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(54) High-nitrogen austentic stainless steel

(57) A high-nitrogen austenitic stainless steel, containing 0.005 mass%≤C≤0.25 mass%; 15.0 mass%≤Cr≤35.0 mass%; 0.2 mass%<Mn<10.0 mass%; 0.05 mass%≤Mo≤8.0 mass%; 0.01 mass%≤Cu≤4.0 mass%; 0.01 mass%≤Ni<5.0 mass%; 0.8 mass%<N≤1.8 mass%; Si≤2.0 mass%; P≤0.03 mass%; S≤0.05 mass%; Al≤0.030 mass%; O≤0.020 mass%, and the balance substantially including Fe and impurities, and having a PRE (=(Cr+3.3Mo+16N)/Mn (mass%)) of not less than 5 and a CRE (= Cr+1.5Mo+2N+Cu (mass%)) of not less than 27.

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to high-nitrogen austenitic stainless steel and, more specifically, high-nitrogen austenitic stainless steel which is excellent in seawater corrosion resistance and strength, and nonmagnetic.

2.Description of the Related Art

[0002] Austenitic stainless steel is generally excellent in corrosion resistance, but may cause corrosion depending on its using environment. For example, it is known that, when austenitic stainless steel is dipped in a halide aqueous solution, the passive film is broken by a halogen ion such as Cl^- or Br^-, causing local corrosion (pitting, crevice corrosion). For prevention of such a local corrosion, the following are known to be effective:

(1) Strengthening of passive film by increasing the amount of Cr
(2) Reduction of active dissolution by addition of Mo, increase in amount of Ni, or the like
(3) Addition of N.

[0003] Therefore, for application in seawater or in marine environment, materials described below, for example, have been used, or uses thereof have been examined:

(1) Austenitic stainless steel improved in corrosion resistance by addition of Cr and/or Mo (e.g., SUS316)
(2) Duplex stainless steel rich in Cr and Mo which are effective for corrosion resistance and adjusted in components so that the ratio of austenite phase is about 50% (e.g., SUS329J1, SUS329J4L, etc.)
(3) Austenitic stainless steel largely increased in amounts of Cr and Mo, with Cr (wt%) +3Mo (wt%) +10N (wt%)≥38 (so-called super stainless steel, e.g., SUS836L)
(4) Ni-based alloy (e.g., Hastelloy-C276, Inconel 625, etc.)
(5) Ti alloy.

[0004] The super stainless steel is excellent in seawater corrosion resistance, however, it is hard to say that it has sufficient strength. On the other hand, the application of Ni-based alloy and Ti alloy has also been examined for a portion requiring strength and corrosion resistance, however, the Ni-based alloy and Ti alloy are expensive and of excessive quality. Accordingly, development of inexpensive and reliable stainless steel is requested, and various proposals have been conventionally made.

[0005] For example, there is disclosed in Patent Reference 1 (Japanese Patent Application Laid-Open No. 10-183303), an austenitic steel alloy, containing 17.5%Cr-4%Mo-11%Mn-0.02%C-0.88%N-0.01%Ni, and the balance Fe; and an austenitic steel alloy, containing 14%Cr-6%Mo-12%Mn-0.9%N, and the balance Fe. It is described inx the same reference that corrosion resistance as high as that of super austenite can be ensured by adopting such a composition.

[0006] Further, there is disclosed in Patent Reference 2 (Japanese Patent Application Laid-Open No. 2000-309857), a stainless steel, containing C:0.003-0.012 wt%, Cr: 15 . 08-25 . 02 wt%, Mn:0.01-0.16 wt%, Mo: 1 . 03-9. 21 wt%, Ni : 2 . 05-23 . 41 wt%, N: 0 . 31-1 . 45 wt%, and the balance Fe, and having a pitting resistance equivalent PRE(=Cr(wt%) +3Mo(wt%)+10N(wt%)) which satisfies a predetermined relation with an area ratio (A%) of nonmetallic inclusion and a diameter (D μm) thereof. It is described in the same reference that, when the area ratio of nonmetallic inclusion and the diameter thereof are certain values or less, then reduction in corrosion resistance which is resulted from that the non-metallic inclusion becomes coating defect of the passive film can be suppressed.

[0007] Further, there is disclosed in Patent Reference 3 (Japanese Patent Application Laid-Open No. 2002-235153), a high-strength, high-corrosive resistance nonmagnetic stainless steel, containing C: not more than 0.15%, Si: not more than 1.0%, Mn : 3.0-12.0%, P: not more than 0.030%, Ni: not more than 0.50%, Cr:15.0-21.0%, N:0.70-1.50%, Al: not more than 0.020%, 0: not more than 0.020%, and the balance Fe. It is described in the same reference that Ni allergy resulted from elution of Ni can be suppressed by controlling the amount of Ni to not more than 0.5%; increased strength and nonmagnetic property can be attained by increasing the amount of N instead of Ni; and excellent corrosion resistance can be ensured by reducing the amount of Mn.

[0008]

[Patent Reference 1] Japanese Patent Application Laid-Open No. 10-183303
[Patent Reference 2] Japanese Patent Application Laid-Open No. 2000-309857

[Patent Reference 3] Japanese Patent Application Laid-Open No. 2002-235153

[0009] In the austenitic steel alloy disclosed in Patent Reference 1, 11-12% of Mn is added in order to enhance the nitrogen solbility. However, it is hard to say that adaptation of such a composition with high Mn can provide sufficient corrosion resistance (particularly, pitting resistance) in seawater.
In the stainless steel disclosed in Patent Reference 2, Mn is hardly added, in order to enhance the corrosion resistance in seawater, while Ni is further added. However, in such a component range for perfectly dissolving Cr nitrides which are harmful to seawater corrosion resistance, solution treatment at an extremely high temperature is needed. Solution treatment at a temperature exceeding 1250°C is disadvantageous for actual manufacture of a product in respect of grain coarsening and increase in manufacturing cost. Further, non-dissolved Cr nitrides may be left depending on temperature restrictions on existing solution treatment facilities, and sufficient seawater corrosion resistance cannot be obtained.
On the other hand, the high-strength, high-corrosion resistant nonmagnetic stainless steel disclosed in Patent Reference 3 is improved in corrosion resistance because a large amount of N is included, and the amount of Mn is suppressed; and has properly high strength. Further, this stainless steel can be used also for accessories, biomedical implants and the like, because it is nonmagnetic and safe for human body. However, further improvement in strength and corrosion resistance is demanded for the use in more severe conditions.

SUMMARY OF THE INVENTION

[0010] An object of the present invention is to provide a high-nitrogen austenitic stainless steel having seawater corrosion resistance as high as that of austenitic super stainless steel and strength as high as that of duplex stainless steel.
Another object of the present invention is to provide a high-nitrogen austenitic stainless steel capable of reducing Cr nitrides which are harmful to corrosion resistance without increasing the manufacturing cost by performing solution treatment in a practical temperature range of from 1050 to 1250°C.
A further object of the present invention is to provide a high-nitrogen austenitic stainless steel having strength equal to or more than that of Ni-based alloy or Ti-based alloy by performing cold working to such a high-nitrogen austenitic stainless steel.
Further, an additional object of the present invention is to provide a high-nitrogen austenitic stainless steel which is nonmagnetic.

