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(54) **AUSTENITE-BASED HEAT-RESISTANT ALLOY**

(57) There is provided an austenitic heat resistant alloy having a chemical composition that contains, in mass percent: C: 0.03 to 0.25%, Si: 0.01 to 2.0%, Mn: 0.10 to 0.50%, P: 0.030% or less, S: 0.010% or less, Cr: 13.0 to 30.0%, Ni: 25.0 to 45.0%, Al: 2.5 to 4.5%, Nb:

0.01 to 2.00%, N: 0.05% or less, Ti: 0 to 0.20%, W: 0 to 6.0%, Mo: 0 to 4.0%, Zr: 0 to 0.10%, B: 0 to 0.0100%, Cu: 0 to 5.0%, REM: 0 to 0.10%, Ca: 0 to 0.050%, Mg: 0 to 0.050%, and the balance: Fe and impurities.

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to an austenitic heat resistant alloy.

BACKGROUND ART

10 **[0002]** Olefins (C_nH_{2n}) such as ethylene (C_2H_4) are produced by subjecting hydrocarbons (naphtha, natural gas, ethane, etc.) to heat decomposition. Specifically, olefinic hydrocarbons (ethylene, propylene, etc.) are obtained by supplying hydrocarbons and steam to an inside of a pipe that is installed in a reactor and made of a high Cr-high Ni alloy, typically 25Cr-25Ni alloys or 25Cr-38Ni alloys, or is made of a stainless steel, typically SUS304 or the like, and by adding heat from an outer surface of the pipe, so that a heat decomposition reaction of the hydrocarbons occurs on an inner surface of the pipe.

15 **[0003]** As a demand of synthetic resins has increased in recent years, a tendency of a higher temperature has become stronger in use conditions of a pyrolytic furnace pipe for ethylene plant, from a viewpoint of increasing an ethylene yield. The inner surface of such a pyrolytic furnace pipe is exposed to a carburizing atmosphere, and thus there is a demand for a heat resistant material that is excellent in high temperature strength and carburization resistance properties.

20 **[0004]** Moreover, as carburization proceeds, a phenomenon called coking in which carbon precipitates on the inner surface of the pyrolytic furnace pipe occurs during operation. As a precipitation amount in the coking increases, a harmful effect on the operation, such as an increase in pressure loss and a decrease in heating efficiency, arises. Therefore, in a practical operation, oxidization and removal of the precipitating carbon by supplying air and steam, what is called a decoking operation, are performed periodically, which however raises a major problem such as an operation stop during the decoking operation and an increase in number of work person-hours.

25 **[0005]** Prior art includes developments of materials each having improved carburization resistance properties. For example, JP2001-40443A (Patent Document 1) proposes a Ni-based heat resistant alloy that is excellent in hot workability, weldability, and carburization resistance properties. However, a Ni-based alloy is difficult to produce because a γ' phase, which is a brittle phase, precipitates at high temperature, narrowing a temperature range that allows hot working.

30 **[0006]** Hence, there is a development of a Fe-based austenitic stainless steel for improvement of the hot workability. For example, WO 2017/119415 (Patent Document 2) proposes an austenitic heat resistant alloy that keeps a high creep strength and a high toughness even in a high-temperature environment.

LIST OF PRIOR ART DOCUMENTS

35 PATENT DOCUMENT

[0007]

Patent Document 1: JP 2001-40443A

40 Patent Document 2: WO 2017/119415

SUMMARY OF INVENTION

TECHNICAL PROBLEM

45 **[0008]** The austenitic heat resistant alloy described in Patent Document 2 forms an alumina layer on its surface while being used at high temperature, which not only provides high corrosion resistances but also allows the austenitic heat resistant alloy to have a long-term high-temperature strength and an excellent toughness. However, Patent Document 2 has no sufficient investigation on the carburization resistance properties, leaving room for improvement.

50 **[0009]** The present invention has an objective to provide an austenitic heat resistant alloy that keeps a high creep strength and excellent carburization resistance properties even in its use in a high temperature environment.

SOLUTION TO PROBLEM

55 **[0010]** The present invention is made to solve the problem described above, and the gist of the present invention is the following austenitic heat resistant alloy.

(1) An austenitic heat resistant alloy having a chemical composition consisting of, in mass percent:

C: 0.03 to 0.25%;
 Si: 0.01 to 2.0%;
 Mn: 0.10 to 0.50%;
 P: 0.030% or less;
 S: 0.010% or less;
 Cr: 13.0 to 30.0%;
 Ni: 25.0 to 45.0%;
 Al: 2.5 to 4.5%;
 Nb: 0.05 to 2.00%;
 N: 0.05% or less;
 Ti: 0 to 0.20%;
 W: 0 to 6.0%;
 Mo: 0 to 4.0%;
 Zr: 0 to 0.10%;
 B: 0 to 0.0100%;
 Cu: 0 to 5.0%;
 REM: 0 to 0.10%;
 Ca: 0 to 0.050%;
 Mg: 0 to 0.050%; and
 the balance: Fe and impurities.

