(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 915 893 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
09.09.2015 Bulletin 2015/37

(21) Application number: **13850082.2**

(22) Date of filing: **29.10.2013**

(51) Int Cl.:
C22C 38/00 *(2006.01)* ***C22C 38/58*** *(2006.01)*

(86) International application number:
PCT/JP2013/079292

(87) International publication number:
WO 2014/069467 (08.05.2014 Gazette 2014/19)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **30.10.2012 JP 2012238872**
23.01.2013 JP 2013010188

(71) Applicant: **Kabushiki Kaisha Kobe Seiko Sho (Kobe Steel, Ltd.)**
Kobe-shi, Hyogo 651-8585 (JP)

(72) Inventors:
- **MIYAMURA Takeo**
  Kobe-shi,Hyogo 651-2271 (JP)
- **NAMBA Shigenobu**
  kobe - shi , Hyogo 651-2271 (JP)

(74) Representative: **Müller-Boré & Partner**
Patentanwälte PartG mbB
Friedenheimer Brücke 21
80639 München (DE)

(54) AUSTENITIC STAINLESS STEEL

(57) Disclosed is an austenitic stainless steel containing C of 0.01 to 0.15 percent by mass, Si of 0.10 to 1.00 percent by mass, Mn of 0.10 to 2.50 percent by mass, Ni of 15.0 to 25.0 percent by mass, Cr of 20.0 to 30.0 percent by mass, Nb of 0.10 to 0.80 percent by mass, Ta of 0.20 to 1.00 percent by mass, B of 0.0005 to 0.0050 percent by mass, N of 0.10 to 0.35 percent by mass, S of 0.0050 percent by mass or less (excluding 0 percent by mass), and P of 0.050 percent by mass or less (excluding 0 percent by mass) with the remainder including iron and inevitable impurities.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention generally relates to austenitic stainless steels. In particular, the present invention relates to an austenitic stainless steel for use in high-temperature and oxidizing environments such as in thermal power generation boiler tubes.

Background Art

[0002] Renewable energy such as sunlight receives attention so as to maintain stable power supply, but thermal power generation is still a main electric power generation system when seen from a global perspective. In particular, coal fired power generation enjoys abundant resources and low material cost and is considered to grow mainly in emerging nations. The coal fired power generation, however, emits CO_2 in a large amount per generated energy. To solve the disadvantage and to provide higher generation efficiency, power boilers are designed to use steam at a higher temperature under higher pressure. Under these circumstances, materials for boiler tubes for use in heat-exchange units of the boilers require higher and higher heat resistance year by year.

[0003] Such thermal power generation boiler tubes employ austenitic stainless steels that have excellent high-temperature strengths and oxidation resistance. Of the boiler tubes, portions to be exposed to a high-temperature and highly corrosive environment employ 25Cr stainless steels typified by steel-use stainless (SUS) 310. The boiler tubes (steel tubes) are exposed not only to a high-temperature environment of 500°C to 700°C, but also to high-pressure steam passing through the inside of the steel tubes and thereby require excellent creep properties. Based on conventional knowledge, various attempts have been made to improve creep strength.

[0004] Typically, Patent Literature (PTL) 1 discloses a technique of controlling the contents of Ti, Nb, Zr, Ta, and C to appropriate proportions. PTL 2 discloses a technique of incorporating trace amounts of oxygen and titanium (Ti) into an austenitic stainless steel to restrain the formation of duplex grains. PTL 3 discloses a technique of controlling the contents typically of P, Al, and V in an austenitic stainless steel further containing Cu, Nb, and N. PTL 4 discloses a technique of controlling the contents of Mo, W, and N in an austenitic steel.

[0005] In addition, the boiler tubes require better toughness. The boiler tubes, if having poor toughness, may be susceptible to crack or tear caused by impact or shock loaded upon operation and/or inspection and may burst with higher possibility.

[0006] For better toughness, reduction in contents of Si, Al, S (sulfur), and O (oxygen) in stainless steels are believed to be effective. Typically, existing materials for thermal power generation boiler tubes have reduced Si and Al contents within such ranges as to offer deoxidation effects so as to restrain the formation of brittle phases such as sigma (σ) phase. These materials further include Mn, Ca, and Mg so as to reduce the influence of sulfur (S) (see, for example, PTL 5 and 6).

[0007] Separately, tantalum (Ta) may be added to 25Cr-20Ni and other heat-resistant stainless steels. PTL 7 to 11 describe that Ta and other elements such as Ti, Nb, V, Mo, W, and Re, when added selectively, may allow stainless steels to have better corrosion resistance, better hot workability, and higher high-temperature strengths due to carbon fixation.

Citation List

Patent Literature

[0008]

PTL 1: Japanese Unexamined Patent Application Publication (JP-A) No. Sho59(1984)-23855
PTL 2: JP-A No. 2004-250783
PTL 3: JP-A No. 2004-323937
PTL 4: JP-A No. 2012-1749
PTL 5: JP-A No. Hei7(1995)-278757
PTL 6: JP-A No. Hei4(1992)-358043
PTL 7: JP-A No. 2004-156126
PTL8: JP-A No. 2002-69591
PTL 9: JP-A No. 2006-291290
PTL 10: PCT International Publication Number WO 2009/044802
PTL 11: PCT International Publication Number WO 2009/044796

Summary of Invention

Technical Problem

[0009] Disadvantageously, however, the techniques according to PTL 1 and 2 fail to offer sufficient creep strengths; and the techniques according to PTL 3 and 4 require the addition of expensive metals such as W, Mo, and Cu in several percent by mass and inevitably suffer from increased cost. Kagi-Kaishaku (KA) SUS 310J1HTB and other JIS standardized steels serving as existing boiler materials contain nitrogen (N) in high contents and fail to enjoy the synergistic effect of nitrogen with another element as in the technique disclosed in PTL 4 and fail to have higher creep strengths.

