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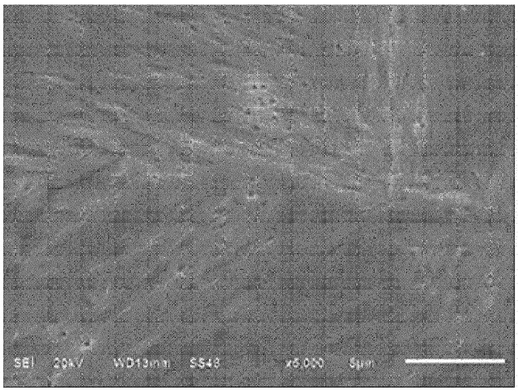
(54) # HIGHLY ANTICORROSIVE MARTENSITIC STAINLESS STEEL, AND MANUFACTURING METHOD THEREFOR

(57) Disclosed is a highly anticorrosive martensitic stainless steel having uniformly distributed fine chromium carbide so as to have improved corrosion resistance and being applicable as tableware with suitable hardness when strengthened by heat treatment, and a manufacturing metho therefor.

The highly anticorrosive martensitic stainless steel according to an embodiment of the present disclosure includes, in percent by weight (wt%), 0.14 to 0.21% of C, 0.05 to 0.11% of N, 0.1 to 0.6% of Si, 0.4 to 1.2% of Mn, 14.0 to 17.0% of Cr, 0.2 to 0.32% of C+N, and the balance of Fe and inevitable impurities, has a PREN value, represented by Formula (1), of 16 or more, and has a precipitation temperature of chromium carbide of 950°C or lower.

FIG.3



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Description

[Technical Field]

[0001] The present disclosure relates to a highly anticorrosive martensitic stainless steel and a manufacturing method therefor, and more particularly, to a highly anticorrosive martensitic stainless steel applicable as a material for tableware and a manufacturing method therefor.

[Background Art]

[0002] In general, materials for edge tools widely used in our daily lives such as knives, scissors, razors, and scalpels, which are medical instruments, require high hardness in order to maintain cutting performance and abrasion resistance and require excellent corrosion resistance because they are used in contact with moisture or stored in a humid atmosphere. Accordingly, high carbon martensitic stainless steels having high hardness are widely used as the materials for edge tools.

[0003] Materials for edge tools that require high hardness are highly brittle. Thus, the materials for edge tools need to be softened to a certain level or more for easy processing. To this end, edge tools are manufactured by using a batch annealing furnace (BAF) or a high-temperature continuous annealing process to facilitate heat treatment of a brittle material.

[0004] During an annealing process, fine particles of chromium carbide are distributed and precipitated in a ferrite matrix as a result of reactions between carbon and chromium. As a solid carbon content decreases in the matrix, the resultant material may be easily applied to a stainless steel manufacturing process such as rolling and acid pickling. Besides, the fine chromium carbide particles uniformly distributed in the ferrite matrix enable rapid resolidification of chromium and carbon to an austenite phase of high temperature during a hardening heat treatment process performed by an edge tool manufacturer and improve hardness and corrosion resistance of the martensitic stainless steel after quenching.

[0005] However, when the contents of carbon, nitrogen, and chromium, which are increased to improve hardness and corrosion resistance of a martensitic stainless steel for edge tools, exceed certain levels, hardness excessively increases thereby causing problems of workability deterioration during a polishing process to obtain gloss and surface defects, and a precipitation temperature of chromium carbide increases thereby causing problems of an increase in hardening heat treatment temperature and deterioration of corrosion resistance due to residual chromium carbide.

[0006] Therefore, in order to obtain a martensitic stainless steel having excellent corrosion resistance and hardness suitable for a polishing process, there is a need to develop a steel material and establish an annealing pattern so that fine chromium carbide is uniformly distributed and a precipitation temperature of chromium carbide is appropriately controlled to facilitate decomposition at a hardening heat treatment temperature.

[Disclosure]

[Technical Problem]

[0007] To solve the above-described problems, provided is a hot-rolled, annealed martensitic stainless steel sheet having improved corrosion resistance by uniformly distributing fine chromium carbonitride in a matrix and having an appropriate hardness during hardening heat treatment, a highly anticorrosive martensitic stainless steel using the same, and a manufacturing method therefor.

[Technical Solution]

[0008] In accordance with an aspect of the present disclosure, a hot-rolled, annealed highly anticorrosive martensitic stainless steel sheet includes, in percent by weight (wt%), 0.14 to 0.21% of C, 0.05 to 0.11% of N, 0.1 to 0.6% of Si, 0.4 to 1.2% of Mn, 14.0 to 17.0% of Cr, 0.2 to 0.32% of C+N, and the balance of Fe and inevitable impurities, wherein chromium carbide or chromium nitride is distributed in a microstructure at a density of 25 particles/100 μm^2, a precipitation temperature of chromium carbide is 950°C or lower, and a PREN value, represented by Formula (1) below, is 16 or more:

$$(1)\ \mathrm{Cr} + 3.3\ \mathrm{Mo} + 16\ \mathrm{N}$$

(wherein Cr, Mo, and N represent contents (wt%) of each alloying element).

[0009] In addition, according to an embodiment of the present disclosure, the hot-rolled, annealed highly anticorrosive martensitic stainless steel sheet may have an elongation of 20% or more.

[0010] In accordance with another aspect of the present disclosure, a highly anticorrosive martensitic stainless steel includes, in percent by weight (wt%), 0.14 to 0.21% of C, 0.05 to 0.11% of N, 0.1 to 0.6% of Si, 0.4 to 1.2% of Mn, 14.0 to 17.0% of Cr, 0.2 to 0.32% of C+N, and the balance of Fe and inevitable impurities, wherein a PREN value, represented by Formula (1) below, is 16 or more, a value, represented by Formula (2) below, is 950 or less:

$$(1)\ \mathrm{Cr} + 3.3\ \mathrm{Mo} + 16\ \mathrm{N}$$

$$(2)\ 674 + 569\ \mathrm{C} - 4.17\ \mathrm{Si} + 0.46\ \mathrm{Mn} + 10.3\ \mathrm{Cr} + 193\ \mathrm{N}$$

(wherein Cr, Mo, N, C, Si, and Mn represent contents (wt%) of each alloying element).

[0011] In addition, according to an embodiment of the present disclosure, the highly anticorrosive martensitic stainless steel may have a Rockwell hardness of 47 to 53 HRC.