(2) The austenitic heat resistant alloy according to the above (1), wherein the chemical composition contains, in mass percent, B: 0.0010 to 0.0100%.

(3) The austenitic heat resistant alloy according to the above (1) or (2), wherein in a case where the alloy is heated in the atmosphere containing steam at 900°C for 20 hours and subsequently heated in an H₂-CH₄-CO₂ atmosphere at 1100°C for 96 hours, a continuous alumina layer having a thickness ranging from 0.5 to 15 μm is formed on a surface of the alloy.

(4) The austenitic heat resistant alloy according to the above (3), wherein in the case where the alloy is heated in the atmosphere containing steam at 900°C for 20 hours and subsequently heated in the H₂-CH₄-CO₂ atmosphere at 1100°C for 96 hours, a layer having a Cr-Mn-based spinel structure formed on the alumina layer has a thickness of 5 μm or less.

ADVANTAGEOUS EFFECTS OF INVENTION

[0011] According to the present invention, an austenitic heat resistant alloy that keeps a high creep strength and excellent carburization resistance properties even in its use in a high temperature environment can be obtained.

DESCRIPTION OF EMBODIMENTS

[0012] The present inventors conducted investigations and studies about carburization resistance properties of an austenitic heat resistant alloy in a high-temperature environment at 1000°C or more (hereinafter, referred to simply as "high temperature environment"), and obtained the following findings.

[0013] Carburization resistance properties at high temperature can be kept by forming a continuous alumina layer on a surface of a base metal. The formation of the alumina layer is promoted by presence of Cr. This effect is called the third element effect (TEE) of Cr. In a very early stage of oxidation, Cr is preferentially oxidized on the surface of the base metal, forming a chromia layer.

[0014] This consumes oxygen in the surface of the base metal, decreasing an oxygen partial pressure. As a result, Al does not undergo internal oxidation but forms the continuous alumina layer in proximity to the surface. Afterward, oxygen used by the chromia layer is taken by the alumina layer, by which a protective layer made only of alumina is eventually formed. Therefore, to form a continuous alumina layer having a protectability, Cr needs to be contained at a certain content or more.

[0015] Here, in a case where a heat resistant alloy is used in a form of a pyrolytic furnace pipe, it is not possible to completely prevent the occurrence of coking. This requires a decoking operation to be performed periodically. At that time, the decoking removes even the alumina layer formed on the surface of the base metal. Therefore, when the heat resistant alloy is reused in the high temperature environment, it is desirable that the continuous alumina layer recovers itself immediately.

[0016] However, if the layer having the "Cr-Mn-based spinel structure" (in the following description, also referred to as "Cr-Mn spinel layer") is produced excessively in the use, Cr in an outer layer of the base metal runs short. This

restrains the TEE as a period of the use increases, which causes Al to undergo internal oxidation, forming discontinuous alumina layers on the surface. As a result, the alumina becomes unable to fulfill a function as the protective layer.

[0017] That is, in order to keep self-recovery properties of the alumina layer for a long time, it is necessary to restrain the formation of the Cr-Mn spinel layer on the surface of the base metal. To this end, it is necessary to reduce a content of Mn in the base metal.

[0018] The present invention is made based on the findings described above. Requirements of the present invention will be described below in detail.

1. Chemical Composition

[0019] The reasons for limiting contents of elements are as described below. In the following description, the symbol "%" for the contents means "percent by mass."

C: 0.03 to 0.25%

[0020] C (carbon) forms carbides, increasing the creep strength. Specifically, C binds with alloying elements to form fine carbides in crystal grain boundaries and grains in the use in the high-temperature environment. The fine carbides increase deformation resistance, thereby increasing the creep strength. If a content of C is excessively low, this effect is not obtained. In contrast, if the content of C is excessively high, a large number of coarse eutectic carbides are formed in a solidification micro-structure of the heat resistant alloy after casting. The eutectic carbides remain coarse in the micro-structure even after solution treatment, thus decreasing a toughness of the heat resistant alloy. In addition, the remaining coarse eutectic carbides make it difficult for the fine carbides to precipitate in the use in the high-temperature environment, decreasing the creep strength. Accordingly, the content of C is to range from 0.03 to 0.25%. A lower limit of the content of C is preferably 0.04%, more preferably 0.05%. An upper limit of the content of C is preferably 0.23%, more preferably 0.20%.

