

(19)



(11)

**EP 3 730 655 A1**

(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 153(4) EPC

(43) Date of publication:

**28.10.2020 Bulletin 2020/44**

(21) Application number: **18891912.0**

(22) Date of filing: **28.11.2018**

(51) Int Cl.:

<b>C22C 38/42</b> (2006.01)	<b>C22C 38/44</b> (2006.01)
<b>C22C 38/46</b> (2006.01)	<b>C22C 38/48</b> (2006.01)
<b>C22C 38/00</b> (2006.01)	<b>C22C 38/50</b> (2006.01)
<b>C21D 8/02</b> (2006.01)	<b>C21D 9/46</b> (2006.01)
<b>C21D 1/18</b> (2006.01)	<b>C22C 38/02</b> (2006.01)
<b>C22C 38/04</b> (2006.01)	<b>C22C 38/06</b> (2006.01)

(86) International application number:

**PCT/KR2018/014855**

(87) International publication number:

**WO 2019/124793 (27.06.2019 Gazette 2019/26)**

(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: **24.12.2017 KR 20170178924**

(71) Applicant: **POSCO**

**Gyeongsangbuk-do 37859 (KR)**

(72) Inventor: **HONG, Soon-Taik**

**Pohang-si, Gyeongsangbuk-do 37877 (KR)**

(74) Representative: **Potter Clarkson**

**The Belgrave Centre**

**Talbot Street**

**Nottingham NG1 5GG (GB)**

(54) **HIGH STRENGTH STEEL SHEET AND MANUFACTURING METHOD THEREFOR**

(57) A high strength steel sheet according to an aspect of the present invention comprises, by weight %, 0.05-0.20% of C, 0.15-0.55% of Si, 0.9-1.75% of Mn, 0.001-0.05% of Al, 0.03 % or less of P, 0.03% or less of S, 0.05-0.3% of Cr, 0.05-0.6% of Ni, 0.005-0.35% of Cu, 0.05-0.2% of Mo, 0.005-0.07% of V, 0.005-0.04% of Nb, 0.0005-0.005% of Ca, 0.005-0.025% of Ti, 0.002-0.006%

of N, less than 0.0005% of B, the balance of Fe and inevitable impurities, with the proviso of satisfying the relation that Cu + Ni + Cr + Mo: 1.5% or less; Cr + Mo: 0.4% or less; V + Nb: 0.1% or less; and Ca/S: 1.0 or higher and may include a combined structure of tempered martensite and tempered bainite as a microstructure.

**EP 3 730 655 A1**

**Description**

[Technical Field]

5 **[0001]** The present disclosure relates to a high strength steel plate and a manufacturing method therefor, and more particularly, to a high strength steel plate having excellent tensile strength and impact toughness, particularly suitable for a nuclear reactor containment container, and a manufacturing method therefor.

[Background Art]

10 **[0002]** Various materials are used for the structures and facilities of a nuclear power plant according to the type, usage, and safety properties thereof. In particular, a nuclear reactor containment vessel utilizes a steel material, and A516-70 steel produced by a normalizing process is mainly used as a thick steel plate material.

15 **[0003]** However, such A516-70 steel has insufficient tensile strength (about 500 Mpa) to ensure the nuclear power plant's safety, and, thus, a range of use thereof may be extremely limited. That is, since the A516-70 steel has relatively low tensile strength, when used to manufacture a nuclear reactor containment vessel, there may be a risk of damage or explosion due to the failure to withstand the high pressure inside. Accordingly, there may be an urgent need to develop a material suitable for a nuclear reactor containment container while having tensile strength of a certain level or more.

20 **[0004]** In order to improve the tensile strength, if a relatively large amount of expensive alloying elements is added to a steel material or a separate heat treatment is performed, tensile strength may be hardly improved, but an increase in costs due to the addition of the alloying elements may be inevitable, and there may be other incidental problems involved.

25 **[0005]** Patent Document 1 discloses a high strength steel plate with improved tensile strength, which may be a high strength steel plate that may be used for a nuclear reactor containment vessel. However, the steel plate disclosed in Patent Document 1 has a level of tensile strength that may be used as a steel plate for a nuclear reactor containment vessel, but may not be suitable as a material for a nuclear reactor containment vessel due to deteriorations in low-temperature toughness and nil-ductility transition temperature properties.

(Patent Document 1) Korea Patent Publication No. 10-2010-0076745 (published on July 6, 2010)

[Disclosure]

30

[Technical Problem]

35 **[0006]** According to an aspect of the present disclosure, a high strength steel plate having excellent tensile strength, low-temperature toughness, and nil-ductility transition temperature properties, particularly suitable for a nuclear reactor containment container of a nuclear power plant, and a manufacturing method therefor, may be provided.

**[0007]** The problems of the present disclosure to be solved are not limited to the above-mentioned contents. Those skilled in the art will have no difficulty in understanding additional problems of the present disclosure from the overall contents of this specification.

40 [Technical Solution]

45 **[0008]** According to an aspect of the present disclosure, a high strength steel plate includes, by weight: 0.05 to 0.20% of C, 0.15 to 0.55% of Si, 0.9 to 1.75% of Mn, 0.001 to 0.05% of Al, 0.03% or less of P, 0.03% or less of S, 0.05 to 0.3% of Cr, 0.05 to 0.6% of Ni, 0.005 to 0.35% of Cu, 0.05 to 0.2% of Mo, 0.005 to 0.07% of V, 0.005 to 0.04% of Nb, 0.0005 to 0.005% of Ca, 0.005 to 0.025% of Ti, 0.002 to 0.006% of N, less than 0.0005% of B, and a balance of Fe, with inevitable impurities, satisfies relationships of Cu + Ni + Cr + Mo: 1.5% or less, Cr + Mo: 0.4% or less, V + Nb: 0.1% or less, and Ca/S: 1.0 or higher, and includes a combined structure of tempered martensite and tempered bainite as a microstructure.

