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- **Imakawa, Kazunari**
Shunan-shi
Yamaguchi 746-0023 (JP)
- **Nakamura, Sadayuki**
Shunan-shi
Yamaguchi 746-0023 (JP)
- **Oku, Manabu**
Shunan-shi
Yamaguchi 746-0023 (JP)

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

(74) Representative: **Carstens, Dirk Wilhelm**
Wagner & Geyer
Gewürzmühlstrasse 5
80538 München (DE)

(72) Inventors:
• **Tomita, Takeo**
Shunan-shi
Yamaguchi 746-0023 (JP)

(54) **Ferritic stainless steel material for automobile exhaust gas passage components**

(57) To provide a ferritic stainless steel material for automobile exhaust gas passage components usable in a high-temperature range over 900°C and even over 950°C. The ferritic stainless steel material has excellent heat resistance and low-temperature toughness and has a composition comprising, in terms of % by mass, at most 0.03 % of C, at most 1 % of Si, from 0.6 to 2 % of Mn, at most 3 % of Ni, from 10 to 25 % of Cr, from 0.3 to 0.7 % of Nb, from more than 1 to 2 % of Cu, from 1 to 2.5 % of

Mo, from 1 to 2.5 % of W, at most 0.15 % of Al, from 0.03 to 0.2 % of V, and at most 0.03 % of N, and optionally containing any of B, Co, W, Ti, Zr, REM and Ca with a balance of Fe and inevitable impurities, and the composition satisfies restrictive formulae $1.2Nb + 5Mo + 6Cu \geq 11.5$ and $15Nb + 2Mo + 0.5Cu \geq 10.5$. The steel material has a texture where the total amount of Nb and Mo existing as a precipitation phase is at most 0.2 % by mass.

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Description

BACKGROUND OF THE INVENTION

5 [0001] The present invention relates to a ferritic stainless steel material for use as automobile exhaust gas passage components, in particular to a ferritic stainless steel material for use as automobile exhaust gas passage components, which has excellent heat resistance and low-temperature toughness favorable for exhaust gas upstream passage components where the material temperature may be over 900°C or further over 950°C, for example, exhaust manifolds, catalyst converters, front pipes and the like.

10 [0002] Heretofore, two typical ferritic steel species are used properly for automobile exhaust gas passage components, depending on the service temperature range of the components. One is a steel species such as typically SUS429 steel mainly applied to the components of which the maximum ultimate temperature of the material may be on a level of 750°C; and the other is a steel species such as typically SUS444 steel mainly applied to the components of which the maximum ultimate temperature of the material may be on a level of 850°C.

15 [0003] For satisfying the recent requirements for emission control and mileage regulation, exhaust gas temperatures tend to be higher, and on the presumption that the material temperature in exhaust gas passage upstream components may actually rise up to about 1000°C, the requirements for heat-resistant materials may be expected to increase for those components. Conventional SUS444 steel (18Cr-2Mo-0.5Nb steel) would be difficult to apply to the components that are exposed to such high temperatures. In order that the materials are durable to use at such high temperatures, those merely having high tensile strength at high temperatures are not enough and it is a matter of importance that the 0.2 % yield strength of the materials at high temperature, which is an index of the stress under which the materials begin to undergo plastic deformation, is high.

20 [0004] With the increase in various devices to be fitted in an engine room, the limitation to the housing space for exhaust gas components is increasing more than before. Accordingly, exhaust gas passage upstream components are required to have excellent workability into various shapes. In particular, not only as plates but also as pipes, the components are required to have excellent workability durable to severe working into complicated shapes. Further, exhaust gas passage components are also required to have good low-temperature toughness.

25 [0005] Heretofore, various ferritic stainless steels having improved heat resistance such as those mentioned below have been developed and are being put into practical use.

30 [0006] Patent Reference 1 shows a ferritic stainless steel of which the composition and the texture are so controlled that it may surely have a sufficient amount of solid solution Nb so as to be durable to use in a temperature range over 900°C and may have a tensile strength of 20 MPa at 950°C. However, this has no description relating to 0.2 % yield strength, and the durability of the steel in a case where the material temperature has actually risen up to about 1000°C is not confirmed. In this, any special consideration is not taken for thermal fatigue resistance and low-temperature toughness.

