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(54) **HIGH STRENGTH / CORROSION-RESISTANT,.AUSTENITIC STAINLESS STEEL WITH CARBON - NITROGEN COMPLEX ADDITIVE, AND METHOD FOR MANUFACTURING SAME**

HOCHFESTER KORROSIONSBESTÄNDIGER AUSTENITISCHER EDELSTAHL MIT KOHLENSTOFF-STICKSTOFF-KOMPLEXZUSATZ UND HERSTELLUNGSVERFAHREN DAFÜR

ACIER INOXYDABLE AUSTÉNITIQUE TRÈS RÉSISTANT MÉCANIQUEMENT ET À LA CORROSION, COMPRENANT UN ADDITIF COMPLEXE DE CARBONE ET D'AZOTE, ET PROCÉDÉ DE FABRICATION CORRESPONDANT

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(56) References cited:
EP-A1- 1 229 142
DE-A1- 2 118 072
JP-A- 9 249 940
JP-A- 11 241 145
JP-A- 2000 192 194
JP-A- 2001 011 579
KR-A- 20050 055 838
KR-A- 20060 110 103
KR-A- 20090 034 194

- **WHITE W ET AL: "Metallographic observations on the formation and occurrence of ferrite, sigma phase, and carbides in austenitic stainless steels", METALLOGRAPHY, AMERICAN ELSEVIER, NEW YORK, NY, US, vol. 3, no. 1, 1 March 1970 (1970-03-01), pages 35-50, XP023901147, ISSN: 0026-0800, DOI: 10.1016/0026-0800(70)90003-0 [retrieved on 1970-03-01]**
- **J SIMMONS: "Strain hardening and plastic flow properties of nitrogen-alloyed Fe-17Cr-(8-10)Mn-5Ni austenitic stainless steels", ACTA MATERIALIA, vol. 45, no. 6, 1 June 1997 (1997-06-01), pages 2467-2475, XP055097199, ISSN: 1359-6454, DOI: 10.1016/S1359-6454(96)00343-6**
- **IRVING MELVIN BERNSTEIN ET AL: "Residual and Minor Elements in Stainless Steels", HANDBOOK OF STAINLESS STEELS, XX, XX, 1 January 1977 (1977-01-01), pages 14-1, XP002430954,**

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a fabrication method of a C + N austenitic stainless steel having high mechanical strength and excellent corrosion resistance.

2. Description of the Related Art

[0002] Generally, unlike carbon steels whose mechanical properties such as strength and ductility can be improved through thermo-mechanical treatments or phase transformation by various heat treatments, it is difficult to improve the mechanical properties of austenitic stainless steels using the heat treatment methods. Thus, the austenitic stainless steels mainly depend on the addition of alloying elements for the improvement of most properties.

[0003] Therefore, the most important technical subject in the development of new alloy is to ensure optimum properties including strength, ductility or corrosion resistance, with low fabrication costs by minimizing a content of a high priced alloying element or by replacing it with economical alloying elements.

[0004] Most austenitic stainless steels reported in the previous studies or inventions contain 16~20 wt.% chromium (Cr), 6~12 wt.% nickel (Ni), 0~2 wt.% molybdenum (Mo), and 0.03~ 0.15 wt.% carbon (C), and exhibit 500~600 MPa of tensile strength, and 40% of elongation.

[0005] Among the above-mentioned alloying elements, nickel (Ni) is an effective austenite stabilizing element which contributes to the improvement of formability. More than 65 % of the total supply amount of nickel (Ni) is consumed for the production of austenitic stainless steels.

[0006] Nevertheless, the price of nickel (Ni) had kept increasing since 2001 by more than 700 % for the following six years, and particularly, it was doubled in 2007, therefore, the price of nickel (Ni) has become a major index in determining cost of stainless steels. In addition to the economical point of view, nickel (Ni) also gives adverse effects to human health and environment since nickel (Ni) can cause allergic reaction to human skin and give off toxic gas during recycling.

[0007] Accordingly, in order to resolve the problems associated with the conventional stainless steels having a high content of nickel (Ni), Fe-Cr-Mn alloys (or STS 200 alloy), and high-nitrogen austenitic stainless steels with desirable physicochemical properties owing to the addition of nitrogen (N) have been developed.

[0008] Nitrogen (N) is a highly effective austenite-stabilizing element, and provides various advantages, including solid solution hardening, less reduction in ductility accompanied by the increase in mechanical strength, and enhanced corrosion resistance. So far, the high-nitrogen stainless steel has not been commercialized due to the difficulty in the fabrication process to ensure high nitrogen (N) content in the steel. Recently, various studies have been conducted to develop effective fabrication processing methods, as a result, pressurized induction melting, pressurized electroslag remelting (PESR), powder metallurgy, and solution nitriding under nitrogen gas atmosphere have been suggested.

[0009] However, the major obstacle to the commercialization of the high-nitrogen stainless steel is the requirement for a special fabrication processing facilities such as pressurized induction melting furnace or PESR, which requires expensive equipments and complicated processing steps.

[0010] The pressurizing processing is particularly required for the fabrication of a large-sized ingot of the high-nitrogen stainless steel, since the pressurizing processing ensures high nitrogen (N) content in the liquid metal and minimizes the delta ferrite gap, which significantly reduces the nitrogen (N) solubility during the solidification. Thus, a modification of conventional melting equipment or an incorporation of new equipments for the pressurizing process are inevitable to fabricate the high-nitrogen stainless steels employing the pressurized melting facility, therefore, the high-nitrogen stainless steel has not been commercialized yet.

EP 1 229 142 A1 discloses high-strength, high corrosion-resistant and nonmagnetic stainless steels comprising 0.15% by weight or less of C, 1.0% or less of Si, 3.0 to 12.0% of Mn, 0.030% or less of P, 0.50% or less of Ni, 15.0 to 21.0% of Cr, 0.70 to 1.50% of N, 0.020% or less of Al and 0.020% or less of O, and a remainder of Fe and inevitable impurities. The fabrication of these steels requires pressurized melting furnaces such as a high frequency induction furnace.