50 **[0009]** The tempered martensite may be included in 30 to 60 area% in the microstructure, the tempered bainite may be included in 40 to 70 area% in the microstructure, and the sum of the tempered martensite and the tempered bainite may be 100 area%.

**[0010]** The tempered martensite may be included in 40 to 60 area% in the microstructure, and the tempered bainite may be included in 40 to 60 area% in the microstructure.

**[0011]** A nil-ductility transition temperature of the steel plate may be -50°C or lower.

**[0012]** Tensile strength of the steel plate may be 600 MPa or more.

55 **[0013]** Charpy impact toughness of the steel plate may be 250 J or more at -60°C.

**[0014]** A grain aspect ratio (a long axis/short axis ratio) of the microstructure may be 1.1 to 2.5.

**[0015]** According to an aspect of the present disclosure, a method of manufacturing a high strength steel plate, includes: reheating a steel slab at 1050 to 1250°C, the steel slab comprising, by weight: 0.05 to 0.20% of C, 0.15 to 0.55% of Si,

## EP 3 730 655 A1

0.9 to 1.75% of Mn, 0.001 to 0.05% of Al, 0.03% or less of P, 0.03% or less of S, 0.05 to 0.3% of Cr, 0.05 to 0.6% of Ni, 0.005 to 0.35% of Cu, 0.05 to 0.2% of Mo, 0.005 to 0.07% of V, 0.005 to 0.04% of Nb, 0.0005 to 0.005% of Ca, 0.005 to 0.025% of Ti, 0.002 to 0.006% of N, less than 0.0005% of B, and a balance of Fe, with inevitable impurities, satisfying relationships of Cu + Ni + Cr + Mo: 1.5% or less, Cr + Mo: 0.4% or less, V + Nb: 0.1% or less, and Ca/S: 1.0 or higher, rolling the slab in a temperature range of  $T_{nr}$  to  $T_{nr} + 100^{\circ}\text{C}$  to provide a steel plate, austenizing the steel plate in a temperature range of 870 to 950°C, quenching the austenized steel plate to a temperature range of 300°C or lower, and tempering the quenched steel plate in a temperature range of 595 to 700°C.

**[0016]** An accumulated reduction amount of the rolling may be 50 to 90%.

**[0017]** A grain aspect ratio (a long axis/short axis ratio) of a microstructure of the steel plate by the rolling may be controlled to have a range of 1.1 to 2.5.

**[0018]** The austenizing may be performed for a time period of  $1.6 * t$  (where, t denotes a thickness (mm) of the steel plate) + (10 to 30 minutes).

**[0019]** The tempering may be performed for a time period of  $2.4 * t$  (where, t denotes a thickness (mm) of the steel plate) + (10 to 30 minutes).

[Advantageous Effects]

**[0020]** According to a preferred aspect of the present disclosure, a high strength steel plate securing a tensile strength of 600 MPa or more, a Charpy impact toughness of 250 J or more at -60°C, and a nil-ductility transition temperature of -50°C or lower, to be particularly suitable for a nuclear reactor containment container of a nuclear power plant, and a manufacturing method therefor, may be provided.

[Best Mode for Invention]

**[0021]** The present disclosure relates to a high strength steel plate and a manufacturing method therefor, and, hereinafter, preferred embodiments of the present disclosure will be described. Embodiments of the present disclosure may be modified in various forms, and the scope of the present disclosure should not be construed as being limited to embodiments to be described below. These embodiments may be provided to those skilled in the art to further detail the present disclosure.

**[0022]** Hereinafter, the steel composition of the present disclosure will be described in more detail. Hereinafter, unless otherwise indicated, % representing the content of each element is based on weight.

**[0023]** A high strength steel plate according to an embodiment of the present disclosure may include, by weight: 0.05 to 0.2% of C, 0.15 to 0.55% of Si, 0.9 to 1.75% of Mn, 0.001 to 0.05% of Al, 0.03% or less of P, 0.03% or less of S, 0.05 to 0.3% of Cr, 0.05 to 0.6% of Ni, 0.005 to 0.35% of Cu, 0.05 to 0.2% of Mo, 0.005 to 0.07% of V, 0.005 to 0.04% of Nb, 0.0005 to 0.005% of Ca, 0.005 to 0.025% of Ti, 0.002 to 0.006% of N, less than 0.0005% of B, and a balance of Fe, with inevitable impurities.

Carbon (C) : 0.05 to 0.2%

**[0024]** Since carbon (C) may be an effective element for securing strength, the present disclosure may limit a lower limit of the carbon (C) content to 0.05% to prevent a decrease in strength on a matrix phase. When carbon (C) is excessively added, toughness and weldability may be deteriorated, making it unsuitable for use for a nuclear reactor containment container, and the present disclosure may limit an upper limit of the carbon (C) content to 0.2%. Therefore, the carbon (C) content of the present disclosure may be 0.05 to 0.2%, and a more preferable carbon (C) content may be 0.08 to 0.15%.

Silicon (Si): 0.15 to 0.55%

**[0025]** Silicon (Si) may be an element added for a deoxidation effect, a solid solution strengthening effect, and an impact transition temperature increasing effect. Therefore, the present disclosure may limit a lower limit of the silicon (Si) content to 0.15% to achieve this effect. A preferred lower limit of the silicon (Si) content may be 0.2%, and a more preferred lower limit of the silicon (Si) content may be 0.3%. When the silicon (Si) is excessively added, weldability of the steel plate may be deteriorated and an oxide film may be severely formed on a surface of the steel plate. Therefore, the present disclosure may limit an upper limit of the silicon (Si) content to 0.55%. A preferred upper limit of the silicon (Si) content may be 0.5%, and a more preferred upper limit of the silicon (Si) content may be 0.4%.