35 [0007] Patent Reference 2 shows a ferritic stainless steel having excellent high-temperature strength at 900°C and having excellent low-temperature toughness. However, this has no description relating to 0.2 % yield strength, and in this, the measures for sufficiently securing the durability in a case where the material temperature has actually risen up to 1000°C or so could not be said to be always satisfactory.

40 [0008] Patent Reference 3 describes a ferritic stainless steel having good high-temperature strength at 950°C and good workability. However, this shows nothing relating to 0.2 % yield strength, and in this, it is not certain as to whether or not the material could be actually durable to exposure to about 1000°C or so. No special consideration is taken for low-temperature toughness.

45 [0009] Patent Reference 4 shows an Fe-Cr alloy of which the thermal expansion coefficient is lowered. However, there is taken no intension of improving the high-temperature strength of the material in a temperature range of about 1000°C or so.

50 [0010] Patent Reference 5 describes a ferritic stainless steel having excellent thermal fatigue resistance and good low-temperature toughness. In this, however, the material was evaluated for the high-temperature strength in terms of the 0.2 % yield strength thereof at 600°C, and its durability is not clear in a case where the material temperature has actually risen up to about 1000°C.

55 [0011] Patent Reference 6 shows a ferritic stainless steel for exhaust gas system components to be used at a temperature of not lower than 700°C. Regarding high-temperature strength, however, this shows only the tensile strength data of the material at 600°C and 850°C, and it is not clear as to whether or not the material could be resistant to exposure to temperatures of 1000°C or so. In addition, this has no description relating to low-temperature toughness.

Patent Reference 1: JP 2959934

Patent Reference 2: JP 2696584

Patent Reference 3: JP 3468156

Patent Reference 4: JP 2005-206944A

Patent Reference 5: JP 2006-117985A

Patent Reference 6: JP 2000-303149A

5 **[0012]** A method capable of stably realizing a material that exhibits excellent durability when used at a temperature over 900°C and satisfies both good low-temperature toughness and good workability is not as yet established (see the above Patent References).

SUMMARY OF THE INVENTION

10 **[0013]** An object of the present invention is to provide a ferritic stainless steel material for automobile exhaust gas passage components, which simultaneously satisfies 0.2 % yield strength at high temperature of 1000°C, thermal fatigue resistance, low-temperature toughness and workability all on a high level and which, even when used under the condition where the material temperature actually reaches a high-temperature range of higher than 900°C and even higher than
15 950°C, still exhibits excellent durability.

[0014] To attain the object as above, the invention provides a ferritic stainless steel material having excellent heat resistance and low-temperature toughness for automobile exhaust gas passage components, which has a composition essentially containing, in terms of % by mass, at most 0.03 % of C, at most 1 % of Si, from 0.6 to 2 % of Mn, at most 3 % of Ni, from 10 to 25 % of Cr, from 0.3 to 0.7 % of Nb, from more than 1 to 2 % of Cu, from 1 to 2.5 % of Mo, from 1 to 2.5 % of W, at most 0.15 % of Al, from 0.03 to 0.2 % of V, and at most 0.03 % of N, and optionally containing at least one of Ti and Zr in an amount of less than 1 % in total, or further containing at least one of B in an amount of at most 0.02 % and Co in an amount of at most 2 %, or further containing at least one of REM (rare earth element) and Ca in an amount of at most 0.1 % in total, with a balance of Fe and inevitable impurities, the composition satisfying the following formulae (1) and (2), and which has a texture where the total amount of Nb and Mo existing as a precipitation phase is
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25 at most 0.2 % by mass:

$$1.2Nb + 5Mo + 6Cu \geq 11.5 \quad (1),$$

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$$15Nb + 2Mo + 0.5Cu \geq 10.5 \quad (2).$$

35 **[0015]** In the above formulae (1) and (2), the element code is substituted with the content of the corresponding element expressed in terms of % by mass.

[0016] "Ferritic stainless steel material for automobile exhaust gas passage components" means a steel material processed for final annealing under heat at a temperature higher than 1000°C (for example, from 1050 to 1100°C) (this may be simply referred to as "final annealing") in a process of producing automobile exhaust gas passage components.
40 For example, in case where a steel sheet is welded and formed into a pipe, then shaped and worked, and thereafter processed for final annealing, the pipe after the final annealing corresponds to the ferritic stainless steel material for automobile exhaust gas passage components as referred to herein. In case where a steel sheet is processed for final annealing, the steel sheet after the final annealing, and the pipe, cylindrical casing or the like obtained by further working the final annealed sheet correspond to the ferritic stainless steel material for automobile exhaust gas passage components.
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[0017] Of the above-mentioned steel materials, those for use for exhaust gas components that are to be within a material temperature range over 900°C or further over 950°C are especially preferred subjects in the invention.

