literature

[0008]

PLT 1: Japanese Unexamined Patent Publication No. 2006-37176 A2
PLT 2: Japanese Patent No. 3446667 B2
PLT 3: WO2003/004714 Al
PLT 4: Japanese Patent No. 3468156 B2
PLT 5: Japanese Patent No. 3397167 B2
PLT 6: Japanese Unexamined Patent Publication No. 2008-240143 Al

Summary of Invention

Technical Problem

[0009] The inventors engaged in studies on steel ingredients not containing Nb, They studied in case of adding Cu and considered the effect of fine dispersion of Cu precipitates and thereby improving the high temperature strength. In addition, they engaged in detailed studies on the all important oxidation resistance in the heat-resistant steel sheet. As a result, examples of the oxidation resistance dropped sharply were found in steel which large amounts of Cu were added, compared with the steel to which Cu was not added, in the region exceeding 900°C. In particular, this trend was seen in the low Cr steel.

[0010] In exhaust system members, there is a possibility of the exhaust gas temperature rising despite of the non-steady state. It is preferable to be able to maintain a stable oxidation resistance even over 900°C. Further, it can be used as a member which high strength is not required.

[0011] From the above description, the present invention has an object to improve the oxidation resistance of the Cu steel and to provide the heat-resistant ferritic stainless steel sheet which has excellent oxidation resistance.

Solution to Problem

[0012] In the present invention, for the purpose of providing a low cost heat-resistant material, the inventors studied in detail a new ferritic stainless steel which keeps addition of the expensive Nb and Mo to a minimum and utilizes the relative inexpensive Cu to enable suitable use for exhaust parts. As a result, they invented the Cu ferritic stainless steel having excellent heat resistance and filed patent applications for them (Japanese Patent Application No. 2010-055944 and Japanese Patent Application No. 2010-072889).

[0013] In the present invention, the inventors further studied in detail the oxidation resistance and discovered the occurrence of the phenomenon of the oxidation resistance rapidly deteriorating in the temperature region of over 900°C in the case of low Cr steel to which Cu is added. Further, they found that this phenomenon is correlated to the formation of a γ-phase directly under the oxide scale. They also found that the formation of a γ-phase causes the oxidation resistance to fall as a general trend. However, they found that even if a γ-phase is formed with a small amount, a sufficient oxidation resistance can be maintained. The inventors studied the addition of various alloy ingredients based on these new findings and discovered that a correlation is seen between the γ-value which is defined by the following formula (1) and the oxidation resistance:

$$\gamma = 23[\%Ni]+9[\%Cu]+7[\%Mn]-11.5[\%Cr]-11.5[\%Si]-52[\%Al]-49[[Ti\%]-4([\%C]+[\%N])]-23[\%V]-12[\%Mo]-47[\%Nb]+189 \quad (1)$$

[0014] This formula is based on the Castro formula (following formula (2)) for evaluation of the stability of the γ-phase (following formula (2)). In formula (2), carbon and nitrogen have direct effects on the stabilization of the γ-phase. On the other hand, in the high purity ferritic stainless steel which is covered by the present invention, at 1000°C or less, carbon and nitrogen are substantially fixed by Ti as carbonitrides, and do not directly contribute to γ-stability. Further, the effect by Ti is limited to the part of Ti not fixed as carbonitrides. Therefore, based on the above such thinking, formula (2) was modified and the above formula (1) was derived.

$$\gamma p = 420[\%C]+470[\%N]+23[\%Ni]+9[\%Cu]+7[\%Mn]-11.5[\%Cr]-11.5[\%Si]-52[\%Al]-49[[Ti\%]-23[\%V]-12[\%Mo]-47[\%Nb]+189 \quad (2)$$

[0015] The above formula (1) is an indicator which shows easily formation of the γ-phase in high purity ferritic stainless steel at 900°C to 1000°C. The larger the γp value, the easier it is for the γ-phase to be formed as a general trend. In accordance with this formula (1), if the γ-value is a certain value (35) or less, even at 930°C, abnormal oxidation and scale spalling no longer occur and the oxidation resistance is remarkably improved. That is, by mutually adjusting the alloy ingredients according to this formula, it is possible to improve the high temperature strength by the addition of Cu, and obtain the heat-resistant ferritic stainless steel having excellent oxidation resistance.

