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(71) Applicants:
- **BABCOCK-HITACHI KABUSHIKI KAISHA**
  1-Chiyoda-ku
  Tokyo 101-0021 (JP)
- **Fujita, Toshio**
  Bunkyo-ku, Tokyo 1130023 (JP)

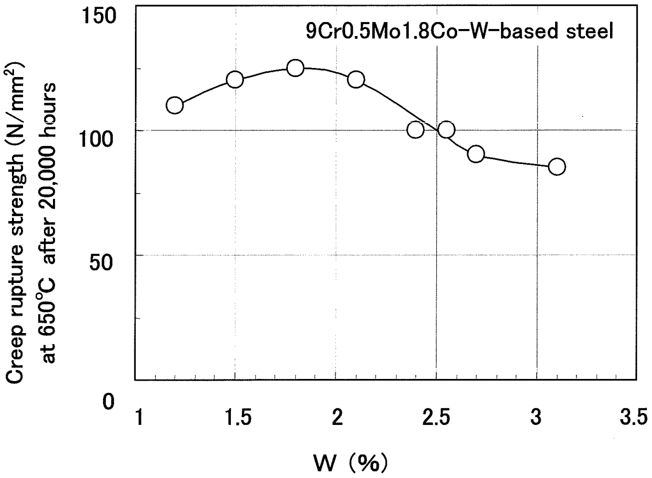
(72) Inventors:
- **FUJITA, Toshio**
  Bunkyo-ku Tokyo 1130023 (JP)
- **SATO, Takashi**
  Kure-shi, Hiroshima 7378508 (JP)
- **TAMURA, Kohji**
  Kure-shi, Hiroshima 7378508 (JP)

(74) Representative: **TBK-Patent**
Bavariaring 4-6
80336 München (DE)

(54) FERRITIC HEAT-RESISTANT STEEL

(57) Disclosed is a ferritic heat-resistant steel which has the following chemical composition (by weight) : C: 0.01-0.10%; Si: 0.30-1.0%; P: 0.02 or less; S: 0.010% or less; Mn: 0.2-1.2%; Ni: 0.3% or less; Cr: 8.0-11.0%; Mo: 0.1-1.2%; W: 1.0-2.5%; V: 0.10-0.30%; Nb: 0.02-0.12%; Co: 0.01-4.0%; N: 0.01-0.08%; B: not less than 0.001% and less than 0.010%; Cu: 0.3% or less; and Al: 0.010% or less, provided that the chemical composition satisfies the following equations: Mo (%) + 0.5xW(%) = 1.0-1.6, and C(%) + N(%) = 0.02-0.15%, and which comprises a tempered martensite single-phase tissue produced by thermal refining. The steel shows an excellent long-term creep rupture strength even when used at a steam temperature around 650˚C and also has excellent steam oxidizability. When the value represented by the equation: Al(%) + 0.1xNi(%) is adjusted to 0.02 or less, the creep strength can be more stabilized.

FIG.2



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Description

Technical Field

[0001] The present invention relates to a ferritic heat-resistant steel, and more specifically, to a high-strength steel for boiler steel pipes suitable for an ultra supercritical pressure thermal power plant with improved power generation efficiency.

Background Art

[0002] Recently, in thermal power plants, the temperature and pressure of steam conditions have been raised for improvement in plant efficiency in view of global environmental issues such as CO_2 emissions reduction. Now, plants which can raise the steam temperature from the current maximum main steam temperature around 600 °C to 650 °C, ultimately, to 700 °C have been developed and studied domestically and internationally. According to such a steam temperature rise, a heat-resistant steel with high creep rupture strength is required at high-temperature and pressure resistant portions of a boiler. Therefore, for heat transfer pipes of a boiler, an austenitic heat-resistant steel having excellent corrosion resistance and creep rupture strength has been increasingly used.

[0003] On the other hand, in the case of a thick pipe with a large diameter like a header or piping, when this austenitic heat-resistant steel is used, the linear expansion coefficient becomes higher and the heat transfer coefficient becomes smaller than those of the ferritic heat-resistant steel. Therefore, when the plant starts or stops, a great thermal stress is applied to these header and piping and the header and piping are easily damaged due to thermal fatigue. In addition, the increase in material cost and process cost causes an economic problem. Therefore, development of new ferritic heat-resistant steel with high creep rupture strength and excellent corrosion resistance has been demanded. As an example of such ferritic heat-resistant steel, a material obtained by increasing the proportion of Cr in a conventional steel of 9% Cr and 1% MoNbV and adding alloy elements of W and Co, etc. , has been proposed (for example, Japanese Patent No. 2528767).

[0004] However, for example, when a ferriticheat-resistant steel is used for a boiler that will reach a steam temperature around 650 °C, the ferritic heat-resistant steel contains many W and other alloy elements, so that during long-term use, aggregation and coarsening of fragile intermetallic compounds or carbide occur. Therefore, it has been found that the creep rupture strength lowers during long-term use for several tens of thousands of hours or longer. Particularly, at a high temperature around 650 °C much higher than 600 °C, so-called fluting that involves sudden lowering in creep strength after about several tens of thousands of hours is a great obstacle in the development of a high-Cr steel (for example, Non-Patent Document 1).

