(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 265 784 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:
25.10.2023 Bulletin 2023/43

(21) Application number: **21911281.0**

(22) Date of filing: **29.11.2021**

(51) International Patent Classification (IPC):
C22C 38/46 $^{(2006.01)}$ ***C22C 38/44*** $^{(2006.01)}$
C22C 38/42 $^{(2006.01)}$ ***C21D 9/46*** $^{(2006.01)}$
C21D 8/02 $^{(2006.01)}$

(52) Cooperative Patent Classification (CPC):
C21D 8/02; C21D 9/46; C22C 38/42; C22C 38/44; C22C 38/46

(86) International application number:
PCT/KR2021/017715

(87) International publication number:
WO 2022/139214 (30.06.2022 Gazette 2022/26)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **21.12.2020 KR 20200180359**

(71) Applicant: **POSCO Co., Ltd**
Pohang-si, Gyeongsangbuk-do 37859 (KR)

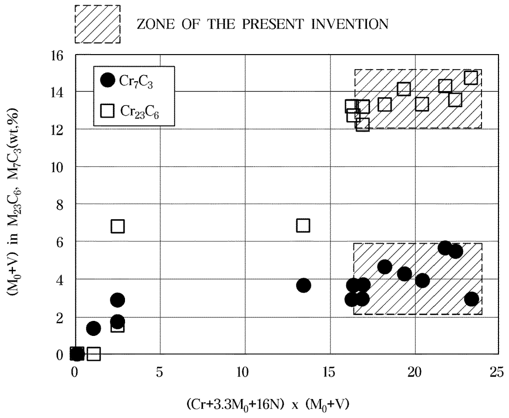
(72) Inventors:
- **SONG, Byoung-jun**
  Pohang-si Gyeongsangbuk-do 37667 (KR)
- **KWON, Youngjin**
  Pohang-si Gyeongsangbuk-do 37655 (KR)
- **JO, Gyujin**
  Pohang-si Gyeongsangbuk-do 37655 (KR)
- **CHU, Nayeon**
  Pohang-si Gyeongsangbuk-do 37669 (KR)

(74) Representative: **Nederlandsch Octrooibureau**
P.O. Box 29720
2502 LS The Hague (NL)

(54) MARTENSITIC STAINLESS STEEL WITH IMPROVED STRENGTH AND CORROSION RESISTANCE, AND MANUFACTURING METHOD THEREFOR

(57) Disclosed is a martensitic stainless steel with improved strength and corrosion resistance. The disclosed martensitic stainless steel sheet comprises, in percent by weight (wt%), 0.3 to 0.5% of C, 0.01 to 0.025% of N, 0.3 to 0.5% of Si, 0.4 to 0.6 of Mn, 13.1 to 14.5% of Cr, 0.95 to 1.10% of Mo, 0.05 to 0.3% of V, 0.3 to 0.5% of Ni, 0.001 to 0.5% of Cu, and the balance being Fe and inevitable impurities, and satisfies Formula (1). Formula (1): $16.4 \leq (Cr+3.3Mo+16N)*(Mo+V) \leq 23.3$, wherein Cr, N, Mo, and V denote the contents (wt%) of respective elements.

【FIG. 1】



Description

[Technical Field]

[0001] The present disclosure relates to a martensitic stainless steel and a method of manufacturing the same, and more particularly, to a martensitic stainless steel applicable to various parts such as home appliances, automobile compressor parts, and doctor blades, and a method of manufacturing the same.

[Background]

[0002] In general, stainless steels are classified according to their chemical composition or metal structure. Based on metal structure, stainless steel may be classified into an austenite system, a ferrite system, a martensite system, and a dual-phase system.

[0003] Martensitic stainless steel, which has excellent hardness and wear resistance but is very brittle and has low elongation, has a different carbon content depending on the application. For example, a brake disc and an anchor, which do not require high wear resistance, use 0.1% or less of carbon, type 1 cutlery use 0.1 to 0.3% of carbon, kitchen knives, scissors, and surgical knives, which require high wear resistance, use 0.3 to 0.7% of carbon, and industrial knives use 1% or more of carbon.

[0004] STS 420, a representative martensitic stainless steel with 12 to 15% of chromium, is the most widely used because of its excellent strength, hardness, and corrosion resistance.

[0005] To ensure strength and hardness, martensitic stainless steels utilize a tempered martensitic structure in which the austenitic phase, which is a high-temperature stable phase, is formed by introducing a hardening heat treatment into a microstructure in which chromium carbide is dispersed in a ferrite base after annealing, and then generated by rapid cooling. The tempered martensite is a very hard structure and its hardness increases as the content of dissolved carbon increases.

[0006] Meanwhile, wear resistance of the martensitic stainless steel may be ensured by a certain fraction of carbides remaining or precipitating after heat treatment. Carbon reacts with chromium to precipitate in the form of chromium carbide, so as the concentration of Cr in a base decreases, corrosion resistance decreases.

[0007] In addition, the larger the size of the residual carbide, the more difficult it is to be easily decomposed into a base, resulting in deviations in hardness and corrosion resistance. In a fatigue environment, the life of the material is shortened because the stress concentration provides a starting point for crack initiation.

[0008] On the other hand, martensitic stainless steel with high brittleness needs to be softened to facilitate machining and is therefore subjected to a batch annealing furnace (BAF) process for easy heat treatment workability. During annealing in a wound coil state, a thermal history deviation occurs in a longitudinal direction thereof. In particular, at the 1/2 point in the longitudinal direction the heating and cooling rates are the slowest, so that the size of carbides becomes coarse, the deviation is maintained after cold rolling, causing the deviation in the physical properties of a final material.

[0009] Accordingly, the development of martensitic stainless steel and the establishment of heat treatment conditions that may suppress material variation while ensuring hardness, strength, and corrosion resistance equal to or greater than those of existing high carbon materials is required.

[Summary]

[Technical Problem]

[0010] The present disclosure provides a martensitic stainless steel with improved strength and corrosion resistance while ensuring hardness by optimizing a content of Mo and V, and a method of manufacturing the same.

[Technical Solution]

[0011] One aspect of the present disclosure provides a hot-rolled annealed martensitic stainless steel sheet with improved strength and corrosion resistance comprising, in percent by weight (wt%), 0.3 to 0.5% of C, 0.01 to 0.025% of N, 0.3 to 0.5% of Si, 0.4 to 0.6 of Mn, 13.1 to 14.5% of Cr, 0.95 to 1.10% of Mo, 0.05 to 0.3% of V, 0.3 to 0.5% of Ni, 0.001 to 0.5% of Cu, and the reminder of Fe and inevitable impurities, and satisfying Formula (1) below:

$$\text{Formula (1):} \quad 16.4 \leq (Cr+3.3Mo+16N)*(Mo+V) \leq 23.3$$

wherein Cr, N, Mo, and V denote contents (wt%) of elements, respectively.

[0012] Furthermore, Formula (2) below may be satisfied:

$$\text{Formula (2): } -14 \leq -36442 + 248\mathrm{C} + 365\mathrm{Cr} + 373\mathrm{Mo} + 530\mathrm{V} + 365\mathrm{Fe} + 350\mathrm{Si} + 312\mathrm{Mn} + 331\mathrm{Ni} + 506\mathrm{C} \leq 50$$

wherein C, Cr, Mo, V, Fe, Si, Mn, Ni, and Cu denote wt% of the respective elements.

[0013] Furthermore, Formula (3) below may be satisfied:

$$\text{Formula (3): } 0.37 \leq \mathrm{C+N} \leq 0.43.$$

[0014] Furthermore, Formula (4) below may be satisfied:

$$\text{Formula (4): } 1.0 \leq \mathrm{Mo+V} \leq 1.35.$$

[0015] Furthermore, the hot-rolled annealed martensitic stainless steel sheet may further include a ferrite as a base structure, a primary carbide represented by $(\mathrm{Cr, Fe, Mo, V})_7\mathrm{C}_3$, and a secondary carbide represented by $(\mathrm{Cr, Fe, Mo, V})_{23}\mathrm{C}_6$.

[0016] Furthermore, the wt% of (Mo+V) in the primary carbide may be 2.93 to 5.67%.