## EP 3 730 655 A1

Manganese (Mn): 0.9 to 1.75%

5 **[0026]** Manganese (Mn) may be an effective element for securing strength, and the present disclosure may limit a lower limit of the manganese (Mn) content to 0.9% to achieve this effect. A preferred lower limit of the manganese (Mn) content may be 1.0%, and a more preferred lower limit of the manganese (Mn) content may be 1.2%. Manganese (Mn) may be combined with sulfur (S) to form a non-metallic inclusion such as MnS. When manganese (Mn) is added excessively, elongation at room temperature and low-temperature toughness may be deteriorated. Therefore, the present disclosure may limit an upper limit of the manganese (Mn) content to 1.75%. A preferred upper limit of the manganese (Mn) content may be 1.7%, and a more preferred upper limit of the manganese (Mn) content may be 1.6%.

10 Aluminum (Al): 0.001 to 0.05%

15 **[0027]** Since aluminum (Al) may be an element as a strong deoxidizer, the present disclosure may limit a lower limit of the aluminum (Al) content to 0.001% for a deoxidation effect in a steelmaking process. When aluminum (Al) is added excessively, the deoxidation effect may be saturated, but manufacturing costs may be increased. The present disclosure may limit an upper limit of the aluminum (Al) content to 0.05%. The aluminum (Al) content is more preferably 0.01 to 0.04%.

Phosphorus (P): 0.03% or less

20 **[0028]** Phosphorus (P) may be an element that impairs low-temperature toughness. Therefore, P may be desirable to have its content managed to be as low as possible. Since Phosphorus (P) may be an element that may be inevitably contained in a steelmaking process, may take excessive cost to completely remove it, the present disclosure may limit an upper limit of the phosphorus (P) content to 0.03%. A preferred upper limit of the phosphorus (P) content may be 0.02%, and a more preferred upper limit of the phosphorus (P) content may be 0.01%.

25 Sulfur (S) : 0.03% or less

30 **[0029]** Sulfur (S) may be also an element that adversely affects low-temperature toughness, together with phosphorus (P). Therefore, S may be desirable to have its content managed to be as low as possible. Since sulfur (S) may be an element that may be inevitably contained in a steelmaking process, like phosphorus (P), and may take excessive cost to completely remove it, the present disclosure may limit an upper limit of the sulfur (S) content to 0.03%. A preferred upper limit of the sulfur (S) content may be 0.02%, and a more preferred upper limit of the sulfur (S) content may be 0.01%.

35 Chromium (Cr): 0.05 to 0.3%

40 **[0030]** Since chromium (Cr) may be an element contributing to an increase in strength, the present disclosure may limit a lower limit of the chromium (Cr) content to 0.05% to achieve this effect. Chromium (Cr) may be an expensive element. When Cr is added excessively, it is not preferable from a viewpoint of economic efficiency. Therefore, the present disclosure may limit an upper limit of the chromium (Cr) content to 0.3%. Therefore, the chromium (Cr) content of the present disclosure may be 0.05 to 0.3%, and is more preferably 0.05 to 0.2%.

Nickel (Ni): 0.05 to 0.6%

45 **[0031]** Nickel (Ni) may be an effective element for improving low-temperature toughness. Therefore, the present disclosure may limit a lower limit of the nickel (Ni) content to 0.05% to achieve this effect. Nickel (Ni) may be an expensive element. When Ni is excessively added, an increase in production cost may occur. Therefore, the present disclosure may limit an upper limit of the nickel (Ni) content to 0.6%. Therefore, the nickel (Ni) content of the present disclosure may be 0.05 to 0.6%, and is more preferably 0.2 to 0.6%.

50 Copper (Cu): 0.005 to 0.35%

55 **[0032]** Copper (Cu) may be an effective element for increasing strength. Therefore, the present disclosure may limit a lower limit of the copper (Cu) content to 0.005% to achieve this effect. Copper (Cu) may be an expensive element. When Cu is excessively added, an increase in production cost may occur. Therefore, the present disclosure may limit an upper limit of the copper (Cu) content to 0.35%. Therefore, the copper (Cu) content of the present disclosure may be 0.005 to 0.35%, and is more preferably 0.01 to 0.3%.

## EP 3 730 655 A1

Molybdenum (Mo): 0.05 to 0.2%

5 **[0033]** Molybdenum (Mo) may be an alloy element effective for improving strength, and may be an element that prevents crack generation caused by sulfide. Therefore, the present disclosure may limit a lower limit of the molybdenum (Mo) content to 0.05% to achieve this effect. Molybdenum (Mo) may be also an expensive element. When Mo is excessively added, an increase in production cost may occur. Therefore, the present disclosure may limit an upper limit of the molybdenum (Mo) content to 0.2%. Therefore, the molybdenum (Mo) content of the present disclosure may be 0.05 to 0.2%, and is more preferably 0.1 to 0.2%.

10 Vanadium (V): 0.005 to 0.07%

15 **[0034]** Vanadium (V) may be an effective element for improving low-temperature toughness. Therefore, the present disclosure may limit a lower limit of the vanadium (V) content to 0.005% to achieve this effect. Vanadium (V) may be also an expensive element. When V is excessively added, an increase in production cost may occur. Therefore, the present disclosure may limit an upper limit of the vanadium (V) content to 0.07%. Therefore, the vanadium (V) content of the present disclosure may be 0.005 to 0.07%, and is more preferably 0.01 to 0.07%.

Niobium (Nb): 0.005 to 0.04%

20 **[0035]** Niobium (Nb) may be an element that may be dissolved in austenite to increase hardenability of the austenite. In addition, niobium (Nb) may be an element that is precipitated as carbonitride (Nb(C,N)) matching with a matrix, together with titanium (Ti), and may be a major element for obtaining a tensile strength of 600 MPa or more for which the present disclosure seeks. Therefore, the present disclosure may limit a lower limit of the niobium (Nb) content to 0.005% to achieve this effect. When niobium (Nb) is excessively added, coarse precipitates may occur in the process of continuous casting, and Nb may act as a starting point for hydrogen-induced cracking (HIC). Therefore, the present disclosure may limit an upper limit of the niobium (Nb) content to 0.04%. Therefore, the niobium (Nb) content of the present disclosure may be 0.005 to 0.04%, and is more preferably 0.01 to 0.03%.

