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(54) **HEAT-RESISTANT COMPONENT FOR CHEMICAL PROCESSING APPARATUS AND METHOD FOR PRODUCING SAME**

(57) A heat-resistant component for a chemical processing apparatus is formed from a ferritic Cr-steel that contains Cr in an amount of from 13% by weight to 30% by mass. The ferritic Cr-steel has a creep rate of 1 × 10^{-5}/h or less at 700°C under stress of 100 MPa, and an oxidation weight gain of 10 mg/cm^2 or less after being maintained in a 650°C water vapor for 1,000 h. The heat-resistant component for a chemical processing apparatus is produced by hot working the ferritic Cr-steel in a temperature range of 850 to 1,200°C, forming the ferritic Cr-steel into a component shape, subjecting the steel to an annealing treatment in a temperature range of 1,000 to 1,250°C, and cooling the steel to 400°C or less at a cooling rate of 100°C/min or higher.

Fig.2

EP 2 447 384 A1
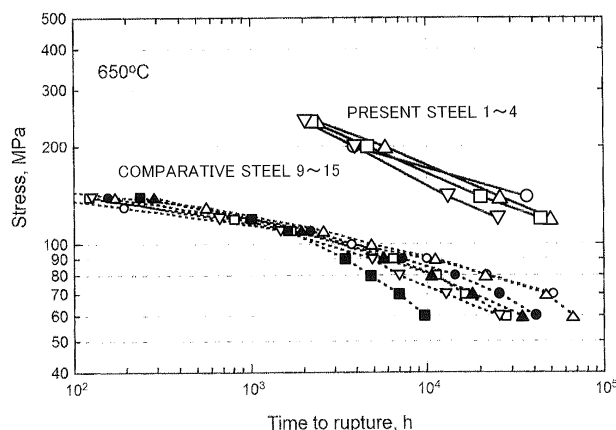
Description

Technical Field

[0001] The present invention relates to heat-resistant components for use in chemical processing apparatuses used mainly for causing chemical reactions for a feedstock through high-temperature chemical treatment, such as in petroleum refineries that heat and fractionate petroleum, and in heating and synthesizing apparatuses that synthesize desired compounds through chemical reactions caused by heating a feedstock.

Background Art

[0002] From the safety standpoint, heat-resistant components used in portions in contact with a feedstock in the high-temperature chemical treatment by a chemical processing apparatus (hereinafter, referred to as "heat-resistant component for a chemical processing apparatus") require long-hour durability. Examples of such heat-resistant components for a chemical processing apparatus include valves, pipes, pressure vessels, and flanges. Generally, chemically stable ferritic high Cr-steel with sufficient strength is used as the material of the heat-resistant components.
[0003] In recent years, high heating temperatures of 650°C and higher are desired for improving heat efficiency and synthesis techniques. It is difficult, however, to meet such demands with the performance of the conventional heat-resistant components.
[0004] The devices used in high temperatures are designed according to the allowable stress formulated based on the creep strength, because the creep strength of ferritic high Cr-steel greatly drops at high temperatures above 650°C.
[0005] On the other hand, Ni-based superalloy is known as a heat-resistant material, as described in Patent Document 1. However, it is not known whether the Ni-based superalloy is applicable to heat-resistant components for a chemical processing apparatus.

Patent Document 1: JP-A-2007-332412

Disclosure of Invention

Problems that the Invention is to Solve

[0006] Under these circumstances, it is an object of the present invention to provide a heat-resistant component for a chemical processing apparatus, and a producing process thereof with which safety can be ensured even at high temperatures of 650°C and higher.

Means for Solving the Problems

[0007] In order to solve the foregoing problems, the present invention provides a heat-resistant component for a chemical processing apparatus that performs a high-temperature chemical treatment for a feedstock at 650°C or higher, **characterized in that** the heat-resistant component is formed from a ferritic Cr-steel of a chemical composition that mainly includes, in % by mass,

Cr: 13 to 30%,
Ni: 1×10^{-1} to 2.5%,
C: 1×10^{-3} to 1×10^{-1}%, and
N: 1×10^{-3} to 1×10^{-1}%,

wherein the ferritic Cr-steel allows for inclusion of an additional component and unavoidable impurities, includes Fe as the remaining part, and forms a ferrite phase.
[0008] It is preferable in the heat-resistant component for a chemical processing apparatus that Ni is added in an amount that satisfies the relationship Ni > 10(C + N), where Ni, C, and N each represent the amount of each component added (in % by mass), when C is added in 1×10^{-2}% by mass or more and/or Ni is added in 1×10^{-2}% by mass or more.
[0009] It is preferable in the heat-resistant component for a chemical processing apparatus that the ferrite phase is 70 volume% or more.
[0010] It is preferable in the heat-resistant component for a chemical processing apparatus that the additional component is one or more of the following in % by mass,

Mo: 5×10^{-1} to 5%,

W: 5×10^{-1} to $1 \times 10\%$,
V: 5×10^{-2} to $4 \times 10^{-1}\%$,
Nb: 1×10^{-2} to $1 \times 10^{-1}\%$,
Co: 1×10^{-1} to $1 \times 10\%$, and
B: 2×10^{-3} to $4 \times 10^{-3}\%$, and

that at least one of carbide, nitride, and intermetallic compound is precipitated in crystal grains.

[0011]   It is preferable in the heat-resistant component for a chemical processing apparatus that Mo and W are added in amounts that satisfy the relationship Mo + 0.5W ≥ 3.0% by mass, where Mo and W each represent the amount of each component added (in % by mass).

[0012]   The present invention also provides a heat-resistant component for a chemical processing apparatus that performs a high-temperature chemical treatment for a feedstock at 650°C or higher, **characterized in that** the heat-resistant component is formed from a ferritic Cr-steel that contains Cr in an amount of from 13% by mass to 30% by mass, wherein the ferritic Cr-steel has a creep rate of 1×10^{-5}/h or less at 700°C under stress of 100 MPa, and an oxidation weight gain of 10 mg/cm^2 or less after being maintained in a 650°C water vapor for 1,000 h.

[0013]   The present invention also provides a process for producing a heat-resistant component for a chemical processing apparatus, the process including hot working the ferritic Cr-steel of the foregoing chemical composition in a temperature range of 850 to 1,200°C, forming the ferritic Cr-steel into a component shape, subjecting the steel to an annealing treatment in a temperature range of 1,000 to 1,250°C, and cooling the steel to 400°C or less at a cooling rate of 100°C/min or higher.

Advantage of the Invention

[0014]   A heat-resistant component for a chemical processing apparatus and a producing process thereof according to the present invention realize a chemical processing apparatus that can perform the conventionally difficult high-temperature operation at 650°C or higher temperatures. The material of the heat-resistant component for a chemical processing apparatus is ferritic Cr-steel, a material belonging to the commonly used ferritic high Cr-steels. The heat-resistant component is thus highly practical. The invention is therefore applicable to various techniques, including the current production techniques and quality management techniques, and is very convenient because hardly any additional limitations are imposed.