[0005] These header and piping are exposed for a long time to high-temperature steam that is an internal fluid of a boiler steel pipe. When the high-Cr ferrite steel is used at a high temperature around 650 °C, production of oxidized scale due to steam becomes pronounced (for example, Proceedings of Workshop, pp. 153 described above), so that the scale growth and exfoliation, and scale scattering to the downstream also come into question. To solve these problems, a special method by addition of noble metals (Non-Patent Document 2) has also been proposed, however, this greatly increases the material cost, so that it has not been made practicable.

[0006] According to Non-Patent Document 3, improvement in creep rupture strength by adding components of V, Nb, N, Mo, W, and B, etc. , to high-chromium steel containing 9 to 12% of chromium is described. Some of the high-chromium steels of the Non-Patent Document 3 realize creep rupture strength at a temperature around 600 °C during long-term use, however, the creep rupture strength at a temperature around 650 °C is much lower than that at 600 °C.

[0007] The inventors previously developed a ferritic heat-resistant steel with high creep rupture strength at a temperature around 650 °C and applied for a patent (Japanese Laid-Open Patent Publication No. 2005-23378).

Patent Document 1: Japanese Patent Publication No. 2528767 Patent Document 2: Japanese Laid-Open Patent Publication No. 2005-23378
Non-Patent Document 1: R. Viswanathan et al., "Materials for Ultrasupercritical Coal-fired Power Plant Boilers" (p. 146-157); R. Blum et al., "Materials Development in Thermie Project for 700°C USC Plant" (pp. 158-176), Committee of the 8th Ultra-Steel Workshop, Steel Research Center, National Institute for Materials Science, July 22, 2004
Non-Patent Document 2: Haruyama et al., "Influence of Pd addition on the steam oxidation behavior of 9Cr ferrite steel, " Material and Process, The Iron and Steel Institute of Japan, March 2003, Vol. 16, No. 3, p. 648
Non-Patent Document 3: Gabrel J et al., "Status of development of the VM12 steel for tubular applications in advanced power plants," Proceedings of the 8th Liége Conference Part II, Materials for Advanced Power Engineering 2006, Forschungszentrum Jülich GmbH, September 2006, p. 1065-1075

Disclosure of the Invention

Problem to be Solved by the Invention

[0008] The ferritic heat-resistant steel described in Patent Document 2, developed earlier by the present inventors, has high creep rupture strength at a temperature around 650 °C, however, its long-term strength is insufficient, and there is room for improvement in steam oxidation resistance (improvement in property of oxidation due to steam inside the pipe). Thus, the conventionally proposed alloys are insufficient in property as a material to be used at a temperature around 650 °C. Further, a ferritic heat-resistant steel which has high creep rupture strength at a temperature around 650 °C, and maintains stably the strength for a long period of time, and is excellent in steam oxidation resistance has been demanded.

[0009] An object of the present invention is to provide a high-strength ferritic heat-resistant steel which is excellent in long-term creep rupture strength and steam oxidation in the case where it is used at a temperature around 650 °C in comparison to conventional materials.

Means for Solving the Problem

[0010] The object of the present invention is achieved by the following solution means.

[0011] A first aspect of the invention provides a ferritic heat-resistant steel which has the following chemical composition (by weight) : carbon (C) : 0.01-0.10%; silicon (Si): 0.30-1.0%; phosphorus (P) : 0.020% or less; sulfur (S) : 0.010% or less, manganese (Mn): 0.2-1.2%; nickel (Ni): 0.3% or less; chromium (Cr) : 8.0-11.0%, molybdenum (Mo) : 0.1-1.2%; tungsten (W): 1.0-2.5%; vanadium (V): 0.10-0.30%; niobium (Nb): 0.02-0.12%; cobalt (Co) : 0.01-4.0%; nitrogen (N): 0.01-0.08%; boron (B) : not less than 0.001% and not more than 0.010%; copper (Cu): 0.3% or less; aluminum (Al): 0.010% or less, provided that the amount of (Mo%+0.5×W%) is limited to 1.0-1.6, and the amount of (C%+N%) is limited to 0.02-0.15%, and which comprises a tempered martensite single-phase tissue produced by thermal refining.

[0012] A second aspect of the invention provides the ferritic heat-resistant steel according to the first aspect, which has the chemical composition in which the amount of (Al%+0,1×Ni%) is limited to 0.02% by weight or less.

[0013] A third aspect of the invention provides the ferritic heat-resistant steel according to the first or second aspect, containing 30% by weight or less of δ ferrite.

[0014] Carbon (C) is an element important for forming carbide (M23C6, M6C, M7C3, etc.) that contributes to strengthening of a high-Cr ferritic heat-resistant steel. Conventional practical steels require about 0.1-0.12% of carbon, however, if the carbon content exceeds 0.10%, it promotes aggregation and coarsening and lowers the creep rupture strength, so that in the present invention, the carbon content is set to 0.10% or less to stabilize long-term creep strength. The lower the C content, the higher the creep rupture strength, however, if the C content is less than 0.01%, the toughness deteriorates, so that the C content is set to 0.01-0.10% as a practical steel. Fine control of the C content requires advanced techniques in steelmaking, however, in particular, by reducing the C content from about 0.1% of a conventional steel to 0.08% or less, the Ac1 point (transformation point) is greatly raised, and the long-term creep rupture strength can be further improved.