[0018] According to the invention, there is provided a ferritic stainless steel material for automobile exhaust gas passage components, which satisfies all the requirements of high-temperature strength durable to exposure to high
50 temperature of 1000°C, good thermal fatigue resistance, good workability and good low-temperature toughness. The material meets the recent tendency in the art toward elevated exhaust gas temperatures and brings about an broadened latitude in planning exhaust gas passage upstream components.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

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[0019] In the invention, it is important to increase the high-temperature strength (0.2 % yield strength) of the steel material at a level of 1000°C with keeping high the high-temperature strength (0.2 % yield strength) thereof at a level of 600°C. It is extremely effective to make the steel material have high strength both in the two temperature ranges for

keeping high the thermal fatigue resistance thereof. As a result of various investigations, it is desirable that the 0.2 % yield strength at 600°C and the 0.2 % yield strength at 1000°C of the steel material are both at least 1.5 times higher than the yield strength at the same temperatures of SUS444 steel. Concretely, it is desirable that the 0.2 % yield strength at 600°C of the steel material is at least 200 MPa and the 0.2 % yield strength at 1000°C thereof is at least 15 MPa. It has been found that the material having such high-temperature strength characteristics has good high-temperature fatigue resistance satisfactory for practical use when it receives repeated temperature change between ordinary temperature and 1000°C or so as automobile exhaust gas passage components.

[0020] In the invention, Cu is used for improving the high-temperature strength of the steel material in a temperature range including 600°C (range of from about 500 to 800°C). Specifically, when Cu is added to the steel material, an ϵ -Cu phase is precipitated at a temperature of around 600°C, and this finely disperses in the matrix of the material to thereby express a precipitation-reinforcing phenomenon. In order that the steel material can keep the high-temperature strength (0.2 % yield strength) in the temperature range higher by at least about 1.5 times than that of SUS444 steel, it is necessary to take advantage of Nb and Mo solid solution reinforcement in addition to the precipitation of the ϵ -Cu phase. As a result of various investigations, controlling the constitutive ingredients in order that the content of Nb, Mo and Cu could satisfy the formula (1) makes it possible to increase the high-temperature range of at most 800°C strength of the steel material by at least about 1.5 times that of SUS444 steel.

$$1.2\text{Nb} + 5\text{Mo} + 6\text{Cu} \geq 11.5 \quad (1).$$

[0021] In a temperature range over 800°C, solid solution of the ϵ -Cu phase is further promoted, and the effect of Cu to enhance the high-temperature strength of the steel material is weakened. In order to increase the high-temperature strength (0.2 % yield strength) at 1000°C of the steel material by at least about 1.5 times that of SUS444 steel, it is important to fully take advantage of the solid solution reinforcement with Nb and Mo. As the solid solution of Cu is also effective for enhancing the high-temperature strength, it is also utilized. As a result of various investigations, it has been found that the constitutive ingredients must be controlled so as to satisfy the formula (2).

$$15\text{Nb} + 2\text{Mo} + 0.5\text{Cu} \geq 10.5 \quad (2).$$

[0022] The coefficient of Nb in formula (2) corresponds to the increase in the 0.2 % yield strength (MPa) at 1000°C per 0.1 % by mass of Nb; and the coefficient of Mo and Cu each correspond to the increase in the 0.2 % yield strength (MPa) at 1000°C per 1 % by mass of Nb and Cu, respectively.

[0023] However, in order to increase the 0.2 % yield strength of the steel material at high temperature of 1000°C by at least about 1.5 times that of SUS444 steel, the composition that satisfies the above formula (2) is not enough. More detailed investigations have confirmed that, in particular, it is extremely important to make the steel material have a metal texture in which the Nb and Mo precipitates are reduced as much as possible. Concretely, after final annealing, the steel material must have a texture condition in which the total amount of Nb and Mo existing as a precipitation phase therein is at most 0.2 % by mass.