Brief Description of Drawings

[0015]

FIG. 1 is a graph representing the influence of cooling rate on creep rupture time at 650°C.
FIG. 2 is a graph representing the results of a creep test performed at 650°C.
FIG. 3 is a graph representing the relationship between creep rate and time at 700°C under stress of 100 MPa.
FIG. 4 is a graph representing the relationship between creep rate and time at 750°C under stress of 50 MPa.
FIG. 5 is a graph representing creep rupture time at 750°C.
FIG. 6 is a graph representing oxidation weight gain in a 650°C water vapor.
FIG. 7 is a graph representing the temperature dependence of linear expansion coefficient.

Mode for Carrying Out the Invention

[0016]   The ferritic Cr-steel used for a heat-resistant component for a chemical processing apparatus of the present invention is a material that has excellent high temperature strength, heat resistance, oxidation resistance, and high toughness even at high temperatures above 650°C (here and below, the temperature is represented in units of 50°C), and that can withstand use under high temperature and high pressure for extended time periods while undergoing only a limited decrease in strength.

[0017]   The ferritic Cr-steel used for the heat-resistant component for a chemical processing apparatus is produced by hot working a ferritic Cr-steel ingot in a temperature range of 850 to 1,200°C and forming the ferritic Cr-steel into a predetermined shape, and then subjecting the steel to an annealing treatment in a temperature range of 1,000 to 1,250°C, and cooling the steel to 400°C or less at a cooling rate of 100°C/min or higher.

[0018]   The hot working temperature such as in hot forging is 850 to 1,200°C, preferably 950 to 1,150°C, more preferably 1,000 to 1,100°C. Above the upper limit temperature, an abrupt decrease in ductility may occur. Below the lower limit temperature, deformation resistance increases, which may lead to processing defects such as cracking.

[0019] The temperature of the annealing treatment is 1,000 to 1,250°C, preferably 1,000 to 1,200°C, more preferably 1,050 to 1,150°C. Above the upper limit temperature, serious coarsening of crystal grains may occur, which can be detrimental to various properties of the steel, including toughness, ductility, and weldability. Below the lower limit temperature, it may not be possible to completely melt the steel and to exhibit a sufficient strength.

[0020] Temperatures of 400°C and higher may cause precipitation of a second phase in the process of cooling from the annealing temperature, because of the fast precipitation rate of second-phase compounds such as carbides, nitrides, and intermetallic compounds. In order to control such precipitation of the second phase, the cooling rate of the cooling to 400°C or less following the annealing treatment is 100°C/min or higher, preferably 120°C/min or higher, more preferably 150°C/min or higher. Below the lower limit, a coarse second phase may precipitate at the crystal grain boundary during the cooling process, and it becomes difficult to disperse and precipitate a fine second phase in the crystal grains. In this case, sufficient strength may not be developed because of the failure to effectively control the precipitation state of the second phase for strength improvement.

[0021] The ferritic Cr-steel produced as above has a minimum creep rate of 1.0×10^{-4}/h or less at 700°C under stress of 100 MPa. A minimum creep rate exceeding the upper limit causes creep deformation during high-temperature use. This may lead to an early loss of functionality in components such as valves that require high dimension accuracy, or may encourage corrosion or oxidation.

[0022] Further, the ferritic Cr-steel has a creep rupture time of preferably 1,000 hr or more at 750°C under stress of 80 MPa, 5,000 hr or more at 750°C under stress of 50 MPa, and 10,000 hr or more at 750°C under stress of 30 MPa. A creep rupture time below the lower limit shortens the creep rupture lifetime that depends on the load generated during the operation of the chemical processing apparatus, and may thus present difficulties in ensuring a sufficient creep rupture lifetime in practical applications.

[0023] Further, the ferritic Cr-steel has a sufficiently small oxidation weight gain of 10 mg/cm^2 or less after being maintained in a 650°C water vapor for 1,000 h. The ferritic Cr-steel thus excels in high-temperature oxidation resistance, and can ensure safety at high temperatures of 650°C and higher. Oxidative degradation becomes likely and performance becomes unstable with an oxidation weight gain in excess of this upper limit.

[0024] Increasing the additive amount of Cr generally improves not only the oxidation resistance but the corrosion resistance of iron and steel materials. Thus, the ferritic Cr-steel with excellent oxidation resistance also excels in corrosion resistance.

[0025] The ferritic Cr-steel has a linear expansion coefficient of 15×10^{-6} or less in a temperature range of from room temperature to 850°C. Above the upper limit, the amounts of thermal expansion and contraction at the start-up and stopping of the chemical processing apparatus increase, and it becomes difficult to produce heat-resistant components with high dimension accuracy.

[0026] The ferritic Cr-steel in the form of, for example, a steel ingot to be subjected to hot working is a ferritic Cr-steel, or a ferritic high Cr-steel as it is called, whose chemical composition is adjusted to include the components below (here and below, % means % by mass).

(1) C: 1×10^{-3} to 1×10^{-1}%

[0027] C needs to be added in at least 1×10^{-3}% to improve creep strength. The upper limit of the C additive amount is 1×10^{-1}%, because the excess addition lowers toughness. When C is added in 1×10^{-2}% or more, it is preferable that Ni > 10 (C + N), where Ni, C, and N each represent the additive amount of each component (in % by mass).

(2) Cr: 13 to 30%

[0028] It is essential that Cr is added in 13% or more. In actual practice, Cr is added in preferably 13.5% or more to ensure a 70 volume% or more of the ferrite phase, and to improve oxidation resistance. The upper limit of Cr additive amount is 30%, because a Cr additive amount in excess of 30% notably lowers toughness.

(3) N: 1×10^{-3} to 1×10^{-1}%

[0029] N needs to be added in at least 1×10^{-3}% to improve creep strength. The upper limit of N additive amount is 1×10^{-1}%, because the excess addition lowers toughness. When N is added in 1×10^{-2}% or more, it is preferable that Ni > 10 (C + N), as with the case of C.

(4) Ni: 1×10^{-1} to 2.5%

[0030] Ni needs to be added in at least 1×10^{-1}% to improve toughness. When C and/or N are added in 1×10^{-2}% or more, it is preferable that the Ni additive amount satisfy Ni > 10 (C + N) to ensure toughness, as above. The upper

limit of Ni additive amount is 2.5%, because the excess addition lowers the percentage volume of the ferrite phase.

[0031] As presented in Table 2 below, comparative steels 7 and 8 with the Ni additive amount satisfying Ni ≥ 10 (C + N) (Ni, C, and N each represent the additive amount of each component (in % by mass)) have small Charpy impact values, regardless of the cooling rate. On the other hand, the water-cooled materials of the steels 1 to 4 of the present invention satisfying the relationship Ni > 10 (C + N) have sufficiently greater Charpy impact values than those of the comparative steels 7 and 8.