[0015] Silicon (Si) was an element necessary as a deoxidizing agent for producing steel. However, recently, vacuum deoxidation has become possible, and it becomes possible to obtain a low-Si steel by vacuum deoxidation, and vacuum deoxidation has also been used for obtaining a high-Cr heat-resistant steel. Si is an element that improves the oxidation resistance, and to obtain steam oxidation resistance necessary as a 600°C-class boiler material, at least 0.30% of Si is necessary. To obtain steam oxidation resistance sufficient as a 650°C-class boiler material, it is generally preferable that the scale thickness is 200 micrometers or less.

[0016] On the other hand, if a large amount of Si over 1.0% is added, production of Laves phase of tungsten (W), etc. are promoted, and ductibility is lowered due to grain boundary segregation, etc. Therefore, when attaching importance to the creep strength, the Si content tends to be made low, and this is an obstacle in using the steel at a temperature around 650 °C.

[0017] However, in the present invention, it was found that according to the effect of reducing M23C6 carbide aggregation and coarsening by aluminum (Al) described later, high creep strength could be obtained even if the Si content was increased. Therefore, to obtain steam oxidation resistance sufficient as a 650 °C-class boiler material, the Si content is set to 0.30-1.0%. When emphasizing the ductibility of steel, the Si content is set to 0.30-0.80% (Fig. 1) since a high Si content lowers the ductibility.

[0018] 0.2% or more of manganese (Mn) is necessary as a deoxidizing agent, and at the same time, manganese is useful as an austenite forming element for restraining production of δ ferrite. However, if it is added by an amount over 1.2%, the Ac1 transformation point lowers, and the creep strength lowers. Therefore, the Mn content is limited to 0.2-1.2%.

[0019] Phosphorus (P) and sulfur (S) are low-melting point elements, so that if their contents are high, they harmfully influence the creep rupture strength, so that the lower the contents of these the better. However, it is difficult to completely remove P and S, and if their contents are extremely low, it causes an increase in material cost, so that it is not necessary to make the contents extremely low, and P is limited to 0.020% or less and S is limited to 0.010% or less.

[0020] Chromium (Cr) is an important element that provides a steel with oxidation resistance and steam oxidation resistance, however, if its content is more than 11%, it forms δ ferrite and lowers the toughness, and precipitation of M23C6 carbide, etc., and growth coarsening due to the precipitation become pronounced and lower the long-term creep strength. Therefore, the Cr content must be set to 11% or less. In the present invention, the steam oxidation resistance is improved by adding a large amount of Si, however, its effect is insufficient if the Cr content is less than 8%, so that the Cr content is set to 8 to 11%.

[0021] Molybdenum (Mo) is an effective element for increasing the creep rupture strength by fine precipitation of carbide. Therefore, the molybdenum content necessary for strengthening by precipitation of carbide is at least 0.1% or more, however, if molybdenum over 1. 2% is added and 0.1% ormore of W is contained, δ ferrite is produced, and aggregation and coarsening of M23C6 carbide containing Mo occur and lead to creep strength lowering. Therefore, the Mo content is set to 0.1 to 1.2%.

[0022] Tungsten (W) is an element most important for increasing the creep rupture strength of this steel by precipitation strengthening of carbide and solution hardening in base metal. It had been conventionally said that addition of about 3% of W is effective, and if 4% or more is added, M23C6 carbide and Laves phase (Fe2W) including W aggregate and coarsen and lower the creep rupture strength. However, it was found that even an addition of about 3% lowered the long-term creep rupture strength, so that the content is reduced to be low and is set to 2.5% or less with which creep rupture strength of 100 N/mm^2 or more at 650°C after 20,000 hours is obtained (Fig. 2). If the content is less than 1.0%, from the data shown in Fig. 2, it is presumed that the creep rupture strength cannot be improved, so that the content is set to 1.0 to 2.5%. W influences the creep strength in combination with Mo, so that the content of W only is regulated, and the value of (Mo%+0.5×W%) is set to 1.0 to 1. 6% effective for improvement in creep rupture strength.

[0023] Cobalt (Co) is an austenite forming element, and prevents production of δ ferrite without greatly lowering the Ac1 transformation point, so that it is an important element. The amount of δ ferrite changes depending on quantities of other alloy elements to be added, however, by adding at least 0.01%, and 4.0% at most of cobalt (Co), production of δ ferrite can be sufficiently prevented.

[0024] Vanadium (V) is an element that forms carbide of V and effectively increases the creep rupture strength at a relatively small amount, and at least 0.10% must be added for forming carbide of V. However, if the content is more than 0.30%, the carbide of V aggregates and coarsens and lowers the creep rupture strength, so that the content is set to 0.10 to 0.30%.

[0025] Niobium (Nb) forms Nb (C, N) (carbonitride of niobium) that is stable carbonitride and can increase the creep rupture strength even with supply of a small amount, however, if the content is more than 0.12%, it is not good for long-term strength although short-term strength is improved. If it is less than 0.02%, precipitated Nb (C, N) is in short supply and strengthening is insufficient, so that the content is set to 0.02 to 0.12%.