30 Calcium (Ca): 0.0005 to 0.005%

35 **[0036]** Calcium (Ca) may be combined with sulfur (S) to form a CaS precipitate, and may thus be an effective element for suppressing formation of MnS. Therefore, the present disclosure may limit a lower limit of the calcium (Ca) content to 0.0005% to achieve this effect. When calcium (Ca) is excessively added, Ca may react with oxygen in steel to produce CaO, which may be a non-metallic inclusion. Therefore, the present disclosure may limit an upper limit of the calcium (Ca) content to 0.005%. Therefore, the calcium (Ca) content of the present disclosure may be 0.0005 to 0.005%, and is more preferably 0.001 to 0.003%.

Titanium (Ti): 0.005 to 0.025%

40 **[0037]** An appropriate content of titanium (Ti) may be fluidly limited according to the content of nitrogen (N). When the content of titanium (Ti) is relatively small, compared to the content of nitrogen (N), an amount of TiN produced may be relatively small, which may be disadvantageous for fine-graining. When titanium (Ti) is added in an excessive amount, TiN may become coarse during a heating operation to reduce an effect of inhibiting grain growth. Therefore, in consideration of the content (e.g., 0.002 to 0.006%) of nitrogen (N), the content of titanium (Ti) of the present disclosure may be 0.005 to 0.025%, and is more preferably 0.01 to 0.02%.

Nitrogen (N): 0.002 to 0.006%

50 **[0038]** Nitrogen (N) may be widely known as an element that plays a role in increasing toughness of a base material and impact toughness of a heat-affected zone (HAZ) by forming a TiN precipitate with titanium (Ti) to refine grains. In this regard, according to the present disclosure, nitrogen (N) may be an element that should be added to achieve the purpose of grain refinement. Therefore, the present disclosure may limit a lower limit of the nitrogen (N) content to 0.002% to achieve this effect. When the nitrogen (N) content is excessively added, an amount of TiN may be excessively increased and low-temperature toughness may be reduced. Therefore, the present disclosure may limit an upper limit of the nitrogen (N) content to 0.006%. Therefore, the nitrogen (N) content of the present disclosure may be 0.002 to 0.006%, and is more preferably 0.002 to 0.004%.

## EP 3 730 655 A1

Boron (B): less than 0.0005%

5 **[0039]** In the present disclosure, the content of boron (B) may be actively suppressed, but excessive cost may be consumed to completely remove boron (B), which may be inevitably introduced during a steelmaking process. Therefore, the present disclosure may limit the boron (B) content to less than 0.0005%. A preferred boron (B) content is 0.0002% or less, and a more preferred boron (B) content is 0.0001% or less.

**[0040]** A high strength steel plate according to an aspect of the present disclosure may satisfy relationships of Cu + Ni + Cr + Mo: 1.5% or less, Cr + Mo: 0.4% or less, V + Nb: 0.1% or less, and Ca/S: 1.0 or higher.

10 **[0041]** Hereinafter, the relationships of the present disclosure will be described in more detail.

Cu + Ni + Cr + Mo: 1.5% or less

Cr + Mo: 0.4% or less

V + Nb: 0.1% or less

15 Ca/S: 1.0 or higher

20 **[0042]** The relationships of Cu + Ni + Cr + Mo, Cr + Mo, and V + Nb may be values that are respectively limited in the basic specification (ASTMA20) regarding steel for a pressure vessel, and the content of Cu + Ni + Cr + Mo may be limited to 1.5% or less, the content of Cr + Mo may be limited to 0.4% or less, and the content of V + Nb may be limited to 0.1% or less. In addition, a ratio of Ca/s may be an essential composition ratio of spheroidizing an MnS inclusion to improve hydrogen-induced crack resistance. When the ratio of Ca/s is less than 1.0, it may be difficult to expect the effect, the ratio may be limited to satisfy 1.0 or more.

**[0043]** Hereinafter, the microstructure of the present disclosure will be described in more detail.

25 **[0044]** A high strength steel plate according to an aspect of the present disclosure may include a combined structure of tempered martensite and tempered bainite as a microstructure.

Microstructure: combined structure of tempered martensite and tempered bainite

30 **[0045]** When quenching and tempering a steel material provided with the above-described alloy composition, a microstructure of the steel material may have a microstructure of tempered martensite and tempered bainite. In the present disclosure, the tempered martensite and the tempered bainite may include 30 to 60 area% and 40 to 70 area%, respectively, and a tensile strength of 600 MPa, a nil-ductility transition temperature of -50°C or lower, and a Charpy impact toughness of 250 J or more at -60°C may be effectively secured. A preferred area fraction of tempered martensite is 40 to 60%, and a preferred area fraction of tempered bainite is 40 to 60%. In addition, the sum of area fractions of the tempered martensite and the tempered bainite may be 100%.

35 Grain Aspect Ratio:  $1.1 \leq \text{Long axis/Short axis} \leq 2.5$

40 **[0046]** In the present disclosure, in order to secure high impact toughness and strength, a grain aspect ratio (a ratio of long axis/short axis) may be controlled within a certain range, and the grain aspect ratio may be controlled by a rolling (a recrystallization control rolling) process. When the grain aspect ratio is less than 1.1, a shape of the grain may be rounded, surface energy thereof may become small, and it may be difficult to expect refinement of the grain. Therefore, it may be difficult to secure sufficient impact toughness and strength. In addition, when the grain aspect ratio exceeds 2.5, a rolling load for forming the grain becomes too high, and impact toughness may be lowered, which is not preferable. Therefore, the present disclosure may limit the grain aspect ratio (the ratio of long axis/short axis) to have a range of 45 1.1 to 2.5.