[0017] Furthermore, the wt% of (Mo+V) in the secondary carbide may be 12.2 to 14.8%.

[0018] Furthermore, the particle size of the primary carbide may be 10 μm or less.

[0019] Furthermore, carbide deviation in a longitudinal direction may be 10 pieces/100 μm^2 or less.

[0020] After cold-rolled, the distribution density of carbide may be 42 to 58 pieces/100 μm^2.

[0021] Another aspect of the present disclosure provides a method of manufacturing a martensitic stainless steel with improved strength and corrosion resistance. The method includes hot-rolling a slab including, in percent by weight (wt%), 0.3 to 0.5% of C, 0.01 to 0.025% of N, 0.3 to 0.5% of Si, 0.4 to 0.6% of Mn, 13.1 to 14.5% of Cr, 0.95 to 1.10% of Mo, 0.05 to 0.3% of V, 0.3 to 0.5% of Ni, 0.001 to 0.5% of Cu, and the reminder of Fe and inevitable impurities, and satisfying the Formula (1) below; batch annealing in a temperature range of 600 to 900°C immediately after hot-rolled; cold rolling the hot-rolled annealed material; and hardening heat treatment the cold-rolled material; wherein Formula (1): $16.4 \leq (\mathrm{Cr}+3.3\mathrm{Mo}+16\mathrm{N})*(\mathrm{Mo}+\mathrm{V}) \leq 23.3$ in Formula (1), Cr, N, Mo, and V denote contents (wt%) of elements, respectively.

[0022] Furthermore, the hot-rolled annealed material may further include a ferrite as a base structure, a primary carbide represented by $(\mathrm{Cr, Fe, Mo, V})_7\mathrm{C}_3$, and a secondary carbide represented by $(\mathrm{Cr, Fe, Mo, V})_{23}\mathrm{C}_6$.

[0023] Furthermore, the wt% of (Mo+V) in the primary carbide may be 2.93 to 5.67%.

[0024] Furthermore, the wt% of (Mo+V) in the secondary carbide may be 12.2 to 14.8%.

[0025] Furthermore, the particle size of the primary carbide may be 10 μm or less.

[0026] Furthermore, after cold-rolled, 42 to 58 pieces/100 μm^2 or less of carbides are distributed therein.

[0027] Furthermore, the hardening heat treatment may further include quenching at a temperature range of 980 to 1,050°C and tempering at a temperature of 400 to 600°C for 1 minute to 1 hour.

[0028] Furthermore, the Vickers hardness may be 520 to 650 Hv after the hardening.

[0029] Furthermore, the method may further include satisfying Formula (2) below:

$$\text{Formula (2): } -14 \leq -36442 + 248\mathrm{C} + 365\mathrm{Cr} + 373\mathrm{Mo} + 530\mathrm{V} + 365\mathrm{Fe} + 350\mathrm{Si} + 312\mathrm{Mn} + 331\mathrm{Ni} + 506\mathrm{Cu} \leq 50$$

wherein C, Cr, Mo, V, Fe, Si, Mn, Ni, and Cu denote wt% of the respective elements.

[0030] Furthermore, the method may further include satisfying Formula (3) and (4) below:

$$\text{Formula (3): } 0.37 \leq \mathrm{C+N} \leq 0.43,$$

and

$$\text{Formula (4): } 1.0 \le \text{Mo+V} \le 1.35.$$

[Advantageous Effects]

[0031] Various embodiments of the present disclosure may provide a martensitic stainless steel with improved strength and corrosion resistance while ensuring hardness, and a method of manufacturing the same.

[Brief Description of Drawings]

[0032]

FIG. 1 is a graph illustrating a relationship between (Cr+3.3Mo+16N)*(Mo+V) values and Mo+V contents in the carbide of a martensitic stainless steel according to an embodiment of the present disclosure.

FIG. 2 is a graph illustrating a relationship between (Cr+3.3Mo+16N)*(Mo+V) values and the sizes of primary carbides represented by $(Cr, Fe, Mo, V)_7C_3$ of a martensitic stainless steel according to an embodiment of the present disclosure.

FIG. 3 is a graph illustrating a relationship between (Cr+3.3Mo+16N)*(Mo+V) values and a hot-rolled annealed carbide distribution of a martensitic stainless steel according to an embodiment of the present disclosure.

FIG. 4 is a photograph of scanning electron micrographs (SEM) showing chromium carbides in a microstructure after hardening heat treatment of Comparative Example 4, after tempering.

FIG. 5 is a photograph of SEM showing chromium carbides in a microstructure after hardening heat treatment of Example 1, after tempering.

[Best Mode]

[0033] A hot-rolled annealed martensitic stainless steel sheet with improved strength and corrosion resistance according to an embodiment of the present disclosure includes, in percent by weight (wt%), 0.3 to 0.5% of C, 0.01 to 0.025% of N, 0.3 to 0.5% of Si, 0.4 to 0.6 of Mn, 13.1 to 14.5% of Cr, 0.95 to 1.10% of Mo, 0.05 to 0.3% of V, 0.3 to 0.5% of Ni, 0.001 to 0.5% of Cu, and the reminder of Fe and inevitable impurities, and satisfies Formula (1) below:

$$\text{(1)} \qquad 16.4 \le (\text{Cr}+3.3\text{Mo}+16\text{N})*(\text{Mo}+\text{V}) \le 23.3,$$

wherein Cr, N, Mo, and V denote contents (wt%) of elements, respectively.

[Detailed Description of the Embodiments]

[0034] 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 a clear description of the disclosure, and sizes of elements may be exaggerated for clarity.

[0035] Throughout the specification, the term "include" an element does not preclude other elements but may further include another element unless otherwise stated.

[0036] As used herein, the singular forms are intended to include the plural forms as well, unless the context clearly indicates otherwise. Hereinafter, embodiments of the present disclosure will be described in detail with reference to the accompanying drawings.

[0037] The present inventors have made various studies to improve the corrosion resistance of high carbon martensitic stainless steel and to minimize material deviation, and then have found those described below.

[0038] To improve corrosion resistance, a method of increasing the Cr content may be considered. However, the increase in the Cr content is not a desirable goal of development because it increases the cost of manufacture.

[0039] A hot-rolled annealed material, produced by typical continuous casting, hot-rolling, and batch annealing processes, has a ferrite as its base structure and contains chromium carbides. Chromium carbides include a primary chromium carbide represented by M_7C_3 (M is Cr: Fe = 73.6%: 17.2%) having a size of several tens to hundreds of μm formed by central segregation of Cr and C during casting, and a secondary chromium carbide precipitated preferentially along grain boundaries and martensitic lath grain boundaries during batch annealing and represented by $M_{23}C_6$ (M is Cr: Fe = 73%: 19.3%).

[0040] In particular, if the size of the primary chromium carbide distributed in the center of the material is coarse at 10 μm or more, the primary chromium carbide remains without being decomposed after hot-rolling and batch annealing. Although cold rolling is performed by applying a certain degree of rolling reduction, it is difficult to segment and consequently remains coarse carbides of 3 μm or more. In addition, although cold rolling is performed by applying a certain degree of rolling reduction, it is difficult to segment and consequently remains coarse carbides of 3 μm or more.

[0041] Residual carbides reduce a re-solubility rate to an austenitic phase during hardening heat treatment, thereby lowering the hardness and corrosion resistance of martensitic stainless steel, which is the final material, and also causing local material imbalance.

[0042] The present inventors found that above a certain amount of Mo and V content allows for preventing coarsening of chromium carbide, securing uniform physical properties (e.g., corrosion resistance, hardness) by diversifying the precipitation sites of chromium carbide, and enabling rapid re-dissolution of chromium and carbon into a high-temperature austenite phase in a subsequent hardening heat treatment step, thereby improving corrosion resistance and strength.

[0043] Hereinafter, various embodiments according to the present disclosure will be described in detail with reference to the accompanying drawings. First, martensitic stainless steel will be described, and then a method of producing martensitic stainless steel will be described.