[0011] Recently, *H. Berns et al.* disclosed austenitic steels in the International Patent Application No. PCT/EP2005/008960, which contain minimum contents of nickel (Ni), 16~21 wt.% chromium (Cr), 16~21 wt.% manganese (Mn), 0.5~2 wt.% molybdenum (Mo), and 0.8 wt.% or more of carbon (C) and nitrogen (N) content ([C+N]), as a suggestion to solve the problems in the fabrication process mentioned above. However, the invention disclosed by *H. Berns et al.* contains a relatively high manganese (Mn) content, which subsequently degrades corrosion resistance.

[0012] The present inventors have developed and completed a C+N austenitic stainless steel with an increased economic efficiency, high strength and excellent corrosion resistance, in which carbon (C) and nitrogen (N) as interstitial elements are added simultaneously instead of nickel (Ni). Therefore, the content of high priced nickel (Ni) can be

minimized, and the strength and corrosion resistance can be improved through controlling the contents of the two interstitial elements of carbon (C) and nitrogen (N) (C+N, C/N) and those of the substitutional elements of manganese (Mn), chromium (Cr), molybdenum (Mo) and tungsten (W) (Mn+Cr, Mn/Cr, or 0.5W+Mo). In addition, this alloy is further economically competitive than the conventional high-nitrogen stainless steels because it can be produced by the conventional melting furnace excluding pressurized process.

SUMMARY OF THE INVENTION

[0013] An aspect of the present invention is to resolve the problems mentioned above, and accordingly, it is an object of the present invention to provide a fabrication method of a C+N austenitic stainless steel which has increased strength and excellent corrosion resistance through controlling the contents of the interstitial elements (C+N, C/N) and those of the substitutional elements (Mn+Cr, Mn/Cr, or 0.5W+Mo).

[0014] The present invention provides a fabrication method of the austenitic stainless steel with high mechanical strength and excellent corrosion resistance, which consists of: 8 to 12 wt.% manganese (Mn); 15 to 20 wt.% chromium (Cr); 2 wt.% or less nickel (Ni); 0.6 to 1.0 wt.% of total C+N content, with 0.3 or higher wt.% nitrogen (N); 4 wt.% or less tungsten (W); 2 wt.% or less molybdenum (Mo); a balance of iron (Fe); and unavoidable impurities, the fabrication method comprising:

master alloy charging in which a master alloy for the stainless steel having the composition of 8 to 12 wt.% manganese (Mn); 15 to 20 wt.% chromium (Cr); 2 wt.% or less nickel (Ni); 0.6 to 1.0 wt.% of total C+N content, with 0.3 or higher wt.% nitrogen (N); 4 wt.% or less tungsten (W); 2 wt.% or less molybdenum (Mo); a balance of iron (Fe); and unavoidable impurities is charged into a vacuum melting furnace;
vacuum maintaining in which the vacuum melting furnace with the master alloy charged therein is maintained under vacuum;
master alloy melting in which the vacuum melting furnace is heated and the master alloy is melted;
nitrogen (N) content adjusting in which nitrogen gas is injected into the vacuum melting furnace to make nitrogen content in the C+N austenitic stainless steel as indicated above;
melted alloy agitating in which the melted master alloy is agitated;
ingot forming in which an ingot is formed by pouring the agitated melted alloy from the vacuum melting furnace;
hot-rolling the formed ingot; and
performing water quenching of the hot-rolled stainless steel to prevent precipitation of carbide which degrades the mechanical property and corrosion resistance,

wherein the nitrogen (N) content adjusting comprises:

nitrogen gas injecting in which nitrogen gas is injected to the interior of the vacuum melting furnace; and

pressure adjusting in which the partial pressure of nitrogen gas of the interior of the vacuum melting furnace is adjusted to 1 atm.

[0015] As described herein, a C+N austenitic stainless steel is provided, to which carbon (C) and nitrogen (N) as interstitial elements are added simultaneously, so that the content of nickel (Ni) is minimized, which is high-priced alloying element, and harmful to an environment and a human health. As a result, the developed austenitic stainless steel provides improved economic efficiency.

[0016] With the fabrication method according to the present invention, it is possible to fabricate an alloy with economic manufacturing cost, and hence the price competitiveness of the alloy can be increased. Furthermore, the austenitic stainless steel according to one embodiment provides favorable mechanical properties of a tensile strength higher than 850 MPa and an uniform elongation more than 45 %, which are obtained through controlling the contents of the interstitial elements (C+N, C/N) and those of the substitutional elements (Mn+Cr, Mn/Cr, or 0.5W+Mo). In addition, the invented alloy also provides an excellent corrosion resistance and a biocompatibility due to the highly alloyed nitrogen (N) and minimized content of nickel (Ni) which causes allergic reaction to the human body. Therefore, the austenitic stainless steel obtainable according to the present invention is efficiently applicable in the fabrication of a variety of functional components including medical biosubstances, watches and accessories, as well as the fields of the conventional structural austenitic stainless steel and offshore structures, desalination plants, materials for oil and gas installing/mining, and materials for transportation facilities, which require high level of strength and corrosion resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The above and/or other aspects of what is described herein will be more apparent by describing certain exem-

plary embodiments with reference to the accompanying drawings, in which:

FIG. 1 is a graphical representation of a variation of the nitrogen (N) solubility as a function of temperature of Fe-Cr-Mn based alloys and Fe-Cr-Mn-0.4C based alloys obtained according to an embodiment of the present invention;
FIG. 2 is a flowchart of a fabricating method for the C+N austenitic stainless steel with high mechanical strength and excellent corrosion resistance obtained according to an embodiment of the present invention;
FIG. 3 is a flowchart illustrating in detail the 4th step of adjusting of nitrogen (N) contents in the fabricating steps of the C+N austenitic stainless steel with high strength and excellent corrosion resistance obtained according to an embodiment of the present invention; and
FIG. 4 is a graphical representation for the comparison of pitting corrosion resistance among the examples of the present invention and comparative examples.

