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(54) AUSTENITIC STAINLESS STEEL

(57) An austenitic stainless steel, which comprises by mass%, C: 0.04 to 0.18%, Si $\leq$ 1.5%, Mn $\leq$ 2.0%, Ni: 6 to 30%, Cr: 15 to 30%, N: 0.03 to 0.35%, sol. Al $\leq$ 0.03% and further contains one or more elements selected from Nb $\leq$ 1.0%, V $\leq$ 0.5% and Ti $\leq$ 0.5%, with the balance being Fe and impurities, and among the impurities P $\leq$ 0.04%, S $\leq$ 0.03%, Sn $\leq$ 0.1%, As $\leq$ 0.01%, Zn $\leq$ 0.01%, Pb $\leq$ 0.01% and Sb $\leq$ 0.01%, and satisfy the conditions $P1 = S + \{(P + Sn)/2\} + \{(As + Zn + Pb + Sb)/5) \leq 0.06$ and $0.2 \leq P2 = Nb + 2(V + Ti) \leq 1.7 - 10 \times P1$ has high strength and excellent resistance to cracking due to grain boundary embrittlement in the welded portion during the use at high temperatures. Therefore, the said steel can be suitably used as materials for constructing machines and equipment, such as power plant boilers, which are to be used at high temperatures for a long period of time.

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Description

TECHNICAL FIELD

[0001] The present invention relates to an austenitic stainless steel. More particularly, the present invention relates to a high strength austenitic stainless heat resistant steel which is to be used in constructing high temperature machines and equipment, such as power plant boilers, and is excellent in resistance to cracking at weld heat affected zone due to grain boundary embrittlement during use at high temperatures.

BACKGROUND ART

[0002] In recent years, the operation conditions for power plant boilers and the like have become higher temperature and higher pressure ones on a worldwide scale in consideration of environmental deterioration. Therefore, these austenitic stainless heat resistant steels which are to be used as materials for superheater tubes and reheater tubes are required to have increased high temperature strength.

[0003] In such a technological background, various austenitic stainless steels have been disclosed.

[0004] For example, the Patent Document 1 discloses a Cu-, Nb- and N-containing austenitic stainless steel excellent in high temperature strength and ductility in which the ratio of Nb (%) / Cu (%) is 0.05 to 0.2 and the content of undissolved Nb, after a solution heat treatment, is within the range of $0.04 \times$ Cu (%) to $0.085 \times$ Cu (%).

[0005] Furthermore, the Patent Document 2 discloses an austenitic stainless steel improved in hot workability by employing such contents of Ca, Mg, O and S that satisfy the relationship $3.0 \leq \{(Ca + Mg) - 0.1 \times O\} / S \leq 15.0$.

[0006] The Patent Document 3 discloses an austenitic stainless steel excellent in high temperature strength and hot workability, which contains 2 to 6% of Cu and one or more elements selected from Y, La, Ce and Nd for a total content level of 0.01 to 0.2% and has a numerical value of a formula expressed in terms of the Mn, Mg, Ca, Y, La, Ce and Nd contents and the Al, Cu and S contents which is in a specified range.

[0007] Furthermore, the Patent Document 4 discloses an austenitic stainless steel, excellent in creep characteristics and hot workability, which satisfies the three relationships, namely the relationship between P and Cu, the relationship between sol. Al and N, and the relationship between O and Cu, respectively.

[0008] While these austenitic stainless heat resistant steels are generally used at high temperatures after welding fabrication, they encounter the problem of an occurrence of cracking in the weld heat affected zone (hereinafter referred to as "HAZ") after a long period of use at high temperatures.

[0009] For example, in the Non-Patent Documents 1 and 2, it is pointed out that the welded portion of 18Cr-8Ni type austenitic stainless heat resistant steels, undergo intergranular cracking in the HAZ after a long period of heating.

[0010] The Non-Patent Document 3 describes investigations made in search of means for preventing intergranular cracking in the HAZ in the welded portion of 18Cr-8Ni-Nb type austenitic stainless heat resistant steels, if heated for a long period of time.

[0011]

Patent Document 1: JP 2000-256803 A
Patent Document 2: JP 2001-49400 A
Patent Document 3: JP 2000-328198 A
Patent Document 4: JP 2004-323937 A
Non-Patent Document 1: R. N. Younger et al.: Journal of the Iron and Steel Institute, October (1960), p. 188
Non-Patent Document 2: R. N. Younger et al.: British Welding Journal, December (1961), p. 579
Non-Patent Document 3: Naiki et al.: Ishikawajima Harima Engineering Review, Vol. 15 (1975), No. 2, p. 209

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0012] In the above-mentioned Patent Documents 1 to 4, there is no consideration is of cracking which occurs in the HAZ resulting from a long period of use at high temperatures after welding fabrication.

[0013] The Non-Patent Documents 1 and 2 suggest that such carbides as $M_{23}C_6$ and NbC may be factors influencing the intergranular cracking in the HAZ; however, the mechanisms of action thereof have not been elucidated.

[0014] The Non-Patent Document 3 proposes measures based on a finding, from the welding process viewpoint, that the reductions in welding residual stress by application of an appropriate post weld heat treatment are effective in preventing cracking. According to that document, differences in strength between grains strengthened by Nb(C, N) and grain boundaries are factors which cause of intergranular cracking in the HAZ; however, there is no mention of factors causing grain boundary (intergranular) embrittlement.

[0015] Therefore, the above-mentioned Non-Patent Documents 1 to 3 suggest nothing about measures, from the material viewpoint, for preventing cracking in the HAZ on the occasion of using high strength austenitic stainless heat resistant steels, such as those recently proposed in the said Patent Documents 1 to 4, for instance, for a prolonged period of time.

[0016] Thus, while the phenomenon of cracking in the HAZ during a long period of use is known for long for austenitic stainless heat resistant steels, the mechanisms thereof have not yet been elucidated and the art has no established measures, in particular from the material viewpoint, against such cracking.

[0017] In addition, a large number of austenitic stainless heat resistant steels proposed recently, contain various alloying elements added thereto for attaining increases in strength and therefore show an increasing susceptibility toward such cracking in the welded portion during a long period of use at high temperatures, as mentioned above.

[0018] In view of the above-mentioned state of affairs, it is an objective of the present invention to provide a high strength austenitic stainless steel, excellent in resistance to cracking due to grain boundary embrittlement in the HAZ and suited for use as a material for constructing machines and equipment, such as power plant boilers, which are to be used at high temperatures for a prolonged period of time.

MEANS FOR SOLVING THE PROBLEMS

[0019] The present inventors made detailed investigations of cracks occurred in the welded portions used at high temperatures for a long period of time in the austenitic stainless steels used as materials for constructing machines and equipment to be used at high temperatures for a prolonged period of time, in order to prevent cracking in the HAZ and to provide steels which have excellent resistance to cracking due to grain boundary embrittlement.

[0020] As a result, the following findings (a) to (c) were obtained first.

[0021]

(a) Cracking occurs at grain boundaries of the so-called "coarse-grained HAZ" exposed to high temperatures during the welding.

[0022]

(b) The fractured surface of each crack is poor in ductility, and also the grain boundary-embrittling elements such as P, S and Sn are found concentrated on the fractured surface.

[0023]

(c) The microstructure in the vicinity of a crack shows a large amount of fine carbides and nitrides that have precipitated intragranularly.

[0024] The present inventors made the following conclusions (d) to (f) from the above findings (a) to (c).

[0025]

(d) The crack occurred in the HAZ is a result of the opening of grain boundaries, which have been weakened due to the segregation of such elements as P, S and Sn at grain boundaries during weld thermal cycles or the subsequent use at high temperatures, due to their undergoing external stress.

[0026]

(e) Due to abundant intragranular precipitates such as fine carbides and nitrides, the intragranular deformation is hindered, and therefore stress concentration occurs at grain boundary. Cracking then tends to occur readily because of the effect superimposed on the weakening of grain boundaries.