[0012] In addition, according to an embodiment of the present disclosure, the highly anticorrosive martensitic stainless steel may have a pitting potential is 180 mV or more in a 3.5% NaCl aqueous solution at 25°C.

[0013] In accordance with an aspect of the present disclosure, a method for manufacturing a highly anticorrosive martensitic stainless steel includes: hot rolling a slab including, in percent by weight (wt%), 0.14 to 0.21% of C, 0.05 to 0.11% of N, 0.1 to 0.6% of Si, 0.4 to 1.2% of Mn, 14.0 to 17.0% of Cr, 0.2 to 0.32% of C+N, and the balance of Fe and inevitable impurities; batch annealing the hot-rolled steel material; and hardening heat-treating the hot-rolled, annealed steel material, wherein the batch annealing includes s a first cracking process performed in a temperature range of 720 to 900°C for 5 to 25 hours and a second cracking process performed in a temperature range of 500 to 700°C for 5 to 15 hours, and the hot-rolled, annealed steel material includes ferrite as a matrix in which chromium carbide or chromium nitride is distributed at a density of 25 particles/100 μm^2 or more.

[0014] In addition, according to an embodiment of the present disclosure, the batch annealing may further include a pre-cracking process performed in a temperature range of 400 to 600°C for 5 to 10 hours before the first cracking process.

[0015] In addition, according to an embodiment of the present disclosure, the temperature may be raised at a rate of 40 to 200°C/h after the pre-cracking process until the first cracking process.

[0016] In addition, according to an embodiment of the present disclosure, the temperature may be lowered at a rate of 10°C/h or more after the first cracking process until the second cracking process.

[0017] In addition, according to an embodiment of the present disclosure, the hardening heat-treating may include an austenitizing treatment process performed at a temperature of 1,000°C or higher for 1 minute or more, and a quenching process to room temperature at a rate of 0.15°C/s or more.

[0018] In addition, according to an embodiment of the present disclosure, the hardening heat-treating may further include a deep freezing process performed in a temperature range of -150 to -50°C for 10 seconds to 5 minutes and a tempering process performed in a temperature range of 400 to 600°C for 30 minutes to 2 hours, after the quenching process.

[Advantageous Effects]

[0019] The hot-rolled, annealed martensitic stainless steel sheet according to the present disclosure may have enhanced workability by uniformly distributing fine chromium carbide in a microstructure.

[0020] In the highly anticorrosive martensitic stainless steel, a chromium carbide may not be retained after hardening heat treatment by lowering the precipitation temperature of a carbide, and thus excellent corrosion resistance may be obtained even without containing relatively high contents of chromium and carbon. In addition, a martensitic stainless steel having a hardness suitable for tableware may be provided.

[Description of Drawings]

[0021] FIG. 1 is a scanning electron microscope (SEM) image of chromium carbide of a microstructure of a hot-rolled, annealed steel sheet of Steel Type F.

[0022] FIG. 2 is an SEM image of chromium carbide of a microstructure of a hot-rolled, annealed steel sheet of Steel Type B after hardening heat treatment.

[0023] FIG. 3 is an SEM image of chromium carbide of a microstructure of a hot-rolled, annealed steel sheet of Steel Type F after hardening heat treatment.

[Best Mode]

[0024] A hot-rolled, annealed highly anticorrosive martensitic stainless steel sheet according to an embodiment of the present disclosure includes, in percent by weight (wt%), 0.14 to 0.21% of C, 0.05 to 0.11% of N, 0.1 to 0.6% of Si, 0.4 to 1.2% of Mn, 14.0 to 17.0% of Cr, 0.2 to 0.32% of C+N, and the balance of Fe and inevitable impurities, wherein chromium carbide or chromium nitride is distributed in a microstructure at a density of 25 particles/100 μm^2, a precipitation temperature of chromium carbide is 950°C or lower, and a PREN value, represented by Formula (1) below, is 16 or more:

$$(1)\ \mathrm{Cr} + 3.3\ \mathrm{Mo} + 16\ \mathrm{N}$$

(wherein Cr, Mo, and N represent contents (wt%) of each alloying element).

[Modes of the Invention]

[0025] Hereinafter, embodiments of the present disclosure will be described in detail with reference to the accompanying drawings. The following embodiments are provided to fully convey the spirit of the present disclosure to a person having ordinary skill in the art to which the present disclosure belongs. The present disclosure is not limited to the embodiments shown herein but may be embodied in other forms. In the drawings, parts unrelated to the descriptions are omitted for clear description of the disclosure and sizes of elements may be exaggerated for clarity.

[0026] Throughout the specification, the term "include" an element does not preclude other elements but may further include another element, unless otherwise stated.

[0027] As used herein, the singular forms are intended to include the plural forms as well, unless the context clearly indicates otherwise.

[0028] Martensitic stainless steels for edge tools, particularly for tableware, require high corrosion resistance and hardness. After hot rolling and annealing, fine chromium carbide and/or chromium nitride (hereinafter, referred to as chromium carbonitride) are uniformly distributed in a ferrite matrix and hardening heat treatment is performed for rapid resolidification into a high-temperature austenite phase. In this case, chromium carbonitride is easily resolidified and the following conditions are required to obtain a martensite structure having excellent corrosion resistance.

[0029] First, fine chromium carbonitride should be formed in a ferrite matrix of a hot-rolled, annealed steel material, and then a precipitation temperature thereof should be low. In the case of conventional type 420 martensitic stainless steels, a precipitation temperature of chromium carbonitride is high due to a high C content of 0.3% or more and coarse chromium carbonitride is locally formed because the chromium carbonitride are precipitated and grow preferentially in grain boundaries, and thus a resolidification rate into an austenite phase decreases during hardening heat treatment, thereby causing deterioration of hardness and corrosion resistance. In addition, in the case where the precipitation temperature of chromium carbonitride is high even when carbon is contained in an amount of 0.2 to 0.3%, a higher temperature should be applied to completely decompose chromium carbonitride during hardening heat treatment, and thus a lot of energy is consumed by a final manufacturer to increase a hardening heat treatment temperature, thereby increasing energy costs, or the chromium carbonitride is retained due to limited heating capacity of a heat treatment furnace. When the chromium carbonitride is retained, the carbide acts as an origin of corrosion, and thus expected enhancement of corrosion resistance may not be obtained even by adding a high content of chromium.