* Description of the main reference numerals of FIGs. 2 and 3*

S100: charging of master alloy	S200: maintaining of vacuum
S300: melting of master alloy	S400: adjusting of nitrogen content
S420: injecting of nitrogen gas	S440: adjusting of pressure
S500: agitating of melted alloy	S600: forming of ingot
S700: hot rolling	S800: water quenching

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0018] Certain exemplary embodiments will now be described in greater detail with reference to the accompanying drawings.

[0019] According to one embodiment, a fabrication method of C+N austenitic stainless steel with high strength and excellent corrosion resistance, consists of: 8 to 12 wt.% manganese (Mn); 15 to 20 wt.% chromium (Cr); 2 wt.% or less nickel (Ni); 4 wt.% or less tungsten (W); 2 wt.% or less molybdenum (Mo); 0.6 to 1.0 wt.% of C+N content, with 0.3 or higher wt.% nitrogen (N); a balance of iron (Fe); and unavoidable impurities.

[0020] The ratio of manganese (Mn) to chromium (Cr) (Mn/Cr) ranges from 0.5 to 1.0.

[0021] According to one embodiment, since the manganese (Mn) content in this invention is lower than that of the stainless steel disclosed by *H. Berns et al.* (i.e., 16 to 21 wt.% manganese (Mn)) in the International Patent Application No. PCT/EP2005/008960, improved pitting resistance is obtained.

[0022] The total manganese (Mn) and chromium (Cr) content ([Mn+Cr]) is 30 wt.% or less.

[0023] The nitrogen (N) content is 0.3 wt.% or more.

[0024] The total tungsten (W) and molybdenum (Mo) content (0.5W+Mo) is 3 wt.% or less. If 0.5W+Mo content exceeds 3 wt.%, the manufacturing cost increases, the amount of remaining delta ferrite increases, and the harmful second phase is formed.

[0025] The alloying elements of the austenitic stainless steel obtainable according to an embodiment of the present invention will be explained in greater detail below.

[0026] Although nickel (Ni) effectively stabilizes the austenitic phase, considering the high price and the adverse effect to environment and human health, the nickel (Ni) content is limited as low as possible. However, considering that the addition of a minute amount of nickel (Ni) to the austenitic stainless steel can improve hot and/or cold formability and suppress the formation of delta ferrite during solidification from the liquid phase, the nickel (Ni) is added within a limit of 2 wt.%.

[0027] Chromium (Cr) is an essential alloying element required to ensure the corrosion resistance for the stainless steel, and most austenitic stainless steels contain 15 wt.% or more chromium (Cr). However, excessively-added chromium (Cr) causes a formation of surplus delta ferrite remaining after solidification, and promotes a precipitation of various second phases during heat treatment, which degrade the corrosion resistance and formability of the stainless steel. Hence, the chromium (Cr) content is limited within a range of 15~20 wt.% in the stainless steel.

[0028] Manganese (Mn) is an austenite-stabilizing element that can substitute for high-priced nickel (Ni). In addition, when added to the stainless steel, manganese (Mn) works to increase nitrogen (N) solubility and, consequently, mechanical strength of the material is enhanced. However, excessively-added manganese (Mn) usually combines with sulfur (S) or oxygen (O) in the stainless steel matrix, forming nonmetallic inclusions such as manganese sulfide (MnS) or manganese oxide (MnO). The nonmetallic inclusions act as initiation sites for the pitting corrosion, thus they degrade the resistance to pitting corrosion of the austenitic stainless steel. Therefore, the manganese (Mn) content is limited within a range of 8~12 wt.%

[0029] Molybdenum (Mo) also improves corrosion resistance of an austenitic stainless steel, similar to chromium (Cr).

However, excessively-added molybdenum (Mo) can cause to increase the amount of delta ferrites remaining after solidification, and like chromium (Cr), induce a formation of harmful second phases. In addition, alloying a large amount of Mo can increase the fabrication cost. Therefore, the molybdenum (Mo) content is limited to 2 wt.% or less.

[0030] Tungsten (W) can efficiently substitute for molybdenum (Mo), because tungsten (W) has an ability to stabilize the ferrite phase and to improve pitting corrosion resistance, corresponding to 1/2 equivalent of molybdenum (Mo) content. In addition, tungsten (W) increases high-temperature strength and creep resistance of the stainless steel. And also, Tungsten (W) improves general corrosion resistance in a non-oxidizing atmosphere, promotes passivation of metals, and improves resistance to pitting corrosion of alloys. However, being a ferrite-stabilizing element, an excessive presence of tungsten (W) in stainless steels can increase the amount of delta ferrite, and also raise the fabrication cost similar to the molybdenum (Mo). Therefore, tungsten (W) content is limited to 4 wt.% or less. Furthermore, in order to attain high corrosion resistance with economic fabrication cost, 0.5W+Mo content is limited to 3 wt.% or less.

[0031] Nitrogen (N), along with carbon (C) and manganese (Mn), is added as the austenite-stabilizing element to substitute for nickel (Ni) with the above-mentioned problems, and to increase strength without causing considerable degradation of ductility, and to promote corrosion resistance including pitting corrosion resistance. Accordingly, 0.3 wt.% or more of nitrogen (N) content has to be used for such effects. However, excessive nitrogen (N) can cause degradation in ductility and ductile-to-brittle transition.

[0032] Like nitrogen (N), carbon (C) is added to stabilize the austenite phase, and acts to improve the mechanical strength of the stainless steel through solid solution hardening. However, the excessive C can degrade the toughness, and form carbides such as $M_{23}C_6$ or M_6C at a grain boundary, which sensitize the grain boundary resulting in a decrease in the corrosion resistance.