[0027]

(f) As a mode of cracking, similar to the cracking which occurred in the welded portion after a long period of use at high temperatures, there may be mentioned such as the SR cracking in low alloy steels, as mentioned by Ito et al. in the Journal of the JWS, Vol. 41 (1972), No. 1, p. 59. However, this SR cracking in those low alloy steels is a cracking occurring in the step of a short period SR heat treatment after welding, which is quite different in timing from the cracking which occurs in the welded portion after a long period of use at high temperatures which is the target of the present invention. In addition, the base metal (and the HAZ) has a ferritic microstructure and the mechanisms of occurrence of SR cracking therein are quite different from those in the austenitic microstructure, which is also a target of the present invention. Therefore, as a matter of course, the measures for preventing the above-mentioned SR cracking in low alloy steels as such, cannot be applied as a measure for preventing the occurrence of cracking in the welded portion after a long period of use at high temperatures.

[0028] Therefore, the present inventors made further detailed investigations using various austenitic stainless steels in order to prevent the occurrence of cracking in the welded portion after a long period of use at high temperatures. As a result, the following important findings (g) to (1) were obtained.

[0029]

(g) In order to prevent the above-mentioned occurrence of cracking in the welded portion after a long period of use at high temperatures, it is most effective to restrict the contents of grain boundary-embrittling elements, specifically P, S, Sn, Sb, Pb, Zn and As, within respective specific ranges.

[0030]

(h) The reason why cracking can be prevented by restricting the contents of the above-mentioned grain boundary-embrittling elements is that weakening the intergranular binding force can be inhibited by reducing the grain boundary segregation of the above-mentioned elements during weld thermal cycles or during the subsequent use at high temperatures.

[0031]

(i) In particular, the cracking in austenitic stainless steels containing 15 to 30% of Cr and 6 to 30% of Ni on the percent by mass basis is concerned, among the elements mentioned above, S is most harmful, followed by P and Sn. And, in order to prevent the above-mentioned cracking, it becomes essential that the value of the parameter P1 defined by the formula (1) below is derived by taking into consideration the weight of the influences of the respective elements should be not more than 0.06. In the formula, each element symbol represents the content by mass percent of the element concerned:

$$P1 = S + \{(P + Sn) / 2\} + \{(As + Zn + Pb + Sb) / 5\} \cdots (1).$$

[0032]

(j) The susceptibility to cracking of the above-mentioned welded portion used at high temperatures for a long period of time can be reduced by controlling the contents of Nb, V, Ti, C and N within respective specific ranges and thereby inhibits the excessive formation of fine intragranular precipitates.

[0033]

(k) It is possible to attain further reductions in susceptibility to cracking and ensure the desired high levels of creep strength by adjusting the contents of Nb, V and Ti within respective specific ranges according to the contents of grain boundary-embrittling elements such as P, S, Sn, Sb, Pb, Zn and As mentioned above. That is to say, when the contents of Nb, V, Ti, C and N are adjusted within respective specific ranges, it becomes possible to ensure the desired levels of creep strength by allowing the precipitation of the appropriate amounts of fine intragranular carbonitrides and, on the other hand, to prevent excessive intragranular strengthening due to fine intragranular precipitates and to alleviate the stress concentration at grain boundary thereby reduces the susceptibility to cracking in the coarse-grained HAZ.

[0034]

(1) In particular, in the case of austenitic stainless steels containing 0.04 to 0.18% of C and 0.03 to 0.35% of N as expressed in terms of percent by mass, required levels of creep strength can be ensured when the value of the parameter P2 defined by the formula (2) below is set to not less than 0.2. Further, the susceptibility to cracking in the coarse-grained HAZ can be reduced when the upper limit of the value of the said parameter P2 is set to [1.7 -

10 × P1]; in the formula, each element symbol represents the content by mass percent of the element concerned:

$$P2 = Nb + 2(V + Ti) \cdots (2).$$

[0035] The present invention has been accomplished on the basis of the above-described findings. The main points of the present invention are the austenitic stainless steels shown in the following (1) to (4).

[0036]

(1) An austenitic stainless steel, which comprises by mass percent, C: 0.04 to 0.18%, Si: not more than 1.5%, Mn: not more than 2.0%, Ni: 6 to 30%, Cr: 15 to 30%, N: 0.03 to 0.35%, sol. Al: not more than 0.03% and further contains one or more elements selected from Nb: not more than 1.0%, V: not more than 0.5% and Ti: not more than 0.5%, with the balance being Fe and impurities, in which the contents of P, S, Sn, As, Zn, Pb and Sb among the impurities are P: not more than 0.04%, S: not more than 0.03%, Sn: not more than 0.1%, As: not more than 0.01%, Zn: not more than 0.01%, Pb: not more than 0.01% and Sb: not more than 0.01%, and the values of P1 and P2 defined respectively by the following formula (1) and formula (2) satisfy the conditions P1 ≤ 0.06 and 0.2 ≤ P2 ≤ 1.7 - 10 × P1;

$$P1 = S + \{(P + Sn) / 2\} + \{(As + Zn + Pb + Sb) / 5\} \cdots (1),$$

$$P2 = Nb + 2(V + Ti) \cdots (2);$$

In the formulas (1) and (2), each element symbol represents the content by mass percent of the element concerned.

[0037] (2) An austenitic stainless steel, which comprises by mass percent, C: 0.05 to 0.15%, Si: not more than 1.0%, Mn: not more than 2.0%, Ni: 6 to 13%, Cr: 15 to 25%, N: 0.03 to 0.15%, sol. Al: not more than 0.03% and further contains one or more elements selected from Nb: not more than 1.0%, V: not more than 0.5% and Ti: not more than 0.5%, with the balance being Fe and impurities, in which the contents of P, S, Sn, As, Zn, Pb and Sb among the impurities are P: not more than 0.04%, S: not more than 0.03%, Sn: not more than 0.1%, As: not more than 0.01%, Zn: not more than 0.01%, Pb: not more than 0.01% and Sb: not more than 0.01%, and the values of P1 and P2 defined respectively by the following formula (1) and formula (2) satisfy the conditions P1 ≤ 0.06 and 0.3 ≤ P2 ≤ 1.7 - 10 × P1;

$$P1 = S + \{(P + Sn) / 2\} + \{(As + Zn + Pb + Sb) / 5\} \cdots (1),$$

$$P2 = Nb + 2(V + Ti) \cdots (2);$$

In the formulas (1) and (2), each element symbol represents the content by mass percent of the element concerned.

[0038] (3) An austenitic stainless steel, which comprises by mass percent, C: 0.04 to 0.18%, Si: not more than 1.5%, Mn: not more than 2.0%, Ni: more than 13% to not more than 30%, Cr: 15 to 30%, N: 0.10 to 0.35%, sol. Al: not more than 0.03% and further contains one or more elements selected from Nb: not more than 1.0%, V: not more than 0.5% and Ti: not more than 0.5%, with the balance being Fe and impurities, in which the contents of P, S, Sn, As, Zn, Pb and Sb among the impurities are P: not more than 0.04%, S: not more than 0.03%, Sn: not more than 0.1%, As: not more than 0.01%, Zn: not more than 0.01%, Pb: not more than 0.01% and Sb: not more than 0.01%, and the values of P1 and P2 defined respectively by the following formula (1) and formula (2) satisfy the conditions P1 ≤ 0.06 and 0.2 ≤ P2 ≤ 1.3 - 10 × P1;

$$P1 = S + \{(P + Sn) / 2\} + \{(As + Zn + Pb + Sb) / 5\} \cdots (1),$$

$$P2 = Nb + 2(V + Ti) \cdots (2);$$

In the formulas (1) and (2), each element symbol represents the content by mass percent of the element concerned.

