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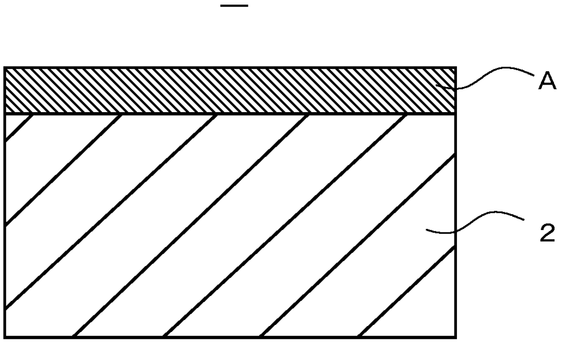
(54) FERRITIC HEAT-RESISTANT STEEL AND FERRITIC HEAT TRANSFER MEMBER

(57) This invention provides a ferritic heat transfer member (4) that is excellent in heat transfer characteristics and steam oxidation resistance properties, and a heat resistant ferritic steel (1) that is capable of realizing the ferritic heat transfer member (4). The heat resistant ferritic steel (1) includes a base material (2), and an oxidized layer A on the surface of the base material (2). The base material (2) has a chemical composition containing, in mass%: C: 0.01 to 0.3%, Si: 0.01 to 2.0%, Mn: 0.01 to 2.0%, Cr: 7.0 to 14.0%, N: 0.005 to 0.15%, and sol. Al: 0.001 to 0.3%, and one or more types of element selected from a group consisting of Mo, Ta, W and Re in a total amount of 0.5 to 7.0%, with the balance being Fe and impurities. An oxidized layer A includes a chemical composition containing, in mass%: Cr and Mn in a total amount of 20 to 45%, and one or more types of element selected from a group consisting of Mo, Ta, W and Re in a total amount of 0.5 to 10%.

FIG. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to a heat resistant steel and a heat transfer member, and more particularly relates to a heat resistant ferritic steel and a ferritic heat transfer member which are used under a high-temperature steam oxidation environment or the like.

BACKGROUND ART

[0002] From the viewpoints of suppressing the emission of CO_2 gas and economic efficiency, there is a demand to improve the power generation efficiency in thermal power plants. Therefore, there is a trend of increasing temperature and pressure of turbine steam in thermal power plants. Heat transfer members that are used in thermal power plants are exposed to high temperature and high pressure steam for long time periods. A heat transfer member is, for example, a boiler pipe. When exposed to high temperature steam for a long time period, oxide scale forms on the surface of the heat transfer member. If the steam oxidation resistance properties of the heat transfer member are insufficient, a large amount of oxide scale will form on the surface of the heat transfer member. The heat transfer member thermally expands and contracts due to starting and stopping of the boiler. Therefore, if a large amount of oxide scale is formed, the oxide scale will peel off and cause a blockage in the pipe. Furthermore, in a case where a large amount of oxide scale is formed, thermal conduction from outside the pipe to inside the pipe is inhibited by the oxide scale. Therefore, in order to maintain the temperature within the pipe at a high temperature, it will be necessary to apply a greater amount of heat from the outside. An increase in the temperature of the pipe causes a reduction in the creep strength. Therefore, high steam oxidation resistance properties are required for heat transfer members that are to be used in equipment such as thermal power boilers, turbines or steam pipes.

[0003] For example, a heat resistant austenitic steel and a heat resistant ferritic steel have been developed as materials that meet the demands regarding such properties. A heat resistant austenitic steel is, for example, a heat resistant austenitic steel having a Cr content of 18 to 25 mass%. A heat resistant ferritic steel is, for example, a heat resistant ferritic steel having a Cr content of 8 to 13 mass%. A heat resistant ferritic steel is less expensive than a heat resistant austenitic steel. A heat resistant ferritic steel also has a lower coefficient of thermal expansion and a higher thermal conductivity than a heat resistant austenitic steel. Therefore, a heat resistant ferritic steel is suitable as the material for a pipe in a thermal power plant. However, the Cr content of a heat resistant ferritic steel is lower than the Cr content of a heat resistant austenitic steel. Consequently, the steam oxidation resistance properties of the heat resistant ferritic steel are lower than the steam oxidation resistance properties of the heat resistant austenitic steel. Therefore, there is a need for a heat resistant ferritic steel that is excellent in steam oxidation resistance properties.

[0004] A heat resistant ferritic steel which inhibits oxide scale from falling off is disclosed, for example, in Japanese Patent Application Publication No. 11-92880 (Patent Literature 1). The heat resistant ferritic steel disclosed in Patent Literature 1 is a heat resistant ferritic steel containing a high Cr content that forms an oxide film on the surface during use, in which ultra-fine oxides having a diameter of 1 micron or less are formed at the boundary with the oxide film or in the vicinity thereof. Patent Literature 1 describes that, as a result, the adhesiveness between the oxide film and the base metal improves.

[0005] A method for improving steam oxidation resistance properties by increasing the Cr concentration at the surface of a heat resistant ferritic steel is disclosed, for example, in Japanese Patent Application Publication No. 2007-39745 (Patent Literature 2). According to the method disclosed in Patent Literature 2, powder particles containing Cr are caused to be carried at the surface of a heat resistant ferritic steel containing Cr, and a Cr-oxide layer having a high Cr concentration is formed on the ferritic steel surface under a high temperature. Patent Literature 2 describes that, according to this method, the (steam) oxidation resistance of a ferritic steel containing Cr can be easily and economically improved.

[0006] A method for improving oxidation resistance by forming a Cr-oxide coating on the surface of a heat resistant ferritic steel is disclosed, for example, in Japanese Patent Application Publication No. 2013-127103 (Patent Literature 3). An antioxidation treatment method for a heat resistant ferritic steel described in Patent Literature 3 includes subjecting a heat resistant ferritic steel containing chromium to a heat treatment under a gas atmosphere with a low oxygen partial pressure that consists of a gaseous mixture of carbon dioxide gas with an inert gas to thereby form an oxide coating that contains chromium on the surface of the heat resistant steel. Patent Literature 3 describes that, according to this method, the Cr concentration in the scale is increased, and the oxidation resistance of the heat resistant ferritic steel can be easily and economically improved.

[0007] A heat resistant ferritic steel in which steam oxidation resistance properties are improved by depositing Cr on the surface of the heat resistant ferritic steel is disclosed, for example, in Japanese Patent Application Publication No. 2009-179884 (Patent Literature 4). The heat resistant ferritic steel disclosed in Patent Literature 4 is a heat resistant ferritic steel that is used under a high-temperature and highpressure steam environment, and has on its surface a Cr oxide film which is formed by subjecting Cr that was deposited by a shot peening treatment using a shot material of powdery Cr to a pre-oxidizing treatment. Patent Literature 4 describes that, because a protection film of oxides with oxidation resistance is formed on the heat resistant steel prior to use in an oxidation environment, the steam oxidation resistance properties of the heat resistant ferritic steel are improved.

CITATION LIST

PATENT LITERATURE

[0008]

Patent Literature 1: Japanese Patent Application Publication No. 11-92880
Patent Literature 2: Japanese Patent Application Publication No. 2007-39745
Patent Literature 3: Japanese Patent Application Publication No. 2013-127103
Patent Literature 4: Japanese Patent Application Publication No. 2009-179884

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0009] However, even when the aforementioned techniques are used, in some cases the heat transfer characteristics and steam oxidation resistance properties of a heat transfer member cannot be increased sufficiently. As described above, various kinds of studies have been conducted regarding methods for suppressing the formation of oxide scale by forming Cr oxides on the surface of a heat transfer member. However, the thermal conductivity of Cr oxides is low. Therefore, if Cr oxides are formed, even though the steam oxidation resistance properties of the heat transfer member will increase, the heat transfer characteristics will decrease.

[0010] An objective of the present invention is to provide a ferritic heat transfer member that is excellent in heat transfer characteristics and steam oxidation resistance properties, and a heat resistant ferritic steel capable of realizing the ferritic heat transfer member.

SOLUTION TO PROBLEM

[0011] A heat resistant ferritic steel according to the present embodiment includes a base material, and an oxidized layer A on a surface of the base material. The base material has a chemical composition consisting of, in mass%, C: 0.01 to 0.3%, Si: 0.01 to 2.0%, Mn: 0.01 to 2.0%, P: 0.10% or less, S: 0.03% or less, Cr: 7.0 to 14.0%, N: 0.005 to 0.15%, sol. Al: 0.001 to 0.3%, one or more types of element selected from a group consisting of Mo: 0 to 5.0%, Ta: 0 to 5.0%, W: 0 to 5.0% and Re: 0 to 5.0%: 0.5 to 7.0% in total, Cu: 0 to 5.0%, Ni: 0 to 5.0%, Co: 0 to 5.0%, Ti: 0 to 1.0%, V: 0 to 1.0%, Nb: 0 to 1.0%, Hf: 0 to 1.0%, Ca: 0 to 0.1%, Mg: 0 to 0.1%, Zr: 0 to 0.1%, B: 0 to 0.1%, and rare earth metal: 0 to 0.1%, with the balance being Fe and impurities. The oxidized layer A includes a chemical composition containing, in mass%, Cr and Mn in a total amount of 20 to 45%. The oxidized layer A includes a chemical composition containing, in mass%, one or more types of element selected from a group consisting of Mo, Ta, W and Re in a total amount of 0.5 to 10%.

[0012] A ferritic heat transfer member according to the present embodiment includes a base material, and an oxide film on a surface of the base material. The base material has the chemical composition described above. The oxide film includes an oxidized layer B and an oxidized layer C. The oxidized layer B contains, in vol%, 80% or more in total of Fe_3O_4 and Fe_2O_3. The oxidized layer C is disposed between the oxidized layer B and the base material. A chemical composition of the oxidized layer C contains, in mass%, Cr and Mn: more than 5% to 30% in total, and one or more types of element selected from a group consisting of Mo, Ta, W and Re: 1 to 15% in total.

ADVANTAGEOUS EFFECTS OF INVENTION

[0013] The heat resistant ferritic steel and the ferritic heat transfer member according to the present embodiment are excellent in heat transfer characteristics and steam oxidation resistance properties.

BRIEF DESCRIPTION OF DRAWINGS

[0014]

FIG. 1 is a sectional view of a heat resistant ferritic steel according to the present embodiment.

FIG. 2 is a sectional view of a ferritic heat transfer member according to the present embodiment.

DESCRIPTION OF EMBODIMENTS

[0015] The present embodiment is described in detail hereunder while referring to the drawings. Identical or equivalent portions in the drawings are assigned the same reference symbols, and a description of such portions is not duplicated.