**[0047]** Hereinafter, a manufacturing method of the present disclosure will be described in more detail.

50 **[0048]** A high strength steel plate according to an aspect of the present disclosure may be manufactured by reheating a steel slab at 1050 to 1250°C, the steel slab including, by weight: 0.05 to 0.20% of C, 0.15 to 0.55% of Si, 0.9 to 1.75% of Mn, 0.001 to 0.05% of Al, 0.03% or less of P, 0.03% or less of S, 0.05 to 0.3% of Cr, 0.05 to 0.6% of Ni, 0.005 to 0.35% of Cu, 0.05 to 0.2% of Mo, 0.005 to 0.07% of V, 0.005 to 0.04% of Nb, 0.0005 to 0.005% of Ca, 0.005 to 0.025% of Ti, 0.002 to 0.006% of N, less than 0.0005% of B, and a balance of Fe, with inevitable impurities, satisfying relationships of Cu + Ni + Cr + Mo: 1.5% or less, Cr + Mo: 0.4% or less, V + Nb: 0.1% or less, and Ca/S: 1.0 or higher, rolling the slab in a temperature range of  $T_{nr}$  to  $T_{nr} + 100^\circ\text{C}$  to provide a steel plate, austenizing the steel plate in a temperature range of 870 to 950°C, quenching the austenized steel plate to a temperature range of 300°C or lower, and tempering the quenched steel plate in a temperature range of 595 to 700°C.

55 **[0049]** Since an alloy composition and a content of the slab of the present disclosure correspond to the alloy composition and the content of the high strength steel plate described above, a description of the alloy composition and the content of the slab of the present disclosure may be replaced with the description of the alloy composition and the content of

## EP 3 730 655 A1

the steel plate described above.

Slab Reheating Operation: 1050 to 1250°C

5 **[0050]** In the present disclosure, a slab provided with the above-described alloy composition may be reheated at a temperature range of 1050 to 1250°C. This is because, when a reheating temperature thereof is less than 1050°C, it may be difficult to sufficiently dissolve solute atoms, and when a reheating temperature thereof exceeds 1250°C, an austenite grain size may be excessively coarsened and properties of a steel plate may be deteriorated.

10 **[0051]** Recrystallization Control Rolling Operation: a temperature range of  $T_{nr}$  to  $(T_{nr} + 100^\circ\text{C})$ , an accumulated reduction amount of 50 to 90% at a rolling reduction ratio of 10% or more per rolling pass

15 **[0052]** The recrystallization control rolling operation refers to a rolling operation to be performed at a temperature, equal to or higher than an unrecrystallized temperature. In this case, the unrecrystallized temperature  $T_{nr}$  may be derived by the following Equation 1, which has been already known. In the following Equation 1, a unit of each alloy element is weight%.

[Equation 1]

20 
$$T_{nr} (^{\circ}\text{C}) = 887 - 464 \times \text{C} + 890 \times \text{Ti} + 363 \times \text{Al} - 357 \times \text{Si} + (6445 \times \text{Nb} - 644$$
  
25 
$$\times \text{Nb}^{1/2}) + (732 \times \text{V} - 230 \times \text{V}^{1/2})$$

30 **[0053]** In order to improve strength, it may be necessary to refine an average particle diameter of prior austenite to 30  $\mu\text{m}$  or less in the recrystallization control rolling operation. When the average particle diameter of the prior austenite exceeds 30  $\mu\text{m}$ , strength and toughness of a product may not be sufficiently exhibited. Therefore, a safety level high enough for a nuclear reactor containment vessel may not be guaranteed. To this end, in the present disclosure, the rolling operation may be performed in a temperature range of  $T_{nr}$  to  $T_{nr} + 100^\circ\text{C}$ .

35 **[0054]** In this case, a rolling reduction ratio of 10% or more may be applied per rolling pass, to finally perform the rolling operation in an accumulated reduction amount of 50 to 90%. Such a reduction amount may be provided to control an average size (30  $\mu\text{m}$  or less) of a microstructure required in the present disclosure and a grain aspect ratio (a long axis/short axis ratio) to 1.1 to 2.5. Therefore, when the accumulated reduction amount is less than 50%, it may be difficult to expect a refinement effect of the microstructure and a control effect of the grain aspect ratio. When the accumulated reduction amount exceeds 90%, a rolling load may be excessively applied, which may cause a problem in process.

40 **[0055]** Heat Treatment and Quenching Operation: quenching after austenizing the steel plate for a time period of  $1.6 * t$  (where,  $t$  denotes a thickness (mm) of the steel plate) + (10 to 30 minutes) in a temperature range of 870 to 950°C

45 **[0056]** The quenching operation may be an important process for obtaining a combined structure of tempered martensite and tempered bainite, and may be necessary to strictly control process conditions to form a microstructure capable of securing a tensile strength of 600 MPa or more, a -60°C Charpy impact toughness of 250J or more, and a nil-ductility transition temperature property of -50°C or lower.

50 **[0057]** In the present disclosure, the austenizing operation may be performed for a time period of  $1.6 * t$  (where,  $t$  denotes a thickness (mm) of the steel plate) + (10 to 30 minutes) in a temperature range of 870 to 950°C. The austenizing operation may be a heat treatment for austenizing the structure before the quenching operation. When a temperature range of the heat treatment is less than 870°C, it may be difficult to re-solidify the solute elements, and thus it may be difficult to secure strength. When a temperature range of the heat treatment exceeds 950°C, growth of grains may occur and coarse grains may occur, to impair low-temperature toughness. Therefore, a temperature range of the austenizing operation of the present disclosure may be limited to a temperature range of 870 to 950°C.

