



EP 4 265 786 A1

(12)

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

(43) Date of publication:

25.10.2023 Bulletin 2023/43

(51) International Patent Classification (IPC):

C22C 38/58 (2006.01)

C22C 38/54 (2006.01)

C22C 38/48 (2006.01)

C22C 38/44 (2006.01)

C21D 9/46 (2006.01)

C21D 8/02 (2006.01)

(21) Application number: **21906841.8**

(52) Cooperative Patent Classification (CPC):

C21D 8/02; C21D 9/46; C22C 38/44; C22C 38/48;

C22C 38/54; C22C 38/58

(22) Date of filing: **04.11.2021**

(86) International application number:

PCT/KR2021/015868

(87) International publication number:

WO 2022/131536 (23.06.2022 Gazette 2022/25)

(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: **18.12.2020 KR 20200179082**

(71) Applicant: **POSCO Co., Ltd**

Pohang-si, Gyeongsangbuk-do 37859 (KR)

(72) Inventors:

- YU, Seng-Ho**
Pohang-si, Gyeongsangbuk-do 37877 (KR)
- CHO, Nam-Young**
Seoul 06194 (KR)

(74) Representative: **Meissner Bolte Partnerschaft**

mbB

Widenmayerstrasse 47

80538 München (DE)

(54) **HIGH HARDNESS ARMORED STEEL HAVING EXCELLENT LOW-TEMPERATURE IMPACT TOUGHNESS, AND MANUFACTURING METHOD THEREFOR**

(57) The present invention can provide: armored steel having high hardness and excellent low-temperature impact toughness to provide excellent ferroelasticity; and a manufacturing method therefor.

EP 4 265 786 A1

Description**Technical Field**

5 [0001] The present disclosure relates to a material appropriate for armored vehicles, explosion-proof structures, and the like, and more particularly to armored steel having excellent low-temperature impact toughness and having high hardness, and a manufacturing method therefor.

Background Art

10 [0002] Armored steel is a material of which a surface is made very hard for its main function of blocking bullets, and is used where protection is required, such as for an exterior of armored vehicles used on the battlefield. Since bulletproof performance is directly related to human life, research to improve the performance of bulletproof materials has been actively conducted in the past, and recently, a non-ferrous material such as titanium and aluminum has been developed.

15 [0003] The non-ferrous material has an advantage of weight reduction compared to a steel material, but is relatively expensive and has poor workability. As compared to the non-ferrous material, since the steel material is relatively inexpensive and may change physical properties such as harness relatively easily, the steel material is widely used as a material for self-propelled artillery, wheeled armored vehicles, and the like.

20 [0004] Hardness is one of the most important physical properties for securing the performance of armor steel, but simple high hardness does not guarantee bulletproof performance. A high hardness characteristic is a factor that increases resistance to bullets penetrating through a material, but the material having high hardness may be relatively easily broken, so the high hardness characteristic cannot necessarily guarantee excellent bulletproof performance. Therefore, there is a need to develop a material that can simultaneously secure brittle fracture resistance to external impact as well as high hardness characteristics rather than simply promoting high hardness of the material.

25 (Prior art Document)

[0005] (Patent Document) Korean Patent Publication No. 10-2018-0043788 (published on April 30, 2018)

Summary of Invention

Technical Problem

30 [0006] An aspect of the present disclosure is to provide armored steel having high hardness characteristics and excellent low-temperature impact toughness and a manufacturing method therefor.

35 [0007] An object of the present disclosure is not limited to the above description. The object of the present disclosure will be understood from the entire content of the present specification, and a person skilled in the art to which the present disclosure pertains will understand an additional object of the present disclosure without difficulty.

40 Solution to Problem

[0008] According to an aspect of the present disclosure, a high-hardness armored steel having excellent low-temperature impact toughness includes, by weight: 0.29 to 0.37% of carbon (C), 1.0 to 2.0% of silicon (Si), 0.5 to 1.6% of manganese (Mn), 0.5 to 1.2% of nickel (Ni), 0.4 to 1.5% of chromium (Cr), 0.05% or less of phosphorus (P), 0.02% or less of sulfur (S), 0.006% or less of nitrogen (N), 0.07% or less of aluminum (Al) (excluding 0%), 0.1 to 0.5% of molybdenum (Mo), 0.01 to 0.05% of niobium (Nb), 0.0002 to 0.005% of boron (B), 0.0005 to 0.004% of calcium (Ca), with a balance of iron (Fe) and inevitable impurities, satisfying the following [Relational Expression 1], wherein a tempered martensite base structure including retained austenite is included as a microstructure.

50 [Relational Expression 1]

$$10 * [C] * [Si] \geq 4$$

55 [0009] In Relational Expression 1, [C] and [Si] refer to contents (weight %) of carbon (C) and silicon (Si) included in the steel sheet, and 0 is substituted when the corresponding element is not intentionally added.

[0010] The armored steel may further include, by weight: at least one of 0.005 to 0.025% of titanium (Ti) and 0.2% or less of vanadium (V).

[0011] A fraction of the tempered martensite may be 90% or more by area, and a fraction of the retained austenite may be 1% by area to 10% by area.

[0012] The armored steel may have a surface hardness of 460 to 540 HB, and an impact absorption energy of 19 J or more at -40°C.

5 [0013] The armored steel may have a thickness of 5 to 40 mm.

[0014] According to an aspect of the present disclosure, a manufacturing method for a high-hardness armored steel having excellent low-temperature impact toughness includes operations of: preparing a steel slab including, by weight: 0.29 to 0.37% of carbon (C), 1.0 to 2.0% of silicon (Si), 0.5 to 1.6% of manganese (Mn), 0.5 to 1.2% of nickel (Ni), 0.4 to 1.5% of chromium (Cr), 0.05% or less of phosphorus (P), 0.02% or less of sulfur (S), 0.006% or less of nitrogen (N), 10 0.07% or less of aluminum (Al) (excluding 0%), 0.1 to 0.5% of molybdenum (Mo), 0.01 to 0.05% of niobium (Nb), 0.0002 to 0.005% of boron (B), 0.0005 to 0.004% of calcium (Ca), with a balance of iron (Fe) and inevitable impurities, satisfying the following [Relational Expression 1]; heating the steel slab in a temperature range of 1050 to 1250°C; rough rolling the heated steel slab in a temperature range of 950 to 1150°C; subjecting the heated steel slab to finish hot rolling in a temperature range of 850 to 950°C after the rough rolling to manufacture a hot-rolled steel sheet; performing a primary 15 heat-treatment of heating the hot-rolled steel sheet to a temperature range of 880 to 930°C and then cooling the same to a cooling end temperature of 150°C or lower at a cooling rate of 10°C/s or more; and performing a secondary heat treatment of heating the primarily heat-treated hot-rolled steel sheet to a temperature range of 350°C or lower and maintaining the same.