[0016] The present inventors conducted various studies regarding heat resistant ferritic steels and ferritic heat transfer members. As a result, the present inventors obtained the following findings.

(1) The heat resistant ferritic steel of the present embodiment can be utilized as a heat transfer member such as a boiler pipe. A heat transfer member such as a boiler pipe comes in contact with high temperature steam. If exposed to high temperature steam for a long time period, oxide scale forms on the surface of the heat transfer member. Oxide scale is composed of various oxides and impurities. The oxides are, for example, Fe_3O_4, Fe_2O_3 and Cr_2O_3. The oxide scale forms an oxide film on the surface of the heat transfer member.

(2) If the thermal conductivity of the oxide film is low, the heat transfer characteristics with respect to the transfer of heat from outside of the heat transfer member to inside of the heat transfer member decrease. Therefore, in order to maintain the inside of the heat transfer member at a high temperature, the necessity arises to apply a large amount of heat from the outside of the heat transfer member, and thus the heat transfer characteristics of the boiler decrease. In a case where a large amount of heat is applied from outside of the heat transfer member, the creep strength of the heat transfer member may also decrease in some cases. Therefore, it is preferable that the thermal conductivity of the oxide film is high. However, in a case where the thermal conductivity of the oxide film is too high, the heat of high temperature steam is transmitted to the inner surface of the heat transfer member. Because the transmitted heat promotes an oxidation reaction on the inner surface of the heat transfer member, a large amount of oxide scale arises on the inner surface of the heat transfer member. The large amount of oxide scale peels off from the inner surface of the heat transfer member. In a case where the heat transfer member is a pipe, the oxide scale that peeled off causes a blockage in the pipe. Therefore, it is necessary for the thermal conductivity of the oxide film to be controlled within a certain fixed range.

(3) If the thickness of the oxide scale is too thick, thermal conduction from the outside of the heat transfer member to the inside of the heat transfer member will be inhibited. Therefore, the heat transfer characteristics of the boiler will decrease. Accordingly, it is preferable that the thickness of the oxide film is as thin as possible.

(4) Among the aforementioned oxides, Fe_3O_4 and Fe_2O_3 are formed in a thermodynamically stable manner under a high-temperature steam oxidation environment (hereunder, also referred to as a "high-temperature steam environment"). The thermal conductivity of Fe_3O_4 and Fe_2O_3 is also high. Accordingly, the thermal efficiency of the boiler will be improved if an oxide film containing a large amount of Fe_3O_4 and Fe_2O_3 is formed on the surface of a heat transfer member that comes in contact with high temperature steam. However, the thermal conductivity of an oxide film containing a large amount of Fe_3O_4 and Fe_2O_3 is too high. Therefore, if only such an oxide film is formed, as described above, a large amount of oxide scale will arise on the inner surface of the heat transfer member.

(5) In general, in a heat transfer member such as a boiler pipe, in many cases the Cr concentration of the inner surface of the pipe is increased, and an oxide film containing a large amount of Cr_2O_3 is formed on the inner surface of the heat transfer member. By this means, formation of a large amount of oxide scale is suppressed and the steam oxidation resistance properties of the heat transfer member improve. However, the thermal conductivity of an oxide film containing a large amount of Cr_2O_3 is low. Consequently, the heat transfer characteristics of the heat transfer member decrease. Therefore, the heat transfer characteristics of the boiler cannot be improved by means of only such an oxide film.

(6) Therefore, an oxide film that includes two layers which are an oxidized layer having excellent heat transfer characteristics and an oxidized layer that compatibly combines both steam oxidation resistance properties and heat transfer characteristics is formed on the inner surface of a heat transfer member under a high-temperature steam environment. By this means, both excellent heat transfer characteristics and excellent steam oxidation resistance properties can be compatibly realized.

(7) When an oxidized layer contains Fe_3O_4 and Fe_2O_3 in a total amount of 80% or more in volume ratio, the thermal conductivity of the oxidized layer is high. Consequently, the heat transfer characteristics of the boiler can be improved. Therefore, an oxidized layer B containing Fe_3O_4 and Fe_2O_3 in a total amount of 80% or more in volume ratio is formed on the surface of the heat transfer member that comes in contact with high temperature steam.

(8) On the other hand, as the oxidized layer that compatibly combines both steam oxidation resistance properties and heat transfer characteristics, an oxidized layer C is formed between the oxidized layer B and the base material. The oxidized layer C contains Cr and Mn in a total amount in a range of more than 5% to 30 mass%, and one or more types of elements selected from a group consisting of Mo, Ta, W and Re in a total amount in a range of 1 to 15 mass%.

[0017] Cr oxides and Mn oxides improve the steam oxidation resistance properties of the base material. However, if the Cr content is too high, the heat transfer characteristics of the oxide film decrease. If the Mn content is too high, the creep strength of the base material decreases. Therefore, the oxidized layer C contains Cr and Mn in a total amount in a range of more than 5% to 30 mass%.

[0018] When Mo, Ta, W and Re are contained in the oxidized layer C, the thermal conductivity of the oxidized layer C increases. However, if the content of these elements is too high, in some cases the steam oxidation resistance properties of the oxidized layer C decrease. Accordingly, the oxidized layer C contains one or more types of element selected from a group consisting of Mo, Ta, W and Re in a total amount in a range of 1 to 15 mass%.

[0019] Thus, the oxidized layer C exhibits excellent heat transfer characteristics and excellent steam oxidation resistance properties.

[0020] (9) In order to form the oxidized layer B and oxidized layer C under a high-temperature steam environment, it is necessary to form the oxidized layer A on the base material in advance. The chemical composition of the oxidized layer A contains, in mass%, Cr and Mn in a total amount in a range of 20 to 45%. The chemical composition of the oxidized layer A contains, in mass%, one or more types of element selected from a group consisting of Mo, Ta, W and Re in a total amount in a range of 0.5 to 10%. When used in a high-temperature steam environment, the oxidized layer A changes to an oxide film including the oxidized layer B and the oxidized layer C. The term "high temperature" refers to, for example, a temperature in the range of 500 to 650°C.

[0021] A heat resistant ferritic steel according to the present embodiment that was completed based on the above findings includes a base material, and an oxidized layer A on the surface of the base material. The base material has a chemical composition consisting of, in mass%, C: 0.01 to 0.3%, Si: 0.01 to 2.0%, Mn: 0.01 to 2.0%, P: 0.10% or less, S: 0.03% or less, Cr: 7.0 to 14.0%, N: 0.005 to 0.15%, sol. Al: 0.001 to 0.3%, one or more types of element selected from a group consisting of Mo: 0 to 5.0%, Ta: 0 to 5.0%, W: 0 to 5.0% and Re: 0 to 5.0%: 0.5 to 7.0% in total, Cu: 0 to 5.0%, Ni: 0 to 5.0%, Co: 0 to 5.0%, Ti: 0 to 1.0%, V: 0 to 1.0%, Nb: 0 to 1.0%, Hf: 0 to 1.0%, Ca: 0 to 0.1%, Mg: 0 to 0.1%, Zr: 0 to 0.1%, B: 0 to 0.1%, and rare earth metal: 0 to 0.1%, with the balance being Fe and impurities. The oxidized layer A includes a chemical composition containing, in mass%, 20 to 45% in total of Cr and Mn. The oxidized layer A includes a chemical composition containing, in mass%, 0.5 to 10% in total of one or more types of element selected from a group consisting of Mo, Ta, W and Re.

[0022] The heat resistant ferritic steel according to the present embodiment is excellent in heat transfer characteristics and steam oxidation resistance properties.

[0023] The chemical composition of the base material of the aforementioned heat resistant ferritic steel may contain one or more types of element selected from a group consisting of Cu: 0.005 to 5.0%, Ni: 0.005 to 5.0% and Co: 0.005 to 5.0%.

[0024] The chemical composition of the aforementioned base material may contain one or more types of element selected from a group consisting of Ti: 0.01 to 1.0%, V: 0.01 to 1.0%, Nb: 0.01 to 1.0% and Hf: 0.01 to 1.0%.

[0025] The chemical composition of the aforementioned base material may contain one or more types of element selected from a group consisting of Ca: 0.0015 to 0.1%, Mg: 0.0015 to 0.1%, Zr: 0.0015 to 0.1%, B: 0.0015 to 0.1% and rare earth metal: 0.0015 to 0.1%.

[0026] A ferritic heat transfer member according to the present embodiment includes a base material, and an oxide film on the surface of the base material. The base material has the chemical composition described above. The oxide film includes an oxidized layer B and an oxidized layer C. The oxidized layer B contains, in vol%, 80% or more in total of Fe_3O_4 and Fe_2O_3. The oxidized layer C is disposed between the oxidized layer B and the base material. The chemical composition of the oxidized layer C contains Cr and Mn in a total amount in a range of more than 5% to 30 mass%, and contains one or more types of element selected from a group consisting of Mo, Ta, W and Re in a total amount in a range of 1 to 15 mass%.

[0027] The ferritic heat transfer member according to the present embodiment is excellent in heat transfer characteristics and steam oxidation resistance properties.

[0028] Preferably, the oxidized layer B contains Cr and Mn in a total amount of not more than 5 mass%.

[0029] Preferably, the oxidized layer C contains not more than 5 vol% of Cr_2O_3.

[0030] In this case, the thermal conductivity of the oxide film is improved by suppressing the amount of precipitated Cr_2O_3 that has low thermal conductivity. Therefore, the heat transfer characteristics of the boiler can be enhanced.

[0031] Hereunder, the heat resistant ferritic steel and the ferritic heat transfer member according to the present embodiment are described in detail. The symbol "%" in relation to an element means "mass%" unless specifically stated otherwise.

[Heat resistant ferritic steel]

[0032] The shape of the heat resistant ferritic steel according to the present embodiment is not particularly limited. The heat resistant ferritic steel is, for example, a steel pipe, a steel bar, or a steel plate. Preferably, the heat resistant ferritic steel is a heat resistant ferritic steel pipe. An oxidation treatment is performed on the base material of the heat resistant ferritic steel according to the present embodiment. An oxidized layer A is formed on the surface of the base material of the heat resistant ferritic steel by the oxidation treatment.

[0033] FIG. 1 is a sectional view of the heat resistant ferritic steel according to the present embodiment. Referring to FIG. 1, a heat resistant ferritic steel 1 includes a base material 2 and an oxidized layer A. The heat resistant ferritic steel 1 that includes the base material 2 and the oxidized layer A is used as a heat transfer member under a high-temperature steam environment. As a result, the oxidized layer A changes to an oxide film 3 that includes an oxidized layer B and an oxidized layer C.