[0033] For these reasons, the total content of carbon (C) and nitrogen (N) ([C+N]) in the stainless steel according to an embodiment of the present invention is limited within a range of 0.6~1.0 wt.%

[0034] Meanwhile, FIG. 1 illustrates the result of the calculated nitrogen (N) solubility at 1 atm of partial pressure of nitrogen gas in Fe-Cr-Mn based ternary alloys (i.e., Fe-18Cr-10Mn, Fe-15Cr15Mn, and Fe-13Cr-20Mn alloys) in absence of carbon (C), and that in Fe-Cr-Mn-0.4C based ternary alloys containing 0.4 wt.% carbon (C). Referring to FIG. 1, the nitrogen (N) solubility in liquid phase metal decreases from 0.38 wt.% to 0.3 wt.% by the addition of carbon (C). However, since the decrease in the nitrogen (N) solubility is significantly restrained due to the reduction in the delta ferrite formation during the solidification by the addition of carbon (C), the loss of alloyed nitrogen (N) can be lowered. This phenomenon occurs due to the increased stability of the austenitic phase at high temperature and the decreased stability of the ferritic phase by the addition of carbon (C). On this concept, when the carbon (C) and nitrogen (N) are added simultaneously to the stainless steel matrix, the targeted nitrogen (N) solubility can be achieved at atmospheric pressure (i.e., 1 atm of partial pressure of nitrogen gas).

[0035] Furthermore, the reason for the limitation of the carbon (C) and nitrogen (N) content (C+N) within a range of 0.6~1.0 wt.% will be explained below. Added nitrogen (N) increases a free electron density of the austenitic matrix, which in turn promotes metallic bonding character and strengthens the short-range ordering in the austenitic matrix. Due to such characteristic atomic bonding induced by the addition of nitrogen (N), it is possible to restrict the generation of harmful second phases by the segregation of an alloying element, and hence improve the ductility and the corrosion resistance. In other words, the physical basis of the improvement of general properties of the steel by the addition of nitrogen (N) can be found from the increase of free electron density. On the other hand, the addition of carbon (C) does not show a noticeable influence on the free electron density of the steel, unlike nitrogen (N) in a predetermined content range. However, in case of the combined addition of carbon (C) and nitrogen (N) to the stainless steel matrix, the stainless steel exhibits a remarkably increased free electron density compared to those of the alloys where the only nitrogen (N) is added due to the synergistic effect between the two elements,. The free electron density gradually increases with carbon (C) and nitrogen (N) content ([C+N]), and reaches the maximum value at 0.85 wt.% of [C+N] before it starts to decrease. Therefore, based on the above-mentioned physical basis, and also to prevent a generation of undesirable secondary precipitate phases caused by an excessive addition of carbon (C) and nitrogen (N), the total C+N content is limited within a range of 0.6~1.0 wt.% according to one embodiment of the present invention.

[0036] Furthermore, the fabrication method of a C+N austenitic stainless steel with high strength and excellent corrosion resistance according to the present invention includes the steps of: S100; charging of master alloy, in which a master alloy is charged into a vacuum melting furnace, and the chemical composition of the master alloy is (all in weight percent) pure iron, Fe-50%Mn, Fe-60%Cr, Fe-58.8%Cr-6.6%N, 75.1%Mn-17.4%Fe-6.8%C, tungsten (W) and/or molybdenum (Mo); S200; maintaining of vacuum, in which the vacuum melting furnace with the master alloy charged is maintained under vacuum; S300; melting of master alloy, in which the vacuum melting furnace is heated and the master alloy is melted; S400; adjusting of nitrogen (N) content, in which nitrogen gas is injected into the vacuum melting furnace; S500; agitating of melted alloy, in which the melted master alloy is agitated; S600; forming of ingot, in which an ingot is formed by pouring the melted alloy from the vacuum melting furnace; S700; hot-rolling the formed ingot; and S800; water quenching for the hot-rolled stainless steel to prevent precipitation of carbide which affects detrimentally the mechanical property and the corrosion resistance.

[0037] The maintaining of vacuum step (S200) is the step of maintaining the vacuum level inside the vacuum melting furnace at 10^{-3} torr or lower.

[0038] The step of adjusting of N content (S400) includes two steps of; injecting nitrogen gas (S420), in which the nitrogen gas is injected to the vacuum melting furnace, and adjusting pressure (S440), in which the partial pressure of nitrogen gas in the vacuum melting furnace is adjusted to 1 atm.

[0039] The embodiments of the present invention are applicable to the fabrication of the austenitic stainless steel with high strength and excellent corrosion resistance in various forms of stainless steels including cast, forged and rolled stainless steels with economic manufacturing cost and raw material costs.

[0040] The austenitic stainless steel obtainable according to one embodiment of the present invention exhibits 850 MPa or higher of tensile strength and 45 % or higher of uniform elongation (see Table 2). Furthermore, the excellent corrosion resistance of the austenitic stainless steel obtainable according to one embodiment of the present invention was confirmed by measuring anodic polarization behavior in a 1 M NaCl solution at a potential scan rate (dV/dt) of 2 mV/s.

[0041] Consequently, the austenitic stainless steel with carbon (C) and nitrogen (N) obtainable according to an embodiment of the present invention can be fabricated by the atmospheric induction melting process excluding the pressurizing process which was essential in the conventional fabrication of high-nitrogen steel. Since it is possible to fabricate the alloy with economic manufacturing cost, the price competitiveness of the developing alloy increases. Moreover, by controlling the contents of the interstitial elements (C+N, C/N), and those of the substitutional elements contents (Mn+Cr, Mn/Cr, or 0.5W+Mo), the high tensile strength (850 MPa or higher) and favorable uniform elongation (45 % or higher) assuring formability are successfully attained, and the corrosion resistance is improved. Additionally, since the harmful nickel (Ni) content is minimized, the austenitic stainless steel obtainable according to the present invention is effectively applicable to not only the fields of the conventional structural austenitic stainless steels and offshore structures, desalination plants, materials for oil and gas installing/mining, and materials for transportation facilities, which require high level of mechanical strength and corrosion resistance, but also the fabrication of a variety of functional components including medical biosubstances, watches and accessories.

[0042] Exemplary embodiments and examples of the present invention will be explained in greater detail below. However, it should be understood that the embodiments and examples are explained only for the illustrative purpose, and therefore, the concept of the present invention is not limited by the exemplary embodiments.

