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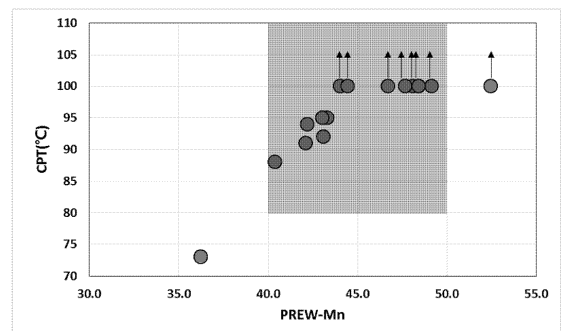
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(54) **HIGHLY CORROSION-RESISTANT AUSTENITIC STAINLESS STEEL HAVING EXCELLENT IMPACT TOUGHNESS AND HOT WORKABILITY**

(57) Disclosed is a highly corrosion-resistant austenitic stainless steel having excellent impact toughness and hot workability. According to one embodiment of the disclosed highly corrosion-resistant austenitic stainless steel, the highly corrosion-resistant austenitic stainless steel includes, in percent by weight (wt%), 0.03% or less (excluding 0) of carbon (C), 1.0% or less of silicon (Si), 1.0% or less of manganese (Mn), 18 to 24% of chromium (Cr), 16 to 24% of nickel (Ni), 5 to 7% of molybdenum (Mo), 0.1 to 2.0% of copper (Cu), 1.0% or less of tungsten (W), 0.18 to 0.3% of nitrogen (N), 0.02 to 0.1% of aluminum (Al), 0.01% or less of oxygen (O), 0.002 to 0.01% calcium (Ca), less than 0.001% of sulfur (S), and the remainder of iron (Fe) and inevitable impurities, and satisfies an O/Al ratio of 0.01 to 0.12 and a S/Ca ratio of 0.01 to 0.4.

[FIG. 1]



Description

[Technical Field]

[0001] The present disclosure relates to a highly corrosion-resistant austenitic stainless steel having excellent impact toughness and hot workability. The austenitic stainless steel according to the present disclosure may be applied as materials for industrial facilities such as desulfurization facilities, heat exchangers, desalination facilities, and food and beverage facilities.

[Background Art]

[0002] Austenitic stainless steels have been used in a wide range of industrial applications due to excellent corrosion resistance, workability, and weldability. STS 316 stainless steels, which have improved corrosion resistance and are manufactured by adding 2% molybdenum (Mo) to STS 304 stainless steels characterized by 18Cr-8Ni components, have been applied to various industrial fields such as kitchens, home appliances, and industrial facilities.

[0003] Corrosion resistance of austenitic stainless steels may be obtained by adding elements such as Cr, Mo, and N. However, increases in contents of these elements such as Cr, Mo, and N added thereto cause precipitation of intermetallic compounds such as a σ phase in a matrix structure to deteriorate corrosion resistance and impact toughness and thus hot workability significantly deteriorates thereby.

[0004] To solve such problems, Patent Documents 1 and 2 disclose techniques for inhibiting formation of the sigma (σ) phase by adding tungsten (W) instead of molybdenum (Mo). However, it is not preferable to add W instead of Mo because a highly alloyed austenitic stainless steel should generally include components within standard ranges. In addition, when a large amount of W is contained, there is a risk that another intermetallic compound such as a chi (χ) phase may be precipitated.

[0005] In Patent Document 3, the sigma phase (σ) is controlled by adjusting a sigma (σ) equivalent (SGR) represented by the following equation to 18 or less. However, in Patent Document 3, only Cr, Mo, N, Mn, and Cu are limitedly considered as alloying elements affecting the control of the sigma (σ) phase, and there is still a problem that intermetallic compounds such as the sigma (σ) phase are still precipitated in a matrix structure.

$$\text{SGR} = \text{Cr} + 2\text{Mo} - 40\text{N} + 0.5\text{Mn} - 2\text{Cu}$$

[0006] (Patent Document 0001) Korean Patent Laid-open Publication No. 10-2001-0026770 (April 06, 2001)

[0007] (Patent Document 0002) Korean Patent Laid-open Publication No. 10-1999-0005962 (September 15, 2000)

[0008] (Patent Document 0003) US Patent Publication No. 2015-0050180 (February 19, 2015)

[Disclosure]

[Technical Problem]

[0009] To solve the aforementioned problems, the present disclosure provides a highly corrosion-resistant austenitic stainless steel having hot workability together with excellent corrosion resistance and impact toughness.

[Technical Solution]

[0010] In accordance with an aspect of the present disclosure, a highly corrosion-resistant austenitic stainless steel having excellent impact toughness and hot workability includes, in percent by weight (wt%), 0.03% or less (excluding 0) of carbon (C), 1.0% or less of silicon (Si), 1.0% or less of manganese (Mn), 18 to 24% of chromium (Cr), 16 to 24% of nickel (Ni), 5 to 7% of molybdenum (Mo), 0.1 to 2.0% of copper (Cu), 1.0% or less of tungsten (W), 0.18 to 0.3% of nitrogen (N), 0.02 to 0.1% of aluminum (Al), 0.01% or less of oxygen (O), 0.002 to 0.01% calcium (Ca), less than 0.001% of sulfur (S), and the remainder of iron (Fe) and inevitable impurities, and satisfies an O/Al ratio of 0.01 to 0.12 and a S/Ca ratio of 0.01 to 0.4.

[0011] In each highly corrosion-resistant austenitic stainless steel having excellent impact toughness and hot workability according to the present disclosure, an impact toughness value (CNV_{TH}) represented by Formula (1) below may be 80 or more.

$$(1) \text{CNV}_{\text{TH}} = 336 - 1432 \cdot \text{C} - 22.1 \cdot \text{Si} + 64.1 \cdot \text{Mn} + 8.5 \cdot \text{Cr} + 0.11 \cdot \text{Ni} \\ - 10.1 \cdot \text{Mo} - 3.3 \cdot \text{Cu} + 22.1 \cdot \text{W} - 392 \cdot \text{N} - 293 \cdot (\text{T}_{\sigma}/\text{T})$$

[0012] In Formula (1), C, Si, Mn, Cr, Ni, Mo, Cu, W, and N denote contents (wt%) of the alloying elements, T_{σ} refers to a temperature at which the sigma (σ) phase is completely, thermodynamically decomposed, and T refers to an actual solution heat treatment temperature.