[Chemical composition of base material 2]

[0034] The base material 2 has the following chemical composition.

C: 0.01 to 0.3%

[0035] Carbon (C) stabilizes austenite. C also increases the creep strength of the base material by solid-solution strengthening. However, if the C content of the base material 2 is too high, an excessive amount of carbides precipitate, and the workability and weldability of the base material 2 will decrease. Accordingly, the C content is set in a range of 0.01 to 0.3%. A preferable lower limit of the C content is 0.03%, and a preferable upper limit of the C content is 0.15%.

Si: 0.01 to 2.0%

[0036] Silicon (Si) deoxidizes the steel. Si also improves the steam oxidation resistance properties of the base material 2. However, if the Si content is too high, the toughness of the base material 2 decreases. Accordingly, the Si content is set in a range of 0.01 to 2.0%. A preferable lower limit of the Si content is 0.05%, and more preferably is 0.1%. A preferable upper limit of the Si content is 1.0%, and more preferably is 0.5%.

Mn: 0.01 to 2.0%

[0037] Manganese (Mn) deoxidizes the steel. Mn also combines with S in the base material 2 to form MnS, and suppresses grain-boundary segregation of S. Thus, the hot workability of the base material 2 improves. However, if the Mn content is too high, the base material 2 becomes brittle and, in addition, the creep strength of the base material 2 decreases. Accordingly, the Mn content is set in a range of 0.01 to 2.0%. A preferable lower limit of the Mn content is 0.05%, and more preferably is 0.1%. A preferable upper limit of the Mn content is 1.0%, and more preferably is 0.8%.

P: 0.10% or less

[0038] Phosphorus (P) is an impurity. P segregates at crystal grain boundaries of the base material 2, and decreases the hot workability of the base material 2. P also concentrates at the boundary between the oxide film 3 and the base material 2, and reduces the adhesiveness of the oxide film 3 with respect to the base material 2. Accordingly, the P content is preferably as low as possible. The P content is set to 0.10% or less, and preferably is 0.03% or less. A lower limit of the P content is, for example, 0.005%.

S: 0.03% or less

[0039] Sulfur (S) is an impurity. S segregates at crystal grain boundaries of the base material 2, and decreases the hot workability of the base material 2. S also concentrates at the boundary between the oxide film 3 and the base material 2, and reduces the adhesiveness of the oxide film 3 with respect to the base material 2. Accordingly, the S content is preferably as low as possible. The S content is set to 0.03% or less, and preferably is 0.015% or less. A lower limit of the S content is, for example, 0.0001%.

Cr: 7.0 to 14.0%

[0040] Chromium (Cr) improves the steam oxidation resistance properties of the base material 2. Cr is also contained in the oxide film 3 as oxides defined by Cr_2O_3 and $(Fe, Cr)_3O_4$. The Cr oxides improve the steam oxidation resistance properties of the base material 2. The Cr oxides also improve the adhesiveness of the oxide film 3 with respect to the base material 2. However, if the Cr content is too high, the concentration of Cr_2O_3 in the oxide film 3 becomes high and the heat transfer characteristics of the oxide film 3 will decrease. Accordingly, the Cr content is set in a range of 7.0 to

14.0%. A preferable lower limit of the Cr content is 7.5%, and more preferably is 8.0%. A preferable upper limit of the Cr content is 12.0%, and more preferably is 11.0%.

N: 0.005 to 0.15%

[0041] Nitrogen (N) dissolves in the base material 2, and increases the strength of the base material 2. In addition, N forms nitrides with alloy elements in the base material 2 and precipitates in the base material 2, thereby increasing the strength of the base material 2. However, if the N content is too high, the nitrides coarsen and the toughness of the base material 2 decreases. Accordingly, the N content is set in a range of 0.005 to 0.15%. A preferable lower limit of the N content is 0.01%. A preferable upper limit of the N content is 0.10%.

sol. Al: 0.001 to 0.3%

[0042] Aluminum (Al) deoxidizes the steel. However, if the Al content is too high, the hot workability of the base material 2 decreases. Accordingly, the Al content is set in a range of 0.001 to 0.3%. A preferable lower limit of the Al content is 0.005%, and a preferable upper limit of the Al content is 0.1%. In the present embodiment, the term "A1 content" means the soluble Al (sol. Al).

[0043] 0.5 to 7.0% in total of one or more types of element selected from a group consisting of:

Mo: 0 to 5.0%,
Ta: 0 to 5.0%,
W: 0 to 5.0%, and
Re: 0 to 5.0%

[0044] One or more types of element selected from a group consisting of molybdenum (Mo), tantalum (Ta), tungsten (W) and rhenium (Re) is contained. Hereinafter, these elements are also referred to as "specific oxidized layer forming elements". The specific oxidized layer forming elements form the oxidized layer A on the surface of the base material 2. The specific oxidized layer forming elements also form the oxide film 3 including the oxidized layer B and the oxidized layer C under a high-temperature steam environment of 500 to 650°C. These effects are obtained if even one type of these elements is contained. However, if the content of the specific oxidized layer forming elements is too high, the toughness, ductility and workability of the base material 2 will decrease. Accordingly, the Mo content is set in a range of 0 to 5.0%, the Ta content is set in a range of 0 to 5.0%, the W content is set in a range of 0 to 5.0% and the Re content is set in a range of 0 to 5.0%. A preferable lower limit of the Mo content is 0.01%, and more preferably is 0.1%. A preferable lower limit of the Ta content is 0.01%, and more preferably is 0.1%. A preferable lower limit of the W content is 0.01%, and more preferably is 0.1%. A preferable lower limit of the Re content is 0.01%, and more preferably is 0.1%. A preferable upper limit of the Mo content is 4.0%, and more preferably is 3.0%. A preferable upper limit of the Ta content is 4.0%, and more preferably is 3.0%. A preferable upper limit of the W content is 4.0%, and more preferably is 3.0%. A preferable upper limit of the Re content is 4.0%, and more preferably is 3.0%. The total content of the specific oxidized layer forming elements is set in the range of 0.5 to 7.0%. A preferable lower limit of the total content of the specific oxidized layer forming elements is 0.6%, and more preferably is 1.0%. A preferable upper limit of the total content of the specific oxidized layer forming elements is 6.5%, and more preferably is 6.0%.

[0045] The balance of the base material 2 of the heat resistant ferritic steel according to the present embodiment is Fe and impurities. In the present embodiment, the term "impurities" refers to substances which are mixed in from ore or scrap that is utilized as a raw material of the steel or from the environment of the production process or the like, and are substances that are contained within a range that does not adversely affect a heat transfer member 4 according to the present embodiment. The impurities include, for example, oxygen (O), arsenic (As), antimony (Sb), thallium (Tl), lead (Pb) and bismuth (Bi).

[0046] The base material 2 of the heat resistant ferritic steel according to the present embodiment may further contain the following elements in lieu of a part of Fe.

[0047] Cu: 0 to 5.0%
Ni: 0 to 5.0%
Co: 0 to 5.0%
Copper (Cu), nickel (Ni) and cobalt (Co) are optional elements, and need not be contained. If contained, these elements stabilize austenite. By this means, retention of delta ferrite that lowers the shock resistance of the base material 2 is suppressed. This effect is obtained if even one type of these elements is contained. However, if the content of these elements is too high, the long-term creep strength of the base material 2 will decrease. Accordingly, the Cu content is set in a range of 0 to 5.0%, the Ni content is set in a range of 0 to 5.0%, and the Co content is set in a range of 0 to 5.0%. A preferable upper limit of the Cu content is 3.0%, and more preferably is 2.0%. A preferable upper limit of the Ni

content is 3.0%, and more preferably is 2.0%. A preferable upper limit of the Co content is 3.0%, and more preferably is 2.0%. A preferable lower limit of the content of each of these elements is 0.005%.

[0048] Ti: 0 to 1.0%
V: 0 to 1.0%
Nb: 0 to 1.0%
Hf: 0 to 1.0%
Titanium (Ti), vanadium (V), niobium (Nb) and hafnium (Hf) are optional elements and need not be contained. If contained, these elements combine with carbon and nitrogen to form carbides, nitrides or carbo-nitrides. These carbides, nitrides and carbo-nitrides act to perform precipitation strengthening of the base material 2. This effect is obtained if even one type of these elements is contained. However, if the content of these elements is too high, the workability of the base material 2 will decrease. Accordingly, the Ti content is set in a range of 0 to 1.0%, the V content is set in a range of 0 to 1.0%, the Nb content is set in a range of 0 to 1.0% and the Hf content is set in a range of 0 to 1.0%. A preferable upper limit of the Ti content is 0.8%, and more preferably is 0.4%. A preferable upper limit of the V content is 0.8%, and more preferably is 0.4%. A preferable upper limit of the Nb content is 0.8%, and more preferably is 0.4%. A preferable upper limit of the Hf content is 0.8%, and more preferably is 0.4%. A preferable lower limit of the content of each of these elements is 0.01%.

[0049] Ca: 0 to 0.1%
Mg: 0 to 0.1%
Zr: 0 to 0.1%
B: 0 to 0.1%
Rare earth metal: 0 to 0.1%
Calcium (Ca), magnesium (Mg), zirconium (Zr), boron (B) and rare earth metal (REM) are optional elements, and need not be contained. If contained, these elements increase the strength, workability and oxidation resistance of the base material 2. This effect is obtained if even one type of these elements is contained. However, if the content of these elements is too high, the toughness and weldability of the base material 2 will decrease. Accordingly, the Ca content is set in a range of 0 to 0.1%, the Mg content is set in a range of 0 to 0.1%, the Zr content is set in a range of 0 to 0.1%, the B content is set in a range of 0 to 0.1% and the REM content is set in a range of 0 to 0.1%. A preferable upper limit of the Ca content is 0.05%. A preferable upper limit of the Mg content is 0.05%. A preferable upper limit of the Zr content is 0.05%. A preferable upper limit of the B content is 0.05%. A preferable upper limit of the REM content is 0.05%. A preferable lower limit of the content of each of these elements is 0.0015%. Herein, the term "REM" refers to one or more types of element selected from a group consisting of yttrium (Y) which is the element with atomic number 39, the elements from lanthanum (La) with atomic number 57 to lutetium (Lu) with atomic number 71 that are lanthanides, and the elements from actinium (Ac) with atomic number 89 to lawrencium (Lr) with atomic number 103 that are actinides.