[0024] Not only for keeping the high-temperature strength of the steel material but also for keeping well the workability, the low-temperature toughness and the weldability thereof, it is extremely effective to make the steel material have the above-mentioned texture condition after final annealing. In case where the amount of Nb or Mo added is considerably large, the amount of the solid solution Mo or the solid solution Nb can be sufficiently secured even when the total amount of Nb and Mo existing as a precipitation phase is more than 0.2 % by mass, and the high-temperature strength of the steel material at 1000°C could be increased owing to their solid solution reinforcement. In this case, however, it is difficult to enhance both the low-temperature toughness and the workability of the steel material.

[0025] "Total amount (% by mass) of Nb and Mo existing as a precipitation phase" can be determined as follows: The residue of the precipitation phase as extracted out through constant potential electrolysis in a water-free solvent electrolytic solution (SPEED method) is analyzed for elementary quantification, and the total mass of Nb and Mo in the residue is divided by the total mass of the dissolved matrix and the extracted precipitation phase in electrolysis, and this is expressed as percentage.

[0026] For obtaining the texture condition where the total amount of Nb and Mo existing as a precipitation phase is at most 0.2 % by mass, the cooling rate from 1050°C to 500°C in the cooling step in the final annealing must be controlled to at least 5°C/sec. For example, in case where a pipe produced by welding is applied to automobile exhaust gas passage components, a steel sheet before formed into a pipe, or after formed into a pipe but before used as the component, may be processed at least once for final annealing that comprises soaking under heat at 1050 to 1100°C for from 0 to 10

minutes followed by cooling from 1050°C to 500°C at a cooling rate of at least 5°C/sec. Insofar as the steel material is processed once to thereby have the texture condition as above before used as an automobile exhaust gas passage component, any superfluous precipitation phase of Nb and Mo would not form when the automobile exhaust gas passage component formed of the steel material is used under heat at a temperature of 1000°C or so, and practically, therefore, the high-temperature strength and the low-temperature toughness of the steel material would not worsen.

[0027] The alloying ingredients are described below.

[0028] C and N are generally effective for improving creep strength and other high-temperature strength properties but degrade oxidation resistant property, workability, low-temperature toughness and weldability when contained in excess. In the invention, both C and N are limited to a content of at most 0.03 % by mass.

[0029] Si is effective for improving high-temperature oxidation resistance. However, when added in excess, it increases hardness and thus degrades workability and low-temperature toughness. In the invention, the Si content is limited to at most 1 % by mass.

[0030] Mn improves high-temperature oxidation resistance, especially scale peeling resistance. In order to sufficiently secure high-temperature oxidation resistance on a level of 1000°C, the Mn content must be at least 0.6 % by mass. However, Mn impairs workability and weldability when added in excess. Further, Mn is an austenite-stabilizing element that when added in a large amount facilitates martensite phase formation and thus causes a decline in thermal fatigue resistance and workability. The Mn content is therefore limited to at most 2 % by mass, preferably at most 1.5 % by mass, more preferably less than 1.5 % by mass.

[0031] Ni contributes to improvement of low-temperature toughness, but when added too much, it may lower cold elongation. In the invention, the acceptable Ni content is up to 3 % by mass, but more preferably, the Ni content is at most 0.6 % by mass.

[0032] Cr stabilizes ferrite phase and contributes to improvement of oxidation resistance, an important property of high-temperature materials. In the invention, the Cr content is secured to be at least 15 % by mass for sufficiently exhibiting its effect. However, too much Cr makes the steel material brittle and worsens the workability thereof, and therefore the Cr content is not more than 25 % by mass.

[0033] Nb is effective for increasing high-temperature strength in a temperature range of around 600°C or so by solid solution reinforcement, but the invention takes advantage of the solid solution reinforcing effect of Nb for securing high-temperature strength in a high temperature range of higher than 900°C. For this, the Nb content must be at least 0.3 % by mass, and it must satisfy the above-mentioned formula (2). In addition, as so mentioned in the above, the invention must secure the steel texture condition where the total amount of Nb and Mo existing as a precipitation phase is at most 0.2 % by mass. In this connection, Nb has a strong affinity for C and N, therefore readily forming precipitates that may lower high-temperature strength, low-temperature toughness, workability and other properties. Accordingly, the Nb content is limited to at most 0.7 % by mass.