20 [Relational Expression 1]

$$10 * [C] * [Si] \geq 4$$

25 [0015] In Relational Expression 1, [C] and [Si] refer to contents (weight %) of carbon (C) and silicon (Si) included in the steel slab, and 0 is substituted when the corresponding element is not intentionally added.

[0016] The steel slab may further include, by weight: at least one of 0.005 to 0.025% of titanium (Ti) and 0.2% or less of vanadium (V).

[0017] A residence time during the primary heat treatment may be $1.3t * 10$ minutes (t: plate thickness (mm)) or more.

30 [0018] A holding time during the secondary heat treatment may be $1.9t + 10$ minutes (t: plate thickness (mm)) or more.

[0019] The solution to the above problems does not enumerate all the features of the present disclosure, and various beneficial merits of the present disclosure are not limited to the descriptions above, and may be more easily understood in a process of describing specific exemplary embodiments in the present disclosure.

35 Advantageous Effects of Invention

[0020] As set forth above, according to the present disclosure, armored steel having excellent low-temperature toughness while having ultra-high hardness may be provided.

40 [0021] The present disclosure may provide armored steel having a target level of physical properties without performing a further heat treatment from optimization of alloy compositions and manufacturing conditions, and thus, is economically favorable.

[0022] The effect of the present disclosure is not limited to the above, and may be interpreted as including an effect that can be inferred from the description described below by those skilled in the art.

45 Best Mode for Invention

50 [0023] The present disclosure relates to a high-hardness armored steel having excellent low-temperature impact toughness and a manufacturing method therefor. 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 the embodiments described below. The present embodiments are provided to those skilled in the art to further elaborate the present disclosure.

55 [0024] The present inventors have studied in depth, in order to provide a steel material having excellent physical properties such as high hardness characteristics, low-temperature impact toughness, and the like, which are essentially required physical properties, as a material which may be appropriately applied to wheeled armored vehicles, explosion-proof structures, and the like.

[0025] In particular, the bulletproof performance of the steel material was intended to be improved by an economically favorable method, and thus, the present disclosure was provided.

[0026] Hereinafter, armored steel according to an aspect of the present disclosure will be described in more detail.

[0027] Hereinafter, a steel composition of the present disclosure will be described in more detail. Hereinafter, % represents a content of each element based on weight, unless otherwise particularly specified.

5 Carbon (C): 0.29 to 0.37%

[0028] Carbon (C) is an element which is effective for improving strength and hardness in steel having a low-temperature transformation phase such as a martensite or bainite phase, and is effective for improving hardenability. In order to sufficiently obtain the effect described above, 0.29% or more of carbon (C) may be included. Preferably, a lower limit of a content of carbon (C) may be 0.30%, and more preferably, the lower limit of the content of carbon (C) may be 0.31%.
10 However, when carbon (C) is excessively added, there may be a concern that weldability and toughness of steel are deteriorated, so in the present disclosure, an upper limit of the content of carbon (C) may be limited to 0.37%. Preferably, the upper limit of the content of carbon (C) may be 0.36%.

15 Silicon (Si): 1.0 to 2.0%

[0029] Silicon (Si) is an element which is effective for improving strength due to solid solution strengthening together with a deoxidation effect, and is also an element suppressing formation of carbides such as cementite in a steel material containing a certain amount or more of C to promote production of residual austenite. In particular, since residual austenite which is uniformly distributed in steel having a low-temperature transformation phase such as martensite and bainite 20 may effectively contribute to improvement of impact toughness without strength reduction. Therefore, in order to sufficiently obtain the effect described above, in the present disclosure, 1.0% or more of silicon (Si) may be included. Preferably, a lower limit of a content of silicon (Si) may be 1.1%, and more preferably, the lower limit of the content of silicon (Si) may be 1.2%. However, when silicon (Si) is excessively added, weldability may be rapidly deteriorated, so in the present disclosure, an upper limit of the content of silicon (Si) may be limited to 2.0%. Preferably, the upper limit 25 of the content of silicon (Si) may be 1.9%, and more preferably, the upper limit of the content of silicon (Si) may be 1.8%.

Manganese (Mn): 0.5 to 1.6%

[0030] Manganese (Mn) is an element favorable to suppress production of ferrite and lower an Ar3 temperature, thereby improving quenching properties of steel to increase strength and toughness. In order to obtain a target level of 30 hardness in the present disclosure, 0.5% or more of manganese (Mn) may be included. Preferably, a lower limit of a content of manganese (Mn) may be 0.6%, and more preferably, the lower limit of the content of manganese (Mn) may be 0.7%. However, when manganese (Mn) is excessively added, there may be a concern that weldability is deteriorated and center segregation is encouraged to deteriorate the physical properties in the center part of steel, so in the present 35 disclosure, an upper limit of the content of manganese (Mn) may be limited to 1.6%. Preferably, the upper limit of the content of manganese (Mn) may be 1.5%, and more preferably, the upper limit of the content of manganese (Mn) may be 1.45%.

40 Nickel (Ni): 0.5 to 1.2%

[0031] Nickel (Ni) is an element favorable to improve both strength and toughness of steel. In order to obtain the effect described above, in the present disclosure, 0.5% or more of nickel (Ni) may be included. Preferably, a lower limit of a content of nickel (Ni) may be 0.6%, and more preferably, the lower limit of the content of nickel (Ni) may be 0.7%. However, nickel (Ni) is an expensive element, when nickel (Ni) is excessively added, manufacturing costs may be greatly 45 increased, so in the present disclosure, an upper limit of the content of nickel (Ni) may be limited to 1.2%. Preferably, the upper limit of the content of nickel (Ni) may be 1.17%, and more preferably, the upper limit of the content of nickel (Ni) may be 1.15%.