[Oxidized layer A]

[0050] An oxidation treatment is performed on the base material 2 having the aforementioned chemical composition. The oxidized layer A is formed on the surface of the base material 2 by the oxidation treatment. The heat resistant ferritic steel 1 having the base material 2 and the oxidized layer A on the surface of the base material 2 is used under a high-temperature steam environment. Under a high-temperature steam environment, the oxidized layer A changes to the oxide film 3 that is excellent in heat transfer characteristics, while maintaining steam oxidation resistance properties. That is, the oxidized layer A is a starting material for forming the oxide film 3 that includes the oxidized layer B and the oxidized layer C. Although the mechanism by which the oxidized layer A changes into the oxide film 3 is not certain, it is surmised that the oxidized layer A principally contributes to formation of the oxidized layer C.

[0051] The thickness of the oxidized layer A is not particularly limited. If the oxidized layer A is formed even slightly, the oxide film 3 will be formed. The thickness of the oxidized layer A is preferably not less than 0.2 μm. In this case, under a high-temperature steam environment, the oxide film 3 can be uniformly formed on the surface of the base material 2 in a stable manner. Therefore, it is easy to completely cover the base material 2 with the oxide film 3. As a result, the thermal conductivity at the surface of the ferritic heat transfer member 4 increases. More preferably, the thickness of the oxidized layer A is not less than 1.0 μm. Although the upper limit of the thickness of the oxidized layer A is not particularly limited, in consideration of mass productivity, the upper limit is preferably not more than 20 μm.

[0052] The thickness of the oxidized layer A is determined by the following method. The heat resistant ferritic steel 1 that was subjected to an oxidation treatment that is described later is cut perpendicularly to the surface thereof. In a case where the heat resistant ferritic steel 1 is a steel pipe, the heat resistant ferritic steel 1 is cut perpendicularly to the axial direction of the steel pipe. A cross-section including the surface of the heat resistant ferritic steel 1 is observed using a scanning electron microscope (SEM) manufactured by JEOL Ltd. In a case where the heat resistant ferritic steel 1 is a steel pipe, SEM is used to observe a cross-section that includes the inner surface of the steel pipe. The observation magnification is 2000 times. In the observation visual field, the thickness of the oxidized layer on the surface of the heat resistant ferritic steel 1 (the inner surface in a case where the heat resistant ferritic steel 1 is a steel pipe) is measured. The measurement is made on four different cross-sections of the heat resistant ferritic steel 1. In a case where the heat resistant ferritic steel 1 is a steel pipe, measurement is performed at four locations at a pitch of 45°. The average value of the measurement results is adopted as the thickness of the oxidized layer A.

[0053] The chemical composition of the oxidized layer A contains a total content of 20 to 45% of Cr and Mn. If the total content of Cr and Mn in the oxidized layer A is less than 20%, the total content of Cr and Mn in the oxidized layer C will be 5% or less under a high-temperature steam environment. In this case, the thermal conductivity of the oxidized layer C will be too high. In such case, the steam oxidation resistance properties of the ferritic heat transfer member 4 will decrease. On the other hand, if the total content of Cr and Mn in the oxidized layer A is more than 45%, the total content of Cr and Mn in the oxidized layer C will be more than 30% under a high-temperature steam environment. In this case, the thermal conductivity of the oxidized layer C will be too low. As a result, the heat transfer characteristics of the ferritic heat transfer member 4 will decrease. Therefore, the chemical composition of the oxidized layer A contains Cr and Mn in a total amount in a range of 20 to 45%. A preferable lower limit of the total content of Cr and Mn in the oxidized layer A is 22%. A preferable upper limit of the total content of Cr and Mn in the oxidized layer A is 40%.

[0054] The chemical composition of the oxidized layer A further contains a total of 0.5 to 10% of one or more types of element selected from the group consisting of Mo, Ta, W and Re (specific oxidized layer forming elements). If the total content of the specific oxidized layer forming elements of the oxidized layer A is less than 0.5%, the total content of the specific oxidized layer forming elements of the oxidized layer C will be less than 1% under a high-temperature steam environment. In this case, the thermal conductivity of the oxidized layer C will be too low. As a result, the heat transfer characteristics of the ferritic heat transfer member 4 will decrease. On the other hand, if the total content of the specific oxidized layer forming elements of the oxidized layer A is more than 10%, under a high-temperature steam environment the total content of the specific oxidized layer forming elements of the oxidized layer C will be more than 15%. In this case, the thermal conductivity of the oxidized layer C will be too high. As a result, the steam oxidation resistance properties of the ferritic heat transfer member 4 will decrease. Therefore, the chemical composition of the oxidized layer A contains the specific oxidized layer forming elements in a total amount that is in a range of 0.5 to 10%. A preferable lower limit of the total content of the specific oxidized layer forming elements is 1%. A preferable upper limit of the total content of the specific oxidized layer forming elements is 8%.

[0055] The total content of Cr and Mn and the total content of the specific oxidized layer forming elements (Mo, Ta, W and Re) in the oxidized layer A is calculated by the following method. The heat resistant ferritic steel 1 that was subjected to an oxidation treatment that is described later is cut perpendicularly to the surface thereof. In a case where the heat resistant ferritic steel 1 is a steel pipe, the heat resistant ferritic steel 1 is cut perpendicularly to the axial direction of the steel pipe. A cross-section including the surface of the heat resistant ferritic steel 1 is observed using a scanning electron microscope (SEM) manufactured by JEOL Ltd. The oxidized layer A that appears with a comparatively white contrast of the surface of the heat resistant ferritic steel 1 (inner surface in a case where the heat resistant ferritic steel 1 is a steel pipe) is identified. At the center of the thickness of the oxidized layer A, an elemental analysis is performed using a field emission electron probe micro analyzer (FE-EPMA) manufactured by JEOL Ltd. The conditions for the elemental analysis are: detector: 30 mm^2 SD, accelerating voltage: 15 kV, and measurement time period: 60 secs. The elemental analysis is made on four different cross-sections of the heat resistant ferritic steel 1. In a case where the heat resistant ferritic steel 1 is a steel pipe, elemental analysis is performed at four locations at a pitch of 45°. Among the compositions for the respective elements that are obtained, a composition from which the quantities of oxygen (O) and carbon (C) are excluded is taken as 100%. The proportion (mass%) of the total amount of Cr and Mn is calculated. The proportion (mass%) of the total content of specific oxidized layer forming elements (Mo, Ta, W and Re) is calculated. Average values of the elemental analysis values obtained at the four locations are adopted as the total content (mass%) of Cr and Mn in the oxidized layer A, and the total content (mass%) of the specific oxidized layer forming elements (Mo, Ta, W and Re) in the oxidized layer A.

[Method for producing heat resistant ferritic steel 1]

[0056] A method for producing the heat resistant ferritic steel 1 according to the present embodiment includes a preparation process and an oxidation treatment process. In the preparation process, the base material 2 having the aforementioned chemical composition is prepared. The base material 2 is produced from a starting material having the aforementioned chemical composition. The starting material may be a slab, a bloom or a billet produced by a continuous casting process. The starting material may also be billet produced by an ingot-making process. A heating temperature when producing the starting material is, for example, in a range of 850 to 1200°C.

[0057] For example, in the case of producing a steel pipe, the prepared starting material is charged into a reheating furnace or a soaking pit and heated. The heated starting material is subjected to hot working to produce the base material 2. The hot working is, for example, the Mannesmann process. The Mannesmann process subjects the starting material to piercing-rolling using a piercing machine to thereby form the starting material into a material pipe. Thereafter, the starting material is subjected to drawing and rolling as well as sizing using a mandrel mill and a sizing mill. The temperature for the hot working is, for example, in a range of 850 to 1200°C. By this means, the base material 2 is produced as a seamless steel pipe. A process for producing the base material 2 is not limited to the Mannesmann process, and the base material 2 may be produced by subjecting the starting material to hot extrusion or hot forging. In addition, the base material 2 produced by hot working may be subjected to a heat treatment or may be subjected to cold working. The base material 2 may also be a steel plate. In the case of producing the base material 2 as a steel plate, the starting material is subjected to hot working to produce the base material 2 as a steel plate. The steel plate may also be processed into a steel pipe by welding to produce the base material 2 as a welded steel pipe.

[Oxidation treatment process]

[0058] An oxidation treatment is performed on the aforementioned base material 2. The oxidation treatment is performed by heating the base material 2 in a gas atmosphere containing CO, CO_2 and N_2. The CO/CO_2 ratio of the gas used for the oxidation treatment is 0.6 or more in volume ratio. By making the CO/CO_2 ratio 0.6 or more, preferential oxidation of Fe can be suppressed. As a result, the oxidized layer A containing Cr and Mn in a total amount of 20 mass% or more and also containing specific oxidized layer forming elements in a total amount of 0.5 mass% or more is formed on the surface of the base material 2. The oxidized layer A changes into the oxide film 3 after the steam oxidation treatment that is described later. Although an upper limit of the CO/CO_2 ratio is not particularly provided, an upper limit of 2.0 is preferable in consideration of operational practicability.

[0059] On the other hand, in the present embodiment, the $(CO+CO_2)/N_2$ ratio of the gas that is used in the oxidation treatment is set as not more than 1.0 in volume ratio. If the $(CO+CO_2)/N_2$ ratio is more than 1.0, the base material 2 will carburize. Therefore, Cr and Mn in the oxidized layer A will form carbides. As a result, the total content of Cr and Mn in the oxidized layer A will be less than 20%. Although a lower limit of the $(CO+CO_2)/N_2$ ratio is not particularly provided, a lower limit of 0.1 is preferable in consideration of operational practicability.

[0060] The temperature for the oxidation treatment is in a range of 900 to 1130°C. If the oxidation treatment temperature is less than 900°C, because outward diffusion of specific elements in the base material 2 will be slow, the total content of specific oxidized layer forming elements in the oxidized layer A will be too low. In this case, under a high-temperature steam environment, the total content of specific oxidized layer forming elements in the oxidized layer C will be too low. As a result, the thermal conductivity of the oxidized layer C will be too low. Consequently, the thermal conductivity at the surface of the ferritic heat transfer member 4 will decrease. Therefore, the heat transfer characteristics of the ferritic heat transfer member 4 will decrease. If the oxidation treatment temperature is more than 1130°C, because the diffusion of Cr and Mn will be fast, the total content of Cr and Mn in the oxidized layer A will be more than 45%. As a result, under a high-temperature steam environment, the total content of Cr and Mn in the oxidized layer C will be more than 30%. In this case, the thermal conductivity of the oxidized layer C will be too low. As a result, the heat transfer characteristics of the ferritic heat transfer member 4 will decrease. Accordingly, the oxidation treatment temperature is set in the range of 900 to 1130°C. A preferable lower limit of the oxidation treatment temperature is 920°C, and more preferably is 950°C. A preferable upper limit of the oxidation treatment temperature is 1120°C.

