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- **OKADA, Hirokazu**
Tokyo 100-8071 (JP)
- **YOSHIZAWA, Mitsuru**
Tokyo 100-8071 (JP)
- **ONO, Toshihide**
Tokyo 100-8071 (JP)

(71) Applicant: **Nippon Steel Corporation**

Tokyo 100-8071 (JP)

(74) Representative: **Zimmermann & Partner**

Patentanwälte mbB

Postfach 330 920

80069 München (DE)

(72) Inventors:

- **SEMBA, Hiroyuki**
Tokyo 100-8071 (JP)

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

(57) Provided is an austenitic heat resistant alloy having a chemical composition consisting of, in mass %: C: 0.02 to 0.12%; Si: 2.0% or less; Mn: 3.0% or less; P: 0.030% or less; S: 0.015% or less; Cr: 20.0% or more and less than 28.0%; Ni: more than 35.0% and 55.0% or less; Co: 0 to 20.0%; W: 4.0 to 10.0%; Ti: 0.01 to 0.50%; Nb: 0.01 to 1.0%; Mo: less than 0.50%; Cu: less than 0.50%; Al: 0.30% or less; N: less than 0.10%; Mg: 0 to 0.05%; Ca: 0 to 0.05%; REM: 0 to 0.50%; V: 0 to 1.5%; B: 0 to 0.01%; Zr: 0 to 0.10%; Hf: 0 to 1.0%; Ta: 0 to

8.0%; Re: 0 to 8.0%; and the balance: Fe and impurities, wherein a shortest distance from a center portion to an outer surface portion of a cross section of the alloy is 40 mm or more, the cross section being perpendicular to a longitudinal direction of the alloy, an austenite grain size number at the outer surface portion is -2.0 to 4.0, an amount of Cr which is present as a precipitate satisfies $[Cr_{PB}/Cr_{PS} \leq 10.0]$, and $[YS_S/YS_B \leq 1.5]$ and $[TS_S/TS_B \leq 1.2]$ are satisfied at a room temperature.

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Description

TECHNICAL FIELD

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

[0002] Conventionally, for thermal power generation boilers, chemical plants and the like which are used in a high temperature environment, 18-8 austenitic stainless steels, such as SUS304H, SUS316H, SUS321H, and SUS347H, have been used as materials for apparatuses.

[0003] In recent years, however, ultra super critical boilers, where temperature and pressure of steam are increased to enhance efficiency, have been newly installed worldwide. The use conditions of apparatuses in such a high temperature environment have become extremely severe, and therefore, properties which materials being used are required to possess have become strict. Under such circumstances, using 18-8 austenitic stainless steel, which is conventionally used, has become extremely insufficient in terms of not only corrosion resistance but also high temperature strength, particularly creep rupture strength.

[0004] To overcome the above problems, various studies have been made. For example, Patent Documents 1 to 4 disclose austenitic steel excellent in high temperature strength and corrosion resistance. Further, Patent Document 5 discloses austenitic stainless steel excellent in high temperature strength and corrosion resistance. According to Patent Documents 1 to 5, the amount of Cr is increased to 20% or more, and W and/or Mo are contained so as to enhance high temperature strength.

LIST OF PRIOR ART DOCUMENTS

PATENT DOCUMENT

[0005]

Patent Document 1: JP61-179833A

Patent Document 2: JP61-179834A

Patent Document 3: JP61-179835A

Patent Document 4: JP61-179836A

Patent Document 5: JP2004-3000A

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0006] Large-sized structural members made of a material for apparatuses, such as thermal power generation boilers or chemical plants, are hot rolled or hot forged and then subjected to final heat treatment without cold rolling before putting into use. Accordingly, the grain size is relatively large. For this reason, usually, there is a problem that 0.2% proof stress and tensile strength at a room temperature, which are defined as the specifications of materials, are lower than those of a material obtained by performing final heat treatment after cold rolling.

[0007] In addition to the above, in a large-sized structural member, a cooling speed at the time of performing heat treatment varies largely from region to region and hence, there is a variation from region to region in the amount of solid solution elements which contribute to strengthening the member as precipitates during use at a high temperature. There is also a problem that creep rupture strength varies due to such variation. Accordingly, it is difficult to adopt steel disclosed in Patent Documents 1 to 5 to a large-sized structural member.

[0008] The present invention has been made to overcome the above problems, and an objective of the present invention is to provide an austenitic heat resistant alloy and a method for producing the same which exhibits sufficient 0.2% proof stress and tensile strength at a room temperature, and sufficient creep rupture strength at a high temperature in large-sized structural members.

SOLUTION TO PROBLEM

[0009] The present invention has been made to overcome the above problems, and the gist of the present invention is the following austenitic heat resistant alloy and method for producing the same.

[0010]

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

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C: 0.02 to 0.12%;
 Si: 2.0% or less;
 Mn: 3.0% or less;
 P: 0.030% or less;
 S: 0.015% or less;
 Cr: 20.0% or more and less than 28.0%;
 Ni: more than 35.0% and 55.0% or less;
 Co: 0 to 20.0%;
 W: 4.0 to 10.0%;
 Ti: 0.01 to 0.50%;
 Nb: 0.01 to 1.0%;
 Mo: less than 0.50%;
 Cu: less than 0.50%;
 Al: 0.30% or less;
 N: less than 0.10%;
 Mg: 0 to 0.05%;
 Ca: 0 to 0.05%;
 REM: 0 to 0.50%;
 V: 0 to 1.5%;
 B: 0 to 0.01%;
 Zr: 0 to 0.10%;
 Hf: 0 to 1.0%;
 Ta: 0 to 8.0%;
 Re: 0 to 8.0%; and
 the balance: Fe and impurities, wherein

a shortest distance from a center portion to an outer surface portion of a cross section of the alloy is 40 mm or more,
 the cross section being perpendicular to a longitudinal direction of the alloy,
 an austenite grain size number at the outer surface portion is -2.0 to 4.0,
 an amount of Cr which is present as a precipitate obtained by an extraction residue analysis satisfies a following
 formula (i), and
 mechanical properties at a room temperature satisfy following formula (ii) and formula (iii):

$$Cr_{PB}/Cr_{PS} \leq 10.0 \dots (i)$$

$$YS_S/YS_B \leq 1.5 \dots (ii)$$

$$TS_S/TS_B \leq 1.2 \dots (iii)$$

where meaning of each symbol in the formulas is as follows:

Cr_{PB} : amount of Cr which is present at center portion as precipitate obtained by extraction residue analysis
 Cr_{PS} : amount of Cr which is present at outer surface portion as precipitate obtained by extraction residue analysis
 YS_B : 0.2% proof stress at center portion
 YS_S : 0.2% proof stress at outer surface portion
 TS_B : tensile strength at center portion
 TS_S : tensile strength at outer surface portion.