[0013] In each highly corrosion-resistant austenitic stainless steel having excellent impact toughness and hot workability according to the present disclosure, a PREW-Mn value represented by Formula (2) below may be from 40 to 50.

$$(2) \text{PREW-Mn} = \text{Cr} + 3.3 \cdot (\text{Mo} + 0.5 \cdot \text{W}) + 16 \cdot \text{N} - 0.5 \cdot \text{Mn}$$

[0014] In Formula (2), Cr, Mo, W, N, and Mn denote contents (wt%) of the respective alloying elements.

[0015] In each highly corrosion-resistant austenitic stainless steel having excellent impact toughness and hot workability according to the present disclosure, a σ phase area ratio measured in an area of 26 mm² at a depth of 1/4 to 3/4 in thickness from the surface at a magnification of 50 $\times$ may be 1.0% or less.

[0016] In each highly corrosion-resistant austenitic stainless steel having excellent impact toughness and hot workability according to the present disclosure, the critical pitting temperature may be 80°C or higher.

[Advantageous Effects]

[0017] According to the present disclosure, a highly corrosion-resistant austenitic stainless steel having excellent hot workability together with excellent corrosion resistance and impact toughness and may be provided and the austenitic stainless steel may be applied as materials for industrial facilities such as desulfurization facilities, heat exchangers, desalination facilities, and food and beverage facilities.

[0018] Excellent corrosion resistance may be obtained by adjusting a PREW-Mn value in a range of 40 to 50 within alloying elements suggested in the present disclosure and inhibiting formation of intermetallic compounds, excellent impact toughness may be obtained by adjusting alloying elements and heat treatment conditions to have an impact toughness value (CNV_{TH}) of 80 or more, and excellent hot workability may be obtained by adjusting contents of elements used in trace amounts to satisfy an O/Al ratio of 0.01 to 0.12 and a S/Ca ratio of 0.01 to 0.4.

[Description of Drawings]

[0019]

FIG. 1 is a graph showing critical pitting temperatures (CPT) of samples of Examples with respect to PREW-Mn.

FIG. 2 is a graph showing S/Ca and O/Al values of samples of Examples.

[Best Mode]

[0020] The highly corrosion-resistant austenitic stainless steel having excellent impact toughness and hot workability according to an embodiment of the present disclosure includes, in percent by weight (wt%), 0.03% or less (excluding O) of carbon (C), 1.0% or less of silicon (Si), 1.0% or less of manganese (Mn), 18 to 24% of chromium (Cr), 16 to 24% of nickel (Ni), 5 to 7% of molybdenum (Mo), 0.1 to 2.0% of copper (Cu), 1.0% or less of tungsten (W), 0.18 to 0.3% of nitrogen (N), 0.02 to 0.1% of aluminum (Al), 0.01% or less of oxygen (O), 0.002 to 0.01% calcium (Ca), less than 0.001% of sulfur (S), and the remainder of iron (Fe) and inevitable impurities, and satisfies an O/Al ratio of 0.01 to 0.12 and a S/Ca ratio of 0.01 to 0.4.

[Modes of the Invention]

[0021] Hereinafter, preferred embodiments of the present disclosure will now be described. However, the present disclosure may be embodied in many different forms and should not be construed as being limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the disclosure to those skilled in the art.

[0022] The terms used herein are merely used to describe particular embodiments. Thus, an expression used in the

singular encompasses the expression of the plural, unless it has a clearly different meaning in the context. In addition, it is to be understood that the terms such as "including" or "having" are intended to indicate the existence of features, steps, functions, components, or combinations thereof disclosed in the specification, and are not intended to preclude the possibility that one or more other features, steps, functions, components, or combinations thereof may exist or may be added.

[0023] Meanwhile, unless otherwise defined, all terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Thus, these terms should not be interpreted in an idealized or overly formal sense unless expressly so defined herein. As used herein, the singular forms are intended to include the plural forms as well, unless the context clearly indicates otherwise.

[0024] In addition, the terms "about", "substantially", etc. used throughout the specification mean that when a natural manufacturing and substance allowable error are suggested, such an allowable error corresponds a value or is similar to the value, and such values are intended for the sake of clear understanding of the present invention or to prevent an unconscious infringer from illegally using the disclosure of the present invention.

[0025] A highly corrosion-resistant austenitic stainless steel having excellent impact toughness and hot workability according to an embodiment of the present disclosure may include, in percent by weight (wt%), 0.03% or less of carbon (C), 1.0% or less of silicon (Si), 1.0% or less of manganese (Mn), 18 to 24% of chromium (Cr), 16 to 24% of nickel (Ni), 5 to 7% of molybdenum (Mo), 0.1 to 2.0% of copper (Cu), 1.0% or less of tungsten (W), 0.18 to 0.3% of nitrogen (N), 0.02 to 0.1% of aluminum (Al), 0.01% or less of oxygen (O), 0.002 to 0.01% calcium (Ca), less than 0.001% of sulfur (S), and the remainder of iron (Fe) and inevitable impurities.

[0026] Hereinafter, reasons for numerical limitations on the contents of alloy components in the embodiment of the present disclosure will be described. Hereinafter, the composition of the component indicates wt% unless otherwise stated.

Carbon (C): 0.03 wt% or less (excluding 0)

[0027] C is a strong austenite phase-stabilizing element and increases strength by solid solution strengthening effects. However, when the C content is excessive, C easily binds to a carbide-forming element such as Cr, which is effective on corrosion resistance, in boundaries of an austenite phase to form a carbide, and the formed carbide lowers the Cr content around grain boundaries, thereby deteriorating corrosion resistance. Therefore, an upper limit of the C content may be set to 0.03 wt%.