[0011] In order to overcome the above-mentioned problems, the high-nitrogen austenitic stainless steel according to the present invention comprises:

$0.005 \text{ mass\%} \le C \le 0.25 \text{ mass\%}$;
$15.0 \text{ mass\%} \le Cr \le 35.0 \text{ mass\%}$;
$0.2 \text{ mass\%} < Mn < 10.0 \text{ mass\%}$;
$0.05 \text{ mass\%} \le Mo \le 8.0 \text{ mass\%}$;
$0.01 \text{ mass\%} \le Cu \le 4.0 \text{ mass\%}$;
$0.01 \text{ mass\%} \le Ni \le 5.0 \text{ mass\%}$;
$0.8 \text{ mass\%} \le N \le 1.8 \text{ mass\%}$;
$Si \le 2.0 \text{ mass\%}$;
$P \le 0.03 \text{ mass\%}$;
$S \le 0.05 \text{ mass\%}$;
$Al \le 0.030 \text{ mass\%}$;
$0 \le 0.020 \text{ mass\%}$; and

the balance substantially containing Fe and impurities[KK1], and having:

PRE represented by the equation (1) and of not less than 5,

$$PRE = (Cr + 3.3Mo + 16N)/Mn \text{ (mass\%)} \ldots (1)$$

and
CRE represented by the equation (2) and of not less than 27,

$$\mathrm{CRE} = \mathrm{Cr}+1.5\mathrm{Mo}+2\mathrm{N}+\mathrm{Cu}\ (\mathrm{mass\%})\ \ldots\ (2).$$

In this case, the high-nitrogen austenitic stainless steel preferably has a composition which can make the diameter of Cr nitrides to not more than 2 μm by the solution treatment of 1050 to 1250°C.
The high-nitrogen austenitic stainless steel preferably has an index of stability of austenitic phase: Ni_{eq}-Cr_{eq} of not less than 0, wherein
Ni_{eq} = Ni+Co+0.5Mn+0.3Cu+25N+30C
Cr_{eq} = Cr+2Si+1.5Mo+5V+5.5Al+1.75Nb+1.5Ti+0.75W.

[0012] When the content of each component element is optimized so that the PRE and the CRE are within predetermined ranges, high strength can be obtained in addition to improvement in seawater corrosion resistance. The optimization of the content of each component element enables dissolution of Cr nitrides with diameter of not less than 2 μm by the solution treatment of 1050 to 1250°C. When the content of each component is optimized so that the index of stability of austenite phase: Ni_{eq}-Cr_{eq} is not less than 0, high-nitrogen austenitic stainless steel which is nonmagnetic even after strong cold working can be obtained. Further, when the high-nitrogen austenitic stainless steel having such a component is subjected to cold working, high strength equal to or more than that of Ni-based alloy or Ti-based alloy can be obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

Fig. 1A is a view schematically showing a crevice forming tool; and
Fig. 1B is a view schematically showing a test piece with the crevice forming tool fixed thereto.

DETAILED DESCRIPTION OF THE INVENTION

[0014] One embodiment of the present invention will be then described in detail.
The high-nitrogen austenitic stainless steel according to the present invention includes elements described below, and the balance substantially containing Fe and inevitable impurities. The kinds and component ranges of additive elements and the limitation reasons thereof are as follows.
In this specification, "mass%" means "mass percent," which is defined by the equation (A):

$$(\mathrm{mass\ \%}) = (\text{amount of each element} \ / \ \text{total amount of all elements of steel or alloy etc.}) \times 100 \ldots (\mathrm{A}).$$

Further, "MPa" is a unit, and 1 MPa equals to 1 × 10^6 N/m^2.[KK2]

[0015] (1) 0.005 mass%≤C≤0.25 mass%
C is an austenite forming element, which is contributable to stabilization of austenite phase and effective for suppression of nitrogen blow. It also contributes to improvement in strength because it is an interstitial element. On the other hand, addition of C exceeding 0 .25 mass% reduces the [KK3] solubility of N, and also reduces dissolved-Cr in a base phase by formation of Cr carbides, causing deterioration of corrosion resistance. Therefore, the addition amount of C is set preferably to from not less than 0.005 mass% to not more than 0.25 mass%, more preferably to from not less than 0.005 mass% to not more than 0.20 mass%, and even more preferably to from not less than 0.01 mass% to not more than 0.15 mass%.

[0016] (2) 15.0 mass%≤Cr≤35.0 mass%
Cr remarkably increases the solubility of N, thus, it is not only effective for suppression of nitrogen blow but also largely contributable to improvement in corrosion resistance and strength. Namely, Cr is an important element. Cr is a ferrite forming element, therefore, excessive addition thereof makes austenite phase unstable, so that nonmagnetic property cannot be kept. Further, the residual amount of non-dissolved Cr nitrides in solution treatment is increased, causing remarkable reduction in corrosion resistance. Further, precipitation of σ-phase which causes deterioration of toughness and ductility is promoted. Therefore, the addition amount of Cr is set preferably to from not less than 15.0 mass% to not more than 35.0 mass%, more preferably to from more than 21.0 mass% to not more than 32.0 mass%, and even more preferably to from more than 24.0 mass% to not more than 30.0 mass%.

[0017] (3) 0.2 mass%<Mn<10.0 mass%
Mn is an austenite forming element, which contributes to stabilization of austenite phase. It remarkably increases the solubility of N, therefore, it is effective for suppression of nitrogen blow. Further, it reduces the temperature at which below-mentioned Cr nitride dissolves[KK4]. It is effective also as a deoxidizing or desulfurizing element. On the other hand, excessive addition of Mn causes deterioration of pitting resistance. Therefore, the addition amount of Mn is set preferably to from more than 0.2 mass% to less than 10.0 mass%, more preferably to from more than 0.2 mass% to not more than 8.0 mass%, and even more preferably to from not less than 2.0 mass% to not more than 7.0 mass%.

[0018] (4) 0.05 mass%≤Mo≤8.0 mass%
Mo increases the solubility of N and remarkably improves corrosion resistance. It also improves strength as a solid-solution strengthening element. On the other hand, excessive addition of Mo makes austenite phase unstable, inducing N blow, and also makes it difficult to ensure the nonmagnetic property. Further, the excessive addition causes formation of a brittle phase and it causes reduction in toughness and ductility, these are also detrimental to forging. Further, the amount of non-dissolved Cr nitrides in solution treatment is increased, causing remarkable reduction in corrosion resistance. Therefore, the addition amount of Mo is set preferably to from not less than 0.05 mass% to not more than 8.0 mass%, more preferably to from not less than 0.05 mass% to not more than 2.5 mass%, and even more preferably to from not less than 0.10 mass% to less than 2.5 mass%.

[0019] (5) 0.01 mass%≤Cu≤4.0 mass%
Cu is an austenite forming element, which contributes to stabilization of austenite phase. It also contributes to improvement in crevice corrosion resistance. On the other hand, excessive addition of Cu increases the amount of non-dissolved Cr nitrides in solution treatment, causing deterioration of corrosion resistance and reduction in hot workability. Therefore, the addition amount of Cu is set preferably to from not less than 0.01 mass% to not more than 4.0 mass%, more preferably to from not less than 0.02 mass% to not more than 2.0 mass%, and even more preferably to from not less than 0.05 mass% to not more than 1.5 mass%.

[0020] (6) 0.01 mass%≤Ni<5.0 mass%
Ni is an austenite forming element, which contributes to stabilization of austenite phase. On the other hand, excessive addition of Ni increases the amount of non-dissolved Cr nitrides in solution treatment, causing deterioration of corrosion resistance. Therefore, the addition amount of Ni is set preferably to from not less than 0.01 mass% to less than 5.0 mass%, more preferably to from not less than 0.01 mass% to less than 3.0 mass%, and even more preferably to from more than 0.5 mass% to less than 3.0 mass%.