(2) The austenitic heat resistant alloy described in the above (1), wherein
 the chemical composition contains one or more elements selected from a group consisting of, in mass %:

Mg: 0.0005 to 0.05%;
 Ca: 0.0005 to 0.05%;
 REM: 0.0005 to 0.50%;

V: 0.02 to 1.5%;
 B: 0.0005 to 0.01%;
 Zr: 0.005 to 0.10%;
 Hf: 0.005 to 1.0%;
 Ta: 0.01 to 8.0%; and
 Re: 0.01 to 8.0%.

- (3) The austenitic heat resistant alloy described in the above (1) or (2), wherein 10,000-hour creep rupture strength at 700°C in the longitudinal direction at the center portion is 100 MPa or more.
 (4) A method for producing an austenitic heat resistant alloy, the method including the steps of:

performing hot working on an ingot or a cast piece having the chemical composition described in the above (1) or (2); and
 thereafter performing heat treatment where the ingot or the cast piece is heated to a heat-treatment temperature T (°C) ranging from 1100 to 1250°C, is held for 1000 D/T to 1400 D/T (min), and is cooled with water, wherein symbol "D" denotes a maximum value (mm) of a linear distance between an arbitrary point on an outer edge of a cross section of the alloy and another arbitrary point on the outer edge, the cross section being perpendicular to a longitudinal direction of the alloy.

- (5) The method for producing an austenitic heat resistant alloy described in the above (4), wherein in the step of performing the hot working, the working is performed one or more times in a direction substantially perpendicular to the longitudinal direction.

ADVANTAGEOUS EFFECTS OF INVENTION

[0011] The austenitic heat resistant alloy of the present invention has small variation in mechanical properties from region to region, and is excellent in creep rupture strength at a high temperature.

DESCRIPTION OF EMBODIMENTS

[0012] Hereinafter, the respective requirements of the present invention are described in detail.

1. Chemical composition

[0013] The reasons for limiting respective elements are as follows. In the description made hereinafter, symbol "%" for content refers to "mass%".

C: 0.02 to 0.12%

[0014] C (carbon) forms carbides so that C is an indispensable element for maintaining high temperature tensile strength and creep rupture strength required for an austenitic heat resistant alloy. Accordingly, it is necessary to set a content of C to 0.02% or more. However, when the C content exceeds 0.12%, not only undissolved carbides are formed, but also Cr carbides increase and hence, mechanical properties, such as ductility and toughness, and weldability deteriorate. Accordingly, the C content is set to a value ranging from 0.02 to 0.12%. The C content is preferably 0.05% or more and 0.10% or less.

Si: 2.0% or less

[0015] Si (silicon) is contained as a deoxidizing element. Further, Si is an element effective in increasing oxidation resistance, steam oxidation resistance and the like. Si is also an element which facilitates the flow of a casting material. However, when a content of Si exceeds 2.0%, the formation of intermetallic compounds, such as a σ phase, is promoted and hence, stability of micro-structure at a high temperature deteriorates, thus lowering toughness and ductility. When the Si content exceeds 2.0%, weldability is also lowered. Accordingly, the Si content is set to 2.0% or less. When importance is placed on structural stability, the Si content is preferably set to 1.0% or less. When a deoxidizing action is sufficiently ensured by other elements, it is not particularly necessary to set the lower limit of the Si content. However, when importance is placed on a deoxidizing action, oxidation resistance, steam oxidation resistance and the like, the Si content is preferably set to 0.05% or more, and more preferably set to 0.10% or more.

Mn: 3.0% or less

[0016] Mn (manganese) has a deoxidizing action in the same manner as Si, and also has an action of fixing S, which is inevitably contained in the alloy, as a sulfide, thus improving ductility at a high temperature. However, when a content of Mn exceeds 3.0%, the precipitation of intermetallic compounds, such as a σ phase, is promoted and hence, structural stability, and mechanical properties, such as high temperature strength, deteriorate. Accordingly, the Mn content is set to 3.0% or less. The Mn content is preferably 2.0% or less, and more preferably 1.5% or less. It is not necessary to set the lower limit of the Mn content. However, when importance is placed on an action of improving ductility at a high temperature, the Mn content is preferably set to 0.10% or more, and more preferably set to 0.20% or more.

P: 0.030% or less

[0017] P (phosphorus) is inevitably mixed in the alloy as an impurity, and remarkably lowers weldability and ductility at a high temperature. Accordingly, a content of P is set to 0.030% or less. It is preferable to reduce the P content to as much as possible. The P content is preferably set to 0.020% or less, and more preferably set to 0.015% or less.

S: 0.015% or less

[0018] S (sulfur) is inevitably mixed in the alloy as an impurity in the same manner as P, and remarkably lowers weldability and ductility at a high temperature. Accordingly, a content of S is set to 0.015% or less. When importance is placed on hot workability, the S content is preferably set to 0.010% or less, more preferably set to 0.005% or less, and further preferably set to 0.003% or less.

Cr: 20.0% or more and less than 28.0%

[0019] Cr (chromium) is an important element which excellently exhibits an action of improving corrosion resistance, such as oxidation resistance, steam oxidation resistance, and high temperature corrosion resistance. However, when a content of Cr is less than 20.0%, these advantageous effects cannot be obtained. On the other hand, when the Cr content increases, particularly to 28.0% or more, the micro-structure is made unstable due to the precipitation of a σ phase or the like, and weldability also deteriorates. Accordingly, the Cr content is set to a value ranging of 20.0% or more and less than 28.0%. The Cr content is preferably 21.0% or more, and more preferably 22.0% or more. Further, the Cr content is preferably 26.0% or less, and more preferably 25.0% or less.