[0016] The present invention was made based on the above-type stainless e discovery and has as its gist the following:

(1) A ferritic stainless steel sheet having excellent heat resistant and oxidation resistance comprising: by mass%, C: 0.015% or less, N: 0.020% or less, P: 0.04% or less, S: 0.01% or less, Si: 0.3 to 1.5%, Mn: 0.3 to 0.7%, Cr: 11.0 to 17.0%, Cu: 0.8 to 1.5%, Ni: 0.05 to 1.0%, V: 0.5% or less, Al: 0.01 to 0.1%, and Ti: 10(C+N) to 0.3%; the amounts of the elements being mutually adjusted such that the γ-value which is defined by the following formula (1), becomes 35 or less, and has a balance of Fe and unavoidable impurities:

$$\gamma = 23[\%Ni]+9[\%Cu]+7[\%Mn]-11.5[\%Cr]-11.5[\%Si]-52[\%Al]-49[[Ti\%]-4([\%C]+[\%N])]-23[\%V]-12[\%Mo]-47[\%Nb]+189 \quad (1).$$

(2) Furthermore, the ferritic stainless steel sheet having excellent heat-resistance and oxidation resistance as set forth in (1), wherein the stainless steel sheet further comprises, by mass%, at least one or more of Nb: 0.001 to 0.3%, Mo: 0.01 to 0.5%, and B: 0.0003 to 0.0050%.

(3) Furthermore, the ferritic stainless steel sheet having excellent heat-resistance and oxidation resistance as set forth in (1) or (2), wherein the stainless steel sheet further comprises, by mass%, at least one or more of Zr: 1.0% or less, Sn: 1.0% or less, and Co: 0.5% or less.

Advantageous Effects of Invention

[0017] According to the present invention, the heat-resistant ferritic stainless steel sheet is obtained even if not adding the expensive Nb and Mo. By applying this in particular to the exhaust system members of automobiles, boilers, etc. a great effect can be obtained in protecting the environments and lowering the costs of parts.

Description of Embodiments

[0018] Here, absence of defined lower limits means inclusion of up to the level of unavoidable impurities. The reasons for limitation of the present invention will be explained as below. "%" means mass%.

[0019] C degrades the shapeability and corrosion resistance and causes a drop in the high temperature strength. The smaller the content, the higher temperature strength is obtained. Therefore the content of C was 0.015% or less. Furthermore, excessive reduction would increase the refining costs. Considering oxidation resistance, the content of C is 0.002 to 0.010% preferably.

[0020] N, like C, degrades the shapeability and corrosion resistance and causes a drop in the high temperature strength. The smaller the content, the higher temperature strength is obtained. Therefore the content of N was 0.020% or less. Furthermore, excessive reduction would increase the refining costs. Considering oxidation resistance, the content of N is 0.002 to 0.015% preferably.

[0021] P is an ingredient which is unavoidably contained in the steel. But if included in over 0.04%, the toughness falls, the upper limit of P was 0.04%.

[0022] S is an ingredient which is unavoidably contained in steel. But in the present invention, when included in over 0.01%, CaS easily forms. So the upper limit was 0.01%. Further, the content of S which is less than 0.0005% would cause an extremely large increase in the steelmaking costs. So the lower limit is 0.0005% preferably.

[0023] Si is an element which improves the oxidation resistance and is a ferrite stabilizing element. Si is essential in the present invention and is positively added. Its effect is exhibited at 0.3% or more. Further, if over 1.5%, the workability remarkably falls and scale spalling is promoted. The upper limit was 1.5%. If considering the balance of the workability and the oxidation resistance, the content of Si which is 0.4% to 1.0% is more preferable.

