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(54) AUSTENITIC HEAT-RESISTANT ALLOY AND METHOD FOR MANUFACTURING SAME

(57) Provided is an austenitic heat resistant alloy having high creep strength and high toughness even in a high temperature environment. This austenitic heat resistant alloy has a chemical composition consisting of: in mass%, C: 0.03 to less than 0.25%, Si: 0.01 to 2.0%, Mn: not more than 2.0%, Cr: 10 to less than 30%, Ni: more than 25 to 45%, Al: more than 2.5 to less than 4.5%, Nb: 0.2 to 3.5%, N: not more than 0.025%, with the balance being Fe and impurities, wherein P and S in the impurities are respectively, P: not more than 0.04% and S: not more than 0.01%. In the structure, a total volume ratio of precipitates having a circle equivalent diameter of not less than 6 μm is not more than 5%.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a heat resistant alloy and a method for producing the same, and more specifically to an austenitic heat resistant alloy and a method for producing the same.

BACKGROUND ART

[0002] Conventionally, 18-8 stainless steel has been used for a heat resistant steel in facilities such as boilers and chemical plants, which are used in high temperature environments. The 18-8 stainless steel is an austenitic stainless steel containing about 18% of Cr and about 8% of Ni, and is, for example, SUS304H, SUS316H, SUS321H, and SUS347H in the JIS standard.

[0003] In recent years, use conditions of facilities in high temperature environments have become significantly harsh, and there is a need for high creep strength even higher than that of the 18-8 stainless steel. Further recently, the Advanced-Ultra Super Critical pressure power generation plan has been promoted in which a conventional steam temperature of about 600°C is increased to not less than 700°C in a boiler for thermal power generation. Moreover, to improve operation efficiency, increasing the operation temperature is also planned in chemical plants. For steel materials to be used in these high temperature environments, high creep strength as well as excellent corrosion resistance is required.

[0004] Heat resistant materials with enhanced corrosion resistance have been proposed in Japanese Patent Application Publication No. 02-115348 (Patent Literature 1) and Japanese Patent Application Publication No. 07-316751 (Patent Literature 2). An Al_2O_3 film is to be formed on surfaces of these heat resistant alloys in a high temperature range during use since these alloys have a high Al content. The film provides excellent corrosion resistance.

[0005] However, the above-described heat resistant alloys disclosed in Patent Literatures 1 and 2 may exhibit insufficient creep strength in a high temperature environment of not less than 700°C.

[0006] As a heat resistant material having a high creep strength in a high temperature environment of not less than 700°C, a heat resistant alloy containing Ni and Co, and also containing a γ' phase (Ni_3Al) as a strengthening phase has been developed. Examples of such heat resistant alloy include Ni-based Alloys 617, 263, and 740. However, alloying raw materials for those heat resistant alloys are expensive. Further, since these alloys have low workability, production cost thereof tends to be high.

[0007] Accordingly, heat resistant alloys which are inexpensive than the above-described Ni-base alloys and are excellent in creep strength have been proposed in Japanese Patent Application Publication No. 2014-43621 (Patent Literature 3) and Japanese Patent Application Publication No. 2013-227644 (Patent Literature 4).

[0008] The austenitic heat resistant alloy disclosed in Patent Literature 3 has a chemical composition containing, in mass%, C: less than 0.02%, Si: not more than 2%, Mn: not more than 2%, Cr: 15 to 26%, Ni: 20 to 35%, Al: not more than 0.3%, P: not more than 0.04%, S: not more than 0.01%, and N: not more than 0.05%, and further containing one or more kinds selected from Ti: not more than 3.0% (including 0%), V: not more than 3.0% (including 0%), Nb: less than 2.3% (including 0%), and Ta: not more than 2.0% (including 0%), wherein a condition of f1: 1.5 to 6.0 where f1 = 2Ti + 2V + Nb + (1/2)Ta is satisfied, with the balance being Fe and impurities. Patent Literature 3 states that the above-described austenitic heat resistant alloy has excellent high temperature strength and toughness due to precipitation strengthening by a Laves phase and a γ' phase.

[0009] The austenitic heat resistant alloy disclosed in Patent Literature 4 has a chemical composition consisting of, in mass%, C: less than 0.02%, Si: 0.01 to 2%, Mn: not more than 2%, Cr: not less than 20% and less than 28%, Ni: more than 35% and not more than 50%, W: 2.0 to 7.0%, Mo: less than 2.5% (including 0%), Nb: less than 2.5% (including 0%), Ti: less than 3.0% (including 0%), Al: not more than 0.3%; P: not more than 0.04%, S: not more than 0.01%, and N: not more than 0.05%, with the balance being Fe and impurities, wherein the chemical composition further satisfies f1: 1.0 to 5.0, where f1 = 1/2W + Mo; f2: 2.0 to 8.0, where f2 = 1/2W + Mo + Nb +2Ti; and f3: 0.5 to 5.0, where f3 = Nb + 2Ti. Patent Literature 4 states that the above-described austenitic heat resistant alloy has excellent high temperature strength and toughness due to precipitation strengthening by a Laves phase and a γ' phase.

CITATION LIST

PATENT LITERATURE

[0010]

Patent Literature 1: Japanese Patent Application Publication No. 02-115348

Patent Literature 2: Japanese Patent Application Publication No. 07-316751
Patent Literature 3: Japanese Patent Application Publication No. 2014-43621
Patent Literature 4: Japanese Patent Application Publication No. 2013-227644

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0011] However, as in the heat resistant alloys of Patent Literatures 3 and 4, in a case of an alloy which takes advantage of strengthening mechanism by a Laves phase and a γ' phase, creep strength and toughness may deteriorate after long-hours aging.