Ni: more than 35.0% and 55.0% or less

[0020] Ni (nickel) is an element which makes the austenitic structure stable, and is also an element important to ensure corrosion resistance. To maintain the balance with the Cr content, it is necessary to set a content of Ni to more than 35.0%. On the other hand, excessively high Ni content increases costs and hence, the Ni content is set to 55.0% or less. The Ni content is preferably 40.0% or more, and more preferably 42.0% or more. Further, the Ni content is preferably 50.0% or less, and more preferably 48.0% or less.

Co: 0 to 20.0%

[0021] It is not always necessary to contain Co (cobalt). However, in the same manner as Ni, Co makes the austenitic structure stable, and also contributes to enhancing creep rupture strength. Accordingly, Co may be contained in lieu of a part of Ni. However, when a content of Co exceeds 20.0%, the effect is saturated and hence, economic efficiency is lowered. Accordingly, the Co content is set to a value ranging from 0 to 20.0%. The Co content is preferably 15.0% or less. When it is desired to obtain the advantageous effects, the Co content is preferably set to 0.5% or more.

W: 4.0 to 10.0%

[0022] W (tungsten) is dissolved in a matrix, thus not only contributing to enhancing creep rupture strength as a solid-solution strengthening element, but also precipitating as a Fe_2W Laves phase or a Fe_7W_6 μ phase so that creep rupture strength is significantly enhanced. Accordingly, W is an important element. However, when a content of W is less than 4.0%, the advantageous effects cannot be obtained. On the other hand, even if the W content is set to more than 10.0%, an effect of enhancing strength is saturated, and structural stability and ductility at a high temperature deteriorate. Accordingly, the W content is set to a value ranging from 4.0 to 10.0%. The W content is preferably 5.0% or more, and more preferably 5.5% or more. Further, the W content is preferably 9.0% or less, and more preferably 8.5% or less.

Ti: 0.01 to 0.50%

[0023] Ti (titanium) is an element which forms carbo-nitrides, thus having an effect of enhancing creep rupture strength. However, when a content of Ti is less than 0.01%, sufficient effects cannot be obtained. On the other hand, when the Ti content exceeds 0.50%, ductility at a high temperature is lowered. Accordingly, the Ti content is set to a value ranging from 0.01 to 0.50%. The Ti content is preferably set to 0.05% or more, and more preferably set to 0.10% or more. Further, the Ti content is preferably set to 0.40% or less, and more preferably set to 0.35% or less.

Nb: 0.01 to 1.0%

[0024] Nb (niobium) has an action of forming carbo-nitrides, thus enhancing creep rupture strength. However, when a content of Nb is less than 0.01%, sufficient effects cannot be obtained. On the other hand, when the Nb content exceeds 1.0%, ductility at a high temperature is lowered. Accordingly, the Nb content is set to a value ranging from 0.01 to 1.0%. The Nb content is preferably 0.10% or more. Further, the Nb content is preferably 0.90% or less, and more preferably 0.70% or less.

Mo: less than 0.50%

[0025] Mo (molybdenum) is an element which is dissolved in a matrix, thus contributing to enhancing creep rupture strength as a solid-solution strengthening element and hence, Mo has been conventionally considered as an element having substantially the same action as W. However, the inventors of the present invention have made studies, and found the following. When Mo is contained in combination in an alloy which contains the amounts of W and Cr, a σ phase may precipitate after long-term use and hence, creep rupture strength, ductility and toughness may be lowered. Accordingly, it is desirable to reduce a content of Mo as much as possible, and the Mo content is set to less than 0.50%. It is preferable to limit the Mo content to less than 0.20%.

Cu: less than 0.50%

[0026] In the present invention, Cu (copper) lowers a fusing point, thus lowering hot workability and weldability. Accordingly, it is desirable to reduce a content of Cu as much as possible, and the Cu content is set to less than 0.50%. It is preferable to limit the Cu content to less than 0.20%.

Al: 0.30% or less

[0027] Al (aluminum) is an element which is contained as a deoxidizer for molten steel. However, when a content of Al exceeds 0.30%, ductility at a high temperature deteriorates. Accordingly, the Al content is set to 0.30% or less. The Al content is preferably 0.25% or less, and more preferably 0.20% or less. When it is desired to obtain the advantageous effect, the Al content is preferably set to 0.01% or more, and more preferably set to 0.02% or more.

N: less than 0.10%

[0028] N (nitrogen) is an element having an action of making the austenitic structure stable, and is an element inevitably contained when an ordinary melting method is adopted. However, in the present invention where Ti is contained as an indispensable element, it is preferable to reduce a content of N as much as possible so as to prevent Ti from being consumed by the formation of TiN. However, in the case of atmospheric melting, it is difficult to extremely reduce the N content. Accordingly, the N content is set to less than 0.10%.

[0029] In the chemical composition of the austenitic heat resistant alloy of the present invention, the balance consists of Fe and impurities. It is preferable to set a content of Fe to 0.1 to 40.0%. In this embodiment, "impurity" means a component which is mixed in industrially producing the alloy due to various causes, such as raw materials including ores or scrap, or production steps, and which is allowed to be mixed without adversely affecting the present invention.

[0030] The austenitic heat resistant alloy of the present invention may further contain one or more kinds selected from a group consisting of Mg, Ca, REM, V, B, Zr, Hf, Ta, and Re.

[0031] Any of Mg, Ca or REM has an action of fixing S as sulfides to enhance high temperature ductility. Accordingly, when it is desired to obtain greater high temperature ductility, one or more kinds of these elements may be positively contained within the following range.