[0030] Accordingly, the present disclosure provides an alloy composition of a highly anticorrosive martensitic stainless steel having enhanced corrosion resistance and appropriate hardness when hardening heat treatment is performed by uniformly distributing fine chromium carbonitride in a matrix by size regulation of a batch annealing pattern and by controlling a precipitation temperature of the chromium carbonitride at a low level for complete decomposition during hardening heat treatment.

[0031] A hot-rolled, annealed martensitic stainless steel sheet according to an embodiment of the present disclosure includes, in percent by weight (wt%), 0.14 to 0.21% of C, 0.05 to 0.11% of N, 0.1 to 0.6% of Si, 0.4 to 1.2% of Mn, 14.0 to 17.0% of Cr, 0.2 to 0.32% of C+N, and the balance of Fe and inevitable impurities.

[0032] Hereinafter, reasons for numerical limitations on the contents of alloying elements in the embodiment of the present disclosure will be described. Hereinafter, the unit of the component indicates wt% unless otherwise stated.

[0033] The content of carbon (C) is from 0.14 to 0.21%.

[0034] When the C content is low, hardness decreases after hardening heat treatment, so that cutting performance and abrasion resistance may be not obtained. Therefore, in the present disclosure, C may be added in an amount of 0.14% or more. However, an excess of C may cause excessive formation of the chromium carbonitride and increase the precipitation temperature, so that the chromium carbonitride retained after hardening heat treatment deteriorates corrosion resistance and increases a risk of formation of coarse carbide in an annealed structure due to carbon segregation. Therefore, an upper limit of the C content is controlled to 0.21% in the present disclosure. More preferably, the C content may be in the range of 0.145 to 0.17%.

[0035] The content of nitrogen (N) is from 0.05 to 0.11%.

[0036] As an element added to improve both corrosion resistance and hardness, N does not cause local fine segregation so as not to form coarse precipitates in a product when added thereto instead of C. To obtain such effects, in the present disclosure, N may be added in an amount of 0.05% or more, preferably 0.08% or more. However, when the N content is excessive out of melting capacity of a molten steel during casting, and thus it may be difficult to control the alloying elements and pin hole defects may occur on the surface. In addition, the martensitic stainless steel for tableware according to the present disclosure does not require a high hardness exceeding a Rockwell hardness of 53 HRC but requires a high gloss for aesthetic properties. Therefore, an upper limit of the N content may be controlled to 0.11%.

[0037] The content of silicon (Si) is from 0.1 to 0.6%.

[0038] Si is an element essentially added for deoxidation. In consideration thereof, Si may be added in an amount of 0.1% or more in the present disclosure. However, an excess of Si deteriorates acid pickling performance, thereby increasing embrittlement. Therefore, an upper limit of the Si content may be controlled to 0.6% in the present disclosure.

[0039] The content of manganese (Mn) is from 0.4 to 1.2%.

[0040] Mn is an element essentially added for deoxidation. In the present disclosure, Mn is added in an amount of 0.4% or more to compensate for stability of austenite decreased by the lowered contents of C and Ni and to obtain solid solubility of N. However, an excess of Mn may deteriorate the surface quality of the steel and form retained austenite in a finally heat-treated material and thus it may be difficult to obtain hardness. Therefore, an upper limit of the Mn content may be controlled to 1.2%. More preferably, the Mn content may be in the range of 0.8 to 1.1%.

[0041] The content of chromium (Cr) is from 14.0 to 17.0%.

[0042] Cr is a representative element enhancing corrosion resistance of a stainless steel and increasing solid solubility of N. In the present disclosure, Cr is added in an amount of 14.0% or more to obtain sufficient corrosion resistance. However, an excess of Cr may increase manufacturing costs and increase fine segregation of the Cr component in the structure to cause local coarsening of chromium carbonitride, thereby reducing corrosion resistance and hardness of the hardening heat-treated material. Therefore, an upper limit of the Cr content is controlled to 17.0% in the present disclosure. Preferably, the Cr content may be controlled to be greater than 14.5% and less than 15.5%.

[0043] A sum of the C content and the N content is from 0.2 to 0.32%.

[0044] C and N may be added in an amount of 0.2% or more to obtain hardness of a steel after hardening heat treatment, preferably, in an amount of 0.23% or more to obtain the number of carbonitride particles. Meanwhile, when the C+N content is excessive, a fraction of distributed chromium carbonitride increases while batch annealing a hot-rolled steel sheet and thus elongation may deteriorate. In the present disclosure, an upper limit of the C+N content is controlled to 0.32%. In addition, in the case of a martensitic stainless steel for tableware, a high hardness excessing a hardness of 53 HRC, which is required for general-use edge tools, is not required and a high gloss is required for aesthetic properties. In the case where the hardness after hardening heat treatment exceeds 53 HRC in the manufacture of high gloss tableware, workability deteriorates during a polishing process to obtain gloss and surface defects such as wave patterns occur on the surface, thereby deteriorating productivity. Therefore, the upper limit of the C+N content may be controlled to 0.28% to prevent excessive hardening and adjust hardness to an appropriate range.

[0045] The remaining component of the composition of the present disclosure is iron (Fe). However, the composition may include unintended impurities inevitably incorporated from raw materials or surrounding environments, and thus addition of other alloy components is not excluded. These impurities are known to any person skilled in the art of manufacturing and details thereof are not specifically mentioned in the present disclosure.

[0046] Also, in addition to controlling the content of each alloying element to the above-described conditions, the relationship therebetween may be further limited as follows.

[0047] The hot-rolled, annealed martensitic stainless steel sheet and the hardening heat-treated martensitic stainless steel according to the present disclosure may have a pitting resistance equivalent number (PREN), represented by Formula (1) below, of 16 or more.

$$(1)\ \mathrm{Cr} + 3.3\ \mathrm{Mo} + 16\ \mathrm{N}$$

[0048] In addition to controlling the content of each alloying element to the above-described conditions, excellent corrosion resistance may be obtained by controlling the content of each alloying element to satisfy a value of Formula (1) of 16.5 or more.

[0049] A method for manufacturing a hot-rolled, annealed martensitic stainless steel sheet in which fine chromium carbonitride is distributed before hardening heat treatment will be described.