Examples 1 to 8. Fabrication of austenitic stainless steel according to the present invention

[0043] In the fabrication of an austenitic stainless steel according to an embodiment of the present invention, a ferrochromium master alloy (e.g., Fe-60%Cr master alloy) was used as a chromium (Cr) source which hardly melts due to the high melting point, and a ferromanganese master alloy (e.g., Fe-50%Mn master alloy) was used as a manganese (Mn) source to prevent a generation of manganese (Mn) fume and a segregation in molten metal due to the low vapor pressure.

[0044] Referring to FIGs. 2 and 3, at the step of S100, a master alloy consisting of Fe-50%Mn, Fe-60%Cr, pure iron, Fe-58.8%Cr-6.6%N for controlling the nitrogen (N) content, 75.1%Mn-17.4%Fe-6.8%C for controlling the carbon (C) content, tungsten (W) and/or molybdenum (Mo), was charged into a vacuum melting furnace. At the step of S200, the vacuum melting furnace was degassed until the vacuum level became 10^{-3} torr or below, and the vacuum level was maintained. At the step of S300, the vacuum melting furnace was heated so that the master alloy and the pure iron were sufficiently melted. At the step of S400, nitrogen (N) content was adjusted by introducing nitrogen gas into the vacuum melting furnace when the master alloy and the pure iron were melted (at the step of S420), and by adjusting the internal partial pressure of nitrogen gas to 1 atm during melting (at the step of S440). At the step of S500, the melted alloy was agitated by electromagnetic induction agitation so that the segregation of the alloying element was avoided. At the step of S600, when the temperature of the melted metal of the master alloy and pure iron reached 1450 °C during the agitating step of S500, an ingot was formed by pouring the melted alloy from the vacuum melting furnace. At the step of S700, the ingot was fabricated in forms of a plate, tube, rod, wire or the like, through hot rolling, and at the step of S800, water quenching treatment was done to prevent the precipitation of carbides which generally degrade the mechanical properties and corrosion resistance.

Comparative examples 1 to 3. Commercial austenitic stainless steels

[0045] The commercially-available austenitic stainless steels (i.e., AISI 304, AISI 316, AISI 316L) were used.

Comparative examples 4 and 5

[0046] The austenitic stainless steels were fabricated according to a composition disclosed by *H. Berns et al.* in the Patent Application No. PCT/EP2005/008960.

[0047] The compositions of the austenitic stainless steels of the examples and the comparative examples are listed in table 1.

[Table 1] (wt.%)

Alloy	Cr	Mn	Ni	Mo	W	N	C	C+N
Ex.1	18.10	9.47	-	2.17	-	0.38	0.48	0.86
Ex.2	17.85	9.72	1.25	2.05	-	0.42	0.49	0.91
Ex.3	17.98	9.79	-	-	2.01	0.39	0.48	0.87
Ex.4	17.71	9.85	1.21	-	2.00	0.36	0.55	0.91
Ex.5	18.12	9.63	0.10	1.16	2.00	0.38	0.53	0.91
Ex.6	17.73	9.97	1.23	1.15	1.99	0.39	0.52	0.91
Ex.7	17.68	9.84	-	-	3.80	0.41	0.56	0.97
Ex.8	17.65	9.73	1.17	-	3.77	0.43	0.54	0.97
Comp.1	18.00	2.00	8.00	-	-	-	0.08	0.08
Comp.2	17.00	2.00	12.00	2.50	-	-	0.08	0.08
Comp.3	17.00	2.00	12.00	2.50	-	-	0.03	0.03
Comp.4	18.54	17.86	0.45	0.52	-	0.54	0.66	1.20
Comp.5	17.97	17.8	0.36	0.51	-	0.58	0.48	1.06

Experiment 1. Measurement of tensile properties

[0048] The tensile properties of the examples and the comparative examples fabricated according to the embodiments of the present invention are listed in table 2.

[Table 2]

Alloy	Yield strength (MPa)	Tensile strength (Mpa)	Uniform elongation (%)
Ex.1	529	980	62.1
Ex.2	559	973	46.3
Ex.3	537	960	52.3
Ex.4	493	903	59.3
Ex.5	523	899	51.1
Ex.6	528	927	49.4
Ex.7	476	868	55.7
Ex.8	532	930	50.8
Comp.1	205	515	40.0 (total elongation)
Comp.2	205	515	40.0 (total elongation)
Comp.3	170	480	40.4 (total elongation)
Comp.4	533	1019	62.8
Comp.5	500	940	59.0

[0049] As table 2 illustrates, compared to the commercial austenitic stainless steels of comparative examples 1 to 3 which exhibited the yield strength of 170~205 MPa, the tensile strength of 480~515 MPa, and the elongation of 40 %, the examples fabricated according to the present invention exhibited superior mechanical properties, which were 476~559 MPa of yield strength, 868~980 MPa of tensile strength, and 46.3~62.1% of uniform elongation.

[0050] Furthermore, the examples fabricated according to the present invention exhibited comparable mechanical properties to those of the C+N austenitic stainless steels (comp. 4 and comp. 5) disclosed by *H. Berns et al.,* which showed the yield strength of 500~533 MPa, the tensile strength of 940~1019 MPa, and the uniform elongation of 59.0~62.8%.

[0051] Accordingly, the austenitic stainless steel obtainable according to an embodiment of the present invention minimizes nickel (Ni) content and exhibits superior mechanical properties in comparison with the commercial austenitic stainless steels. Therefore, the austenitic stainless steel obtainable according to the present invention can replace the conventional austenitic stainless steels.

Experiment 2. Measurement of corrosion resistance

[0052] In order to measure the corrosion resistance of the austenitic stainless steels obtainable according to the present invention, anodic polarization behavior of the sample was observed, as a result, the pitting potential was measured. Samples of austenitic stainless steels obtained according to the examples of the present invention and comparative examples were immersed in a 1 M NaCl solution at a room temperature, and the potential was increased at a potential scan rate (dV/dt) of 2 mV/s. The polarization responses are represented in FIG. 4 and the measured pitting potentials are listed in table 3.