[0024] Mn is an element which improves the oxidation resistance and in particular is an element which improves the scale spalling resistance, and is an essential element in the present invention. However, it has the effect of increasing the increase in oxidation. If excessively added, abnormal oxidation easily occurs. Further, it is an austenite-forming element, in the present invention, the suitable range was 0.3 to 0.7%. If considering the workability, the content of Mn which is 0.3 to 0.6% is more preferable.

[0025] Cr, in the present invention, is an essential element for securing oxidation resistance and corrosion resistance. If Cr is less than 11.0%, the effect does not appear. The lower limit was 11.0%. Further, Cr is a ferrite stabilizing element. If over 17.0%, due to the amount of Cr, the α-phase stabilizes, and there is no longer a need to mutually adjust the elements. Therefore, the upper limit of the amount of Cr of the present invention was 17.0%. That is, the present invention, the lower the Cr is in the steel, the better effect exhibits. The preferable range is 12.0% to 15.0%.

[0026] Cu is an element which is effective for improving the high temperature strength, in particular the high temperature strength in the medium temperature range of 600 to 800°C or so. The precipitation strengthening due to formation of Cu precipitates in this temperature region is the main cause. Furthermore, even if over 900°C, this has a certain extent of strength improving effect. This effect appears at 0.8% or more, so the lower limit was 0.8%. Further, if adding over 1.5%, the oxidation resistance and the workability deteriorate, so the upper limit was 1.5%. If considering the balance of the high temperature strength, oxidation resistance, and workability, the content of Cu which is 1.0 to 1.4% is preferable.

[0027] Ni is an element which improves the corrosion resistance and the high temperature salt damage resistance. Its effect is exhibited with addition of 0.05% or more. However, this is an austenite stabilizing element, so excessive addition would cause the oxidation resistance to drop. Therefore, the upper limit is 1.0%. If considering the workability, addition of a trace amount is preferable, the content of Ni which is 0.05 to 0.50% is more suitable.

[0028] V is added since it is a ferrite stabilizing element. However, if over 0.5%, the hot rolled plate falls in toughness, the upper limit is 0.5%. If considering the steelmaking costs and workability, the content of V which is 0.03% to 0.5% is preferable.

[0029] Al is an element which is added as a deoxidizing element and is also added in accordance with need for improving the oxidation resistance. Further, it is a ferrite stabilizing element and improves the oxidation resistance. Excessive addition causes hardening and a remarkable drop in the uniform elongation and also causes the toughness to remarkably fall, so the upper limit was 0.1%. Furthermore, if considering the formation of surface defects, weldability, and manufacturability, the content of Al which is 0.01 to 0.05% is preferable.

[0030] Ti is an element which bonds with C and N to improve the corrosion resistance, intergranular corrosion resistance, room temperature ductility, and deep drawability. In particular, the exhaust system members etc. for which the steel sheet of the present invention is used, are usually welded structures. So intergranular corrosion resistance is essential. The amount of addition of Ti is important. These effects appear at 10(C+N)% or more. The lower limit was 10 (C+N)%. Further, on the other hand, if adding over 0.3%, the oxidation resistance falls. The upper limit was 0.3%. If considering the workability and the manufacturability, the content of Ti which is 10(C+N) to 0.25% is preferable.

[0031] To improve the oxidation resistance in the ranges of these alloy elements, it is necessary to mutually adjust the elements so that the γ-value given by the following formula (1) becomes 35 or less. If over 35, a γ-phase is easily formed under the scale at a high temperature region of over 900°C and abnormal oxidation easily occurs, so this is not preferable., Note that the effect of unavoidable impurities is considered to be zero. The grounds for deriving the formula (1) are as follows:

$$\gamma = 23[\%Ni]+9[\%Cu]+7[\%Mn]-11.5[\%Cr]-11.5[\%Si]-52[\%Al]-49[[Ti\%]-4([\%C]+[\%N])]-23[\%V]-12[\%Mo]-47[\%Nb]+189 \quad (1)$$

[0032] In the present invention, the following elements may also be added in accordance with the desired properties.