[0034] Cu is an important element in the invention. Specifically, as so mentioned in the above, the invention takes advantage of the fine dispersion precipitation phenomenon of the ϵ -Cu phase of the steel material to thereby enhance the strength thereof at around 600°C (from about 500 to 850°C) and to improve the thermal fatigue resistance thereof. In a high temperature range over 850°C, Cu further plays a role of assisting the high-temperature strength-enhancing effect of Nb and Mo, based on the solid solution enhancement with Cu. As a result of various studies, the Cu content must be at least more than 1 % by mass for satisfactorily attaining these effects. However, too much Cu worsens workability, low-temperature toughness and weldability, and therefore the uppermost limit of the Cu content is limited to 2 % by mass.

[0035] Mo, like Nb, is effective for increasing high temperature strength by solid solution reinforcement. Especially in the invention, the high temperature strength in a high temperature range over 900°C must be increased, and Mo addition in an amount of at least 1 % by mass is indispensable. As so mentioned in the above, the invention must secure the steel texture condition where the total amount of Nb and Mo existing as a precipitation phase is at most 0.2 % by mass. Excess Mo addition may result in formation of carbide and Laves phase (Fe_2Mo), thereby impairing high temperature strength and low-temperature toughness. Accordingly, the Mo content is limited to at most 2.5 % by mass.

[0036] W is an element effective for increasing high temperature strength in a high temperature range over 900°C, and in the invention, the W content must be at least 1 % by mass. However, excess W addition impairs workability, and therefore, the W content must be at most 2.5 % by mass, more preferably at most 2 % by mass.

[0037] Al is used as a deoxidizer in a steel making, and acts for improving high temperature oxidation resistance. However, too much Al addition has negative influences on surface properties, workability, weldability and low-temperature toughness. Accordingly, Al is added within a range of at most 0.15 % by mass.

[0038] V contributes to improvement of high-temperature strength when added in combination with Nb and Cu. When existing along with Nb, V improves workability, low-temperature toughness, resistance to grain boundary corrosion susceptibility, and toughness of weld heat affected zone. In order to sufficiently attain all these effects, V is added in the invention in an amount of at least 0.03 % by mass. However, excessive addition of V impairs workability and low-temperature toughness. Accordingly, the V content is limited to at most 0.2 % by mass.

[0039] Ti and Zr are elements effective for improving high-temperature strength; and if desired, at least one of these may be added. However, excessive addition impairs toughness. In case where at least one of Ti and Zr is added, the total content thereof must be less than 1 % by mass.

5 [0040] B and Co, like Ni, are elements contributing to low-temperature toughness. If desired, one or two of B and Co may be added. However, excessive addition lowers cold elongation; and therefore, the B content is at most 0.02 % by mass and the Co content is at most 2 % by mass. More effectively, the B content is from 0.0005 to 0.02 % by mass.

10 [0041] REM (rare earth element) and Ca are elements that contribute to high-temperature oxidation resistance. If desired, at least one of these may be added. More effectively, the total content of REM and Ca is at least 0.001 % by mass. However, excessive addition thereof may have some negative influences on producibility, and therefore, the total content of REM and Ca is limited to at most 0.1 % by mass.

15 [0042] The stainless steel material of the invention may be produced by preparing a stainless steel having a controlled composition as above according to an ordinary steel melting method, then working it into a steel sheet having a predetermined thickness according to an ordinary stainless steel sheet producing method, thereafter welding it into a pipe, or shaping and further working it. In this process, in the final annealing step where the steel is heated at 1050 to 1100°C, it is important to cool the steel from 1050°C to 500°C at a controlled cooling rate of at least 5°C/sec as so mentioned in the above. Overstepping the cooling condition, the steel could hardly have a texture condition where the total amount of Nb and Mo existing as a precipitation phase is at most 0.2 % by mass, and it may be difficult to enhance the high-temperature strength (0.2 % yield strength) of the steel material at 1000°C stably on a level of at least about 1.5 times that of SUS444. Under the condition, in addition, the low-temperature toughness of the steel material may also be lowered.