[0012] An objective of the present invention is to provide an austenitic heat resistant alloy having high creep strength and high toughness even in a high temperature environment.

SOLUTION TO PROBLEM

[0013] An austenitic heat resistant alloy according to the present embodiment has a chemical composition consisting of: in mass%, C: 0.03 to less than 0.25%, Si: 0.01 to 2.0%, Mn: not more than 2.0%, Cr: 10 to less than 30%, Ni: more than 25 to 45%, Al: more than 2.5 to less than 4.5%, Nb: 0.2 to 3.5%, N: not more than 0.025%, Ti: 0 to less than 0.2%, W: 0 to 6%, Mo: 0 to 4%, Zr: 0 to 0.1%, B: 0 to 0.01%, Cu: 0 to 5%, rare earth metals: 0 to 0.1%, Ca: 0 to 0.05%, and Mg: 0 to 0.05%, with the balance being Fe and impurities, wherein P and S in the impurities are respectively P: not more than 0.04% and S: not more than 0.01%. In the structure, a total volume ratio of precipitates having a circle equivalent diameter of not less than 6 μm is not more than 5%. Where, the precipitates are, for example, carbides, nitrides, NiAl, and α-Cr.

ADVANTAGEOUS EFFECTS OF INVENTION

[0014] The austenitic heat resistant alloy according to the present embodiment has a high temperature strength for long hours and excellent toughness even in a high temperature environment.

DESCRIPTION OF EMBODIMENTS

[0015] The present inventors have conducted investigation and research on creep strength and toughness of austenitic heat resistant alloys in a high temperature environment of not less than 700°C (hereinafter, simply referred to as a "high temperature environment"), and have obtained the following findings.

[0016] As described so far, a heat resistant alloy containing a Laves phase and γ' phase such as Ni_3Al has a high creep strength in a high temperature environment. However, since these precipitation phases are coarsened when used for long hours in a high temperature environment, creep strength and toughness of the heat resistant alloy deteriorate.

[0017] On the other hand, provided that precipitates such as carbides, nitrides, NiAl, α-Cr, and the like can be caused to precipitate in a finely dispersed manner during use of the heat resistant alloy in a high temperature environment, it is possible to maintain a high creep strength and high toughness even in long-hours use. These precipitates cover grain boundaries, thereby increasing grain boundary strength. Further, when these precipitates precipitate inside grains, deformation resistance of the heat resistant alloy is increased, thereby increasing the creep strength.

[0018] To increase the creep strength and toughness by the above-described fine precipitates, the structure of the heat resistant alloy before use is controlled as follows.

[Limitation of amount of precipitates having a circle equivalent diameter of not less than 6 μm]

[0019] In a solidified structure after casing of a heat resistant alloy, precipitates such as carbides, nitrides, NiAl, α-Cr, and the like (hereinafter, simply referred to as "precipitates") are present. These precipitates are generated in a liquid phase in which solution elements that are present between dendrites are condensed. These precipitates have typically coarse shapes, and are non-uniformly dispersed in the structure. Therefore, the toughness of the heat resistant alloy deteriorates.

[0020] Further, even when subjected to solution treatment, these precipitates are not likely to dissolve, remaining in a coarse state. When these precipitates remain in a coarse state in a heat resistant alloy, it is not likely that fine precipitates are formed during use in a high temperature environment. Therefore, a total volume ratio of coarse precipitates in a heat resistant alloy is preferably as low as possible.

[0021] Provided that the total volume ratio of precipitates having a circle equivalent diameter of not less than 6 μm (hereinafter, referred to as "coarse precipitates") is not more than 5% in the structure of a heat resistant alloy, an enough amount of fine precipitates can be caused to precipitate during use of heat resistant alloy in a high temperature environment, and thus high creep strength and high toughness can be obtained.

[0022] To make the total volume ratio of coarse precipitates in the structure not more than 5%, the C content in the heat resistant alloy is made to be less than 0.25%. Further, the reduction of area during hot forging is made not less than 30%. In this case, coarse precipitates are uniformly dispersed by hot forging. Because of that, in a solution treatment in a later step, precipitates can be dissolved, and thus the total volume ratio of coarse precipitates will be not more than 5%.

[0023] The austenitic heat resistant alloy according to the present embodiment, which has been completed based on the above findings, has a chemical composition consisting of, in mass%, C: 0.03 to less than 0.25%, Si: 0.01 to 2.0%, Mn: not more than 2.0%, Cr: 10 to less than 30%, Ni: more than 25 to 45%, Al: more than 2.5 to less than 4.5%, Nb: 0.2 to 3.5%, N: not more than 0.025%, Ti: 0 to less than 0.2%, W: 0 to 6%, Mo: 0 to 4%, Zr: 0 to 0.1%, B: 0 to 0.01%, Cu: 0 to 5%, rare earth metals: 0 to 0.1%, Ca: 0 to 0.05%, and Mg: 0 to 0.05%, with the balance being Fe and impurities, wherein P and S in the impurities are respectively, P: not more than 0.04% and S: not more than 0.01%. In the structure, the total volume ratio of precipitates having a circle equivalent diameter of not less than 6 μm is not more than 5%.