[0050] A hot-rolled martensitic stainless steel material having the above-described alloy composition is subjected to continuous casting or steel ingot casting to prepare a slab and the slab is hot-rolled to prepare a hot-rolled steel sheet ready for processing. Subsequently, the prepared hot-rolled steel sheet is batch-annealed, to obtain excellent workability, before starting processing such as fine rolling to a thickness applicable to edge tools. After the batch annealing, the microstructure may include ferrite as a matrix, and fine chromium carbide may be uniformly distributed therein. The hot-rolled, annealed martensitic stainless steel material is manufactured into a martensitic stainless steel by subsequent hardening heat treatment.

[0051] First, the batch annealing will be described.

[0052] The batch annealing includes a first cracking process and a second cracking process. Also, the batch annealing may optionally include a pre-cracking process before the first cracking process.

[0053] The pre-cracking process is a cracking step, previously performed before the first cracking process, to uniformly raise the temperature over the entire material. According to an embodiment, the pre-cracking process may be performed in a temperature range of 400 to 600°C for 5 to 10 hours.

[0054] When the heating temperature is below 400°C or exceeds 600°C, the temperature cannot be uniformly raised over the entire material. In addition, when the heating time is less than 5 hours or exceeds 10 hours, the temperature cannot be uniformly raised over the entire material.

[0055] The first cracking process is a step of uniformly distributing chromium carbonitride in the microstructure of the hot-rolled steel sheet. According to an embodiment, the first cracking process may be performed at a constant temperature in a temperature range of 720 to 900°C for 5 to 25 hours.

[0056] When the heating temperature is below 720°C, agglomerates of chromium carbonitride may be formed locally in grain boundaries. When the heating temperature exceeds 900°C, coarse chromium carbonitride is formed in grain boundaries.

[0057] In addition, when the heating time is less than 5 hours, the size of chromium carbonitride may be decreased, but chromium carbonitride may be distributed intensively in a portion. When the heating time exceeds 25 hours, chromium carbonitride particles adjacent to each other are combined to be locally coarsened.

[0058] Chromium carbide agglomerates or coarse chromium carbide may cause non-uniformity of a material, thereby deteriorating ductility and deteriorating rigidity ductility, and corrosion resistance of a final product. To prevent this, in the present disclosure, the heating temperature of the first cracking process is controlled in the range of 720 to 900°C, and the heating time is controlled in the range of 5 to 25 hours.

[0059] The second cracking process is a step of spheroidizing chromium carbonitride. By spheroidizing chromium carbonitride, workability of a subsequent processing operation may be improved. According to an embodiment, the second cracking process may be performed at a constant temperature in a temperature range of 500 to 700°C for 5 to 15 hours.

[0060] For spheroidization of chromium carbonitride, a heating temperature of 500°C or higher is required. On the contrary, when the heating temperature exceeds 700°C, spheroidized chromium carbonitride excessively grow and the number thereof decreases, thereby deteriorating ductility. In addition, when the heating time is less than 5 hours, chromium carbonitride is not spheroidized. When the heating time exceeds 15 hours, chromium carbonitride excessively grows, thereby deteriorating ductility.

[0061] The temperature may be raised at a rate of 40 to 200°C/h after the pre-cracking process until the first cracking process.

[0062] When the heating rate is less than 40°C/h, a time required for passing through a temperature range of 700 to 750°C in which chromium carbonitride coarsens increases, and thus the chromium carbonitride coarsen and the number of the chromium carbonitride particles distributed in the microstructure decreases, thereby deteriorating ductility. On the contrary, when the heating rate exceeds 200°C/h, a time required for passing through the temperature range in which chromium carbonitride coarsens decreases, and thus fine chromium carbonitride may be obtained. However, chromium carbonitride is non-uniformly distributed due to insufficient time for distribution of chromium carbonitride.

[0063] After the first cracking process, the temperature may be lowered at a rate of 10°C/h or more until the second cracking process.

[0064] When the cooling rate is less than 10°C/h, the time required for passing through the temperature range in which chromium carbonitride coarsens increases, and thus the chromium carbonitride coarsens and it is difficult to obtain high corrosion resistance and high hardness.

[0065] After the second cracking process, air cooling may be performed.

[0066] In the above-described batch annealing, carbon reacts with chromium to form chromium carbide and nitrogen also reacts with chromium to form chromium nitride in the microstructure. As a result, the content of solute C decreases in the microstructure, thereby improving workability and the steel sheet may be easily applied to a subsequent steel making process and processed to a desired final shape. The hot-rolled, annealed martensitic stainless steel sheet according to an embodiment of the present disclosure may have an elongation of 20% or more. The chromium nitride also enhances hardness and corrosion resistance of the martensite structure after rapid cooling by hardening heat treatment.

[0067] In addition, the fine chromium carbonitride uniformly distributed in the microstructure by the above-described batch annealing process may enable rapid resolidification of carbon, nitrogen, and chromium to a high-temperature austenite phase during the subsequent hardening heat-treating process and improve hardness and corrosion resistance of the martensite structure after rapid cooling.

[0068] According to the present disclosure, fine chromium carbonitride may be uniformly distributed in the microstructure of the hot-rolled, annealed martensitic stainless steel sheet by the above-described batch annealing process, and chromium carbonitride may be distributed in the microstructure at a density of 25 particles/100 μm^2 or more. When the chromium carbonitride is distributed in the microstructure at a density less than 25 particles/100 μm^2, ductility deteriorates due to the small number and the large size of the chromium carbonitride, and resolidification of chromium and carbon is difficult in the subsequent hardening heat treatment, and thus a desired hardness cannot be obtained.

[0069] According to the present disclosure, after being processed to a final shape, the batch-annealed hot-rolled, annealed martensitic stainless steel material is subjected to the hardening heat treatment to prepare a martensitic stainless steel.

[0070] The hardening heat treatment may include an austenitizing treatment process, and a quenching process, and may further include a deep freezing process and a tempering process, if required.

[0071] The austenitizing treatment process is a step of transforming the matrix of the steel material from ferrite to austenite.

[0072] In this process, the chromium carbonitride is resolidified in the matrix in the form of chromium, carbon, and nitrogen, and thus hardness of the martensitic stainless steel may be enhanced after the subsequent quenching or deep freezing process.