50 Chromium (Cr): 0.4 to 1.5%

[0032] Chromium (Cr) is an element of increasing quenching properties of steel to improve strength, and effectively contributing to securing hardness in a surface part and a center part of steel. In addition, since chromium (Cr) is a relatively inexpensive element, chromium (Cr) is also an element for economically securing hardness and toughness. In order to obtain the effect described above, in the present disclosure, 0.4% or more of chromium (Cr) may be included. Preferably, a lower limit of a content of chromium (Cr) may be 0.5%. However, when chromium (Cr) is excessively added, weldability may be deteriorated, so in the present disclosure, an upper limit of the content of chromium (Cr) may be limited to 1.5%. Preferably, the upper limit of the content of chromium (Cr) may be 1.4%, and more preferably, the upper limit of the content of chromium (Cr) may be 1.3%.

Phosphorous (P): 0.05% or less

[0033] Phosphorus (P) is an element which is inevitably contained in steel, and is also an element which deteriorates toughness of the steel. Thus, it is preferred to lower a content of P as much as possible. In the present disclosure, even in the case of including phosphorus (P) up to 0.05%, the physical properties of the steel are not significantly influenced, and thus, an upper limit of the content of phosphorus (P) may be limited to 0.05%. More favorably, the content thereof may be limited to 0.03% or less. However, 0% may be excluded considering an inevitably contained level.

Sulfur (S): 0.02% or less

[0034] Sulfur (S) is an element which is inevitably contained in steel, and is also an element forming MnS inclusions to deteriorate toughness of steel. Thus, it is preferred to lower a content of S as much as possible. In the present disclosure, even in the case of including sulfur (S) up to 0.02%, the physical properties of the steel are not significantly influenced, and thus, an upper limit of the content of sulfur (S) may be limited to 0.02%. More favorably, the content thereof may be limited to 0.01% or less. However, 0% may be excluded considering an inevitably contained level.

Nitrogen (N): 0.006% or less

[0035] Nitrogen (N) is an element which is favorable to improve strength of steel by forming precipitates in steel, but when a content of nitrogen (N) is more than a certain level, which may rather cause deterioration in toughness of steel. In the present disclosure, there is no difficulty in securing strength even when N is not contained, so in the present disclosure, an upper limit of a content of nitrogen (N) may be limited to 0.006%. However, 0% may be excluded considering an inevitably contained level.

Aluminum (Al): 0.07% or less (excluding 0%)

[0036] Aluminum (Al) is an element effective for lowering an oxygen content in molten steel as a deoxidizing agent of steel. However, when aluminum (Al) is excessively added, cleanliness of steel may be impaired, so in the present disclosure, an upper limit of a content of aluminum (Al) may be limited to 0.07%.

[0037] On the other hand, when the content of aluminum (Al) is excessively lowered, a load may occur in a steelmaking process and manufacturing costs may be increased, and thus, in the present disclosure, 0% may be excluded from a lower limit of the content of aluminum (Al), and the lower limit thereof may be 0.01%.

Molybdenum (Mo): 0.1 to 0.5%

[0038] Molybdenum (Mo) is an element favorable to increase quenching properties of steel, and in particular, to improve hardness of a thick material having a certain thickness or more. In order to obtain the effect described above, in the present disclosure, 0.1% or more of molybdenum (Mo) may be included. Preferably, a lower limit of a content of molybdenum (Mo) may be 0.15%, and more preferably, the lower limit of the content of molybdenum (Mo) may be 0.2%. However, when molybdenum (Mo) is excessively added, not only manufacturing costs may be increased, but also weldability may be deteriorated, so in the present disclosure, an upper limit of the content of molybdenum (Mo) may be limited to 0.5%. Preferably, the upper limit of the content of molybdenum (Mo) may be 0.48%, and more preferably, the upper limit of the content of molybdenum (Mo) may be 0.45%.

Niobium (Nb): 0.01 to 0.05%

[0039] Niobium (Nb) is an element which is effective for increasing hardenability of austenite by being dissolved in austenite, and increasing strength of steel and suppressing growth of austenite crystal grains by forming carbonitrides such as Nb(C,N). In order to sufficiently obtain the effect described above, in the present disclosure, 0.01% or more of niobium (Nb) may be included. However, when niobium (Nb) is excessively added, coarse precipitates may be formed to become a starting point of brittle fracture, so in the present disclosure, an upper limit of a content of niobium (Nb) may be limited to 0.05%. Preferably, the upper limit of the content of niobium (Nb) content may be 0.04%.

Boron (B): 0.0002 to 0.005%

[0040] Boron (B) is an element effectively contributing to strength improvement by increasing quenching properties of steel even with a small addition amount thereof. In order to sufficiently obtain the effect, in the present disclosure, 0.0002% or more of boron (B) may be contained. Preferably, a lower limit of a content of boron (B) may be 0.0005%,

and more preferably, the lower limit of the content of boron (B) may be 0.001%. However, when boron (B) is excessively added, toughness and weldability of steel may be rather deteriorated, so in the present disclosure, an upper limit of the content of boron (B) may be limited to 0.005%. Preferably, the upper limit of the content of boron (B) may be 0.004%, and more preferably, the upper limit of the content of boron (B) may be 0.003%.

5

Calcium (Ca): 0.0005 to 0.004%

10

[0041] Calcium (Ca) an element having a good binding force with sulfur (S) and producing CaS on the periphery (around) MnS, thereby suppressing elongation of MnS to improve toughness in a direction perpendicular to a rolling direction. In addition, CaS produced by adding Ca has an effect of increasing corrosion resistance under a humid external environment. In order to sufficiently obtain the effect described above, 0.0005% or more of Ca may be included. Preferably, a lower limit of a content of calcium (Ca) may be 0.001%. However, when calcium (Ca) is excessively added, defects such as nozzle clogging, or the like, may be caused in a steelmaking operation, so in the present disclosure, an upper limit of the content of calcium (Ca) may be limited to 0.004%. Preferably, the upper limit of the content of calcium (Ca) may be 0.003%.