[0032] The ferritic Cr-steel can be reinforced with the controlled precipitation of at least one of carbide, nitride, and intermetallic compound, specifically, by the fine dispersion and precipitation within the crystal grains. This is effective for improving creep strength. To this end, the ferritic Cr-steel allows for addition of the components below in its chemical composition, in addition to the foregoing components.

(5) Mo: 5×10^{-1} to 5%

[0033] Mo is a chemical component effective for precipitating an intermetallic compound, and can improve creep strength. Mo may be added in 5×10^{-1}% or more. The upper limit of Mo additive amount is preferably 5%, because the excess addition may lower toughness.

(6) W: 5×10^{-1} to 1×10%

[0034] As with Mo, W is a chemical component effective for precipitating an intermetallic compound, and can improve creep strength. W may be added in 5×10^{-1}% or more. The upper limit of W additive amount is preferably 1×10%, because the excess addition may lower toughness.

[0035] Note that Mo and W may be added to satisfy the relationship Mo + 0.5W ≥ 3.0% (Mo and W each represent the additive amount (in % by mass)), so as to ensure a sufficient amount of intermetallic compound precipitation.

(7) V: 5×10^{-2} to 4×10^{-1}%

[0036] V forms carbides or nitrides effective for improving creep strength. V maybe added in 5×10^{-2}% or more. The upper limit of V additive amount is preferably 4×10^{-1}%, because the excess addition is not necessarily effective for the formation of carbides and nitrides.

(8) Nb: 1×10^{-2} to 1×10^{-1}%

[0037] As with V, Nb forms carbides or nitrides effective for improving creep strength. Nb may be added in 1×10^{-2}% or more. The upper limit of Nb additive amount is preferably 1×10^{-1}%, because the excess addition is not necessarily effective for the formation of carbides and nitrides.

(9) Co: 1×10^{-1} to 1×10%

[0038] Co is a component effective for miniaturizing the precipitated carbide, nitride, and intermetallic compound, and for improving creep strength. Co may be added in 1×10^{-1}% or more. The upper limit of Co additive amount is preferably 1×10%, because the excess addition may lower the percentage volume of the ferrite phase.

(10) B: 2×10^{-3} to 4×10^{-3}%

[0039] B is a component effective for miniaturizing and stabilizing the precipitates, and for strengthening the grain boundary. B may be added in 2×10^{-3}% or more. The upper limit of B additive amount is preferably 4×10^{-3}%, because the excess addition may lead to formation of boron nitride, and may not be necessarily effective for improving creep strength.

(11) Mn: 5×10^{-2} to 8×10^{-1}%

[0040] Mn is a component effective as a deoxidant. Mn may be added in 5×10^{-2}% or more. The upper limit of Mn additive amount is preferably 8×10^{-1}%, because the excess addition is detrimental to strength and toughness.

(12) Si: 5×10^{-2} to 5×10^{-1}%

[0041] Si is a component effective as a deoxidant. Si may be added in 5×10^{-2}% or more. The upper limit of Si additive

amount is preferably 5×10^{-1}%, because the excess addition accelerates the coarsening of the precipitates and lowers strength.

[0042] The remaining parts of the ferritic Cr-steel chemical composition are Fe and unavoidable impurities.

[0043] Preferably, the ferritic Cr-steel forms at least 70 volume% of the ferrite phase to improve creep strength. A tempered martensite structure with 70 volume% or more of the ferrite phase is unstable at high temperatures, whereas the ferrite phase has high structure stability at high temperatures. As presented in Table 2, furnace cooling of the steels 2 to 4 of the present invention makes the percentage volume of the ferrite phase less than 70% because of the slow cooling rate following the annealing treatment. However, the percentage volume of the ferrite phase becomes 70% or more when the cooling rate down to 400°C or less is 100°C/min or higher in water cooling. Thus, as represented in FIG. 1, the water-cooled materials of the steels 2 to 4 of the present invention have creep rupture times about 10 times longer than those of the furnace cooled materials.

[0044] Further, as presented in FIG. 2, the steels 1 to 4 of the present invention have longer creep rupture times than the comparative steels 9 to 15 in which the Cr additive amount is less than 13% and the percentage volume of the ferrite phase is less than 70%.

[0045] Examples are described below.

[0046] In the following Examples, a round bar was assumed to be a component, and various properties were measured. As noted above, the heat-resistant component for a chemical processing apparatus of the present invention is a heat-resistant component used in portions in contact with a feedstock in the high-temperature chemical treatment in a chemical processing apparatus, and may be, for example, a valve, a pipe, a pressure vessel, or a flange. It would be easily anticipated and understood that the heat-resistant component for a chemical processing apparatus produced from the ferritic Cr-steel has properties comparable to those of the ferritic Cr-steel used as the material.

Examples

[0047] The round bars of steels 1 to 8 with the chemical compositions presented in Table 1 (steels 1 to 6 of the present invention, and comparative steels 7 and 8) were each prepared from a 10-kg steel ingot subjected to 850 to 1,150°C hot forging to have a diameter of 15 mm. After 1,200°C annealing treatment, each specimen was cooled by furnace cooling or water cooling.

[0048] Note that Table 1 also presents the chemical compositions of the existing ferritic heat-resistant steels (steels 9 to 15; comparative steels).

[0049] Table 1 also presents steel 16 (comparative steel). The chemical composition of comparative steel 16 is such that Ni and Cr are added in amounts below the lower limits for the steels of the present invention.