20 EXAMPLES

25 [0043] Ferritic stainless steels shown in Table 1 were produced according to a steel melting method, and then worked into cold-rolled annealed steel sheets having a thickness of 2 mm according to a process of hot rolling, annealing of hot-rolled sheets, cold rolling and final annealing. The final annealing was attained under the condition as simulated for final annealing of steel materials for exhaust gas passage components. The final annealing condition was as follows: After heated at 1050°C with soaking for 1 minute, the steels except some comparative samples (such as No. 21) were cooled from 1000°C to 500°C at a mean cooling rate of at least 5°C/sec. The cooling rate was monitored with a thermocouple attached to the surface of each sample. Samples of the cold-rolled annealed steel sheets thus obtained after the final

30 annealing were tested and analyzed for various properties of exhaust gas passage components.

Table 1

Steel No.	Chemical Ingredients (mass%)													Left Side of Formula (1)	Left Side of Formula (2)	
	C	Si	Mn	Ni	Cr	Mo	Nb	Cu	W	Al	V	N	Others			
Invention Steels	1	0.005	0.19	0.65	0.02	17.8	1.35	0.47	1.68	1.55	0.04	0.04	0.009		17.39	10.59
	2	0.006	0.25	0.60	0.01	18.2	1.65	0.56	1.05	1.25	0.05	0.04	0.010		15.22	12.23
	3	0.007	0.16	0.79	0.02	16.5	1.55	0.56	1.06	1.59	0.01	0.05	0.012		14.78	12.03
	4	0.010	0.14	0.80	0.02	24.7	1.98	0.43	1.54	1.84	0.01	0.04	0.009		19.66	11.18
	5	0.008	0.08	1.12	0.02	18.0	2.06	0.39	1.48	1.51	0.02	0.05	0.008	Ti:0.08	19.65	10.71
	6	0.006	0.09	1.16	0.02	20.4	2.45	0.45	1.45	1.78	0.02	0.12	0.012	Zr:0.09	21.49	12.38
	7	0.007	0.12	1.25	0.01	22.5	1.36	0.65	1.39	1.97	0.03	0.04	0.016		15.92	13.17
	8	0.009	0.06	1.35	0.02	20.9	2.03	0.69	1.88	1.48	0.03	0.06	0.012	REM: 0.04,Ca0.01	22.26	15.35
	9	0.010	0.06	0.77	0.03	15.9	2.05	0.45	1.79	1.66	0.04	0.05	0.008	Ti:0.15,Co: 0.01	21.53	11.75
	10	0.010	0.08	0.60	0.01	18.8	2.16	0.35	1.95	1.74	0.04	0.07	0.007	B:0.0012	22.92	10.55
Comparative Steels	21	0.006	0.06	0.75	0.02	18.5	1.22	0.55	1.40	1.88	0.03	0.07	0.011		15.16	11.39
	22	0.009	0.12	0.51	0.02	16.5	0.21	0.19	1.46	2.04	0.02	0.05	0.012	Ti:0.15	10.04	4.00
	23	0.005	0.24	1.12	0.01	17.2	0.88	0.22	0.68	2.16	0.01	0.04	0.009		8.74	5.40
	24	0.005	0.29	1.18	0.01	18.9	1.55	0.58	2.25	2.55	0.03	0.06	0.008		21.95	12.93
	25	0.009	0.06	0.69	0.01	20.4	1.30	0.69	0.42	0.18	0.04	0.11	0.009		9.85	13.16
	26	0.007	0.12	0.48	0.02	19.2	1.45	0.41	2.08	0.00	0.01	0.06	0.012		20.22	10.09
	27	0.008	0.19	0.75	0.02	2.04	2.55	0.12	1.88	0.88	0.02	0.04	0.016		24.17	7.84
	28	0.008	0.06	0.69	0.03	22.9	1.68	0.79	1.12	1.24	0.02	0.03	0.015		16.07	15.77
	29	0.008	0.08	0.56	0.02	24.8	2.30	0.71	0.78	1.84	0.02	0.05	0.008	B:0.0015	17.03	15.64
	30	0.007	0.15	0.84	0.01	15.9	3.58	0.55	1.69	1.05	0.02	0.05	0.009		28.70	16.26

Underlined: Outside the scope of the invention.

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[0044] The samples (after final annealing) were tested and analyzed for the total amount of Nb and Mo existing as a precipitation phase therein (this is expressed as "amount of precipitated Nb + precipitated Mo"), and the 0.2 % yield strength at 600°C, the 0.2 % yield strength at 1000°C, the low-temperature toughness and the cold workability thereof in the manner mentioned below.