Mg: 0.05% or less

[0032] Mg (magnesium) has an action of fixing S, which inhibits ductility at a high temperature, as sulfides, thus improving high temperature ductility. Accordingly, Mg may be contained so as to obtain this advantageous effect. However, when a content of Mg exceeds 0.05%, cleanliness is lowered, and high temperature ductility is impaired on the contrary. Accordingly, when Mg is contained, the amount of Mg is set to 0.05% or less. The Mg content is more preferably set to 0.02% or less, and further preferably set to 0.01% or less. On the other hand, to obtain the advantageous effect with certainty, the Mg content is preferably set to 0.0005% or more, and more preferably set to 0.001% or more.

Ca: 0.05% or less

[0033] Ca (calcium) has an action of fixing S, which inhibits ductility at a high temperature, as sulfides, thus improving high temperature ductility. Accordingly, Ca may be contained so as to obtain this advantageous effect. However, when a content of Ca exceeds 0.05%, cleanliness is lowered, and high temperature ductility is impaired on the contrary. Accordingly, when Ca is contained, the amount of Ca is set to 0.05% or less. The Ca content is more preferably set to 0.02% or less, and further preferably set to 0.01% or less. On the other hand, to obtain the advantageous effect with certainty, the Ca content is preferably set to 0.0005% or more, and more preferably set to 0.001% or more.

REM: 0.50% or less

[0034] REM has an action of fixing S as sulfides, thus improving high temperature ductility. REM also has an action of improving adhesiveness of a Cr_2O_3 protection film on a steel surface, thus improving oxidation resistance particularly when the alloy is repeatedly oxidized. Further, REM contributes to strengthening grain boundaries, thus having an action of enhancing creep rupture strength and creep rupture ductility. However, when a content of REM exceeds 0.50%, the amount of inclusions, such as an oxide increases and hence, workability and weldability are impaired. Accordingly, when REM is contained, the amount of REM is set to 0.50% or less. The REM content is more preferably set to 0.30% or less, and further preferably set to 0.15% or less. On the other hand, to obtain the advantageous effects with certainty, the REM content is preferably set to 0.0005% or more, more preferably set to 0.001% or more, and further preferably set to 0.002% or more.

[0035] REM indicates 17 elements in total, including Sc, Y, and the lanthanoids. The REM content means the total content of these elements.

[0036] The total content of Mg, Ca and REM may be 0.6% or less. However, the total content is more preferably 0.4% or less, and further preferably 0.2% or less.

[0037] Any of V, B, Zr, or Hf has an action of enhancing high temperature strength and creep rupture strength. Accordingly, when it is desired to obtain greater high temperature strength and greater creep rupture strength, the alloy may positively contain one or more kinds of these elements within the following range.

V: 1.5% or less

[0038] V (vanadium) has an action of forming carbo-nitrides to enhance high temperature strength and creep rupture strength. Accordingly, V may be contained so as to obtain these advantageous effects. However, when a content of V exceeds 1.5%, high temperature corrosion resistance is lowered and, further, ductility and toughness deteriorate due to the precipitation of a brittle phase. Accordingly, when V is contained, the amount of V is set to 1.5% or less. The V content is more preferably set to 1.0% or less. On the other hand, to obtain the advantageous effect with certainty, the V content is preferably set to 0.02% or more, and more preferably set to 0.04% or more.

B: 0.01% or less

[0039] B (boron) is present in carbide or in a matrix. B has not only an action of promoting micronization of precipitated carbide, but also an action of strengthening grain boundaries, thus enhancing creep rupture strength. However, when a content of B exceeds 0.01%, ductility at a high temperature is lowered, and a fusing point is also lowered. Accordingly, when B is contained, the amount of B is set to 0.01% or less. The B content is more preferably 0.008% or less, and further preferably 0.006% or less. On the other hand, to obtain the advantageous effects with certainty, the B content is preferably set to 0.0005% or more, more preferably set to 0.001% or more, and further preferably set to 0.0015% or more.

Zr: 0.10% or less

[0040] Zr (zirconium) is an element which promotes micronization of carbo-nitrides, and which enhances creep rupture

strength as a grain boundary strengthening element. However, when a content of Zr exceeds 0.10%, ductility at a high temperature is lowered. Accordingly, when Zr is contained, the amount of Zr is set to 0.10% or less. The Zr content is more preferably 0.06% or less, and further preferably 0.05% or less. On the other hand, to obtain the advantageous effects with certainty, the Zr content is preferably set to 0.005% or more, and more preferably set to 0.01% or more.

Hf: 1.0% or less

[0041] Hf (hafnium) has an action of contributing to strengthening precipitation as carbo-nitrides, thus enhancing creep rupture strength. Accordingly, Hf may be contained so as to obtain these advantageous effects. However, when a content of Hf exceeds 1.0%, workability and weldability are impaired. Accordingly, when Hf is contained, the amount of Hf is set to 1.0% or less. The Hf content is more preferably set to 0.8% or less, and further preferably set to 0.5% or less. On the other hand, to obtain the advantageous effects with certainty, the Hf content is preferably set to 0.005% or more, more preferably set to 0.01% or more, and further preferably set to 0.02% or more.

[0042] The total content of V, B, Zr, and Hf is preferably 2.6% or less, and more preferably 1.8% or less.

[0043] Either one of Ta or Re dissolves in austenite forming a matrix, thus having an action of solid-solution strengthening. Accordingly, when it is desired to obtain greater high temperature strength and creep rupture strength due to an action of solid-solution strengthening, one or both of these elements may be positively contained within the following range.

Ta: 8.0% or less

[0044] Ta (tantalum) has an action of forming carbo-nitrides, and also has an action of enhancing high temperature strength and creep rupture strength as a solid-solution strengthening element. Accordingly, Ta may be contained so as to obtain these advantageous effects. However, when a content of Ta exceeds 8.0%, workability and mechanical properties are impaired. Accordingly, when Ta is contained, the amount of Ta is set to 8.0% or less. The Ta content is more preferably set to 7.0% or less, and further preferably set to 6.0% or less. On the other hand, to obtain the advantageous effects with certainty, the Ta content is preferably set to 0.01% or more, more preferably set to 0.1% or more, and further preferably set to 0.5% or more.