[Table 3]

Alloy	Pitting potentials (E_{pit}), V_{SCE}
Ex 1	No pitting (1.0 or above)
Ex.2	No pitting (1.0 or above)
Ex.3	No pitting (1.0 or above)
Ex.4	No pitting (1.0 or above)
Ex.5	No pitting (1.0 or above)
Ex.6	No pitting (1.0 or above)
Ex.7	No pitting (1.0 or above)
Ex.8	No pitting (1.0 or above)
Comp.1	0.311
Comp.2	0.417
Comp.3	0.496
Comp.4	0.557
Comp.5	0.692

[0053] As illustrated in FIG. 4 and table 3, examples 1 to 8 obtained according to the present invention did not exhibit an occurrence of the pitting corrosion. Contrarily, the pitting corrosion occurred at 0.311~0.496 V_{SCE} on the commercial stainless steels of comparative examples 1 to 3, and also occurred at 0.557~0.692 V_{SCE} on the conventional C+N stainless steel of comparative examples 4 and 5, respectively. Accordingly, it is clear that the austenitic stainless steels fabricated according to the embodiments of the present invention have superior resistance to pitting corrosion than those of the comparative examples.

[0054] Consequently, compared to the commercial austenitic stainless steels or conventional C+N austenitic stainless steels, the austenitic stainless steel obtainable according to the embodiments of the present invention has minimized nickel (Ni) content and exhibits superior mechanical properties with increased corrosion resistance. Therefore, the austenitic stainless steel obtainable according to the present invention can replace the conventional austenitic stainless steels.

Claims

1. A fabrication method of the C+N austenitic stainless steel with high mechanical strength and excellent corrosion resistance, which consists of: 8 to 12 wt.% manganese (Mn); 15 to 20 wt.% chromium (Cr); 2 wt.% or less nickel

(Ni); 0.6 to 1.0 wt.% of total C+N content, with 0.3 or higher wt.% nitrogen (N); 4 wt.% or less tungsten (W); 2 wt.% or less molybdenum (Mo); a balance of iron (Fe); and unavoidable impurities, the fabrication method comprising:

master alloy charging in which a master alloy for the stainless steel having the composition of 8 to 12 wt.% manganese (Mn); 15 to 20 wt.% chromium (Cr); 2 wt.% or less nickel (Ni); 0.6 to 1.0 wt.% of total C+N content, with 0.3 or higher wt.% nitrogen (N); 4 wt.% or less tungsten (W); 2 wt.% or less molybdenum (Mo); a balance of iron (Fe); and unavoidable impurities is charged into a vacuum melting furnace;
vacuum maintaining in which the vacuum melting furnace with the master alloy charged therein is maintained under vacuum;
master alloy melting in which the vacuum melting furnace is heated and the master alloy is melted;
nitrogen (N) content adjusting in which nitrogen gas is injected into the vacuum melting furnace to make nitrogen content in the C+N austenitic stainless steel as indicated above;
melted alloy agitating in which the melted master alloy is agitated;
ingot forming in which an ingot is formed by pouring the agitated melted alloy from the vacuum melting furnace;
hot-rolling the formed ingot; and
performing water quenching of the hot-rolled stainless steel to prevent precipitation of carbide which degrades the mechanical property and corrosion resistance,

wherein the nitrogen (N) content adjusting comprises:

nitrogen gas injecting in which nitrogen gas is injected to the interior of the vacuum melting furnace; and
pressure adjusting in which the partial pressure of nitrogen gas of the interior of the vacuum melting furnace is adjusted to 1 atm.

2. The fabrication method of claim 1, in the vacuum maintaining step, the vacuum level inside the vacuum melting furnace is kept at 10^{-3} torr or lower.

Patentansprüche

1. Herstellungsverfahren für den C+N austenitischen nichtrostenden Stahl mit hoher mechanischer Festigkeit und ausgezeichneter Korrosionsbeständigkeit, welcher die folgenden Bestandteile hat: 8 bis 12 Gew.-% Mangan (Mn); 15 bis 20 Gew.-% Chrom (Cr); höchstens 2 Gew.-% Nickel (Ni); 0,6 bis 1,0 Gew.-% Gesamtgehalt an C+N, wobei Stickstoff (N) mindestens 0,3 Gew.-% ausmacht; höchstens 4 Gew.-% Wolfram (W); höchstens 2 Gew.-% Molybdän (Mo); wobei Eisen (Fe) und unvermeidbare Verunreinigungen den Rest ausmachen, wobei das Herstellungsverfahren Folgendes umfasst:

Beschicken mit einer Vorlegierung, wobei ein Vakuumschmelzofen mit einer Vorlegierung für den nichtrostenden Stahl beschickt wird, welche sich aus 8 bis 12 Gew.-% Mangan (Mn); 15 bis 20 Gew.-% Chrom (Cr); höchstens 2 Gew.-% Nickel (Ni); einem Gesamtgehalt an C+N von 0,6 bis 1,0 Gew.-%, wobei Stickstoff (N) mindestens 0,3 Gew.-% ausmacht; höchstens 4 Gew.-% Wolfram (W); höchstens 2 Gew.-% Molybdän (Mo) zusammensetzt, wobei Eisen (Fe) und unvermeidbare Verunreinigungen den Rest ausmachen,
Aufrechterhalten des Vakuums, wobei der Vakuumschmelzofen mit der darin befindlichen Vorlegierung unter Vakuum gehalten wird;
Schmelzen der Vorlegierung, wobei der Vakuumschmelzofen aufgeheizt und die Vorlegierung geschmolzen wird;
Einstellen des Gehalts an Stickstoff (N), wobei Stickstoffgas in den Vakuumschmelzofen eingeleitet wird, damit der Stickstoffgehalt in dem C+N austenitischen Stahl die oben genannten Werte erreicht;
Rühren der geschmolzenen Legierung, wobei die geschmolzene Vorlegierung gerührt wird;
Bilden eines Barrens, wobei ein Barren gebildet wird, indem die gerührte geschmolzene Legierung aus den Vakuumschmelzofen abgegossen wird;
Walmwalzen des Barrens nach dessen Bildung; und
Durchführen einer Wasserabschreckung des warmgewalzten nichtrostenden Stahls, um eine Abscheidung von Carbid zu verhindern, welche die mechanische Eigenschaft und die Korrosionsbeständigkeit verschlechtert,
wobei das Einstellen des Gehalts an Stickstoff (N) Folgendes umfasst:

Einleiten von Stickstoffgas, wobei Stickstoffgas in den Innenraum des Vakuumschmelzofens eingeleitet wird; und

Einstellen des Drucks, wobei der Partialdruck des Stickstoffgases im Innenraum des Vakuumschmelzofens auf 1 atm eingestellt wird.