[0033] Nb is expensive, but is an element which improves the high temperature strength and is a ferrite stabilizing element. When Nb adds even in a trace amount, Nb can improve the heat resistance and oxidation resistance. The effect appears at 0.001% or more. When adding over 0.3%, the effect of improving the high temperature strength becomes smaller. The upper limit was 0.3%.

[0034] Mo is also expensive, but is an element which improves the high temperature strength and is a ferrite stabilizing element. When Mo adds even in a trace amount, Mo can improve the heat resistance and oxidation resistance. The effect appears at 0.01% or more. When adding over 0.5%, the effect of improving the high temperature strength becomes smaller. The upper limit was made 0.5%.

[0035] B is an element which improves the secondary workability at the time of press forming a product. This effect acts from 0.0003%, so the lower limit was 0.0003%. Excessive addition results in hardening and a problem with intergranular corrosion due to the formation of precipitates of Cr and B. Further, the problem of weld cracks also arises. The upper limit was 0.0050%. Furthermore, if considering the manufacturability, the content of B is 0.0003 to 0.0015% preferably.

[0036] Zr is a more powerful carbonitride forming element than Ti. It can fix carbonitrides at a higher temperature, so can be expected to have the effect of lowering the austenite phase stability. However, excessive addition causes a drop in the manufacturability. The upper limit was 1.0%.

[0037] Sn is an element which has a large atomic radius and is effective for solution strengthening at a high temperature. Sn is an element which results in only a little drop in mechanical properties at room temperature, and is added in accordance with need. However, if excessively added, the manufacturability and the weldability fall. The upper limit was

1.0%.

[0038] Co is an element which improves the high temperature strength, but if excessively added, the manufacturability falls. The upper limit was 0.5%.

[0039] Next, the method of production will be explained. The method of production of the steel sheet of the present invention is comprised of the steps of steelmaking, hot rolling, pickling, cold rolling, and annealing and pickling. In the steelmaking, the steel which contains the above essential ingredients and ingredients which are added in accordance with need is suitably produced in a converter and then secondarily refined. The produced molten steel is made into a slab by a known casting method (continuous casting). The slab is heated to a predetermined temperature and is hot rolled by continuous rolling to a predetermined plate thickness. Regarding the cold rolling conditions, the cold rolling of the stainless steel sheet is usually performed by reverse rolling by a Sendzimir rolling mill or one-directional rolling by a tandem rolling mill. In the present invention, any rolling method may be employed, but tandem rolling is superior in productivity compared with Sendzimir rolling and also raises the r-value indicator of workability. It is preferable to perform the cold rolling by a tandem rolling mill which a roll diameter is a 400 mm or more.

[0040] From the viewpoint of the productivity, the annealing of the hot rolled plate which is usually performed in the production of ferritic stainless steel sheet is preferably omitted, but the hot rolled plate may also be annealed.

[0041] The other steps of the method of production are not particularly defined. The hot rolling conditions, hot rolled plate thickness, cold rolled sheet annealing temperature, atmosphere, etc. may be suitably selected. Further, after the cold rolling and annealing, temper rolling may be performed or a tension leveler may be applied. Furthermore, the final sheet thickness may be suitably selected in accordance with the demanded thickness of the member.