[0044] A hot-rolled annealed martensitic stainless steel sheet having improved strength and corrosion resistance according to an aspect of the present disclosure includes, in percent by weight (wt%), 0.3 to 0.5% of C, 0.01 to 0.025% of N, 0.3 to 0.5% of Si, 0.4 to 0.6% of Mn, 13.1 to 14.5% of Cr, 0.95 to 1.10% of Mo, 0.05 to 0.3% of V, 0.3 to 0.5% of Ni, 0.001 to 0.5% of Cu, and the reminder of Fe and inevitable impurities.

[0045] Hereinafter, reasons for numerical limitations on the contents of alloying elements in the embodiment of the present disclosure will be described. Hereinafter, the unit is wt% unless otherwise stated.

[0046] The content of carbon (C) is 0.3 to 0.5%.

[0047] C is an essential element to ensure the hardness of martensitic stainless steel and is added in an amount of 0.3% or more to secure hardness after quenching/tempering heat treatment. However, if the C content is excessive, chromium carbide is excessively formed and accordingly the corrosion resistance of the material itself is lowered, and there is a risk of toughness deterioration due to the increase and residual coarse carbide. Therefore, the upper limit may be limited to 0.5% and the C content is preferably 0.36 to 0.4%.

[0048] The content of nitrogen (N) is 0.01 to 0.025%.

[0049] N, an element added to improve corrosion resistance and hardness at the same time, does not cause local fine segregation although N is added instead of C, which has the advantage of not forming coarse precipitates in the product. To achieve such an effect, 0.01% or more of N is added in the present disclosure. However, if the N content is excessive, there is a risk of forming Cr nitride, which is a low-temperature precipitated phase, and an excessive retained austenite phase, so the upper limit may be limited to 0.025% to ensure fatigue properties.

[0050] The C+N content is 0.37 to 0.43%.

[0051] The hardness of the martensitic stainless steel may be ensured by controlling the contents of C and N, which are interstitial elements, to 0.37% or more. However, the rolling force increases during the hot-rolling process as C+N increases, leading to a decrease in manufacturability and a reduction in toughness. Therefore, the range of the C+N value may be controlled to 0.37 to 0.43%, considering the hardness and manufacturability of the final material.

[0052] The content of silicon (Si) is 0.3 to 0.5%.

[0053] Si, an element added essentially for deoxidation, serves to improve strength. 0.3% or more of Si is added in the present disclosure. However, if the Si content is excessive, there is a risk of forming a scale on the surface of the steel sheet during hot-rolling, thereby degrading the surface quality. Therefore, the upper limit may be limited to 0.5%.

[0054] The content of manganese (Mn) is 0.4 to 0.6%.

[0055] Mn, an element added to improve strength and hardenability, combines with sulfur (S), which is inevitably contained during the manufacturing process, to form MnS, thereby suppressing cracks caused by S. 0.4% or more of Mn is added in the present disclosure. However, if the Mn content is excessive, there is a risk of impairing the surface quality and toughness of the steel. Therefore, the upper limit may be limited to 0.6%.

[0056] The content of chromium (Cr) is 13.1 to 14.5%.

[0057] Cr, a basic element enhancing corrosion resistance, serves to improve hardness and wear resistance by forming chromium carbide. 13.1% or more of Cr is added in the present disclosure. However, if the Cr content is excessive, the manufacturing cost increases, and the hardenability increases. Therefore, the upper limit may be limited to 14.5%.

[0058] The content of molybdenum (Mo) is 0.95 to 1.10%.

[0059] Mo, an element improving corrosion resistance, suppresses decarburization, and improving hardenability, and serves to fine carbide by replacing Cr in chromium carbide. In the present disclosure, 0.95% or more of Mo is added. However, if the Mo content is excessive, the manufacturing cost increases, and the hardenability increases. Therefore, the upper limit may be limited to 1.10%.

[0060] The content of vanadium (V) is 0.05 to 0.3%.

[0061] V is an element effective in suppressing coarsening of chromium carbide by forming carbides, preventing coarsening of crystal grains during heat treatment, and improving wear resistance. In the present disclosure, 0.05% or more of V is added. However, if the V content is excessive, the manufacturing cost increases and there is a risk of lowering the toughness. Therefore, the upper limit may be limited to 0.3%.

[0062] The Mo+V content is 1.0 to 1.35%.

[0063] By controlling the content of Mo and V, which preferentially react with C instead of Cr to form carbides, to 1.0% or more, corrosion resistance may be improved and crystal grains of chromium carbide may be finely secured. However, considering that the above effect is saturated and the price competitiveness of the material decreases as the Mo+V content increases, the range of Mo+V value may be controlled to 1.0 to 1.35%.

[0064] The content of nickel (Ni) is 0.3 to 0.5%.

[0065] Ni, an essential element added to ensure an austenitic structure in a hot working region of martensitic stainless steel, serves to improve corrosion resistance and hardenability. In the present disclosure, 0.3% or more of Ni is added. However, if the Ni content is excessive, the manufacturing cost increases and there is a risk of reducing machinability. Therefore, the upper limit may be limited to 0.5%.

[0066] The content of copper (Cu) is 0.001 to 0.5%.

[0067] Cu, an element for forming an austenite phase, serves to improve strength, hardness, and corrosion resistance. In the present disclosure, 0.001% or more of Cu is added. However, if the Cu content is excessive, the manufacturing cost increases, the hot workability decreases, and there is a risk of forming a precipitate phase, such as CuS, which is detrimental to corrosion resistance due to reaction with S. Therefore, the upper limit may be limited to 0.5%.

[0068] 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. The impurities are not specifically mentioned in the present disclosure, as they are known to any person skilled in the art of manufacturing.

[0069] On the other hand, the hot-rolled annealed martensitic stainless steel sheet having improved strength and corrosion resistance according to an embodiment of the present disclosure satisfies the following formula (1).

$$(1) \qquad 16.4 \leq (Cr+3.3Mo+16N)*(Mo+V) \leq 23.3$$

(wherein Cr, N, Mo, and V denote contents (wt%) of elements, respectively).

[0070] In general, the Pitting Resistance Equivalent Number (PREN) is represented as Cr+3.3Mo+16N. The higher the PREN*(Mo+V) value, the better the corrosion resistance. The present disclosure attempts to ensure corrosion resistance even in a humid environment, such as a compressor, by controlling the PREN value to 16.4 or more in Formula (1), in addition to limiting the content of the alloying elements to the above conditions.

[0071] In the process of manufacturing martensitic stainless steel, the hot-rolled annealed material produced through a batch annealing process has a ferrite as its base structure and contains chromium carbide. Chromium carbide includes a primary chromium carbide represented by M_7C_3 (M is Cr: Fe = 73.6%: 17.2%) having a size of several tens to hundreds of μm formed by central segregation of Cr and C during casting and a secondary chromium carbide precipitated preferentially along grain boundaries during batch annealing and represented by $M_{23}C_6$ (M is Cr: Fe = 73%: 19.3%).

[0072] The primary carbide formed during slab cooling has limitations in controlling its size and distribution during hot-rolling and cold-rolling processes.

[0073] In the present disclosure, when martensitic stainless steel is manufactured by hardening heat treatment including a quenching/tempering continuous heat treatment, the influence of Mo and V, which may improve the corrosion resistance of steel after the quenching/tempering by fining carbides, is also considered, and thus the optimized Formula (1) is derived.

[0074] FIG. 1 is a graph illustrating a relationship between (Cr+3.3Mo+16N)*(Mo+V) values and the Mo+V content in a carbide of a martensitic stainless steel according to an embodiment of the present disclosure. FIG. 2 is a graph illustrating a relationship between (Cr+3.3Mo+16N)*(Mo+V) values and the size of a primary carbide represented by $(Cr, Fe, Mo, V)_7C_3$ of a martensitic stainless steel according to an embodiment of the present disclosure.

[0075] Referring to FIG. 1 and FIG. 2, as the value of (Cr+3.3Mo+16N)*(Mo+V) increases, it can be seen that Cr in the chromium carbide is replaced by Mo and V, and the carbide is finely derived.

[0076] In addition, in the present disclosure, Formula (2) is derived in consideration of the change in the properties of carbides during hardening heat treatment.