2. Herstellungsverfahren nach Anspruch 1, wobei, im Schritt des Aufrechterhaltens des Vakuums, das Vakuum im Vakuumschmelzofen bei einem Niveau von höchstens 10^{-3} torr gehalten wird.

Revendications

1. Procédé de fabrication d'acier inoxydable austénitique C+N possédant une résistance mécanique élevée et une résistance excellente à la corrosion, qui est constitué par : de 8 à 12 % en poids de manganèse (Mn) ; de 15 à 20 % en poids de chrome (Cr) ; 2 % en poids ou moins de nickel (Ni) ; de 0,6 à 1,0 % en poids d'une teneur totale en C+N, avec 0,3 % en poids ou plus d'azote (N) ; 4 % en poids ou moins de tungstène (W) ; 2 % en poids ou moins de molybdène (Mo) ; le reste étant du fer (Fe) et des impuretés inévitables, le procédé de fabrication comprenant :

le chargement d'un alliage maître, dans lequel on charge dans un four de fusion sous vide un alliage maître pour l'acier inoxydable possédant la composition suivante : de 8 à 12 % en poids de manganèse (Mn) ; de 15 à 20 % en poids de chrome (Cr) ; 2 % en poids ou moins de nickel (Ni) ; de 0,6 à 1,0 % en poids d'une teneur totale en C+N, avec 0,3 % en poids ou plus d'azote (N) ; 4 % en poids ou moins de tungstène (W) ; 2 % en poids ou moins de molybdène (Mo) ; le reste étant du fer (Fe) et des impuretés inévitables ;
le maintien du vide, dans lequel on maintient sous vide le four de fusion sous vide dans lequel on a chargé l'alliage maître ;
la mise en fusion de l'alliage maître, dans laquelle on chauffe le four de fusion sous vide et on porte à fusion l'alliage maître ;
le réglage de la teneur en azote (N), dans lequel on injecte de l'azote gazeux dans le four de fusion sous vide pour obtenir la teneur en azote de l'acier inoxydable austénitique C+N, telle qu'indiquée ci-dessus ;
l'agitation de l'alliage en fusion, dans laquelle on agite l'alliage maître en fusion ;
la formation d'un lingot, dans laquelle on forme un lingot en versant l'alliage agité en fusion à partir du four de fusion sous vide ;
le laminage à chaud du lingot obtenu ; et
la mise en oeuvre d'une trempe à l'eau de l'acier inoxydable soumis à un laminage à chaud afin d'empêcher une précipitation du carbure, qui dégrade les propriétés mécaniques et la résistance à la corrosion ;

dans lequel le réglage de la teneur en azote (N) comprend :

l'injection d'azote gazeux, dans laquelle on injecte de l'azote gazeux à l'intérieur du four de fusion sous vide ; et
le réglage de la pression, dans laquelle on règle à 1 atm la pression partielle de l'azote gazeux à l'intérieur du four de fusion sous vide.

2. Procédé de fabrication selon la revendication 1 dans lequel, dans l'étape de maintien du vide, le niveau de vide à l'intérieur du four de fusion sous vide est maintenu à une valeur de 10^{-3} torr ou moins.

FIG. 1

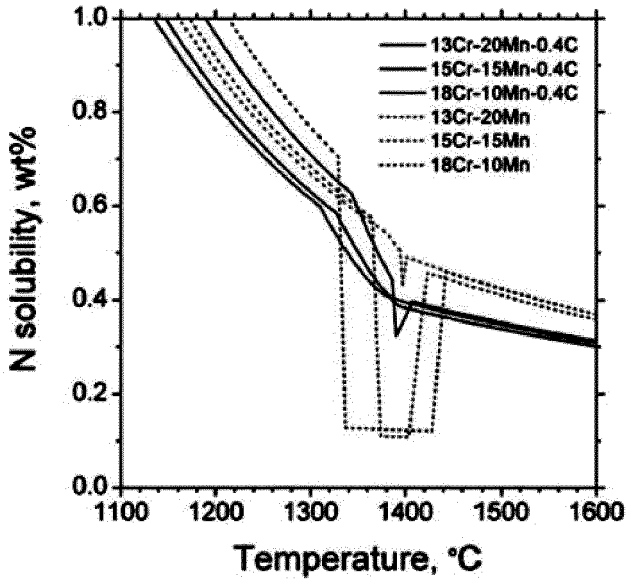

1.0
0.8
0.6
0.4
0.2
0.0
N solubility, wt%
1100
1200
1300
1400
1500
1600
Temperature, °C
13Cr-20Mn-0.4C
15Cr-15Mn-0.4C
18Cr-10Mn-0.4C
13Cr-20Mn
15Cr-15Mn
18Cr-10Mn