55 **[0058]** In addition, in the present disclosure, the austenizing operation may be performed for a time period of  $1.6 * t$  (where,  $t$  denotes a thickness (mm) of the steel plate) + (10 to 30 minutes). When a time period of the austenizing operation is excessively short, an effect of sufficient austenizing may not be expected due to insufficient heating time, and it may be difficult to homogenize the structure. When a time period of the austenizing operation is excessively long, production time may be prolonged and productivity may be deteriorated. Therefore, a time period of the austenizing operation of the present disclosure may be limited to  $1.6 * t$  (where,  $t$  denotes a thickness (mm) of the steel plate) + (10 to 30 minutes). For reference, in the steel plate manufacturing process, when  $1.6 * t$  is set as a heating time period, and a target temperature is reached, 10 to 30 minutes may be set as a maintenance time period to perform the austenizing operation.

**[0059]** The steel plate, after the austenizing operation, may be quenched, preferably water-cooled, to be transformed to a combined structure of martensite and bainite. Conditions for the quenching operation in the present disclosure is

## EP 3 730 655 A1

not particularly limited, and any rapid quenching method including a water cooling operation may be applied to the quenching operation of the present disclosure. In order to obtain a microstructure desired by the present disclosure, after the austenizing operation is finished, the steel plate may be cooled to a temperature range of 300°C or lower.

**[0060]** Tempering Operation:  $2.4 \times t$  (where, t denotes a thickness (mm) of the steel plate) + (10 to 30 minutes) in a temperature range of 595 to 700°C

**[0061]** In the present disclosure, in order to secure excellent tensile strength, nil-ductility transition temperature, and low-temperature toughness properties, a tempering operation of the quenched steel material to 300°C or lower may be used to remove residual stress in a structure thereof. Therefore, tempered martensite and tempered bainite may be formed.

**[0062]** A temperature range of the tempering operation of the present disclosure may be limited to 595 to 700°C. This may be because, when a temperature range of the tempering operation is less than 595°C, carbides and the like may be not smoothly precipitated, and when a temperature range of the tempering operation exceeds 700°C, strength of the steel material may be lowered.

**[0063]** In addition, the tempering operation of the present disclosure may be carried out for a time period of  $2.4 * t$  (where, t denotes a thickness (mm) of the steel plate) + (10 to 30 minutes) to obtain a sufficient tempering effect. For reference, in the steel plate manufacturing process, when  $2.4 * t$  is set as a heating time period, and a target temperature is reached, 10 to 30 minutes may be set as a maintenance time period to perform the tempering operation.

[Mode for Invention]

**[0064]** Hereinafter, the present disclosure will be described in more detail through examples. However, it may be necessary to note that the embodiments described below may be only intended to further illustrate the present disclosure and may be not intended to limit the scope of the present disclosure.

**[0065]** A slab provided with the alloy composition of Table 1 below was prepared.

[Table 1]

Composition (wt%)	IS a	IS b	IS c	CS d	CS e	CS f
C	0.10	0.09	0.12	0.06	0.07	0.09
Mn	1.51	1.58	0.92	1.30	1.35	0.78
Al	0.02	0.03	0.032	0.035	0.030	0.032
Si	0.35	0.36	0.36	0.35	0.34	0.36
P	0.009	0.010	0.008	0.008	0.010	0.010
S	0.0010	0.0008	0.0011	0.0013	0.0014	0.0012
Cu	0.03	0.04	0.03	0.05	-	-
Ni	0.50	0.55	0.53	0.05	0.15	0.10
Cr	0.05	0.05	0.06	0.03	0.05	0.04
Mo	0.15	0.18	0.17	0.15	0.10	0.16
V	0.030	0.025	0.030	0.003	0.005	0.030
Nb	0.012	0.014	0.013	0.013	0.012	0.015
B	-	-	-	0.0015	0.0012	0.0007
Ti	0.012	0.010	0.013	0.013	0.012	0.013
N	0.0028	0.0035	0.0034	0.0028	0.0035	0.0032
Ca	0.0020	0.0019	0.0021	0.0018	0.0021	0.0020
IS: Inventive Steel, CS: Comparative Steel						

**[0066]** Test pieces were prepared by performing a reheating operation, a recrystallization control rolling operation, an austenizing operation, a quenching operation, and a tempering operation using respective slabs made of the compositions of Inventive Steel and Comparative Steel, as illustrated in Table 2 below. Properties such as strength, low-temperature toughness, and nil-ductility transition temperature were evaluated, and the results therefrom are illustrated in Table 3

### EP 3 730 655 A1

below. In Table 3 below, the low-temperature impact toughness may be evaluated as a Charpy impact energy value obtained by performing a Charpy impact test on a specimen having a V notch at -60°C. In addition, the nil-ductility transition temperature may be a result value according to the drop-weight test transition temperature set by the ASTM E208-06 method.

5

10

15

20

25

30

35

40

45

50

55

5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55

[Table 2]

Condition	Steel Plate Thickness (mm)	Slab Reheating Temp. (°C)	Rolling Temp. (°C)	Recrystallization Control Rolling Cumulative Reduction Amount (%)	Grain Aspect Ratio*	Austenizing Temp. (°C)	Tempering Temp. (°C)	
IS a	a-1	45	1200	780	60	1.75	900	680
	a-2	80	1180	780	55	1.95	920	660
	a-3	100	1100	790	50	1.25	910	650
	a-4	50	1100	790	45	1.01	910	660
IS b	b-1	45	1150	780	70	2.15	910	680
	b-2	80	1100	780	60	2.00	920	660
	b-3	100	1100	790	55	1.65	900	650
IS c	50	1150	780	75	1.98	900	660	
CS d	d-1	45	1200	780	20	1.02	920**	680
	d-2	100	1150	790	30	1.05	900**	650
CS e	100	1100	780	40	1.06	900**	650	
CS f	80	1150	790	55	1.03	900	650	