[0010] The techniques described in PTL 5 to 11 may allow stainless steels to have toughness maintained at certain high level even upon exposure to a high-temperature environment (e.g., at 500°C to 700°C) for a long time. These techniques, however, are considered not to meet the heat resistance requirement that becomes severer year by year, as described above.

[0011] The present invention has been made under such circumstances. It is an object of the present invention to provide an austenitic stainless steel that can develop excellent creep strength in a high-temperature environment over a long term without the addition of large amounts of expensive metals such as W, Mo, and Cu. It is another object of the present invention to provide an austenitic stainless steel that can maintain excellent toughness even after exposure to a high-temperature environment for a long term. Solution to Problem

[0012] After intensive investigations, the present inventors have found that an austenitic stainless steel, when incorporated with tantalum (Ta) in a content within a specific range, can have excellent toughness even after an aging heat treatment, where the aging heat treatment simulates a use environment typically in a boiler, namely, an environment in which the stainless steel is exposed to a high temperature for a long term. In addition, the present inventors have found that the austenitic stainless steel containing Ta in a content within a specific range, when containing Nb and Ta in contents with a specific ratio therebetween, can have higher creep strength.

[0013] The present invention has been made based on these findings. Specifically, the present invention provides an austenitic stainless steel that contains C in a content of 0.01 to 0.15 percent by mass, Si in a content of 0.10 to 1.00 percent by mass, Mn in a content of 0.10 to 2.50 percent by mass, Ni in a content of 15.0 to 25.0 percent by mass, Cr in a content of 20.0 to 30.0 percent by mass, Nb in a content of 0.10 to 0.80 percent by mass, Ta in a content of 0.20 to 1.00 percent by mass, B in a content of 0.0005 to 0.0050 percent by mass, N in a content of 0.10 to 0.35 percent by mass, S in a content of 0.0050 percent by mass or less (excluding 0 percent by mass), and P in a content of 0.050 percent by mass or less (excluding 0 percent by mass) with the remainder including iron and inevitable impurities.

[0014] The austenitic stainless steel according to the present invention may contain Ta in a content of 0.25 to 0.8 percent by mass to exhibit particularly excellent toughness after aging.

[0015] The austenitic stainless steel according to the present invention may contain Nb in a content of 0.10 to 0.60 percent by mass and may have a ratio of Ta to Nb of 0.8 to 4.0 to exhibit particularly excellent creep strength.

[0016] The austenitic stainless steel according to the present invention may further include at least one of groups (a) and (b) below. The resulting austenitic stainless steel can have higher high-temperature strength and/or better oxidation resistance depending on an element to be contained. The groups (a) and (b) are as follows:

(a) at least one element selected from the group consisting of W in a content of 4 percent by mass or less, Mo in a content of 4 percent by mass or less, Cu in a content of 4 percent by mass or less, at least one rare-earth element in a content of 0.15 percent by mass or less, Ca in a content of 0.005 percent by mass or less, and Mg in a content of 0.005 percent by mass or less; and

(b) at least one element, in a total content of 0.4 percent by mass or less, selected from the group consisting of V in a content of 0.2 percent by mass or less, Ti in a content of 0.2 percent by mass or less, Zr in a content of 0.2 percent by mass or less, and Hf in a content of 0.2 percent by mass or less.

Advantageous Effects of Invention

[0017] The austenitic stainless steel according to an embodiment of the present invention can maintain excellent toughness even after exposure to a high-temperature environment for a long term. In another embodiment, the austenitic stainless steel according to the present invention can develop excellent creep strength in a high-temperature environment over a long term without the addition of large amounts of expensive metals such as Mo and Cu.

Description of Embodiments

[0018] Next, embodiments of the present invention will be described in detail below.

[0019] An austenitic stainless steel according to one embodiment of the present invention contains C in a content of

0.01 to 0.15 percent by mass, Si in a content of 0.10 to 1.00 percent by mass, Mn in a content of 0.10 to 2.50 percent by mass, Ni in a content of 15.0 to 25.0 percent by mass, Cr in a content of 20.0 to 30.0 percent by mass, Nb in a content of 0.10 to 0.80 percent by mass, Ta in a content of 0.20 to 1.00 percent by mass, B in a content of 0.0005 to 0.0050 percent by mass, N in a content of 0.10 to 0.35 percent by mass, S in a content of 0.0050 percent by mass or less (excluding 0 percent by mass), and P in a content of 0.050 percent by mass or less (excluding 0 percent by mass) with the remainder including iron and inevitable impurities.

[0020] The austenitic stainless steel according to the embodiment of the present invention has chemical compositions in Ni and Cr contents equivalent to a 25Cr-20Ni austenitic stainless steel, but includes specific chemical compositions (C, Si, Mn, Ni, Cr, Nb, Ta, B, N, S, and P) as mentioned below. Operations of these elements and reasons for specifying the content ranges of the elements are as follows.

C: 0.01 to 0.15 percent by mass

[0021] Carbon (C) forms carbides in a high-temperature use environment and allows the steel to have higher high-temperature strength and higher creep strength necessary as a heat-exchanger tube. Carbon may be contained in a content of 0.01 percent by mass or more so as to ensure certain amounts of precipitated carbides acting as a strengthening mechanism. However, carbon, if contained in an excessively high content of greater than 0.15 percent by mass, may form coarse carbides to fail to offer still further strengthening. The carbon content is preferably 0.03 percent by mass or more, and more preferably 0.05 percent by mass or more; and is preferably 0.10 percent by mass or less, and more preferably 0.07 percent by mass or less.