[0061] The oxidation treatment time period is in a range of 1 minute to 1 hour. If the oxidation treatment time period is too short, because concentration of the specific oxidized layer forming elements will occur, the total content of the specific oxidized layer forming elements in the oxidized layer A will be more than 10%. Therefore, under a high-temperature steam environment, the total content of the specific oxidized layer forming elements in the oxidized layer C will be more than 15%. As a result, the thermal conductivity at the surface of the ferritic heat transfer member 4 will be too high. On the other hand, if the oxidation treatment time period is too long, productivity will decrease. When taking productivity into consideration, a shorter oxidation treatment time period is preferable. Furthermore, if the oxidation treatment time period is too long, the total content of Cr and Mn in the oxidized layer A will be less than 20% because Fe will preferentially oxidize. Thus, the oxidation treatment time period is set in the range of 1 minute to 1 hour. Preferably, an upper limit of the oxidation treatment time period is 30 minutes, and more preferably is 20 minutes. Preferably, a lower limit of the oxidation treatment time period is 3 minutes.

[0062] A tempering treatment (low-temperature annealing) may be performed after the oxidation treatment. In addition, although the oxidation treatment may be performed on the entire base material 2, the oxidation treatment may also be performed only on a face of the base material 2 which comes in contact with high temperature steam (for example, the inner surface of a steel pipe).

[0063] The oxidation treatment may be performed once, or may be performed multiple times. After the oxidation treatment, degreasing or cleaning or the like may be performed to remove dirt or oil that adhered to the surface of the base material 2. The oxidized layer A will not be affected even if degreasing or cleaning or the like is performed. Even if degreasing or cleaning or the like is performed, it will not affect formation of the oxide film 3 thereafter.

[0064] The heat resistant ferritic steel 1 of the present embodiment can be produced by the production method described above.

[Ferritic heat transfer member 4]

[0065] The ferritic heat transfer member 4 according to the present embodiment includes a base material 2 and an oxide film 3. The base material 2 of the ferritic heat transfer member 4 is the same as the base material of the heat resistant ferritic steel 1 that is described above. Accordingly, the chemical composition of the base material 2 of the ferritic heat transfer member 4 is the same as the chemical composition of the base material 2 of the heat resistant ferritic steel 1 that is described above. The shape of the ferritic heat transfer member 4 according to the present embodiment is not particularly limited. The ferritic heat transfer member 4 is, for example, a pipe, a bar or a plate material. In the case where the ferritic heat transfer member 4 has a tubular shape, the ferritic heat transfer member 4 is used, for example, as a boiler pipe. Accordingly, the ferritic heat transfer member 4 is preferably a ferritic heat-transfer pipe.

[0066] FIG. 2 is a sectional view of the ferritic heat transfer member 4 according to the present embodiment. Referring to FIG. 2, the ferritic heat transfer member 4 includes the base material 2 and the oxide film 3. The oxide film 3 includes the oxidized layer B and the oxidized layer C.

[Oxide film 3]

[0067] The oxide film 3 is formed on the surface of the base material 2 by performing a steam oxidation treatment on the heat resistant ferritic steel 1 having the base material 2 and the oxidized layer A. Referring to FIG. 2, the oxide film 3 is an oxide film including two layers, namely, the oxidized layer B and the oxidized layer C. Because the oxide film 3 includes the oxidized layer B, the oxide film 3 is excellent in heat transfer characteristics. Because the oxide film 3 includes the oxidized layer C, the oxide film 3 is excellent in both steam oxidation resistance properties and heat transfer characteristics. That is, the oxide film 3 is not just excellent in steam oxidation resistance properties, but is also excellent in heat transfer characteristics. The oxidized layer B is formed as the uppermost layer of the ferritic heat transfer member 4. The oxidized layer C is disposed between the oxidized layer B and the base material 2. In a case where the ferritic heat transfer member 4 is a boiler pipe, the oxidized layer B corresponds to the inner surface side of the boiler pipe, and the base material 2 corresponds to the outer surface side of the boiler pipe. In this case, the oxidized layer B comes in contact with high temperature steam.

[Oxidized layer B]

[0068] The oxidized layer B contains, in vol%, a total of 80% or more of Fe_3O_4 and Fe_2O_3. The thermal conductivity of Fe_3O_4 and Fe_2O_3 is high. Accordingly, the thermal conductivity of the oxidized layer B is high, and heat imparted from the outside of the ferritic heat transfer member 4 is transferred to the inside of the ferritic heat transfer member 4 without being significantly decreased. Therefore, the heat transfer characteristics of the boiler can be improved. Preferably, the oxidized layer B contains, in vol%, a total of 90% or more of Fe_3O_4 and Fe_2O_3. Preferably, the Fe_2O_3 content of the oxidized layer B is less than 20 vol%. More preferably, the oxidized layer B is composed of Fe_3O_4.

[0069] In some cases a part of Cr and Mn contained in the base material 2 forms an oxide and is contained in the oxidized layer B. The thermal conductivity of Cr_2O_3, in particular, is low. Therefore, the Cr_2O_3 content of the oxidized layer B is preferably low. Accordingly, the chemical composition of the oxidized layer B preferably contains, in mass%, not more than 5% of Cr and Mn in total. More preferably, the chemical composition of the oxidized layer B contains, in mass%, not more than 3% of Cr and Mn in total.

[0070] A preferable thickness of the oxidized layer B is 10 to 400 μm.

[Oxidized layer C]

[0071] The oxidized layer C is disposed between the oxidized layer B and the base material 2, and contacts the base material 2.

[0072] The chemical composition of the oxidized layer C contains Cr and Mn in a total amount in a range of more than 5% to 30%. In the oxidized layer C, Cr and Mn are present as oxides represented by the chemical formula $(Fe, M)_3O_4$. In the formula, Cr and Mn are substituted for M. The oxides represented by the chemical formula $(Fe, M)_3O_4$ are oxides that have a so-called spinel crystal structure that is the same as Fe_3O_4, and in which a part of Fe is substituted with Cr and Mn. In a case where the total amount of Cr and Mn contained in the oxidized layer C is 5% or less, the proportion of Fe_3O_4 and Fe_2O_3 in the oxidized layer C cannot be kept low. In this case, the thermal conductivity of the oxidized layer C becomes too high. Consequently, a large amount of oxide scale arises on the inner surface of the ferritic heat transfer member 4. On the other hand, in a case where the total amount of Cr and Mn contained in the oxidized layer C is greater than 30%, the thermal conductivity of the oxidized layer C becomes too low. In this case, the heat transfer characteristics of the boiler decrease. Accordingly, the content of Cr and Mn in the oxidized layer C is set in a range of more than 5% to 30% in total. By this means, the thermal conductivity of the oxidized layer C can be controlled within an appropriate range while maintaining the steam oxidation resistance properties. A preferable lower limit of the total content of Cr and Mn in the oxidized layer C is 10%, and more preferably is 13%. A preferable upper limit of the total content of Cr and Mn in the oxidized layer C is 28%, and more preferably is 25%.

[0073] The oxidized layer C contains one or more types of element selected from a group consisting of Mo, Ta, W and Re in a total amount in a range of 1 to 15%. If the total content of the specific oxidized layer forming elements (Mo, Ta, W and Re) of the oxidized layer C is less than 1%, the thermal conductivity of the oxidized layer C will be too low. On the other hand, if the total content of the specific oxidized layer forming elements of the oxidized layer C is more than 15%, the thermal conductivity of the oxidized layer C will be too high. In such case, the steam oxidation resistance properties of the ferritic heat transfer member 4 will decrease. Accordingly, the total content of the specific oxidized layer forming elements in the oxidized layer C is in the range of 1 to 15%. A preferable upper limit of the total content of the specific oxidized layer forming elements (Mo, Ta, W and Re) in the oxidized layer C is 10%, and more preferably is 9%. A preferable lower limit of the total content of the specific oxidized layer forming elements (Mo, Ta, W and Re) in the oxidized layer C is 1.5%.

[0074] In addition, preferably a major portion of the oxidized layer C is oxides having the aforementioned spinel crystal structure, and the oxidized layer C contains Cr_2O_3 in an amount that is not more than 5 vol%. By suppressing formation of Cr_2O_3 which has low thermal conductivity to an amount that is not more than 5 vol% and causing the formation of oxides having a spinel crystal structure, the thermal conductivity of the oxidized layer C can be controlled to be within an appropriate range. The content of Cr_2O_3 in the oxidized layer C is preferably 5 vol% or less, and more preferably is 3 vol% or less.

[0075] The thermal conductivity of the oxidized layer C is preferably controlled within a range of 1.2 to 3.0 $W \cdot m^{-1} \cdot K^{-1}$. If the thermal conductivity of the oxidized layer C is 1.2 $W \cdot m^{-1} \cdot K^{-1}$ or more, thermal conduction from the outside of the ferritic heat transfer member 4 to the inside of the ferritic heat transfer member 4 is not inhibited, and the heat transfer characteristics of the boiler stably increase. On the other hand, if the thermal conductivity of the oxidized layer C is not more than 3.0 $W \cdot m^{-1} \cdot K^{-1}$, the heat of high temperature steam that is transferred to the surface of the base material 2 can be stably controlled. By this means, excessive heating of the surface of the base material 2 is suppressed, and an oxidation reaction at the surface of the base material 2 is suppressed. Therefore, formation of a large amount of oxide scale at the surface of the base material 2 is stably suppressed. As a result, the steam oxidation resistance properties of the ferritic heat transfer member 4 stably increase. Accordingly, the thermal conductivity of the oxidized layer C is preferably controlled within the range of 1.2 to 3.0 $W \cdot m^{-1} \cdot K^{-1}$. In this case, it is easy to improve the steam oxidation resistance properties of the ferritic heat transfer member 4 without loss of the heat transfer characteristics. In the oxidized layer C, a preferable lower limit of the thermal conductivity is 1.3 $W \cdot m^{-1} \cdot K^{-1}$, and more preferably is 1.4 $W \cdot m^{-1} \cdot K^{-1}$. In the oxidized layer C, a preferable upper limit of the thermal conductivity is 2.8 $W \cdot m^{-1} \cdot K^{-1}$, and more preferably is 2.5 $W \cdot m^{-1} \cdot K^{-1}$.