Re: 8.0% or less

[0045] Re (rhenium) has an action of enhancing high temperature strength and creep rupture strength mainly as a solid-solution strengthening element. Accordingly, Re may be contained so as to obtain these advantageous effects. However, when a content of Re exceeds 8.0%, workability and mechanical properties are impaired. Accordingly, when Re is contained, the amount of Re is set to 8.0% or less. The Re content is more preferably set to 7.0% or less, and further preferably set to 6.0%. On the other hand, to obtain the advantageous effects with certainty, the Re content is preferably set to 0.01% or more, more preferably set to 0.1% or more, and further preferably set to 0.5% or more.

[0046] The total content of Ta and Re is preferably 14.0% or less, and more preferably 12.0% or less.

2. Grain size

Austenite grain size number at outer surface portion: -2.0 to 4.0

[0047] When an austenitic grain size at an outer surface portion is extremely large, 0.2% proof stress and tensile strength at a room temperature are lowered. On the other hand, when an austenitic grain size at an outer surface portion is extremely small, it becomes impossible to maintain high creep rupture strength at a high temperature. Accordingly, the austenite grain size number at the outer surface portion is set to a value ranging from -2.0 to 4.0. In a production process for a Ni-based alloy, by properly adjusting a heat-treatment temperature and holding time after hot working and a cooling method, it is possible to set the grain size number at the outer surface portion to a value which falls within the range after final heat treatment.

3. Size

Shortest distance from center portion to outer surface portion: 40 mm or more

[0048] As described above, in a large-sized structural member, in addition to a problem that 0.2% proof stress and tensile strength at a room temperature are lowered, there is also a problem that creep rupture strength varies from region to region. However, the austenitic heat resistant alloy according to the present invention exhibits sufficient 0.2% proof stress and tensile strength at a room temperature, and sufficient creep rupture strength at a high temperature in large-

sized structural members. That is, the present invention can obtain remarkable advantageous effects in members having a thick wall.

[0049] Accordingly, in the austenitic heat resistant alloy of the present invention, the shortest distance from the center portion to the outer surface portion of a cross section is set to 40 mm or more, the cross section being perpendicular to a longitudinal direction. To obtain more remarkable advantageous effects of the present invention, the shortest distance from the center portion to the outer surface portion is preferably 80 mm or more, and more preferably 100 mm or more. In this embodiment, the shortest distance from the center portion to the outer surface portion refers to a radius (mm) of a cross section when an alloy has a columnar shape, and the shortest distance refers to a half-length (mm) of the short side of a cross section when an alloy has a quadrangular prism shape, for example.

[0050] As described later, the heat resistant alloy according to the present invention is obtained by performing hot working, such as hot forging or hot rolling on an ingot, or a cast piece, obtained by continuous casting or the like, for example. When an ingot is used, the longitudinal direction of a heat resistant alloy substantially refers to a direction along which a top portion and a bottom portion of the ingot are connected. When a cast piece is used, the longitudinal direction of a heat resistant alloy substantially refers to the longitudinal direction of the cast piece.

4. Amount of Cr which is present as precipitate obtained by extraction residue analysis

[0051]

$$Cr_{PB}/Cr_{PS} \leq 10.0 \dots (i)$$

where meaning of each symbol in the formula (i) is as follows:

Cr_{PB} : amount of Cr which is present at center portion as precipitate obtained by extraction residue analysis

Cr_{PS} : amount of Cr which is present at outer surface portion as precipitate obtained by extraction residue analysis

[0052] In a production process for an alloy, after heat treatment, which is performed after the hot working, is performed, undissolved Cr precipitations (mainly carbides) are generated at crystal grain boundaries or within grains. Particularly at the center portion of the alloy, a cooling speed is slower than that at the outer surface portion of the alloy and hence, the amount of Cr precipitates tends to increase. Accordingly, when a value of Cr_{PB}/Cr_{PS} exceeds 10.0, it becomes impossible to maintain high creep rupture strength at a high temperature. On the other hand, it is not necessary to set the lower limit value of Cr_{PB}/Cr_{PS} . However, there is a tendency that the amount of precipitates increases more at the center portion than at the outer surface portion and hence, Cr_{PB}/Cr_{PS} is preferably set to 1.0 or more.

[0053] An extraction residue analysis is performed by the following procedure. First, test coupons for measuring Cr precipitates are obtained from the center portion and the outer surface portion of the cross section of an alloy specimen, the cross section being perpendicular to the longitudinal direction of the alloy specimen. The surface area of each test coupon is obtained and, thereafter, only the base metal of the alloy specimen is completely electrolyzed in a 10% acetylacetone - 1% tetramethyl ammonium chloride - methanol solution under an electrolysis condition of 20 mA/cm². Then, the solution after electrolysis is performed is filtered through a 0.2 μm filter to extract precipitates as a residue. Thereafter, the extracted residue is decomposed with an acid, and is analyzed using an inductively coupled plasma emission spectrophotometer (ICP-AES) to measure a content (mass%) of Cr contained as undissolved Cr precipitate, and a value of Cr_{PB}/Cr_{PS} is obtained based on the measured value.

5. Mechanical properties

[0054]

$$YS_S/YS_B \leq 1.5 \dots (ii)$$

$$TS_S/TS_B \leq 1.2 \dots (iii)$$

where meaning of each symbol in the formulas is as follows:

YS_B : 0.2% proof stress at center portion

YSs: 0.2% proof stress at outer surface portion

TS_B: tensile strength at center portion

TS_S: tensile strength at outer surface portion

[0055] In a large-sized structural member, a cooling speed at the time of performing heat treatment varies from region to region and hence, there is a tendency that great variations occur in mechanical properties from region to region due to the difference in the cooling speed. If there is a large difference in 0.2% proof stress and tensile strength at a room temperature between the center portion and the outer surface portion of the large-sized structural member, there arises a problem that some regions do not satisfy the specifications.

[0056] Accordingly, with respect to the austenitic heat resistant alloy according to the present invention, mechanical properties at a room temperature satisfy the formula (ii) and formula (iii). It is not necessary to set the respective lower limit values of these formulas. However, there is a tendency that mechanical characteristics at the center portion are inferior to mechanical characteristics at the outer surface portion and hence, either one of formula (ii) or formula (iii) is preferably set to 1.0 or more.