[0073] According to an embodiment, the austenitizing treatment process may be performed by heat treatment at a temperature of 1,000°C or higher for 1 minute or more. In this case, both of chromium and carbon may be resolidified during the austenitizing treatment in accordance with a precipitation temperature of the chromium carbide ($Cr_{23}C_6$). A desired precipitation temperature of the chromium carbide of the present disclosure is 950°C or lower. The precipitation temperature of the chromium carbide may vary according to the composition of the alloying elements and may be expressed by Formula (2) below. As shown in Formula (2), as the contents of chromium and carbon increase, the precipitation temperature of the chromium carbide increases.

$$(2)\ 674 + 569\ C - 4.17\ Si + 0.46\ Mn + 10.3\ Cr + 193\ N$$

[0074] In the case where a large amount of chromium is contained to enhance corrosion resistance or large amounts of carbon and nitrogen are contained to enhance hardness, the precipitation temperature of the chromium carbide increases, and thus there are limitations on the temperature range of austenitizing. As described above, the chromium carbide may not be completely resolidified but may be retained in actual hardening heat treatment due to facility problems caused by limited heating capacity or an increase in energy costs. In this case, corrosion resistance may deteriorate. Therefore, in the present disclosure, all of the chromium and carbon added thereto may contribute to corrosion resistance by controlling the precipitation temperature of the chromium carbide to 950°C or lower as well as by adjusting the alloy composition.

[0075] When the austenitizing treatment temperature is below 1,000°C, it may be difficult to completely decompose the chromium carbide and a treatment time may increase, thereby deteriorating economic feasibility. Meanwhile, when the austenitizing treatment temperature is too high, energy costs increase to deteriorate economic feasibility, the amount of resolidified carbide increases to excessively form retained austenite, thereby deteriorating hardness, and the grains grow excessively. Therefore, it is preferable to control the austenitizing treatment temperature to 1,200°C or lower.

[0076] In addition, when the austenitizing treatment time is less than 1 minute, it is difficult to completely decompose chromium carbide making it difficult to obtain a desired hardness. When the austenitizing treatment time increases, grains grow excessively, thereby causing retained austenite. Therefore, it is preferable to control the austenitizing treatment time to 30 minutes or less.

[0077] The quenching process is a step of transforming the austenite structure to a martensite having a high hardness via rapid cooling to room temperature at a cooling rate of 0.15°C/s or more after the austenitizing treatment. By cooling at a cooling rate of 0.2°C/s or more, a higher martensite hardness may be obtained.

[0078] The deep freezing process is a step of additionally transforming the retained austenite structure to the martensite structure by further cooling the steel material quenched to room temperature to an extremely low temperature. By the deep freezing process, the hardness of the steel material may further be increased. According to an embodiment, the deep freezing process may be performed by subzero heat treatment performed at a temperature of -150 to -50°C for 10 seconds to 5 minutes.

[0079] The tempering process is a step of imparting toughness to a martensite structure, which has high embrittlement due to high hardness, after the deep freezing process. According to an embodiment, the tempering process may be performed in a temperature range of 400 to 600°C for 30 minutes to 2 hours.

[0080] According to the present disclosure, by the above-described hardening heat treatment, the ferrite structure may be finally transformed into the martensite structure and desired hardness and corrosion resistance may be obtained. For example, an area fraction of chromium carbonitride retained in a cross-section of the material after resolidification by hardening heat-treating may be 2% or less.

[0081] The highly anticorrosive martensitic stainless steel according to an embodiment of the present disclosure may have a pitting potential of 180 mV or more in a 3.5% NaCl aqueous solution at 25°C. This may be obtained by completely resolidifying the carbide by controlling the PREN value, represented by Formula (1), to 16.0 or more and controlling the precipitation temperature of chromium carbide to 950°C or lower.

[0082] The highly anticorrosive martensitic stainless steel according to an embodiment of the present disclosure may have a Rockwell hardness of 47 to 53 HRC.

[0083] Among martensitic stainless steels for edge tools, those for tableware do not require a high hardness and a high hardness exceeding 53 HRC is not required therefor because there may be a problem in working productivity during polishing to obtain gloss. A hardness of 49 to 53 HRC is suitable for a blade and a hardness of 47 to 51 HRC is suitable for a handle for tableware knives. Therefore, in the present disclosure, the upper limit of the C+N content is controlled to 0.32%, and the contents of the alloying elements are limited to the above-described ranges to obtain an appropriate hardness even when they are completely resolidified by controlling the precipitation temperature of chromium carbide. Accordingly, the highly anticorrosive martensitic stainless steel of the present disclosure may have a Rockwell hardness of 47 to 53 HRC.

[0084] Hereinafter, the present disclosure will be described in more detail with reference to the following examples.

Examples

[0085] Steels including the alloying elements shown in Table 1 below were cast and hot-rolled, followed by heat treatment for batch annealing. The batch annealing was conducted by performing a pre-cracking process at 500°C for 7 hours, raising the temperature at a rate of about 100°C/h, performing a first cracking process at 840°C for 10 hours, lowering the temperature at a rate of 15°C/h, maintaining at 580°C for 10 hours, and performing an air cooling process.

Table 1

Steel type	Composition (wt%)						precipitation temperature of Cr carbide (°C)	Occurrence of pin hole	Remarks
	C	Si	Mn	Cr	Mo	N			
A	0.6500	0.29	0.69	13.12	0.01	0.156	1,208	×	Comparative Steel 1
B	0.2530	0.42	0.45	15.36	0.01	0.195	1,012	◦	Comparative Steel 2
C	0.2445	0.47	0.46	15.35	0.01	0.114	991	×	Comparative Steel 3
D	0.150	0.50	0.45	13.50	0.01	0.080	911	×	Comparative Steel 4
E	0.1460	0.51	0.48	13.45	0.01	0.095	912	◦	Comparative Steel 5
F	0.1620	0.31	0.98	14.97	0.01	0.095	937	×	Inventive Steel

[0086] Table 1 shows precipitation temperature (°C) of chromium carbonitride and occurrence of pine holes on the surface of the steel materials caused by nitrogen gas as ◦ and ×.

[0087] Pine holes were formed on the surface of steel type B because a large amount of N, out of the range of the present disclosure, was added. Although the N content was appropriate, pin holes were formed in steel type E because the N content exceeds the solid solubility of N due to the low content of Cr, which affects solid solubility of nitrogen, and relatively low contents of C and Mn, which are austenite-stabilizing elements, thereby generating nitrogen gas. No pin holes were formed in steel type F having the alloy composition within the range of the present disclosure, and the precipitation temperature of the chromium carbide was low as 937°C and thus steel type F may be efficiently applied to hardening heat treatment which will be described below.