Table 1

Specimen No.		Component (Mass%)												
		C	Si	Mn	Ni	Cr	Mo	V	Nb	W	Co	N	B	Fe
The present steel	1	0.051	0.20	0.50	1.99	14.94	0.99	0.20	0.051	6.05	0.01	0.041	0.0029	Remaining
	2	0.049	0.20	0.51	1.21	15.02	1.00	0.20	0.051	6.04	2.96	0.042	0.0028	Remaining
	3	0.048	0.21	0.51	1.60	15.00	1.00	0.20	0.050	6.03	2.95	0.044	0.0026	Remaining
	4	0.048	0.23	0.51	2.00	14.96	0.99	0.20	0.050	6.07	2.98	0.036	0.0029	Remaining
	5	0.047	0.21	0.51	0.42	14.93	1.00	0.20	0.050	6.05	2.96	0.041	0.0029	Remaining
	6	0.048	0.20	0.51	0.78	15.00	1.00	0.20	0.050	6.05	2.96	0.042	0.0029	Remaining
Comparative steel	7	0.110	0.24	0.49	0.02	15.21	0.98	0.20	0.051	2.95	-	0.072	0.0028	Remaining
	8	0.100	0.20	0.48	-	14.88	1.01	0.19	0.045	6.01	2.96	0.002	0.0028	Remaining
	9	0.110	0.10	0.41	0.17	9.26	0.42	0.16	0.057	1.67	-	0.046	0.0020	Remaining
	10	0.098	0.29	0.42	0.13	9.50	0.36	0.19	0.062	1.74	-	0.046	0.0020	Remaining
	11	0.120	0.28	0.61	0.34	10.50	0.36	0.21	0.060	2.05	-	0.069	0.0029	Remaining
	12	0.140	0.26	0.65	0.40	11.03	0.29	0.20	0.070	1.95	-	0.064	0.0030	Remaining
	13	0.120	0.30	0.60	0.32	10.65	0.34	0.19	0.050	1.89	-	0.054	0.0029	Remaining
	14	0.130	0.31	0.60	0.36	10.65	0.33	0.19	0.050	1.87	-	0.057	0.0024	Remaining
	15	0.110	0.27	0.59	0.33	12.10	0.34	0.19	0.060	1.82	-	0.066	0.0030	Remaining
	16	0.100	0.24	0.44	0.04	8.74	0.94	0.21	0.076	-	-	0.058	-	Remaining

[0050] These test pieces were subjected to a Charpy impact test at 100°C. The results are presented in Table 2.

[0051] Impact value smaller comparative steels 7 and 8 in which Ni was added in small amounts outside the rate for the steels of the present invention, regardless of the cooling rate after the annealing treatment. In contrast, the steels 1 to 4 of the present invention had greater impact values of 300J/cm^2 or more than the furnact cooled materials and comparative steels 7 and 8 in water cooling with a high cooling fate, though the values were small in furnace cooling that involves a lower cooling rate.

Table 2

Specimen No.	Impact value at 100°C (J/cm^2)		Percentage volume of ferrite phase (%)		Remarks
	Furnace cooling	Water cooling	Furnace cooling	Water cooling	
1	6	300	94	100	
2	6	333	56	83	
3	5	367	48	77	
4	6	366	40	72	
7	12	32	100	100	Out of Ni range, Out of Co range
8	5	12	-	91	Out of Ni range

[0052] FIG. 1 is a graph representing the influence of cooling rate on creep rupture time at 650°C in the steels 2 to 4 of the present invention. It can be seen that the water-cooled materials with a high cooling rate have creep rupture times about 10 times longer than those of the furnace cooled materials involving a low cooling rate.

[0053] Table 3 represents the measured data used to create FIG. 1.

Table 3

Stress (MPa)	Creep rupture time at 650°C (hr)					
	The present steel 2		The present steel 3		The present steel 4	
	Water cooling	Furnace cooling	Water cooling	Furnace cooling	Water cooling	Furnace cooling
240	2405	-	2222	-	2008	-
200	5789	-	4620	-	3911	-
140	25776	1507	20074	1478	13211	1810
120	49380	2883	43299	3063	25076	3508

[0054] It was confirmed that required cooling rate conditions include an annealing treatment within a temperature range of 1,000 to 1,250°C, and the subsequent cooling to 400°C--a temperature that essentially does not allow for precipitation of carbides, rides, and intermetallic compounds--at a high cooling rate that can suppress the precipitation of these components, specifically at 100°C/min or higher.

[0055] FIG. 2 is a graph representing the results of a creep test at 650°C.

[0056] It can be seen that the steels 1 to 4 of the present invention have higher creep strengths than comparative steels 9 to 15 in which Cr is added in less than 13% by mass, and in which the percentage volume of the ferrite phase is less than 70%.

[0057] Table 4 represents the measured data used to create FIG. 2.

Table 4

Stress (MPa)	Creep rupture time at 650°C (hr)										
	The present steel				Comparative steel						
	1	2	3	4	9	10	11	12	13	14	15
240	-	2405	2222	2008	-	-	-	-	-	-	-
200	3834	5789	4620	3911	-	-	-	-	-	-	-
180	-	-	-	-	-	6	-	-	-	-	-

(continued)

Stress (MPa)	Creep rupture time at 650°C (hr)										
	The present steel				Comparative steel						
	1	2	3	4	9	10	11	12	13	14	15
160	-	-	-	-	11	20	-	-	-	-	-
140	36418	25776	20074	13211	66	171	122	127	157	289	241
130	-	-	-	-	194	564	-	-	-	-	-
120	-	49380	43299	25076	-	-	804	670	985	1004	1008
110	-	-	-	-	1689	2589	1670	1478	2171	1934	1615
100	-	-	-	-	3739	4831	-	-	-	-	-
90	-	-	-	-	10002	11219	6473	4853	7249	5721	3412
80	-	-	-	-	21717	21505	11283	6966	14462	10713	4783
70	-	-	-	-	50871	46437	16377	12802	25632	18158	6909
60	-	-	-	-	-	65959	27733	25438	40713	34223	9734

[0058]   FIG. 3 is a graph representing the relationship between creep rate and time at 700°C under stress of 100 MPa.

[0059]   It can be seen that the creep rates of the stells 2 and 4 of the present invention are only about 1/1,000 of the creep rates of comparative stells 9 to 11, and that the creep rupture times are least about 100 times longer.

[0060]   Table 5 represents the minimum creep rates obtained from FIG. 3. The steels 2 and 4 of the present invention have a minimum creep rate of 1.0×10^{-4}/h or less, or 1.0×10^{-5}/h or less. 1.0×10^{-5}/h or less.

Table 5

700°C, Stress 100 MPa	
Tested material	Minimum creep rate (h^{-1})
The present steel 2	2.0×10^{-6}
The present steel 4	1.9×10^{-6}
Comparative steel 9	2.1×10^{-3}
Comparative steel 10	1.1×10^{-3}
Comparative steel 11	2.5×10^{-3}

[0061]   FIG. 4 is a graph representing the relationship between creep rate and time at 750°C under stress of 50 MPa.

[0062]   The steel 4 of the present invention did not rupture during the course of testing. The creep rates of the stells 2 and 4 of the present invention were only 1/100 or less of the creep rates of comparative steels 9 and 13, and the creep rupture times were at least about 100 times longer.

[0063]   Table 6 represents the measured data used to create FIG. 4.

Table 6

750°C, Stress 50 MPa	
Tested material	Minimum creep rate (h^{-1})
The present steel 2	1.1×10^{-6}
The present steel 4	7.4×10^{-7}
Comparative steel 9	5.3×10^{-4}
Comparative steel 13	5.2×10^{-4}

[0064]   FIG. 5 is a graph representing creep rupture time at 750°C.