Si: 0.01 to 2.0%

[0021] Silicon (Si) deoxidizes the heat resistant alloy. In addition, Si increases corrosion resistances (oxidation resistance and steam oxidation resistance) of the heat resistant alloy. Si is an element that is contained unavoidably, but in a case where the deoxidation can be performed sufficiently by other elements, a content of Si may be as low as possible. In contrast, if the content of Si is excessively high, the hot workability is decreased. Accordingly, the content of Si is to range from 0.01 to 2.0%. A lower limit of the content of Si is preferably 0.02%, more preferably 0.03%. An upper limit of the content of Si is preferably 1.0%, more preferably 0.3%.

Mn: 0.10 to 0.50%

[0022] Manganese (Mn) binds with S contained in the heat resistant alloy to form MnS, increasing the hot workability of the heat resistant alloy. However, if a content of Mn is excessively high, the heat resistant alloy becomes excessively hard, decreasing in the hot workability and the weldability. In addition, the excessively high content of Mn causes the production of the Cr-Mn spinel layer described above, which inhibits the TEE, inhibiting uniform formation of the alumina layer. Accordingly, the content of Mn is to range from 0.10 to 0.50%. An upper limit of the content of Mn is preferably 0.40%, more preferably 0.30%, still more preferably 0.20%.

P: 0.030% or less

[0023] Phosphorus (P) is an impurity. P decreases the weldability and the hot workability of the heat resistant alloy. Accordingly, the content of P is to be 0.030% or less. The content of P is preferably as low as possible.

S: 0.010% or less

[0024] Sulfur (S) is an impurity. S decreases the weldability and the hot workability of the heat resistant alloy. Accordingly, a content of S is to be 0.010% or less. The content of S is preferably as low as possible.

Cr: 13.0 to 30.0%

[0025] Chromium (Cr) increases corrosion resistances (oxidation resistance, steam oxidation resistance, etc.) of the heat resistant alloy in the high temperature environment. In addition, Cr brings about the TEE, promoting the uniform

formation of the alumina layer. However, if a content of Cr is excessively high, the formation of the chromia layer becomes predominant, and the formation of the alumina layer is rather inhibited. Accordingly, the content of Cr is to range from 13.0 to 30.0%. A lower limit of the content of Cr is preferably 15.0%. An upper limit of the content of Cr is preferably 25.0%, and more preferably 20.0%.

Ni: 25.0 to 45.0%

[0026] Nickel (Ni) stabilizes austenite. In addition, Ni binds with Al to form fine NiAl, increasing the creep strength. Moreover, Ni has an effect of increasing the corrosion resistances of the heat resistant alloy as well as an effect of increasing the carburization resistance properties by decreasing a diffusion velocity of C in the steel. If a content of Ni is excessively low, these effects are not obtained. In contrast, if the content of Ni is excessively high, these effects level off, and furthermore, the hot workability is decreased. In addition, the excessively high content of Ni increases a raw-material cost. Accordingly, the content of Ni is to range from 25.0 to 45.0%. A lower limit of the content of Ni is preferably 30.0%. An upper limit of the content of Ni is preferably 40.0%, more preferably 35.0%.

Al: 2.5 to 4.5%

[0027] Aluminum (Al) forms the alumina layer, which is excellent in the carburization resistance properties, in the use in the high temperature environment. In addition, Al binds with Ni to form the fine NiAl, increasing the creep strength. If a content of Al is excessively low, these effects are not obtained. In contrast, if the content of Al is excessively high, a structural stability is decreased, and a strength is decreased. Accordingly, the content of Al is to range from 2.5 to 4.5%. A lower limit of the content of Al is preferably 2.8%, more preferably 3.0%. An upper limit of the content of Al is preferably 3.8%. In the austenitic heat resistant alloy according to the present invention, the content of Al means a total amount of Al contained in the alloy.

Nb: 0.05 to 2.00%

[0028] Niobium (Nb) forms intermetallic compounds (Laves phase and Ni₃Nb phase) to be precipitation strengthening phases, so as to bring about precipitation strengthening in the crystal grain boundaries and the grains, increasing the creep strength of the heat resistant alloy. In contrast, if a content of Nb is excessively high, the intermetallic compounds are produced excessively, decreasing the toughness and the hot workability of the alloy. The excessively high content of Nb additionally decreases a toughness after long-time aging. Accordingly, the content of Nb is to range from 0.05 to 2.00%. A lower limit of the content of Nb is preferably 0.50%, more preferably 0.80%. An upper limit of the content of Nb is preferably 1.20%, more preferably 1.00%.