Si: 0.1 to 1.0 percent by mass

[0022] Silicon (Si) has a deoxidation action in a molten steel Silicon, even if contained in a trace amount, may effectively allow the steel to have better oxidation resistance. To allow the element to exhibit the effects effectively, the Si content may be controlled to 0.1 percent by mass or more. However, Si, if contained in an excessively high content of greater than 1.0 percent by mass, may cause the formation of sigma (σ) phase and may cause the austenitic stainless steel to have inferior toughness. The Si content is preferably 0.2 percent by mass or more, and more preferably 0.3 percent by mass or more; and is preferably 0.7 percent by mass or less, and more preferably 0.5 percent by mass or less.

Mn: 0.1 to 2.5 percent by mass

[0023] Manganese (Mn) has a deoxidation action in the molten steel as with Si and functionally stabilizes austenite. To allow the element to exhibit the effects effectively, the Mn content may be controlled to 0.1 percent by mass or more. However, Mn, if contained in an excessively high content of greater than 2.5 percent by mass, may adversely affect the hot workability. The Mn content is preferably 0.5 percent by mass or more, and more preferably 1.0 percent by mass or more; and is preferably 2.0 percent by mass or less, and more preferably 1.5 percent by mass or less.

P: 0.05 percent by mass or less (excluding 0 percent by mass)

[0024] Phosphorus (P) is an inevitable impurity. Phosphorus, if contained in a higher content, may adversely affect the weldability. To prevent this, the phosphorus content may be controlled to 0.05 percent by mass or less. The phosphorus content may be controlled preferably to 0.04 percent by mass or less, and more preferably to 0.03 percent by mass or less.

S: 0.005 percent by mass or less (excluding 0 percent by mass)

[0025] Sulfur (S) is an inevitable impurity. Sulfur, if contained in a higher content, may adversely affect the hot workability. To prevent this, the sulfur content may be controlled to 0.005 percent by mass or less. The sulfur content may be controlled preferably to 0.003 percent by mass or less, and more preferably to 0.001 percent by mass or less.

Ni:15 to 25 percent by mass

[0026] Nickel (Ni) functionally stabilizes austenite. To maintain the austenite phase, Ni may be contained in a content of 15 percent by mass or more. However, Ni, if contained in an excessively high content of greater than 25 percent by mass, may cause increased cost. The Ni content is preferably 17 percent by mass or more, and more preferably 19 percent by mass or more; and is preferably 23 percent by mass or less, and more preferably 21 percent by mass or less.

Cr: 20 to 30 percent by mass

[0027] Chromium (Cr) s essential for the austenitic stainless steel to exhibit corrosion resistance as a stainless steel. To allow the element to offer excellent corrosion resistance, Cr may be contained in a content of 20 percent by mass or more. However, Cr, if contained in an excessively high content of greater than 30 percent by mass, may cause an increased amount of ferrite phase that causes reduction of high-temperature strength. The Cr content is preferably 22 percent by mass or more, and more preferably 24 percent by mass or more; and is preferably 28 percent by mass or less, and more preferably 26 percent by mass or less.

Nb: 0.1 to 0.8 percent by mass

[0028] Niobium (Nb) precipitates as carbides, nitrides, or carbonitrides to allow the steel to have higher high-temperature strength and higher creep strength. In addition, these precipitates may suppress grain coarsening, promote chromium diffusion, and thereby secondarily allow the steel to have better corrosion resistance. To surely allow the particles to precipitate in necessary amounts for exhibiting these effects effectively, Nb may be contained in a content of 0.1 percent by mass or more. However, Nb, if contained in an excessively high content of greater than 0.8 percent by mass, may cause the precipitates to coarsen to thereby cause the austenitic stainless steel to have inferior toughness. The Nb content is preferably 0.15 percent by mass or more, more preferably 0.2 percent by mass or more, and furthermore preferably 0.25 percent by mass or more; and is preferably 0.6 percent by mass or less.

Ta: 0.20 to 1.00 percent by mass

[0029] Precipitate formations are classified into precipitation at grain boundaries and precipitation inside of grains. It has been known that the particles precipitated at grain boundaries, if covering the grain boundaries, cause the steel to have inferior toughness. Tantalum (Ta), when contained, can reduce the amounts of particles precipitated at grain boundaries and allows the steel to have excellent toughness after aging. In contrast, Ta allows carbides and carbonitrides to precipitate in grains to offer precipitation strengthening and thereby makes the steel have higher creep strength. In addition, Ta is dissolved in Z phase (CrNbN) precipitated in the austenitic stainless steel and allows the steel to have still higher creep strength. To offer these effects, Ta may be contained in a content of 0.20 percent by mass or more. However, Ta, if contained in an excessively high content of greater than 1.00 percent by mass, may cause the formation of excessive amounts of precipitates and cause the austenitic stainless steel to have inferior ductility and poor economic efficiency. For the Ta content, the lower limit is preferably 0.25 percent by mass or more, and more preferably 0.30 percent by mass or more; and the upper limit is preferably 0.80 percent by mass or less, and more preferably 0.60 percent by mass or less.

B: 0.0005 to 0.005 percent by mass

[0030] Boron (B) is dissolved in the steel and functionally promotes the formation of $M_{23}C_6$ carbides, where M represents a carbide-forming element. Such $M_{23}C_6$ carbides act as one of main strengthening mechanisms. To be sure that the element exhibits these effects effectively, the boron content may be 0.0005 percent by mass or more. However, boron, if contained in an excessively high content, may cause inferior hot workability and/or inferior weldability. To prevent this, the boron content may be controlled to 0.005 percent by mass or less. The boron content is preferably 0.001 percent by mass or more, and more preferably 0.0015 percent by mass or more; and is preferably 0.003 percent by mass or less, and more preferably 0.0025 percent by mass or less.