[0039] (4) The austenitic stainless steel according to any one of the above (1) to (3), which contains, by mass percent, one or more elements of one or more groups selected from the first to third groups listed below in lieu of a part of Fe:

First group: Cu: not more than 4%, Mo: not more than 2%, W: not more than 2%, Co: not more than 1%, Ta: not more than 0.1%, Zr: not more than 0.1% and Hf: not more than 0.1%;
Second group: B: not more than 0.012%; and
Third group: Ca: not more than 0.02%, Mg: not more than 0.02% and rare earth element: not more than 0.1%.

[0040] The term "rare earth element" (hereinafter referred to as "REM") refers to a total of 17 elements including Sc, Y and lanthanoid collectively, and the REM content mentioned above means the content of one or the total content of two or more of the REM.

[0041] Hereinafter, the above-mentioned inventions (1) to (4) related to the austenitic stainless steels are referred to as "the present invention (1)" to "the present invention (4)", respectively. They are sometimes collectively referred to as "the present invention".

EFFECTS OF THE INVENTION

[0042] The austenitic stainless steels of the present invention have high strength and excellent resistance to cracking due to grain boundary embrittlement in welded portions during use at high temperatures. Consequently, they can be used as materials for constructing machines and equipment, such as power plant boilers, which are to be used at high temperatures for a prolonged period of time.

BEST MODES FOR CARRYING OUT THE INVENTION

[0043] In the following, the reasons for restricting the contents of the component elements of the austenitic stainless steels in the present invention are described in detail. In the following description, the symbol "%" for the content of each element means "% by mass".

C: 0.04 to 0.18%

[0044] C is an element having an austenite-stabilizing effect and at the same time it forms fine intragranular carbonitrides with N and thereby it contributes toward improvements in high temperature strength. In order to obtain the above-mentioned effects, it is necessary that the content of C be not less than 0.04%. However, when the C content is excessive, in particular when it exceeds 0.18%, C causes over precipitation of fine intragranular carbonitrides during use at high temperatures. Thereby this inhibits the intragranular deformation and causes stress concentration at grain boundary to increase the susceptibility to cracking due to grain boundary embrittlement in the coarse-grained HAZ. In addition, it sometimes forms a large amount of intergranular carbides upon exposure to weld thermal cycles or during use at high temperatures causes the formation of Cr-depleted layers in the vicinity of grain boundaries, which leads to deterioration of corrosion resistance. Therefore, the content of C is set to 0.04 to 0.18%. The lower limit of the C content is preferably 0.05% and the upper limit thereof is preferably 0.13%.

[0045] In the case of the present invention (2) according to which the Ni content is 6 to 13% and the Cr content is 15 to 25%, the content of C is preferably 0.05 to 0.15%. The content range of C in this case is more preferably 0.07 to 0.13%.

[0046] In the case of the present invention (3) according to which the Ni content is more than 13% to not more than 30% and the Cr content is 15 to 30%, the C content range of 0.04 to 0.15% is preferable out of the above-mentioned range of 0.04 to 0.18%.

Si: not more than 1.5%

[0047] Si is an element having a deoxidizing effect. It is also effective in increasing corrosion resistance and oxidation resistance at high temperatures. However, when the content thereof is excessive, in particular at a content level exceeding 1.5%, it deteriorates the stability of the austenite phase, thus creep strength and toughness are deteriorated. Therefore, the content of Si is set to not more than 1.5%. The content of Si is preferably not more than 1.0%.

[0048] The more preferable Si content in the practice of the present invention is not more than 0.8%.

[0049] It is not necessary to particularly specify any lower limit in the Si content; however, an extreme reduction of Si content results in failure to attain a sufficient deoxidizing effect, hence in deterioration in cleanliness of the steel and, in addition, in an increased production cost. Therefore, the lower limit of the Si content is preferably 0.02%.

Mn: not more than 2.0%

[0050] Mn, like Si, has a deoxidizing effect. Mn also contributes toward stabilization of the austenite phase. However, when the content thereof is excessive, in particular at a content level exceeding 2.0%, it causes embrittlement and thus deteriorates the creep ductility and toughness. Therefore, the content of Mn is set to not more than 2.0%. More preferably, the content of Mn is not more than 1.5%.

[0051] It is not necessary to particularly specify any lower limit in the Mn content; however, an extreme reduction of Mn content results in failure to attain a sufficient deoxidizing effect, hence in deterioration in cleanliness of the steel and, in addition, in an increased production cost. Therefore, the lower limit of the Mn content is preferably 0.02%.

Ni: 6 to 30%

[0052] Ni is effective in obtaining the austenitic microstructure and also is an essential element for ensuring the structural stability during a long period of use and thus obtaining the desired level of creep strength. In order to sufficiently produce the effects mentioned above within the Cr content range to be mentioned below, it is necessary that the Ni content be not less than 6%. On the other hand, the addition of Ni, which is an expensive element, at a content level exceeding 30% results in an increase in cost. Therefore, the content of Ni is set to 6 to 30%. The lower limit of the Ni content is preferably 7% and the upper limit thereof is preferably 28%.

Cr: 15 to 30%

[0053] Cr is an essential element for ensuring the oxidation resistance and corrosion resistance at high temperatures and, in order to obtain the said effects, it is necessary that the Cr content be not less than 15%. However, when the content thereof is excessive, in particular at a content level exceeding 30%, it deteriorates the stability of the austenite phase at high temperatures and thus causes a decrease in creep strength. Therefore, the content of Cr is set to 15 to 30%. The preferable lower limit of the Cr content is 16% and the preferable upper limit thereof is 28%.

[0054] When the stability of the austenite phase and/or cost is taken into consideration, the combination of the Ni content and Cr content is preferably as follows, as defined in the present invention (2): Ni: 6 to 13% and Cr: 15 to 25%, more preferably Ni: 7 to 12% and Cr: 16 to 20%.

[0055] In order to ensure the stability of the austenite phase at high temperatures as well as high corrosion resistance, the combination of the Ni content and Cr content is preferably as follows, as defined in the present invention (3): Ni: more than 13% to not more than 30% and Cr: 15 to 30%, more preferably Ni: 15 to 28% and Cr: 18 to 28%.

N: 0.03 to 0.35%

[0056] N is an austenite-forming element and is also an element soluble in the matrix and forms, like C, fine intragranular carbonitrides and thus it is an essential element for ensuring the creep strength at high temperatures. In order to obtain these effects sufficiently, the content of N is required to be not less than 0.03%. N is also effective in enhancing corrosion resistance. However, when the N content is excessive, in particular at a content level exceeding 0.35%, it causes precipitation of a large amount of fine intragranular carbonitrides during use at high temperatures to thereby inhibit intragranular deformation and cause stress concentration at grain boundary, with the result that the susceptibility to cracking due to grain boundary embrittlement in the coarse-grained HAZ is increased. Therefore, the content of N is set to 0.03 to 0.35%. The preferable lower limit of the N content is 0.05% and the preferable upper limit thereof is 0.30%.

[0057] When the Ni content is 6 to 13% and the Cr content is 15 to 25%, the content of N is preferably 0.03 to 0.15%. The content range of N in this case is more preferably 0.05 to 0.12%.

[0058] When the Ni content is more than 13% to not more than 30% and the Cr content is 15 to 30%, the content of N is preferably 0.10 to 0.35%. The content range of N in this case is more preferably 0.15 to 0.30%.

Sol. Al: not more than 0.03%

[0059] Al has a deoxidizing effect but, at high addition levels, it markedly impairs the cleanliness and deteriorates the workability and ductility; in particular, when the Al content exceeds 0.03% as sol. Al ("acid-soluble Al"), it causes marked decreases in workability and ductility. Therefore, the content of sol. Al is set to not more than 0.03%. The lower limit of the sol.Al content is not particularly restricted. However the lower limit of the sol.Al content is preferably 0.0005%.