15

[0042] In addition to the above-described alloy composition, armored steel of the present disclosure may further include the following elements for the purpose of favorably securing target physical properties.

20

[0043] Specifically, the armored steel of the present disclosure may further include at least one of titanium (Ti) and vanadium (V).

25

Titanium (Ti): 0.005 to 0.025%

30

[0044] Titanium (Ti) is an element which maximizes the effect of boron (B), which is an element favorable to improve quenching properties of steel. That is, titanium (Ti) is bonded to nitrogen (N) in steel to be precipitated into TiN to reduce the content of solid-solubilized N, while suppressing formation of BN of B therefrom to increase solid-solubilized B, thereby maximizing improvement of quenching properties. In order to sufficiently obtain the effect described above, 0.005% or more of titanium (Ti) may be contained. However, when titanium (Ti) is excessively added, coarse TiN precipitates may be formed and toughness of steel may be deteriorated, so in the present disclosure, an upper limit of the content of titanium (Ti) may be limited to 0.025%.

35

Vanadium (V): 0.2% or less (including 0%)

40

[0045] Vanadium (V) is an element favorable to form a VC carbide when reheating after hot rolling, thereby suppressing growth of austenite crystal grains and improving quenching properties of steel to secure strength and toughness. However, since vanadium (V) is a relatively expensive element, an upper limit of a content of vanadium (V) may be limited to 0.2% in consideration of manufacturing costs.

45

[0046] The armored steel according to an aspect of the present disclosure may include a remainder of Fe and other inevitable impurities in addition to the components described above. However, since in the common manufacturing process, unintended impurities may be inevitably incorporated from raw materials or the surrounding environment, the component may not be excluded. Since these impurities are known to any person skilled in the common manufacturing process, the entire contents thereof are not particularly mentioned in the present specification. In addition, further addition of effective ingredients other than the above-mentioned ingredients is not entirely excluded.

[0047] The armored steel according to an aspect of the present disclosure may satisfy the following [Relational Expression 1].

50

[Relational Expression 1]

$$10 * [C] * [Si] \geq 4$$

55

[0048] In Relational Expression 1, [C] and [Si] refer to contents (weight %) of carbon (C) and silicon (Si) included in the steel sheet, and 0 is substituted if the corresponding element is not intentionally added.

[0049] The inventors of the present disclosure have conducted in-depth research on a method capable of securing high-hardness characteristics and excellent low-temperature impact toughness of a steel sheet at the same time, and have derived that it is effective to control not only a content range of each respective alloy composition, but also a relative content range of the specific alloy composition included in the steel sheet. In the present disclosure, not only the content range of each respective alloy composition included in the steel sheet is controlled to be within a certain range, but also the relative content range of carbon (C) and silicon (Si) is controlled to be within a certain range, as illustrated in [Relational

Expression 1], so that high hard characteristics and excellent low-temperature impact toughness may be effectively compatible. $10^*[\text{C}]^*[\text{Si}]$ defined by the Relational Expression 1 may be 4.3 or more.

[0050] The armored steel of the present disclosure having the alloy composition described above may have a tempered martensite base structure including retained austenite as a microstructure, and may further include other inevitable structures. In this case, preferably, a fraction of retained austenite may be 1% by area to 10% by area, and a fraction of tempered martensite may be 90% or more by area.

[0051] Retained austenite is a structure remaining without being completely phase transformed into martensite during a rapid cooling heat treatment, and has relatively low hardness but excellent toughness as compared to martensite. For this effect, the armor steel of the present disclosure may include 1% or more by area of retained austenite, more preferably 2% or more by area of retained austenite. On the other hand, when the retained austenite is excessively formed, the low-temperature impact toughness greatly increases, but it is difficult to secure target hardness characteristics. Therefore, in the present disclosure, an upper limit of the fraction of the retained austenite may be set to be 10% by area. The upper limit of the fraction of the retained austenite may be 5% by area, and a lower limit of the fraction of the tempered martensite may be 95% by area.

[0052] Meanwhile, the armor steel of the present disclosure may have the above-described microstructural configuration over the entire thickness.

[0053] The armor steel of the present disclosure having the above-described alloy composition and the proposed microstructure may have a thickness of 5 to 40 mm, and have a surface hardness of 460 to 540HB, exhibiting ultra-high hardness, and an impact absorption energy of 19 J or more at -40°C, exhibiting excellent low-temperature toughness.

[0054] Here, the surface hardness refers to an average value of three measurements after milling a surface of the armored steel at 2 mm in a thickness direction using a Brinell hardness tester (load: 3000 kgf, 10 mm tungsten injection port).

[0055] Hereinafter, a manufacturing method for armored steel according to an aspect of the present disclosure will be described in more detail.

[0056] A steel slab having a predetermined component is prepared. Since the steel slab of the present disclosure has an alloy composition corresponding to the alloy composition of the hot-rolled steel sheet described above (including [Relational Expression 1]), a description of the alloy composition of the steel slab is substituted for the description of the alloy composition of the above-described hot-rolled steel sheet.

[0057] In brief, the armored steel may be manufactured by preparing a steel slab satisfying the alloy composition described above, and then subjecting the steel slab to the processes of [heating - rolling - primary heat treatment (quenching) - secondary heat treatment (tempering)]. Hereinafter, each process condition will be described in detail.

[Steel slab heating process]

[0058] First, a steel slab having the alloy composition proposed in the present disclosure is prepared, which may be then heated in a temperature range of 1050 to 1250°C.

[0059] When the temperature is lower than 1050°C during the heating, deformation resistance of steel is increased, so that a subsequent rolling process may not be effectively performed. On the other hand, when the temperature is higher than 1250°C, austenite crystal grains are coarsened, so that non-uniform structure may be formed.

[0060] Therefore, the steel slab may be heated in a temperature range of 1050 to 1250°C.

[Rolling process]

[0061] The steel slab heated as described above may be rolled, and then may be subjected to rough rolling and finish hot rolling to manufacture a hot-rolled steel sheet.