[0024] The above-described chemical composition may contain, in mass%, one or more kinds selected from the group consisting of, Ti: 0.005 to less than 0.2%, W: 0.005 to 6%, Mo: 0.005 to 4%, Zr: 0.0005 to 0.1%, and B: 0.0005 to 0.01%.

[0025] The above-described chemical composition may contain, in mass%, one or more kinds selected from the group consisting of, Cu: 0.05 to 5%, and rare earth metals: 0.0005 to 0.1%.

[0026] The above-described chemical composition may contain, in mass%, one or more kinds selected from the group consisting of, Ca: 0.0005 to 0.05% and Mg: 0.0005 to 0.05%.

[0027] A method for producing the above-described austenitic heat resistant alloy includes steps of: performing hot forging at a reduction of area of not less than 30% on a starting material having the above-described chemical composition; producing an intermediate material by performing hot working on the starting material after hot forging; and performing solution treatment at 1100 to 1250°C on the intermediate material.

[0028] Hereinafter, an austenitic heat resistant alloy of the present embodiment will be described in detail. The symbol "%" relating to elements means, unless otherwise stated, mass%.

[Chemical composition]

[0029] The austenitic heat resistant alloy of the present embodiment is, for example, an alloy pipe. The chemical composition of the austenitic heat resistant alloy contains the following elements.

C: 0.03 to less than 0.25%

[0030] Carbon (C) forms carbides and increases creep strength. Specifically, C combines with an alloy element to form fine carbides at crystal grain boundaries and in crystal grains during use in a high temperature environment. The fine carbides increase deformation resistance and increase creep strength. When the C content is too low, this effect cannot be obtained. On the other hand, when the C content is too high, a large number of coarse eutectic carbides are formed in a solidified structure after casting of the heat resistant alloy. Since the eutectic carbides remain coarse in the structure even after solution treatment, they deteriorate toughness of the heat resistant alloy. Further, if the coarse eutectic carbides remain, fine carbides are not likely to precipitate during use in a high temperature environment, and thus creep strength decreases. Thus, the C content is 0.03 to less than 0.25%. A lower limit of the C content is preferably 0.05%, and more preferably 0.08%. An upper limit of C content is preferably 0.23%, and more preferably 0.20%.

Si: 0.01 to 2.0%

[0031] Silicon (Si) deoxidizes a heat resistant alloy. Si further improves corrosion resistance (oxidation resistance and steam oxidation resistance) of a heat resistant alloy. While Si is an element that is inevitably contained, the Si content may be as small as possible when deoxidization is sufficiently carried out by other elements. On the other hand, when the Si content is too high, hot workability deteriorates. Therefore, the Si content is 0.01 to 2.0%. A lower limit of the Si content is preferably 0.02%, and more preferably 0.03%. An upper limit of the Si content is preferably 1.0%.

Mn: not more than 2.0%

[0032] Manganese (Mn) is inevitably contained. Mn combines with S contained in a heat resistant alloy to form MnS, thereby improving hot workability of the heat resistant alloy. However, when the Mn content is too high, the heat resistant alloy becomes too hard, and hot workability and weldability deteriorate. Therefore, the Mn content is not more than 2.0%. A lower limit of the Mn content is preferably 0.1%, and more preferably 0.2%. An upper limit of the Mn content is preferably

1.2%.

Cr: 10 to less than 30%

[0033] Chromium (Cr) improves corrosion resistance (oxidation resistance, steam oxidation resistance, etc.) of a heat resistant alloy in a high temperature environment. Cr further finely precipitates as α-Cr during use in a high temperature environment to increase creep strength. When the Cr content is too low, these effects cannot be obtained. On the other hand, when the Cr content is too high, the stability of the structure deteriorates, and the creep strength decreases. Therefore, the Cr content is 10 to less than 30%. A lower limit of the Cr content is preferably 11%, and more preferably 12%. An upper limit of the Cr content is preferably 28%, and more preferably 26%.

Ni: more than 25 to 45%

[0034] Nickel (Ni) stabilizes austenite. Ni further improves the corrosion resistance of a heat resistant alloy. When the Ni content is too low, such effect cannot be obtained. On the other hand, when the Ni content is too high, not only such effect is saturated, but also hot workability deteriorates. Further, when the Ni content is too high, the raw material cost increases. Therefore, the Ni content is more than 25 to 45%. A lower limit of the Ni content is preferably 26%, and more preferably 28%. An upper limit of the Ni content is preferably 44%, and more preferably 42%.

Al: more than 2.5 to less than 4.5%

[0035] Aluminum (Al) combines with Ni to form fine NiAl during use in a high temperature environment, thereby increasing creep strength. Al further improves corrosion resistance in a high temperature environment of not less than 1000°C. When the Al content is too low, these effects cannot be obtained. On the other hand, when the Al content is too high, structural stability deteriorates, and strength decreases. Therefore, the Al content is more than 2.5 to less than 4.5%. A lower limit of the Al content is preferably 2.55%, and more preferably 2.6%. An upper limit of the Al content is preferably 4.4%, and more preferably 4.2%. In the austenitic heat resistant alloy according to the present invention, the Al content means the total Al amount contained in the steel material.