[0026] Nitrogen (N) increases the creep rupture strength by precipitation strengthening by forming nitride of V and solution hardening of itself. However, nitrogen over 0.08% forms too much nitride and causes aggregation and coarsening, and lowers the creep rupture strength, so that the nitrogen content is set to 0.08% or less. If the nitrogen content is less than 0.01%, the effect of increasing the creep rupture strength is insufficient, so that the nitrogen content is set to 0.01 to 0.08%. The creep rupture strength based on N has a close correlation with the amount of C, and when (C%+N%) is limited to 0.02 to 0.15%, the highest creep rupture strength is obtained.

[0027] Nickel (Ni) is an element effective for improving the toughness and restraining production of δ ferrite, and in a conventional boiler steel, it is added by about 0.5% without special limitation. However, it was found that addition of nickel greatly lowered the Ac1 transformation point and harmfully influenced the long-term creep strength, so that in view of the creep rupture strength, it is preferable that the nickel content is lowered to be not more than 0.1%. However, for this, at the time of steelmaking, the amount of nickel to be mixed from scrap steel, the furnace wall, and ladle, etc., must be minimized, and this increases the steelmaking technical limitations, so that the upper limit of the nickel content is set to 0.3% as a practical steel. Ni may not be contained.

[0028] Aluminum (Al) is conventionally added as a deoxidizing agent and a crystal grain refining agent. However, excessive addition of 0.010% or more of Al captures nitrogen that is effective for improving the creep strength as Al nitride, and is incrassated on the surface of M23C6 carbide and promotes diffusion of Cr, and accelerates aggregation and coarsening of M23C6 carbide. The present inventors also found that when the Al content exceeded a predetermined value, even if it was a very small amount, it greatly lowered the long-term creep strength after several tens of thousands of hours at a temperature around 650 °C. In a conventional practical steel, the toughness is improved by adding Al up to about 0.03%, however, in the heat-resistant steel of the present invention, by reducing the Al content to 0.01% or less, the long-term creep strength at 650 °C is greatly increased.

[0029] It was conventionally very difficult to reduce the Al content to such an extremely low level. However, recently, it became possible to manufacture an extremely-low level Al steel by means of vacuum carbon deoxidation method. The increase in Si content in the steel of the present invention is also one of the features, and even if the deoxidation effect of Al is lost, the deoxidation effect of Si can be used, so that the amount of oxygen in the steel can be reduced. Al may not be contained.

[0030] Fig. 3 shows the creep rupture strength at 650 °C in materials with variously changedAl quantities and Ni quantities on the vertical axis, and the Al quantities on the horizontal axis. As creep rupture strength at 650 °C after 100,000 hours, to obtain about 100 N/mm^2, strength over 100 N/mm^2 after 20,000 hours is required. Therefore, for example, when the Ni amount is about 0.3%, the Al amount is reduced to 0.005% or less. When the Ni amount is 0.1% or less, the allowable range of the Al amount can be widened.

[0031] The steel of the present invention has a feature in that Al and Ni that are elements especially harmful for stabilizing the creep strength are reduced, and reduction of these is essential. The same test results as in Fig. 3 are shown in Fig. 4 by rewriting the Al amount on the horizontal axis into Al amount + (0.1×Ni amount). From these test results, as a range of the Al amount and Ni amount with which creep rupture strength over 100 N/mm^2 is reliably obtained, (Al%+0.1×Ni%) is limited to 0.02% or less.

[0032] Copper (Cu) has an effect of restraining production of δ ferrite when mixed as an impurity into copper as in the case of Co. However, mixture of Cu may lower the long-term creep rupture strength at a temperature of 600 °C or more, so that it is limited to 0.3% or less. Cu may not be contained.

[0033] Boron (B) is a grain boundary strengthening element (element that strengthens crystal grain boundaries), and remarkably increases the creep rupture strength even at a small amount. It dissolves into M23C6 carbide and restrains aggregation and coarsening of M23C6 carbide to increase the creep rupture strength, so that at least 0.001% of B is added. However, if 0.010% or more of B is added, weldability of the steel is greatly deteriorated, so that the additive amount of B is set to less than 0.10%.

[0034] The major chemical component ranges of the ferritic heat-resistant steel of the present invention are as described above, however, it may contain amounts of the following elements less than the contents described below in units of percent by weight as impurities.

[0035] Ta<0.2%, Ti<0.1%, Zr<0.2%, La<0.1%, Ce<0.1%, Pd<0.2%, Re<0.5%, Hf<0.3%

[0036] These elements also have the effect of increasing the strength as follows:

Ta: forms TaC and strengthens the base metal.
Ti: forms TiC and strengthens the base metal.
Zr: forms ZrC and strengthens the base metal.
La, Ce: lowers the proportion of oxygen in the steel and increases the creep rupture strength.
Pd: improves the creep rupture strength and oxidation resistance (steam oxidation resistance).
Re: strengths the base metal.
Hf: forms HfC and strengthens the base metal.