N: 0.10 to 0.35 percent by mass

[0031] Nitrogen (N) is dissolved in the steel to cause solute strengthening and thereby allows the steel to have higher high-temperature strength. Thus, the element is one of important elements that bear high-temperature strength of the austenitic stainless steel according to the embodiment of the present invention. To allow the element to have the effects effectively, nitrogen may be contained in a content of 0.10 percent by mass or more. However, nitrogen, if contained in an excessively high content of greater than 0.35 percent by mass, may adversely affect the hot workability. The nitrogen content is preferably 0.20 percent by mass or more, and more preferably 0.23 percent by mass or more; and is preferably 0.30 percent by mass or less, and more preferably 0.27 percent by mass or less.

Remainder: iron and inevitable impurities

[0032] The austenitic stainless steel according to the embodiment of the present invention contains the elements as above, with the remainder including iron and inevitable impurities. Such impurities include Sn, Pb, Sb, As, Zn, and other low-melting-point metallic elements derived from scrap materials. The low-melting-point metallic elements cause the steel to have inferior strength at grain boundaries upon hot working and/or upon use in a high-temperature environment. To prevent this and to improve hot workability and embrittlement cracking resistance after long-term use, the contents of metallic elements having the low-melting-point are desirably controlled at low levels.

[0033] The austenitic stainless steel according to the one embodiment of the present invention has been described above. The austenitic stainless steel according to an embodiment of the present invention, when having a Ta content of 0.25 to 0.8 percent by mass, can exhibit particularly excellent toughness after aging, as described above. Reasons for this will be described below.

[0034] Precipitate formations are classified into precipitation at grain boundaries and precipitation inside of grains, as described above. The precipitates formed at grain boundaries, when covering the grain boundaries, cause the steel to have inferior toughness, as has been known The present inventors, however, have found that Ta, when contained in the austenitic stainless steel in a content of 0.25 to 0.8 percent by mass, can particularly effectively contribute to reduction of amounts of particles precipitated at grain boundaries. This can allow the steel to exhibit excellent toughness after aging. From this viewpoint, Ta is particularly preferably contained in a content of 0.3 percent by mass or more. In contrast, Ta is an expensive metal and, when added, causes increased cost. To prevent this and to offer better toughness, Ta may be contained in a content of preferably 0.6 percent by mass or less, and more preferably 0.5 percent by mass or less.

[0035] The austenitic stainless steel contains Ta in a content within the specific range and contains other elements than Ta in appropriately controlled contents, as above. The austenitic stainless steel can thereby have excellent toughness (toughness value) after an aging heat treatment, where the aging heat treatment simulates a use environment typically in a boiler, namely, an environment in which the stainless steel is exposed to a high temperature for a long term. This will be concretely described in experimental examples below. The austenitic stainless steel according to the embodiment of the present invention is therefore advantageously usable as a material for heat-exchanger tubes typically of boilers (boiler tubes). Specifically, the austenitic stainless steel according to the embodiment of the present invention maintains excellent toughness even after exposure to a high-temperature environment for a long term typically in a boiler, can endure shock (impact) occurring during operation and/or during inspection, and is usable as a material for a boiler tube that can maintain its reliability over a long term.

[0036] In another embodiment, the austenitic stainless steel according to the present invention has a Nb content of 0.10 to 0.60 percent by mass and has a ratio of the Ta content to the Nb content of 0.8 to 4.0 as described above. The austenitic stainless steel in this embodiment can exhibit particularly excellent creep strength. Reasons for this will be described below.

[0037] Niobium (Nb) precipitates in the steel as Nb(C,N) and/or Z phase (CrNbN), thus contributes to precipitation strengthening, and makes the steel have higher creep strength. The present inventors have found that Nb, when contained in a content of 0.10 to 0.60 percent by mass, may exhibit these effects particularly advantageously. In addition, Ta, when contained in a ratio of Ta to Nb (Ta/Nb) within a predetermined range, may be dissolved in the Z phase in an optimum amount and allows the steel to have higher creep strength. The austenitic stainless steel, if having a ratio Ta/Nb of less than 0.8, may include solute tantalum in a small amount and may fail to have higher creep strength in an expected manner. In contrast, the austenitic stainless steel, if having a ratio Ta/Nb of greater than 4.0, may have inferior ductility due to a large amount of solute tantalum and may suffer from poor economic efficiency. To avoid these, the ratio Ta/Nb may be controlled to the range of from 0.8 to 4.0.

[0038] In another embodiment, the austenitic stainless steel according to the present invention may further include at least one of groups (a) and (b) below. In this embodiment, the austenitic stainless steel can have higher high-temperature strength and/or better oxidation resistance depending on an element to be contained The groups (a) and (b) are as follows:

(a) at least one element selected from the group consisting of W in a content of 4 percent by mass or less, Mo in a content of 4 percent by mass or less, Cu in a content of 4 percent by mass or less, at least one rare-earth element in a content of 0.15 percent by mass or less, Ca in a content of 0.005 percent by mass or less, and Mg in a content of 0.005 percent by mass or less; and

(b) at least one element, in a total content of 0.4 percent by mass or less, selected from the group consisting of V in a content of 0.2 percent by mass or less, Ti in a content of 0.2 percent by mass or less, Zr in a content of 0.2 percent by mass or less, and Hf in a content of 0.2 percent by mass or less.