[0062] First, the heated steel slab is roughly rolled in a temperature range of 950 to 1150°C to be manufactured into a bar, which may be then subjected to finish hot rolling in a temperature range of 850 to 950°C.

[0063] When the temperature is lower than 950°C during the rough rolling, a rolling load is increased to reduce the steel slab relatively weakly, and thus, deformation is not sufficiently transferred to a center of the slab in the thickness direction, and as a result, defects such as voids may not be removed. On the other hand, when the temperature thereof is higher than 1150°C, recrystallization granularity is coarsened, which may be harmful to toughness.

[0064] When the temperature is lower than 850°C during the finish hot rolling, two-phase region rolling is performed, so that there is a concern that ferrite may be produced in the microstructure. On the other hand, when the temperature thereof is higher than 950°C, the granularity of the final structure is coarsened to deteriorate low-temperature toughness.

[Primary heat treatment (quenching) process]

[0065] The hot-rolled steel sheet manufactured through the rolling process described above is air cooled to room

temperature, and then heated to a residence time of $1.3t + 10$ minutes (t : plate thickness (mm)) or more in a temperature range of 880 to 930°C.

[0066] The heating is performed for reverse transformation of a hot-rolled steel sheet composed of ferrite and pearlite into an austenite single phase. When a heating temperature is lower than 880°C, austenitization is not sufficiently achieved, and coarse soft ferrite is mixed, and thus hardness of a final product may be deteriorated. On the other hand, when the temperature thereof is higher than 930°C, there is an effect of increasing quenching properties due to coarse austenite crystal grains, but there is a disadvantage in terms of thermal efficiency during mass production. Therefore, heating during a primary heat treatment is preferably performed in a range of 880 to 930°C. A lower limit of the heating temperature is more preferably 885°C, even more preferably 890°C, and most preferably 895°C. In addition, an upper limit of the heating temperature is more preferably 925°C, even more preferably 920°C, and most preferably 915°C.

[0067] Meanwhile, when a residence time during the primary heat treatment is less than $1.3t + 10$ minutes (t : plate thickness (mm)), austenitization does not sufficiently occur, so that phase transformation by subsequent rapid cooling, that is, a martensitic structure cannot be sufficiently obtained. Therefore, a residence time during the heating is preferably $1.3t + 10$ minutes (t : plate thickness (mm)) or more. The residence time during the heating is more preferably $1.3t + 12$ minutes (t : plate thickness (mm)) or more, even more preferably $1.3t + 13$ minutes (t : plate thickness (mm)) or more, and most preferably $1.5t + 15$ minutes (t : plate thickness (mm)) or more.

[0068] In the present disclosure, an upper limit of the residence time during the primary heat treatment is not particularly limited. However, when the residence time during the heating exceeds $1.3t + 60$ minutes (t : plate thickness (mm)), austenite crystal grains become coarse, so that quenching properties may increase, but there may be a disadvantage in that productivity is relatively lowered. Therefore, the residence time during the heating is preferably $1.3t + 60$ minutes (t : plate thickness (mm)) or less. The residence time during the heating is more preferably $1.3t + 50$ minutes (t : plate thickness (mm)) or less, even more preferably $1.3t + 40$ minutes (t : plate thickness (mm)) or less, and most preferably $1.3t + 30$ minutes (t : plate thickness (mm)) or less.

[0069] Thereafter, the heated hot-rolled steel sheet may be cooled to 120°C or lower at a cooling rate of 10°C/s or more with respect to a plate thickness center portion (e.g., 1/2t point, t : plate thickness (mm)). In this case, the cooling is preferably rapid cooling through water cooling. When the cooling rate is less than 10°C/s or a cooling end temperature is higher than 120°C, there is a concern that a ferrite phase may be formed or a bainite phase may be excessively formed during cooling. Therefore, the cooling is preferably performed to 120°C or lower at a cooling rate of 10°C/s or more. The faster the cooling rate, the more favorable it is to form the microstructure to be obtained in the present disclosure. Meanwhile, in the present disclosure, an upper limit of the cooling rate is not particularly limited, and it may be appropriately set in consideration of facility limitations by any person skilled in the art. The cooling end temperature is more preferably 100°C or lower, even more preferably 80°C or lower, and most preferably 50°C or lower.

[Secondary heat treatment (tempering) process]

[0070] The hot-rolled steel sheet manufactured through the above-described primary heat treatment may be heated to a temperature range of 350°C or lower and maintained for $1.9t + 10$ minutes (t : plate thickness (mm)) or more.

[0071] The reheating is performed to release internal stress of a hot-rolled steel sheet fully composed of martensite after quenching. As dislocation density inside a material thereof decreases through such a tempering heat treatment, hardness may decrease somewhat, but toughness may be secured. In the case of armor steel, since it is necessary not only to have high hardness but also to have excellent low-temperature impact toughness, such a subsequent tempering heat treatment is essential if no special element is added. When a tempering temperature exceeds 350°C, the dislocation density inside the martensite is excessively reduced, and thus hardness of a final product may be lowered. On the other hand, when the tempering temperature is too low, the decrease in hardness can be prevented, but the dislocation density becomes too high, which is disadvantageous in terms of securing impact toughness. In the present disclosure, a lower limit of the tempering temperature is not separately specified, but is preferably 100°C or higher in order to obtain the effect described above. It is preferable to perform tempering, more preferably at a temperature of 125°C or higher, and even more preferably 150°C or higher.

[0072] In the present disclosure, a lower limit of the holding time during the tempering is not particularly limited. However, when the holding time during the tempering is less than $1.9t + 10$ minutes (t : plate thickness (mm)), a thickness center portion compared to the surface thereof may not be sufficiently heated, as the heat treatment is performed at a relatively low temperature for a short time. Therefore, the holding time during the tempering is preferably $1.9t + 10$ minutes (t : plate thickness (mm)) or more. The holding time during the tempering is more preferably $1.9t + 12$ minutes (t : plate thickness (mm)) or more, more preferably $1.9t + 15$ minutes (t : plate thickness (mm)) or less, and most preferably $1.9t + 20$ minutes (t : plate thickness (mm)) or more.