[0076] The volume ratio of Fe_3O_4 and Fe_2O_3 in the oxidized layer B is measured by the following method. The ferritic heat transfer member 4 that has undergone a steam oxidation treatment which is described later is cut perpendicularly to the surface thereof. In a case where the ferritic heat transfer member 4 is a pipe, the ferritic heat transfer member 4 is cut perpendicularly to the axial direction of the pipe. At a cross-section (observation surface) including the oxidized layer B, a chemical composition analysis of the oxidized layer B is performed using a field emission electron probe micro analyzer (FE-EPMA) manufactured by JEOL Ltd. The conditions for the chemical composition analysis are: detector: 30 mm^2 SD, accelerating voltage: 15 kV, and measurement time period: 60 secs. By means of the chemical composition analysis, regions in which Fe and O (oxygen) are detected and Cr is not detected are identified. Next, it is confirmed by means of the chemical composition analysis that all of the identified regions have Fe_3O_4 or Fe_2O_3. Next, the strength of Fe in the oxidized layer B of the observation surface is subjected to binarization processing. At this time, the maximum strength of the grayscale extraction objects is set as 1/10 or more. It is confirmed that all regions other than the identified regions (regions confirmed as having Fe_3O_4 and Fe_2O_3) are included in black regions after binarization. After the binarization processing, the area fraction of black regions in the oxidized layer B of the observation surface is determined, and the resulting value is subtracted from 100%. The obtained area fraction is taken as the volume ratio of Fe_3O_4 and Fe_2O_3 in the oxidized layer B.

[0077] The volume ratio of Cr_2O_3 in the oxidized layer C is measured by the following method. The ferritic heat transfer member 4 that has undergone a steam oxidation treatment which is described later is cut perpendicularly to the surface thereof. In a case where the ferritic heat transfer member 4 is a pipe, the ferritic heat transfer member 4 is cut perpendicularly to the axial direction of the pipe. SEM is used to observe a cross-section (observation surface) including the oxidized layer B and the oxidized layer C, to thereby identify the oxidized layer C. In the SEM observation, the oxidized layer B and the oxidized layer C are distinguished from each other by means of a contrast difference obtained with an SEM backscattered electron image (BSE). The contrast of the oxidized layer B is brighter than the contrast of the oxidized layer C. The volume ratio of Cr_2O_3 in the oxidized layer C is determined by a similar method as the method used for determining the volume ratio of Fe_3O_4 and Fe_2O_3 in the oxidized layer B. That is, at a cross-section (observation surface) including the oxidized layer C, a chemical composition analysis is performed using a field emission electron probe micro analyzer (FE-EPMA) manufactured by JEOL Ltd. The conditions for the chemical composition analysis are: detector: 30 mm^2 SD, accelerating voltage: 15 kV, and measurement time period: 60 secs. By means of the chemical composition analysis, regions in which Cr and O (oxygen) are detected and Fe is not detected are identified. Next, it is confirmed by means of the chemical composition analysis that all of the identified regions have Cr_2O_3. Next, the strength of Cr in the oxidized layer C of the observation surface is subjected to binarization processing. At this time, the maximum strength of the grayscale extraction objects is set as 1/10 or more. It is confirmed that all regions other than the identified regions (regions confirmed as having Cr_2O_3) are included in black regions after binarization. The area fraction of black regions after binarization processing of the observation surface is determined, and the resulting value is subtracted from 100%. The obtained area fraction is taken as the volume ratio of Cr_2O_3 in the oxidized layer C.

[0078] The total content of Cr and Mn and the total content of the specific oxidized layer forming elements (Mo, Ta, W and Re) in the oxidized layer B and the oxidized layer C are determined by a similar method as the method used with respect to the oxidized layer A. In the SEM observation, the oxidized layer B and the oxidized layer C are distinguished from each other by means of a contrast difference obtained with an SEM backscattered electron image (BSE). The contrast of the oxidized layer B is brighter than the contrast of the oxidized layer C. Under the same conditions as used in the case of the oxidized layer A, an elemental analysis is performed at the center of the thickness of the oxidized layer B and the center of the thickness of the oxidized layer C. In a similar manner as in the case of the oxidized layer A, the total content (mass%) of Cr and Mn and the total content (mass%) of the specific oxidized layer forming elements (Mo, Ta, W and Re) are determined based on the compositions of the respective elements that are obtained.

[0079] The thermal conductivity of the oxidized layer C is determined by the following method. After mechanically removing the oxidized layer B of the ferritic heat transfer member 4, the bulk density, specific heat and thermal diffusivity of the oxidized layer C including the base material 2 are measured. Next, after mechanically removing the oxidized layer C, the bulk density, specific heat and thermal diffusivity of the base material 2 are measured in a similar manner. The thermal conductivity κ can be determined by converting the differences between the respective measurement values to measurement values of the oxidized layer C, and substituting the resulting measurement values into the following formula.

$$\kappa = \rho \times C_p \times D$$

[0080] Where, the bulk density is substituted for ρ, the specific heat is substituted for C_p, and the thermal diffusivity is substituted for D.

[0081] A preferable lower limit of the thickness of the oxidized layer C is 10 μm.

[Thickness of oxide film 3]

[0082] Although the thickness of the oxide film 3 is not particularly limited, a thin thickness is preferable. If the oxide film 3 is thin, the heat transfer characteristics of the ferritic heat transfer member 4 increase. Therefore, the heat transfer characteristics of the boiler can be improved. When the ferritic heat transfer member 4 is used for a long time period, the oxide film 3 thickens. The oxide film 3 also thickens in a case where the temperature for a steam oxidation treatment of the ferritic heat transfer member 4 is high. When an oxidation treatment and a steam oxidation treatment that are described later are performed, the oxidized layer B and the oxidized layer C are formed to almost the same thickness. Accordingly, in a case where the oxidized layer C is thin, the oxide film 3 will also be thin.

[0083] The thicknesses of the oxidized layer B and the oxidized layer C are determined by the same method as the method used for determining the thickness of the oxidized layer A. The ferritic heat transfer member 4 that has undergone the steam oxidation treatment which is described later is prepared. The prepared ferritic heat transfer member 4 is observed by means of SEM by the same method as the method used for determining the thickness of the oxidized layer A. The oxidized layer B and the oxidized layer C are distinguished from each other by means of a contrast difference obtained with an SEM backscattered electron image. The contrast of the oxidized layer B is darker than the contrast of the oxidized layer C. The respective thicknesses of the oxidized layer B and the oxidized layer C are determined by the same method as the method used for determining the thickness of the oxidized layer A.

[Method for producing ferritic heat transfer member 4]

[0084] A method for producing ferritic heat transfer member 4 according to the present embodiment includes a steam oxidation treatment process.

[Steam oxidation treatment process]

[0085] A steam oxidation treatment is performed on the heat resistant ferritic steel that underwent the aforementioned oxidation treatment. The steam oxidation treatment is performed by exposing the heat resistant ferritic steel to steam at a temperature in a range from 500 to 650°C. An upper limit of the time period of the steam oxidation treatment is not particularly limited as long as the treatment time period is not less than 100 hours. By performing the steam oxidation treatment, the oxidized layer A changes to the oxide film 3 that includes the oxidized layer B and the oxidized layer C. By this means, the oxide film 3 that includes the oxidized layer B and the oxidized layer C is formed on the base material 2.

[0086] The ferritic heat transfer member 4 according to the present embodiment can be produced by the above processes. A similar effect as the effect obtained in a case of performing the steam oxidation treatment is obtained by exposing the heat resistant ferritic steel 1 of the present embodiment under a high-temperature steam environment. That is, if the heat resistant ferritic steel 1 of the present embodiment is exposed under a high-temperature steam environment for not less than 100 hours, the ferritic heat transfer member 4 can be produced even without performing a steam oxidation treatment.

EXAMPLES

[0087] Respective cast pieces having the chemical compositions shown in Table 1 were produced, and an oxidation treatment and a steam oxidation treatment were performed under the conditions illustrated in Table 2. Specifically, ingots having the chemical compositions shown in Table 1 were prepared. Each of the obtained ingots was subjected to hot rolling and cold rolling to produce a steel plate, which was adopted as the base material. A test specimen was prepared from each of the obtained base materials, and each test specimen was subjected to an oxidation treatment under the conditions shown in Table 2.

[Table 1]

[0088]

TABLE 1

Steel No.	Chemical Composition (mass%; balance is Fe and impurities)									
	C	Si	Mn	P	S	Cr	N	sol.Al	Mo,Ta,W,Re	Others
1	0.07	0.20	0.33	0.013	0.001	11.6	0.02	0.01	1.6W	-
2	0.11	0.25	0.40	0.015	<0.001	8.9	0.04	0.006	0.9Mo	0.2V
3	0.08	0.15	0.48	0.009	0.002	9.0	0.03	0.02	0.5Mo, 1.9W	0.06Nb, 0.004B
4	0.08	0.25	0.49	0.011	0.004	9.1	0.01	0.02	2.8Ta	2.6Co, 0.05Zr, 0.02Ca
5	0.07	0.11	0.16	0.013	0.002	8.8	0.04	0.01	2.2Re	0.02Nd
6	0.08	0.18	0.56	0.011	0.002	9.2	0.03	0.02	0.8Mo	0.25Ti, 0.01Mg
7	0.07	0.14	0.51	0.013	0.002	8.9	0.04	0.01	2.0W	0.3Hf
8	0.05	0.08	0.21	0.014	0.001	9.1	0.03	0.03	0.5Ta, 4.3Re	0.3Cu, 1.2Ni, 0.03Ce
9	0.12	0.31	0.55	0.014	0.002	8.9	0.03	0.02	0.6Mo, 1.6W	0.05Nb, 0.03Nd
10	0.11	0.32	0.41	0.011	0.003	9.4	0.04	0.01	-	-
11	0.11	0.16	0.45	0.013	0.001	15.4	0.02	0.02	1.5Mo	1.6Cu, 1.3Ni
12	0.15	0.25	0.64	0.009	0.002	5.2	0.04	0.02	0.9Mo	0.2V
13	0.09	0.33	0.32	0.013	0.001	9.6	0.03	0.01	8.1W	0.03La, 0.003B

[Table 2]

[0089]