[0065]   The steels 2 and 4 of the present invention did not rupture during the course of testing under stresses of 50 MPa and 30 MPa. Further, the steels 2 and 4 of the present invention tested under stresses of 80 to 50 MPa had creep rupture times at least about 100 times longer than the rupture times of comparative steels 9 to 15. It can also be seen that the creep rupture times are longer thatn those of the austenite heat-resistant steel (steel No. X: SUS316) presented in Table 7. Further, it can be seen that, even under stress of 30 MPa, the steels 2 and 4 of the present invention have

creep rupture times comparable to that of SUS316.

[0066]   Tables 7 and 8 represent the measured data used to create FIG. 5. Table 7 represents the creep rupture time (h) of the austenite steel SUS316 (steel No. X) at 750°C. Table 8 represents the mean values for the steel No. X presented in Table 7, along with the creep rupture times (h) of the steels 2 and 4 of the present invention, comparative steels 9 to 15, and X measured at 750°C.

Table 7

Creep rupture time of austenite steel SUS316 (steel No.X) at 750°C (h)									
Stress (MPa)	88	69	61	53	47	41	37	33	26
Run 1	127	555	1371	1725	5547	5384	9613	11188	33279
Run 2	135	577		2095		6564	23693	18173	37610
Run 3	145	615		2137		8302		23024	44459
Run 4	162	641		2651		8873		33224	46417
Run 5	163	656		2691		9266			53844
Run 6	170	680		2726		11767			130478
Run 7	173	802		2735					
Run 8	194			2979					
Mean value	159	647	1371	2467	5547	8359	16653	21402	57681

Table 8

Creep rupture time at 750°C (hr)										
Stress (MPa)	The present steel		Comparative steel							
	2	4	9	10	11	12	13	14	15	Steel No.X
88										159
80	2173	3550								
69										647
61										1371
60					24					
53										2467
50	9033	>16154	97	97		108	92			
47										5547
41										8359
40			430	362	326	516	392	239	204	
37										16653
35				579		970			384	
33										11188
30	>21023	>20973	1994	1488	1043		1730	1018	667	
26										57681
25			3621	3079	2333	3882			1307	
20			5713	5050		7884	7115	4209	2819	

[0067]   FIG. 6 is a graph representing the oxidation weight gain in a 650°C water vapor. The oxidation weight gain was measured for the steels 2 and 4 of the present invention, and for comparative steel 16. In the comparative steel 16 with the small Cr additive amount, the oxidation weight gain increased to 15 mg/cm^2 or more after 1,000 h. In contrast, in the steels 2 and 4 of the present invention, the oxidation weight gain remained sufficiently small at 10 mg/cm^2 or less even after 1,000 h. It can be seen from these results that the steels 2 and 4 of the present invention have excellent oxidation resistance at high temperatures.

[0068]   Table 9 represents the measured date used to create FIG. 6. in the table, 2 and 4 correspond to the steels 2 and 4, respectively, of the present invention, and 16 corresponds to comparative steel 16.

Table 9

Time held (h)	Oxidation weight gain in 650°C, water vapor (mg/cm^2)		
	2	4	16
100	5.968	5.862	8.031
500	8.533	8.484	11.010
1000	9.905	9.307	15.310

[0069] FIG. 7 is a graph representing the temperature dependence of expansion coefficient. The graph represents the results of the comparison of the linear expansion coefficients of the steels of the present invention and practical heat-resistant materials.

[0070] The steels 2 and 4 of the present invention were heated from room temperature to 1,000°C at a rate of 1,000°C/h, and the thermal expansion was measured to determine a linear expansion coefficient at each temperature. The linear expansion coefficients of the practical heat-resistant materials are values specified in the boiler and pressure vessel specifications of the American Society of Mechanical Engineers (ASME).

[0071] Table 10 represents the measured data used to create FIG. 7.

Table 10

Temperature °C	Linear expansion coefficient ($\times 10^{-6}$)							
	The present steel		Comparative steel					
			Ferrite steel		Austenite steel		Ni-based superalloy	
	2	4	9Cr-1Mo	12Cr, 13Cr	18Cr-8Ni	25Cr-20Ni	NCF600	NCF800
50	8.8	10.9	10.8	11.1	15.9	15.2	12.8	14.9
150	9.3	11.1	11.7	11.9	17.7	16.8	13.9	16.4
250	9.9	11.4	12.4	12.2	18.8	17.2	14.9	17.0
350	10.4	11.6	13.0	12.5	19.3	17.9	15.5	17.5
450	11.0	11.8	13.5	12.9	19.8	18.5		18.0
550	11.6	12.0	14.1	13.2	20.7	19.2		18.6
650	12.1	12.2	15.1	13.3	21.6	20.0		19.4
750	12.7	12.4		13.4	21.1	20.9		20.7
850	13.2	12.6						23.7

Industrial Applicability

[0072] The present invention realizes a heat-resistant component for a chemical processing apparatus with which safety can be ensured even at high temperatures of 650°C and higher. The invention enables a high-temperature operation of a chemical processing apparatus at high temperatures of 650°C and higher. The material of the heat-resistant component for a chemical processing apparatus is ferritic Cr-steel, and thus the heat-resistant component is highly practical. The invention is applicable to various techniques, including the current production techniques and quality management techniques, and is very convenient because hardly any additional limitations are imposed.

Claims

1. A heat-resistant component for a chemical processing apparatus that performs a high-temperature chemical treatment for a feedstock at 650°C or higher,
   characterized in that the heat-resistant component is formed from a ferritic Cr-steel of a chemical composition that mainly includes, in % by mass,
   Cr: 13 to 30%,
   Ni: 1×10^{-1} to 2.5%,
   C: 1×10^{-3} to 1×10^{-1}%, and
   N: 1×10^{-3} to 1×10^{-1}%,

wherein the ferritic Cr-steel allows for inclusion of an additional component and unavoidable impurities, includes Fe as the remaining part, and forms a ferrite phase.

2. The heat-resistant component for a chemical processing apparatus according to claim 1, wherein Ni is added in an amount that satisfies the relationship Ni > 10(C + N), where Ni, C, and N each represent the amount of each component added (in % by mass), when C is added in 1×10^{-2}% by mass or more and/or Ni is added in 1×10^{-2}% by mass or more.

3. The heat-resistant component for a chemical processing apparatus according to claim 1 or 2, wherein the ferrite phase is 70 volume% or more.

4. The heat-resistant component for a chemical processing apparatus according to claim 1 or 2,
   wherein the additional component is one or more of the following in % by mass, Mo: 5×10^{-1} to 5%,
   W: 5×10^{-1} to 1×10%,
   V: 5×10^{-2} to 4×10^{-1} %,
   Nb: 1×10^{-2} to 1×10^{-1}%,
   Co: 1×10^{-1} to 1×10%, and
   B: 2×10^{-3} to 4×10^{-3}%, and
   wherein at least one of carbide, nitride, and intermetallic compound is precipitated in crystal grains.