IS: Inventive Steel, CS: Comparative Steel  
 \* Grain aspect ratio: Long grain/short grain  
 \*\* Quenching temperatures of Comparative Steel are normalizing temperatures

[Table 3]

	Condition	Tempered Martensite Structural Fraction (%)	Tempered Bainite Structural Fraction (%)	YS (MPa)	TS (MPa)	-60°C Impact Toughness (J)***	NDT Transition Temp. (°C)****	
IS a	a-1	56	44	634	649	334	-80	IE 1
	a-2	51	49	641	641	324	-70	IE 2
	a-3	48	52	628	634	313	-65	IE 3
	a-4	62	38	580	701	58	-40	CE 1
IS b	b-1	58	42	642	660	324	-85	IE 4
	b-2	50	50	648	652	318	-70	IE 5
	b-3	45	55	634	635	334	-70	IE 6
IS c	C	55	45	542	650	320	-80	IE 7
CS d	d-1	85	15	370	639	180	-40	CE 2
	d-2	80	20	365	630	172	-45	CE 3
CS e	E	82	18	358	630	193	-40	CE 4
CS f	F	85	15	443	650	140	-30	CE 5
IE: Inventive Example, CE: Comparative Example, IS: Inventive Steel, CS: Comparative Steel *** Impact toughness: impact toughness in a T direction (having a V-notch in a direction, perpendicular to a rolling direction) **** NDT transition temperature: transition temperature of the drop-weight test conducted by the ASTM208-06 method.								

**[0067]** As in the results of Tables 2 and 3, it can be seen that Inventive Examples 1 to 7 have microstructures of 30 to 60% of tempered martensite and 40 to 70% of tempered bainite, and secure a tensile strength of 600 MPa or more, an impact toughness of 300 J or more at -60°C, and a nil-ductility transition temperature property of -50°C or lower.

**[0068]** In a case of Comparative Example 1, it can be seen that, since a steel composition satisfies the defined steel composition of the present disclosure, but an accumulated reduction amount of a recrystallization control rolling operation does not satisfy the defined scope of the present disclosure, the area fractions of a microstructure defined by the present disclosure are not satisfied, and a nil-ductility transition temperature property at -50°C or lower is, thus, not secured.

**[0069]** In addition, in cases of Comparative Examples 2 to 5, it can be seen that, since steel compositions do not satisfy the defined steel composition of the present disclosure, a microstructure has 80 area% or more of tempered martensite and 20 area% or less of tempered bainite, and tensile strength, impact toughness, and nil-ductility transition temperature properties are thus deteriorated.

**[0070]** Therefore, since a steel plate according to an embodiment of the present disclosure may control a steel composition, a microstructure, and manufacturing operations under optimal conditions, to secure tensile strength of 600 MPa or more, Charpy impact toughness of 250 J or more at -60°C, and a nil-ductility transition temperature of -50°C or lower, a high strength steel plate having properties suitable for a nuclear reactor containment vessel may be provided.

**[0071]** While example embodiments have been illustrated and described above, it will be apparent to those skilled in the art that modifications and variations could be made without departing from the scope of the present disclosure as defined by the appended claims.

## Claims

1. A high strength steel plate comprising, by weight: 0.05 to 0.20% of C, 0.15 to 0.55% of Si, 0.9 to 1.75% of Mn, 0.001

## EP 3 730 655 A1

to 0.05% of Al, 0.03% or less of P, 0.03% or less of S, 0.05 to 0.3% of Cr, 0.05 to 0.6% of Ni, 0.005 to 0.35% of Cu, 0.05 to 0.2% of Mo, 0.005 to 0.07% of V, 0.005 to 0.04% of Nb, 0.0005 to 0.005% of Ca, 0.005 to 0.025% of Ti, 0.002 to 0.006% of N, less than 0.0005% of B, and a balance of Fe, with inevitable impurities, satisfying relationships of Cu + Ni + Cr + Mo: 1.5% or less, Cr + Mo: 0.4% or less, V + Nb: 0.1% or less, and Ca/S: 1.0 or higher, and comprising a combined structure of tempered martensite and tempered bainite as a microstructure.

2. The high strength steel plate according to claim 1, wherein the tempered martensite comprises 30 to 60 area% in the microstructure, the tempered bainite comprises 40 to 70 area% in the microstructure, and the sum of the tempered martensite and the tempered bainite is 100 area%.

3. The high strength steel plate according to claim 2, wherein the tempered martensite comprises 40 to 60 area% in the microstructure, and the tempered bainite comprises 40 to 60 area% in the microstructure.

4. The high strength steel plate according to any one of claims 1 to 3, wherein a nil-ductility transition temperature of the steel plate is  $-50^{\circ}\text{C}$  or lower.

5. The high strength steel plate according to any one of claims 1 to 3, wherein tensile strength of the steel plate is 600 MPa or more.

6. The high strength steel plate according to any one of claims 1 to 3, wherein Charpy impact toughness of the steel plate is 300J or more at  $-60^{\circ}\text{C}$ .

7. The high strength steel plate according to any one of claims 1 to 3, wherein a grain aspect ratio (a long axis/short axis ratio) of the microstructure is 1.1 to 2.5.