TABLE 2

Test No.	Steel No.	Oxidation Treatment				Oxidized Layer A			Steam Oxidation Treatment		Oxidized Layer B		Oxidized Layer C			Performance Evaluation	
		Temperature (°C)	Time (mins)	CO/CO_2 Ratio	$(CO+CO_2)/N_2$ Ratio	Thickness (μm)	Total Amount Cr+ (mass%)	Total Amount of Mo+Ta+W+Re (mass%)	Temperature (°C)	Time (hours)	Fe_3O_4 Volume Ratio (%)	Total Amount of Cr+Mn (mass%)	Cr_2O_3 Volume Ratio (%)	Total Amount of Cr+Mn (mass%)	Total Amount of Mo+Ta+W+Re (mass%)	Thermal Conductivity of Oxidized Layer C ($W \cdot m^{-1} \cdot K^{-1}$)	Thickness of Oxidized Layer C (μm)
1	1	1050	10	1.2	0.2	2.3	41.7	2.0	560	5000	Fe_3O_4 (96)	1.2	4.7	25.6	2.1	1.3	23.5
2	1	1150	1	0.8	0.5	12.5	49.2	2.5	560	5000	Fe_3O_4 (97)	4.2	8.5	35.4	3.3	1.0	13.2
3	2	1060	20	1.0	0.6	4.6	35.9	1.3	600	5000	Fe_3O_4 (99)	<0.1	<0.1	20.4	2.0	1.5	34.2
4	2	-	-	-	-	-	-	-	600	5000	Fe_3O_4 (85)	6.5	10.2	26.8	0.8	1.0	20.9
5	2	850	15	1.2	0.3	0.2	32.2	0.4	600	5000	Fe_3O_4 (100)	<0.1	<0.1	19.6	0.4	1.0	25.4
6	2	1050	12	1.3	0.8	2.6	30.5	1.8	600	5000	Fe_3O_4 (94)	0.3	<0.1	20.7	3.3	1.7	37.9
7	2	1070	20	0.4	0.2	4.1	8.2	0.7	630	5000	$Fe_2O_3+Fe_3O_4$ (65)	<0.1	<0.1	3.7	3.2	3.4	77.8
8	2	1080	80	1.6	0.4	6.9	6.5	1.8	600	5000	Fe_3O_4 (100)	<0.1	<0.1	3.2	3.1	3.2	72.8
9	3	1010	2	1.6	0.3	1.1	22.8	8.7	630	5000	Fe_3O_4 (97)	<0.1	<0.1	12.4	13.5	2.5	52.6
10	3	1130	30	0.7	0.2	23.5	34.5	0.7	560	5000	Fe_3O_4 (100)	<0.1	1.1	27.4	1.1	1.2	31.7
11	3	1040	15	0.9	0.5	1.9	34.2	3.4	600	5000	Fe_3O_4 (98)	<0.1	<0.1	19.1	6.0	2.0	34.2
12	4	960	20	1.2	0.3	1.3	25.6	5.6	560	5000	Fe_3O_4 (100)	<0.1	<0.1	18.3	13.5	2.7	43.5
13	5	1120	5	0.9	0.3	3.2	28.9	4.3	560	5000	Fe_3O_4 (93)	0.8	2.5	24.1	4.8	1.7	32.8
14	6	1060	10	1.0	0.2	2.4	28.5	0.9	560	5000	Fe_3O_4 (95)	<0.1	<0.1	21.0	1.9	1.4	22.6
15	7	1060	10	1.0	0.7	3.5	27.6	2.6	560	5000	Fe_3O_4 (98)	<0.1	<0.1	19.3	5.8	2.0	34.6
16	8	1080	0.5	1.2	0.4	0.5	24.2	12.9	560	5000	Fe_3O_4 (100)	<0.1	<0.1	11.5	17.2	3.5	65.4
17	9	1050	12	1.1	0.4	1.8	30.4	1.6	630	5000	Fe_3O_4 (100)	<0.1	<0.1	22.4	2.5	1.5	25.2

(continued)

Test No.	Steel No.	Oxidation Treatment				Oxidized Layer A			Steam Oxidation Treatment		Oxidized Layer B		Oxidized Layer C			Performance Evaluation	
		Temperature (°C)	Time (mins)	CO/CO_2 Ratio	$(CO+CO_2)/N_2$ Ratio	Thickness (µm)	Total Amount Cr+ (mass%)	Total Amount of Mo+Ta+W+Re (mass%)	Temperature (°C)	Time (hours)	Fe_3O_4 Volume Ratio (%)	Total Amount of Cr+Mn (mass%)	Cr_2O_3 Volume Ratio (%)	Total Amount of Cr+Mn (mass%)	Total Amount of Mo+Ta+W+Re (mass%)	Thermal Conductivity of Oxidized Layer C ($W \cdot m^{-1} \cdot K^{-1}$)	Thickness of Oxidized Layer C (µm)
18	10	1050	10	1.1	0.3	4.5	28.6	<0.1	560	5000	Fe_3O_4 (100)	<0.1	3.8	26.4	<0.1	1.1	24.3
19	11	1040	15	1.1	0.4	1.3	47.6	2.7	600	5000	Fe_3O_4 (95)	0.4	34.2	56.7	3.4	0.8	18.9
20	12	1060	12	1.0	0.3	13.2	16.3	2.1	600	5000	Fe_3O_4 (97)	<0.1	<0.1	1.3	2.2	3.3	82.4
21	13	1060	15	1.0	0.3	2.9	22.9	13.9	580	5000	Fe_3O_4 (95)	<0.1	<0.1	13.2	18.6	3.8	72.5
22	2	1060	20	1.0	1.3	2.4	10.6	0.7	600	5000	Fe_3O_4 (97)	<0.1	<0.1	4.6	1.2	3.4	70.1

[Oxidized layer A thickness measurement test]

[0090] The thickness of the oxidized layer A of each test specimen was determined by the method described above. The results are shown in Table 2.

[Oxidized layer A metallic element content measurement test]

[0091] The content of each metallic element in a cross-section of each test specimen was determined by the method described above. For the oxidized layer A, the total content (mass%) of Cr and Mn, and the total content (mass%) of Mo, Ta, W and Re were determined. The results are shown in Table 2.

[0092] Each test specimen was subjected to a steam oxidation treatment under the conditions in Table 2. Each of the obtained test specimens was subjected to the following measurement tests.

[Tests to measure Fe_3O_4 and Fe_2O_3 volume ratio in oxidized layer B, and Cr_2O_3 volume ratio in oxidized layer C]

[0093] The total volume ratio of Fe_3O_4 and Fe_2O_3 in a cross-section (that is, a cross-section of the oxidized layer B) of each test specimen was determined by the method described above. Furthermore, the volume ratio of Cr_2O_3 in a cross-section of the oxidized layer C was determined. The results are shown in Table 2.

[Metallic element content measurement test]

[0094] The content of each metallic element in a cross-section of each test specimen was determined by the method described above. With respect to the oxidized layer B, the total content (mass%) of Cr and Mn was determined. The results are shown in Table 2. With respect to the oxidized layer C, the total content (mass%) of Cr and Mn, and the total content (mass%) of Mo, Ta, W and Re were determined. The results are shown in Table 2.

[Oxidized layer C thermal conductivity measurement test]

[0095] The thermal conductivity of the oxidized layer C of each test specimen was determined by the method described above. The results are shown in Table 2.

[Oxidized layer C thickness measurement test]

[0096] The thickness of the oxidized layer C of each test specimen was determined by the method described above. The results are shown in Table 2.

[Evaluation results]

[0097] Referring to Table 1 and Table 2, the chemical compositions and production conditions of the steels of Test Nos. 1, 3, 6, 9 to 15 and 17 were appropriate. Therefore, the oxidized layer A of each of these Test Nos. contained Cr and Mn in a total amount in a range of 20 to 45%, and contained one or more types of element selected from the group consisting of Mo, Ta, W and Re in a total amount in a range of 0.5 to 10%. As a result, the oxidized layer B formed on the base material after the steam oxidation treatment contained Fe_3O_4 and Fe_2O_3 in a total amount of 80% or more in vol%. In addition, the total content of Cr+Mn in the oxidized layer C was in a range of more than 5% to 30%, and the total content of the specific oxidized layer forming elements was in a range of 1 to 15%. As a result, the thermal conductivity of the oxidized layer C was within the range of 1.2 to 3.0 $W \cdot m^{-1} \cdot K^{-1}$, and thus exhibited excellent thermal conductivity. In addition, the thickness of the oxidized layer C was not more than 60 μm, and thus exhibited excellent steam oxidation resistance properties.

[0098] In contrast, in Test No. 2, although the chemical composition was appropriate, the oxidation treatment temperature was too high, and consequently the total amount of Cr and Mn in the oxidized layer A was more than 45%. Therefore, the Cr+Mn amount in the oxidized layer C was more than 30%, and the thermal conductivity was less than 1.2 $W \cdot m^{-1} \cdot K^{-1}$.

[0099] In Test No. 4, although the chemical composition was appropriate, an oxidation treatment was not performed, and the oxidized layer A was not formed. Consequently, the thermal conductivity of the oxidized layer C was less than 1.2 $W.m^{-1} \cdot K^{-1}$. It is considered that because the total amount of the specific oxidized layer forming elements in the oxidized layer C was less than 1%, the thermal conductivity was decreased.

[0100] In Test No. 5, although the chemical composition was appropriate, because the oxidation treatment temperature was too low, the total amount of the specific oxidized layer forming elements in the oxidized layer A was 0.4%, which was too low. Consequently, the total amount of the specific oxidized layer forming elements in the oxidized layer C was less than 1.0%. As a result, the thermal conductivity of the oxidized layer C was 1.0 $W{\cdot}m^{-1}{\cdot}K^{-1}$, which was too low.

[0101] In Test No. 7, although the chemical composition was appropriate, the CO/CO_2 ratio in the oxidation treatment was less than 0.6. Therefore, the total content of Cr and Mn in the oxidized layer A was less than 20%. Consequently, the total content of Cr and Mn in the oxidized layer C was not more than 5%, and the thermal conductivity of the oxidized layer C was more than 3.0 $W{\cdot}m^{-1}{\cdot}K^{-1}$. Further, because the Fe_3O_4 volume ratio in the oxidized layer B was less than 80%, the inward flux of oxygen was large and growth of the oxidized layer C was promoted, and the thickness of the oxidized layer C was more than 60 μm.

[0102] In Test No. 8, although the chemical composition was appropriate, the oxidation treatment time period was too long. Therefore, the total content of Cr and Mn in the oxidized layer A was 6.5%, which was too low. Consequently, the total content of Cr and Mn in the oxidized layer C was 3.2%, which was too low. As a result, the thermal conductivity of the oxidized layer C was 3.2 $W{\cdot}m^{-1}{\cdot}K^{-1}$, which was too high. Furthermore, in Test No. 8, the thickness of the oxidized layer C was more than 60 μm. It is considered that this was because the thermal conductivity of the oxidized layer C was too high.