[0021] (7) 0.8 mass%≤N≤1.8 mass%
N is one of the most important elements in the present invention. N is an interstitial element, which is very effective for improvement in strength, for stabilization of austenite phase, and for improvement in corrosion resistance. On the other hand, excessive addition of N induces generation of N blow and also makes a large amount of non-dissolved Cr nitrides or large amounts of Ti, Nb, and V nitrides remain in steel in solution treatment, causing remarkable reduction in corrosion resistance. Therefore, the addition amount of N is set preferably to from more than 0.8 mass% to not more than 1.8 mass%, and more preferably to from more than 0.8 mass% to not more than 1.5 mass%.

[0022] (8) Si≤2.0 mass%
Although Al is more effective than Si as a deoxidizing element for general steel, excessive addition of Al in high-nitrogen steel causes formation of AlN which leads to remarkable reduction in corrosion resistance, toughness and ductility. Therefore, as an main deoxidizing element, it is preferable to use Si with an essential element Mn. Since Si is a ferrite forming element, excessive addition thereof makes austenite phase unstable, inducing N blow, and also makes it difficult to ensure the nonmagnetic property. Further, the excessive addition is not only detrimental to forging, but also it remarkably deteriorates the toughness and ductility of steel. The residual amount of non-dissolved Cr nitrides after solution treatment is also increased, causing remarkable reduction in corrosion resistance. Therefore, the addition amount of Si is set preferably to not more than 2.0 mass%, more preferably to from not less than 0.01 mass% to not more than 1.0 mass%, and even more preferably to from not less than 0.01 mass% to not more than 0.50 mass%.

[0023] (9) P≤0.03 mass%
Excessive addition of P causes reduction in hot workability, grain boundary strength, toughness and ductility, while excessive reduction of P causes a rise of manufacturing cost. Therefore, the content of P is preferably set to not more than 0.03 mass%.

(10) S≤0.05 mass%
Although S is effective for improvement in machinability, excessive addition thereof causes reduction in hot workability and causes deterioration of corrosion resistance by formation of MnS. On the other hand, excessive reduction of S causes a rise of manufacturing cost. Therefore, the content of S is set preferably to not more than 0.05 mass%, and more preferably to not more than 0.01 mass%.

[0024] (11) Al≤0.030 mass%
Al is very effective as a deoxidizing element similarly to Si and Mn. In this steel, however, if the addition amount of Al is more than 0.03 mass%, formation of AlN progresses, causing remarkable reduction in corrosion resistance, toughness

and ductility. Therefore, the addition amount of Al is set preferably to not more than 0.030 mass%, more preferably to not more than 0.025 mass%, and even more preferably to not more than 0.020 mass%.

(12) 0≤0.020 mass%

Addition of O exceeding 0.020 mass% reduces the cleanliness of steel, causing remarkable deterioration of corrosion resistance. Therefore, the content of 0 is set preferably to not more than 0.020 mass%, more preferably to not more than 0.015 mass%, and even more preferably to not more than 0.010 mass%.

[0025] The high-nitrogen austenitic stainless steel according to the present invention is characterized in that PRE is not less than 5 and CRE is not less than 27, in addition to that various additive elements are within the above-mentioned ranges.

The "PRE" means a pitting resistance equivalent[KK5], which is a value represented by the following equation (1). In the equation (1), N, Cr and Mo are used as elements which improve the pitting resistance and Mn is used as element which deteriorates the pitting resistance.

$$PRE = (Cr+3.3Mo+16N)/Mn \text{ (mass\%)} \ldots (1)$$

When the PRE is not less than 5, a pitting resistance equal to or more than that of super stainless steel (e.g., SUS836L) is obtained. The PRE is more preferably not less than 7.

The "CRE" means a crevice corrosion resistance equivalent[KK6], which is a value represented by the following equation (2). In the equation (2), Cr, Mo, N and Cu are used as elements which reduce a critical pH.

$$CRE = Cr+1.5Mo+2N+Cu \text{ (mass\%)} \ldots (2)$$

When the CRE is not less than 27, a crevice corrosion resistance equal to or more than that of super stainless steel (e.g., SUS836L) is obtained. The CRE is preferably not less than 30.

[0026] The high-nitrogen austenitic stainless steel according to the present invention may contain, further, one or more second additive elements as described below, in addition to the various elements described above. The component range of each element and the limitation reason thereof are as follows.

(13) 0.01 mass%≤W≤8.0 mass%

W contributes to improvement in corrosion resistance similarly to Mo, and also contributes to improvement in strength as a solid-solution strengthening element. On the other hand, excessive addition of W causes reduction in toughness and ductility by formation of a brittle phase similarly to Mo, and is also detrimental to forging. The amount of non-dissolved Cr nitrides in solution treatment is also increased, causing remarkable reduction in corrosion resistance. Therefore, the addition amount of W is set preferably to from not less than 0.01 mass% to not more than 8.0 mass%, and more preferably to from not less than 0.05 mass% to not more than 1.5 mass%.

(14) 0.01 mass%≤Co≤5.0 mass%

Co contributes to improvement in corrosion resistance and to improvement in strength. On the other hand, excessive addition of Co leads to rise of cost, and it increases the amount of non-dissolved Cr nitrides in solution treatment, causing remarkable reduction in corrosion resistance. Therefore, the addition amount of Co is set preferably to from not less than 0.01 mass% to not more than 5.0 mass%, more preferably to from not less than 0.05 mass% to not more than 4.5 mass%, and even more preferably to from not less than 0.1 mass% to not more than 4.0 mass%.

[0027] The high-nitrogen austenitic stainless steel according to the present invention may further contain one or more third additive elements as described below, in addition to the above-mentioned various elements or instead of the above-mentioned second additive elements. The component range of each element and the limitation reason thereof are as follows.

(15) 0.01 mass%≤Ti≤0.5 mass%

Ti bonds to C and/or N to contribute to improvement in strength and to grain refining. On the other hand, excessive addition of Ti makes large amounts of oxides and/or nitrides remain in steel, causing reduction in corrosion resistance. It also reduces the effective amount of dissolved N, causing reduction in strength. Therefore, the addition amount of Ti is set preferably to from not less than 0.01 mass% to not more than 0.5 mass%, more preferably to from not less than 0.02 mass% to not more than 0.4 mass%, and even more preferably to from not less than 0.03 mass% to not more than 0.3 mass%.

[0028] (16) 0.01 mass%≤Nb≤0.5 mass%

Nb bonds to C and/or N similarly to Ti to contribute to improvement in strength and to grain refining. On the other hand, excessive addition of Nb makes large amounts of oxides and/or nitrides remain in steel, causing reduction in corrosion resistance. It also reduces the effective amount of dissolved N, causing reduction in strength. Therefore, the addition amount of Nb is set preferably to from not less than 0.01 mass% to not more than 0.5 mass%, more preferably to from not less than 0.02 mass% to not more than 0.4 mass%, and even more preferably to from not less than 0.03 mass% to not more than 0.3 mass%.

[0029] (17) $0.01\ \text{mass}\% \leq V < 1.0\ \text{mass}\%$
V bonds to C and/or N similarly to Ti and Nb to contribute to improvement in strength and to grain refining. On the other hand, excessive addition of V makes large amounts of oxides and/or nitrides remain in steel, causing reduction in corrosion resistance. It also reduces the effective amount of dissolved N, causing reduction in strength. Therefore, the addition amount of V is set preferably to from not less than 0.01 mass% to less than 1.0 mass%, more preferably to from not less than 0.02 mass% to not more than 0.9 mass%, and even more preferably to from not less than 0.03 mass% to not more than 0.8 mass%.