Silicon (Si): 1.0 wt% or less

[0028] Si is a ferrite phase-stabilizing element, enhances corrosion resistance, and serves as a deoxidizer. However, an excess of Si promotes precipitation of intermetallic compounds such as sigma (σ) phase, thereby deteriorating mechanical properties related to impact toughness and corrosion resistance and causing cracks during hot rolling. Therefore, an upper limit of the Si content may be set to 1.0 wt%.

Manganese (Mn): 1.0 wt% or less

[0029] Mn is an austenite phase stabilizing element and enhances solid solubility of N. However, an excess of Mn may cause formation of inclusions such as MnS to deteriorate corrosion resistance. Therefore, an upper limit of the Mn content may be set to 1.0 wt%.

Chromium (Cr): 18 to 24 wt%

[0030] Cr is a representative element effective on enhancing corrosion resistance of stainless steel. In the present disclosure, the Cr may be added in an amount of 18 wt% or more to obtain excellent corrosion resistance having a PREW-Mn of 40 or more. However, because Cr is a ferrite phase-stabilizing element, an excess of Cr may cause an increase in ferrite fractions to deteriorate hot workability and promote formation of the σ phase to deteriorate mechanical properties and corrosion resistance. Therefore, an upper limit of the Cr content may be set to 24 wt%.

Nickel (Ni): 16 to 24 wt%

[0031] Ni is the strongest austenite phase-stabilizing element and may be added in an amount of 16 wt% or more to maintain the austenite phase. However, as the Ni content increases, costs for raw materials increase, and therefore an upper limit of the Ni content may be set to 24 wt%.

Molybdenum (Mo): 5.0 to 7.0 wt%

[0032] Mo is a ferrite phase-stabilizing element and enhances corrosion resistance. In the present disclosure, to obtain excellent corrosion resistance having a PREW-Mn value of 40 or more, Mo may be added in an amount of 5.0 wt% or more. Although Mo is effective on mechanical properties and corrosion resistance during annealing processes, but Mo is known to form the σ phase during aging heat treatment, hot rolling, or welding. Thus, an excess Mo content may promote formation of the σ phase to deteriorate mechanical properties and corrosion resistance. Therefore, an upper limit of the Mo content may be set to 7.0 wt%.

Copper (Cu): 0.1 to 2.0 wt%

[0033] Cu, as an austenite phase-stabilizing element, inhibits phase transformation into a martensite phase during cold deformation and enhances corrosion resistance in a sulfur atmosphere. To this end, Cu may be added in an amount of 0.1 wt% or more. However, an excess of Cu may deteriorate pitting corrosion resistance in a chlorine atmosphere and deteriorate hot workability. Therefore, an upper limit of the Cu content may be set to 2.0 wt%.

Tungsten (W): 1.0 wt% or less

[0034] W is a ferrite phase-stabilizing element and enhances corrosion resistance. Also, due to a large atomic radius, W is known as an element effective on inhibiting formation of the σ phase by preventing diffusion of Cr and Mo at a high temperature. However, a highly alloyed austenitic stainless steel may include components within standard ranges, and an excess of W may promote precipitation of intermetallic compounds such as a chi (χ) phase to deteriorate corrosion resistance and impact toughness and deteriorate hot workability. Therefore, an upper limit of the W content may be set to 1.0 wt%.

Nitrogen (N): 0.18 to 0.3 wt%

[0035] N is an austenite phase-stabilizing element and enhances corrosion resistance in a chlorine atmosphere. Therefore, N may be added in an amount of 0.18 wt% or more to enhance corrosion resistance. However, an excess of N deteriorates hot workability, and thus an upper limit of the N content may be set to 0.3 wt%.

Aluminum (Al): 0.02 to 0.1 wt%

[0036] Al, serving as a strong deoxidizer, binds to oxygen to form slag and remove oxygen from molten steel, thereby improving hot workability of steel. In view of this property, Al may be added in an amount of 0.02 wt% or more. However, an excess of Al may cause formation of nonmetallic inclusions thereby deteriorating cleanliness of steel and also cause formation of AlN thereby deteriorating impact toughness. Therefore, an upper limit of the Al content may be set to 0.1 wt%.

Oxygen (O): 0.01 wt% or less

[0037] O deteriorates hot workability of steel by segregating to grain boundaries. Thus, it is preferable to decrease the O content as low as possible, and an upper limit of the O content may be adjusted to 0.01 wt%. To further improve hot workability, the O content may preferably be adjusted to 0.0035 wt% or less.

Calcium (Ca): 0.002 to 0.01 wt%

[0038] Ca is an element serving as a deoxidizer and bind to S contained in molten steel to form a stable CaS compound, thereby inhibiting a tendency of sulfur segregation to grain boundaries resulting in enhancement of hot workability of steel. In view of this property, Ca may be added in an amount of 0.002 wt% or more. However, an excess of Ca may cause formation of non-metallic inclusions increasing a risk of lowering cleanliness of the steel. Accordingly, it is preferable to adjust an upper limit of the Ca content to 0.01 wt%. To increase cleanliness of the steel, the upper limit of the Ca content may be set to 0.0045 wt%.

Sulfur (S): less than 0.001 wt%

[0039] S is an element deteriorating hot workability by segregating to grain boundaries. Therefore, an upper limit of the S content may be controlled to be less than 0.001 wt%.

[0040] The remaining component of the present disclosure is iron (Fe). However, since in a common steel manufacturing

process, unintended impurities may be inevitably incorporated from raw materials or the surrounding environment, they may not be excluded. Since these impurities are known to any person skilled in the common steel manufacturing process, the entire contents thereof are not particularly mentioned in the present specification.