[0039] Hereinafter the elements and their contents to be contained in the austenitic stainless steel according to this embodiment will be described.

W: 4 percent by mass or less and Mo: 4 percent by mass or less

[0040] Tungsten (W) and molybdenum (Mo) offer solute strengthening and effectively allow the steel to have higher high-temperature strength. These elements, when contained according to necessity, allow the austenitic stainless steel to have higher high-temperature strength. However, tungsten, if contained in an excessively high content of greater than 4 percent by mass, may form coarse intermetallic compounds to cause the austenitic stainless steel to have inferior hot ductility. To prevent this, the tungsten content is preferably 4 percent by mass or less (excluding 0 percent by mass), more preferably 3 percent by mass or less, and furthermore preferably 2 percent by mass or less.

[0041] Mo, if contained in an excessively high content of greater than 4 percent by mass, may adversely affect the hot workability. To prevent this, the Mo content is preferably 4 percent by mass or less (excluding 0 percent by mass), more preferably 3 percent by mass or less, and furthermore preferably 2 percent by mass or less.

[0042] To allow the element to exhibit the above-mentioned effects effectively, the tungsten content is preferably 0.1 percent by mass or more, and more preferably 0.5 percent by mass or more. Likewise, the Mo content is preferably 0.1 percent by mass or more, and more preferably 0.5 percent by mass or more. However, these elements cause increased cost, although they exhibit the above-mentioned effects. The contents of these elements are preferably set depending on the necessary magnitude of strengthening and an allowable cost.

Cu: 4 percent by mass or less

[0043] Copper (Cu) forms conformable precipitates in the steel and allows the steel to have significantly higher creep high-temperature strength and acts as one of main strengthening mechanisms in the stainless steel. The term "conformable precipitates" refers to precipitates having an atomic arrangement continuous with that of the parent metal. However, Cu, if contained in an excessively high content of greater than 4 percent by mass, may be saturated in its effects. To prevent this, the Cu content is preferably 4 percent by mass or less (excluding 0 percent by mass), more preferably 3.7 percent by mass or less, and furthermore preferably 3.5 percent by mass or less. To allow the element to exhibit the effects, the Cu content is preferably 0.2 percent by mass or more, more preferably 2 percent by mass or more, and furthermore preferably 2.5 percent by mass or more.

Rare-earth element: 0.15 percent by mass or less

[0044] Rare-earth elements usable herein are exemplified by seventeen elements including Sc and Y as well as lanthanoid elements typified by La, Ce, and Nd.

[0045] The rare-earth elements effectively allow the stainless steel to have better oxidation resistance and can restrain the formation of oxidized scale on the inner surface of a heat-exchanger tube through which high-temperature and high-pressure steam passes. The rare-earth element or elements, if contained in an excessively high content of greater than 0.15 percent by mass, may cause the grain boundaries to partially melt in a high-temperature environment to adversely affect the hot workability. To prevent this, the rare-earth element content is preferably 0.15 percent by mass or less, more preferably 0.1 percent by mass or less, and furthermore preferably 0.05 percent by mass or less. To allow the elements to exhibit the effects effectively, the rare-earth element content is preferably 0.01 percent by mass or more, more preferably 0.015 percent by mass or more, and furthermore preferably 0.02 percent by mass or more. The austenitic stainless steel, when configured as above, can give a boiler heat-exchanger tube (boiler tube) having excellent toughness. When to be contained in the steel, the individual rare-earth elements may be added independently to the steel, but may be added as so-called misch metal including these elements. The misch metal, when used, contributes to lower cost for the separation of individual elements and contributes to better profitability.

Ca: 0.005 percent by mass or less and Mg: 0.005 percent by mass or less

[0046] Calcium (Ca) and magnesium (Mg) act as desulfurizing and deoxidizing elements. However, these elements, if contained in excessively high contents, may cause bumping of the molten steel during melting operation and may cause constrains in operations. To prevent this, the Ca and Mg contents are each preferably 0.005 percent by mass or less (excluding 0 percent by mass), and more preferably 0.002 percent by mass or less. To allow the elements to exhibit the effects effectively, the Ca and Mg contents are each preferably 0.0002 percent by mass or more, and more preferably 0.0005 percent by mass or more.

[0047] At least one element, in a total content of 0.4 percent by mass or less, selected from the group consisting of V in a content of 0.2 percent by mass or less, Ti in a content of 0.2 percent by mass or less, Zr in a content of 0.2 percent by mass or less, and Hf in a content of 0.2 percent by mass or less

[0048] Vanadium (V), titanium (Ti), zirconium (Zr), and hafnium (Hf) exhibit effects as with Nb, but when added in combination, may allow the precipitates to be still further stabilized and may effectively allow the steel to maintain high-temperature strength for a long term. However, these elements, if contained in excessively high contents, may fail to be dissolved in the steel and may thereby cause the steel to include larger amounts of inclusions and to have inferior toughness. To prevent this, the contents of V, Ti, Zr, and Hf are each preferably controlled to 0.2 percent by mass or less (excluding 0 percent by mass), more preferably 0.15 percent by mass or less, and furthermore preferably 0.1 percent by mass or less. To allow the elements to exhibit the effects effectively, the contents of V, Ti, Zr, and Hf are each preferably 0.02 percent by mass or more, more preferably 0.04 percent by mass or more, and furthermore preferably 0.06 percent by mass or more. However, when two or more of these elements are contained in a total content of greater than 0.4 percent by mass, may cause larger amounts of undissolved inclusions, as described above. To prevent this, two or more of these elements, when contained in combination, are preferably contained in a total content of 0.4 percent by mass or less.