Nb: 0.2 to 3.5%

[0036] Niobium (Nb) forms a Laves phase and a Ni_3Nb phase which work as precipitation strengthening phases, and precipitation-strengthens crystal grain boundaries and crystal grains, thereby increasing creep strength of a heat resistant alloy. When the Nb content is too low, the above effect cannot be obtained. On the other hand, when the Nb content is too high, the Laves phase and the Ni_3Nb phase are excessively generated, thereby deteriorating toughness and hot workability of the alloy. When the Nb content is too high, toughness after long-hours aging will also deteriorate. Therefore, the Nb content is 0.2 to 3.5%. A lower limit of the Nb content is preferably 0.35%, and more preferably 0.5%. An upper limit of the Nb content is preferably less than 3.2%, and more preferably 3.0%.

N: not more than 0.025%

[0037] Nitrogen (N) stabilizes austenite and is inevitably contained in a usual melting method. In addition, N combines with an alloy element to form fine nitrides at crystal grain boundaries and in crystal grains during use in a high temperature environment. Fine nitrides increase deformation resistance, thereby increasing creep strength. However, when the N content is too high, it forms coarse nitrides which remain undissolved even after solution treatment, thus decreasing toughness of the alloy. Therefore, the N content is not more than 0.025%. An upper limit of the N content is preferably 0.02%, and more preferably 0.01%.

P: not more than 0.04%

[0038] Phosphorus (P) is an impurity. P deteriorates weldability and hot workability of a heat resistant alloy. Therefore, the P content is not more than 0.04%. An upper limit of P content is preferably 0.03%. The P content is preferably as low as possible.

S: not more than 0.01%

[0039] Sulfur (S) is an impurity. S deteriorates weldability and hot workability of a heat resistant alloy. Therefore, the S content is not more than 0.01%. An upper limit of the S content is preferably 0.008%. The S content is preferably as low as possible.

[0040] The balance of the chemical composition of the austenitic heat resistant alloy of the present embodiment consists of Fe and impurities. Herein, the term impurity means what are introduced from ores and scraps as raw materials, or production environments when industrially producing an austenitic heat resistant alloy, and what are permitted within a range not adversely affecting the present invention.

[Optional elements]

[0041] The chemical composition of the above-described austenitic heat resistant alloy may contain, in lieu of part of Fe, one or more kinds selected from the group consisting of Ti, W, Mo, Zr, and B. All of these elements are optional elements, and increase creep strength.

Ti: 0 to less than 0.2%

[0042] Titanium (Ti) is an optional element and may not be contained. When contained, Ti forms a Laves phase and a Ni_3Ti phase, which each act as a precipitation strengthening phase, and creep strength is increased by the precipitation strengthening. However, when the Ti content is too high, the Laves phase and the Ni_3Ti phase are excessively generated, thereby deteriorating high temperature ductility and hot workability. Further, when the Ti content is too high, toughness after long-hours aging deteriorates. Therefore, the Ti content is 0 to less than 0.2%. A lower limit of Ti content is preferably 0.005%, and more preferably 0.01%. An upper limit of Ti content is 0.15%, and more preferably 0.1%.

W: 0 to 6%

[0043] Tungsten (W) is an optional element and may not be contained. When contained, W dissolves into austenite which is the mother phase (matrix), thereby increasing creep strength by solid solution strengthening. Further, W forms a Laves phase at crystal grain boundaries and in crystal grains, thereby increasing creep strength by precipitation strengthening. However, when the W content is too high, the Laves phase is excessively generated, thereby deteriorating high-temperature ductility, hot workability, and toughness. Therefore, the W content is 0 to 6%. A lower limit of the W content is preferably 0.005%, and more preferably 0.01%. An upper limit of W content is preferably 5.5%, and more preferably 5%.

Mo: 0 to 4%

[0044] Molybdenum (Mo) is an optional element and may not be contained. When contained, Mo dissolves into austenite of the mother phase, thereby increasing creep strength by solid solution strengthening. Mo further forms a Laves phase at crystal grain boundaries and in crystal grains, thereby increasing creep strength by precipitation strengthening. However, when the Mo content is too high, the Laves phase is excessively generated, thereby deteriorating high temperature ductility, hot workability and toughness. Therefore, the Mo content is 0 to 4%. A lower limit of the Mo content is 0.005%, and more preferably 0.01%. An upper limit of the Mo content is preferably 3.5%, and more preferably 3%.

Zr: 0 to 0.1%

[0045] Zirconium (Zr) is an optional element and may not be contained. When contained, Zr increases creep strength by grain boundary strengthening. However, when the Zr content is too high, weldability and hot workability of a heat resistant alloy deteriorate. Therefore, the Zr content is 0 to 0.1%. A lower limit of the Zr content is preferably 0.0005%, more preferably 0.001%. An upper limit of the Zr content is preferably 0.06%.

B: 0 to 0.01%

[0046] Boron (B) is an optional element and may not be contained. When contained, B increases creep strength by grain boundary strengthening. However, when the B content is too high, weldability deteriorates. Therefore, the B content is 0 to 0.01%. A lower limit of B is preferably 0.0005%, and more preferably 0.001%. An upper limit of the B content is preferably 0.005%.

[0047] The chemical composition of the above-described austenitic heat resistant alloy may contain, in lieu of part of Fe, one or more kinds selected from the group consisting of Cu and rare earth metals. All of these elements are optional elements, and increase corrosion resistance of a heat resistant alloy.

Cu: 0 to 5%

[0048] Copper (Cu) is an optional element and may not be contained. When contained, Cu facilitates formation of an Al_2O_3 film in the vicinity of the surface, thereby enhancing corrosion resistance of a heat resistant alloy. However, when the Cu content is too high, not only such effect is saturated, but also the high temperature ductility deteriorates. Therefore, the Cu content is 0 to 5%. A lower limit of the Cu content is preferably 0.05%, and more preferably 0.1%. An upper limit of the Cu content is preferably 4.8%, and more preferably 4.5%.