[0030] (18) $0.01\ \text{mass}\% \leq Ta \leq 0.5\ \text{mass}\%$
Ta bonds to C and/or N similarly to Ti, Nb and V to contribute to improvement in strength and to grain refining. On the other hand, excessive addition of Ta makes large amounts of oxides and/or nitrides remain in steel, causing reduction in corrosion resistance. It also reduces the effective amount of dissolved N, causing reduction in strength. Therefore, the addition amount of Ta is set preferably to from not less than 0.01 mass% to not more than 0.5 mass%, more preferably to from not less than 0.02 mass% to not more than 0 .4 mass%, and even more preferably to from not less than 0.03 mass% to not more than 0.3 mass%.

[0031] (19) $0.01\ \text{mass}\% \leq Zr \leq 0.5\ \text{mass}\%$
Zr contributes to improvement in strength. On the other hand, excessive addition of Zr leads to reduction in toughness and ductility. Therefore, the addition amount of Zr is set preferably to from not less than 0.01 mass% to not more than 0 . 5 mass%, more preferably to from not less than 0.03 mass% to not more than 0.4 mass%, and even more preferably to from not less than 0.05 mass% to not more than 0.3 mass%.

[0032] The high-nitrogen austenitic stainless steel according to the present invention may further contain one or more fourth additive elements as described below, in addition to the above-mentioned various elements or instead of the above-mentioned second and/or third additive elements. The component range of each element and the limitation reason thereof are as follows.
(20) $0.001\ \text{mass}\% \leq B \leq 0.01\ \text{mass}\%$
B is effective for improvement in strength and for improvement in hot workability. On the other hand, excessive addition of B rather impairs the hot workability, and deteriorates corrosion resistance. Therefore, the addition amount of B is set preferably to from not less than 0.001 mass% to not more than 0.01 mass%, more preferably to from not less than 0.001 mass% to not more than 0.008 mass%, and even more preferably to from not less than 0.001 mass% to not more than 0.005 mass%.

[0033] (21) $0.001\ \text{mass}\% \leq Ca \leq 0.01\ \text{mass}\%$
(22) $0.001\ \text{mass}\% \leq Mg \leq 0.01\ \text{mass}\%$
Ca and Mg are effective for improving hot workability. Ca is also effective for improving machinability. On the other hand, excessive addition of Ca and Mg rather impairs the hot workability. Therefore, the addition amounts of Ca and Mg are set, respectively, preferably to not less than 0.001 mass% to not more than 0.01 mass%, more preferably to from not less than 0.001 mass% to not more than 0.008 mass%, and even more preferably to from not less than 0.001 mass% to not more than 0.005 mass%.

[0034] The high-nitrogen austenitic stainless steel according to the present invention may further contain one or more fifth additive elements as described below, in addition to the above-mentioned various elements, or instead of the above-mentioned second, third and/or fourth additive elements. The component range of each element and the limitation reason thereof are as follows. (23) $0.005\ \text{mass}\% \leq Te \leq 0.05\ \text{mass}\%$
Te contributes to improvement in machinability. On the other hand, excessive addition of Te deteriorates corrosion resistance, toughness, ductility, and hot workability. Therefore, the addition amount of Te is set preferably to from not less than 0.005 mass% to not more than 0.05 mass%, and more preferably to from not less than 0.01 mass% to not more than 0.04 mass%.
(24) $0.01\ \text{mass}\% \leq Se \leq 0.20\ \text{mass}\%$
Se contributes to improvement in machinability. On the other hand, excessive addition of Se deteriorates corrosion resistance, toughness, ductility, and hot workability. Therefore, the addition amount of Se is set preferably to from not less than 0.01 mass% to not more than 0.20 mass%, more preferably to from not less than 0.02 mass% to not more than 0.18 mass%, and even more preferably to from not less than 0.05 mass% to not more than 0.15 mass%.

[0035] In the high-nitrogen austenitic stainless steel according to the present invention, it is desirable that $Ni_{eq}-Cr_{eq}$ is not less than 0 in addition that the additive elements are within the above-mentioned ranges.
The "$Ni_{eq}-Cr_{eq}$" means an index of stability of austenite phase, which is represented by using contents of main austenite forming elements and contents of main ferrite forming elements. The "Ni_{eq}" and the "Cr_{eq}" mean values represented by the following equations, respectively.

Ni_{eq} = Ni+Co+0.5Mn+0.3Cu+25N+30C

Cr_{eq}= Cr+2Si+1.5Mo+5V+5.5A1+1.75Nb+1.5Ti+0.75W.

When the Ni_{eq}-Cr_{eq} is not less than 0, the austenite phase can be stably kept even after strong cold working.

[0036] Further, it is preferable that the high-nitrogen austenitic stainless steel according to the present invention has, particularly, a composition which can make the diameter of Cr nitrides to not more than 2 μm by solution treatment of 1050 to 1250°C among the above-mentioned compositions.

The high-nitrogen austenitic stainless steel according to the present invention is subjected, after forging or rolling, to solution treatment for 0.1 to 2 hours at such a heat treatment temperature as to be suitable for the composition of steel for the purpose of ensuring corrosion resistance. The solution treatment is carried out in order to dissolve Cr nitrides and to uniform microstructure. In this case, extinguishment of Cr nitrides with diameter exceeding 2 μm cannot always be attained in steel having any composition by performing solution treatment at a fixed temperature. Therefore, it is necessary to select an optimum solution treatment temperature according to the composition of the steel.

When the solution treatment temperature is excessively low, non-dissolved Cr nitrides with diameter exceeding 2 μm are generally left after solution treatment. Rough Cr nitrides cause reduction in seawater corrosion resistance. On the other hand, an excessively high solution-treatment temperature causes grain coarsening and/or increase in facility cost. In order to suppress the grain coarsening and/or the increase in facility cost while ensuring excellent seawater corrosion resistance, among the above-mentioned compositions, a composition which can make the diameter of non-dissolved Cr nitrides to not more than 2 μm by solution treatment of 1050 to 1250°C is particularly preferred.

[0037] The effect of the high-nitrogen austenitic stainless steel according to the present invention will be then described. The high-nitrogen austenitic stainless steel of the present invention is such that a large amount of N is dissolved to make elements such as Cr, Mn, Mo, Ni, Cu and the like to be proper, and the content of each component element is optimized so that the pitting resistance equivalent PRE and the crevice corrosion resistance equivalent CRE are within predetermined ranges. Therefore, seawater corrosion resistance as high as that of austenitic super stainless steel and high strength equivalent to that of duplex stainless steel are obtained.

When the addition amount of each component element is optimized, rough Cr nitrides harmful to corrosion resistance can be reduced by solution treatment in a practical temperature range of 1050 to 1250°C. Since the solution treatment can be performed at a relatively low temperature, increase in manufacturing cost can be suppressed.

When the content of each component element is optimized so that the index of stability of austenite phase: Ni_{eq}-Cr_{eq} is not less than 0, the austenite phase can be stably kept even after strong cold working. Therefore, high-nitrogen austenitic stainless steel which is nonmagnetic can be obtained.

[0038] Further, when the content of each component element is optimized, and Cr nitrides with diameter of 2 μm or more are dissolved by solution treatment of 1050 to 1250 °C, the tensile strength after solution treatment becomes 1000 MPa or more by solid-solution strengthening of N.

When the content of each component element is optimized, Cr nitrides with diameter of 2 μm or more are dissolved by solution treatment of 1050 to 1250°C, and cold working is performed, then the tensile strength after solution treatment and cold working is increased by solid-solution strengthening and work hardening by N, and high strength equivalent to or more than that of Ni-based alloy or Ti-based alloy can be obtained. Further, the strength after cold working rises in accordance with a reduction ratio. Therefore, if the cold working condition is optimized, the tensile strength after solution treatment and cold working becomes 1800 MPa or more.