[0103] In Test No. 16, although the chemical composition was appropriate, the oxidation treatment time period was too short. Therefore, the total content of the specific oxidized layer forming elements in the oxidized layer A was 12.9%, which was too high. Consequently, the total content of the specific oxidized layer forming elements in the oxidized layer C was 17.2%, which was too high. As a result, the thermal conductivity of the oxidized layer C was 3.5 $W{\cdot}m^{-1}{\cdot}K^{-1}$, which was too high. Furthermore, in Test No. 16, the thickness of the oxidized layer C was more than 60 μm. It is considered that this was because the thermal conductivity of the oxidized layer C was too high.

[0104] In Test No. 18, the steel did not contain any of the specific oxidized layer forming elements. Therefore, even though the production method was appropriate, the total content of the specific oxidized layer forming elements in the oxidized layer A was less than 0.1%, which was too low. Consequently, the total content of the specific oxidized layer forming elements in the oxidized layer C was less than 0.1%, which was too low. As a result, the thermal conductivity of the oxidized layer C was 1.1 $W{\cdot}m^{-1}{\cdot}K^{-1}$, which was too low.

[0105] In Test No. 19, the Cr content was too high. Therefore, even though the production method was appropriate, the total content of Cr and Mn in the oxidized layer A was 47.6%, which was too high. Consequently, the total content of Cr and Mn in the oxidized layer C was 56.7%, which was too high. As a result, the thermal conductivity of the oxidized layer C was 0.8 $W{\cdot}m^{-1}{\cdot}K^{-1}$, which was too low.

[0106] In Test No. 20, the Cr content was too low. Therefore, even though the production method was appropriate, the total content of Cr and Mn in the oxidized layer A was 16.3%, which was too low. Consequently, the total content of Cr and Mn in the oxidized layer C was 1.3%, which was too low. As a result, the thermal conductivity of the oxidized layer C was 3.3 $W{\cdot}m^{-1}{\cdot}K^{-1}$, which was too high. Furthermore, in Test No. 20, the thickness of the oxidized layer C was more than 60 μm. It is considered that this was because the thermal conductivity of the oxidized layer C was too high.

[0107] In Test No. 21, the content of the specific oxidized layer forming elements was too high. Therefore, the total content of the specific oxidized layer forming elements in the oxidized layer A was 13.9%, which was too high. Consequently, the total content of the specific oxidized layer forming elements in the oxidized layer C was 18.6%, which was too high. As a result, the thermal conductivity of the oxidized layer C was 3.8 $W{\cdot}m^{-1}{\cdot}K^{-1}$, which was too high. Furthermore, in Test No. 21 the thickness of the oxidized layer C was more than 60 μm. It is considered that this was because the thermal conductivity of the oxidized layer C was too high.

[0108] In Test No. 22, although the chemical composition was appropriate, the $(CO+CO_2)/N_2$ ratio was more than 1.0. Therefore, the total content of Cr and Mn in the oxidized layer A was 10.6%, which was too low. Consequently, the total content of Cr and Mn in the oxidized layer C was 4.6%, which was too low. As a result, the thermal conductivity of the oxidized layer C was 3.4 $W{\cdot}m^{-1}{\cdot}K^{-1}$, which was too high. Furthermore, in Test No. 22, the thickness of the oxidized layer C was more than 60 μm. It is considered that this was because the thermal conductivity of the oxidized layer C was too high.

[0109] An embodiment of the present invention has been described above. However, the foregoing embodiment is merely an example for implementing the present invention. Accordingly, the present invention is not limited to the above embodiment, and the above embodiment can be appropriately modified within a range that does not deviate from the gist of the present invention.

REFERENCE SIGNS LIST

[0110]

1	Heat Resistant Ferritic Steel
2	Base Material
3	Oxide Film

4	Ferritic Heat Transfer Member
A	Oxidized Layer A
B	Oxidized Layer B
C	Oxidized Layer C

Claims

1. A heat resistant ferritic steel comprising:

    a base material, and
    an oxidized layer A on a surface of the base material;
    wherein:
    the base material has a chemical composition consisting of, in mass%:

        C: 0.01 to 0.3%,
        Si: 0.01 to 2.0%,
        Mn: 0.01 to 2.0%,
        P: 0.10% or less,
        S: 0.03% or less,
        Cr: 7.0 to 14.0%,
        N: 0.005 to 0.15%,
        sol. Al: 0.001 to 0.3%,
        one or more types of element selected from a group consisting of Mo: 0 to 5.0%, Ta: 0 to 5.0%, W: 0 to 5.0% and Re: 0 to 5.0%: 0.5 to 7.0% in total,
        Cu: 0 to 5.0%,
        Ni: 0 to 5.0%,
        Co: 0 to 5.0%,
        Ti: 0 to 1.0%,
        V: 0 to 1.0%,
        Nb: 0 to 1.0%,
        Hf: 0 to 1.0%,
        Ca: 0 to 0.1%,
        Mg: 0 to 0.1%,
        Zr: 0 to 0.1%,
        B: 0 to 0.1%, and
        rare earth metal: 0 to 0.1%,
        with the balance being Fe and impurities; and
        the oxidized layer A has a chemical composition containing, in mass%:

            Cr and Mn: 20 to 45% in total, and
            one or more types of element selected from a group consisting of Mo, Ta, W and Re: 0.5 to 10% in total.

2. The heat resistant ferritic steel according to claim 1, wherein the chemical composition of the base material contains one or more types of element selected from a group consisting of:

    Cu: 0.005 to 5.0%,
    Ni: 0.005 to 5.0%, and
    Co: 0.005 to 5.0%.

3. The heat resistant ferritic steel according to claim 1 or claim 2, wherein the chemical composition of the base material contains one or more types of element selected from a group consisting of:

    Ti: 0.01 to 1.0%,
    V: 0.01 to 1.0%,

Nb: 0.01 to 1.0%, and
Hf: 0.01 to 1.0%.

4. The heat resistant ferritic steel according to any one of claims 1 to 3, wherein the chemical composition of the base material contains one or more types of element selected from a group consisting of:

Ca: 0.0015 to 0.1%,
Mg: 0.0015 to 0.1%,
Zr: 0.0015 to 0.1%,
B: 0.0015 to 0.1%, and
rare earth metal: 0.0015 to 0.1%.

5. A ferritic heat transfer member, comprising:

a base material having a chemical composition according to any one of claims 1 to 4, and
an oxide film on a surface of the base material;
wherein:

the oxide film comprises:

an oxidized layer B containing Fe_3O_4 and Fe_2O_3 in a total amount of 80% or more in vol%, and
an oxidized layer C that is disposed between the oxidized layer B and the base material; and
a chemical composition of the oxidized layer C contains, in mass%:

Cr and Mn: more than 5% to 30% in total, and
one or more types of element selected from a group consisting of Mo, Ta, W and Re: 1 to 15% in total.

6. The ferritic heat transfer member according to claim 5, wherein a chemical composition of the oxidized layer B contains, in mass%:
Cr and Mn: 5% or less in total.

7. The ferritic heat transfer member according to claim 5 or claim 6, wherein the oxidized layer C contains, in vol%, 5% or less of Cr_2O_3.

FIG. 1

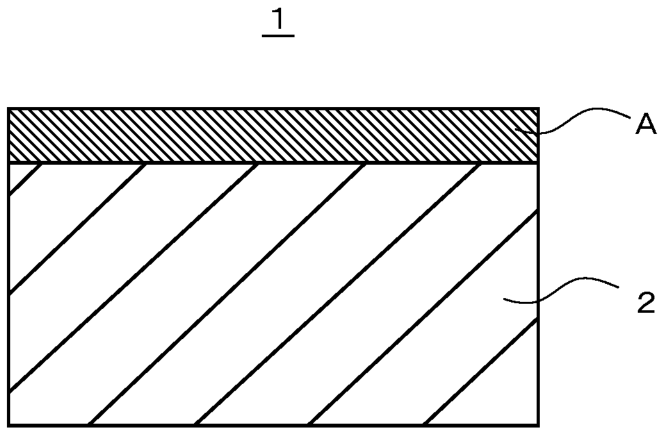
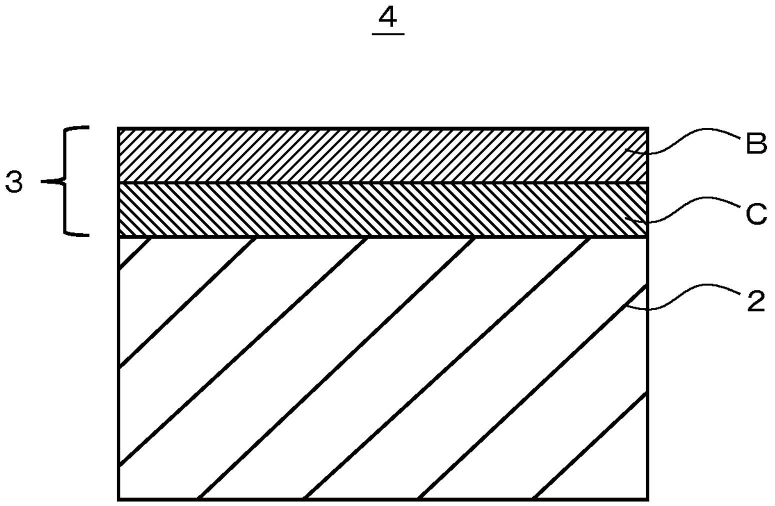


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/024012

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/58*(2006.01)i, *C23C8/10*(2006.01)i, *C21D1/76*(2006.01)n

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-C22C38/60, C23C8/10, C21D1/76, C21D6/00

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	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

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	WO 2013/077363 A1 (Nippon Steel & Sumitomo Metal Corp.), 30 May 2013 (30.05.2013), claims; 0001 to 0002, 0018, 0021, 0034 to 0052, 0063 to 0094, 0105 to 0114; tables 1 to 4 & US 2014/0295194 A1 claims; 0001 to 0002, 0018, 0021, 0038 to 0060, 0071 to 0100, 0111 to 0118; tables 1 to 4 & US 2017/0218496 A1 & EP 2784172 A1 & CN 103946413 A & KR 10-2014-0093954 A & RU 2566122 C1 & ZA 201403446 B & ES 2604714 T3	1-7
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☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 13 September 2017 (13.09.17)	Date of mailing of the international search report 26 September 2017 (26.09.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2007-39745 A (Babcock-Hitachi Kabushiki Kaisha), 15 February 2007 (15.02.2007), (Family: none)	1-7
A	CN 103334056 A (TIANJIN UNIVERSITY OF TECHNOLOGY), 02 October 2013 (02.10.2013), (Family: none)	1-7

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