N: 0.05% or less

[0029] Nitrogen (N) stabilizes austenite and is unavoidably contained through a normal solution process. However, if a content of N is excessively high, coarse carbo-nitrides are formed and remain undissolved even after the solution treatment, decreasing the toughness of the alloy. Accordingly, the content of N is to be 0.05% or less. An upper limit of the content of N is preferably 0.01%.

Ti: 0 to 0.20%

[0030] Titanium (Ti) forms the intermetallic compounds (Laves phase and Ni₃Ti phase) to be the precipitation strengthening phases, so as to bring about the precipitation strengthening, increasing the creep strength. Therefore, Ti may be contained as necessary. However, if a content of Ti is excessively high, the intermetallic compounds are produced excessively, decreasing a high temperature ductility and the hot workability. The excessively high content of Ti additionally decreases the toughness after long-time aging. Accordingly, the content of Ti is to be 0.20% or less. An upper limit of the content of Ti is preferably 0.15%, more preferably 0.10%. Note that the content of Ti is preferably 0.03% or more in a case where an intention is to obtain the above effect.

W: 0 to 6.0%

[0031] Tungsten (W) is dissolved in the austenite being a parent phase (matrix), bringing about solid-solution strengthening to increase the creep strength through. In addition, W forms Laves phases in the crystal grain boundaries and the grains, bringing about the precipitation strengthening to increase the creep strength. Therefore, W may be contained as necessary. However, if a content of W is excessively high, the Laves phases are produced excessively, decreasing the

high temperature ductility, the hot workability, and the toughness. Accordingly, the content of W is to be 6.0% or less. An upper limit of the content of W is preferably 5.5%, more preferably 5.0%. Note that the content of W is preferably 0.005% or more, and more preferably 0.01% or more in a case where an intention is to obtain the above effect.

Mo: 0 to 4.0%

[0032] Molybdenum (Mo) is dissolved in the austenite being the parent phase, bringing about the solid-solution strengthening to increase the creep strength through. In addition, Mo forms the Laves phases in the crystal grain boundaries and the grains, bringing about the precipitation strengthening to increase the creep strength. Therefore, Mo may be contained as necessary. However, if a content of Mo is excessively high, the Laves phases are produced excessively, decreasing the high temperature ductility, the hot workability, and the toughness. Accordingly, the content of Mo is to be 4.0% or less. An upper limit of the content of Mo is preferably 3.5%, more preferably 3.0%. Note that the content of Mo is preferably 0.005% or more, and more preferably 0.01% or more in a case where an intention is to obtain the above effect.

Zr: 0 to 0.10%

[0033] Zirconium (Zr) brings about grain-boundary strengthening, increasing the creep strength. Therefore, Zr may be contained as necessary. However, if a content of Zr is excessively high, the weldability and the hot workability of the heat resistant alloy are decreased. Accordingly, the content of Zr is to be 0.10% or less. An upper limit of the content of Zr is preferably 0.06%. Note that the content of Zr is preferably 0.0005% or more, and more preferably 0.001% or more in a case where an intention is to obtain the above effect.

B: 0 to 0.0100%

[0034] Boron (B) brings about the grain-boundary strengthening, increasing the creep strength. Therefore, B may be contained as necessary. However, if a content of B is excessively high, the weldability is decreased. Accordingly, the content of B is to be 0.0100% or less. An upper limit of the content of B is preferably 0.0050%. Note that the content of B is preferably 0.0001% or more in a case where an intention is to obtain the above effect. The lower limit of the content of B is more preferably 0.0005%, still more preferably 0.0010%, 0.0020% or more, or 0.0030% or more.

Cu: 0 to 5.0%

[0035] Copper (Cu) promotes the formation of the alumina layer in proximity to the surface, increasing the corrosion resistances of the heat resistant alloy. Therefore, Cu may be contained as necessary. However, if a content of Cu is excessively high, the effect levels off, and furthermore, the high temperature ductility is decreased. Accordingly, the content of Cu is to be 5.0% or less. An upper limit of the content of Cu is preferably 4.8%, more preferably 4.5%. Note that the content of Cu is preferably 0.05% or more, and more preferably 0.10% or more in a case where an intention is to obtain the above effect.

REM: 0 to 0.10%

[0036] Rare earth metal (REM) immobilizes S in a form of its sulfide, increasing the hot workability. In addition, REM forms its oxide, increasing the corrosion resistances, the creep strength, and a creep ductility. Therefore, REM may be contained as necessary. However, if a content of REM is excessively high, inclusions such as the oxide are increased, decreasing the hot workability and the weldability, and increasing production costs. Accordingly, the content of REM is to be 0.10% or less. An upper limit of the content of REM is preferably 0.09%, more preferably 0.08%. Note that the content of REM is preferably 0.0005% or more, and more preferably 0.001% or more in a case where an intention is to obtain the above effect.