[0060] One or more elements selected from Nb: not more than 1.0%, V: not more than 0.5% and Ti: not more than 0.5% Nb, V and Ti constitute an important group of elements forming the basis of the present invention. That is to say, these elements precipitate intragranularly in the form of fine carbonitrides and thus act as essential elements for ensuring the creep strength at high temperatures. However, when the content of these elements is excessive, in particular when the contents of Nb and V exceed 1.0% and 0.5% respectively, the carbonitrides rapidly become coarsened during use at high temperatures, causing extreme decreases in creep strength and toughness. In the case of Ti, if the content thereof exceeds 0.5% it causes a marked increase in the susceptibility to liquid cracking on the occasion of welding. Therefore, the content of each of Nb, V and Ti is set to as follows: Nb: not more than 1.0%, V: not more than 0.5% and Ti: not more than 0.5%.

[0061] The upper limit of each of the contents of the above-mentioned elements is preferably as follows: 0.8% for Nb, 0.4% for V, and 0.04% for Ti.

[0062] The steels of the present invention can contain only one or a combination of two or more of the above-mentioned elements selected from Nb, V and Ti. However, in order to secure the required levels of creep strength, it is necessary that the value of the said parameter P2 mentioned hereinabove should be set to not less than 0.2 and, in order to reduce susceptibility to cracking in the coarse-grained HAZ, it is necessary that the upper limit to the value of the said parameter P2 should be set to [1.7 - 10 × P1], as described later herein.

[0063] In the present invention, it is necessary to restrict the contents of P, S, Sn, As, Zn, Pb and Sb among the impurities to not more than the specified levels.

[0064] That is to say, all of the above-mentioned elements segregate at the grain boundaries in the coarse-grained HAZ during weld thermal cycles or during the subsequent use at high temperatures, thus weakening the grain boundary binding force and causing cracking due to grain boundary embrittlement in the coarse-grained HAZ during use at high temperatures. Therefore, first, it is necessary to restrict the contents thereof as follows: P: not more than 0.04%, S: not more than 0.03%, Sn: not more than 0.1%, As: not more than 0.01%, Zn: not more than 0.01%, Pb: not more than 0.01% and Sb: not more than 0.01%.

[0065] Among the elements mentioned above, S exerts the most harmful influence on the cracking due to grain boundary embrittlement in the coarse-grained HAZ during use at high temperatures, followed by the harmful influences of P and Sn, in the austenitic stainless steel of the present invention which contains 15 to 30% of Cr and 6 to 30% of Ni. And in order to prevent the said cracking, it is necessary that the value of the parameter P1, mentioned hereinabove should be not more than 0.06 and that this parameter P1, in relation to the parameter P2, should satisfy the condition [P2 ≤ 1.7 - 10 × P1]. These requirements will be explained below.

The value of the parameter P1: not more than 0.06

[0066] When the value of P1, defined by the said formula (1), that is to say, by [S + {(P + Sn) / 2} + {(As + Zn + Pb + Sb) / 5}], exceeds 0.06, it becomes impossible to prevent the decrease in the grain boundary binding force and, therefore the occurrence of cracking due to grain boundary embrittlement in the coarse-grained HAZ during use at high temperatures of the austenitic stainless steel, according to the present invention, which contains 15 to 30% of Cr and 6 to 30% of Ni cannot be avoided. Therefore, it is necessary that the value of the parameter P1 should be set to not more than 0.06. The value of the parameter P1 is preferably not more than 0.04. It is also preferable that the value of the parameter P1 be reduced as low as possible.

The value of the parameter P2: not less than 0.2 to not more than [1.7-10×P1]

[0067] When the value of P2 defined by the said formula (2), that is to say, by [Nb + 2(V + Ti)], is not less than 0.2, appropriate amounts of fine carbonitrides precipitate intragranularly, and thereby high creep strength can be ensured. Furthermore, when the value of P2 satisfies the condition of not more than [1.7 - 10 x P1], in relation to the above-mentioned parameter P1, it becomes possible to inhibit excessive intragranular strengthening and thereby prevent the above-mentioned cracking in the coarse-grained HAZ. Therefore, the value of the parameter P2 is set to not less than 0.2 to not more than [1.7 - 10 × P1]. The lower limit of the value of the parameter P2 is preferably 0.3, and more preferably 0.4. On the other hand, the upper limit of the value of the parameter P2 is preferably set to [1.5 - 10 × P1], and more preferably [1.3 - 10 × P1].

[0068] In the case of the present invention (2) according to which the Ni content is 6 to 13% and the Cr content is 15 to 25%, the value of the parameter P2 is preferably set to not less than 0.3 to not more than [1.7 - 10 × P1]. In this case, the more preferable lower limit of the value of the parameter P2 is 0.4. And the more preferable upper limit of the value of the parameter P2 is [1.5 - 10 × P1].

[0069] In the case of the present invention (3) according to which the Ni content is more than 13% to not more than 30% and the Cr content is 15 to 30%, the value of the parameter P2 is preferably set to not less than 0.2 to not more than [1.3 - 10 × P1]. In this case, the more preferable lower limit of the value of the parameter P2 is 0.3. And the more preferable upper limit of the value of the parameter P2 is [1.2 - 10 × P1].

[0070] The austenitic stainless steels according to the present inventions (1) to (3) can further selectively contain, according to need, one or more elements of each of the following groups of elements in lieu of a part of Fe:

> First group: Cu: not more than 4%, Mo: not more than 2%, W: not more than 2%, Co: not more than 1%, Ta: not more than 0.1%, Zr: not more than 0.1% and Hf: not more than 0.1%;
> Second group: B: not more than 0.012%; and
> Third group: Ca: not more than 0.02%, Mg: not more than 0.02% and REM: not more than 0.1%.

[0071] That is to say, one or more of the first to third groups of elements may be added, as optional element(s), to the above-mentioned steels and thereby contained therein.

[0072] The above-mentioned optional elements will be explained below.

First group: Cu: not more than 4%, Mo: not more than 2%, W: not more than 2%, Co: not more than 1%, Ta: not more than 0.1%, Zr: not more than 1% and Hf: not more than 0.1%

[0073] Each of Cu, Mo, W, Co, Ta, Zr and Hf being elements of the first group, if added, has the effect of enhancing the high temperature strength. In order to obtain this effect, the said elements may be added to the steels and thereby contained therein. The elements, which are in the first group, are now described in detail.

Cu: not more than 4%

[0074] Cu precipitates finely at high temperatures. Therefore, Cu is an effective element which enhances high temperature strength. Cu is also effective in stabilizing the austenite phase. However, when the content of Cu is increased, the Cu phase precipitation becomes excessive and the above-mentioned susceptibility to cracking due to grain boundary embrittlement in the coarse-grained HAZ increases; in particular when the content of Cu exceeds 4%, the incidence of the cracking due to grain boundary embrittlement in the coarse-grained HAZ becomes markedly high. Therefore, if Cu is added, the content of Cu is set to not more than 4%. The content of Cu is preferably set to not more than 3.8%, and more preferably not more than 3.5%. The content of Cu is still more preferably set to not more than 3%. On the other hand, in order to ensure the above-mentioned effects, the lower limit of the Cu content is preferably set to 0.02%. The lower limit of the Cu content is more preferably 0.05%.

Mo: not more than 2%

[0075] Mo dissolves in the matrix and is an element which makes a contribution to the enhancement of high temperature strength, in particular to the enhancement of creep strength at high temperatures. However, when the content of Mo is increased, the stability of the austenite phase is deteriorated; hence the creep strength is rather low, and moreover, the susceptibility to cracking due to grain boundary embrittlement in the coarse-grained HAZ increases. In particular, when the content of Mo exceeds 2%, the creep strength markedly deteriorates. Therefore, if Mo is added, the content of Mo is set to not more than 2%. The content of Mo is preferably set to not more than 1.8%. On the other hand, in order to ensure the above-mentioned effects, the lower limit of the Mo content is preferably set to 0.05%. The lower limit thereof is more preferably set to 0.08%.