[0041] The austenitic stainless steel according to of the present disclosure may be applied as a material to industrial facilities such as desulfurization facilities, heat exchangers, desalination facilities, and food and beverage facilities. Hereinafter, technical methods for obtaining corrosion resistance of steel according to the present disclosure will be described in detail.

[0042] In general, corrosion resistance of austenitic stainless steels is indirectly expressed by pitting resistance equivalent number (PREN). The pitting resistance equivalent number (PREN) is represented by the following equation using contents of Cr, Mo, and N which are elements affecting corrosion resistance. In the following equation, each alloying element indicates wt% thereof.

$$\text{PREN} = \text{Cr} + 3.3 * \text{Mo} + 16 * \text{N}$$

[0043] However, W is also an element enhancing corrosion resistance of austenitic stainless steels and Mn is an element adversely affecting corrosion resistance by forming water-soluble inclusions. Thus, expressing corrosion resistance using the PREN equation defined above is limited. Accordingly, in the present disclosure, the PREN equation is modified to PREW-Mn represented by the following equation by further considering influences of both W and Mn. In the following equation, each alloying element indicates wt% thereof.

$$\text{PREW-Mn} = \text{Cr} + 3.3 * (\text{Mo} + 0.5 * \text{W}) + 16 * \text{N} - 0.5 * \text{Mn}$$

[0044] In order to obtain sufficient corrosion resistance of steel in an extremely corrosive environment, e.g., an environment containing a large amount of salt such as seawater or an environment containing an acidic substance, the PREW-Mn value may be from 40 to 50. When the PREW-Mn value is less than 40, sufficient corrosion resistance cannot be obtained and thus steel cannot withstand for a long time. On the contrary, when the PREW-Mn value is more than 50, intermetallic compounds, such as a σ phase, precipitated in the matrix structure due to large amounts of Cr, Mo, and W may deteriorate corrosion resistance. As a result of controlling the PREW-Mn value in the range of 40 to 50, a critical pitting temperature of the austenitic stainless steel according to an embodiment of the present disclosure may be 80°C or higher.

[0045] In addition, the austenitic stainless steel according to an embodiment has excellent impact toughness. Hereinafter, technical methods for obtaining impact toughness of steel according to the present disclosure will be described in detail.

[0046] Impact toughness of steel may be determined by intermetallic compounds. The intermetallic compound is mainly a σ phase including Cr and Mo, and the σ phase is precipitated in the matrix structure to deteriorate corrosion resistance, impact toughness, and hot workability. Because increases in the contents of the alloying elements such as Cr and Mo promote formation of the σ phase, the alloying elements need to be appropriately adjusted to inhibit formation of the σ phase.

[0047] In addition, when steel is subjected to solution heat treatment at a high temperature, the elements of the σ phase such as Cr and Mo are diffused into the matrix structure, resulting in decomposition of the σ phase. In general, a solution heat treatment temperature of 316 austenitic stainless steels containing Mo and having excellent corrosion resistance is 1,100°C or higher, and thus a solution heat treatment for decomposing the σ phase according to the present disclosure may be equal to or higher than 1,100°C. However, excessive, high-temperature, and prolonged solution heat treatment affects an apparatus for the heat treatment, and thus the solution heat treatment temperature is controlled to 1,200°C or below.

[0048] Since formation and decomposition of the σ phase are affected by alloying elements and solution heat treatment temperature, conditions for solution heat treatment and the alloying elements need to be appropriately controlled to inhibit the σ phase that deteriorates impact toughness. In the present disclosure, an impact toughness value (CNV_{TH}) as a function of the alloying elements and the solution heat treatment temperature represented by the following equation may be controlled to be 80 or more to obtain impact toughness. The CNV_{TH} value corresponds to a theoretical value of impact toughness according to the present disclosure. In the CNV_{TH} defined below, T_{σ} is a temperature at which the σ phase is completely, thermodynamically decomposed and T is an actual solution heat treatment temperature. In the following CNV_{TH} equation, each alloying element indicates wt% thereof and T has a value of 1,100 to 1,200°C.

$$\text{CNV}_{\text{TH}} = 336 - 1432 \cdot \text{C} - 22.1 \cdot \text{Si} + 64.1 \cdot \text{Mn} + 8.5 \cdot \text{Cr} + 0.11 \cdot \text{Ni} - 10.1 \cdot \text{Mo} - 3.3 \cdot \text{Cu} + 22.1 \cdot \text{W} - 392 \cdot \text{N} - 293 \cdot (\text{T}_\sigma / \text{T})$$

[0049] As a result of controlling the CNV_{TH} value to 80 or more according to the present disclosure, formation of the σ phase may be inhibited. For example, in the austenitic stainless steel of the present disclosure, a σ phase area ratio measured in an area of 26 mm² at a depth of 1/4 to 3/4 in thickness from the surface at a magnification of 50x may be 1.0% or less.

[0050] In addition, the austenitic stainless steel according to the present disclosure has excellent hot workability. Hereinafter, technical methods for obtaining hot workability of steel according to the present disclosure will be described in detail.

[0051] To obtain corrosion resistance of austenitic stainless steels, it is essential to add large amounts of alloying elements such as Cr, Mo, and N to the steel. When contents of these elements such as Cr, Mo, and N increase, grain boundaries are embrittled during hot working due to segregation of impurities to the grain boundaries, thereby deteriorating hot workability. Therefore, to obtain hot workability together with corrosion resistance, it is important to prevent embrittlement of grain boundaries by minimizing segregation of impurities to the grain boundaries while adding the alloying elements such as Cr, Mo, and N.

[0052] Oxygen (O) and sulfur (S) are representative impurities segregated to grain boundaries of austenitic stainless steels. In the present disclosure, excellent hot workability may be obtained by minimizing impurities such as oxygen and sulfur segregated to grain boundaries by controlling elements used in trace amounts.