[0077] More specifically, the present inventors derive Formula (2) by considering a relationship between the fact whether or not a Z phase (where M is 44V+41Cr) and vanadium nitride (where M is 74.2V+5Cr) are formed and the added components. Herein, the Z phase is represented by the contents of C, Cr, and N, which are affected by the addition of Mo and V, which changes the properties of the precipitated carbide, and the Mo+V content in the chromium carbide, and the vanadium nitride is represented by M-N.

$$(2)\ -14 \leq -36442 + 248C + 365Cr + 373Mo + 530V + 365Fe + 350Si + 312Mn + 331Ni + 506Cu \leq 50$$

[0078] Wherein C, Cr, Mo, V, Fe, Si, Mn, Ni, and Cu denote wt% of the respective elements.)

[0079] The present inventors found that as the value of Formula (2) increases, coarsening of the primary carbide may be prevented and the fine secondary carbide may be precipitated. More specifically, when the value of Formula (2) exceeds -14, the added Mo and V replace Cr in the primary and secondary carbides to suppress the coarsening, and the formed Z phase and vanadium nitride precipitate preferentially along the grain boundaries to suppress the formation of secondary chromium carbide ($M_{23}C_6$), which is precipitated long along the grain boundaries. Meanwhile, if the value of Formula (2) is too high, the Z phase and the vanadium nitride themself may act as precipitation sites of the secondary carbide and manufacturing costs may increase, so the value of Formula (2) needs to be limited to 50 or less.

[0080] Martensitic stainless steels are typically machined to their final shape and then subjected to a hardening heat treatment process to secure corrosion resistance and hardness. The hardening heat treatment process is a process in which the material is held at a high temperature of about 1,000 to 1,200°C for a short time and then rapidly cooled to room temperature, which increases the chromium concentration of the base to about 12% by re-dissolving chromium carbide in the high-temperature austenite phase. As a result, this creates a dense layer of chromium oxide, which is a thin passivation film, on a surface of the material, thereby improving the corrosion resistance of the material.

[0081] Furthermore, as the austenite phase containing re-dissolved carbon or nitrogen is transformed into the martensite phase during rapid cooling, the hardness of the material is improved. At this time, if the size of the spheroidized chromium carbide distributed in the base structure is large, it is difficult to re-dissolve chromium carbide in the high-temperature austenite phase, so that the concentration of chromium and carbon present in the base structure decreases, resulting in a lowering of the corrosion resistance and hardness of the material.

[0082] On the contrary, if the size of chromium carbide is fine, it is easy to re-dissolve chromium carbide even in short heat treatment, so that the concentration of chromium, carbon, and nitrogen in the base structure increases, thereby improving the corrosion resistance and hardness.

[0083] Therefore, in order to ensure the corrosion resistance and hardness of high carbon martensitic stainless steels at the same time, it is required to finely and uniformly distribute chromium carbide in materials prior to the hardening heat treatment process, such as hot-rolled annealed materials.

[0084] In the present disclosure, the addition of Mo and V suppresses the growth of carbides due to the substitution of Cr in the primary and secondary chromium carbides, and preferentially combines with C to form fine carbides, so that the precipitation sites of the primary and secondary chromium carbides is preoccupied., resulting in uniform micronization and distribution of the carbides.

[0085] More specifically, a hot-rolled annealed martensitic stainless steel sheet having improved strength and corrosion resistance according to an embodiment of the present disclosure has the ferrite as its base structure and includes the primary carbide represented by $(Cr, Fe, Mo, V)_7C_3$ and the secondary carbide represented by $(Cr, Fe, Mo, V)_{23}C_6$.

[0086] Mo and V form carbides in a compound with Cr, so the Cr content in the carbides may be reduced, and the concentration of chromium in the base structure may be increased by forming fine carbides.

[0087] More specifically, the wt% of (Mo+V) in the primary carbide represented by $(Cr, Fe, Mo, V)_7C_3$ is 2.93 to 5.67%, and the particle size of the primary carbide is 10 μm or less. The wt% of (Mo+V) in the secondary carbide represented by $(Cr, Fe, Mo, V)_{23}C_6$ is 12.2 to 14.8%.

[0088] Furthermore, when Mo and V are added, the Z phase represented by M(C, N) (where M is 44V+41Cr) and the vanadium nitride represented by M-N (where M is 74.2V+5Cr) are formed. The Z phase and the vanadium nitride themself then act as precipitation sites of the secondary carbide, so that the carbides may be finely and uniformly distributed.

[0089] For example, the hot-rolled annealed martensitic stainless steel sheet having improved strength and corrosion resistance according to an embodiment of the present disclosure has a carbide deviation of 10 pieces/100 μm^2 or less in a longitudinal direction thereof.

[0090] In addition, the hot-rolled annealed martensitic stainless steel sheet of the present disclosure has, after cold-rolled, 42 to 58 pieces/100 μm^2 of chromium carbides distributed in the microstructure.

[0091] Next, a method of manufacturing martensitic stainless steel according to another embodiment of the present disclosure will be described.

[0092] A method of manufacturing martensitic stainless steel with improved strength and corrosion resistance according to another embodiment of the present disclosure is provided. The method includes hot-rolling a slab that includes, in percent by weight (wt%), 0.3 to 0.5% of C, 0.01 to 0.025% of N, 0.3 to 0.5% of Si, 0.4 to 0.6% of Mn, 13.1 to 14.5% of Cr, 0.95 to 1.10% of Mo, 0.05 to 0.3% of V, 0.3 to 0.5% of Ni, 0.001 to 0.5% of Cu, and the reminder of Fe and inevitable impurities and satisfies the following formula (1), performing a batch annealing heat treatment in a temperature range of 600 to 900°C immediately after hot-rolled, cold rolling the hot-rolled annealed material, and performing a hardening heat treatment of the cold-rolled material.

$$(1) \qquad 16.4 \leq (Cr+3.3Mo+16N)*(Mo+V) \leq 23.3$$

[0093] The reasons for the numerical limitation of the alloying element contents are as described above.

[0094] The stainless steel including the above compositions is manufactured into a slab by continuous casting or ingot casting, and manufactured into a hot-rolled steel sheet capable of being processed by hot-rolling treatment.

[0095] Next, the manufactured hot-rolled steel sheet is softened by batch annealing heat treatment to ensure good workability before further processing, such as precision rolling to a thickness suitable for crafting (e.g., swords, tools, etc.)

[0096] Typically, during the batch annealing of a hot-rolled coil in a wound state, a thermal history deviation occurs during the cooling/reheating processes, causing a variation in the physical properties of a final material. More specifically, immediately after hot-rolling, as the wound coil comes into contact with the outside air, a partial cooling deviation occurs in the wound coil, and accordingly, a martensitic structure is formed in an area where the cooling rate is high, resulting in deriving a non-uniform microstructure.

[0097] To minimize a time for air-cooling at room temperature of the hot-rolled coil, which is wound in the temperature range of 800 to 900°C after being hot-rolled, an embodiment of the present disclosure is configured to prevent phase transformation to martensite by introducing a batch annealing heat treatment immediately after hot-rolling.

[0098] The batch annealing may be performed at a temperature ranging from 600 to 900°C to ensure uniform distribution of carbides. If the annealing temperature is low, the martensite phase may be remained due to insufficient driving force for annealing to the ferrite and carbide phases. If the annealing temperature is too high, reverse transformation to the austenite phase may occur, resulting in coarsening of the grain boundaries, and intensive formation of coarse chromium carbides at the grain boundaries during the cooling process. Considering such an annealing temperature, the temperature range of the batch annealing heat treatment is limited to 600 to 900°C.

[0099] According to the present disclosure, the hot-rolled annealed martensitic stainless material, which has been subjected to the batch annealing heat treatment, may be manufactured into martensitic stainless steel through a process of hardening heat treatment after machining to a final shape.

[0100] The hardening heat treatment may further include an austenizing treatment, a quenching treatment, and a tempering treatment.

[0101] The austenizing treatment is a process of transforming the base structure of the steel material from ferrite to austenite. According to one example, the austenizing treatment may include a heat treatment at a temperature of 1,000°C or more for 1 minute or more.