[0073] After tempering, it can be cooled to room temperature by air cooling. Through such a tempering process, the hot-rolled steel sheet according to an aspect of the present disclosure may have softened tempered martensite as a base structure.

[0074] The hot-rolled steel sheet obtained through the above-described series of manufacturing processes is a steel material having a thickness of 5 to 40 mm, and can provide excellent bullet-proof resistance by securing high hardness and high toughness.

5 Mode for Invention

[0075] Hereinafter, armored steel of the present disclosure and a manufacturing method therefor will be described in more detail through specific examples. It should be noted that the following examples are only for understanding of the present disclosure, and are not intended to specify the scope of the present disclosure. The scope of the present disclosure may be determined by the matters described in the claims and the matters reasonably inferred therefrom.

10 (Example)

[0076] After preparing a steel slab having alloy compositions of Table 1 below, [heating - rolling - heat treatment (quenching) - heat treatment (tempering)] were performed according to process conditions illustrated in Table 2 below to manufacture each hot-rolled steel sheet. In this case, after being water cooled to a cooling end temperature, air cooling was applied to room temperature. The tempering performed thereafter also applied air cooling to room temperature after performing a heat treatment at a specific temperature. Alloy compositions not listed in Table 1 refer to unavoidable impurities and iron (Fe). In addition, a part marked with "-" in Table 1 means that the corresponding component was not intentionally added, which is preferable to be interpreted as 0% by weight within an error range.

25

30

35

40

45

50

55

[Table 1]

Steel type	Alloy composition (weight %)											[Relative Expression 1]				
	C	Si	Mn	P*	S*	Ni	Cr	Mo	Nb	V	Al	Ca*	Ti	B*	N*	
A	0.49	1.25	1.16	74	16	1.12	0.81	0.27	0.03	0.03	0.03	27	0.015	20	50	6.13
B	0.24	0.21	0.89	72	20	0.25	0.56	0.44	0.01	-	0.04	21	-	19	45	0.50
C	0.31	1.43	0.94	71	21	0.92	0.72	0.39	0.02	0.04	0.03	20	-	17	44	4.43
D	0.34	1.29	1.22	75	23	0.79	0.56	0.42	0.04	-	0.03	19	-	18	49	4.39
E	0.36	1.37	1.45	76	19	1.13	0.68	0.28	0.03	-	0.04	16	0.012	21	45	4.93
F	0.29	1.08	0.62	73	20	0.66	0.43	0.15	0.02	-	0.03	18	0.014	20	43	3.13

P*, S*, Ca*, B*, and N* are represented in units of ppm

[Table 2]

Spec imen No.	Stee 1 type	Thic knes (mm)	Slab heat ing (°C)	Rolling		First heat treatment (quenching)				Second heat treatment (tempering)	
				Rough rollin 9 (°C)	Finish hot rolling (°C)	Heati ng tempe ratur e (°C)	Resid ence time (min.)	Cooling end tempe ratur e (°C)	Cooli ng rate (°C/ s)	Heatin 9 temper ature (°C)	Holdin g time (min.)
1	A	12	1171	1034	886	908	31	23	50.6	224	46
2	A	18	1125	1018	924	910	37	29	38.8	206	57
3	A	40	1159	1046	911	905	68	22	25.7	217	100
4	B	40	1159	1046	911	905	25	19	63.4	432	40
5	B	10	1165	1040	887	909	47	23	45.5	561	58
6	B	20	1154	1035	916	915	74	24	26.6	306	97
7	C	5	1180	1065	871	902	31	17	71.1	214	38
8	C	15	1176	1063	899	900	45	26	47.5	421	52
9	C	25	1165	1025	923	910	54	23	44.6	223	68
10	D	12	1159	1059	890	911	38	25	64.7	212	44
11	D	25	1163	1024	915	904	55	21	49.8	230	59
12	D	40	1155	1030	922	906	72	224	27.9	226	94
13	E	40	1153	1027	934	899	73	46	26.3	215	14
14	E	25	1149	1029	928	913	54	37	45.9	227	60
15	E	25	1164	1022	909	907	57	29	43.6	391	62
16	E	10	1147	1055	861	909	36	30	65.2	208	39
17	F	15	1150	1062	892	903	40	28	47.3	294	41

[0077] Thereafter, a microstructure and mechanical properties of each hot-rolled steel sheet were measured, and the results thereof were shown in Table 3.

[0078] The microstructure of each hot-rolled steel sheet was cut into an arbitrary size as a specimen to manufacture a mirror surface, a Nital etching solution was used to corrode the specimen, and then an optical microscope and a scanning electron microscope (SEM) were used to observe a 1/2t point which was a thickness center portion. In this case, a fraction of the microstructure was measured by electron back-scattered diffraction (EBSD) analysis.

[0079] In addition, hardness and toughness of each hot-rolled steel sheet were measured using a Brinell hardness tester (load: 3000 kgf, 10 mm tungsten injection port) and a Charpy impact tester, respectively. In this case, in the surface hardness, an average value of three measurements after a milling process of the surface of the hot-rolled sheet at 2 mm was used, and in the Charpy impact test, a specimen was collected at 1/4t point in the thickness direction, and then an average value of three measurements at -40°C was used.

[Table 3]

Specime n No.	Steel type	Microstructure (area %)			Surface hardness (HB)	Impact toughness (J, @-40°C)
		TM	F or B	R- γ		
1	A	96	-	4	612	16
2	A	97	-	3	626	15
3	A	97	-	3	615	14

(continued)

Specime n No.	Steel type	Microstructure (area %)			Surface hardness (HB)	Impact toughness (J, @-40°C)
		TM	F or B	R- γ		
4	B	100	-	0	346	29
5	B	100	-	0	317	32
6	B	99	-	1	453	22
7	C	97	-	3	502	29
8	C	100	-	0	428	34
9	C	97	-	3	489	31
10	D	98	-	2	514	24
11	D	97	-	3	507	26
12	D	56	B:42, F: 2	0	405	50
13	E	100	-	0	573	16
14	E	97	-	3	493	28
15	E	100	-	0	386	31
16	E	98	-	2	526	24
17	F	99	-	1	447	28

TM: Tempered martensite, B: Bainite, F: Ferrite R- γ : Retained austenite

[0080] As shown in Tables 1 to 3, it can be seen that specimens satisfying the alloy composition and process conditions of the present disclosure have a surface harness of 460 to 540 HB and an impact absorption energy of 19 J or more at -40°C, but specimens not satisfying at least one of the alloy compositions or process conditions of the present disclosure do not have a surface hardness of 460 to 540 HB or an impact absorption energy of 19 J or more at -40°C at the same time.