Rare earth metals: 0 to 0.1%

[0049] Rare earth metals (REM) are optional elements and may not be contained. When contained, REM each immobilize S as a sulfide, thereby improving hot workability. REM further form oxides to improve corrosion resistance, creep strength, and creep ductility. However, when the REM content is too high, inclusions such as oxides increase, thereby deteriorating hot workability and weldability, and increasing production cost. Therefore, the REM content is 0 to 0.1%. A lower limit of the REM content is preferably 0.0005%, and more preferably 0.001%. An upper limit of the REM content is preferably 0.09%, and more preferably 0.08%.

[0050] The term REM as used herein is a general term for a total of 17 elements including Sc, Y and lanthanoide series. When the REM contained in a heat resistant alloy is one kind of these elements, a REM content means the content of that element. When the REM contained in the heat resistant alloy is not less than two kinds, the REM content means the total content of those elements. REM are generally contained in Mischmetal. Therefore, REM may be added in the form of Mischmetal such that the REM content is within the above-described range.

[0051] The chemical composition of the above-described austenitic heat resistant alloy may contain, in lieu of part of Fe, one or more kinds selected from the group consisting of Ca and Mg. All of these elements are optional elements, and improve hot workability of a heat resistant alloy.

Ca: 0 to 0.05%

[0052] Calcium (Ca) is an optional element and may not be contained. When contained, Ca immobilizes S as a sulfide, thereby improving hot workability. On the other hand, when the Ca content is too high, toughness, ductility and cleanliness deteriorate. Therefore, the Ca content is 0 to 0.05%. A lower limit of Ca is preferably 0.0005%. An upper limit of the Ca content is preferably 0.01%.

Mg: 0 to 0.05%

[0053] Magnesium (Mg) is an optional element and may not be contained. When contained, Mg immobilizes S as a sulfide, thereby improving hot workability of a heat resistant alloy. On the other hand, when the Ca content is too high, toughness, ductility and cleanliness deteriorate. Therefore, the Ca content is 0 to 0.05%. A lower limit of Ca is preferably 0.0005%. An upper limit of the Ca content is preferably 0.01%.

[Total volume ratio of precipitates (coarse precipitates) having a circle equivalent diameter of not less than 6 μm: not more than 5%]

[0054] As described so far, in the austenitic heat resistant alloy of the present embodiment, fine precipitates are caused to precipitate during use in a high temperature environment, and thus creep strength and maintaining toughness are increased. Examples of the precipitate include carbides, nitrides, NiAl, and α-Cr. When the precipitate is coarse, creep strength and toughness deteriorate. Therefore, coarse precipitates are preferably as small in amount as possible in a heat resistant alloy before use. Provided that the total volume ratio of precipitates having a circle equivalent diameter of not less than 6 μm (coarse precipitates) is not more than 5% in the structure of the heat resistant alloy, fine precipitates are caused to precipitate during use in a high temperature environment, and thus creep strength and toughness are increased. An upper limit of the total volume ratio of coarse precipitates is preferably 4%, and more preferably 3%. Here, the circle equivalent diameter of a precipitate means a diameter (μm) of a circle which has the same area as that of the precipitate.

[Measurement method of total volume ratio of coarse precipitates in structure]

[0055] A total volume ratio of coarse precipitates in the structure of an austenitic heat resistant alloy of the present embodiment can be measured by the following method.

[0056] A test specimen of a vertical section to the surface is sampled from a heat resistant alloy material. For example, when the austenitic heat resistant alloy material is an alloy pipe, a test specimen is sampled from a middle portion of wall thickness of a section normal to the axial direction.

[0057] After a section (observation surface) of the sampled test specimen is polished, the observation surface is etched by a mixed acid solution of hydrochloric acid and nitric acid. Arbitrary 10 visual fields in the observation surface are imaged by using a scanning electron microscope (SEM) to create SEM images (backscattered electron images). Each visual field is 100 μm × 100 μm.

[0058] In a SEM image, a precipitate and the matrix have different contrast, respectively. By determining area of a precipitate which is identified from difference in contrast, a circle equivalent diameter of each precipitate is calculated. After calculation, precipitates having a circle equivalent diameter of not less than 6 μm (coarse precipitates) are identified.

[0059] A total area of the identified coarse precipitates is determined. Also a proportion (%) of the total area of coarse precipitates to the area of the visual field is determined. Since an area ratio of precipitate corresponds to a volume ratio thereof, the determined proportion of coarse precipitates is defined as a total volume ratio (%) of coarse precipitates.

[0060] The shape of the austenitic heat resistant alloy of the present embodiment is not particularly limited. The austenitic heat resistant alloy is, for example, an alloy pipe. An austenitic heat resistant alloy pipe is used for piping for boilers and a reaction pipe for chemical plants. The austenitic heat resistant alloy may be a plate, a bar, or a wire.

[Production method]

[0061] A production method of an alloy pipe will be described as an example of the method for producing an austenitic heat resistant alloy of the present embodiment. The production method of the present embodiment includes: a step of preparing a starting material having the above-described chemical composition (preparation step); a step of hot forging the prepared starting material (hot forging step); a step of producing an intermediate material by performing hot working on the hot forged starting material (hot working step); and a step of performing solution heat treatment on the intermediate material (solution heat treatment step). Hereinafter, each step will be described.