8. A method of manufacturing a high strength steel plate, comprising:

reheating a steel slab at  $1050$  to  $1250^{\circ}\text{C}$ , the steel slab comprising, by weight: 0.05 to 0.20% of C, 0.15 to 0.55% of Si, 0.9 to 1.75% of Mn, 0.001 to 0.05% of Al, 0.03% or less of P, 0.03% or less of S, 0.05 to 0.3% of Cr, 0.05 to 0.6% of Ni, 0.005 to 0.35% of Cu, 0.05 to 0.2% of Mo, 0.005 to 0.07% of V, 0.005 to 0.04% of Nb, 0.0005 to 0.005% of Ca, 0.005 to 0.025% of Ti, 0.002 to 0.006% of N, less than 0.0005% of B, and a balance of Fe, with inevitable impurities, satisfying relationships of Cu + Ni + Cr + Mo: 1.5% or less, Cr + Mo: 0.4% or less, V + Nb: 0.1% or less, and Ca/S: 1.0 or higher,

rolling the slab in a temperature range of  $T_{nr}$  to  $T_{nr} + 100^{\circ}\text{C}$  to provide a steel plate,

austenizing the steel plate in a temperature range of  $870$  to  $950^{\circ}\text{C}$ ,

quenching the austenized steel plate to a temperature range of  $300^{\circ}\text{C}$  or lower, and

tempering the quenched steel plate in a temperature range of  $595$  to  $700^{\circ}\text{C}$ .

9. The method according to claim 8, wherein an accumulated reduction amount of the rolling is 50 to 90%.

10. The method according to claim 8 or 9, wherein a grain aspect ratio (a long axis/short axis ratio) of a microstructure of the steel plate by the rolling is controlled to have a range of 1.1 to 2.5.


11. The method according to claim 8, wherein the austenizing is performed for a time period of  $1.6 * t$  (where, t denotes a thickness (mm) of the steel plate) + (10 to 30 minutes).

12. The method according to claim 8, wherein the tempering is performed for a time period of  $2.4 * t$  (where, t denotes a thickness (mm) of the steel plate) + (10 to 30 minutes).

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2018/014855

5	A. CLASSIFICATION OF SUBJECT MATTER <i>C22C 38/42(2006.01)i, C22C 38/44(2006.01)i, C22C 38/46(2006.01)i, C22C 38/48(2006.01)i, C22C 38/00(2006.01)i, C22C 38/50(2006.01)i, C21D 8/02(2006.01)i, C21D 9/46(2006.01)i, C21D 1/18(2006.01)i</i> According to International Patent Classification (IPC) or to both national classification and IPC		
	B. FIELDS SEARCHED		
10	Minimum documentation searched (classification system followed by classification symbols) C22C 38/42; B21B 1/26; B21B 3/00; B21B 3/02; C21D 8/02; C22C 38/00; C22C 38/14; C22C 38/38; C22C 38/58; C22C 38/44; C22C 38/46; C22C 38/48; C22C 38/50; C21D 9/46; C21D 1/18		
	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		
15	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS (KIPO internal) & Keywords: steel plate, C, Si, Mn, Al, P, S, Cr, Ni, Cu, Mo, V, Nb, Ca, Ti, N, B, tempered martensite, tempered bainite, nuclear reactor, low temperature toughness, transition temperature		
20	C. DOCUMENTS CONSIDERED TO BE RELEVANT		
	Category*	Citation of document, with indication, where appropriate, of the relevant passages	
		Relevant to claim No.	
	Y	KR 10-0833069 B1 (POSCO) 27 May 2008 See paragraphs [0050], [0052] and claims 2, 4.	1-12
25	Y	KR 10-2010-0076745 A (POSCO) 06 July 2010 See paragraphs [0053], [0054], [0070]-[0074] and claim 5.	1-12
	Y	JP 2015-124435 A (JFE STEEL CORP. et al.) 06 July 2015 See abstract and claims 1-4.	1-12
30	A	KR 10-2015-0126683 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 12 November 2015 See claims 1-7.	1-12
	A	KR 10-2016-0078573 A (POSCO) 05 July 2016 See claims 1-14.	1-12
35	A	KR 10-2011-0061260 A (POSCO) 09 June 2011 See claims 1, 5.	1-12
	A	KR 10-2015-0101735 A (HYUNDAI STEEL COMPANY) 04 September 2015 See claims 1, 6.	1-12
40	<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> 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	"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	
45	"E" earlier application or patent but published on or after the international filing date	"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	
	"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)	"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	
	"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	
	"P" document published prior to the international filing date but later than the priority date claimed		
50	Date of the actual completion of the international search 25 FEBRUARY 2019 (25.02.2019)	Date of mailing of the international search report 25 FEBRUARY 2019 (25.02.2019)	
55	Name and mailing address of the ISA/KR  Korean Intellectual Property Office Government Complex Daejeon Building 4, 189, Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea Facsimile No. +82-42-481-8578	Authorized officer  Telephone No.	

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.

PCT/KR2018/014855

5

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member	Publication date
KR 10-0833069 B1	27/05/2008	NONE	
KR 10-2010-0076745 A	06/07/2010	CN 102264936 A CN 102264936 B EP 2370608 A2 EP 2370608 A4 KR 10-1091306 B1 US 2011-0259481 A1 WO 2010-074473 A2 WO 2010-074473 A3	30/11/2011 18/06/2014 05/10/2011 21/05/2014 07/12/2011 27/10/2011 01/07/2010 23/09/2010
JP 2015-124435 A	06/07/2015	JP 6253974 B2	27/12/2017
KR 10-2015-0126683 A	12/11/2015	BR 112015024854 A2 CN 105209650 A CN 105209650 B EP 2998414 A1 JP 6132017 B2 JP WO2014-185405 A1 KR 10-1709432 B1 MX 2015014099 A TW 201446973 A TW 1509084 B US 2016-0273066 A1 WO 2014-185405 A1	18/07/2017 30/12/2015 07/11/2017 23/03/2016 24/05/2017 23/02/2017 08/03/2017 15/12/2015 16/12/2014 21/11/2015 22/09/2016 20/11/2014
KR 10-2016-0078573 A	05/07/2016	KR 10-1657823 B1	20/09/2016
KR 10-2011-0061260 A	09/06/2011	KR 10-1271990 B1	05/06/2013
KR 10-2015-0101735 A	04/09/2015	NONE	

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- KR 1020100076745 [0005]