[0057] 0.2% proof stress and tensile strength are obtained in such a way that round bar tensile test coupons, each having a parallel portion with a length of 40 mm, are cut out by mechanical processing from the center portion and the outer surface portion of the alloy parallel to the longitudinal direction, and a tensile test is performed on these test coupons at a room temperature. The tensile test is performed in accordance with JIS Z 2241 (2011).

6. Creep rupture strength

[0058] The austenitic heat resistant alloy of the present invention is used in a high temperature environment, thus being required to be excellent in high temperature strength, particularly, in creep rupture strength. Accordingly, 10,000-hour creep rupture strength at 700°C in the longitudinal direction is preferably 100 MPa or more at the center portion of the heat resistant alloy of the present invention.

[0059] Creep rupture strength is obtained by the following method. First, round bar creep rupture test coupons, described in JIS Z 2241 (2011), and having a diameter of 6 mm and a gage length of 30 mm, are cut out by mechanical processing from the center portions of the alloys parallel to the longitudinal direction. Then, a creep rupture test is performed in the atmosphere of 700°C, 750°C, and 800°C to obtain 10,000-hour creep rupture strength at 700°C by a Larson-Miller parameter method. The creep rupture test is performed in accordance with JIS Z 2271 (2010).

7. Production method

[0060] The austenitic heat resistant alloy of the present invention can be produced by performing hot working on an ingot or a cast piece having the above chemical composition. In the above step of performing hot working, processing is performed such that the longitudinal direction of the alloy in the final shape aligns with the longitudinal direction of the ingot or the cast piece forming a starting material. Hot working may be performed only in the longitudinal direction. However, to obtain a more uniform micro-structure at a higher working ratio, hot working may be performed one or more times in a direction substantially perpendicular to the longitudinal direction. After the hot working is performed, hot working of another method, such as hot extrusion, may be further performed when necessary.

[0061] In producing the austenitic heat resistant alloy of the present invention, after the above step, final heat treatment described below is performed so as to minimize variation in metal micro-structure and mechanical properties from region to region, thus maintaining high creep rupture strength.

[0062] First, the alloy on which hot working was performed is heated to a heat-treatment temperature T (°C) ranging from 1100 to 1250°C, and is held for 1000 D/T to 1400 D/T (min) within such a range. In this embodiment, symbol "D" denotes the diameter (mm) of the alloy when the alloy has a columnar shape, and "D" denotes a diagonal distance (mm) when the alloy has a quadrangular prism shape, for example. That is, symbol "D" denotes the maximum value (mm) of a linear distance between an arbitrary point on the outer edge of the cross section of the alloy and another arbitrary point on the outer edge, the cross section being perpendicular to a longitudinal direction of the alloy.

[0063] When the heat-treatment temperature is less than 1100°C, the amount of undissolved chromium carbide or the like increases, thus lowering creep rupture strength. On the other hand, when the heat-treatment temperature exceeds 1250°C, grain boundaries are dissolved or grains are remarkably coarsened so that ductility is lowered. Accordingly, it is more desirable to set the heat-treatment temperature to 1150°C or above and 1230°C or below. Further, when the holding time is less than 1000 D/T (min), undissolved chromium carbide at the center portion increases so that Cr_{PB}/Cr_{PS} falls outside a range defined by the present invention. On the other hand, when the holding time exceeds 1400 D/T (min), grain at the outer surface portion is coarsened so that the austenite grain size number falls outside the range defined by the present invention.

[0064] Immediately after the alloy is heated and held, the alloy is cooled with water. This is because when a cooling

speed becomes lower, particularly at the center portion of the alloy, a large amount of undissolved Cr precipitates is generated at crystal grain boundaries or within grains so that there is a possibility that the formula (i) is not satisfied.

[0065] Hereinafter, the present invention is described more specifically with reference to examples. However, the present invention is not limited to these examples.

EXAMPLE

[0066] Alloys having the chemical compositions shown in Table 1 were melted in a high-frequency vacuum furnace to prepare ingots each having an outer diameter of 550 mm, and a weight of 3t.

[Table 1]

Table 1

Alloy	Chemical composition (in mass%, balance: Fe and impurities)																				
	C	Si	Mn	P	S	Cr	Ni	Co	W	Ti	Nb	Mo	Cu	Al	N	Mg	Ca	REM	V	B	Others
1	0.075	0.38	1.12	0.008	0.001	21.5	41.3	-	4.6	0.41	0.73	0.08	0.15	0.14	0.031	-	-	-	-	-	-
2	0.043	0.42	0.95	0.006	0.002	25.3	44.2	7.3	8.4	0.22	0.45	0.05	0.07	0.03	0.015	-	-	-	-	0.0051	-
3	0.090	0.40	1.07	0.010	0.001	26.8	48.5	-	6.1	0.15	0.29	0.06	0.11	0.25	0.026	0.0012	0.002	0.01	0.6	-	Zr0.01,Ta:1.4
4	0.041	0.43	1.24	0.009	0.003	24.6	51.1	-	5.2	0.17	0.24	0.13	0.08	0.09	0.019	-	-	0.06	-	0.0063	Hf0.3,Re:1.2
5	0.030	0.51	1.06	0.011	0.002	27.5	53.7	-	4.8	0.25	0.71	0.34	0.21	0.16	0.024	-	-	0.11	-	-	-
6	0.064	0.24	1.57	0.014	0.001	23.4	47.2	-	6.4	0.47	0.60	0.07	0.13	0.20	0.018	-	-	-	-	0.0017	-
7	0.102	0.78	0.59	0.008	0.001	25.6	50.6	-	5.7	0.19	0.43	0.09	0.10	0.09	0.034	-	-	-	-	-	Zr0.05
8	0.056	0.43	1.25	0.012	0.001	20.9	38.4	-	4.9	0.20	0.39	0.11	0.15	0.12	0.072	-	-	-	0.7	-	-
9	0.048	0.69	1.68	0.015	0.002	24.7	52.1	-	6.5	0.34	0.25	0.14	0.08	0.17	0.044	-	0.009	-	-	-	-
A	0.073	0.40	1.08	0.007	0.001	21.7	41.6	-	4.5	0.45	0.73	0.05	0.14	0.10	0.035	-	-	-	-	-	-
B	0.076	0.42	1.10	0.008	0.001	21.4	41.0	-	4.8	0.41	0.75	0.07	0.15	0.11	0.040	-	-	-	-	-	-
C	0.045	0.39	1.05	0.008	0.002	25.0	45.2	7.0	8.2	0.23	0.41	0.08	0.07	0.05	0.025	-	-	-	-	0.0050	-
D	0.044	0.40	1.01	0.007	0.002	24.9	44.8	7.1	8.0	0.24	0.42	0.08	0.08	0.05	0.019	-	-	-	-	0.0052	-
E	0.044	0.42	0.98	0.007	0.001	25.2	45.7	7.4	8.1	0.24	0.44	0.07	0.08	0.04	0.018	-	-	-	-	0.0053	-