[Preparation step]

[0062] Molten steels having the above-described chemical compositions are produced. The molten steels are subjected as needed to a well-known degassing treatment. Using a molten steel, a starting material is produced by casting. The starting material may be an ingot by an ingot-making process, a slab by a continuous casting process, or a cast piece such as a bloom, and a billet.

[Hot forging step]

[0063] The produced starting material is subjected to hot forging to produce a columnar starting material. In the hot forging, the reduction of area defined by Formula (1) is made not less than 30%.

$$\text{Reduction of area} = 100 - (\text{sectional area of starting material after hot forging}/\text{sectional area of starting material before hot forging}) \times 100\ (\%) \quad (1)$$

[0064] As described above, precipitates such as eutectic carbides are present in the structure of the starting material produced by casting. These precipitates are coarse, and a large number of them have a circle equivalent diameter of not less than 6 μm. Such coarse precipitates are not likely to dissolve even in a solution treatment in a later step.

[0065] Provided that the reduction of area is not less than 30% in the hot forging step, the coarse precipitates are broken off during hot forging, thereby decreasing in size. Therefore, the precipitates are more likely to dissolve in the solution heat treatment in a later step. As a result of this, the volume ratio of precipitates having a circle equivalent diameter of not less than 6 μm will become not more than 5%.

[0066] The reduction of area is preferably not less than 35%, and more preferably not less than 40%. Although the upper limit of the reduction of area is not particularly limited, it will be 90% when considering productivity.

[Hot working step]

[0067] The hot forged starting material (columnar starting material) is subjected to hot working, to produce an alloy raw pipe which is the intermediate material. For example, a through hole is formed at a center of the columnar starting material by machining. The columnar starting material formed with a through hole is subjected to hot extrusion, to produce an alloy raw pipe. The alloy raw pipe (intermediate material) may be produced by piercing-rolling of the columnar starting material. The intermediate material after hot working may be subjected to cold working. The cold working is, for example, cold drawing, etc. The intermediate material is produced through the above described steps.

[Solution heat treatment step]

[0068] The produced intermediate material is subjected to solution heat treatment. By the solution heat treatment, precipitates in the intermediate material are dissolved.

[0069] The heat treatment temperature in the solution heat treatment is 1100 to 1250°C. When the heat treatment temperature is less than 1100°C, the precipitates will not sufficiently dissolve and, as a result, the volume ratio of coarse precipitates will be more than 5%. On the other hand, when the heat treatment temperature is too high, austenite grains are coarsened, thus deteriorating productivity.

[0070] When the heat treatment temperature is 1100 to 1250°C, the precipitates sufficiently dissolve, and the total volume ratio of coarse precipitates will be not more than 5%.

[0071] The solution heat treatment time is not particularly limited. The solution heat treatment time is, for example, one minute to one hour.

[0072] The intermediate material after the solution heat treatment may be subjected to pickling treatment for the purpose of removing scales formed on the surface. For the pickling, for example, a mixed acid solution of nitric acid and hydrochloric acid is used. The pickling time is, for example, 30 to 60 minutes.

[0073] Further, the intermediate material after pickling treatment may be subjected to blasting treatment by use of blast media. For example, the blasting treatment is performed on the inner surface of the alloy pipe. In this case, a worked layer is formed on the surface, thereby improving corrosion resistance (oxidation resistance, etc.).

[0074] By the production method described so far, the austenitic heat resistant alloy of the present embodiment is produced. It is noted that a production method of an alloy pipe has been described in the above. However, a plate, a bar, a wire, or the like may be produced by a similar production method (the preparation step, hot forging step, hot working step, and solution heat treatment step).

EXAMPLES

[Production method]

[0075] Molten steels having chemical compositions shown in Table 1 were produced by using a vacuum melting furnace.

[Table 1]

[0076]

TABLE 1

Test No.	Chemical composition (mass%, the balance being Fe and impurities)										
	C	Si	Mn	Cr	Ni	Al	Nb	N	P	S	Others
1	0.120	0.14	1.13	20.31	35.69	3.14	0.74	0.0021	0.011	0.004	-
2	0.150	0.18	1.31	25.14	40.66	3.56	0.94	0.0037	0.008	0.006	-
3	0.060	0.13	0.96	28.67	30.69	3.22	1.85	0.0012	0.013	0.006	Mg: 0.0025
4	0.210	0.20	0.64	18.97	41.45	3.87	1.72	0.0021	0.012	0.008	Ca: 0.0021
5	0.120	0.18	1.25	24.36	28.21	4.42	2.45	0.0021	0.008	0.006	B : 0.003
6	0.140	0.14	1.41	21.64	35.64	2.84	0.65	0.0018	0.003	0.009	Ti: 0.14
7	0.080	0.16	1.09	22.65	32.67	3.65	2.46	0.0021	0.011	0.004	W: 4.57
8	0.160	0.20	1.25	19.04	33.67	3.14	2.28	0.0023	0.012	0.006	Zr: 0.03
9	0.110	0.19	1.02	21.36	31.69	3.24	1.17	0.0011	0.010	0.007	Mo: 2.14
10	0.065	0.89	1.18	15.09	28.09	3.94	1.94	0.0227	0.025	0.008	REM: 0.032
11	0.079	0.04	1.26	24.03	40.95	3.52	3.01	0.0112	0.021	0.007	Cu: 3.56

(continued)