Production of Austenitic Stainless Steel According to Present Invention

[0049] The austenitic stainless steel according to the embodiment of the present invention may be produced typically by melting a steel while adding individual elements to give the chemical compositions in primary refining, and sequentially performing production processes such as secondary refining according to a common procedure. Examples

[0050] Next, the present invention will be illustrated specifically with reference to several examples that take desired advantageous effects of the present invention.

Experimental Example 1: Experimental example relating to toughness after aging

[0051] Steels having chemical compositions given in Test Nos. 1A to 19A in Table 1 below were melted in a vacuum induction furnace (VIF), formed into 20-kg ingots, hot-forged to dimensions of 120 mm wide by 20 mm thick, subjected to a heat treatment at 1250°C, and cold-rolled to a thickness of 13 mm. The steels were subjected again to a heat treatment at 1220°C for 5 minutes and taken as base metals (base steels).

[0052] Of the steels according to Test Nos. 1A to 19A in Table 1, the steels of Test Nos. 1A to 12A are steels having chemical compositions within ranges specified in the present invention for austenitic stainless steels excellent particularly in toughness after aging. These are steels according to the present invention. The steels of Test Nos.13A to 19A are steels having chemical compositions out of the ranges specified in the present invention for the austenitic stainless steels excellent particularly in toughness after aging. These are comparative steels. Of these steels, the steel of Test No.19A corresponds to the existing steel "KA-SUS 310J1HTB". The steel (Test No.19A) corresponding to "KA-SUS 310J1HTB" belongs to 25Cr-20Ni austenitic stainless steels and is a steel grade having been actually used in boiler heat-exchanger tubes (boiler tubes). Italicized and underlined numerical values in Table 1 refer to data out of the chemical composition ranges specified in the present invention. The symbol "-" in Table 1 indicates that an element in question is not added. A material for rare-earth elements to be added was a misch metal including Ce, La, and Nd.

[Table 1]

Test No.	Chemical compositions* (in mass percent)										
	Ta	C	Si	Mn	P	S	Ni	Cr	Nb	B	N	Others
1A	028	0.06	0.44	1.31	0.014	0.0005	19.4	25.0	0.23	0.0009	0.23	
2A	0.40	0.05	0.36	1.34	0.015	0.0011	20.0	24.8	0.25	0.0012	0.23	
3A	0.40	0.06	0.45	1.45	0.025	0.0008	20.1	24.2	0.22	0.0048	0.26	
4A	027	0.07	0.32	1.32	0.032	0.0010	22.5	24.9	0.28	0.0021	0.25	
5A	0.33	0.08	0.43	1.30	0.043	0.0028	18.4	22.8	0.32	0.0019	0.26	
6A	0.42	0.06	0.62	1.19	0.016	0.0036	23.6	27.5	020	0.0008	027	
7A	0.25	0.02	0.28	0.48	0.010	0.0021	18.9	23.6	0.39	0.0021	0.31	Cu:1.5
8A	0.28	0.04	0.56	220	0.014	0.0015	16.9	21.8	0.31	0.0018	0.28	Mo:1.0, Rare-earth elements:0.03
9A	0.51	0.09	0.72	1.56	0.033	0.0009	23.1	29.0	0.29	0.0012	0.22	W:2.2
10A	0.66	0.11	0.39	0.95	0.025	0.0004	21.1	25.6	0.27	0.0016	0.18	Ca:0.002
11A	0.38	0.08	0.51	1.54	0.018	0.0010	22.2	25.1	0.32	0.0013	0.23	Mg:0.0003, Rare-earth elements:0.01
12A	0.42	0.06	0.40	1.05	0.011	0.0007	19.2	28.4	0.27	0.0014	0.27	V:0.06, Zr:0.04. Ti.0.06
13A	*0.04*	0.09	0.39	1.40	0.030	0.0021	22.1	26.7	0.27	0.0018	0.25	
14A	0.25	0.06	0.25	121	0.031	0.0018	19.8	25.0	*0.81*	0.0022	0.28	
15A	*0.84*	0.07	0.49	1.42	0.031	0.0014	18.7	23.8	0.38	0.0022	0.24	
16A	*0.02*	0.10	0.29	0.97	0.030	0.0032	21.6	26.1	0.32	0.0018	0.23	
17A	0.43	0.07	*1.12*	1.21	0.025	0.0012	20.5	26.1	0.29	0.0015	0.25	
18A	0.49	0.05	0.40	1.12	0.032	*0.0052*	23.7	28.7	0.52	0.0014	0.26	
19A	-	0.06	0.32	1.21	0.015	0.0021	19.5	24.2	0.46	0.0012	025	

*Remainder: Iron and inevitable impurities

[0053] The base metals were machined to give samples of 40 mm by 60 mm and subjected to an aging heat treatment in an atmospheric furnace at 700°C for 300 hrs. After the aging heat treatment, the samples were cooled with water, retrieved from the furnace, and formed into V-notched test specimens having a notch depth of 2 mm according to JIS Z 2242. Each two V-notched test specimens as Charpy impact test specimens were prepared per each steel type (N = 2). The test specimens were subjected to Charpy impact tests at 0°C in conformity with JIS Z 2242. Measurement results (toughness values (Charpy impact values [J/cm^2])) of the Charpy impact tests are indicated in Table 2 below.

[Table 2]

Test No.	Toughness value (0°C) J/cm^2
	After 300-hr aging heat treatment
1A	61.7
2A	69.9
3A	63.5
4A	58.4
5A	46.8
6A	49.3
7A	61.1
8A	66.5
9A	71.2
10A	73.2
11A	68.2
12A	56.8
13A	43.6
14A	34.1
15A	35.6
16A	39.5
17A	31.5
18A	22.4
19A	42.6

[0054] The measurement results indicated in Table 2 give following considerations.