[0037] Here, in the present invention, REM refers to Sc (scandium), Y (yttrium), and lanthanoids, 17 elements in total, and the content of REM means a total content of these elements. In industrial practice, the lanthanoids are added in a form of misch metal.

Ca: 0 to 0.050%

[0038] Calcium (Ca) immobilizes S in a form of its sulfide, increasing the hot workability. Therefore, Ca may be contained as necessary. However, if a content of Ca is excessively high, the toughness, the ductility, and a cleanliness are decreased. Accordingly, the content of Ca is to be 0.050% or less. An upper limit of the content of Ca is preferably 0.030%,

more preferably 0.010%. Note that the content of Ca is preferably 0.0005% or more in a case where an intention is to obtain the above effect.

Mg: 0 to 0.050%

[0039] Magnesium (Mg) immobilizes S in a form of its sulfide, increasing the hot workability. Therefore, Mg may be contained as necessary. However, if a content of Mg is excessively high, the toughness, the ductility, and the cleanliness are decreased. Accordingly, the content of Mg is to be 0.050% or less. An upper limit of the content of Mg is preferably 0.030%, more preferably 0.010%. Note that the content of Mg is preferably 0.0005% or more in a case where an intention is to obtain the above effect.

[0040] The balance of the chemical composition described above is Fe and impurities. The term "impurities" as used herein means components that are mixed in the alloy in producing the alloy industrially due to raw materials such as ores and scraps, and various factors of a producing process, and are allowed to be mixed in the alloy within ranges in which the impurities have no adverse effect on the present invention.

2. Layer

[0041] As described above, it is preferable for the austenitic heat resistant alloy according to the present invention to immediately form the continuous alumina layer having a protectability in the high temperature environment. Specifically, in a case where the alloy is heated in the atmosphere containing steam at 900°C for 20 hours and subsequently heated in an H₂-CH₄-CO₂ atmosphere at 1100°C for 96 hours, it is preferable that the continuous alumina layer having a thickness ranging from 0.5 to 15 μm is formed on the surface of the alloy. Note that the treatment of heating the alloy in the atmosphere containing steam at 900°C for 20 hours is directed to performing the decoking in advance.

[0042] If the thickness of the alumina layer formed by the treatment is less than 0.5 μm, the layer is broken in a short time in a high temperature carburizing environment, failing to keep the corrosion resistances. In contrast, if the thickness of the layer is more than 15 μm, the layer cannot withstand its internal stress and is prone to form a crack. Note that whether the alumina layer is continuous is evaluated by observing a cross section of the layer under a scanning electron microscope (SEM).

[0043] Additionally, it is preferable that the formation of the Cr-Mn spinel layer is restrained in the high-temperature environment. Specifically, in the case where the alloy is heated in the atmosphere containing steam at 900°C for 20 hours and subsequently heated in an H₂-CH₄-CO₂ atmosphere at 1100°C for 96 hours, it is preferable that the thickness of the layer having the Cr-Mn-based spinel structure formed on the alumina layer is 5 μm or less.

[0044] If the thickness of the Cr-Mn spinel layer is more than 5 μm, a Cr depleted zone is produced in the outer layer of the base metal, due to which the TEE is restrained as a period of the use increases.

3. Producing Method

[0045] As an example of a method for producing the austenitic heat resistant alloy according to the present invention, a method for producing an alloy pipe will be described. The producing method in the present embodiment includes a preparation step, a hot forging step, a hot working step, a cold working step, and a solution heat treatment step described below. The producing method may further include a scale removing step after the solution heat treatment step. The steps will be each described below.

[Preparation Step]

[0046] A molten steel having the chemical composition described above is produced. The molten steel is subjected to a well-known degassing treatment as necessary. The molten steel is cast to be produced into a starting material. The starting material may be an ingot made by an ingot-making process, or may be a cast piece such as a slab, bloom, and billet made by a continuous casting process.

[Hot Forging Step]

[0047] Hot forging is performed on the cast starting material to produce a cylindrical starting material. In the hot forging, its area reduction ratio defined by Formula (i) is set at 30% or more.

Area reduction ratio = $100 - (\text{cross-sectional area of starting material after hot working} / \text{cross-sectional area of starting material before hot forging}) \times 100 (\%)$ (i)

[Hot Working Step]

[0048] Hot working is performed on the hot-forged cylindrical starting material to produce an alloy hollow shell. For example, a through hole is formed at a center of the cylindrical starting material by machining. Hot extrusion is performed on the cylindrical starting material with the through hole formed to produce the alloy hollow shell. The alloy hollow shell may be produced by performing piercing-rolling on the cylindrical starting material.