[0037] The ferriticheat-resistant steel of the present invention is normalized at a temperature of 1, 050 to 1, 100 °C and tempered at a temperature of 750 to 800 °C after molten and forged, and then used as a tempered martensite tissue. From the standpoint of obtaining toughness, a single phase of tempered martensite tissue is desirable. However, when it is used as a high-temperature boiler member, in the case where some degree of lowering in toughness is permitted, it is allowed that the amounts of ferrite forming elements such as Cr and Si, etc., are set to be comparatively large in the limited ranges described above to precipitate δ ferrite. In view of toughness and creep rupture strength, it is known that a volume ratio of δ ferrite over 35% lowers the strength and toughness, so that the volume ratio is limited to 30% or less.

[0038] The steel of the present invention is characterized by containing C reduced to the half, lowered Al and Ni, and increased Si in comparison to the idea of the conventional high-Cr heat-resistant steel. By the compound effect of these, the stability of the creep strength is improved for the first time, and at the same time, the oxidation resistance (steam oxidation resistance) is improved, whereby a high-Cr ferritic heat-resistant steel usable up to 650 °C is achieved. It is possible to employ various manufacturing methods according to the purpose of use of the steel, and the steel can be used not only as a steel pipe but also as a steel sheet.

[0039] In addition, the ferritic heat-resistant steel of the present invention has creep rupture strength remarkably improved in comparison to the conventional ferritic heat-resistant steel, and has strength and ductibility stable even during long-term use. Therefore, by applying this steel to a high-temperature pressure resistant portion of an ultra supercritical pressure boiler, the steam temperature can be raised to about 650 °C, and the plant efficiency of a thermal power plant can be improved. Further, growth and exfoliation of steam oxidized scale and damage of devices due to scattering of steam oxidized scale can be reduced. Therefore, the durability of the plant is also improved, and a remarkable effect in fuel consumption reduction such as coal and CO_2 emissions reduction in the thermal power plant can be obtained.

Brief Description of the Drawings

[0040]

Fig. 1 is a diagram showing results of the oxidation test using steam when the Si amount was changed in 9CrWCo-based steel of the present invention;

Fig. 2 is a diagram showing results of the creep rupture test when the W amount was changed in the 9CrWCo-based steel of the present invention;

Fig. 3 is a diagram showing results of the creep rupture test by showing the Al amount on the horizontal axis when the Al and Ni amounts were changed in the 9CrWCo-based steel of the present invention; and

Fig. 4 is a diagram of the same test results as of Fig. 3 by rewriting the Al amount on the horizontal axis into (Al+0.1×Ni) amount.

Best Mode for Carrying Out the Invention

[0041] Hereinafter, examples / embodiments of the present invention will be described by using actual examples.

[0042] The heat-resistant steels having the chemical compositions shown in Table 1 of the present examples and comparative steels were molten in a vacuum induction melting furnace, and forged into 50kg ingots, respectively. The comparative steel A is nominal 9Cr1MoNbV steel, comparative steels B and C are nominal 9Cr0.5Mo1.8WNbV steels, and all of these have been made practicable as boiler steels. After forming steel sheets with a thickness of 20 millimeters by hot forging, the steel sheets were normalized at 1,050 °C for 60 minutes and tempered at 780 °C for 60 minutes, and then subjected to a creep rupture test. In addition, small-sized sheet-like test specimens were processed from the steel sheets, and subjected to an oxidation test by using steam at 650 ° C.

[Table 1]

(wt%)

	C	Si	Mn	P	S	Cr	Mo	W	V	Nb	Ni
Steel A of the present invention	0.043	0.51	0.50	0.003	0.001	8.9	0.45	1.80	0.19	0.051	0.005
Steel B of the present invention	0.048	0.43	0.49	0.002	0.001	9.0	0.47	1.71	0.20	0.057	0.008
Steel C of the present invention	0.075	0.40	0.48	0.003	0.001	9.2	0.50	1.90	0.18	0.060	0.007
Steel D of the present invention	0.019	0.60	0.52	0.003	0.001	9.5	0.45	1.81	0.21	0.059	0.010
Steel E of the present invension	0.012	0.75	0.51	0.002	0.001	8.8	0.40	2.00	0.18	0.050	0.015
Steel F of the present invention	0.035	0.55	0.50	0.002	0.001	9.0	0.30	2.02	0.22	0.055	0.010
Comparative steel A	0.100	0.40	0.40	0.008	0.004	8.9	1.02		0.21	0.058	0.28
Comparative steel B	0.110	0.30	0.35	0.010	0.006	9.0	0.48	1.81	0.20	0.062	0.22
Comparative steel C	0.082	0.07	0.42	0.008	0.005	9.1	0.52	1.76	0.19	0.053	0.20

(continued)

	Co	N	B	Al	Cu	Mo+0.5W	C+N	0.1Ni+Al
Steel A of the present invention	1.81	0.046	0.006	0.0010	0.005	1.350	0.089	0.0015
Steel B of the present invention	1.91	0.043	0.005	0.0008	0.005	1.325	0.091	0.0016
Steel C of the present invension	1.70	0.05	0.007	0.0012	0.005	1.450	0.125	0.0019
Steel D of the present invention	1.75	0.062	0.006	0.0009	0.004	1.355	0.081	0.0019
Steel E of the present invention	1.82	0.070	0.005	0.0010	0.005	1.400	0.082	0.0025
Steel F of the present invention	1.75	0.055	0.006	0.0009	0.004	1.310	0.090	0.0019
Comparative steel A	0.00	0.048	0.000	0.007	0.03	1.02	0.15	0.0350
Comparative steel B	0.00	0.051	0.006	0.005	0.05	1.39	0.16	0.0270
Comparative steel C	0.00	0.043	0.006	0.006	0.04	1.40	0.13	0.0260

[0043] 100,000-hour creep rupture strengths at 600°C and 650°C estimated by plotting the results of the creep rupture test of the steels of the examples of the present invention and the comparative steels by temperature as a stress-rupture time diagram and extrapolating these on the long-term side were shown in Table 2.