[0055] The results demonstrated that the steels according to the present invention (Test Nos. 1A to 12A) having chemical compositions within ranges specified in the present invention had more excellent toughness values and less suffered from reduction in toughness after the aging treatment (temper aging) as compared with the existing steel (Test No.19A) and the comparative steels (Test Nos.13A to 18A). The comparative steels had chemical compositions out of the ranges specified in the present invention, where the ranges were specified so as to give austenitic stainless steels according to the present invention excellent particularly in toughness after aging. The results therefore significantly indicated that the steels according to the present invention are advantageously usable as materials for heat-exchanger tubes typically of boilers (boiler tubes). Specifically, the results significantly indicated that the steels according to the present invention can maintain excellent toughness even after exposure to a high-temperature environment for a long term typically in a boiler, can endure impact (shock) occurring during operation and/or during inspection, and can serve as materials for boiler tubes capable of maintaining reliability over a long term.

[0056] The steels of Test No.17A and Test No.18A were samples respectively having Si and S (sulfur) contents out of (greater than the upper limits of) the chemical compositions specified in the present invention. The results demonstrated that the steels having an extremely high silicon (Si) or sulfur (S) content had low toughness values, as indicated by the conventional findings. Specifically, the results demonstrated that the steels of this type, even when containing Ta in a specific content, failed to have sufficiently high toughness values. In other words, the results demonstrated that steels as with Test Nos. 1A to 12A can have better toughness, because these steels are designed to contain Ta in a content within the specific range specified in the present invention while controlling the contents of Si and S within the ranges specified in the present invention.

[0057] Experimental Example 2: Experimental examples relating to creep properties

[0058] Steels having chemical compositions given in Table 3 below were melted in a vacuum induction furnace (VIF) and formed into ingots. The formed 20-kg ingots were hot-forged to dimensions of 130 mm wide by 20 mm thick, subjected to a heat treatment at 1250°C, and cold-rolled to a thickness of 13 mm. The steels were subjected again to a heat treatment at 1220°C for 5 minutes and taken as base metals (Test Nos.1B to 17B).

[0059] Of the base metals according to Test Nos.1B to 17B in Table 3, the base metals of Test Nos. 2B, 3B, 5B, 6B, 7B, 10B, 11B, 13B, 15B, and 17B are base metals as examples having chemical compositions within the ranges specified in the present invention for austenitic stainless steels excellent particularly in creep strength. The base metals of Test Nos.1B, 4B, 8B, 9B, 12B, 14B, and 16B are base metals as comparative examples having chemical compositions out of the ranges specified in present invention for austenitic stainless steels excellent particularly in creep strength. Among them, the base metal of Test No. 8B is a base metal including a steel corresponding to the existing steel "KA-SUS 310J1HTB".

[0060] In general, austenitic stainless steels have the precipitation strengthening of the Nb compound (CrNbN) and tend to have better precipitation strengthening and a longer creep rupture time with an increasing amount (content) of Nb. Ta also contributes to precipitation strengthening as with Nb. In this experimental example, the total sums of the atomic concentrations (atomic percentages) of Ta and Nb were set at approximately the same level among Test Nos.1B to 3B, among 4B to 8B, among 9B to 11B, between 12B and13B, between 14B and 15B, and between 16B to 17B. This was performed so as to distinguish the effect obtained by the total amount of Nb and Ta from the effect obtained by allowing Ta to substitute for part of Nb.

[0061] The base metals were machined to give creep test specimens having a diameter of 6 mm, and the creep test specimens were subjected to creep rupture tests at 700°C and 189 MPa using a multi-specimen creep testing machine. Measured creep rupture times are indicated in Table 3 below.

[Table 3]

Test No.	Chemical compositions* (in mass percent)												Ta+Nb (at%)	Ratio of Ta to Nb	Creep rupture time (hr)	Remarks
	C	Si	Mn	Ni	Cr	Nb	Ta	B	N	S	P	Others				
1B	0.06	0.62	1.48	23.1	28.1	0.20	0.09	0.0007	0.25	0.0032	0.016		0.14	0.5	660	Comparative Example
2B	0.07	0.49	1.42	20.6	24.2	0.16	0.20	0.0023	0.25	0.0016	0.025		0.15	1.1	688	Example
3B	0.05	0.72	1.34	19.7	23.9	0.12	0.26	0.0015	0.24	0.0011	0.043		0.15	2.2	724	
4B	0.05	0.37	1.39	19.9	25.0	0.42	0.08	0.0015	0.24	0.0013	0.021		0.27	0.2	718	Comparative Example
5B	0.06	0.44	1.41	20.2	25.4	0.31	0.28	0.0008	0.23	0.0010	0.017		0.27	0.9	760	Example
6B	0.05	0.36	1.33	19.7	24.6	0.25	0.43	0.0012	0.25	0.0017	0.011		0.28	1.7	810	
6B	0.08	0.50	1.44	20.6	25.1	0.16	0.62	0.0011	0.26	0.0020	0.032		0.28	3.9	801	
8B	0.06	0.32	1.21	20.1	24.7	0.46		0.0012	0.25	0.0021	0.015		0.27	0.0	709	Comparative Example
9B	0.06	0.45	1.31	21.5	26.6	0.59	0.34	0.0032	0.27	0.0008	0.010		0.45	0.6	720	Comparative Example
10B	0.07	0.32	1.13	18.9	24.8	0.41	0.69	0.0021	0.23	0.0010	0.031		0.45	1.7	856	Example
11B	0.08	0.43	1.21	22.5	23.7	0.28	0.98	0.0018	0.26	0.0027	0.025		0.46	3.5	877	
12B	0.04	0.54	1.29	22.9	23.5	0.38	0.20	0.0024	0.28	0.0009	0.022	Mg:0.0012	0.28	0.5	812	Comparative Example
13B	0.04	0.53	1.32	21.7	24.0	0.26	0.41	0.0022	0.29	0.0010	0.021	Mg:0.0009	0.28	1.6	897	Example
14B	0.05	0.33	1.45	17.9	26.5	0.24	0.14	0.0017	0.22	0.0012	0.032	Rare-earth:0.048	0.18	0.6	781	Comparative Example
15B	0.06	0.36	1.50	18.5	25.9	0.15	0.32	0.0015	0.23	0.0013	0.033	Rare-earth:0.045	0.19	2.1	853	Example
16B	0.06	0.39	1.40	21.7	24.9	0.49	0.17	0.0010	0.24	0.0015	0.011	Ca:0.0012	0.34	0.3	704	Comparative Example
17B	0.05	0.38	1.37	22.0	24.6	0.31	0.56	0.0011	0.25	0.0017	0.013	Ca:0.0010	0.35	1.8	835	Example