W: not more than 2%

[0076] W also dissolves in the matrix and is an element which makes a contribution to the enhancement of high temperature strength, in particular to the enhancement of creep strength at high temperatures. However, when the content of W is increased, the stability of the austenite phase is deteriorated; hence the creep strength is rather low, and moreover, the susceptibility to cracking due to grain boundary embrittlement in the coarse-grained HAZ increases. In particular, when the content of W exceeds 2%, the creep strength markedly deteriorates. Therefore, if W is added, the content of W is set to not more than 2%. The content of W is preferably set to not more than 1.8%. On the other hand, in order to ensure the above-mentioned effects, the lower limit of the W content is preferably set to 0.05%. The lower limit thereof is more preferably set to 0.08%.

Co: not more than 1%

[0077] Like Ni, Co is an austenite-forming element; it increases the stability of the austenite phase and makes a contribution to the enhancement of high temperature strength, in particular to the enhancement of creep strength.

However, Co is a very expensive element and, therefore, an increased content thereof results in an increase in cost. In particular when the content of Co exceeds 1%, the cost markedly increases. Therefore, if Co is added, the content of Co is set to not more than 1%. The content of Co is preferably set to not more than 0.9%. On the other hand, in order to ensure the above-mentioned effects, the lower limit of the Co content is preferably set to 0.03%. The lower limit of the Co content is more preferably 0.05%.

Ta: not more than 0.1%

[0078] Ta dissolves in the matrix or precipitates as a carbonitride; it is an element which makes a contribution to the enhancement of high temperature strength, although the effect is not so much compared with Mo, W, V, Nb or Ti. However, when the Ta content is increased, the amount of precipitates increases and thereby toughness deteriorates and moreover the susceptibility to cracking due to grain boundary embrittlement in the coarse-grained HAZ becomes higher. In particular, when the content of Ta exceeds 0.1%, toughness markedly deteriorates and the incidence of cracking due to grain boundary embrittlement in the coarse-grained HAZ also markedly increases. Therefore, if Ta is added, the content of Ta is set to not more than 0.1%. The content of Ta is preferably set to not more than 0.09%. On the other hand, in order to ensure the above-mentioned effect, the lower limit of the Ta content is preferably set to 0.002%. The lower limit of the Ta content is more preferably 0.005%.

Zr: not more than 0.1%

[0079] Zr also dissolves in the matrix or precipitates as a carbonitride; it is an element which makes a contribution to the enhancement of high temperature strength, although the effect is not so much compared with Mo, W, V, Nb or Ti. However, when the Zr content is increased, the amount of precipitates increases and thereby toughness deteriorates and moreover the susceptibility to cracking due to grain boundary embrittlement in the coarse-grained HAZ becomes higher. In particular, when the content of Zr exceeds 0.1%, toughness markedly deteriorates and the incidence of cracking due to grain boundary embrittlement in the coarse-grained HAZ also markedly increases. Therefore, if Zr is added, the content of Zr is set to not more than 0.1%. The content of Zr is preferably set to not more than 0.09%. On the other hand, in order to ensure the above-mentioned effect, the lower limit of the Zr content is preferably set to 0.002%. The lower limit of the Zr content is more preferably 0.005%.

Hf: not more than 0.1%

[0080] Hf also dissolves in the matrix or precipitates as a carbonitride; it is an element which makes a contribution to the enhancement of high temperature strength, although the effect is not so much compared with Mo, W, V, Nb or Ti. However, when the Hf content is increased, the amount of precipitates increases and thereby toughness deteriorates and moreover the susceptibility to cracking due to grain boundary embrittlement in the coarse-grained HAZ becomes higher. In particular, when the content of Hf exceeds 0.1%, toughness markedly deteriorates and the incidence of cracking due to grain boundary embrittlement in the coarse-grained HAZ also markedly increases. Therefore, if Hf is added, the content of Hf is set to not more than 0.1%. The content of Hf is preferably set to not more than 0.09%. On the other hand, in order to ensure the above-mentioned effect, the lower limit of the Hf content is preferably set to 0.002%. The lower limit of the Hf content is more preferably 0.005%.

[0081] The steels of the present invention can contain only one or a combination of two or more of the above-mentioned Cu, Mo, W, Co, Ta, Zr and Hf.

Second group: B: not more than 0.012%

[0082] B, which is the element of the second group, if added, has the effect of strengthening the grain boundaries. In order to obtain this effect, B may be added to the steels and thereby contained therein. B, which is in the second group, is now explained in detail.

B: not more than 0.012%

[0083] B segregates on the grain boundaries and also disperses carbides precipitating on the grain boundaries finely, and is an element which makes a contribution to strengthening the grain boundaries. However, an excessive addition of B lowers the melting point; in particular, when the content of B exceeds 0.012%, the decrease of the melting point becomes remarkable, and therefore, in the step of welding, the liquation cracking on the grain boundaries in the HAZ vicinity to the fusion line occurs. Therefore, if B is added, the content of B is set to not more than 0.012%. The content of B is preferably not more than 0.010%. On the other hand, in order to ensure the above-mentioned effect, the lower limit of the B content is preferably set to 0.0001%. The lower limit of the B content is more preferably 0.0005%.

[0084] Third group: Ca: not more than 0.02%, Mg: not more than 0.02% and REM: not more than 0.1%.
Each of Ca, Mg and REM being elements of the third group, if added, has the effect of increasing the hot workability. In order to obtain this effect, the said elements may be added to the steels and thereby contained therein. The elements, which are in the third group, are now described in detail.

Ca: not more than 0.02%

[0085] Ca has a high affinity for S and so, it has an effect of improving the hot workability. Ca is also effective, although to a slight extent, in reducing the possibility of cracking due to grain boundary embrittlement in the coarse-grained HAZ which is caused by the segregation of S on the grain boundaries. However, an excessive addition of Ca causes deterioration of the cleanliness, in other words, an increase of the index of cleanliness, due to the binding thereof to oxygen; in particular, when the content of Ca exceeds 0.02%, the deterioration of the cleanliness markedly increases and the hot workability rather deteriorates. Therefore, if Ca is added, the content of Ca is set to not more than 0.02%. The content of Ca is preferably not more than 0.015%. On the other hand, in order to ensure the above-mentioned effects, the lower limit of the Ca content is preferably set to 0.0001%. The lower limit of the Ca content is more preferably 0.001%.

Mg: not more than 0.02%

[0086] Mg also has a high affinity for S and so, it has an effect of improving the hot workability. Mg is also effective, although to a slight extent, in reducing the possibility of cracking due to grain boundary embrittlement in the coarse-grained HAZ which is caused by the segregation of S on the grain boundaries. However, an excessive addition of Mg causes deterioration of the cleanliness due to the binding thereof to oxygen; in particular, when the content of Mg exceeds 0.02%, the deterioration of the cleanliness markedly increases and the hot workability rather deteriorates. Therefore, if Mg is added, the content of Mg is set to not more than 0.02%. The content of Mg is preferably not more than 0.015%. On the other hand, in order to ensure the above-mentioned effects, the lower limit of the Mg content is preferably set to 0.0001%. The lower limit of the Mg content is more preferably 0.001%.

REM: not more than 0.1%

[0087] REM has a high affinity for S and so, it has an effect of improving the hot workability. REM is also effective in reducing the possibility of cracking due to grain boundary embrittlement in the coarse-grained HAZ which is caused by the segregation of S on the grain boundaries. However, an excessive addition of REM causes deterioration of the cleanliness due to the binding thereof to oxygen; in particular, when the content of REM exceeds 0.1%, the deterioration of the cleanliness markedly increases and the hot workability rather deteriorates. Therefore, if REM is added, the content of REM is set to not more than 0.1%. The content of REM is preferably not more than 0.08%. On the other hand, in order to ensure the above-mentioned effects, the lower limit of the REM content is preferably set to 0.001%. The lower limit of the REM content is more preferably 0.005%.

[0088] As already mentioned hereinabove, the term "REM" refers to a total of 17 elements including Sc, Y and lanthanoid collectively, and the REM content means the content of one or the total content of two or more of the REM.

[0089] The steel of the present invention may contain one alone or a combination of two or more of the above-mentioned Ca, Mg and REM.