Further, when the content of each component element is optimized, Cr nitrides with diameter of 2 μm or more are dissolved by solution treatment of 1050 to 1250°C, and the cold working condition is optimized, then the tensile strength after solution treatment and cold working becomes 2000 MPa or more by solid-solution strengthening and work hardening by N. Even in such a high strength state, an elongation of not less than 10% can be ensured.

EXAMPLES

[0039] [Examples 1 to 18 and Comparative Examples 1 to 23] [1. Preparation of Samples]

Each of alloys having chemical components shown in Tables 1 and 2 was melted and cast in a pressurized induction furnace, whereby 50 kg of ingot was obtained. The ingot was homogenized, and made to a round bar with ϕ24 by hot forging. The resulting round bar was subjected to solution treatment. As the solution treatment condition, the bar was held at 1050 to 1300°C for 1 hour, and then cooled with water.

The same test was carried out with respect to super stainless steel: SUS836L (Comparative Example 14), duplex stainless steel: SUS329J4L (Comparative Example 15), austenitic stainless steel: SUS316 (Comparative Example 16), Ni-based alloy: Inconel 625 (Comparative Example 17), and Ti (Comparative Example 18) as representatives of existing steel products. The heat treatment was performed in a generally adapted temperature condition.

[0040]

[Table 1]

		C	Si	Mn	P	S	Cu	Ni	Cr	Mo	Co	W	V	Al	Ti
EXAMPLES	1	0.03	0.13	0.4	0.01	0.01	0.16	0.48	27.3	1.30				0.008	
	2	0.03	0.21	1.8	0.02	0.01	0.05	0.20	24.9	1.90	0.23	0.12		0.007	
	3	0.08	0.31	7.9	0.02	0.01	0.23	2.30	31.4	0.92			0.06	0.006	
	4	0.03	0.20	4.2	0.01	0.01	0.72	0.50	17.9	5.80	0.26	0.13		0.006	0.09
	5	0.02	0.11	3.4	0.02	0.01	0.32	1.38	21.2	6.43	0.73			0.005	0.06
	6	0.03	0.22	6.5	0.02	0.01	0.16	0.07	27.1	0.21	0.47	0.15		0.005	
	7	0.05	0.21	7.3	0.02	0.01	0.16	0.09	25.0	2.30	0.32	0.23		0.006	0.02
	8	0.03	0.15	7.7	0.02	0.01	0.43	0.03	21.2	2.43				0.007	
	9	0.06	0.02	9.1	0.02	0.01	0.19	0.09	19.5	3.90			0.07	0.008	
	10	0.22	0.22	7.1	0.02	0.01	0.16	0.07	24.3	3.80	0.47	0.15		0.005	
	11	0.05	0.21	5.8	0.02	0.01	1.39	0.09	23.7	1.75				0.006	
	12	0.06	0.20	5.9	0.02	0.01	0.16	3.80	23.3	3.40		0.05		0.005	
	13	0.04	0.20	7.2	0.02	0.01	0.16	0.22	24.1	2.40	2.10		0.15	0.005	
	14	0.04	0.20	5.4	0.02	0.01	0.16	0.18	25.3	1.74	0.28	1.44		0.005	0.15
	15	0.01	0.28	6.9	0.01	0.01	0.16	0.22	25.0	2.48				0.011	
	16	0.03	0.01	7.8	0.02	0.01	0.16	0.10	24.3	2.10		0.15		0.007	
	17	0.07	0.31	4.5	0.01	0.01	0.13	1.01	23.2	4.20				0.006	
	18	0.05	0.18	8.8	0.01	0.01	0.13	0.05	24.4	2.33				0.005	
	19	0.04	0.20	5.4	0.02	0.01	0.63	2.20	24.6	1.80				0.005	
	20	0.08	0.28	6.9	0.01	0.01	0.16	1.30	25.0	2.45				0.009	
	21	0.03	0.15	8.4	0.02	0.01	0.20	1.10	24.3	2.30				0.007	
	22	0.09	0.31	6.8	0.01	0.01	0.13	1.01	22.1	4.20				0.006	
	23	0.05	0.18	4.5	0.01	0.01	0.51	2.40	24.4	2.33				0.005	
COMPARATIVE EXAMPLES	1	0.03	0.16	1.5	0.02	0.01	0.52	0.16	24.2	1.94	0.15	0.05		0.010	
	2	0.07	0.21	4.0	0.02	0.01	0.15	0.17	22.2	3.90	0.51		0.31	0.055	
	3	0.05	0.20	6.0	0.01	0.01	0.15	0.07	19.2	12.90			0.11	0.008	0.05
	4	0.05	2.44	8.0	0.02	0.01	0.19	0.20	37.2	0.51				0.009	
	5	0.04	0.12	0.1	0.02	0.01	0.21	6.20	27.3	0.56	0.05	0.05		0.007	
	6	0.05	0.14	8.0	0.02	0.01	4.60	0.10	23.2	0.98				0.009	
	7	0.04	0.19	12.8	0.02	0.01	0.14	0.16	13.0	7.99			0.40	0.009	
	8	0.06	0.17	9.7	0.01	0.01	0.16	0.06	23.3	1.54			0.15	0.008	0.03
	9	0.33	0.24	4.0	0.01	0.01	0.14	0.31	26.8	0.54			0.19	0.006	
	10	0.08	0.23	1.2	0.01	0.01	0.14	0.24	29.0	1.01				0.009	0.03
	11	0.02	0.32	9.2	0.01	0.01	0.13	0.06	18.3	2.21				0.005	
	12	0.02	0.17	17.6	0.01	0.01	0.23	0.31	18.4	2.12				0.007	
	13	0.07	0.15	13.0	0.01	0.01	0.20	0.01	17.8	2.02				0.012	
	14	0.02	0.17	0.8	0.02	0.01	0.92	25.1	19.9	6.22				0.009	
	15	0.02	0.21	0.9	0.02	0.01		6.4	24.9	3.98				0.010	
	16	0.04	0.34	1.1	0.03	0.01	0.15	11.8	17.5	2.12				0.025	
	17	0.05	0.31	0.1	0.03	0.01		Bal.	22.1	9.10				0.011	
	18	0.01													Bal.

[0041]

[Table 2]