[Cold Working Step]

[0049] Cold working is performed on the hot-worked alloy hollow shell to produce an intermediate material. The cold working is, for example, cold drawing or the like.

[0050] In a case where the cold working is performed, its area reduction ratio defined by Formula (ii) is set at 15% or more.

Area reduction ratio = $100 - (\text{cross-sectional area of starting material after cold working} / \text{cross-sectional area of starting material before cold working}) \times 100 (\%)$ (ii)

[0051] By performing the cold working at the area reduction ratio of 15% or more, a micro-structure of the base metal becomes close-grained through recrystallization in heat treatment, which enables formation of a more close-grained alumina layer.

[Solution Heat Treatment Step]

[0052] Solution heat treatment is performed on the produced intermediate material. By the solution heat treatment, the carbides and the precipitates included in the intermediate material are dissolved.

[0053] In the solution heat treatment, its heat treatment temperature is 1150 to 1280°C. If the heat treatment temperature is less than 1150°C, the carbides and the precipitates are not dissolved sufficiently, and as a result, the corrosion resistances deteriorate. In contrast, if the heat treatment temperature is excessively high, the crystal grain boundaries are melted. A duration of the solution heat treatment is 1 minute or more, in which the carbides and the precipitates are dissolved.

[Scale Removing Step]

[0054] After the solution heat treatment step, shotblasting may be performed to remove scales formed on the surface. In addition, pickling treatment may be performed to remove the scales. In this case, the intermediate material is immersed in a fluoro-nitric acid at 20 to 40°C made by mixing 5% hydrofluoric acid and 10% nitric acid, for 2 to 10 minutes.

[0055] By the above producing method, the austenitic heat resistant alloy according to the present embodiment is produced. The above description is made about the method for producing an alloy pipe, a plate material, but a bar material, a wire rod, or the like may be produced by a similar producing method.

[0056] The present invention will be described below more specifically with reference to examples, but the present invention is not limited to these examples.

EXAMPLES

[0057] Molten steels having chemical compositions shown in Table 1 were produced using a vacuum furnace. The molten steels were used to produce column-shaped ingots having an outer diameter of 120 mm. The hot forging at an area reduction ratio of 60% was performed on the ingots to produce rectangular-shaped starting materials. Then, the hot rolling and the cold rolling were performed on the rectangular-shaped starting materials to produce plate-shaped intermediate materials having a thickness of 1.5 mm. In the cold rolling, its area reduction ratio was 50%. Subsequently, the intermediate materials were retained at 1200°C for 10 minutes and then water-cooled to be produced into alloy plate materials.

[Table 1]

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[0058]

Table 1

Test No.	Chemical composition (mass %, balance: Fe and impurities)											
	C	Si	Mn	P	S	Cr	Ni	Al	Nb	N	B	Others
1	0.10	0.17	0.16	0.012	0.003	14.96	34.77	2.79	1.01	0.0019	-	-
2	0.15	0.18	0.31	0.008	0.006	13.14	40.66	3.56	0.94	0.0037	-	Ti: 0.12
3	0.12	0.14	0.22	0.009	0.008	28.14	35.10	3.44	0.92	0.0022	0.0031	-
4	0.12	0.11	0.47	0.012	0.007	13.24	35.80	2.98	1.20	0.0019	-	Ca: 0.0052
5	0.15	0.19	0.11	0.007	0.007	21.56	32.80	4.21	0.98	0.0150	0.0078	W: 4.55
6	0.18	0.35	0.35	0.012	0.009	28.25	26.21	4.01	0.97	0.0087	0.0006	Mo: 1.98
7	0.11	0.16	0.44	0.011	0.007	20.11	36.33	3.80	1.21	0.0069	0.0033	Zr: 0.08
8	0.08	0.27	0.21	0.011	0.006	15.30	29.55	3.55	1.22	0.0025	0.0007	Cu: 3.52
9	0.15	0.44	0.16	0.013	0.005	24.33	30.43	3.52	1.52	0.0033	0.0028	REM: 0.014
10	0.18	0.19	0.17	0.011	0.005	17.88	30.05	2.81	1.55	0.0021	0.0045	Mg: 0.0020
11	0.11	0.13	0.44	0.008	0.005	15.33	28.55	4.23	1.05	0.0022	-	-
12	0.10	0.11	0.34	0.020	0.005	18.30	28.94	3.55	1.74	0.0034	-	-
13	0.12	0.19	0.21	0.007	0.001	24.21	38.15	3.24	0.52	0.0340	-	W: 0.55
14	0.82	0.21	0.98	0.013	0.006	23.14	31.64	3.55	1.05	0.0025	0.0022	-
15	0.12	0.14	1.13	0.011	0.004	20.31	35.69	3.14	0.74	0.0021	0.0038	-
16	0.14	0.11	1.04	0.012	0.006	20.64	30.27	1.56	1.49	0.0029	0.0038	-
17	0.16	1.91	0.20	0.021	0.006	25.61	34.55	3.21	0.02	0.0022	0.0025	-
18	0.10	0.16	0.16	0.012	0.001	24.82	39.67	1.99	0.10	0.0086	-	-
19	0.10	0.80	0.54	0.020	0.001	15.05	31.10	2.94	2.20	0.0184	-	-
20	0.14	0.15	0.75	0.008	0.007	28.64	34.90	3.84	2.50	0.0018	-	-