[0090] From the reasons mentioned above, the austenitic stainless steel according to the present invention (4) is defined as the one which contains one or more elements of one or more groups selected from the first to third groups listed below in lieu of a part of Fe in the austenitic stainless steel according to any one of the present inventions (1) to (3).

First group: Cu: not more than 4%, Mo: not more than 2%, W: not more than 2%, Co: not more than 1%, Ta: not more than 0.1%, Zr: not more than 1% and Hf: not more than 0.1%;
Second group: B: not more than 0.012%; and
Third group: Ca: not more than 0.02%, Mg: not more than 0.02% and REM: not more than 0.1%.

[0091] The austenitic stainless steels according to the present inventions (1) to (4) can be produced by selecting the materials to be used in the melting step based on the results of careful and detailed analyses so that, in particular, the contents of Sn, As, Zn, Pb and Sb among the impurities may fall within the above-mentioned respective ranges, namely Sn: not more than 0.1%, As: not more than 0.01%, Zn: not more than 0.01%, Pb: not more than 0.01% and Sb: not more than 0.01% and the values of P1 and P2 respectively defined by the said formula (1) and formula (2) satisfy the conditions $P1 \leq 0.06$ and $0.3 \leq P2 \leq 1.7 - 10 \times P1$, respectively and then melting the materials using an electric furnace, an AOD furnace or a VOD furnace.

[0092] Next, a slab, a bloom or a billet is produced by casting the molten metal, which is prepared by a melting process, into an ingot by the so-called "ingot making method" and subjecting the ingot to hot working, or by continuous casting. Then, in the case of plate manufacturing, for example, the said material is subjected to hot rolling into a plate or a coil shaped sheet. Or, in the case of pipe manufacturing, for instance, any of such materials is subjected to hot working into a tubular product by the hot extrusion pipe manufacturing process or Mannesmann pipe manufacturing process.

[0093] That is to say, the hot working may use any hot working process. For example, in a case where the final product is a steel pipe or tube, the hot working may include the hot extrusion pipe manufacturing process represented by the Ugine-Sejournet process and/or the rolling pipe manufacturing process (Mannesmann pipe manufacturing process) represented by the Mannesmann-Plug Mill rolling process or the Mannesmann-Mandrel Mill rolling process or the like. In a case where the final product is a steel plate or sheet, the hot working may include the typical process of manufacturing a steel plate or a hot rolled steel sheet in coil.

[0094] The end temperature of the hot working is not particularly defined, but may be preferably set to not less than 1030˚C. This is because if the end temperature of the hot working is less than 1030˚C, the dissolution of the carbonitrides of Nb, Ti and V becomes insufficient, and therefore the creep strength and ductility may be impaired.

[0095] The cold working may be carried out after the hot working. For instance, in a case where the final product is a steel pipe or tube, the cold working may include the cold drawing pipe manufacturing process in which the pipe produced by the above-mentioned hot working is subjected to drawing and/or the cold rolling pipe manufacturing process using a cold pilger mill. In a case where the final product is a steel plate or sheet, the cold working may include the typical process of manufacturing a cold rolled steel sheet in coil. Moreover, in order to homogenize the microstructure and to further stabilize the strength, it is preferable to apply strains on the materials and then to perform a heat treatment for obtaining the recrystallization and uniform grains. In order to apply strains, it is recommended that the final working in the case of cold working be carried out at a rate of reduction in area of not less than 10%.

[0096] The final heat treatment after the above-mentioned hot working or the final heat treatment after a further cold working following the hot working may be carried out at a heating temperature of not less than 1030˚C. The upper limit of the said heating temperature is not particularly defined, but a temperature exceeding 1350˚C may cause not only high temperature intergranular cracking or a deterioration of ductility but also very coarse grains. Moreover, the said temperature may cause a marked deterioration of workability. Therefore, the upper limit of the heating temperature is preferably set to 1350˚C.

[0097] The following examples illustrate the present invention more specifically. These examples are, however, by no means limited to the scope of the present invention.

EXAMPLES

(Example 1)

[0098] Austenitic stainless steels A1, A2, B1 and B2 having the chemical compositions shown in Tables 1 and 2 were melted using an electric furnace and cast to form ingots. Each ingot was hot worked by a hot forging and a hot rolling, and then, was subjected to a heat treatment comprising heating at 1200˚C, followed by water cooling and, thereafter subjected to machining to produce steel plates having a thickness of 20 mm, a width of 50 mm and a length of 100 mm.

[0099] The steels A1 and A2 shown in Tables 1 and 2 are steels having chemical compositions which fall within the range regulated by the present invention. On the other hand, the steels B1 and B2 are steels of comparative examples in which the values of the parameters P1 and P2 are out of the ranges regulated by the present invention.

[Table 1]

[0100]

Table 1

Steel	Chemical composition (% by mass) The balance: Fe and impurities														
	C	Si	Mn	Cu	Ni	Cr	Mo	Co	sol.Al	B	N	Nb	V	Ti	S	P
A1	0.07	0.24	0.80	2.79	8.93	18.95	0.31	0.15	0.002	0.0047	0.12	0.500	0.072	0.003	0.0020	0.031
A2	0.06	0.38	1.15	0.08	19.70	24.56	0.11	0.39	0.005	0.0018	0.24	0.444	0.030	0.003	0.0003	0.017
B1	0.08	0.22	0.75	2.85	8.92	18.95	0.35	0.15	0.007	0.0030	0.10	0.595	0.192	0.040	0.0090	0.038
B2	0.06	0.36	1.18	0.08	20.10	25.12	0.10	0.42	0.004	0.0014	0.26	0.480	0.210	0.082	0.0120	0.028

[Table 2]

[0101]

Table 2 (continued from Table 1)

Steel	Chemical composition (% by mass) The balance: Fe and impurities								
	Sn	As	Pb	Zn	Sb	Others	Value of P1	Value of [1.7-10×P1]	Value of P2
A1	0.0700	-	-	-	-	-	0.05	1.18	0.65
A2	0.0160	0.0010	0.0002	0.0010	-	-	0.02	1.53	0.51
B1	0.0700	0.0030	0.0030	0.0030	0.0020	Ca: 0.0001	* 0.07	1.05	* 1.06
B2	0.0800	0.0060	0.0020	0.0030	0.0040	Hf:0.002	* 0.07	1.01	* 1.06

P1=S+{(P+Sn)/2}+{(As+Zn+pb+Sb)/5}
P2=Nb+2(V+Ti)
The mark * indicates falling outside the conditions regulated by the present invention.

[0102] Then, the steel plates made of the steels A1, A2, B1 and B2 were machined for providing each of them with a shape of V-groove with an angle of 30° in the longitudinal direction and a root thickness of 1 mm. Then each of them was subjected to four side-restrained welding onto a commercial SM400C steel plate, 25 mm in thickness, 200 mm in width and 200 mm in length, as standardized in JIS G 3106 (2004) using "DNiCrFe-3" defined in JIS Z 3224 (1999) as a covered electrode.

[0103] Thereafter, each steel plate was subjected to multilayer welding in the groove using the "YNiCr-3" defined in JIS Z 3334 (1999) as a welding wire by the TIG welding method under a heat input condition of 9 to 15 kJ/cm.

[0104] After the above welding procedure, each test specimen was subjected to an aging heat treatment at 650°C for 3000 hours, and a section thereof was mirror-like polished and etched, and then observed using an optical microscope. As a result, cracking due to grain boundary embrittlement was found to have occurred in the coarse-grained HAZ in the steels B1 and B2.

[0105] Next, test specimens, 12 mm × 12 mm × 100 mm in size, were prepared from the middle part in the direction of thickness of each of the above-mentioned steel plates with a thickness of 20 mm, a width of 50 mm and a length of 100 mm. The above-mentioned test specimens were subjected to simulated HAZ thermal cycles of 1350°C for 5 seconds which simulates the weld thermal cycle at the coarse-grained HAZ. Then, brimmed round bar creep test specimens with a soaked potion exposed to the simulated HAZ thermal cycles forming the parallel portion, 6 mm in diameter and 10 mm in length, were cut off from the above test specimens. Regarding the steels A1 and B1, the creep test specimens were subjected to a creep rupture test under the conditions of 650°C and 196 MPa corresponding to a desired base metal strength level of 3000 hours; regarding the steels A2 and B2, which had higher Cr and Ni contents and also had a higher level of creep strength; the creep test specimens were subjected to a creep rupture test under the conditions of 650°C and 216 MPa corresponding to a desired base metal strength level of 3000 hours.