		Nb	O	N	B	Mg	Ca	Ta	Zr	Te	Se	PRE	CRE	Nieq −Creq
EXAMPLES	1		0.002	1.31								131.4	32.0	4.8
	2	0.05	0.003	1.47			0.005					30.4	30.7	10.6
	3		0.002	1.33		0.003						7.1	35.7	8.2
	4	0.04	0.002	1.21								13.4	29.7	6.9
	5		0.002	1.22		0.003	0.002	0.09	0.10	0.03	0.10	18.2	33.6	3.8
	6		0.001	1.20								7.2	30.0	6.7
	7	0.01	0.003	1.24			0.006					7.2	31.1	7.5
	8		0.002	0.93	0.002	0.003						5.7	27.1	3.0
	9		0.001	0.83								5.0	27.2	1.5
	10		0.001	1.08	0.003							7.6	32.3	7.2
	11		0.003	1.18			0.007					8.3	30.1	7.6
	12		0.003	1.26		0.002	0.003					9.3	31.1	11.2
	13	0.05	0.003	1.08				0.06				6.8	30.0	5.2
	14	0.05	0.003	1.06					0.09			8.9	30.2	1.2
	15	0.07	0.002	1.26						0.03		7.7	31.4	6.1
	16		0.005	0.94		0.003	0.006					5.9	29.5	0.8
	17		0.004	1.15								12.3	31.9	4.0
	18		0.003	1.07								5.6	30.2	4.5
	19		0.005	1.14								9.0	30.2	7.1
	20		0.007	1.10								7.3	31.0	5.4
	21		0.005	1.07								5.8	30.1	4.9
	22		0.004	1.10								7.9	30.7	5.6
	23		0.003	1.05								10.9	30.5	4.3
COMPARATIVE EXAMPLES	1		0.029	1.20		0.003			0.11			33.2	30.0	4.6
	2		0.002	1.03				0.11	0.09			12.9	30.3	0.3
	3		0.003	1.19	0.002		0.003	0.10				13.5	41.1	-5.3
	4		0.002	1.02								6.9	40.2	-11.6
	5		0.003	1.26				0.11		0.02	0.10	448.3	30.9	10.6
	6		0.005	1.21	0.003							5.7	31.7	12.2
	7	0.05	0.002	1.21		0.030	0.004					4.6	27.5	10.6
	8	0.05	0.004	0.69								4.1	27.2	-2.9
	9		0.002	1.11								11.6	30.0	10.9
	10		0.004	1.85			0.002					51.6	34.4	18.5
	11		0.002	0.98	0.0024		0.003					4.5	23.7	7.5
	12		0.03	1.02				0.12				2.4	23.9	13.3
	13		0.003	1.01								3.1	23.1	12.7
	14		0.007	0.14								56.9	30.4	0.1
	15		0.004	0.19								45.6	31.3	-19.1
	16		0.005	0.03								22.7	20.9	-7.2
	17		0.005	0.03								-	-	-
	18		0.09	0.01								-	-	-

[0042] [2.Evaluation (1)]
The resulting ingots and round bars were evaluated as follows.

(1) Existence of nitrogen blow:

A test piece was cut out from a bottom portion of each ingot, and visual confirmation of nitrogen blow holes was performed therefor.

(2) Selection of the solution treatment temperature:

The round bar after hot forging was subjected to solution treatment at various temperatures, after that, optional five visual fields thereof were observed by an optical microscope at 400-fold. Thereby, the lowest temperature at which the circle-converted diameter of Cr-based nitrides becomes 2 μm or less was determined. This lowest temperature was selected as the solution treatment temperature.

(3) Tensile strength, critical pitting temperature (CPT) and depassivation pH:

A test piece was sampled from each round bar heat-treated at the selected solution treatment temperature, and a tensile strength, a critical pitting temperature (CPT) and a depassivation pH thereof were measured.
The tensile strength was measured in accordance with JIS Z2241. The critical pitting temperature (CPT) was measured in accordance with JIS G0578.
Further, with respect to the depassivation pH, the test piece was dipped in a 4.9% NaCl aqueous solution the pH of which is adjusted with HCl. A spontaneous potential thereof after the lapse of 24 hours was measured, the pH at the time when the potential transits from the active area to the passive area was determined and taken as the depassivation pH. The depassivation pH is correlative with crevice corrosion resistance, and the crevice corrosion resistance is more excellent as the depassivation pH is smaller.

[0043] The evaluation results of each sample are shown in Table 3.
In Comparative Examples 1, 2 and 9, the CPT was reduced, while the depassivation pH was raised because of excessive O, Al and C. In Comparative Examples 3, 4 and 5, the solution treatment temperature exceeded 1250°C because of excessive Mo, Cr and Ni. In Comparative Example 6, forging crack was caused because of excessive Cu. In Comparative Examples 7 and 8, the CPT was reduced, while the depassivation pH was raised because of excessive Mn and insufficient N. In Comparative Examples 11, 12 and 13, the CPT was reduced, or the depassivation pH was raised because of low PRE or CRE. In Comparative Example 10, N blow was caused in the ingot because of excessive N.
In contrast to this, in Examples 1 to 23, no N blow was caused. The solution treatment temperature was within the range of from 1050 to 1250°C. Further, the tensile strength after solution treatment was 1000 MPa or more in each case, and extremely satisfactory corrosion resistance was shown. The Ni_{eq}-Cr_{eq} was not less than 0 in each case.

[0044]

[Table 3]

		Existence of N-blow	Solution treatment (°C)	Tensile Strength (MPa)	CPT (°C)	Depassivation pH
EXAMPLES	1	None	1250	1150	>70	<0.5
	2	None	1250	1240	>70	<0.5
	3	None	1200	1189	>70	<0.5
	4	None	1150	1150	>70	<0.5
	5	None	1200	1171	>70	<0.5
	6	None	1150	1130	>70	<0.5
	7	None	1150	1160	>70	<0.5
	8	None	1100	1093	>70	0.60
	9	None	1050	1072	>70	0.60
	10	None	1150	1102	>70	<0.5
	11	None	1200	1141	>70	<0.5
	12	None	1200	1170	>70	<0.5
	13	None	1150	1141	>70	<0.5
	14	None	1150	1131	>70	<0.5
	15	None	1150	1201	>70	<0.5
	16	None	1100	1091	>70	<0.5
	17	None	1200	1120	>70	<0.5
	18	None	1150	1008	>70	<0.5
	19	None	1200	1106	>70	<0.5
	20	None	1150	1102	>70	<0.5
	21	None	1150	1114	>70	<0.5
	22	None	1150	1133	>70	<0.5
	23	None	1200	1066	>70	<0.5
COMPARATIVE EXAMPLES	1	None	1250	1144	52.5	1.03
	2	None	1200	1108	47.5	1.13
	3	None	1300	1192	>70	<0.5
	4	None	1300	1207	>70	<0.5
	5	None	1300	1157	>70	<0.5
	6	None	Forging crack	Forging crack	Forging crack	Forging crack
	7	None	1200	1146	45	0.68
	8	None	1100	932	40	0.73
	9	None	1250	1125	50	0.98
	10	Occured	—	—	—	—
	11	None	1150	1098	60	1.23
	12	None	1100	1106	22.5	1.23
	13	None	1100	1104	27.5	1.28
	14	None	1150	692	>70	<0.5
	15	None	1100	702	42.5	<0.6
	16	None	1100	599	5	1.30
	17	None	—	690	>70	<0.5
	18	None	—	420	>70	<0.5

[0045] [3.Evaluation (2)]

With respect to Examples 5, 7, 15 and 16, 50 kg of each ingot was homogenized, and then made into a sheet stock mm in thickness by hot forging and hot rolling. The solution treatment was then performed thereto at a solution treatment temperature selected in Evaluation (1). A test piece was cut out from the resulting sheet stock, and a crevice corrosion dipping test in real seawater for one year was performed. The same test was carried out also with respect to Comparative examples 14, 15, 16 and 18.

A crevice forming tool is shown in Figs. 1A and 1B. The crevice forming tool 10 includes a cylindrical projection 12 having an outside diameter of 23 mm and an inside diameter of 20.5 mm at the tip thereof, as shown in Fig. 1A. The cylindrical projection 12 includes grooves 12a having a width of 1 mm and a depth of 0.5 mm so as to form a total of twenty crevice forming parts 12b. Such a crevice forming tool 10 was fixed to both sides of a test piece 14 by a Ti-made bolt 16a and nut 16b, as shown in Fig. 1B. Namely, a total of forty crevices were formed per one test piece. Three test pieces were suspended in a place 1 m below the sea level and dipped therein for one year. After the test was ended, the number of corroded crevices among a total of one hundred and twenty crevices was measured to determine a crevice corrosion generation rate. The result is shown in Table 4.