[0088] In addition, although the precipitation temperature of the chromium carbide was 990°C or higher in the case where the contents of C and Cr were high, it was confirmed that the precipitation temperature was 950°C or lower when the alloy composition including C and Cr was within the range of the present disclosure.

[0089] The numbers of chromium carbide particles contained in the microstructures of the hot-rolled, annealed steel materials A to F prepared as described above were observed using a scanning electron microscope (SEM) and elongations obtained by a tensile test according to the JIS 13 B standard are shown in Table 2 below.

Table 2

Steel type	C	N	C+N	No. of Cr carbonitride (particles/100 μm^2)	Elongatio n (%)	Remarks
A	0.6500	0.156	0.8060	63	17.6	Comparative Steel 1
B	0.2530	0.195	0.4480	21	19.6	Comparative Steel 2
C	0.2445	0.114	0.3585	32	29.3	Comparative Steel 3
D	0.150	0.080	0.2300	19	28.1	Comparative Steel 4
E	0.1460	0.095	0.2410	17	32.4	Comparative Steel 5
F	0.1620	0.095	0.2570	30	30.2	Inventive Steel

[0090] Referring to Table 2, because steel type A included the C content of 0.6% or more, a large number of chromium carbonitride particles were observed at a density of 60/100 μm^2 or more, but a very low elongation of 17.6% was observed.

[0091] Although both steel types B and C had higher C contents of about 0.25%, the N contents thereof were different. Although steel type B had a higher C+N content than that of steel type C, the number of carbonitride particles was 21 particles/100 μm^2 which is smaller than that of steel type C. This is estimated because the chromium carbonitride coarsened due to a too high fraction of the precipitated chromium carbonitride. In addition, steel type B had a slightly low elongation of 19.6% due to the high C+N content. Although Steel type C had a large number of chromium carbonitride particles of 32 particles/100 μm^2 and a high elongation of 29.3%, there is a high possibility of residual chromium carbonitride after hardening heat treatment due to the high precipitation temperature of chromium carbide of 991°C.

[0092] Although steel types D and E had high elongations of 28% or more, the number of the chromium carbonitride particles was less than 25 per 100 μm^2. This may be estimated because the Cr content was low although the content of C+N was appropriate.

[0093] FIG. 1 is a scanning electron microscope (SEM) image of chromium carbonitride of a microstructure of a hot-rolled, annealed steel sheet of Steel Type F. It was confirmed that fine chromium carbonitride are uniformly distributed in the ferrite matrix of steel type F corresponding to the hot-rolled, annealed steel material according to the inventive steel of the present disclosure. As shown in Table 2, as well as the chromium carbide distribution at a density of about 30/100 μm^2, a high elongation of 30.2% was measured.

[0094] Subsequently, the hot-rolled, annealed martensitic stainless steel material was subjected to austenitizing treatment at 1,050°C and quenching at a cooling rate of 0.27°C/s to prepare a martensitic stainless steel. In Table 3, PREN and pitting potential values are shown to evaluate corrosion resistance, and Rockwell hardness is shown to evaluate hardness. The PREN value was derived by substituting the content (wt%) of each alloying element into Formula (1) and the pitting potential was measured in a 3.5% NaCl aqueous solution at 25°C.

Table 3

Steel type	PREN	Pitting potential (mV)	Hardness (HRC)	Remarks
A	15.65	15	61.0	Comparative Steel 1
B	18.51	240	52.6	Comparative Steel 2
C	17.21	212	54.7	Comparative Steel 3
D	14.81	97	51.2	Comparative Steel 4

(continued)

Steel type	PREN	Pitting potential (mV)	Hardness (HRC)	Remarks
E	15.00	93	51.9	Comparative Steel 5
F	16.52	199	51.4	Inventive Steel

[0095] Steel type A including a high C content of 0.6% or more exhibited the lowest pitting potential because a sensitization phenomenon occurred due to depletion of Cr and chromium carbonitride was retained due to the high precipitation temperature of chromium carbide.

[0096] Although steel type B in which nitrogen gas pin holes were formed by adding N exceeding the solid solubility thereof exhibited the highest PREN value and pitting potential due to the influence of N, steel type B could not be applied to products due to pin holes formed on the surface.

[0097] Although steel type C had a PREN value of 17.21 and a high pitting potential of 212 mV, a hardness of 54.7 HRC, which exceeds an appropriate range of 47 to 53 HRC required to prevent occurrence of surface defects during a polishing process to obtain gloss, was obtained due to the high C content.

[0098] Steel types D and E exhibited similar pitting potential values of about 95 mV and similar hardness values because the contents of Cr and N are similar.

[0099] Steel type F corresponding to the inventive steel according to the present exhibited a PREN value of 16.52, which is greater than 16.0, a high pitting potential value of 199 mV, and an appropriate hardness value of 51.4 HRC.

[0100] FIGS. 2 and 3 are SEM images of chromium carbide of microstructures of hot-rolled steel sheets of steel type B and steel type F after hardening heat treatment. Because steel type B shown in FIG. 2 had a high C+N content, the chromium carbonitride could not be uniformly distributed in the hot-rolled, annealed steel material but coarsen to be segregated. Also, it was confirmed that the chromium carbide could not be resolidified but retained even after hardening heat treatment due to the high precipitation temperature of chromium carbide. On the contrary, in steel type F, as Inventive Steel, it was confirmed that most of the chromium carbonitride was resolidified after hardening heat treatment and the area fraction of the chromium carbonitride retained on the cross-section was 2% or less by controlling the contents of C+N and Cr and the precipitation temperature of chromium carbide.

[0101] 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]

[0102] The martensitic stainless steel according to the present disclosure has improved corrosion resistance and appropriate hardness by hardening heat treatment and thus applicable to a material for tableware.