[0067] The obtained ingots were processed to have a columnar shape with an outer diameter of 120 to 480 mm by

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hot forging, and final heat treatment was performed under conditions shown in Table 2 to obtain alloy member specimens. Alloys 1, 2 and 4 were subjected to forging in a direction substantially perpendicular to the longitudinal direction after hot forging in the longitudinal direction and before final heat treatment and, thereafter, final hot forging was further performed in the longitudinal direction.

[Table 2]

[0068]

Table 2

Alloy	Outer diameter D (mm)	Heat-treatment temperature T (°C)	1000D/T	1400D/T	Holding time (min)	Cooling method
1	450	1180	381	534	480	water cooling
2	350	1200	292	408	360	water cooling
3	200	1150	174	243	220	water cooling
4	480	1150	417	584	540	water cooling
5	250	1210	207	289	260	water cooling
6	300	1200	250	350	310	water cooling
7	120	1180	102	142	130	water cooling
8	300	1180	254	356	295	water cooling
9	520	1200	433	607	570	water cooling
A	450	1180	381	534	660 **	water cooling
B	450	1180	381	534	200 **	water cooling
C	350	1070 **	327	458	340	water cooling
D	350	1270 **	276	386	340	water cooling
E	350	1200	292	408	360	air cooling **
** indicates that production conditions do not satisfy those defined by the present invention.						

[0069] A test coupon for observing micro-structure was obtained from the outer surface portion of each specimen, and the cross section in the longitudinal direction was polished with emery paper and a buff. Thereafter, the test coupon was etched with a mixed acid, and optical microscopic observation was performed. The grain size number on an observation surface was obtained in accordance with a determination method defined by JIS G 0551 (2013) where the grain size number is determined based on crossing line segments (grain size).

[0070] Next, test coupons for measuring the amount of Cr precipitates were obtained from the center portion and the outer surface portion of the cross section of each specimen, the cross section being perpendicular to the longitudinal direction of the specimen. The surface area of each test coupon was obtained and, thereafter, only the base metal of

the alloy specimen was completely electrolyzed in a 10% acetylacetone - 1% tetramethyl ammonium chloride - methanol solution under an electrolysis condition of 20 mA/cm². Then, the solution after electrolysis was performed was filtered through a 0.2 μm filter to extract precipitates as a residue. Thereafter, extracted residue was decomposed with an acid, and was subjected to ICP-AES measurement to measure a content (mass%) of Cr contained as undissolved Cr precipitate and, then, a value of Cr_{PB}/Cr_{PS} was obtained based on the measured value.

[0071] Tensile test coupons, each having a parallel portion with a length of 40 mm, were cut out by mechanical processing from the center portion and the outer surface portion of each specimen parallel to the longitudinal direction, and a tensile test was performed on these test coupons at a room temperature so as to obtain 0.2% proof stress and tensile strength. Further, creep rupture test coupon, having a parallel portion with a length of 30 mm, was cut out by mechanical processing from the center portion of each specimen parallel to the longitudinal direction. Then, a creep rupture test was performed in the atmosphere of 700°C, 750°C, and 800°C to obtain 10,000-hour creep rupture strength at 700°C by a Larson-Miller parameter method.

[0072] These results are collectively shown in Table 3.

[Table 3]

[0073]

Table 3

Alloy	Grain size number at outer surface portion	Cr _{PB} /Cr _{PS}	YS _S /YS _B	TS _S /TS _B	Creep rupture strength#	
1	-1.1	6.9	1.2	1.0	112	Inventive example
2	0.2	3.4	1.3	1.1	128	
3	2.2	5.8	1.0	1.0	115	
4	0.6	7.9	1.2	1.0	118	
5	-0.4	6.5	1.2	1.1	116	
6	-0.7	5.7	1.3	1.1	119	
7	1.2	2.8	1.1	1.0	118	
8	1.0	4.4	1.2	1.0	114	
9	-1.3	8.7	1.4	1.2	118	
A	-2.5 *	6.0	1.6 *	1.3 *	110	Comparative example
B	3.5	4.6	1.1	1.1	92	
C	5.7 *	12.6 *	1.2	1.1	93	
D	-2.8 *	2.4	1.6 *	1.4 *	97	
E	0.5	14.8 *	1.3	1.0	95	
* indicates that conditions fall outside the range of the present invention. # indicates 10,000-hour creep rupture strengths at 700 °C.						

[0074] The alloy A and the alloy B have substantially the same chemical composition as the alloy 1, and are formed into a final shape same as that of the alloy 1 by hot forging. However, a holding time in heat treatment falls outside the production conditions defined by the present invention. Due to such holding time, the alloy A has the result that the grain size number at the outer surface portion falls outside the range defined by the present invention, and a value of YS_S/YS_B and a value of TS_S/TS_B fall outside the range defined by the present invention. Accordingly, the alloy A has a large variation in mechanical characteristics from region to region. The alloy B falls outside the range defined by the present invention with respect to creep rupture strength and, as a result, creep rupture strength of the alloy B is remarkably lower than that of the alloy 1.