[0081] While example embodiments have been shown 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-hardness armored steel having excellent low-temperature impact toughness comprising, by weight:

0.29 to 0.37% of carbon (C), 1.0 to 2.0% of silicon (Si), 0.5 to 1.6% of manganese (Mn), 0.5 to 1.2% of nickel (Ni), 0.4 to 1.5% of chromium (Cr), 0.05% or less of phosphorus (P), 0.02% or less of sulfur (S), 0.006% or less of nitrogen (N), 0.07% or less of aluminum (Al) (excluding 0%), 0.1 to 0.5% of molybdenum (Mo), 0.01 to 0.05% of niobium (Nb), 0.0002 to 0.005% of boron (B), 0.0005 to 0.004% of calcium (Ca), with a balance of iron (Fe) and inevitable impurities, satisfying the following [Relational Expression 1], wherein a tempered martensite base structure including retained austenite is included as a microstructure,

[Relational Expression 1]

$$10 * [C] * [Si] \geq 4$$

in Relational Expression 1, [C] and [Si] refer to contents (weight %) of carbon (C) and silicon (Si) included in the steel, and 0 is substituted when the corresponding element is not intentionally added.

2. The high-hardness armored steel having excellent low-temperature impact toughness of claim 1, wherein the armored

steel further comprises, by weight: at least one of 0.005 to 0.025% of titanium (Ti) and 0.2% or less of vanadium (V) .

5 3. The high-hardness armored steel having excellent low-temperature impact toughness of claim 1, wherein a fraction of the tempered martensite is 90% or more by area, and a fraction of the retained austenite is 1% by area to 10% by area.

10 4. The high-hardness armored steel having excellent low-temperature impact toughness of claim 1, wherein the armored steel has a surface hardness of 460 to 540 HB and an impact absorption energy of 19 J or more at -40°C.

15 5. The high-hardness armored steel having excellent low-temperature impact toughness of claim 1, wherein the armored steel has a thickness of 5 to 40 mm.

20 6. A manufacturing method for a high-hardness armored steel having excellent low-temperature impact toughness, comprising operations of: preparing a steel slab including, by weight: 0.29 to 0.37% of carbon (C), 1.0 to 2.0% of silicon (Si), 0.5 to 1.6% of manganese (Mn), 0.5 to 1.2% of nickel (Ni), 0.4 to 1.5% of chromium (Cr), 0.05% or less of phosphorus (P), 0.02% or less of sulfur (S), 0.006% or less of nitrogen (N), 0.07% or less of aluminum (Al) (excluding 0%), 0.1 to 0.5% of molybdenum (Mo), 0.01 to 0.05% of niobium (Nb), 0.0002 to 0.005% of boron (B), 0.0005 to 0.004% of calcium (Ca), with a balance of iron (Fe) and inevitable impurities, satisfying the following [Relational Expression 1];

25 heating the steel slab in a temperature range of 1050 to 1250°C;
 rough rolling the heated steel slab in a temperature range of 950 to 1150°C;
 subjecting the heated steel slab to finish hot rolling in a temperature range of 850 to 950°C after the rough rolling to manufacture a hot-rolled steel sheet;
 30 performing a primary heat treatment of heating the hot-rolled steel sheet to a temperature range of 880 to 930°C and then cooling the same to a cooling end temperature of 150°C or lower at a cooling rate of 10°C/s or more; and performing a secondary heat treatment of heating the primarily heat-treated hot-rolled steel sheet to a temperature range of 350°C or lower and maintaining the same,

35 [Relational Expression 1]

$$10 * [C] * [Si] \geq 4$$

40 in Relational Expression 1, [C] and [Si] refer to contents (weight %) of carbon (C) and silicon (Si) included in the steel slab, and 0 is substituted when the corresponding element is not intentionally added.

45 7. The manufacturing method for a high-hardness armored steel having excellent low-temperature impact toughness of claim 6, wherein the steel slab further comprises, by weight: at least one of 0.005 to 0.025% of titanium (Ti) and 0.2 % or less of vanadium (V).

50 8. The manufacturing method for a high-hardness armored steel having excellent low-temperature impact toughness of claim 6, wherein a residence time during the primary heat treatment is $1.3t + 10$ minutes (t: plate thickness (mm)) or more.

55 9. The manufacturing method for a high-hardness armored steel having excellent low-temperature impact toughness of claim 6, wherein a holding time during the secondary heat treatment is $1.9t + 10$ minutes (t: plate thickness (mm)) or more.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2021/015868