Examples

[0042] The steel of each of the compositions of ingredients which are shown in Table 1 was produced and cast into a slab. The slab was hot rolled to obtain a 5 mm thick hot rolled coil. After that, the hot rolled coil was pickled and was cold rolled down to a 2 mm thickness, then was annealed and pickled to obtain a product sheet. The annealing temperature of the cold rolled sheet was made 850 to 1000°C so as to make the grain size number about 6 to 8. The annealing time was 120 seconds. In the table, Nos. 1 to 15 are invention steels, while Nos. 16 to 39 are comparative steels. Further, the No. 1A steel and the No. 2A steel are steels of the same ingredients as respectively the No. 1 steel and No. 2 steel but where after the hot rolling, the hot rolled plates are annealed at 850 to 1000°C for 120 seconds, then are pickled in the same way as other steels and, furthermore, cold rolled, annealed, and pickled to obtain the final sheets. From the obtained final sheets, high temperature tensile test pieces were taken, subjected to tensile tests at 800°C and 900°C, and measured for 0.2% yield stress (based on JISG0567). Here, 25 MPa at 800°C and 15 MPa at 900°C, levels substantially equal to those of 0.4Nb-1Si steel currently most generally used as steel for exhaust manifolds, were used as the passing criteria.

[0043] Furthermore, as a test of the oxidation resistance, continuous oxidation tests were run in the air at 900°C and 930°C for 200 hours and the presence of any abnormal oxidation was evaluated (based on JISZ2281). In addition, for the workability at room temperature, JIS No. 13B test pieces were fabricated and subjected to tensile tests in the rolling direction to measure the elongation at break. Here too, 32%, a level substantially equal to that of existing 0.4Nb-1Si steel, was used as the passing criteria.

[0044] Furthermore, to clarify the intergranular corrosion resistance of the weld zone, toe welding was performed using the TIG welding method, then a Strauss test was performed and the presence of intergranular corrosion was studied.

[0045] The test results are shown in Table 1.

Table 1

(mass%)