[Table 2]

	10^5h creep rupture strength (N/mm^2)	
	600°C	650°C
Steel A of the present invention	182	105
Steel B of the present invention	185	103
Steel C of the present invention	188	107
Steel D of the present invention	185	105
Steel E of the present invention	180	102
Steel F of the present invention	185	106
Comparative steel A	92	48
Comparative steel B	135	68
Comparative steel C	140	70

[0044] The steels A and B of the present invention have creep rupture strengths at 650°C after 100,000 hours which are about twice the creep rupture strength of the comparative steel A that was used as a conventional boiler heat-resistant steel for many years, and are about 1. 5 times the creep rupture strength of high-strength comparative steels

B and C, so that A and B have revolutionary strengths. The results of the oxidation test using steam conducted for the steels of the examples and comparative steels are shown in Table 3, and the results show that the growth of oxidized scale due to steam is restrained with respect to the comparative steels, so that it is considered possible that the steels of the present invention are sufficiently usable at a steam temperature of 650 °C.

[Table 3]

	Water vapor oxidized scale thickness (μm) (650°C, 2000h)
Steel A of the present invention	120
Steel B of the present invention	150
Steel C of the present invention	150
Steel D of the present invention	115
Steel E of the present invention	80
Steel F of the present invention	120
Comparative steel A	160
Comparative steel B	200
Comparative steel C	300

[0045] In the present invention, the experiments were performed by setting the normalizing temperature to 1,050 °C, however, a higher creep rupture strength can be obtained by raising the normalizing temperature. However, at the same time, the toughness lowers, so that the normalizing temperature is preferably in the temperature range up to 1,100 °C.
[0046] The ferriticheat-resistant steel of the present invention is suitable, in particular, as a material of a header and a main steam pipe of a superheater of an ultra supercritical pressure boiler with a steam temperature around 650 °C. The ferritic heat-resistant steel of the present invention can be used not only as a thick and large-diameter pipe material but also as a small-diameter heat transfer pipe material.

Industrial Applicability

[0047] The ferriticheat-resistant steel of the present invention is highly industrially applicable not only as a material of a header and a main steam pipe of a superheater and a thick and large-diameter pipe material of an ultra supercritical pressure boiler with a steam temperature around 650 °C but also as a small-diameter heat transfer pipe material.

Claims

1. A ferritic heat-resistant steel which has the following chemical composition (by weight): carbon (C): 0.01-0.10%; silicon (Si): 0.30-1.0%; phosphorus (P): 0.020% or less; sulfur (S): 0.010% or less, manganese (Mn): 0.2-1.2%; nickel (Ni): 0.3% or less; chromium (Cr): 8.0-11.0%, molybdenum (Mo): 0.1-1.2%; tungsten (W): 1.0-2.5%; vanadium (V): 0.10-0.30%; niobium (Nb) : 0.02-0.12%; cobalt (Co) : 0.01-4.0%; nitrogen (N) : 0.01-0.08%; boron (B) : not less than 0.001% and not more than 0.010%; copper (Cu): 0.3% or less; aluminum (Al): 0.010% or less, provided that the amount of (Mo%+0.5xW%) is limited to 1.0-1.6, and the amount of (C%+N%) is limited to 0.02-0.15%, and which comprises a tempered martensite single-phase tissue produced by thermal refining.

2. The ferritic heat-resistant steel according to Claim 1, having the chemical composition in which the amount of (Al%+0.1×Ni%) is limited to 0.02% by weight or less.