[0053] In order to lower the O content in steel, a deoxidization process is important and Al may be used as a main deoxidizer. Al binds to O to form slag and removes oxygen from molten steel, resulting in enhancement of hot workability of steel. However, an excess of Al causes formation of nonmetallic inclusions to deteriorate cleanliness of steel and impact toughness of steel may be deteriorated by formation of AlN. In consideration of these properties, in the present disclosure, changes in O contents by addition of Al are indexed to an O/Al ratio and the O/Al ratio may be adjusted in the range of 0.01 to 0.12.

[0054] In addition, in the present disclosure, Ca, which binds to S contained in molten steel to form a stable CaS compound, is added to steel to reduce the S content in the steel. Ca inhibits a tendency of sulfur segregation to grain boundaries by forming a CaS compound, thereby enhancing hot workability of steel. However, an excess of Ca may cause formation of nonmetallic inclusions, thereby increasing a risk of deteriorating cleanliness of steel. In consideration of these properties, in the present disclosure, changes in S contents by addition of Ca are intended to a S/Ca ratio and the S/Ca ratio may be adjusted in the range of 0.01 to 0.4.

[0055] In the present disclosure, occurrence of cracks at the surface or edges of steel is prevented during hot working by controlling the O/Al ratio in the range of 0.01 to 0.12 and the S/Ca ratio in the range of 0.01 to 0.4.

[0056] According to the present disclosure, excellent corrosion resistance may be obtained by adjusting the PREW-Mn value in the range of 40 to 50, excellent impact toughness may be obtained by adjusting alloying elements and controlling heat treatment conditions to have an impact toughness value (CNV_{TH}) of 80 or more, and excellent hot workability may be obtained by adjusting elements used in trace amounts to satisfy an O/Al ratio of 0.01 to 0.12 and a S/Ca ratio of 0.01 to 0.4.

[0057] Hereinafter, the present disclosure will be described in more detail through examples. However, it is necessary to note that the following examples are only intended to illustrate the present disclosure in more detail and are not intended to limit the scope of the present disclosure. This is because the scope of the present disclosure is determined by matters described in the claims and able to be reasonably inferred therefrom.

Examples

[0058] Steels respectively having the chemical compositions shown in Table 1 below were melted in a vacuum induction melting furnace, hot-rolled, and subjected to solution heat treatment at a temperature of 1,100 to 1,200°C to prepare hot-rolled steel sheets having a thickness of 5 mm.

Table 1

	Alloy composition (wt%)										
	C	Si	Mn	Cr	Ni	Mo	Cu	W	N	Al	O
Example 1	0.020	0.4	0.5	20.0	18.0	6.1	0.7	0.0	0.20	0.07	0.0024
Example 2	0.015	0.5	0.6	20.5	17.4	6.2	1.8	0.0	0.21	0.05	0.0020
Example 3	0.018	0.3	0.8	23.6	20.3	6.5	2.0	0.0	0.28	0.09	0.0010
Example 4	0.015	0.7	0.5	22.8	22.1	6.3	0.3	0.0	0.27	0.08	0.0012
Example 5	0.009	0.6	0.5	19.9	20.5	6.2	0.8	0.0	0.20	0.06	0.0022
Example 6	0.017	0.3	0.6	19.5	23.6	5.9	0.7	0.0	0.22	0.03	0.0030
Example 7	0.026	0.6	0.6	21.5	23.8	5.1	1.8	0.6	0.25	0.09	0.0010
Example 8	0.013	0.2	0.7	18.8	21.0	5.9	1.3	0.5	0.21	0.05	0.0031
Comparative Example 1	0.021	1.2*	0.4	23.0	21.2	6.5	0.9	0.0	0.26	0.05	0.0021
Comparative Example 2	0.023	1.5*	0.5	22.5	23.0	6.1	0.2	0.1	0.26	0.08	0.0020
Comparative Example 3	0.014	0.2	0.6	17.5*	16.2	4.9*	1.2	0.0	0.18	0.05	0.0026
Comparative Example 4	0.018	0.4	0.6	24.5*	23.3	7.2*	0.5	0.0	0.28	0.04	0.0048
Comparative Example 5	0.016	0.8	0.7	20.8	20.3	6.2	0.8	0.1	0.21	0.00*	0.0090
Comparative Example 6	0.018	0.9	0.8	22.7	21.9	6.6	1.0	0.0	0.25	0.01*	0.0084
Comparative Example 7	0.025	0.5	0.3	18.2	16.4	5.5	0.9	0.8	0.18	0.04	0.0052
(* is out of the range defined by the present disclosure.)											

[0059] Table 2 shows PREW-Mn values, critical pitting temperatures (CPT), T_{σ} values, T values, O/Al ratios, S/Ca ratios, surface cracks, σ phase area ratios, and impact toughness values (CNV_{TH} and CNV_{EX}) according to components according to examples and comparative examples.

[0060] The PREW-Mn values of Table 2 are obtained by substituting the contents (wt%) of the respective alloying elements of Table 1 into the following equation.

$$PREW-Mn = Cr + 3.3*(Mo + 0.5*W) + 16*N - 0.5*Mn$$

[0061] The critical pitting temperature (CPT) of Table 2 was obtained by measuring a CRT from the surface according to the ASTM G150 standards, and a higher CPT indicates better corrosion resistance. Among austenitic stainless steels, a CPT of a super austenitic stainless steel having the highest corrosion resistance measured according to the above-described method was 80°C or higher. Based thereon, in the present disclosure, a critical pitting temperature of 80°C or higher was judged as sufficient corrosion resistance.

[0062] In Table 2, T_{σ} is a temperature at which the sigma (σ) phase is completely, thermodynamically decomposed, and T refers to an actual solution heat treatment temperature.

[0063] In Table 2, the O/Al ratio and the S/Ca ratio are obtained by substituting the contents (wt%) of the respective alloying elements of Table 1.

[0064] With regard to the surface crack of Table 2, a case where less than 5 cracks having a length of 5 mm were observed in an area of 150 mm x 250 mm was marked as 'Good', and more than 5 cracks was marked as 'Bad'.