Inventive example

Comparative example

[0059] First, from the materials made by subjecting the rectangular-shaped starting materials to the retention at 1200°C for 10 minutes and the subsequent water cooling, round bar creep rupture test specimens each having a diameter of 6 mm and a gage length of 30 mm, which are described in JIS Z 2241(2011), were taken and subjected to the creep rupture test, under conditions of 1000°C and 10 MPa. The test was conducted in conformity with JIS Z 2271(2010). When a creep rupture time of a test specimen was less than 2000 h, the test specimen was rated as poor (×), when the creep rupture time ranged from 2000 to 3000 h, the test specimen was rated as good (○), and when the creep rupture time was more than 3000 h, the test specimen was rated as excellent (○○).

[0060] Next, two of the alloy plate materials were prepared for each test number, and the two alloy plate materials were subjected to the carburizing treatment described below. One of the two alloy plate materials was subjected to carburizing treatment in which the one alloy plate material was heated in an H₂-CH₄-CO₂ atmosphere, at 1100°C, for 96 hours (once-treated material).

[0061] The once-treated material subjected to the carburizing treatment was cut into halves in a direction perpendicular to its rolling direction. One of the halves was embedded in resin, and its observation surface was polished, by which a test specimen for observation was fabricated. Then, a kind, a thickness, and a form of the formed layer were observed under a SEM. In addition, a surface of the other of the halves subjected to the carburizing treatment was subjected to manual dry polishing using #600 abrasive paper, by which scales and the like on the surface were removed.

[0062] The other of the two alloy plate materials was subjected to a process including carburizing treatment in which the other alloy plate material was heated in the H₂-CH₄-CO₂ atmosphere, at 1100°C, for 96 hours, and after the carburizing treatment, heating the other alloy plate material at 900°C for 20 hours in the atmosphere containing steam, and the process was repeated five times (five-time-treated material).

[0063] Then, from a surface of each of the once-treated material and the five-time-treated material from which scales were removed, a machined chip for analysis including four 0.5-mm-pitch layers was taken, and a concentration of C of the machined chip for analysis was measured by the high frequency combustion infrared absorption method. From the concentration, a concentration of C contained in the starting material is subtracted, by which an increase of C content was determined. In the present invention, a case where the increase of C content was 0.3% or less was evaluated as being excellent in the carburization resistance properties.

[0064] Results of the observation and results of the test are collectively shown in Table 2.

[Table 2]

[0065]

Table 2

Test No.	Creep strength	Cr-Mn spinel layer	Alumina layer		Increase of C content (%)		
		Thickness (μm)	Thickness (μm)	Form	once	five-time	
1	○	-	10	continuous	0.10	0.11	Inventive example
2	○	-	8	continuous	0.17	0.16	
3	○○	-	8	continuous	0.14	0.15	
4	○	5	7	continuous	0.22	0.27	
5	○○	-	10	continuous	0.05	0.08	
6	○	-	8	continuous	0.09	0.08	
7	○○	3	7	continuous	0.19	0.23	
8	○	-	9	continuous	0.11	0.08	
9	○○	-	9	continuous	0.07	0.08	
10	○○	-	7	continuous	0.15	0.15	
11	○	4	7	continuous	0.21	0.22	
12	○	-	8	continuous	0.16	0.23	
13	○	-	8	continuous	0.15	0.14	

(continued)

Test No.	Creep strength	Cr-Mn spinel layer	Alumina layer		Increase of C content (%)		
		Thickness (μm)	Thickness (μm)	Form	once	five-time	
14	×	21	2	discontinuous	0.11	0.15	Comparative example
15	○	21	2	discontinuous	0.83	1.25	
16	○	23	-	none	1.10	1.72	
17	×	-	7	continuous	0.21	0.25	
18	○	-	4	discontinuous	0.32	0.55	
19	○	14	2	discontinuous	0.51	0.89	
20	○	19	2	discontinuous	0.65	1.06	

[0066] Referring to Table 2, regarding Test Nos. 1 to 13, their chemical compositions satisfied the specification according to the present invention, and thus the production of the Cr-Mn spinel layer was restrained, and good alumina layers were formed. As a result, they showed excellent carburization resistance properties.