[0102] In this process, chromium carbide is re-dissolved into the base structure in the form of chromium and carbon, thereby increasing the hardness of the martensitic stainless steel after the subsequent quenching process.

[0103] The quenching treatment is a process of transforming the austenite structure into martensite with high hardness by rapidly cooling from a temperature range of 980 to 1,050°C to room temperature after the austenizing treatment. If the cooling rate is ensured at 0.2 °C/s or higher, a martensitic structure may be secured.

[0104] The tempering treatment is a process of imparting toughness to the brittle martensitic structure due to the high hardness achieved by the quenching treatment. According to an example, the tempering treatment may be performed at a temperature of 400 to 600°C for 1 minute to 1 hour depending on the thickness.

[0105] Through the above hardening heat treatments, the ferrite structure may be finally transformed into the martensite structure, which achieves a desired hardness and corrosion resistance. For example, the Vickers hardness of the material re-dissolved by the hardening heat treatment may be 520 to 650 Hv.

[0106] Hereinafter, the present disclosure will be described in more detail through examples.

[0107] Slabs of various ranges of alloy composition shown in Table 1 were reheated at 1,250°C, rough-rolled, and then finally hot-rolled at 800°C or higher. Next, the hot-rolled plate without cooling to room temperature was placed in a batch annealing furnace at 700°C while maintaining a temperature of 600°C or higher, and subjected to hot-rolling annealing.

[0108] In Table 1 below, Formula (1) is (Cr+3.3Mo+16N)*(Mo+V).

Table 1

Example	C	Si	Mn	Ni	Cu	Cr	Mo	V	N	C+N	Mo+V	Formula(1)
Example 1	0.38	0.4	0.45	0.4	0.05	13.5	1.05	0.07	0.02	0.40	1.12	19.4
Example 2	0.38	0.4	0.45	0.4	0.05	13.5	0.95	0.05	0.02	0.40	1.00	17.0
Example 3	0.38	0.4	0.45	0.4	0.05	13.5	1.1	0.15	0.02	0.40	1.25	21.8
Example 4	0.38	0.4	0.45	0.4	0.05	14.5	1.05	0.07	0.02	0.40	1.12	20.5
Example 5	0.4	0.5	0.6	0.5	0.5	13.9	1.1	0.15	0.025	0.43	1.25	22.4
Example 6	0.36	0.3	0.4	0.3	0.001	13.1	0.95	0.05	0.01	0.37	1.00	16.4
Example 7	0.38	0.4	0.45	0.4	0.05	13.5	1.05	0.3	0.02	0.40	1.35	23.3
Comparative Example 1	0.38	0.4	0.45	0.4	0.05	13.5	0.5	0.001	0.02	0.40	0.5	7.8
Comparative Example 2	0.38	0.4	0.45	0.4	0.05	13.5	0.5	0.04	0.02	0.40	0.54	8.4
Comparative Example 3	0.38	0.4	0.45	0.4	0.05	12.5	1.05	0.07	0.02	0.40	1.12	18.2
Comparative Example4	0.38	0.4	0.45	0.4	0.05	13.5	0.001	0.001	0.02	0.40	0.00	0.0
Comparative Examples	0.38	0.4	0.45	0.4	0.05	13.5	0.001	0.07	0.02	0.40	0.07	1.0
Comparative Example6	0.38	0.4	0.45	0.4	0.05	13.5	0.1	0.07	0.02	0.40	0.17	2.4
Comparative Example7	0.38	0.4	0.45	0.4	0.05	13.5	0.1	0.07	0.02	0.40	0.17	2.4
Comparative Examples	0.3	0.5	0.5	0.2	0.05	13.2	0	0	0.02	0.32	0.00	0.0
Comparative Example9	0.45	0.35	0.55	0.2	0.05	14.0	0	0	0.025	0.48	0.00	0.0
Comparative Example 10	0.5	0.4	0.45	0.2	0.05	14.7	0.65	0.125	0.03	0.53	0.78	13.4

[0109] During the annealing process, whether or not the Z phase represented by M(C, N) (where M is 44V+41Cr) and the vanadium nitride represented by M-N (where M is 74.2V+5Cr) are formed, the average particle size of primary carbide (μm), and the Mo+V content (wt%) in the carbide in the hot-rolled annealed material were sampled from the specimens by the Replical method of the transmission electron microscope (TEM), and the energy dispersive spectrometer (EDS) components of the TEM was measured and shown in Table 2 below.

[0110] Additionally, the hardening heat treatment was performed on the cold-rolled annealed material. More specifically, the cold-rolled annealed material was quenched at a cooling rate of 233°C/s to 300°C after heat treatment at 1,000°C for 420 seconds, followed by tempering at 350°C for 350 seconds. The martensitic stainless steel was finally prepared and the Vickers hardness was measured, and the results were shown in Table 2 below.

Table 2

Example	Formul a (2)	(Mo+V) in M_7C_3	(Mo+V) in $M_{23}C_6$	Whether Z phase precipitation	Whether VN Precipitation	M_7C_3 Size (pm)	Carbide density of cold-rolled annealed steel (piece/100μm^2)	Hardness after tempering (Hv)
Example 1	-10	4.29	14.1	O	O	6.2	49	620
Example 2	-14	3.70	12.2	O	O	10	44	555
Example 3	3	5.67	14.3	O	O	4	53	635
Example 4	-10	3.94	13.3	O	O	7	45	582
Example 5	50	5.54	13.6	O	O	9	55	643
Example 6	-8	3.71	12.8	O	O	5	42	520
Example 7	28	2.93	14.8	O	O	3.5	58	650
Comparative Example 1	-227	2.90	13.2	X	X	19	36	480
Comparative Example 2	-220	2.93	13.2	X	X	16	37	484
Comparative Example 3	-10	4.69	13.3	O	O	12	33	430
Comparative Example 4	-30	0.00	0.0	X	X	67	35	473
Comparative Example 5	-19	1.40	0.0	O	O	50	40	501
Comparative Example 6	-18	1.72	1.5	O	O	25	43	496
Comparative Example 7	-18	2.92	6.8	O	O	14	38	517
Comparative Example 8	-18	0.00	0.0	X	X	38	32	453
Comparative Example 9	-38	0.00	0.0	X	X	74	59	751
Comparative Example 10	-15	3.67	6.9	O	O	45	78	847

[0111] FIG. 1 to FIG. 3 are graphs illustrating a relationship between (Cr+3.3Mo+16N)*(Mo+V) values and the content of Mo+V in the carbide, the size of primary carbides represented by (Cr, Fe, Mo, $V)_7C_3$, and the hot-rolled annealed carbide distribution of the martensitic stainless steel according to an embodiment of the present disclosure. Referring to Table 1, Table 2, and FIG. 1 to FIG. 3, in Examples 1 to 7 in which the Mo and V content, and the values of Formula (1) satisfy the range of 16.4 to 23.3, it can be seen that Cr in chromium carbide is replaced by Mo and V and the carbide is finely derived.

[0112] For example, in Examples 1 to 7, the wt% of (Mo+V) in the primary carbide represented by (Cr, Fe, Mo, $V)_7C_3$ is 2.93 to 5.67%, and the particle size of the primary carbide is 10 μm or less, and the wt% of (Mo+V) in the secondary carbide represented by (Cr, Fe, Mo, $V)_{23}C_6$ is 12.2 to 14.8%.

[0113] This is a result derived from the fact not only that optimized Mo and V suppress the formation of coarse carbides by forming carbides in complex with Cr, but also that the Z phase and the vanadium nitride themself, which are formed during hot-rolling annealing, act as precipitation sites for the secondary carbide.

[0114] Accordingly, after cold rolling, 42 to 58 pieces/ 100 μm^2 of chromium carbide is distributed in the microstructure, and the hardness of the final material is ensured in the range of 520 to 650 Hv.

[0115] On the contrary, in Comparative Examples 4, 8, and 9 in which Mo and V were not added, the Z phase and vanadium nitride were not formed during hot-rolling annealing, and the particle sizes of the primary carbide of the hot-rolled annealed material were derived very coarsely 67 μm, 38 μm, and 74 μm, respectively.