	No.	C	N	Si	Mn	P	S	Cr	Cu	Ni	V	Al	Ti	Nb	Mo	B	Others	C+N	γ	800°C yield stress (MPa)	900°C yield stress (MPa)	900°C oxid. resist.	930°C oxid. resist.	Ord. temp. elong. (%)	Grain bound. corr. resist.	Others
Inv. steel	1	0.005	0.009	1.00	0.30	0.030	0.0015	11.6	0.90	0.02	0.25	0.09	0.25					0.014	34.8	Good	Good	Good	Good	Good	Good	
	1A	Same as No. 1																		Good	Good	Good	Good	Good	Good	Hot rolled plate annealed
	2	0.003	0.010	0.50	0.50	0.020	0.0010	13.5	1.20	0.10	0.10	0.04	0.20					0.013	33.0	Good	Good	Good	Good	Good	Good	
	2A	Same as No. 2																		Good	Good	Good	Good	Good	Good	Hot rolled plate annealed
	3	0.008	0.018	0.40	0.60	0.015	0.0008	15.0	1.40	0.50	0.02	0.01	0.28					0.026	30.6	Good	Good	Good	Good	Good	Good	
	4	0.006	0.011	0.35	0.70	0.025	0.0012	16.5	1.50	0.70	0.05	0.02	0.28					0.017	17.1	Good	Good	Good	Good	Good	Good	
	5	0.007	0.010	0.35	0.50	0.021	0.0007	14.0	1.20	0.10	0.10	0.04	0.20	0.005				0.017	29.5	Good	Good	Good	Good	Good	Good	
	6	0.009	0.009	0.40	0.40	0.030	0.0010	13.0	1.10	0.05	0.15	0.07	0.20	0.05				0.018	33.0	Good	Good	Good	Good	Good	Good	
	7	0.006	0.012	0.80	0.30	0.025	0.0008	13.0	1.20	0.10	0.10	0.04	0.20	0.15				0.018	27.8	Good	Good	Good	Good	Good	Good	
	8	0.009	0.011	1.20	0.30	0.035	0.0012	14.0	1.20	0.10	0.10	0.04	0.22		0.02			0.02	17.9	Good	Good	Good	Good	Good	Good	
	9	0.008	0.010	0.80	0.45	0.035	0.0012	12.0	1.10	0.05	0.15	0.04	0.23	0.2	0.3			0.018	29.7	Good	Good	Good	Good	Good	Good	
	10	0.003	0.010	0.50	0.50	0.020	0.0010	13.5	1.20	0.10	0.10	0.04	0.20			0.0005		0.013	33.0	Good	Good	Good	Good	Good	Good	
	11	0.004	0.011	0.70	0.35	0.020	0.0010	13.0	1.15	0.10	0.10	0.04	0.23	0.05	0.2	0.001		0.015	29.1	Good	Good	Good	Good	Good	Good	
	12	0.003	0.010	0.60	0.50	0.012	0.0010	13.5	1.10	0.10	0.10	0.04	0.20				Zr: 0.1	0.013	30.9	Good	Good	Good	Good	Good	Good	
	13	0.003	0.010	0.50	0.50	0.020	0.0010	13.5	1.10	0.10	0.10	0.04	0.20				Sn: 0.05	0.013	32.1	Good	Good	Good	Good	Good	Good	
	14	0.003	0.010	0.60	0.40	0.020	0.0010	13.2	1.10	0.10	0.10	0.04	0.20				Co: 0.05	0.013	33.7	Good	Good	Good	Good	Good	Good	
	15	0.003	0.010	0.50	0.50	0.020	0.0010	13.5	1.20	0.10	0.10	0.04	0.20	0.1	0.3	0.0015	Co: 0.1	0.013	24.7	Good	Good	Good	Good	Good	Good	
Comp. steel	16	0.003	0.010	0.40	0.70	0.020	0.0026	11.6	1.00	0.10	0.10	0.04	0.20					0.013	55.6	Good	Good	Good	Poor	Good	Good	
	17	0.005	0.012	0.30	0.80	0.015	0.0015	13.5	1.40	0.10	0.10	0.02	0.20					0.017	41.0	Good	Good	Good	Poor	Good	Good	
	18	0.02	0.010	0.39	0.41	0.020	0.0010	13.2	1.00	0.10	0.08	0.03	0.30					0.03	34.7	Good	Poor	Good	Poor	Poor	Good	
	19	0.005	0.025	0.77	0.50	0.025	0.0008	13.7	1.36	0.05	0.08	0.07	0.30					0.03	25.2	Good	Poor	Good	Poor	Poor	Good	
	20	0.006	0.015	0.08	0.40	0.020	0.0010	13.8	1.10	0.10	0.10	0.03	0.25					0.021	32.4	Good	Good	Poor	Poor	Good	Good	
	21	0.004	0.012	1.80	0.35	0.026	0.0012	12.5	1.25	0.05	0.15	0.04	0.20					0.016	27.2	Good	Good	Good	Good	Poor	Good	
	22	0.004	0.012	0.40	0.10	0.020	0.0024	13.5	1.25	0.05	0.12	0.04	0.22					0.016	29.8	Good	Good	Good	Poor	Good	Good	
	23	0.004	0.012	0.60	1.20	0.020	0.0018	13.5	1.00	0.05	0.15	0.04	0.22					0.016	32.2	Good	Good	Good	Poor	Poor	Good	
	24	0.004	0.011	0.60	0.30	0.050	0.0010	13.3	1.25	0.05	0.18	0.06	0.20					0.015	29.5	Good	Good	Good	Good	Good	Good	Hot rolled plate cracked
	25	0.004	0.012	1.10	0.35	0.020	0.0200	13.0	1.30	0.05	0.18	0.09	0.21					0.016	26.2	Good	Good	Good	Good	Good	Good	CaS formed causing drop in corrosion resistance
	26	0.005	0.012	0.60	0.35	0.027	0.0010	10.5	1.25	0.05	0.11	0.04	0.20					0.017	65.1	Poor	Poor	Poor	Poor	Good	Good	
	27	0.004	0.012	0.60	0.30	0.020	0.0010	12.5	0.60	0.05	0.30	0.06	0.20					0.016	30.3	Poor	Poor	Good	Good	Good	Good	
	28	0.006	0.013	0.70	0.36	0.020	0.0023	14.0	1.70	0.05	0.17	0.04	0.20					0.019	26.9	Good	Good	Good	Good	Poor	Good	
	29	0.004	0.012	0.60	0.33	0.018	0.0010	16.0	1.25	1.50	0.30	0.06	0.20					0.016	29.5	Good	Good	Good	Good	Poor	Good	
	30	0.003	0.012	0.60	0.38	0.020	0.0028	12.5	1.40	0.05	0.70	0.04	0.20					0.015	29.7	Good	Good	Good	Good	Poor	Good	
	31	0.004	0.016	0.50	0.40	0.020	0.0010	12.5	1.25	0.05	0.15	0.20	0.24					0.02	33.0	Good	Good	Good	Good	Poor	Good	
	32	0.003	0.012	0.60	0.46	0.019	0.0010	13.8	1.20	0.05	0.10	0.07	0.08					0.015	31.6	Good	Good	Good	Good	Good	Poor	
	33	0.004	0.012	0.70	0.60	0.029	0.0026	13.0	1.25	0.05	0.15	0.04	0.50					0.016	21.2	Good	Good	Good	Good	Poor	Good	
	34	0.004	0.010	0.60	0.51	0.020	0.0010	12.0	1.15	0.05	0.06	0.04	0.20	0.5				0.014	25.2	Good	Good	Good	Good	Poor	Good	
	35	0.005	0.012	0.40	0.35	0.017	0.0012	13.5	1.25	0.05	0.15	0.07	0.18		1.0			0.017	19.4	Good	Good	Good	Good	Poor	Good	
	36	0.004	0.012	0.60	0.41	0.020	0.0021	13.2	1.30	0.05	0.50	0.04	0.20			0.01		0.016	25.8	Good	Good	Good	Good	Poor	Poor	
	37	0.004	0.013	0.50	0.33	0.026	0.0011	14.0	1.28	0.05	0.15	0.04	0.19				Zr: 1.2	0.017	25.7	Good	Good	Good	Good	Poor	Good	Hot rolled plate cracked
	38	0.006	0.012	0.50	0.45	0.021	0.0009	13.5	1.20	0.05	0.21	0.04	0.20				Sn: 1.2	0.018	29.9	Good	Good	Good	Good	Poor	Good	Hot rolled plate cracked
	39	0.004	0.011	0.50	0.36	0.024	0.0013	13.7	1.25	0.05	0.15	0.04	0.17				Co: 0.7	0.015	29.7	Good	Good	Good	Good	Poor	Good	Hot rolled plate cracked