[0067] In particular, regarding steels except those of Test Nos. 4, 7, and 11, their contents of Mn were reduced to 0.35% or less, and thus the production of the Cr-Mn spinel layer was not recognized, and their carburization resistance properties were consequently more excellent than others. In addition, regarding Test Nos. 3, 5, 7, 9, 10, and 13, in which at least one of B and W is contained, resulted in more excellent creep strengths than cases where neither B nor W was contained, or the content of B or W was insufficient.

[0068] In contrast to these, Test Nos. 14 to 20 are comparative examples that did not satisfy the specification according to the present invention. Specifically, Test No. 14 had a high content of C, and Test No. 17 had a low content of Nb, and thus Test No. 14 and Test No. 17 resulted in poor creep strengths.

[0069] Regarding Test Nos. 14 to 16, 19, and 20, because their contents of Mn were high, the Cr-Mn spinel layer was formed, and a Cr depleted zone was produced on each outer layer of their base metals, which restrained the TEE, inhibiting the formation of the alumina layer. Regarding Test Nos. 16 and 18, their contents of Al were low, resulting in insufficient formation of the alumina layer.

[0070] As a result, regarding Test Nos. 14, 15, and 18 to 20, their alumina layers were formed discontinuously, and regarding Test No. 16, no alumina layer was formed. Therefore, these comparative examples resulted in poor carburization resistance properties for both of their once-treated materials and five-time-treated materials.

Claims

1. An austenitic heat resistant alloy having a chemical composition consisting of, in mass percent:

C: 0.03 to 0.25%;
Si: 0.01 to 2.0%;
Mn: 0.10 to 0.50%;
P: 0.030% or less;
S: 0.010% or less;
Cr: 13.0 to 30.0%;
Ni: 25.0 to 45.0%;
Al: 2.5 to 4.5%;
Nb: 0.05 to 2.00%;
N: 0.05% or less;
Ti: 0 to 0.20%;
W: 0 to 6.0%;
Mo: 0 to 4.0%;
Zr: 0 to 0.10%;
B: 0 to 0.0100%;
Cu: 0 to 5.0%;

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REM: 0 to 0.10%;
Ca: 0 to 0.050%;
Mg: 0 to 0.050%; and
the balance: Fe and impurities.

- 5
2. The austenitic heat resistant alloy according to claim 1, wherein the chemical composition contains, in mass percent, B: 0.0010 to 0.0100%.
- 10
3. The austenitic heat resistant alloy according to claim 1 or claim 2, wherein in a case where the alloy is heated in an atmosphere containing steam at 900°C for 20 hours and subsequently heated in an H₂-CH₄-CO₂ atmosphere at 1100°C for 96 hours, a continuous alumina layer having a thickness ranging from 0.5 to 15 μm is formed on a surface of the alloy.
- 15
4. The austenitic heat resistant alloy according to claim 3, wherein in the case where the alloy is heated in the atmosphere containing steam at 900°C for 20 hours and subsequently heated in the H₂-CH₄-CO₂ atmosphere at 1100°C for 96 hours, a layer having a Cr-Mn-based spinel structure formed on the alumina layer has a thickness of 5 μm or less.
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/048342

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C22C38/48 (2006.01) i, C22C38/54 (2006.01) i, C23C8/18 (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)

Int.Cl. C22C38/00-38/60, C23C8/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2019

Registered utility model specifications of Japan 1996-2019

Published registered utility model applications of Japan 1994-2019

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 10-140296 A (SUMITOMO METAL INDUSTRIES, LTD.) 26 May 1998, claims, paragraph [0001], table 1 (Family: none)	1-4
X	CN 103774056 A (UNIV JIANGSU) 07 May 2014, paragraphs [0001], [0019] (Family: none)	1-4



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2017/119415 A1 (NIPPON STEEL & SUMITOMO METAL CORPORATION) 13 July 2017, claims, paragraph [0093], table 1 & EP 3401415 A1, claims, paragraph [0093], table 1 & CN 108474072 A	1-4
A	JP 7-331390 A (SUMITOMO METAL INDUSTRIES, LTD.) 19 December 1995, claims, table 1 (Family: none)	1-4
A	WO 2016/104417 A1 (KUBOTA CORP.) 30 June 2016, claims, paragraphs [0001]-[0003], table 1 & EP 3239311 A1, claims, paragraphs [0001]-[0003], table 1 & JP 2016-125088 A	1-4
A	JP 9-243284 A (KUBOTA CORP.) 19 September 1997, claims, paragraph [0026] (Family: none)	1-4

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2001040443 A [0005] [0007]
- WO 2017119415 A [0006] [0007]