[0116] In Comparative Examples 5, 6, 7, and 10, the Z phase and vanadium nitride were formed during hot-rolling annealing, but the content of Mo and V was not within the range of 16.4 to 23.3 proposed in the present disclosure, so that it was not possible to derive the particle size of the carbide of the hot-rolled annealed material to be 10 μm or less, which is a target.

[0117] In particular, in Comparative Example 10, the content of Mo and V is added in a certain amount or more, but the range of Formula (1) was not satisfied, so that securing of the wt% of (Mo+V) in the secondary carbide is not possible. Accordingly, the chromium carbide may not be finely and uniformly distributed.

[0118] FIG. 4 and FIG. 5 are photographs of scanning electron micrographs (SEM) showing chromium carbides in the microstructure after the hardening heat treatment of Comparative Example 4 and Example 1, respectively, after tempering.

[0119] In Comparative Example 4, it can be seen that the coarsened and segregated carbides remain without being re-dissolved after the hardening heat treatment. Whereas, in Example 1, it can be seen that most of the carbonaceous materials are re-dissolved after the hardening heat treatment and a martensitic structure having a low area fraction of residual carbonitrides is derived.

[0120] As described above, according to an embodiment of the present disclosure, by controlling the alloy components and the relationships, the corrosion resistance of the high carbon martensitic stainless steel can be improved and the material deviation can be minimized.

[0121] While the present disclosure has been particularly described with reference to exemplary embodiments, it should be understood by those 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]

[0122] The hot-rolled annealed martensitic stainless steel sheet according to an embodiment of the present disclosure has improved strength and corrosion resistance while ensuring hardness and is therefore industrially usable.

Claims

1. A hot-rolled annealed martensitic stainless steel sheet with improved strength and corrosion resistance comprising, in percent by weight (wt%), 0.3 to 0.5% of C, 0.01 to 0.025% of N, 0.3 to 0.5% of Si, 0.4 to 0.6 of Mn, 13.1 to 14.5% of Cr, 0.95 to 1.10% of Mo, 0.05 to 0.3% of V, 0.3 to 0.5% of Ni, 0.001 to 0.5% of Cu, and the reminder of Fe and inevitable impurities, and satisfying Formula (1) below:

$$\text{Formula (1):} \quad 16.4 \leq (Cr+3.3Mo+16N)*(Mo+V) \leq 23.3$$

wherein Cr, N, Mo, and V denote contents (wt%) of elements, respectively.

2. The hot-rolled annealed martensitic stainless steel sheet of claim 1, wherein Formula (2) below is satisfied:

$$\text{Formula (2): } -14 \leq -36442+248C+365Cr+373Mo+530V+365Fe+350Si+312Mn+331Ni+506Cu \leq 50$$

wherein C, Cr, Mo, V, Fe, Mn, Ni, and Cu denote wt% of the respective elements.

3. The hot-rolled annealed martensitic stainless steel sheet of claim 1, wherein Formula (3) below is satisfied:

$$\text{Formula (3): } 0.37 \leq C+N \leq 0.43.$$

4. The hot-rolled annealed martensitic stainless steel sheet of claim 1, wherein Formula (4) below is satisfied:

$$\text{Formula (4): } 1.0 \leq Mo+V \leq 1.35.$$

5. The hot-rolled annealed martensitic stainless steel sheet of claim 1, further comprising:

a ferrite as a base structure;
a primary carbide represented by $(Cr, Fe, Mo, V)_7C_3$; and
a secondary carbide represented by $(Cr, Fe, Mo, V)_{23}C_6$.

6. The hot-rolled annealed martensitic stainless steel sheet of claim 5, wherein the wt% of (Mo+V) in the primary carbide is 2.93 to 5.67%.

7. The hot-rolled annealed martensitic stainless steel sheet of claim 5, wherein the wt% of (Mo+V) in the secondary carbide is 12.2 to 14.8%.

8. The hot-rolled annealed martensitic stainless steel sheet of claim 1, wherein a particle size of the primary carbide is 10 μm or less.

9. The hot-rolled annealed martensitic stainless steel sheet of claim 1, wherein a carbide deviation is 10 pieces/100 μm^2 or less in a longitudinal direction.

10. The hot-rolled annealed martensitic stainless steel sheet of claim 1, wherein, after cold-rolled, a distribution density of carbide is 42 to 58 pieces/100 μm^2.

11. A method of manufacturing a martensitic stainless steel with improved strength and corrosion resistance, the method comprising:

hot-rolling a slab including, in percent by weight (wt%), 0.3 to 0.5% of C, 0.01 to 0.025% of N, 0.3 to 0.5% of Si, 0.4 to 0.6% of Mn, 13.1 to 14.5% of Cr, 0.95 to 1.10% of Mo, 0.05 to 0.3% of V, 0.3 to 0.5% of Ni, 0.001 to 0.5% of Cu, and the reminder of Fe and inevitable impurities, and satisfying Formula (1) below;
batch-annealing in a temperature range of 600 to 900°C immediately after hot-rolled;
cold-rolling the hot-rolled annealed material; and
hardening heat treatment of the cold-rolled material;

$$\text{Formula (1): } 16.4 \leq (Cr+3.3Mo+16N)*(Mo+V) \leq 23.3$$

wherein Cr, N, Mo, and V denote contents (wt%) of elements, respectively.

12. The method of claim 11, wherein the hot-rolled annealed material further comprises:

a ferrite as a base structure;

a primary carbide represented by $(Cr, Fe, Mo, V)_7C_3$; and
a secondary carbide represented by $(Cr, Fe, Mo, V)_{23}C_6$.

13. The method of claim 11, wherein the wt% of (Mo+V) in the primary carbide is 2.93 to 5.67%.

14. The method of claim 11, wherein the wt% of (Mo+V) in the secondary carbide is 12.2 to 14.8%.

15. The method of claim 11, wherein a particle size of the primary carbide is 10 μm or less.

16. The method of claim 11, wherein, after cold-rolled, 42 to 58 pieces/100 μm^2 or less of carbides are distributed therein.

17. The method of claim 11, wherein the hardening heat treatment further comprises:

quenching at a temperature range of980 to 1,050°C; and
tempering at a temperature of 400 to 600°C for 1 minute to 1 hour.

18. The method of claim 17, wherein the Vickers hardness is 520 to 650 Hv after the hardening heat treatment.

19. The method of claim 11, further comprising satisfying Formula (2) below:

$$\text{Formula (2)}: -14 \leq -36442+248C+365Cr+373Mo+530V+365Fe+350Si+312Mn+331Ni+506Cu \leq 50$$

wherein C, Cr, Mo, V, Fe, Si, Mn, Ni, and Cu denote wt% of the respective elements.

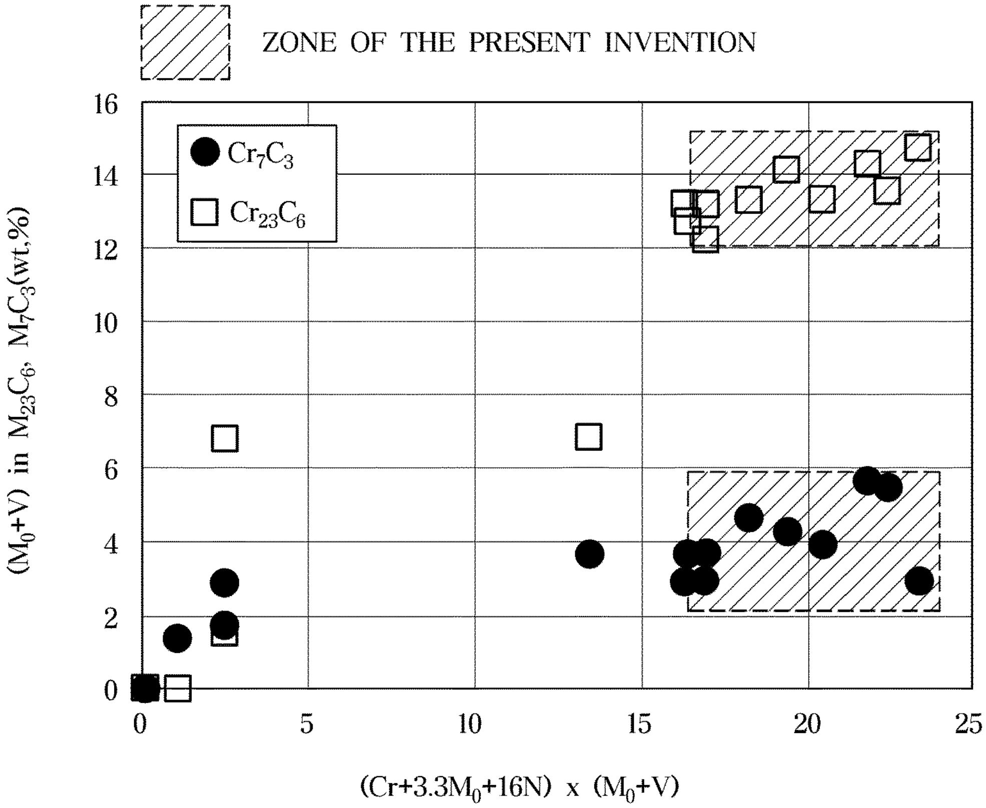
20. The method of claim 11, further comprising satisfying Formula (3) and (4) below:

$$\text{Formula (3)}: 0.37 \leq C+N \leq 0.43,$$

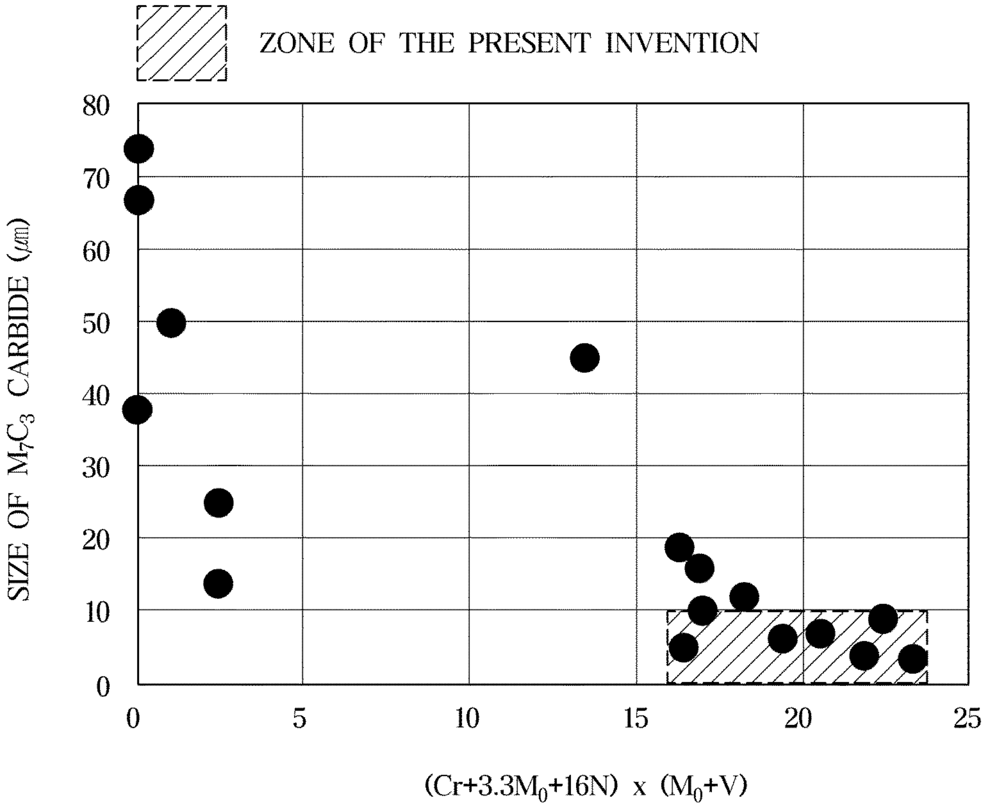
and

$$\text{Formula (4)}: 1.0 \leq Mo+V \leq 1.35.$$

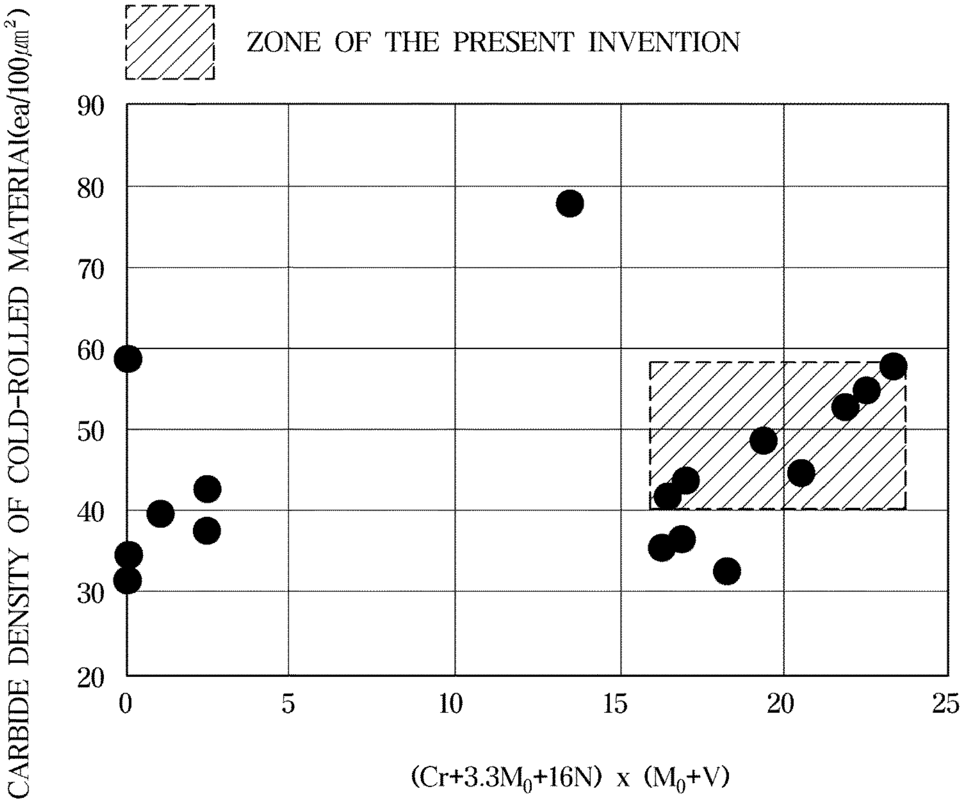
【FIG. 1】


ZONE OF THE PRESENT INVENTION
Cr_7C_3
$Cr_{23}C_6$
(M_0+V) in $M_{23}C_6$, M_7C_3(wt,%)
0
2
4
6
8
10
12
14
16
0
5
10
15
20
25
$(Cr+3.3M_0+16N)$ x (M_0+V)