[0106] The results of the above-mentioned creep rupture test are shown in Table 3. The symbol "○" in the column "ductility" in Table 3 indicates that the reduction of area after rupture was not less than 10%, while the symbol "×" indicates that the reduction of area after rupture was less than 10%. The symbol "○" in the column "creep strength" indicates that the rupture time was longer than 3000 hours.

[Table 3]

[0107]

Table 3

Test No.	Steel	Ductility	Creep strength	Note
1	A1	○	○	Inventive Example
2	A2	○	○	
3	* B1	×	○	Comparative Example
4	* B2	×	○	

(continued)

Test No.	Steel	Ductility	Creep strength	Note
The mark * indicates falling outside the conditions regulated by the present invention.				

[0108] As shown in Table 3, in Test Nos. 1 and 2 in which the steels A1 and A2 having no occurrence of cracking due to grain boundary embrittlement in the coarse-grained HAZ in the welded joint aging test were respectively used and they are examples according to the present invention, each reduction of area after rupture is more than 10% and moreover each rupture time is long, namely exceeds 3000 hours.

[0109] On the contrary, in the comparative examples, that is to say, in Test Nos. 3 and 4 in which the steels B1 and B2 showing a parameter P1 value exceeding 0.06, and a parameter P2 value exceeding the value of $[1.7 - 10 \times P1]$ and having an occurrence of cracking due to grain boundary embrittlement in the coarse-grained HAZ in the welded joint aging test were respectively used, each reduction of area after rupture is low, namely less than 10%, although each rupture time is long, namely longer than 3000 hours.

[0110] From the above-mentioned investigation results, it is apparent that the occurrence of cracking due to grain boundary embrittlement in a welded portion, that is to say, the susceptibility to cracking due to grain boundary embrittlement, can be evaluated in terms of the reduction of area after the rupture in the creep rupture test.

(Example 2)

[0111] Austenitic stainless steels A3 to A13, B3 and B4 having the chemical compositions shown in Tables 4 and 5 were melted using an electric furnace and cast to form ingots. Each ingot was hot worked by a hot forging and a hot rolling, and then, was subjected to a heat treatment comprising heating at 1200˚C, followed by water cooling and, thereafter subjected to machining to produce steel plates having a thickness of 20 mm, a width of 50 mm and a length of 100 mm.

[0112] The steels A3 to A13 shown in Tables 4 and 5 are steels having chemical compositions which fall within the range regulated by the present invention. On the other hand, the steels B3 and B4 are steels of comparative examples in which the value of the parameter P2 is out of the ranges regulated by the present invention.

[Table 4]

[0113]

Table 4

Steel	Chemical composition (% by mass) The balance: Fe and impurities															
	C	Si	Mn	Cu	Ni	Cr	Mo	Co	sol.Al	B	N	Nb	V	Ti	S	P
A3	0.08	0.23	0.80	2.90	9.33	18.54	-	-	0.003	-	0.10	0.500	0.075	0.003	0.0010	0.026
A4	0.08	0.23	0.74	2.88	8.87	18.07	0.21	0.19	0.010	0.0041	0.11	0.520	0.067	0.004	0.0010	0.027
A5	0.08	0.24	0.78	2.87	8.73	18.38	0.22	0.16	0.011	0.0042	0.11	0.502	0.050	0.002	0.0005	0.033
A6	0.08	0.15	0.80	2.77	8.64	18.33	0.45	0.25	0.004	0.0043	0.10	0.489	0.050	-	0.0008	0.036
A7	0.08	0.21	0.82	2.96	8.72	18.39	0.37	0.17	0.007	0.0040	0.10	0.487	0.050	0.004	0.0005	0.032
A8	0.06	0.42	1.20	0.10	19.82	24.46	0.23	0.20	0.017	0.0015	0.26	0.440	0.048	0.005	0.0002	0.017
A9	0.06	0.37	1.15	0.09	19.65	24.91	0.07	0.38	0.004	0.0016	0.25	0.438	0.060	0.007	0.0003	0.017
A10	0.06	0.37	1.14	-	19.47	24.71	-	-	0.004	-	0.24	0.446	0.050	0.005	0.0003	0.018
A11	0.06	0.39	1.11	0.05	19.63	24.26	0.08	0.13	0.005	0.0016	0.24	0.413	0.020	-	0.0002	0.015
A12	0.06	0.38	1.13	0.07	19.53	24.81	0.08	0.26	0.004	0.0015	0.24	0.447	0.040	0.003	0.0005	0.014
A13	0.07	0.20	0.50	3.50	19.80	22.51	-	-	0.006	0.0020	0.26	0.450	0.020	-	0.0100	0.025
B3	0.08	0.22	0.81	2.96	9.04	18.65	0.35	0.13	0.008	0.0038	0.10	0.130	0.022	-	0.0005	0.021
B4	0.15	0.23	1.19	0.06	19.87	25.25	0.22	0.05	0.025	0.0001	0.25	0.010	0.065	0.003	0.0040	0.017

[Table 5]

[0114]

Table 5 (continued from Table 4)

Steel	Chemical composition (% by mass) The balance: Fe and impurities								
	Sn	As	Pb	Zn	Sb	Others	Value of P1	Value of [1.7-10×P1]	Value of P2
A3	0.0400	-	-	-	-	-	0.03	1.36	0.66
A4	0.0170	-	-	-	-	Ca: 0.0001,Mg: 0.0001	0.02	1.47	0.66
A5	0.0090	0.0040	0.0001	0.0010	-	Ca:0.004	0.02	1.47	0.61
A6	0.0050	0.0010	0.0004	0.0010	0.0005	Ca: 0.001,W: 0.1	0.02	1.48	0.59
A7	0.0050	0.0030	0.0005	-	-	Ca: 0.003,Nd: 0.0003,Ta: 0.002	0.02	1.50	0.60
A8	0.0140	-	-	-	-	Ta:0.01	0.02	1.54	0.55
A9	0.0060	0.0010	0.0001	0.0010	-	Ta: 0.002,Ca: 0.0001,Mg: 0.0001	0.01	1.58	0.57
A10	0.0040	0.0010	0.0004	0.0010	0.0003	-	0.01	1.58	0.56
A11	0.0040	0.0010	0.0003	0.0010	-	Ta: 0.002,Ca: 0.0002	0.01	1.60	0.45
A12	0.0010	0.0010	0.0004	0.0010	0.0003	Ta: 0.002,Nd: 0.002,Ce: 0.001	0.01	1.61	0.53
A13	0.0001	-	-	-	-	W:1.50	0.02	1.47	0.49
B3	0.0040	0.0010	-	-	-	Mg:0.0001	0.01	1.57	* 0.18
B4	0.0020	-	-	-	-	Ta:0.002	0.01	1.57	* 0.15

P1=S+{(P+Sn)/2}+1(As+Zn+Pb+Sb)/5}
P2=Nb+2(V+Ti)
The mark * indicates falling outside the conditions regulated by the present invention.

[0115] Test specimens, 12 mm × 12 mm × 100 mm in size, were prepared from the middle part in the direction of thickness of each of the thus-obtained steel plates with a thickness of 20 mm, a width of 50 mm and a length of 100 mm. The above-mentioned test specimens were subjected to simulated HAZ thermal cycles of 1350˚C for 5 seconds which simulates the weld thermal cycle at the coarse-grained HAZ. Then, brimmed round bar creep test specimens with a soaked portion exposed to the simulated HAZ thermal cycles forming the parallel portion, 6 mm in diameter and 10 mm in length, were cut off from the above test specimens. Regarding the steels A3 to A7 and B3, the creep test specimens were subjected to a creep rupture test under the conditions of 650˚C and 196 MPa corresponding to a desired base metal strength level of 3000 hours; regarding the steels A8 to A13 and B4, which had higher Cr and Ni contents and also had a higher level of creep strength; the creep test specimens were subjected to a creep rupture test under the conditions of 650˚C and 216 MPa corresponding to a desired base metal strength level of 3000 hours.