3. The ferritic heat-resistant steel according to Claim 1 or 2, containing 30% by weight or less of δ ferrite.

FIG.1

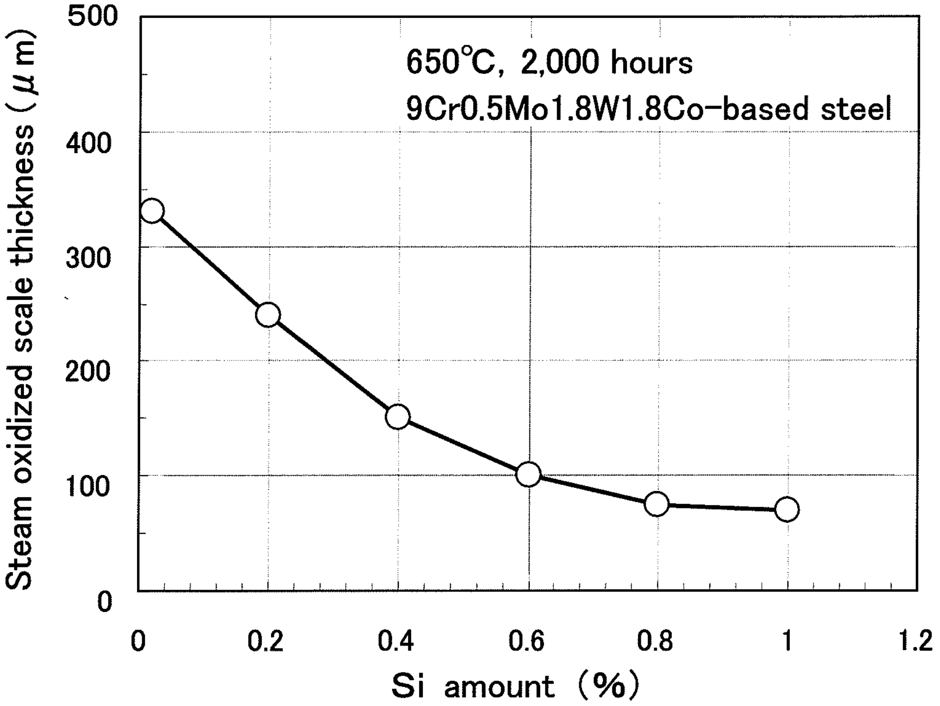

650°C, 2,000 hours
9Cr0.5Mo1.8W1.8Co-based steel
Steam oxidized scale thickness (μm)
500
400
300
200
100
0
0
0.2
0.4
0.6
0.8
1
1.2
Si amount (%)

FIG.2

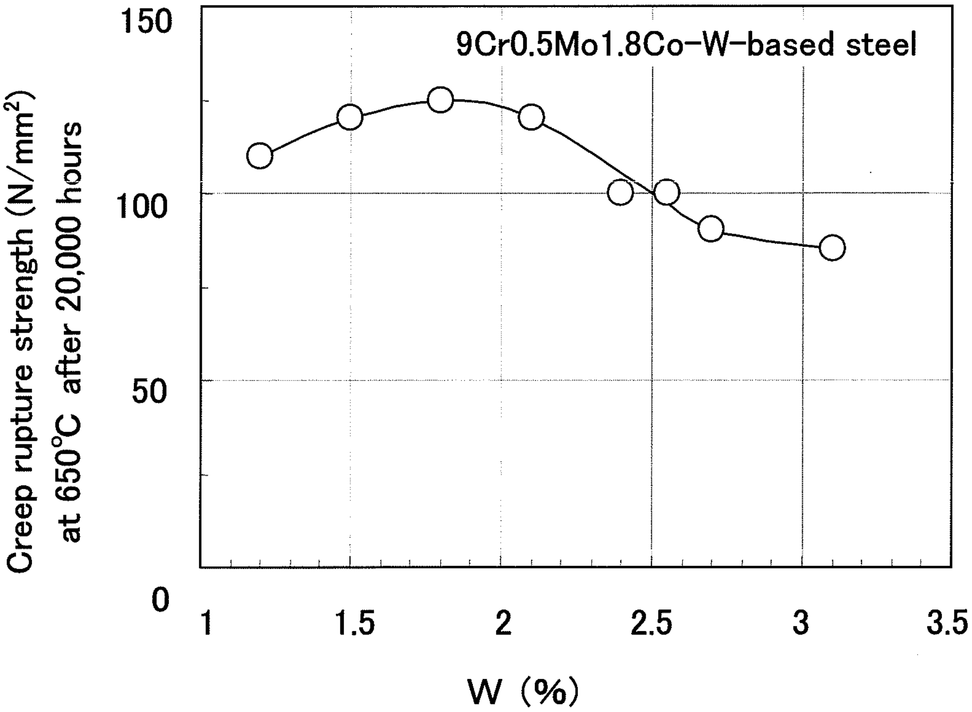

9Cr0.5Mo1.8Co-W-based steel
Creep rupture strength (N/mm²) at 650°C after 20,000 hours
150
100
50
0
1
1.5
2
2.5
3
3.5
W (%)