5. The heat-resistant component for a chemical processing apparatus according to claim 4, wherein Mo and W are added in amounts that satisfy the relationship Mo + 0.5W ≥ 3.0% by mass, where Mo and W each represent the amount of each component added (in % by mass).

6. A heat-resistant component for a chemical processing apparatus that performs a high-temperature chemical treatment for a feedstock at 650°C or higher,
   characterized in that the heat-resistant component is formed from a ferritic Cr-steel that contains Cr in an amount of from 13% by mass to 30% by mass, wherein the ferritic Cr-steel has a creep rate of 1×10^{-5}/h or less at 700°C under stress of 100 MPa, and an oxidation weight gain of 10 mg/cm^2 or less after being maintained in a 650°C water vapor for 1,000 h.

7. A process for producing a heat-resistant component for a chemical processing apparatus,
   the process comprising hot working the ferritic Cr-steel of the chemical composition of claim 1 in a temperature range of 850 to 1,200°C, forming the ferritic Cr-steel into a component shape, subjecting the steel to an annealing treatment in a temperature range of 1,000 to 1,250°C, and cooling the steel to 400°C or less at a cooling rate of 100°C/min or higher.
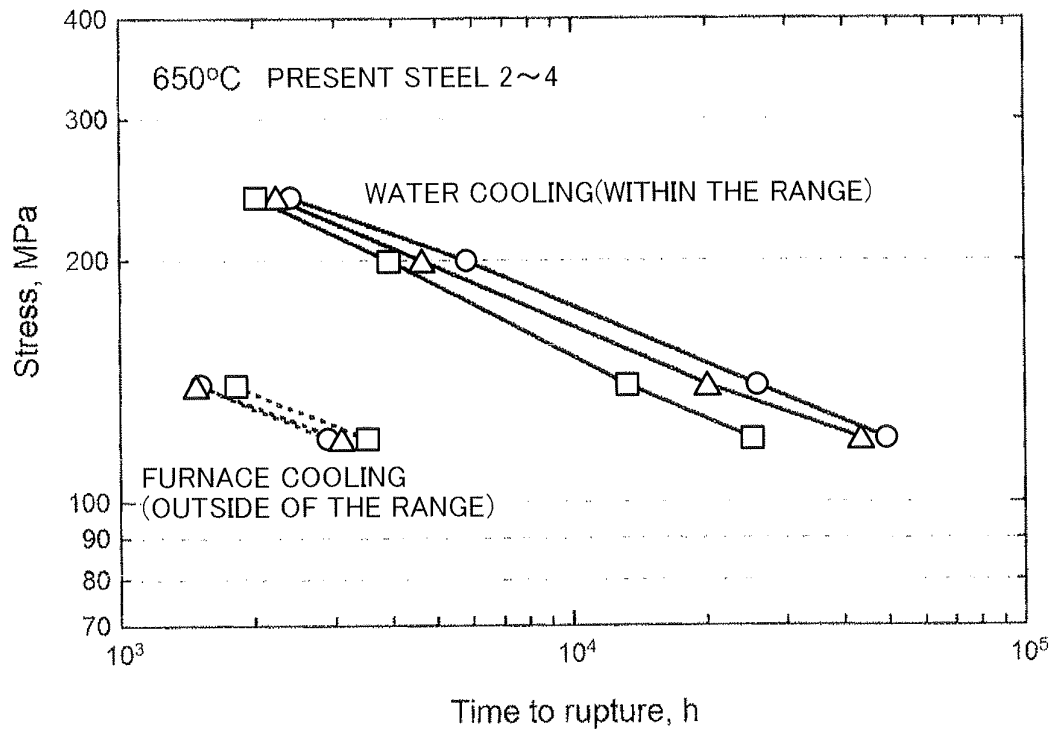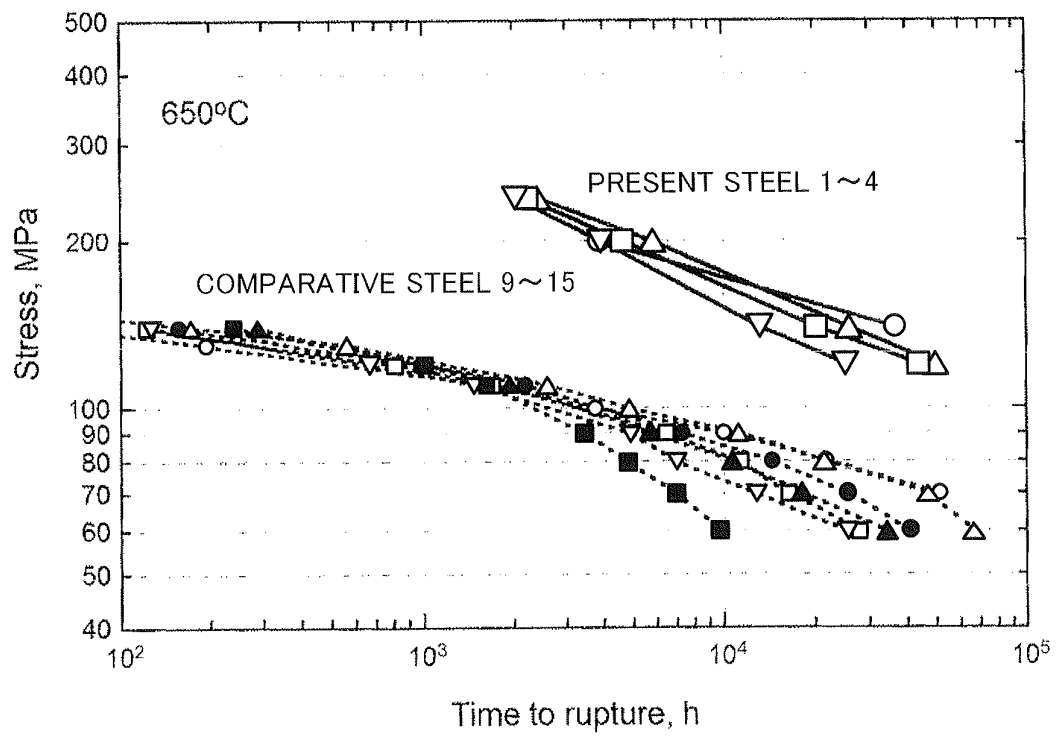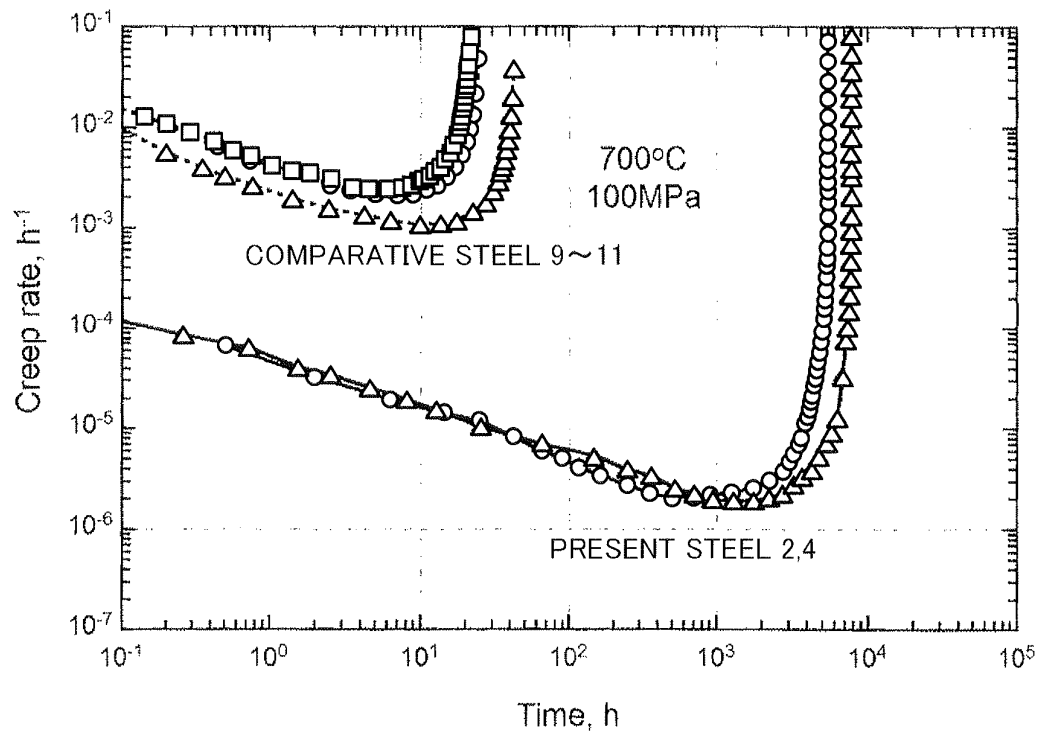
Fig.1