Test No.	Chemical composition (mass%, the balance being Fe and impurities)										
	C	Si	Mn	Cr	Ni	Al	Nb	N	P	S	Others
12	0.815	0.21	0.98	23.14	31.64	3.55	1.05	0.0025	0.013	0.006	-
13	0.140	0.11	1.04	20.64	30.27	1.56	1.49	0.0029	0.012	0.006	-
14	0.110	0.14	0.97	22.64	33.94	5.47	0.99	0.0017	0.011	0.003	-
15	0.151	0.12	0.85	7.69	40.36	2.97	2.81	0.0022	0.007	0.005	-
16	0.140	0.20	1.07	35.68	32.82	3.85	1.07	0.0025	0.006	0.006	-
17	0.220	0.14	1.34	25.66	30.41	3.24	0.49	0.0015	0.002	0.008	-
18	0.140	0.15	0.75	28.64	34.90	3.84	2.50	0.0018	0.008	0.007	-
19	0.090	0.46	0.91	19.89	38.14	2.88	4.11	0.0041	0.004	0.004	-
20	0.157	1.91	1.11	17.38	42.26	3.44	0.07	0.0124	0.001	0.004	-

[0077] The above-described molten steels were used to each produce a columnar ingot (30 kg) having an outer diameter of 120 mm. Each ingot was subjected to hot forging at a reduction of area shown in Table 2 to produce a rectangular starting material. The rectangular starting material was subjected to hot rolling and cold rolling to produce a planar intermediate material having a thickness of 1.5 mm. The intermediate material was subjected to a solution treatment in which the intermediate material was held at a heat treatment temperature shown in Table 2 for 10 minutes. After being held for 10 minutes, the intermediate material was water cooled to produce an alloy plate.

[Table 2]

[0078]

TABLE 2

Test No.	Reduction of area (%) during forging	Total volume ratio (%) of coarse precipitates	Solution heat treatment temperature (°C)	Creep strength (MPa)	Charpy impact value (J/cm^2)
1	52	1.2	1215	152.3	50.3
2	65	1.6	1220	154.6	48.3
3	58	0.8	1185	149.6	55.6
4	75	2.1	1195	156.7	51.3
5	81	1.3	1200	154.3	50.1
6	68	1.4	1225	151.2	51.4
7	74	1.2	1205	155.9	52.3
8	77	2.3	1210	157.6	53.6
9	59	1.1	1200	154.6	52.1
10	70	0.7	1205	150.9	53.6
11	68	0.4	1190	151.2	50.5
12	45	10.4	1225	116.8	24.6
13	56	1.4	1230	120.3	70.2
14	65	1.9	1235	108.2	67.5
15	72	1.5	1215	124.3	70.6
16	68	1.1	1225	114.4	57.8

(continued)

Test No.	Reduction of area (%) during forging	Total volume ratio (%) of coarse precipitates	Solution heat treatment temperature (°C)	Creep strength (MPa)	Charpy impact value (J/cm^2)
17	8.7	8.5	1195	121.1	28.7
18	65	7.7	1040	126.4	25.9
19	43	0.6	1175	164.7	21.9
20	52	1.8	1220	109.6	48.8

[Creep rupture test]

[0079] A test specimen was made from the produced alloy plate. The test specimen was sampled from a central portion of the thickness of the alloy plate in parallel with the longitudinal direction (rolling direction). The test specimen was a round bar specimen, of which diameter of the parallel portion was 6 mm and gauge length was 30 mm. A creep rupture test was conducted by using the test specimen. The creep rupture test was performed in an atmosphere of 700 to 800°C. Based on obtained rupture strength, a creep strength (MPa) at 1.0×10^4 hours at 700°C was determined by the Larson-Miller parameter method.

[Charpy impact test]

[0080] The produced alloy plate was subjected to aging treatment in which it is held for 8000 hours at 700°C, and thereafter was water cooled. A V-notch Charpy impact test specimen specified in JIS Z2242(2005) was sampled from a middle portion in the thickness direction of the plate stock after aging treatment. The notch was formed in parallel with the longitudinal direction of the alloy plate. The test specimen had a width of 5 mm, a height of 10 mm, a length of 55 mm, and a notch depth of 2 mm. At 0°C, a Charpy impact test in accordance with JIS Z2242(2005) was performed to determine an impact value (J/cm^2).

[Test results]

[0081] Test results are shown in Table 2.

[0082] Referring to Table 2, the chemical compositions of Test No. 1 to Test No. 11 were appropriate, and the volume ratios of coarse precipitates were not more than 5%. As a result, the creep strength was not less than 140 MPa, showing excellent creep strength. Further, the Charpy impact values were not less than 40 J/cm^2, thus exhibiting excellent toughness even after long-hours aging treatment.

[0083] On the other hand, in Test No. 12, the C content was too high. Because of that, the volume ratio of coarse precipitates was more than 5%. As a result, the creep strength was less than 140 MPa, and the Charpy impact value was less than 40 J/cm^2.

[0084] In Test No. 13, the Al content was too low. Because of that, the creep strength was less than 140 MPa. This may be because the precipitation amount of NiAl was small.

[0085] In Test No. 14, the Al content was too high. Because of that, the creep strength was less than 140 MPa. Because the Al content was too high, conceivably, the structure was not stabilized, resulting in low creep strength.

[0086] In Test No. 15, the Cr content was too low. Because of that, the creep strength was less than 140 MPa. This may be because the precipitation amount of α-Cr was small.