FIG.3

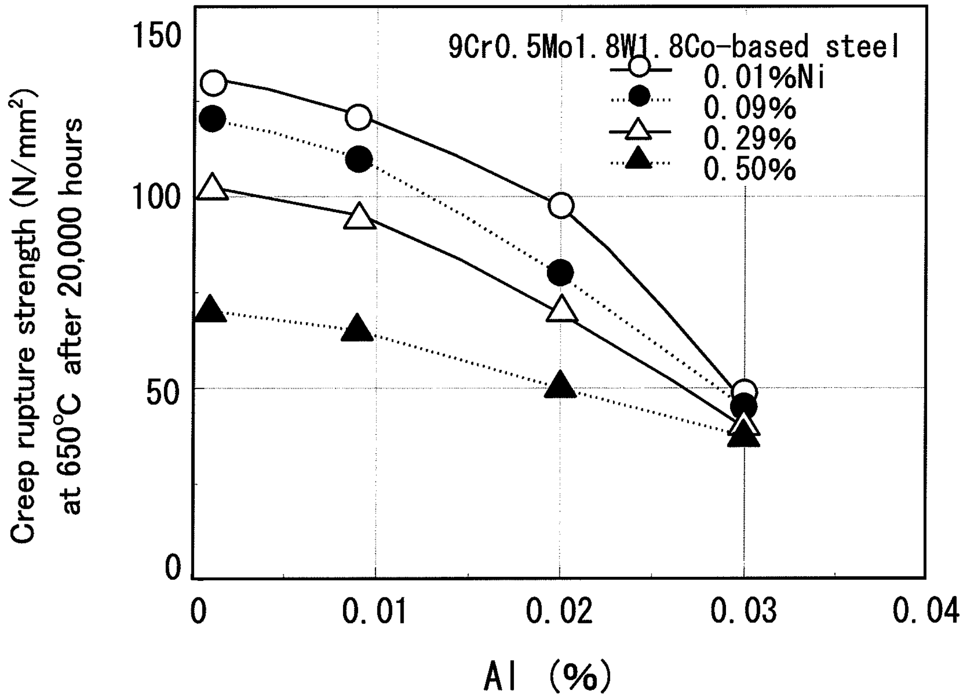
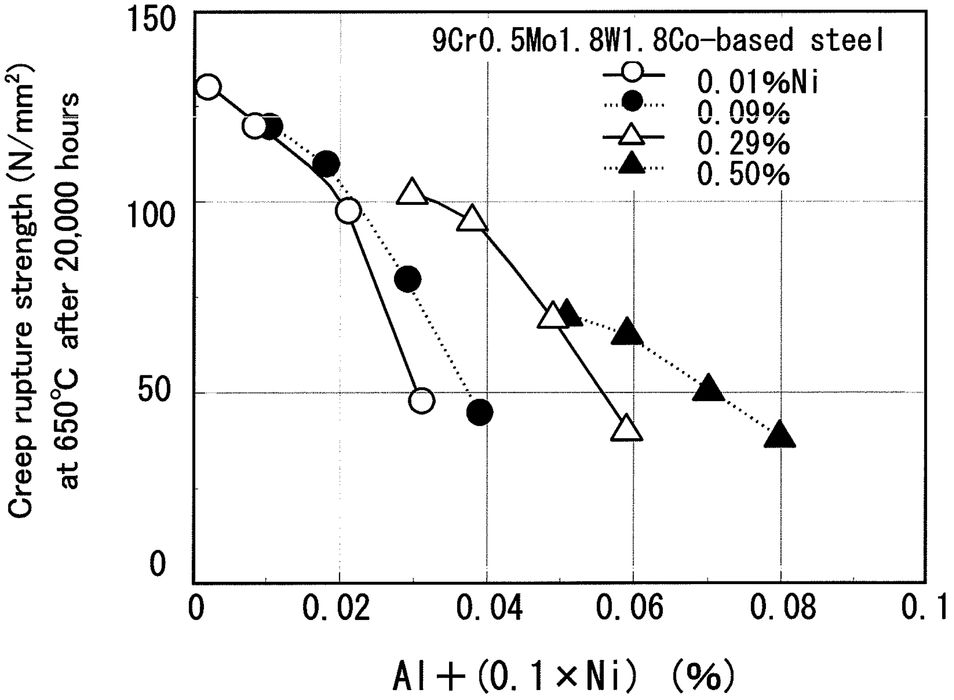

9Cr0.5Mo1.8W1.8Co-based steel
0.01%Ni
0.09%
0.29%
0.50%
Creep rupture strength (N/mm^2) at 650°C after 20,000 hours
150
100
50
0
0
0.01
0.02
0.03
0.04
Al (%)

FIG.4


9Cr0.5Mo1.8W1.8Co-based steel
0.01%Ni
0.09%
0.29%
0.50%
Creep rupture strength (N/mm^2) at 650°C after 20,000 hours
150
100
50
0
0
0.02
0.04
0.06
0.08
0.1
Al+(0.1×Ni) (%)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/051968

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(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, 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	1996-2007
Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2002-180208 A (Babcock-Hitachi Kabushiki Kaisha), 26 June, 2002 (26.06.02), Claims; Par. Nos. [0001], [0021] to [0024] (Family: none)	1-3
A	JP 2002-235154 A (Sumitomo Metal Industries, Ltd.), 23 August, 2002 (23.08.02), Claims; Par. Nos. [0001], [0037], [0043], [0044] (Family: none)	1-3
A	JP 2002-241903 A (Sumitomo Metal Industries, Ltd.), 28 August, 2002 (28.08.02), Claims; Par. Nos. [0001], [0037], [0038] (Family: none)	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 12 March, 2007 (12.03.07)	Date of mailing of the international search report 20 March, 2007 (20.03.07)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

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- Materials Development in Thermie Project for 700°C USC Plant. **R. BLUM et al.** Committee of the 8th Ultra-Steel Workshop. National Institute for Materials Science, 22 July 2004, 158-176 **[0007]**
- Influence of Pd addition on the steam oxidation behavior of 9Cr ferrite steel. **HARUYAMA et al.** Material and Process. The Iron and Steel Institute of Japan, March 2003, vol. 16, 648 **[0007]**
- Status of development of the VM12 steel for tubular applications in advanced power plants. **GABREL J et al.** Proceedings of the 8th Liége Conference Part II, Materials for Advanced Power Engineering 2006. Forschungszentrum Jülich GmbH, September 2006, 1065-1075 **[0007]**