[0046] As clear from Table 1, it is found that steels having compositions of ingredients defined by the present invention have no problem at all in high temperature strength, oxidation resistance, room temperature elongation, and intergranular corrosion resistance and exhibit excellent properties.

[0047] As opposed to these, in the comparative steels of Nos. 16 and 17, the ingredient elements are in the ranges of the present invention, but the γ-values are over 35, so abnormal oxidation occurs at 930°C and the oxidation resistances are inferior. The Nos. 18 and 19 steels respectively have C and N outside the upper limit and are inferior in high temperature strength, oxidation resistance, and workability. The No. 20 steel has insufficient Si and is inferior in oxidation resistance. The No. 21 steel has Si added in excess and is inferior in workability. The No. 22 has little addition of Mn and is inferior in oxidation resistance. The No. 23 steel has Mn added in excess and is inferior in oxidation resistance and workability. The No. 24 has P added in excess, is inferior in toughness, and exhibited fine cracks in the hot rolled plate at the stage of production of steel sheets. The No. 25 steel has S added in excess and was confirmed to have the formation of CaS - the cause of deterioration of the corrosion resistance. The No. 26 steel has a small amount of Cr, and is low in high temperature strength and is inferior in oxidation resistance. The No. 27 steel has a small amount of addition of Cu and is inferior in high temperature strength. The No. 28 steel has Cu added in excess and is inferior in workability. The No. 29 steel has Ni added in excess and is inferior in workability. The No. 30 steel has V added in excess and is inferior in workability. The No. 31 steel has Al added in excess and is inferior in workability. The No. 32 steel has a small amount of addition of Ti and is inferior in intergranular corrosion resistance. The No. 33 steel has Ti added in excess and is inferior in workability. The No. 34 steel has Nb added in excess and is inferior in workability. The No. 35 steel has Mo added in excess and is inferior in workability. The No. 36 steel has B added in excess, is inferior in workability, and is inferior in intergranular corrosion resistance. The Nos. 37, 38, and 39 steels respectively have Zr, Sn, and Co added in excess. But it is found that these steels are inferior in workability, exhibit fine cracks in the hot rolled plates when producing steel sheet, and are inferior in manufacturability.