[0065] The σ phase area ratio of Table 2 is calculated by polishing a cross-section of a steel with a diamond paste having a size of 1 μ m after final annealing, etching the steel with a NaOH solution to prepare a sample in which the σ phase is distinguished from a matrix structure, and consecutively measuring 10 fields of view in an area of 26 mm² at a depth of 1/4 to 3/4 in thickness from the surface of the sample prepared as described above at a magnification of 50 $\times$.

[0066] The CNV_{TH} value of Table 2 is a theoretical value of impact toughness according to the present disclosure. The CNV_{TH} value was calculated by substituting the contents (wt%) of the respective alloying elements, the T_{σ} value, and the T value into the following equation. The calculated CNV_{TH} values are expressed to two decimal places.

$$CNV_{TH} = 336 - 1432*C - 22.1*Si + 64.1*Mn + 8.5*Cr + 0.11*Ni - 10.1*Mo - 3.3*Cu + 22.1*W - 392*N - 293*(T_{\sigma}/T)$$

[0067] The CNV_{EX} values of Table 2 are test results of impact toughness measured by a Charpy V-notch impact test. In the test, the sample is processed to have a thickness of 4 mm and tested at room temperature (25°C).

[0068] Upon comparison between the CNV_{TH} value and the CNV_{EX} value of Table 2, the theoretical value of impact toughness was similar to the test result without deviation, and thus it can be seen that the actual impact toughness may be accurately derived using the CNV_{TH} equation suggested by the present disclosure without a large error.

Table 2

Example	PREW-Mn	CPT (°C)	T_{σ} (°C)	T (°C)	O/Al	S/Ca	Surface Crack	σ area ratio (%)	CNV_{TH}	CNV_{EX} (J)
Example 1	43.08	92	1079	1145	0.034	0.150	Good	0.7	84.12	84
Example 2	44.02	> 100	1084	1129	0.040	0.031	Good	0.7	85.90	86
Example 3	49.13	> 100	1089	1101	0.011	0.095	Good	0.7	85.90	86
Example 4	47.66	> 100	1090	1154	0.015	0.048	Good	0.8	80.12	80
Example 5	43.31	95	1054	1100	0.037	0.240	Good	0.6	88.90	88
Example 6	42.19	94	1000	1103	0.100	0.241	Good	0.3	98.05	98
Example 7	43.02	95	1036	1115	0.011	0.100	Good	0.3	94.91	95

(continued)

Example	PREW-Mn	CPT (°C)	T _σ (°C)	T (°C)	O/Al	S/Ca	Surface Crack	σ area ratio (%)	CNV _{TH}	CNV _{EX} (J)
Example 8	42.105	91	1031	1101	0.062	0.121	Good	0.1	110.42	110
Comparative Example 1	48.41	> 100	1100	1066	0.042	0.057	Good	3.5*	29.99*	30*
Comparative Example 2	46.705	> 100	1133	1107	0.025	0.160	Good	2.9*	33.88*	34*
Comparative Example 3	36.25*	73*	956	1059	0.052	0.214	Good	0.1	112.01	112
Comparative Example 4	52.44*	> 100	1211	1070	0.120	0.250	Good	2.9*	34.92*	35*
Comparative Example 5	44.435	> 100	1079	1094	90.000*	3.200*	Bad	0.6	84.96	85
Comparative Example 6	48.08	> 100	1093	1116	0.840*	1.300*	Bad	0.8	82.05	82
Comparative Example 7	40.4	88	1028	1170	0.130*	0.417*	Bad	0.4	96.04	96
(* is out of the range defined by the present disclosure.)										

[0069] Hereinafter, examples and comparative examples will be comparatively evaluated with reference to Tables 1 and 2.

[0070] Examples 1 to 8 satisfied the composition ranges of alloying elements defined by the present disclosure. In addition, excellent corrosion resistance was obtained according to Examples 1 to 8 by adjusting the PREW-Mn values in the range of 40 to 50 and the critical pitting temperatures to be higher than 80°C. Excellent impact toughness having a CNV_{EX} value of 80 J or more was obtained according to Examples 1 to 8 by controlling the alloying elements and heat treatment conditions such that the σ area ratios were 1.0% or less and the CNV_{TH} values were 80 or more. Excellent hot workability without causing surface cracks during hot working was obtained according to Examples 1 to 8 by controlling the elements used in trace amounts to satisfy the O/Al ratio of 0.01 to 0.12 and the S/Ca ratio of 0.01 to 0.4.

[0071] On the other hand, in Comparative Examples 1 and 2, the Si contents exceeded the upper limit of 1.0 wt% defined in the present disclosure. As a result, precipitation of intermetallic compounds such as the σ phase was promoted, so that the σ area ratios exceeded 1.0% and the impact toughness values were about 32 J indicating poor impact toughness compared to Examples 1 to 8.

[0072] In Comparative Example 3, the Cr content and the Mo content were lower than the lower limits thereof defined in the present disclosure, so that the PREW-Mn was less than 40 and the critical pitting temperature was below 80°C failing to obtain sufficient corrosion resistance.

[0073] In Comparative Example 4, the Cr content and the Mo content exceeded the upper limits thereof defined in the present disclosure, so that the PREW-Mn value was greater than 50, and corrosion resistance deteriorated by precipitation of the intermetallic compounds such as the σ phase in the matrix structure due to excessive amounts of Cr and Mo. Referring to Table 2, the σ area ratio exceeded 1.0%, and thus corrosion resistance deteriorated and impact toughness (35J) deteriorated compared to Examples 1 to 8.

[0074] In Comparative Examples 5 and 6, the Al content and the Ca content were below the lower limits thereof defined in the present disclosure and thus the O/Al ratio and the S/Ca ratio exceeded the upper limits defined in the present disclosure due to relatively higher contents of O and S. Therefore, surface cracks occurred during hot working indicating deterioration of hot workability compared to Examples 1 to 8.