[0116] As mentioned in the above-described "Example 1", the steels A1 and A2, each reduction of area after rupture thereof is more than 10% in the creep rupture test mentioned above, showed no occurrence of cracking due to grain boundary embrittlement in the coarse-grained HAZ. Therefore, only the ones having a reduction of area after rupture of not less than 10% and a rupture time of 3000 hours or longer were judged as capable of realizing the objective of the present invention, hence as "successful".

[0117] The results of above-mentioned creep rupture test are shown in Table 6. The symbol "○" in the column "ductility" indicates that the reduction of area after rupture was not less than 10%. In the column "creep strength", the symbol "○" indicates that the rupture time was 3000 hours or longer, and the symbol "×" indicates that the rupture time was shorter than 3000 hours.

[Table 6]

[0118]

Table 6

Test No.	Steel	Ductility	Creep strength	Note
5	A3	○	○	Inventive Example
6	A4	○	○	
7	A5	○	○	
8	A6	○	○	
9	A7	○	○	
10	A8	○	○	
11	A9	○	○	
12	A10	○	○	
13	A11	○	○	
14	A12	○	○	
15	A13	○	○	
16	* B3	○	×	Comparative Example
17	* B4	○	×	
The mark * indicates falling outside the conditions regulated by the present invention.				

[0119] As shown in Table 6, in each of the examples according to the present invention, that is to say, Test Nos. 5 to 15, in which the steels A3 to A13 were respectively used, each reduction of area after rupture is large, namely not less than 10%, and the rupture time is long, namely longer than 3000 hours.

[0120] On the contrary, in the comparative examples, that is to say, in Test Nos. 16 and 17 in which the steels B3 and B4 having a parameter P2 value less than 0.2 were respectively used, each creep strength is low with the rupture time of shorter than 3000 hours, although each reduction of area after rupture is large, namely not less than 10%.

[0121] From the above-mentioned results of "Example 1" and "Example 2", it is apparent that the steels having chemical compositions which fall within the range regulated by the present invention are high strength austenitic stainless steels excellent in resistance to cracking due to grain boundary embrittlement in the HAZ.

INDUSTRIAL APPLICABILITY

[0122] The austenitic stainless steels of the present invention have high strength and excellent resistance to cracking due to grain boundary embrittlement in the welded portion during use at high temperatures. Consequently, they can be used as materials for constructing machines and equipment, such as power plant boilers, which can be used at high temperatures for a long period of time.

Claims

1. An austenitic stainless steel, which comprises by mass percent, C: 0.04 to 0.18%, Si: not more than 1.5%, Mn: not more than 2.0%, Ni: 6 to 30%, Cr: 15 to 30%, N: 0.03 to 0.35%, sol. Al: not more than 0.03% and further contains one or more elements selected from Nb: not more than 1.0%, V: not more than 0.5% and Ti: not more than 0.5%, with the balance being Fe and impurities, in which the contents of P, S, Sn, As, Zn, Pb and Sb among the impurities are P: not more than 0.04%, S: not more than 0.03%, Sn: not more than 0.1%, As: not more than 0.01%, Zn: not more than 0.01%, Pb: not more than 0.01% and Sb: not more than 0.01%, and the values of P1 and P2 defined respectively by the following formula (1) and formula (2) satisfy the conditions $P1 \leq 0.06$ and $0.2 \leq P2 \leq 1.7 - 10 \times P1$;

$$P1 = S + \{(P + Sn) / 2\} + \{(As + Zn + Pb + Sb) / 5\} \cdots (1),$$

$$P2 = Nb + 2(V + Ti) \cdots (2);$$

wherein each element symbol in the formulas (1) and (2) represents the content by mass percent of the element concerned.

2. An austenitic stainless steel, which comprises by mass percent, C: 0.05 to 0.15%, Si: not more than 1.0%, Mn: not more than 2.0%, Ni: 6 to 13%, Cr: 15 to 25%, N: 0.03 to 0.15%, sol. Al: not more than 0.03% and further contains one or more elements selected from Nb: not more than 1.0%, V: not more than 0.5% and Ti: not more than 0.5%, with the balance being Fe and impurities, in which the contents of P, S, Sn, As, Zn, Pb and Sb among the impurities are P: not more than 0.04%, S: not more than 0.03%, Sn: not more than 0.1%, As: not more than 0.01%, Zn: not more than 0.01%, Pb: not more than 0.01% and Sb: not more than 0.01%, and the values of P1 and P2 defined respectively by the following formula (1) and formula (2) satisfy the conditions $P1 \leq 0.06$ and $0.3 \leq P2 \leq 1.7 - 10 \times P1$;

$$P1 = S + \{(P + Sn) / 2\} + \{(As + Zn + Pb + Sb) / 5\} \cdots (1),$$

$$P2 = Nb + 2(V + Ti) \cdots (2);$$

wherein each element symbol in the formulas (1) and (2) represents the content by mass percent of the element concerned.

3. An austenitic stainless steel, which comprises by mass percent, C: 0.04 to 0.18%, Si: not more than 1.5%, Mn: not more than 2.0%, Ni: more than 13% to not more than 30%, Cr: 15 to 30%, N: 0.10 to 0.35%, sol. Al: not more than 0.03% and further contains one or more elements selected from Nb: not more than 1.0%, V: not more than 0.5% and Ti: not more than 0.5%, with the balance being Fe and impurities, in which the contents of P, S, Sn, As, Zn, Pb and Sb among the impurities are P: not more than 0.04%, S: not more than 0.03%, Sn: not more than 0.1%, As: not more than 0.01%, Zn: not more than 0.01%, Pb: not more than 0.01% and Sb: not more than 0.01%, and the values of P1 and P2 defined respectively by the following formula (1) and formula (2) satisfy the conditions $P1 \leq 0.06$ and $0.2 \leq P2 \leq 1.3 - 10 \times P1$;

$$P1 = S + \{(P + Sn) / 2\} + \{(As + Zn + Pb + Sb) / 5\} \cdots (1),$$

$$P2 = Nb + 2(V + Ti) \cdots (2);$$

wherein each element symbol in the formulas (1) and (2) represents the content by mass percent of the element concerned.

4. The austenitic stainless steel according to any one of claims 1 to 3, which contains, by mass percent, one or more elements of one or more groups selected from the first to third groups listed below in lieu of a part of Fe:

First group: Cu: not more than 4%, Mo: not more than 2%, W: not more than 2%, Co: not more than 1%, Ta: not more than 0.1%, Zr: not more than 0.1% and Hf: not more than 0.1%;
Second group: B: not more than 0.012%; and
Third group: Ca: not more than 0.02%, Mg: not more than 0.02% and rare earth element: not more than 0.1%.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2008/067905

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/60*(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)
C22C38/00, C22C38/60

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	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

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 2003-268503 A (Sumitomo Metal Industries, Ltd.), 25 September, 2003 (25.09.03), & US 2003/0231976 A1	1-4
A	WO 2006/106944 A1 (Sumitomo Metal Industries, Ltd.), 12 October, 2006 (12.10.06), & EP 1867743 A1	1-4
A	JP 6-158234 A (Nippon Steel Corp.), 07 June, 1994 (07.06.94), (Family: none)	1-4
A	JP 41-8043 B1 (Tokushu Seiko Kabushiki Kaisha), 27 April, 1966 (27.04.66), (Family: none)	1-4

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

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search 07 January, 2009 (07.01.09)	Date of mailing of the international search report 20 January, 2009 (20.01.09)
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