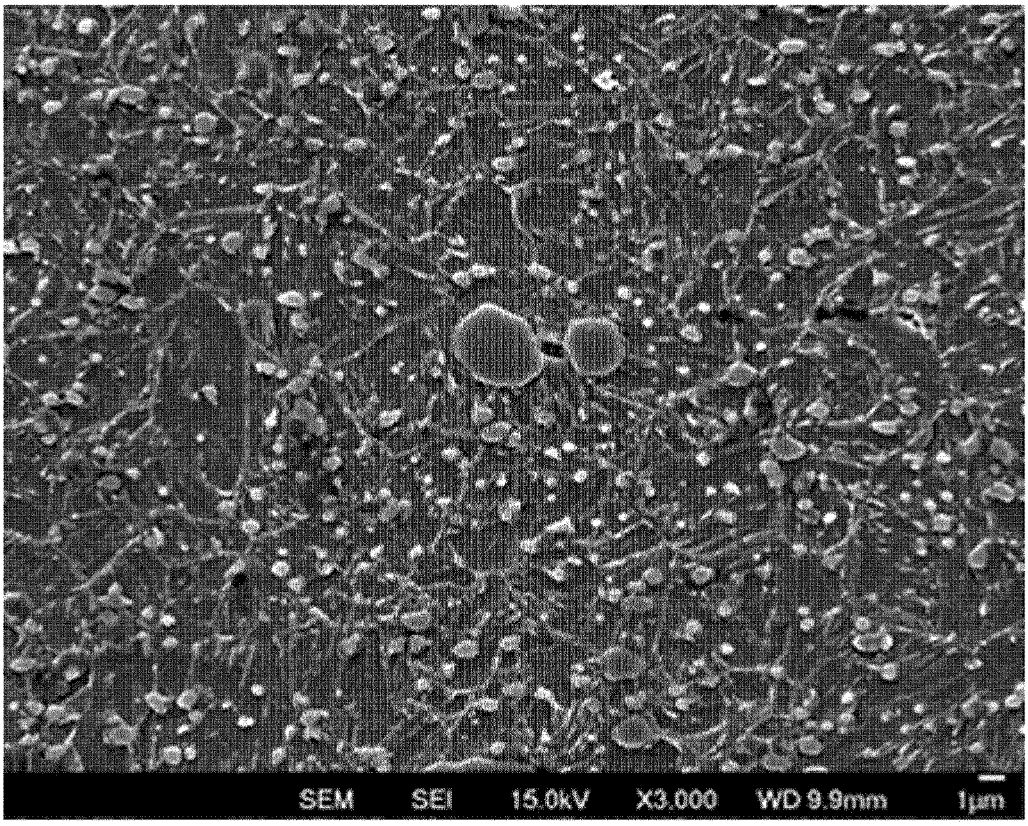
【FIG. 2】


ZONE OF THE PRESENT INVENTION
SIZE OF M_7C_3 CARBIDE (μm)
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
(Cr+3.3M_0+16N) x (M_0+V)

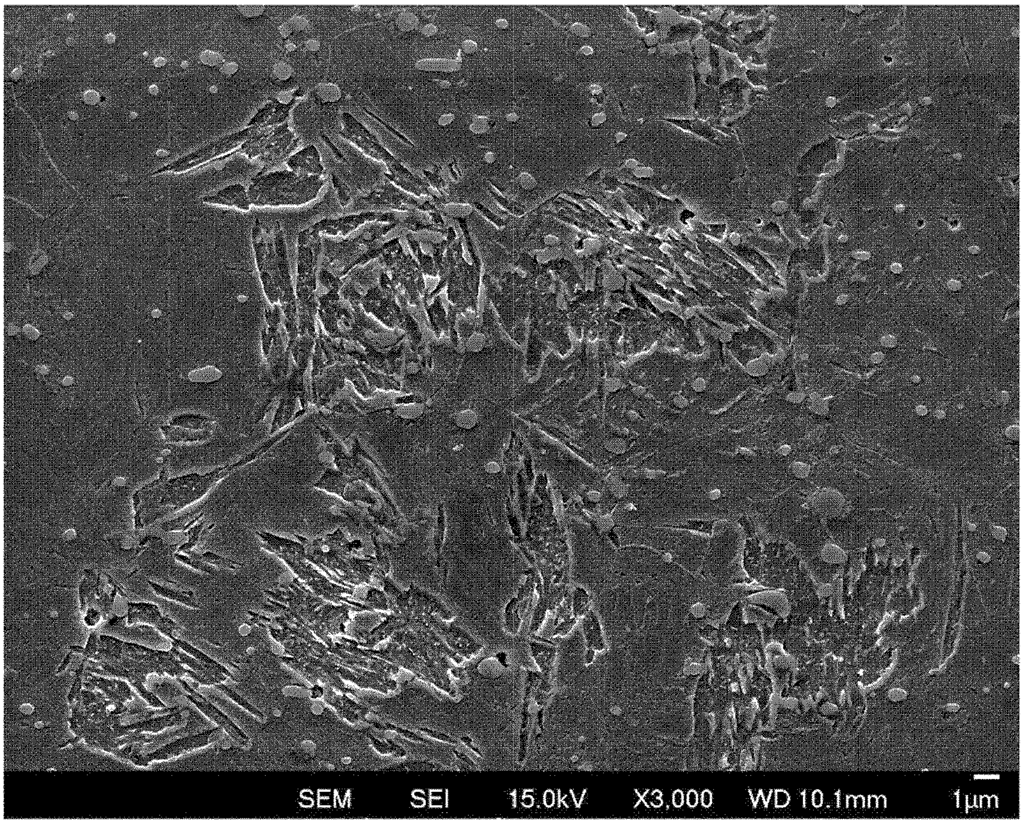
【FIG. 3】


ZONE OF THE PRESENT INVENTION
CARBIDE DENSITY OF COLD-ROLLED MATERIAL(ea/100㎛²)
90
80
70
60
50
40
30
20
0
5
10
15
20
25
(Cr+3.3M0+16N) x (M0+V)

【FIG. 4】



【FIG. 5】



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2021/017715

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/46(2006.01)i; **C22C 38/44**(2006.01)i; **C22C 38/42**(2006.01)i; **C21D 9/46**(2006.01)i; **C21D 8/02**(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C 38/46(2006.01); C22C 38/00(2006.01); C22C 38/02(2006.01); C22C 38/04(2006.01); C22C 38/20(2006.01); C22C 38/22(2006.01); C22C 38/44(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: 스테인리스(stainless), 마르텐사이트(martensite), 몰리브덴(Mo), 바나듐(V), 구리(Cu), 니켈(Ni), 크롬(Cr), 질소(N), 탄화물(carbide), 퀜칭(quenching), 소둔(annealing)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-0210522 B1 (HITACHI, METALS LTD) 15 July 1999 (1999-07-15) See paragraphs [0071] and [0077], claim 4 and tables 3a-3b.	1-20
X	JP 2020-050916 A (NIPPON STEEL STAINLESS STEEL CORP.) 02 April 2020 (2020-04-02) See claims 1 and 3-4.	1-4
A	WO 2020-245285 A1 (AB SANDVIK MATERIALS TECHNOLOGY) 10 December 2020 (2020-12-10) See claims 1 and 13.	1-20
A	CN 106086631 A (CENTRAL IRON & STEEL RESEARCH INSTITUTE) 09 November 2016 (2016-11-09) See claims 1-2.	1-20
A	US 2020-0232076 A1 (UDDEHOLMS AB) 23 July 2020 (2020-07-23) See paragraph [0091] and claim 1.	1-20

☐ 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 **27 April 2022**	Date of mailing of the international search report **27 April 2022**
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.

Form PCT/ISA/210 (second sheet) (July 2019)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2021/017715

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
KR	10-0210522	B1	15 July 1999	CN	1046970	C	01 December 1999
				CN	1145644	A	19 March 1997
				DE	69604341	T2	25 May 2000
				DE	69604341	T3	01 June 2006
				EP	0750687	A1	02 January 1997
				EP	0750687	B1	22 September 1999
				EP	0750687	B2	27 July 2005
				JP	10-504354	A	28 April 1998
				JP	2968844	B2	02 November 1999
				MY	114984	A	31 March 2003
				TW	393518	B	11 June 2000
				US	5714114	A	03 February 1998
				WO	96-21747	A1	18 July 1996
JP	2020-050916	A	02 April 2020	None			
WO	2020-245285	A1	10 December 2020	BR	112021024509	A2	18 January 2022
				CN	112501491	A	16 March 2021
				CN	113966405	A	21 January 2022
				KR	10-2022-0016835	A	10 February 2022
CN	106086631	A	09 November 2016	CN	106086631	B	01 May 2018
US	2020-0232076	A1	23 July 2020	CA	3078221	A1	11 April 2019
				CN	111183240	A	19 May 2020
				EA	202090880	A1	26 June 2020
				EP	3692180	A1	12 August 2020
				JP	2020-536169	A	10 December 2020
				KR	10-2020-0078500	A	01 July 2020
				SE	1751230	A1	06 April 2019
				SE	541151	C2	16 April 2019
				TW	201936946	A	16 September 2019
				WO	2019-070189	A1	11 April 2019

Form PCT/ISA/210 (patent family annex) (July 2019)