[0075] In Comparative Example 7, the Al content and the Ca content were within the ranges defined in the present disclosure. However, in Comparative Example 7, the O/Al ratio and the S/Ca ratio exceeded the upper limits thereof defined in the present disclosure, and therefore surface cracks occurred during hot working indicating deterioration of hot workability compared to Examples 1 to 8.

[0076] Also, the above-described results may be visually confirmed from FIGS. 1 and 2 of the present disclosure. FIG. 1 is a graph showing critical pitting temperatures (CPT) of samples of Examples with respect to PREW-Mn. FIG. 2 is a

graph showing S/Ca and O/Al values of samples of Examples. Shaded areas in the drawings correspond to ranges defined by the present disclosure.

[0077] Referring to FIG. 1, in the case where the PREW-Mn value is out of the range of 40 to 50 defined in the present disclosure and the critical pitting temperature (CPT) is below 80°C or the critical pitting temperature (CPT) exceeds 100°C (Comparative Example 4), intermetallic compounds such as the σ phase is precipitated in the matrix structure due to excessive amounts of Cr and Mo resulting in deterioration of corrosion resistance.

[0078] Referring to FIG. 2, in the case where the S/Ca ratio and the O/Al ratio are out of the ranges defined in the present disclosure (Comparative Examples 5, 6, and 7), surface cracks occurred during hot working may be confirmed. Particularly, in the case of Comparative Example 7 in which the contents of Al and Ca are within the ranges defined in the present disclosure but the S/Ca ratio and the O/Al ratio are out of the ranges defined in the present disclosure, surface cracks occurred during hot working.

[0079] Based on the above-described results, it was confirmed that excellent corrosion resistance was obtained by adjusting the PREW-Mn value in the range of 40 to 50 in the alloying elements defined in the present disclosure, excellent impact toughness was obtained by controlling the alloying elements and heat treatment conditions to have the impact toughness value (CNV_{TH}) of 80 or more, and excellent hot workability was obtained by adjusting the elements used in trace amounts to satisfy the O/Al ratio of 0.01 to 0.12 and the S/Ca ratio of 0.01 to 0.4.

[0080] While the present disclosure has been particularly described with reference to exemplary embodiments, it should be understood by those of skilled in the art that various changes in form and details may be made without departing from the spirit and scope of the present disclosure.

[Industrial Applicability]

[0081] The austenitic stainless steel according to the present disclosure may be applied as materials for industrial facilities such as desulfurization facilities, heat exchangers, desalination facilities, and food and beverage facilities.

Claims

1. A highly corrosion-resistant austenitic stainless steel having excellent impact toughness and hot workability comprising, in percent by weight (wt%), 0.03% or less (excluding 0) of carbon (C), 1.0% or less of silicon (Si), 1.0% or less of manganese (Mn), 18 to 24% of chromium (Cr), 16 to 24% of nickel (Ni), 5 to 7% of molybdenum (Mo), 0.1 to 2.0% of copper (Cu), 1.0% or less of tungsten (W), 0.18 to 0.3% of nitrogen (N), 0.02 to 0.1% of aluminum (Al), 0.01% or less of oxygen (O), 0.002 to 0.01% calcium (Ca), less than 0.001% of sulfur (S), and the remainder of iron (Fe) and inevitable impurities, and satisfying an O/Al ratio of 0.01 to 0.12 and a S/Ca ratio of 0.01 to 0.4.
2. The highly corrosion-resistant austenitic stainless steel according to claim 1, wherein an impact toughness value (CNV_{TH}) represented by Formula (1) below is 80 or more:

$$(1) CNV_{TH} = 336 - 1432 \cdot C - 22.1 \cdot Si + 64.1 \cdot Mn + 8.5 \cdot Cr + 0.11 \cdot Ni - 10.1 \cdot Mo - 3.3 \cdot Cu + 22.1 \cdot W - 392 \cdot N - 293 \cdot (T_{\sigma}/T)$$

wherein in Formula (1) above, C, Si, Mn, Cr, Ni, Mo, Cu, W, and N denote contents (wt%) of the respective alloying elements, T_{σ} is a temperature at which the sigma (σ) phase is completely, thermodynamically decomposed, and T is an actual solution heat treatment temperature.

3. The highly corrosion-resistant austenitic stainless steel according to claim 1, wherein a PREW-Mn value represented by Formula (2) below is from 40 to 50:

$$(2) \text{PREW-Mn} = Cr + 3.3 \cdot (Mo + 0.5 \cdot W) + 16 \cdot N - 0.5 \cdot Mn$$

wherein in Formula (2) above, Cr, Mo, W, N, and Mn denote contents (wt%) of the respective alloying elements.

4. The highly corrosion-resistant austenitic stainless steel according to claim 1, wherein a σ phase area ratio measured in an area of 26 mm² at a depth of 1/4 to 3/4 in thickness from the surface at a magnification of 50× is 1.0% or less.

5. The highly corrosion-resistant austenitic stainless steel according to claim 1, wherein a critical pitting temperature is 80°C or higher.