Claims

1. A hot-rolled, annealed highly anticorrosive martensitic stainless steel sheet comprising, in percent by weight (wt%), 0.14 to 0.21% of C, 0.05 to 0.11% of N, 0.1 to 0.6% of Si, 0.4 to 1.2% of Mn, 14.0 to 17.0% of Cr, 0.2 to 0.32% of C+N, and the balance of Fe and inevitable impurities,

   wherein chromium carbide or chromium nitride is distributed in a microstructure at a density of 25 particles/100 μm^2,
   a precipitation temperature of chromium carbide is 950°C or lower, and
   a PREN value, represented by Formula (1) below, is 16 or more:

   $$(1)\ \mathrm{Cr} + 3.3\ \mathrm{Mo} + 16\ \mathrm{N}$$

   (wherein Cr, Mo, and N represent contents (wt%) of each alloying element).

2. The hot-rolled, annealed highly anticorrosive martensitic stainless steel sheet according to claim 1, wherein an elongation is 20% or more.

3. A highly anticorrosive martensitic stainless steel comprising, in percent by weight (wt%), 0.14 to 0.21% of C, 0.05 to 0.11% of N, 0.1 to 0.6% of Si, 0.4 to 1.2% of Mn, 14.0 to 17.0% of Cr, 0.2 to 0.32% of C+N, and the balance of Fe and inevitable impurities,

   wherein a PREN value, represented by Formula (1) below, is 16 or more,
   a value, represented by Formula (2) below, is 950 or less:

$$(1)\ \mathrm{Cr} + 3.3\ \mathrm{Mo} + 16\ \mathrm{N}$$

$$(2)\ 674 + 569\ \mathrm{C} - 4.17\ \mathrm{Si} + 0.46\ \mathrm{Mn} + 10.3\ \mathrm{Cr} + 193\ \mathrm{N}$$

   (wherein Cr, Mo, N, C, Si, and Mn represent contents (wt%) of each alloying element).

4. The highly anticorrosive martensitic stainless steel according to claim 3, wherein a Rockwell hardness is in a range of 47 to 53 HRC.

5. The highly anticorrosive martensitic stainless steel according to claim 3, wherein a pitting potential is 180 mV or more in a 3.5% NaCl aqueous solution at 25°C.

6. A method for manufacturing a highly anticorrosive martensitic stainless steel, the method comprising:

   hot rolling a slab comprising, in percent by weight (wt%), 0.14 to 0.21% of C, 0.05 to 0.11% of N, 0.1 to 0.6% of Si, 0.4 to 1.2% of Mn, 14.0 to 17.0% of Cr, 0.2 to 0.32% of C+N, and the balance of Fe and inevitable impurities;
   batch annealing the hot-rolled steel material; and
   hardening heat-treating the hot-rolled, annealed steel material,
   wherein the batch annealing comprises a first cracking process performed in a temperature range of 720 to 900°C for 5 to 25 hours and a second cracking process performed in a temperature range of 500 to 700°C for 5 to 15 hours, and
   the hot-rolled, annealed steel material comprises ferrite as a matrix in which chromium carbide or chromium nitride is distributed at a density of 25 particles/100 μm^2 or more.

7. The method according to claim 6, wherein the batch annealing further comprises a pre-cracking process performed in a temperature range of 400 to 600°C for 5 to 10 hours before the first cracking process.

8. The method according to claim 7, wherein the temperature is raised at a rate of 40 to 200°C/h after the pre-cracking process until the first cracking process.

9. The method according to claim 6, wherein the temperature is lowered at a rate of 10°C/h or more after the first cracking process until the second cracking process.

10. The method according to claim 6, wherein the hardening heat-treating comprises an austenitizing treatment process performed at a temperature of 1,000°C or higher for 1 minute or more, and a quenching process to room temperature at a rate of 0.15°C/s or more.

11. The method according to claim 10, wherein the hardening heat-treating further comprises a deep freezing process performed in a temperature range of -150 to -50°C for 10 seconds to 5 minutes and a tempering process performed in a temperature range of 400 to 600°C for 30 minutes to 2 hours, after the quenching process.