[0087] In Test No. 16, the Cr content was too high. Because of that, the creep strength was less than 140 MPa. Because the Cr content was too high, conceivably, the structure was not stabilized, resulting in low creep strength.

[0088] In Test No. 17, the reduction of area during hot forging was less than 30%. Because of that, the total volume ratio of coarse precipitates was more than 5%. As a result, the creep strength was less than 140 MPa, and the Charpy impact value was less than 40 J/cm^2.

[0089] In Test No. 18, the solution heat treatment temperature was less than 1100°C. Because of that, the total volume ratio of coarse precipitates was more than 5%. As a result, the creep rupture strength was less than 140 MPa, and the Charpy impact value was less than 40 J/cm^2.

[0090] In Test No. 19, the Nb content was too high. Because of that, the Charpy impact value was less than 40 J/cm^2.

[0091] In Test No. 20, the Nb content was too low. Because of that, the creep strength was less than 140 MPa.

[0092] So far embodiments of the present invention have been described. However, the above described embodiments are merely examples for carrying out the present invention. Therefore, the present invention will not be limited to the above described embodiments, and can be carried out by appropriately modifying the above described embodiments within the range not departing from the spirit thereof.

INDUSTRIAL APPLICABILITY

[0093] The austenitic heat resistant alloy of the present invention can be widely used in a high temperature environment of not less than 700°C. It is particularly suitable as an alloy pipe to be used such as in boilers for power generation and in plants for chemical industry, which are exposed to a high temperature environment of not less than 700°C.

Claims

1. An austenitic heat resistant alloy comprising a chemical composition, consisting of: in mass%,
   C: 0.03 to less than 0.25%,
   Si: 0.01 to 2.0%,
   Mn: not more than 2.0%,
   Cr: 10 to less than 30%,
   Ni: more than 25 to 45%,
   Al: more than 2.5 to less than 4.5%,
   Nb: 0.2 to 3.5%,
   N: not more than 0.025%,
   Ti: 0 to less than 0.2%,
   W: 0 to 6%,
   Mo: 0 to 4%,
   Zr: 0 to 0.1%,
   B: 0 to 0.01%,
   Cu: 0 to 5%,
   rare earth metals: 0 to 0.1%,
   Ca: 0 to 0.05%, and
   Mg: 0 to 0.05%, with the balance being Fe and impurities, wherein P and S in the impurities are respectively, P: not more than 0.04% and S: not more than 0.01%, and wherein
   in a structure, a total volume ratio of precipitates having a circle equivalent diameter of not less than 6 μm is not more than 5%.

2. The austenitic heat resistant alloy according to claim 1, wherein
   the chemical composition contains one or more kinds selected from the group consisting of, in mass%,
   Ti: 0.005 to less than 0.2%,
   W: 0.005 to 6%,
   Mo: 0.005 to 4%,
   Zr: 0.0005 to 0.1%, and
   B: 0.0005 to 0.01%.

3. The austenitic heat resistant alloy according to claim 1 or 2, wherein
   the chemical composition contains one or more kinds selected from the group consisting of, in mass%,
   Cu: 0.05 to 5%, and
   rare earth metals: 0.0005 to 0.1%.

4. The austenitic heat resistant alloy according to any one of claims 1 to 3, wherein
   the chemical composition contains one or more kinds selected from the group consisting of, in mass%,
   Ca: 0.0005 to 0.05%, and
   Mg: 0.0005 to 0.05%.

5. A method for producing an austenitic heat resistant alloy comprising steps of:

   performing hot forging at a reduction of area of not less than 30% on a starting material having the chemical composition according to any one of claims 1 to 4;
   producing an intermediate material by performing hot working on the starting material after hot forging; and
   performing solution treatment at 1100 to 1250°C on the intermediate material.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/000056

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21D8/00*(2006.01)i, *C22C19/05*(2006.01)i, *C22C30/02*(2006.01)i, *C22C38/58*(2006.01)i, *C22F1/10*(2006.01)i, *C22F1/00*(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)
C22C38/00-38/60, C21D8/00-8/12, C22C19/05, C22C30/00-30/06, C22F1/00-1/18

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)
JSTPlus/JMEDPlus/JST7580(JDreamIII)

C. 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 59-229468 A (Sumitomo Metal Industries, Ltd.), 22 December 1984 (22.12.1984), table 1 (Family: none)	1-5
A	US 2008/0304996 A1 (BRADY, Michael P.), 11 December 2008 (11.12.2008), table 1 & WO 2008/086141 A1	1-5

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

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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

International application No.
PCT/JP2017/000056

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2013/0266477 A1 (YAMAMOTO, Yukinori), 10 October 2013 (10.10.2013), table 2 (Family: none)	1-5
A	CN 103774056 A (JIANGSU UNIVERSITY), 07 May 2014 (07.05.2014), examples (Family: none)	1-5
A	CN 104561821 A (JIANGSU UNIVERSITY), 29 April 2015 (29.04.2015), examples (Family: none)	1-5
A	ZHOU,D.Q et al., Precipitate characteristics and their effects on the high-temperature creep resistance of alumina-forming austenitic stainless steels, Materials Science & Engineering A, 2015.01.12, Vol.622, Page.91-100	1-5
A	YAMAMOTO,Y. et al., Alloying effects on creep and oxidation resistance of austenitic stainless steel alloys employing intermetallic precipitates, Intermetallics, 2008.03, Vol.16 No.3, Page.453-462	1-5

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