Fig.2

Fig.3

700°C
100MPa

COMPARATIVE STEEL 9~11

PRESENT STEEL 2,4

Fig.4

750°C-50MPa

COMPARATIVE STEEL 9,13

PRESENT STEEL 2

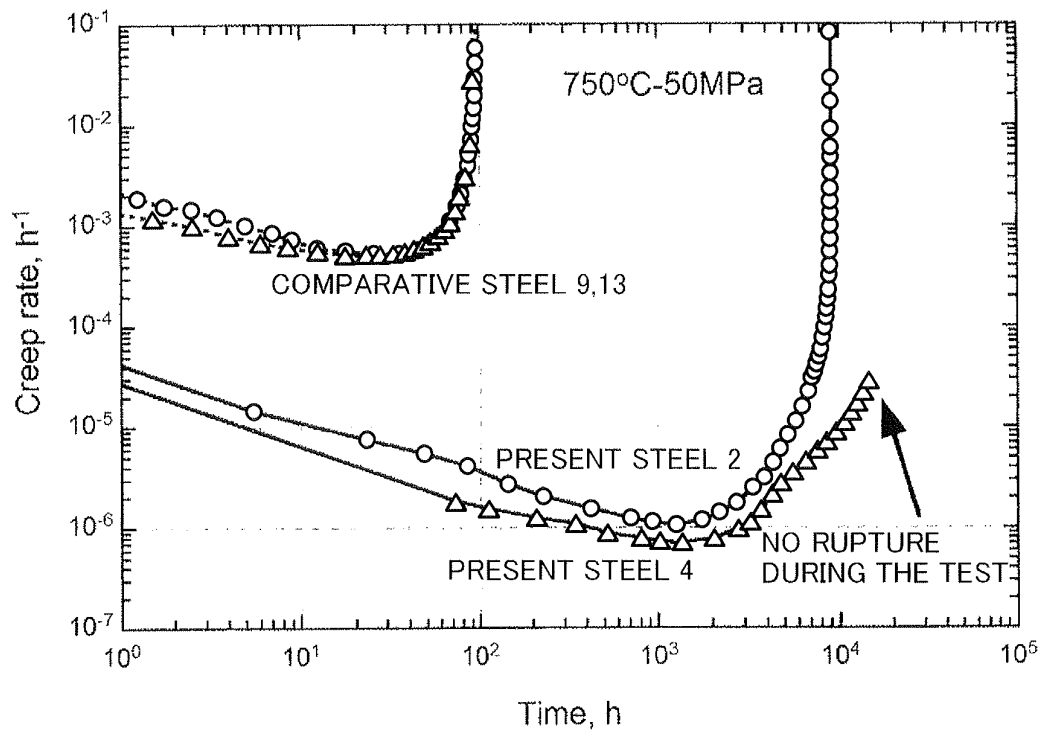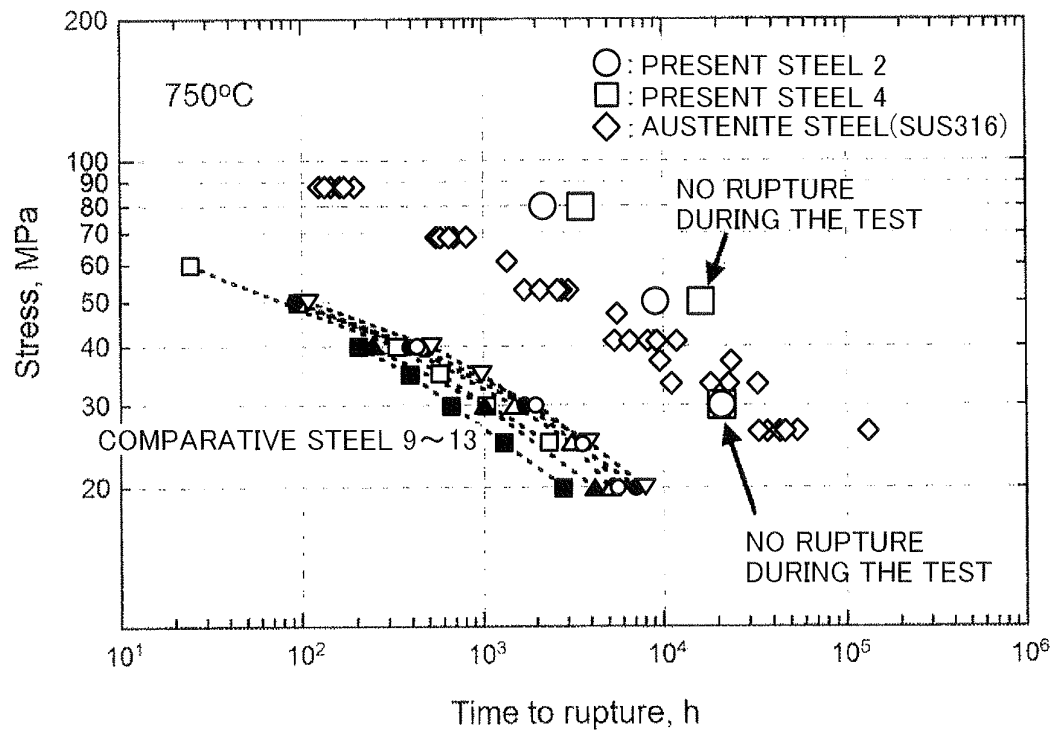PRESENT STEEL 4