[0046]

[Table 4]

	Crevice Corrosion Generation rate (%)	Remarks
Example 5	0	
Example 7	0	
Example 15	0	
Example 16	0	
Comparative example 14	0	SUS836L
Comparative example 15	8	SUS329J4L
Comparative example 16	62	SUS316
Comparative example 18	0	Ti

[0047] In Comparative Examples 15 (corresponding to SUS329J4L) and 16 (corresponding to SUS316), the crevice corrosion generation rates were 8% and 62%, respectively. In Examples 5, 7, 15 and 16, the crevice corrosion generation rate was 0%, and the crevice corrosion resistances were equivalent to those in Comparative Examples 14 (corresponding to SUS836L) and 18 (Ti).

[0048] [4. Evaluation (3)]

For Examples 5, 7 and 15, 50 kg of each ingot was homogenized and made into a wire rod of ϕ12.5 by hot forging and hot rolling. Then, solution treatment was performed thereto at a solution treatment temperature selected in Evaluation (1). Further, the wire rod was made into a wire rod of ϕ8.8 by cold working with a reduction ratio of 50%. A test piece was cut out from the resulting wire rod, and a tensile strength and an elongation thereof were measured. The tensile strength and the elongation were measured in accordance with JIS Z2241. The results are shown in Table 5.

As is apparent from Table 5, each of the steel stocks has a tensile strength after cold working of not less than 2000 MPa, and an elongation of not less than 10%.

[0049]

[Table 5]

	Tensile strength after 50%-Cold working (MPa)	Elongation after 50%-Cold working (%)
Example 5	2235	12.1
Example 7	2254	11.0
Example 15	2273	10.2

[0050] The embodiment of the present invention was described above in detail, but the present invention is never limited to the above-mentioned embodiment, and various modifications can be made within the scope not deviating from the gist of the present invention.

[0051] The high-nitrogen austenitic stainless steel according to the invention can be used in applications requiring seawater resistance, for example, for marine-related equipment, seashore environmental members, structural members for marine structures, seawater-desalination plant members, seawater heat exchanger members, submarine cables,

structural members for submarine structures, mooring ropes, aquaculture fish nets, bridge wires for seashore section, seawater pumps, shafts, fastening members such as bolt, nut and screw, and the like.
This high-nitrogen austenitic stainless steel can be used also for general high-strength, high-corrosive member such as bolts, nuts, cylinder liners, shafts, hubs, connectors, bearings, races, rails, gears, pins, screws, rolls, turbine blades, molds, dies, drills, valves, valve seats, cutters, nozzles, gaskets, rings, springs, industrial furnace members, chemical plant members, medicine producing members, food producing plant members, food producing device members, oil drilling members, petroleum refining plant members, refuse incinerator members, steam turbine members, gas turbine members, reactor members, aircraft members, biomass plant members, and the like.

[0052] Further, steel products reduced in content of Ni are particularly applicable to biological materials and accessories, and can be used, for example, for:

(1) accessories such as necklaces, pierces or rings, back lids for watches, watch bands, eyeglass frames, interdental brushes and the like, which directly touch human bodies;
(2) dental materials such as artificial roots and correction wires, which are used within living bodies;
(3) implant materials such as plates, bolts, nuts, springs, screws, wires, electrodes, artificial bones, and artificial joints;
(4) medical instruments such as injection needles, knives, surgical knives, scissors, forceps, and drills.

[0053] Further, steel products sufficiently ensuring stability of austenite phase can be used as nonmagnetic, high-strength, and high-corrosive resistance materials for:

(1) springs, shafts, bearings, races, pins, dies, and rails for precision electronic parts;
(2) wires and meshes for printed board manufacturing parts;
(3) biological implant electrodes, MRI parts, and MRI-responding biological implant members; and
(4) medicine producing members, hanger members, linear motor car members, semiconductor manufacturing device parts, pincettes, bearing, scissors, cutters, and the like.

Claims

1. A high-nitrogen austenitic stainless steel, comprising:

$0.005\text{ mass\%} \leq C \leq 0.25\text{ mass\%}$;
$15.0\text{ mass\%} \leq Cr \leq 35.0\text{ mass\%}$;
$0.2\text{ mass\%} < Mn < 10.0\text{ mass\%}$;
$0.05\text{ mass\%} \leq Mo \leq 8.0\text{ mass\%}$;
$0.01\text{ mass\%} \leq Cu \leq 4.0\text{ mass\%}$;
$0.01\text{ mass\%} \leq Ni \leq 5.0\text{ mass\%}$;
$0.8\text{ mass\%} < N \leq 1.8\text{ mass\%}$;
$Si \leq 2.0\text{ mass\%}$;
$P \leq 0.03\text{ mass\%}$;
$S \leq 0.05\text{ mass\%}$;
$Al \leq 0.030\text{ mass\%}$;
$O \leq 0.020\text{ mass\%}$, and

having:

PRE represented by an equation (1) and of not less than 5,

$$PRE = (Cr+3.3Mo+16N)/Mn \text{ (mass\%)} \ldots (1)$$

and
CRE represented by an equation (2) and of not less than 27,

$$CRE = Cr+1.5Mo+2N+Cu \text{ (mass\%)} \ldots (2)$$

and

further optionally containing one or more elements selected from the group consisting of:

at least one of:

0.01 mass%$\leq W \leq 8.0$ mass%; and
0.01 mass%$\leq Co \leq 5.0$ mass%;

at least one of:

0.01 mass%$\leq Ti \leq 0.5$ mass%;
0.01 mass%$\leq Nb \leq 0.5$ mass%;
0.01 mass%$\leq V \leq 1.0$ mass%;
0.01 mass%$\leq Ta \leq 0.5$ mass%; and
0.01 mass%$\leq Zr \leq 0.5$ mass%;

at least one of:

0.001 mass%$\leq B \leq 0.01$ mass%;
0.001 mass%$\leq Ca \leq 0.01$ mass%; and
0.001 mass%$\leq Mg \leq 0.01$ mass%;

at least one of:

0.005 mass%$\leq Te \leq 0.05$ mass%; and
0.01 mass%$\leq Se \leq 0.20$ mass%; and

the balance substantially containing Fe and impurities.

2. The high-nitrogen austenitic stainless steel according to claim 1, wherein an index of stability of austenite phase: $Ni_{eq}-Cr_{eq}$ is not less than 0, wherein

$Ni_{eq} = Ni+Co+0.5Mn+0.3Cu+25N+30C$
$Cr_{eq} = Cr+2Si+1.5Mo+5V+5.5A1+1.75Nb+1.5Ti+0.75W$.

3. The high-nitrogen austenitic stainless steel according to claim 1 or 2, wherein tensile strength in a solution-treated state is not less than 1000 MPa.

4. The high-nitrogen austenitic stainless steel according to claim 1 or 2, wherein tensile strength after solution treatment and cold working is not less than 1800 MPa.

5. The high-nitrogen austenitic stainless steel according to claim 1 or 2, wherein tensile strength after solution treatment and cold working is not less than 2000 MPa, and elongation is not less than 10%.

6. The high-nitrogen austenitic stainless steel according to claim 3, wherein tensile strength after solution treatment and cold working is not less than 1800 MPa.

7. The high-nitrogen austenitic stainless steel according to claim 3, wherein tensile strength after solution treatment and cold working is not less than 2000 MPa, and elongation is not less than 10%.

8. The high-nitrogen austenitic stainless steel according to claim 4, wherein tensile strength after solution treatment and cold working is not less than 2000 MPa, and elongation is not less than 10%.