[0075] Alloys C, D, and E have substantially the same chemical composition as the alloy 2, and are formed into a final shape same as that of the alloy 2 by hot forging. The alloy C is lower than the range defined by the present invention with respect to the heat-treatment temperature and hence, the grain size number at the outer surface portion and a value of Cr_{PB}/Cr_{PS} fall outside the ranges defined by the present invention. As a result, creep rupture strength of the alloy C

is remarkably lower than that of the alloy 2.

[0076] The alloy D is higher than the range defined by the present invention with respect to a heat-treatment temperature and hence, the grain size number at the outer surface portion and a value of YS_S/YS_B and a value of TS_S/TS_B fall outside the range defined by the present invention. As a result, creep rupture strength of the alloy D is remarkably lower than that of the alloy 2.

[0077] With regard to the alloy E, a cooling method in final heat treatment was not water cooling but was air cooling and hence, a cooling speed was remarkably low. Accordingly a value of Cr_{PB}/Cr_{PS} falls outside the range defined by the present invention and, as a result, creep rupture strength of the alloy E is remarkably lower than that of the alloy 2. On the other hand, the alloys 1 to 9 which satisfy all specifications of the present invention have small variation in mechanical characteristics, and favorable creep rupture strength.

INDUSTRIAL APPLICABILITY

[0078] The austenitic heat resistant alloy of the present invention has small variation in mechanical properties from region to region, and is excellent in creep rupture strength at a high temperature. Accordingly, the austenitic heat resistant alloy of the present invention is preferably applicable to a large-sized structural member for a thermal power generation boiler, a chemical plant or the like which is used in a high temperature environment.

Claims

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

C: 0.02 to 0.12%;
 Si: 2.0% or less;
 Mn: 3.0% or less;
 P: 0.030% or less;
 S: 0.015% or less;
 Cr: 20.0% or more and less than 28.0%;
 Ni: more than 35.0% and 55.0% or less;
 Co: 0 to 20.0%;
 W: 4.0 to 10.0%;
 Ti: 0.01 to 0.50%;
 Nb: 0.01 to 1.0%;
 Mo: less than 0.50%;
 Cu: less than 0.50%;
 Al: 0.30% or less;
 N: less than 0.10%;
 Mg: 0 to 0.05%;
 Ca: 0 to 0.05%;
 REM: 0 to 0.50%;
 V: 0 to 1.5%;
 B: 0 to 0.01%;
 Zr: 0 to 0.10%;
 Hf: 0 to 1.0%;
 Ta: 0 to 8.0%;
 Re: 0 to 8.0%; and

the balance: Fe and impurities, wherein

a shortest distance from a center portion to an outer surface portion of a cross section of the alloy is 40 mm or more, the cross section being perpendicular to a longitudinal direction of the alloy,

an austenite grain size number at the outer surface portion is -2.0 to 4.0,

an amount of Cr which is present as a precipitate obtained by an extraction residue analysis satisfies a following formula (i), and

mechanical properties at a room temperature satisfy following formula (ii) and formula (iii):

$$Cr_{PB}/Cr_{PS} \leq 10.0 \dots (i)$$

$$YS_S/YS_B \leq 1.5 \dots (ii)$$

$$TS_S/TS_B \leq 1.2 \dots (iii)$$

where meaning of each symbol in the formulas is as follows:

Cr_{PB}: amount of Cr which is present at center portion as precipitate obtained by extraction residue analysis
 Cr_{PS}: amount of Cr which is present at outer surface portion as precipitate obtained by extraction residue analysis
 YS_B: 0.2% proof stress at center portion
 YS_S: 0.2% proof stress at outer surface portion TS_B: tensile strength at center portion
 TS_S: tensile strength at outer surface portion.

2. The austenitic heat resistant alloy according to claim 1, wherein the chemical composition contains one or more elements selected from a group consisting of, in mass %:

Mg: 0.0005 to 0.05%;
 Ca: 0.0005 to 0.05%;
 REM: 0.0005 to 0.50%;
 V: 0.02 to 1.5%;
 B: 0.0005 to 0.01%;
 Zr: 0.005 to 0.10%;
 Hf: 0.005 to 1.0%;
 Ta: 0.01 to 8.0%; and
 Re: 0.01 to 8.0%.

3. The austenitic heat resistant alloy according to claim 1 or claim 2, wherein 10,000-hour creep rupture strength at 700°C in the longitudinal direction at the center portion is 100 MPa or more.

4. A method for producing an austenitic heat resistant alloy, the method comprising the steps of:

performing hot working on an ingot or a cast piece having the chemical composition according to claim 1 or claim 2; and
 thereafter performing heat treatment where the ingot or the cast piece is heated to a heat-treatment temperature T (°C) ranging from 1100 to 1250°C, is held for 1000 D/T to 1400 D/T (min), and is cooled with water, wherein symbol "D" denotes a maximum value (mm) of a linear distance between an arbitrary point on an outer edge of a cross section of the alloy and another arbitrary point on the outer edge, the cross section being perpendicular to a longitudinal direction of the alloy.

5. The method for producing an austenitic heat resistant alloy according to claim 4, wherein in the step of performing the hot working, the working is performed one or more times in a direction substantially perpendicular to the longitudinal direction.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/004824

A. CLASSIFICATION OF SUBJECT MATTER

C22C19/05(2006.01)i, C21D8/00(2006.01)i, C22C38/00(2006.01)i, C22C38/58
(2006.01)i, C22F1/10(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C19/05, C21D8/00, C22C38/00, C22C38/58, C22F1/10

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.
A	JP 2011-63838 A (Sumitomo Metal Industries, Ltd.), 31 March 2011 (31.03.2011), & US 2012/0168038 A1 & WO 2011/033856 A1 & EP 2479300 A1	1-5
A	JP 2004-3000 A (Sumitomo Metal Industries, Ltd.), 08 January 2004 (08.01.2004), & US 2003/0198567 A1 & EP 1357198 A1 & CA 2425398 A1 & CN 1451778 A	1-5
A	JP 2016-37664 A (Nippon Steel & Sumitomo Metal Corp.), 22 March 2016 (22.03.2016), (Family: none)	1-5

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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"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

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Name and mailing address of the ISA/
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3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

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- JP 61179834 A [0005]
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- JP 61179836 A [0005]
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