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[Amount of precipitated Nb + precipitated Mo]

[0045] According to a SPEED method as mentioned above, a sample is tested through constant potential electrolysis at a potential at which the matrix of the sample dissolves but the precipitation phase thereof does not dissolve, and the residue of the extracted precipitation phase is analyzed for elementary determination. The total mass of Nb and Mo in the residue is divided by the total mass of the dissolved matrix and the extracted precipitation phase in electrolysis, and this is expressed as percentage of the amount of precipitated Nb + precipitated Mo. In the SPEED method, used is 10 % acetylacetone + 1 % tetramethylammonium chloride + methyl alcohol solution as a water-free solvent.

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[0.2 % yield strength at 600°C, 1000°C]

[0046] A test piece for tensile strength having a thickness of 2 mm (the pulling direction of the sample is the same as the rolling direction thereof) is tested for tensile strength at 600°C and tensile strength at 1000°C according to JIS G0567. Samples of which the 0.2 % yield strength at 600°C is at least 200 MPa, corresponding to about at least 1.5 times that of SUS444 steel, are good; and those of which the strength is lower than it are not good. Samples of which the 0.2 % yield strength at 1000°C is at least 15 MPa, corresponding to about at least 1.5 times that of SUS444 steel, are good; and those of which the strength is lower than it are not good.

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[Low-temperature toughness]

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[0047] A V-notch Charpy impact test piece is cut out of a sample having a thickness of 2 mm (the direction in which the test piece is hit with a hammer is in parallel to the rolling direction of the sample), and tested in a Charpy impact test at a pitch of 25°C within a range of from -75°C to 25°C according to JIS Z2242, thereby determining the ductility-toughness transition temperature of the sample. Samples of which the transition temperature is not higher than -25°C are rated G (good in point of the low-temperature toughness); and those of which the transition temperature is higher than -25°C are rated NG (not good in point of the low-temperature toughness).

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[Cold workability]

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[0048] Three tensile test pieces (JIS 13B) are cut out of a sample having a thickness of 2 mm in such a manner that the pulling direction thereof could be at an angle of 0°, 45° or 90° relative to the rolling direction thereof. According to JIS 2241, these are tested for tensile strength at break (test times n = 3). The broken pieces are butt-jointed, and the elongation at break (%) thereof is determined. According to the following formula (3), the mean elongation EL_A of the sample is computed, and this EL_A indicates the cold elongation of the tested sample.

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$$EL_A = (EL_L + EL_D + EL_T) \quad (3)$$

[0049] In this, EL_L means the elongation at break of the sample at a pulling direction of 0° (mean value of n = 3); EL_D means the elongation at break at a pulling direction of 45° (mean value of n = 3); and EL_T means the elongation at break at a pulling direction of 90° (mean value of n = 3). Samples having EL_A of at least 30 % are rated G (good in point of the cold workability); and those having EL_A of smaller than 30 % are rated NG (not good in point of the cold workability).

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[0050] The results are shown in Table 2. In Table 2, "cooling rate in final annealing" means the mean cooling rate from 1050°C to 500°C.

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Table 2

Steel No.	Cooling Rate in Final Annealing (°C/sec)	Amount of Precipitated Nb + Precipitated Mo (mass%)	0.2 % Yield Strength at 600°C (MPa)	0.2 % Yield Strength at 1000°C (MPa)	Low-Temperature Toughness	Cold Work ability	
Invention Steels	1	15.2	0.02	230	15	G	G
	2	10.4	0.20	221	17	G	G
	3	8.2	0.16	220	17	G	G
	4	11.2	0.18	254	16	G	G
	5	8.6	0.05	231	19	G	G
	6	10.1	0.06	249	20	G	G
	7	10.6	0.04	230	22	G	G
	8	5.6	0.05	269	23	G	G
	9	11.2	0.06	248	20	G	G
	10	11.5	0.04	264	21	G	G
Comparative Steels	21	4.8	0.25	204	13	NG	NG
	22	5.8	0.02	164	8	G	G
	23	10.2	0.06	176	10	G	G
	24	10.5	0.16	226	16	G	NG
	25	10.6	0.04	140	17	G	G
	26	8.2	0.04	220	11	G	G
	27	8.5	0.67	230	9	NG	G
	NG	10.7	0.58	205	19	G	NG
	29	11.5	1.20	150	17	NG	G
	30	11.6	1.58	220	20	NG	NG

Underlined: Outside the scope of the invention, or unsatisfactory in point of the properties.