9. The high-nitrogen austenitic stainless steel according to claim 6, wherein tensile strength after solution treatment and cold working is not less than 2000 MPa, and elongation is not less than 10%.

Fig. 1A

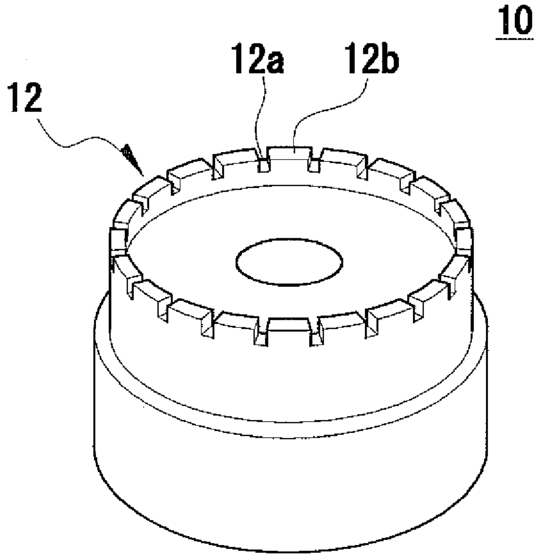
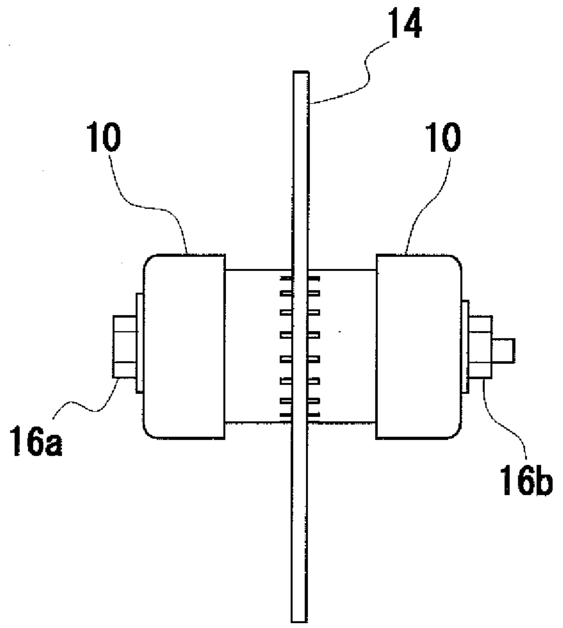


Fig. 1B



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EUROPEAN SEARCH REPORT

Application Number
EP 06 12 3231

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 1 229 142 A (DAIDO STEEL CO LTD [JP]) 7 August 2002 (2002-08-07) * claims 1-7 * * page 2, paragraph 1 - page 5, paragraph 36 * * table 1 * -----	1-9	INV. C22C38/58 C22C38/44 C22C38/42 C22C38/00 C21D6/00
P,X	EP 1 626 101 A (DAIDO STEEL CO LTD [JP]) 15 February 2006 (2006-02-15) * claims 1-6 * * page 2, paragraph 1 - page 8, paragraph 44 * * tables 1-4 * * page 12, paragraph 47 - paragraph 49 * -----	1-9	
D,X	JP 2000 309857 A (NAT RES INST METALS) 7 November 2000 (2000-11-07) * the whole document * -----	1-9	
X	GB 2 055 122 A (INST PO METALLOZNANIE I TEKNO) 25 February 1981 (1981-02-25) * claims 1-4 * * page 1, line 1 - line 55 * -----	1-9	TECHNICAL FIELDS SEARCHED (IPC) C22C C21D
X	DE 196 07 828 A1 (VSG EN & SCHMIEDETECHNIK GMBH [DE] VSG EN UND SCHMIEDETECHNIK GMB [DE]) 17 October 1996 (1996-10-17) * claims 1-11 * * page 2, line 1 - page 3, line 20 * * examples 1,2 * -----	1-9	
D,X	JP 10 183303 A (VSG ENERG & SCHMIEDETECHNIK GM) 14 July 1998 (1998-07-14)	1,3-9	
A	* the whole document * ----- -/--	2	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	20 February 2007	Vlassi, Eleni

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
EP 06 12 3231

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X A	CH 688 862 A5 (BASF AG [DE]) 30 April 1998 (1998-04-30) * claims 1-7 * * page 2, line 1 - page 4, line 22 * -----	1,3-9 2	
X A	CH 688 914 A5 (BASF AG [DE]) 29 May 1998 (1998-05-29) * claims 1-11 * * page 2, line 1 - page 4, line 57 * -----	1,3-9 2	
X	US 6 682 581 B1 (SPEIDEL MARKUS [CH]) 27 January 2004 (2004-01-27) * claims 1-7 * -----	1,3-9	
A	US 4 116 683 A (NIKOLOV IVAN DIMOV ET AL) 26 September 1978 (1978-09-26) * claims 1-4 * -----	1-9	
A	US 6 682 582 B1 (SPEIDEL MARKUS [CH]) 27 January 2004 (2004-01-27) * claims 1-8 * -----	1-9	TECHNICAL FIELDS SEARCHED (IPC)
A	WO 91/16469 A (CARPENTER TECHNOLOGY CORP [US]) 31 October 1991 (1991-10-31) * claims 1-9 * -----	1-9	
A	US 3 904 401 A (MERTZ DAVID L ET AL) 9 September 1975 (1975-09-09) * claims 1-10 * -----	1-9	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	20 February 2007	Vlassi, Eleni

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-02-2007

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1229142 A	07-08-2002	JP 2002235153 A	23-08-2002
		US 2002148537 A1	17-10-2002
EP 1626101 A	15-02-2006	JP 2006052452 A	23-02-2006
		US 2006034724 A1	16-02-2006
JP 2000309857 A	07-11-2000	JP 3598364 B2	08-12-2004
GB 2055122 A	25-02-1981	BG 29797 A1	16-02-1981
		DE 3023590 A1	22-01-1981
		JP 56020151 A	25-02-1981
DE 19607828 A1	17-10-1996	NONE	
JP 10183303 A	14-07-1998	DE 19513407 C1	10-10-1996
		US 5714115 A	03-02-1998
		ZA 9602761 A	30-07-1996
CH 688862 A5	30-04-1998	NONE	
CH 688914 A5	29-05-1998	NONE	
US 6682581 B1	27-01-2004	AU 5676300 A	18-12-2000
		CA 2372563 A1	07-12-2000
		CH 694401 A5	31-12-2004
		CN 1351674 A	29-05-2002
		WO 0073528 A1	07-12-2000
		EP 1198604 A1	24-04-2002
		JP 2003500544 T	07-01-2003
US 4116683 A	26-09-1978	NONE	
US 6682582 B1	27-01-2004	AU 5072400 A	31-01-2001
		CN 1373815 A	09-10-2002
		CN 1495281 A	12-05-2004
		WO 0100897 A1	04-01-2001
		EP 1194605 A1	10-04-2002
		JP 3798317 B2	19-07-2006
		JP 2003503595 T	28-01-2003
WO 9116469 A	31-10-1991	AT 405058 B	25-05-1999
		AT 901191 A	15-09-1998
		CA 2079914 A1	13-10-1991
		GB 2257713 A	20-01-1993
		US 5094812 A	10-03-1992
		US 5308577 A	03-05-1994

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 06 12 3231

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-02-2007

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3904401 A	09-09-1975	CA 1023580 A1	03-01-1978

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 10183303 A **[0005] [0008]**
- JP 2000309857 A **[0006] [0008]**
- JP 2002235153 A **[0007] [0008]**