Note: In the chemical compositions, the remainder includes iron and inevitable impurities.
Note: A blank in the chemical compositions indicates that the composition in question is not contained.

[0062] The results in Table 3 demonstrated that the base metals according to the examples having chemical compositions within the ranges specified in the present invention had longer creep rupture times and had more excellent creep strengths as compared with the base metals according to the comparative examples. The ranges are specified for austenitic stainless steels excellent particularly in creep strength. The base metals according to the comparative examples included the existing steel (Test No. 8B) or included the stainless steels having chemical compositions out of the ranges specified in the present invention.

[0063] The creep strengths were evaluated by comparing stainless steels having total sums of the atomic concentrations of Ta and Nb at approximately the same levels. Typically, the base metal of Test No. 8B (comparative example) is a conventional boiler tube material. A comparison between the base metals of Test Nos. 5B to 7B (examples) and the base metal of Test No. 8B (comparative example) demonstrated that the base metals, when containing Ta substituting for part of Nb, could have more excellent creep strengths as compared with the conventional material.

[0064] The austenitic stainless steels according to the present invention have been described with a certain degree of particularity relating to several embodiments and examples. It should be noted, however, that the present invention be not limited by the details of the description, but rather be construed broadly within its spirit and scope as set out in the accompanying claims. In addition, it is naturally to be understood that various changes and variations made based on the description fall within the true spirit and scope of the present invention.

[0065] The present application is based on Japanese Patent Application No. 2012-238872 filed on October 30,2012 and Japanese Patent Application No. 2013-010188 filed on January 23, 2013, the entire contents of which are incorporated herein by reference.

Industrial Applicability

[0066] The austenitic stainless steels according to the embodiments of the present invention are suitable as materials for thermal power generation boiler tubes, and other parts and apparatuses to be used in a high-temperature and oxidizing environment.

Claims

1. An austenitic stainless steel comprising:

C in a content of 0.01 to 0.15 percent by mass;
Si in a content of 0.10 to 1.00 percent by mass;
Mn in a content of 0.10 to 2.50 percent by mass;
Ni in a content of 15.0 to 25.0 percent by mass;
Cr in a content of 20.0 to 30.0 percent by mass;
Nb in a content of 0.10 to 0.80 percent by mass;
Ta in a content of 0.20 to 1.00 percent by mass;
B in a content of 0.0005 to 0.0050 percent by mass;
N in a content of 0.10 to 0.35 percent by mass;
S in a content of 0.0050 percent by mass or less (excluding 0 percent by mass); and
P in a content of 0.050 percent by mass or less (excluding 0 percent by mass),

with the remainder comprising iron and inevitable impurities.

2. The austenitic stainless steel according to claim 1,
wherein the austenitic stainless steel comprises Ta in a content of 0.25 to 0.8 percent by mass.

3. The austenitic stainless steel according to claim 1,
wherein the austenitic stainless steel comprises Nb in a content of 0.10 to 0.60 percent by mass, and
wherein the austenitic stainless steel has a ratio of the Ta content to the Nb content of 0.8 to 4.0.

4. The austenitic stainless steel according to any one of claims 1 to 3, further comprising at least one of groups (a) and (b) as follows:

(a) at least one element selected from the group consisting of:

W in a content of 4 percent by mass or less;

Mo in a content of 4 percent by mass or less;
Cu in a content of 4 percent by mass or less;
at least one rare-earth element in a content of 0.15 percent by mass or less;
Ca in a content of 0.005 percent by mass or less; and
Mg in a content of 0.005 percent by mass or less; and

(b) at least one element, in a total content of 0.4 percent by mass or less, selected from the group consisting of:

V in a content of 0.2 percent by mass or less;
Ti in a content of 0.2 percent by mass or less;
Zr in a content of 0.2 percent by mass or less; and
Hfin a content of 0.2 percent by mass or less.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/079292

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/58*(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)
C22C1/00-49/14

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	1996-2014
Kokai Jitsuyo Shinan Koho	1971-2014	Toroku Jitsuyo Shinan Koho	1994-2014

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 2006/109727 A1 (Sumitomo Metal Industries, Ltd.), 19 October 2006 (19.10.2006), & JP 2006-291290 A & US 2008/0107559 A1 & CA 2604968 A & KR 10-2007-0119082 A & CN 101194037 A & TWB 00I315346	1-4

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

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Date of the actual completion of the international search 10 January, 2014 (10.01.14)	Date of mailing of the international search report 21 January, 2014 (21.01.14)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/079292

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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