5	A. CLASSIFICATION OF SUBJECT MATTER C22C 38/58(2006.01)i; C22C 38/54(2006.01)i; C22C 38/48(2006.01)i; C22C 38/44(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																			
10	B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C22C 38/58(2006.01); C21D 8/02(2006.01); C21D 9/46(2006.01); C22C 38/00(2006.01); C22C 38/14(2006.01); C22C 38/44(2006.01); C22C 38/60(2006.01)																			
15	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																			
20	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS (KIPO internal) & keywords: 텐퍼드 마르텐사이트(tempered martensite), 오스테나이트(austenite), 냉각 (cooling), 텐퍼링(tempering), 규소(Si)																			
25	C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <tr> <td>Category*</td> <td>Citation of document, with indication, where appropriate, of the relevant passages</td> <td>Relevant to claim No.</td> </tr> <tr> <td>X</td> <td>KR 10-2014-0074981 A (JFE STEEL CORPORATION) 18 June 2014 (2014-06-18) See paragraphs [0098]-[0099], claims 1, 3-4 and 7 and table 2.</td> <td>1-9</td> </tr> <tr> <td>X</td> <td>KR 10-2010-0116608 A (JFE STEEL CORPORATION) 01 November 2010 (2010-11-01) See claims 1-4.</td> <td>1-5</td> </tr> <tr> <td>A</td> <td>KR 10-2019-0076790 A (POSCO) 02 July 2019 (2019-07-02) See paragraph [0106] and claim 1.</td> <td>1-9</td> </tr> <tr> <td>A</td> <td>KR 10-2015-0064223 A (BAOSHAN IRON & STEEL CO., LTD.) 10 June 2015 (2015-06-10) See paragraph [0045] and claim 1.</td> <td>1-9</td> </tr> <tr> <td>A</td> <td>JP 2002-302734 A (KOBE STEEL LTD.) 18 October 2002 (2002-10-18) See claims 1 and 4-6.</td> <td>1-9</td> </tr> </table>		Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	KR 10-2014-0074981 A (JFE STEEL CORPORATION) 18 June 2014 (2014-06-18) See paragraphs [0098]-[0099], claims 1, 3-4 and 7 and table 2.	1-9	X	KR 10-2010-0116608 A (JFE STEEL CORPORATION) 01 November 2010 (2010-11-01) See claims 1-4.	1-5	A	KR 10-2019-0076790 A (POSCO) 02 July 2019 (2019-07-02) See paragraph [0106] and claim 1.	1-9	A	KR 10-2015-0064223 A (BAOSHAN IRON & STEEL CO., LTD.) 10 June 2015 (2015-06-10) See paragraph [0045] and claim 1.	1-9	A	JP 2002-302734 A (KOBE STEEL LTD.) 18 October 2002 (2002-10-18) See claims 1 and 4-6.	1-9
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																		
X	KR 10-2014-0074981 A (JFE STEEL CORPORATION) 18 June 2014 (2014-06-18) See paragraphs [0098]-[0099], claims 1, 3-4 and 7 and table 2.	1-9																		
X	KR 10-2010-0116608 A (JFE STEEL CORPORATION) 01 November 2010 (2010-11-01) See claims 1-4.	1-5																		
A	KR 10-2019-0076790 A (POSCO) 02 July 2019 (2019-07-02) See paragraph [0106] and claim 1.	1-9																		
A	KR 10-2015-0064223 A (BAOSHAN IRON & STEEL CO., LTD.) 10 June 2015 (2015-06-10) See paragraph [0045] and claim 1.	1-9																		
A	JP 2002-302734 A (KOBE STEEL LTD.) 18 October 2002 (2002-10-18) See claims 1 and 4-6.	1-9																		
30	<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.																			
35	* 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																			
40	Date of the actual completion of the international search 18 April 2022																			
45	Date of mailing of the international search report 18 April 2022																			
50	Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon Building 4, 189 Cheongsa-ro, Seo-gu, Daejeon 35208																			
55	Facsimile No. +82-42-481-8578																			

INTERNATIONAL SEARCH REPORT Information on patent family members				International application No. PCT/KR2021/015868		
5	Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)		
10	KR 10-2014-0074981	A 18 June 2014	CN 103857820 A 11 June 2014	CN 103857820 B 21 December 2016	EP 2757171 A1 23 July 2014	EP 2757171 B1 19 April 2017
			JP 2012-031462 A 16 February 2012	JP 5136609 B2 06 February 2013	KR 10-1647902 B1 23 August 2016	KR 10-1660216 B1 26 September 2016
			KR 10-2016-0045932 A 27 April 2016	US 10190186 B2 29 January 2019	US 2014-0377584 A1 25 December 2014	US 2016-0160310 A1 09 June 2016
			US 9290834 B2 22 March 2016	WO 2013-051160 A1 11 April 2013		
	KR 10-2010-0116608	A 01 November 2010	CA 2713195 A1 06 August 2009	CA 2713195 C 26 November 2013	CN 101932745 A 29 December 2010	CN 101932745 B 08 August 2012
			EP 2258887 A1 08 December 2010	EP 2258887 B1 29 July 2015	JP 2009-203549 A 10 September 2009	JP 5365216 B2 11 December 2013
			KR 10-1225404 B1 22 January 2013	MX 2010008404 A 25 October 2010	US 2011-0048589 A1 03 March 2011	US 8840834 B2 23 September 2014
			WO 2009-096595 A1 06 August 2009			
	KR 10-2019-0076790	A 02 July 2019	CN 111479945 A 31 July 2020	EP 3730656 A1 28 October 2020	JP 2021-507999 A 25 February 2021	KR 10-2031446 B1 08 November 2019
			US 2021-0164079 A1 03 June 2021	WO 2019-125083 A1 27 June 2019		
30	KR 10-2015-0064223	A 10 June 2015	AU 2014-243613 A1 23 July 2015	AU 2014-243613 B2 08 September 2016	CN 103205634 A 17 July 2013	CN 103205634 B 01 June 2016
			EP 2980257 A1 03 February 2016	JP 2016-505094 A 18 February 2016	JP 6214674 B2 18 October 2017	KR 10-2017-0055560 A 19 May 2017
			KR 10-2040679 B1 05 November 2019	NZ 708763 A 25 November 2016	US 10208369 B2 19 February 2019	US 2016-0010191 A1 14 January 2016
			WO 2014-154106 A1 02 October 2014	ZA 201504567 B 29 June 2016		
			JP 2002-302734 A 18 October 2002	EP 1365037 A1 26 November 2003	EP 1365037 B1 02 April 2008	JP 2002-309334 A 23 October 2002

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

5 **INTERNATIONAL SEARCH REPORT**
10 **Information on patent family members**

15 International application No.
20 **PCT/KR2021/015868**

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)		Publication date (day/month/year)
10	JP 2003-073773	A		12 March 2003
	JP 2003-171735	A		20 June 2003
	JP 2003-171736	A		20 June 2003
	JP 4188581	B2		26 November 2008
	JP 4188582	B2		26 November 2008
	JP 4188608	B2		26 November 2008
	JP 4188609	B2		26 November 2008
	US 7090731	B2		15 August 2006
15	WO 02-061161	A1		08 August 2002
			
20				
25				
30				
35				
40				
45				
50				
55				

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

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 1020180043788 [0005]