FIG.1

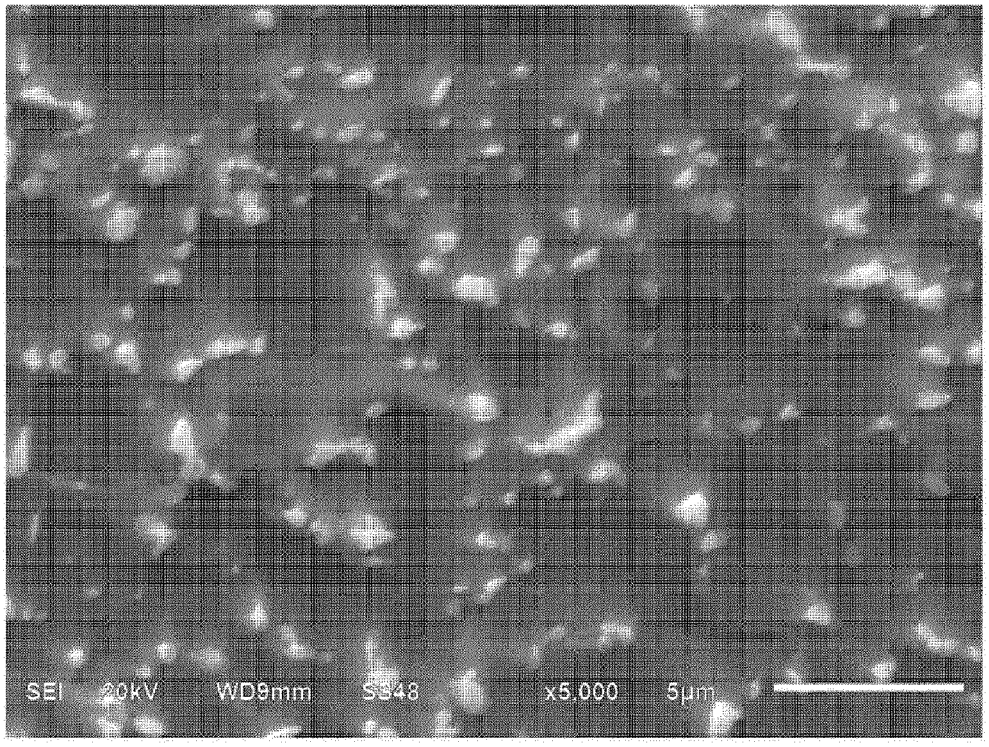


FIG.2

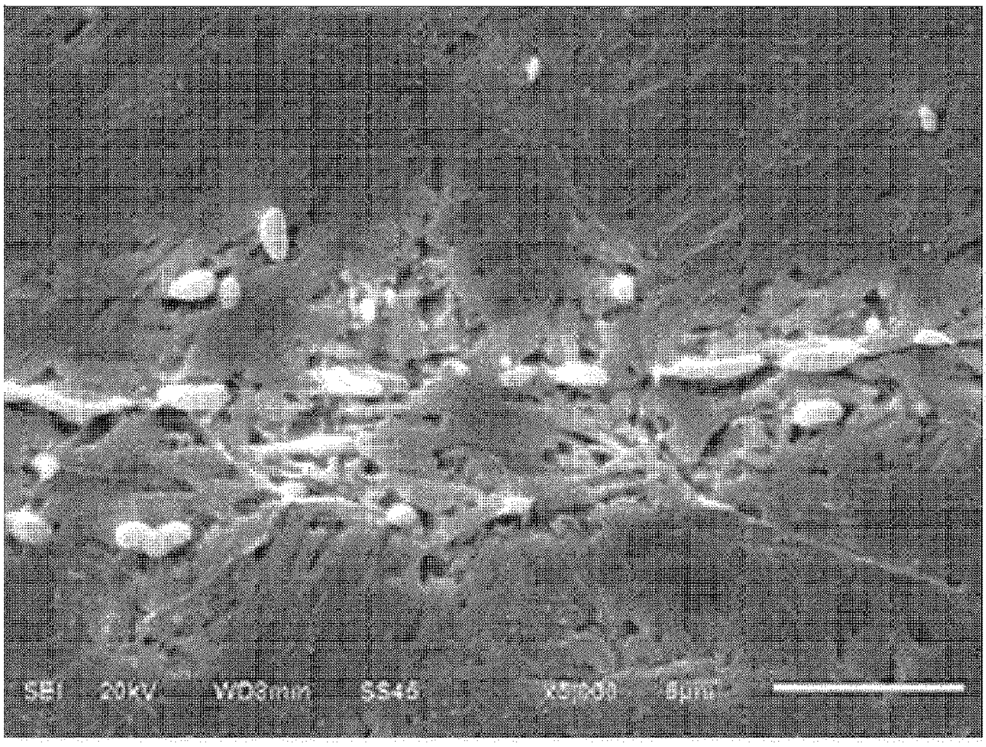
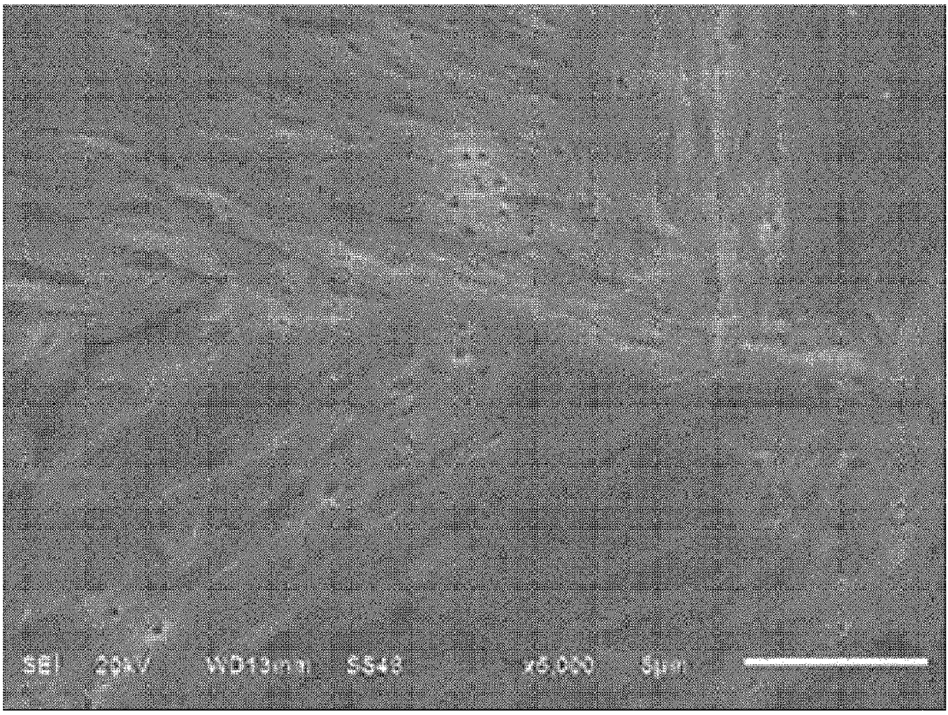


FIG.3



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2020/014029

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/22(2006.01)i; **C22C 38/00**(2006.01)i; **C21D 8/02**(2006.01)i; **C21D 1/26**(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 38/22(2006.01); C21D 8/00(2006.01); C21D 8/02(2006.01); C21D 9/46(2006.01); C22C 38/00(2006.01); C22C 38/18(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: 마르텐사이트(martensite), 스테인리스(stainless), 크롬탄화물(Cr carbide), 크롬질화물(Cr nitride), 내식성(wear resistance)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	CN 101372734 A (BAOSTEEL GROUP CORP.) 25 February 2009 (2009-02-25) See paragraphs [0026]-[0027], [0043], [0049] and [0053], and claim 1, figure 5 and table 2.	3-5 1-2,6-11
Y	KR 10-1834996 B1 (POSCO) 06 March 2018 (2018-03-06) See paragraphs [0027], [0054] and [0072]-[0073] and claims 1 and 4-8.	1-2,6-11
Y	KR 10-1356951 B1 (POSCO) 28 January 2014 (2014-01-28) See claims 6-8.	11
X	KR 10-2005-0054058 A (POSCO) 10 June 2005 (2005-06-10) See claim 1.	3
X	KR 10-0523107 B1 (POHANG IRON & STEEL CO., LTD.) 19 October 2005 (2005-10-19) See claim 1.	3

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search **09 February 2021**	Date of mailing of the international search report **10 February 2021**
Name and mailing address of the ISA/KR **Korean Intellectual Property Office** **Government Complex-Daejeon Building 4, 189 Cheongsa-ro, Seo-gu, Daejeon 35208** Facsimile No. **+82-42-481-8578**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2020/014029

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2019-167630 A (HITACHI METALS LTD.) 03 October 2019 (2019-10-03) See paragraph [0009] and claim 1.	1-11

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2020/014029

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		WO 2017-150738 A1	08 September 2017