[0051] The steel materials of the invention examples that satisfy the requirements for the composition and the amount of precipitated Nb + precipitated Mo all had 0.2 % yield strength at 600°C and 0.2 % yield strength at 1000°C both higher by at least about 1.5 times than those of SUS444 steel, as known from Table 2; and accordingly, they have excellent high-temperature strength in a high temperature range over 850°C, and have sufficiently good thermal fatigue resistance. In addition, their low-temperature toughness and cold workability are also good.

[0052] In contrast, No. 21 is not good, though its composition falls within the scope of the invention. This is because the cooling rate from 1000°C to 500°C in the final annealing was lower than 5°C/sec, and therefore a large amount of Nb and Mo precipitates formed during the cooling step thereby giving a texture condition in which the amount of precipitated Nb + precipitated Mo was too much. This comparative sample was poor in the high-temperature strength at 1000°C, the low-temperature toughness and the cold workability. In No. 22, the content of Mo and Nb was small; and in No. 23, the Cu content was additionally small. Since these do not satisfy the formulas (1) and (2), their high-temperature strength at 600°C and 1000°C was poor. In No. 24, the W content was too much, and therefore, this was poor in the cold workability. In No. 25, the Cu content was low and this did not satisfy the formula (1), and the high-temperature strength at 600°C of this comparative sample was poor. In No. 26, the Cu content was too much, and this did not satisfy the formula (2). In addition, W was not added to it, and therefore the high-temperature strength at 1000°C of the comparative sample was low. In No. 27, the Mo content was too much, and in the texture thereof, the amount of precipitated Nb + precipitated Mo was too much. Its Nb content was too low, and this did not satisfy the formula (2). Its high-temperature strength at 1000°C and its low-temperature toughness were poor. In No. 28, the Nb content was high, and in the texture thereof,

the amount of precipitated Nb + precipitated Mo was too much, and its cold workability was poor. In No. 29, the content of Mo and Nb was high, and in the texture thereof, the amount of precipitated Nb + precipitated Mo was too much, and its low-temperature toughness was poor. In addition, since its Cu content was small, its high-temperature strength at 600°C was low. In No. 30, the Mo content was too high, and in the texture of thereof, the amount of precipitated Nb + precipitated Mo was too much. However, owing to the solid solution of Mo therein, the high-temperature strength at 1000°C of the comparative sample was high, but the low-temperature toughness and the cold workability thereof were poor.

Claims

1. A ferritic stainless steel material having excellent heat resistance and low-temperature toughness for automobile exhaust gas passage components, which has a composition comprising, in terms of % by mass, at most 0.03 % of C, at most 1 % of Si, from 0.6 to 2 % of Mn, at most 3 % of Ni, from 10 to 25 % of Cr, from 0.3 to 0.7 % of Nb, from more than 1 to 2 % of Cu, from 1 to 2.5 % of Mo, from 1 to 2.5 % of W, at most 0.15 % of Al, from 0.03 to 0.2 % of V, and at most 0.03 % of N, with a balance of Fe and inevitable impurities, and satisfying the following formulae (1) and (2), and which has a texture where the total amount of Nb and Mo existing as a precipitation phase is at most 0.2 % by mass:

$$1.2\text{Nb} + 5\text{Mo} + 6\text{Cu} \geq 11.5 \quad (1),$$

$$15\text{Nb} + 2\text{Mo} + 0.5\text{Cu} \geq 10.5 \quad (2).$$

2. The steel material as claimed in claim 1, wherein the composition further contains at least one of Ti and Zr in an amount of less than 1 % in total.
3. The steel material as claimed in claim 1 or 2, wherein the composition further contains at least one of B in an amount of at most 0.02 % and Co in an amount of at most 2 %.
4. The steel material as claimed in any of claims 1 to 3, wherein the composition further contains at least one of REM (rare earth element) and Ca in an amount of at most 0.1 % in total.
5. The steel material as claimed in any of claims 1 to 4, which is used for exhaust gas components of which the material temperature is in a temperature range over 900°C.



EUROPEAN SEARCH REPORT

Application Number
EP 08 01 9006

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