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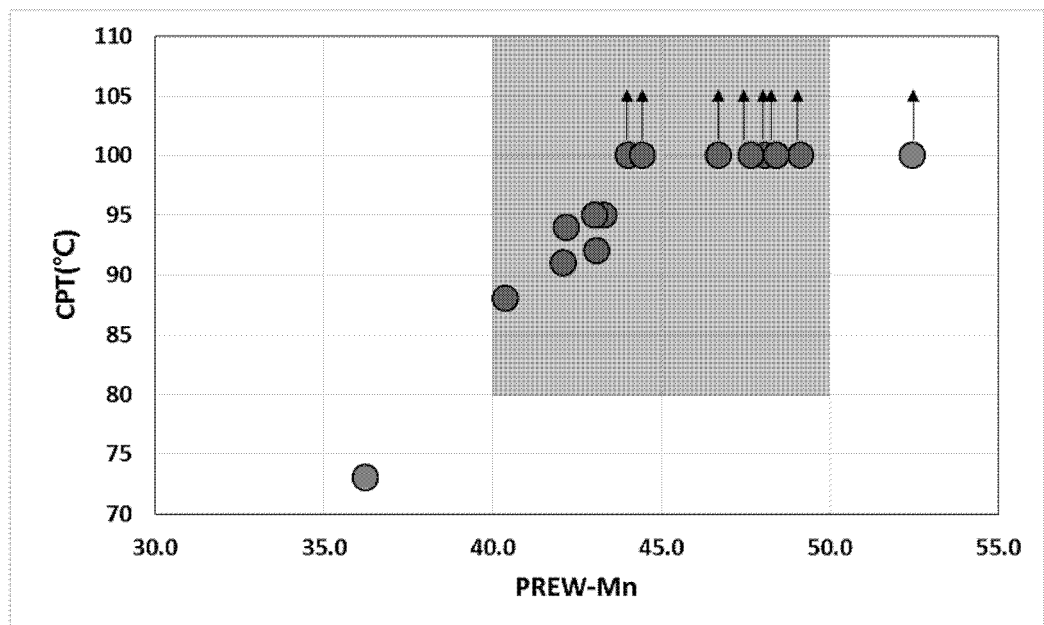
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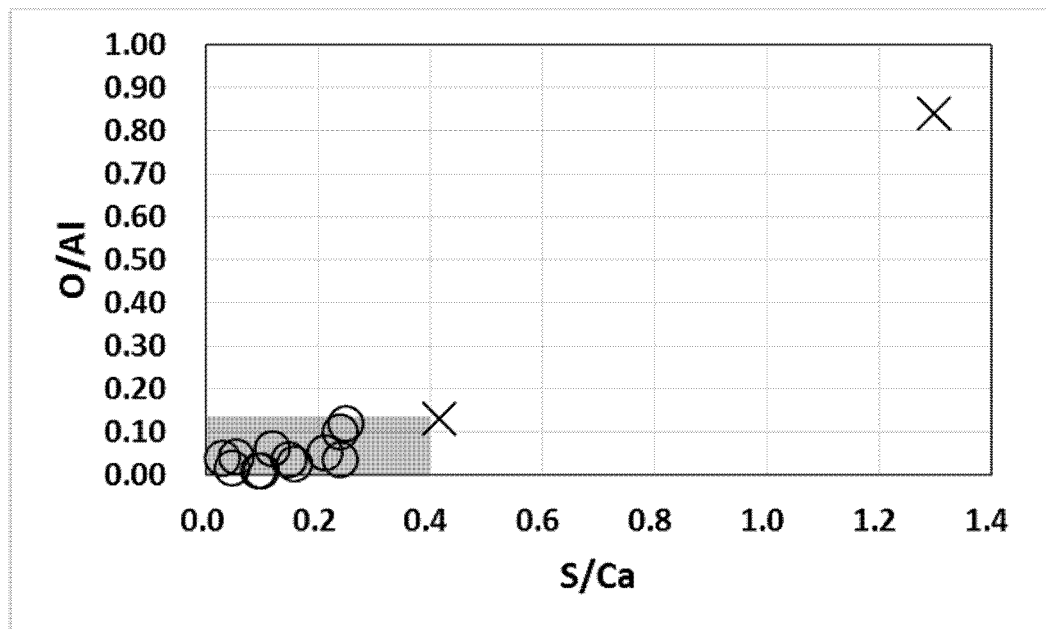
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【FIG. 1】



【FIG. 2】



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2020/008864

A. CLASSIFICATION OF SUBJECT MATTER C22C 38/44(2006.01)i; C22C 38/42(2006.01)i; C22C 38/00(2006.01)i; C22C 38/60(2006.01)i; C21D 8/02(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) C22C 38/44(2006.01); C21D 6/00(2006.01); C21D 8/02(2006.01); C22C 38/00(2006.01); C22C 38/58(2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models: IPC as above Japanese utility models and applications for utility models: IPC as above Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS (KIPO internal) & keywords: 오스테나이트(austenite), 스테인리스(stainless), 인성(toughness), 내식성(corrosion resistance), 시그마상(sigma phase)																		
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>KR 10-1992-0004703 B1 (NIPPON STEEL CORPORATION) 13 June 1992 (1992-06-13) See page 5, claims 1 and 7-9, table 1 and figure 3.</td> <td>1-5</td> </tr> <tr> <td>A</td> <td>JP 2006-213950 A (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORP.) 17 August 2006 (2006-08-17) See claims 1-3.</td> <td>1-5</td> </tr> <tr> <td>A</td> <td>JP 2005-187904 A (MATSUSHITA ELECTRIC IND CO., LTD. et al.) 14 July 2005 (2005-07-14) See claims 1 and 3.</td> <td>1-5</td> </tr> <tr> <td>A</td> <td>KR 10-1998-0021576 A (PARK, Yong Soo et al.) 25 June 1998 (1998-06-25) See pages 3-4 and claims 1-5.</td> <td>1-5</td> </tr> <tr> <td>A</td> <td>JP 2000-034546 A (UGINE SA et al.) 02 February 2000 (2000-02-02) See claim 1.</td> <td>1-5</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	KR 10-1992-0004703 B1 (NIPPON STEEL CORPORATION) 13 June 1992 (1992-06-13) See page 5, claims 1 and 7-9, table 1 and figure 3.	1-5	A	JP 2006-213950 A (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORP.) 17 August 2006 (2006-08-17) See claims 1-3.	1-5	A	JP 2005-187904 A (MATSUSHITA ELECTRIC IND CO., LTD. et al.) 14 July 2005 (2005-07-14) See claims 1 and 3.	1-5	A	KR 10-1998-0021576 A (PARK, Yong Soo et al.) 25 June 1998 (1998-06-25) See pages 3-4 and claims 1-5.	1-5	A	JP 2000-034546 A (UGINE SA et al.) 02 February 2000 (2000-02-02) See claim 1.	1-5
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