Industrial Applicability

[0048] As clear from the above explanation, according to the present invention, it is possible to provide the heat-resistant stainless steel sheet having excellent oxidation resistance even without adding large amounts of expensive alloy elements such as Nb or Mo. In particular, the part costs are reduced and the weight can be lightened by application to exhaust members. The social contribution, including protection of the environments, is extremely great.

Claims

1. ferritic stainless steel sheet having excellent heat resistant and oxidation resistance comprising: by mass%,
C: 0.015% or less,
N: 0.020% or less,
P: 0.04% or less,
S: 0.01% or less,
Si: 0.3 to 1.5%,
Mn: 0.3 to 0.7%,
Cr: 11.0 to 17.0%,
Cu: 0.8 to 1.5%,
Ni: 0.05 to 1.0%,
V: 0.5% or less,
Al: 0.01 to 0.1%, and
Ti: 10(C+N) to 0.3%;
the amounts of the elements being mutually adjusted such that the γ-value which is defined by the following formula (1), becomes 35 or less, and
has a balance of Fe and unavoidable impurities:

$$\gamma = 23[\%Ni]+9[\%Cu]+7[\%Mn]-11.5[\%Cr]-11.5[\%Si]-52[\%Al]-49[[Ti\%]-4([\%C]+[\%N])]-23[\%V]-12[\%Mo]-47[\%Nb]+189 \quad (1).$$

2. The ferritic stainless steel sheet having excellent heat-resistance and oxidation resistance as set forth in claim 1,

wherein said stainless steel sheet further comprises, by mass%, at least one or more of
Nb: 0.001 to 0.3%,
Mo: 0.01 to 0.5%, and
B: 0.0003 to 0.0050%.

3. The ferritic stainless steel sheet having excellent heat-resistance and oxidation resistance as set forth in claim 1 or 2, wherein said stainless steel sheet further comprises, by mass%, at least one or more of
Zr: 1.0% or less,
Sn: 1.0% or less, and
Co: 0.5% or less.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/071765

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/50*(2006.01)i, *C22C38/54*(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00, C22C38/50, C22C38/54

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	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

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 2009-235555 A (Nippon Steel & Sumikin Stainless Steel Corp.), 15 October 2009 (15.10.2009), claims; paragraphs [0010], [0017] to [0027]; table 1 (Family: none)	1-3
A	JP 2008-240143 A (Nippon Steel & Sumikin Stainless Steel Corp.), 09 October 2008 (09.10.2008), claims; tables 1, 2 & WO 2008/105134 A1 & US 2009/0092513 A1 & EP 2058413 A1 & CN 101454471 A	1-3

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 December, 2011 (13.12.11)	20 December, 2011 (20.12.11)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2003/004714 A1 (Nisshin Steel Co., Ltd.), 16 January 2003 (16.01.2003), claims; tables 1, 2 & US 2004/0170518 A1 & EP 1413640 A1 & CN 1524130 A	1-3
A	JP 2008-144199 A (Nisshin Steel Co., Ltd.), 26 June 2008 (26.06.2008), claims; table 1 & US 2008/0138233 A1 & EP 1930461 A1 & CN 101250672 A	1-3
A	JP 2006-117985 A (Nisshin Steel Co., Ltd.), 11 May 2006 (11.05.2006), claims; table 1 (Family: none)	1-3

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2010055944 A **[0012]**
- JP 2010072889 A **[0012]**