NO RUPTURE
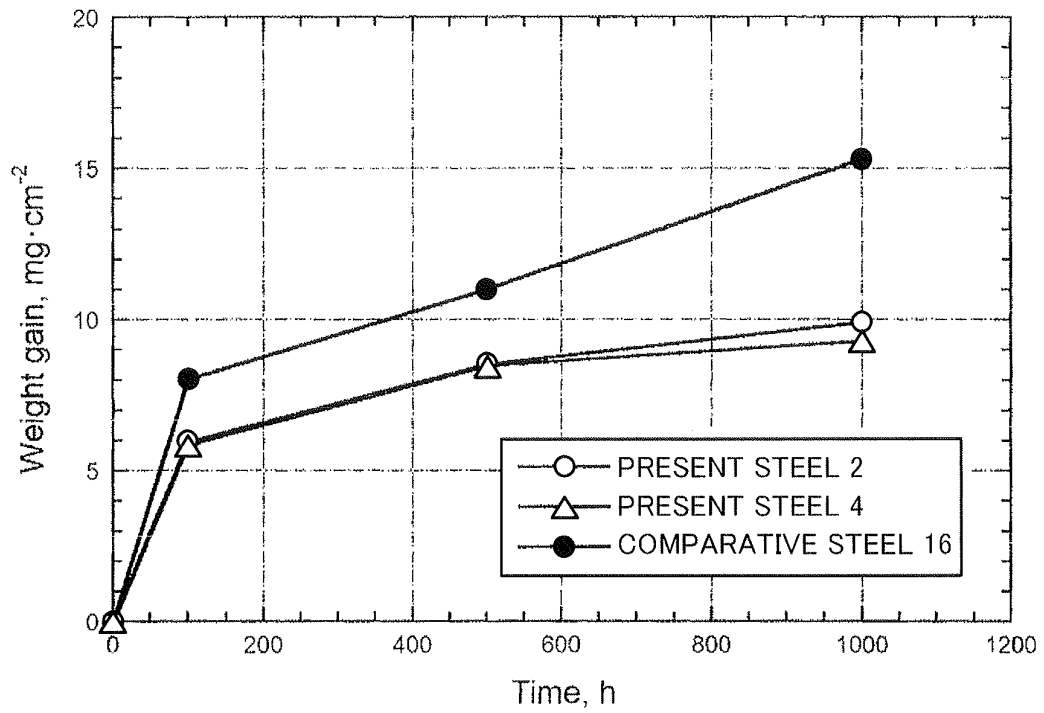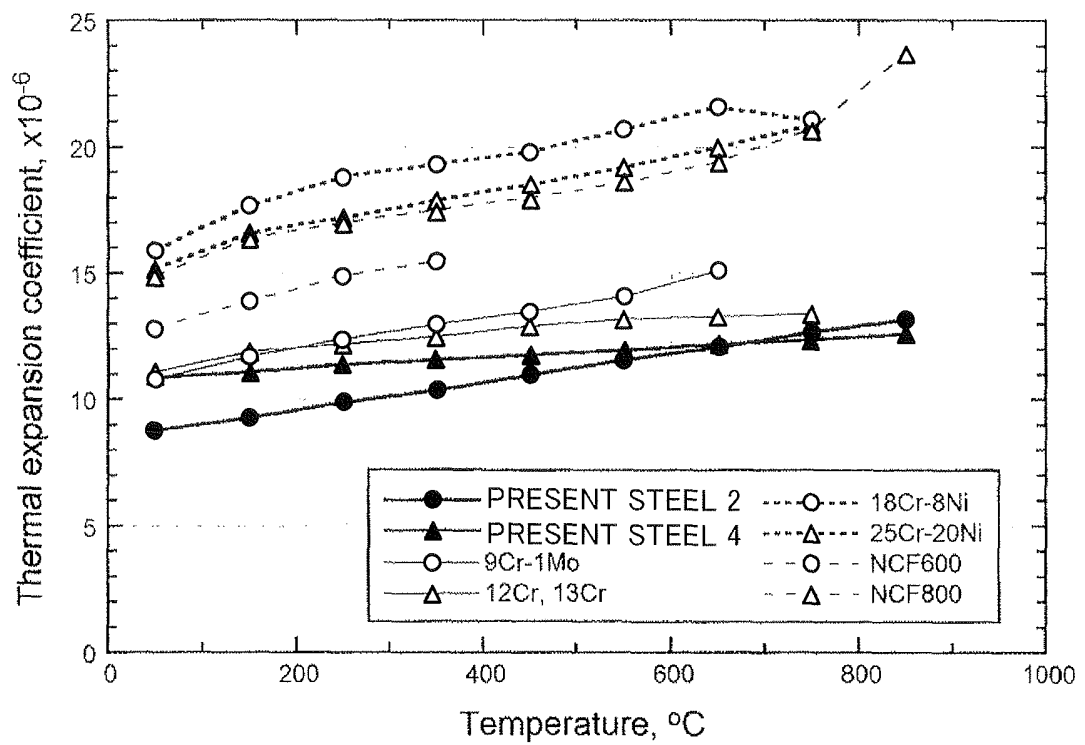DURING THE TEST

Fig.5

Fig.6

Fig.7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/059450

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21D6/00*(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, C21D6/00, 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	1996-2010
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.
X	JP 2003-253402 A (Independent Administrative Institution National Institute for Materials Science), 10 September 2003 (10.09.2003), claims; paragraphs [0003], [0012] to [0013]; examples; tables 1, 2; fig. 1 (Family: none)	1-7
X	JP 2009-102728 A (JFE Steel Corp.), 14 May 2009 (14.05.2009), claims; paragraphs [0001], [0017], [0049], [0067]; examples (Family: none)	1-7

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

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
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"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 August, 2010 (04.08.10)	17 August, 2010 (17.08.10)

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

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/059450

C (Continuation).   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2004-76154 A (JFE Steel Corp.), 11 March 2004 (11.03.2004), claims; paragraphs [0001], [0038] & EP 1553198 A1	1-5
X	JP 11-236650 A (Kawasaki Steel Corp.), 31 August 1999 (31.08.1999), claims; paragraphs [0023], [0025], [0040]; examples (Family: none)	1-5

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2007332412 A **[0005]**