FIG. 2

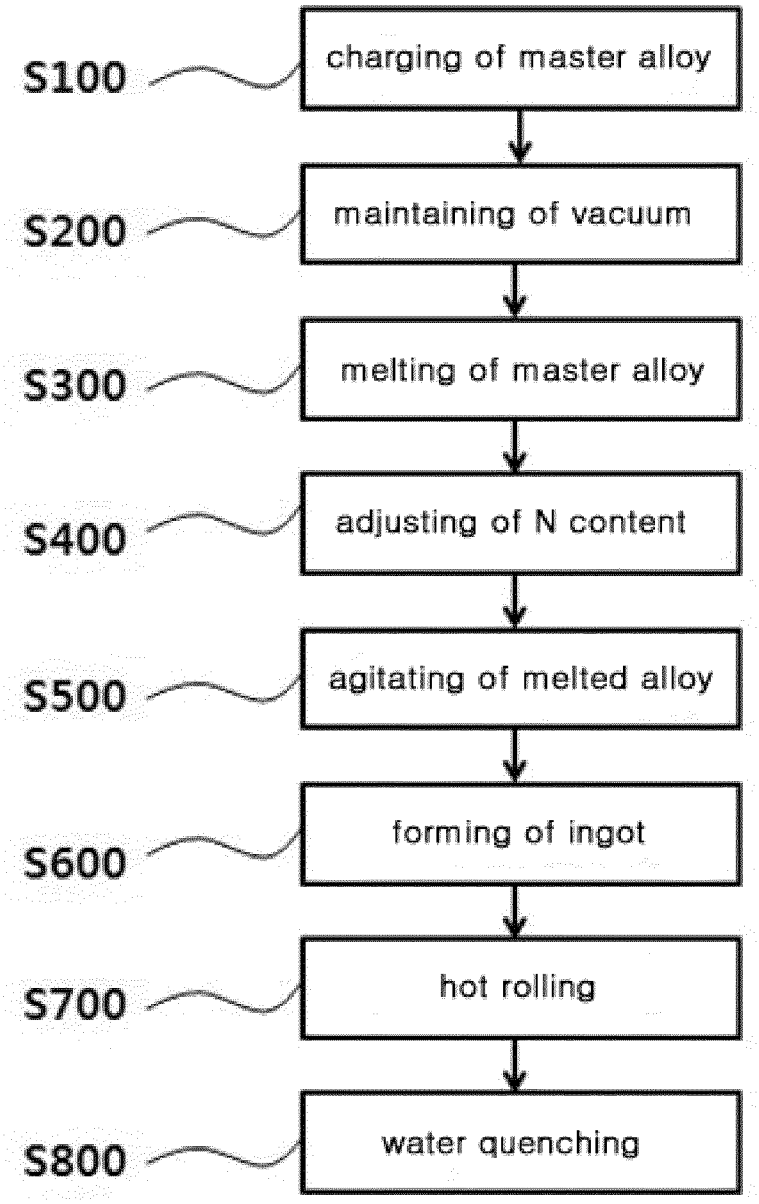

S100
charging of master alloy
S200
maintaining of vacuum
S300
melting of master alloy
S400
adjusting of N content
S500
agitating of melted alloy
S600
forming of ingot
S700
hot rolling
S800
water quenching

FIG. 3

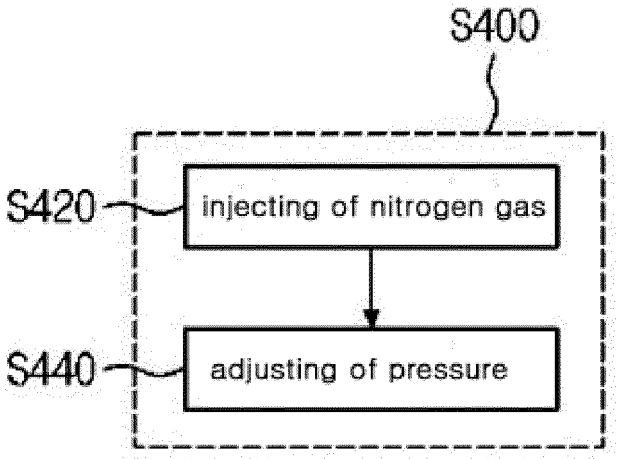
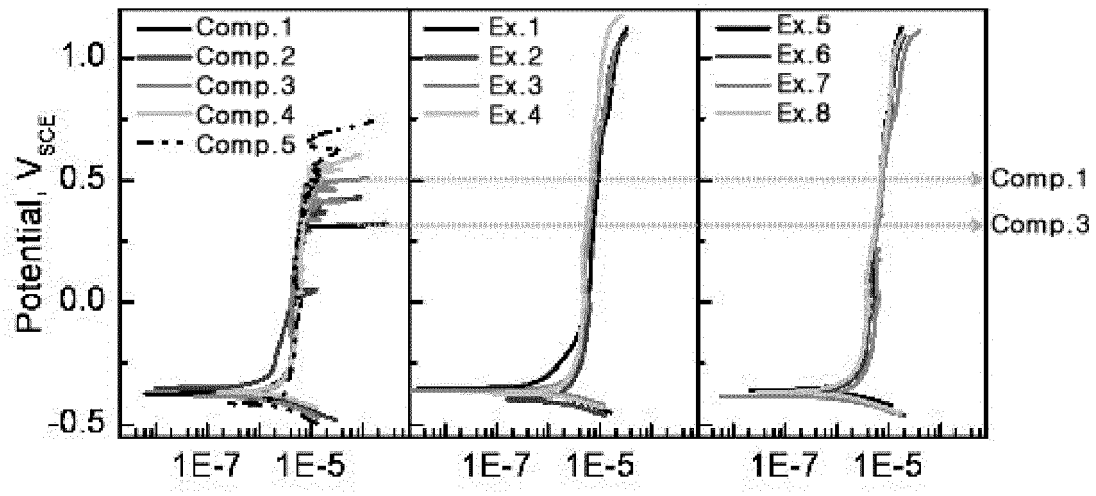

S400
S420
injecting of nitrogen gas
S440
adjusting of pressure

FIG. 4


Comp.1
Comp.2
Comp.3
Comp.4
Comp.5
Ex.1
Ex.2
Ex.3
Ex.4
Ex.5
Ex.6
Ex.7
Ex.8
Potential, V SCE
1.0
0.5
0.0
-0.5
1E-7
1E-5
Comp.1
Comp.3

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 1229142 A1 **[0010]**
- EP 2005008960 W **[0011] [0021] [0046]**