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(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 method for manufacturing same.

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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 an exterior of armored vehicles used in battlefields. 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 hardness 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 important physical properties for securing the performance of armored steel, but simply high hardness does not guarantee bulletproof performance. A high hardness characteristic is a factor that increases resistance to bullets from 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 1) Korean Patent Publication No. 10-2018-0043788 (published on April 30, 2018)

30 Summary of Invention

Technical Problem

35 **[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.

[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

45 **[0008]** According to an aspect of the present disclosure, a high-hardness armored steel having excellent low-temperature impact toughness, includes by weight: 0.18 to 0.25% 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]

$$(A - 200) / 100 \leq 2.0$$

55 **[0009]** In the Relational Expression 1, A refers to a value calculated by the following Relational Expression 2.

[Relational Expression 2]

$$A = 539 - 423*[C] - 30.4*[Mn] - 17.7*[Ni] - 12.1*[Cr] \\ - 7.5*[Mo]$$

[0010] In the Relational Expression 2, [C], [Mn], [Ni], [Cr], and [Mo] refer to contents (weight %) of carbon (C), manganese (Mn), nickel (Ni), chromium (Cr), and molybdenum (Mo) included in the steel sheet, and 0 is substituted when the corresponding element is not intentionally added.

[0011] The armored steel may include, by weight: at least one of 0.005 to 0.025% of titanium (Ti) and 0.2% or less of vanadium (V).

[0012] A fraction of the tempered martensite may be 90% or more by area, and a fraction of retained austenite may be 1% by area to 10% by area.

[0013] The armored steel may have a surface hardness of 360 to 440 HB, and an impact absorption energy of 27J or more at -40°C.

[0014] The armored steel may have a thickness of greater than 40 mm.

[0015] 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: 0.18 to 0.25 % 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]; 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; and cooling the hot-rolled steel sheet to a temperature of 50 to 250 °C at a cooling rate of 3 °C/s or more and then air cooling the same to room temperature.

[Relational Expression 1]

$$(A - 200) / 100 \leq 2.0$$

[0016] In the Relational Expression 1, A refers to a value calculated by the following Relational Expression 2.

[Relational Expression 2]

$$A = 539 - 423*[C] - 30.4*[Mn] - 17.7*[Ni] - 12.1*[Cr] \\ - 7.5*[Mo]$$

[0017] In the Relational Expression 2, [C], [Mn], [Ni], [Cr], and [Mo] refer to contents (weight %) of carbon (C), manganese (Mn), nickel (Ni), chromium (Cr), and molybdenum (Mo) included in the steel slab, and 0 is substituted when the corresponding element is not intentionally added.

[0018] The steel slab may further include, by weight: at least one of 0.005 to 0.25% of titanium (Ti) and 0.2% or less of vanadium (V).

[0019] The hot-rolled steel sheet may have a thickness greater than 40 mm.

[0020] 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.

Advantageous Effects of Invention

[0021] As set forth above, according to the present disclosure, armored steel having excellent low-temperature toughness while having high hardness may be provided.

[0022] In the present disclosure armored steel having a target level of physical properties without performing a further

heat treatment from optimization of an alloy composition and manufacturing conditions may be provided, and thus, is economically favorable.

[0023] 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.

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Best Mode for Invention

[0024] 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.

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[0025] 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 is appropriately applied to tracked armored vehicles, explosion-proof structures, and the like.

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[0026] 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.

[0027] Hereinafter, armored steel according to an aspect of the present disclosure will be described in more detail.

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[0028] 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.

Carbon (C): 0.18 to 0.25%

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[0029] 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, 0.18% or more of carbon (C) may be included. Preferably, a lower limit of a content of carbon (C) may be 0.19%. 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 0.25%. Preferably, the upper limit of the content of carbon (C) may be 0.24%.

30

Silicon (Si): 1.0 to 2.0%

[0030] 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 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 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, since weldability may be rapidly deteriorated, in the present disclosure, an upper limit of the content of silicon (Si) may be limited to 2.0%. Preferably, the upper limit 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%.

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Manganese (Mn): 0.5 to 1.6%

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[0031] 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 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. Therefore, in the present 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 1.4%.

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Nickel (Ni): 0.5 to 1.2%

5 [0032] Nickel (Ni) is an element favorable to improving both strength and toughness of steel. In order to obtain the above-described effects, 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, since nickel (Ni) is an expensive element, when nickel (Ni) is excessively added, manufacturing costs may be greatly 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 1.15%, and more preferably, the upper limit of the content of nickel (Ni) may be 1.1%.

10 Chromium (Cr): 0.4 to 1.5%

15 [0033] 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 sufficiently 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 0.45%, and more preferably, the lower limit of the 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

25 [0034] 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.

30 Sulfur (S): 0.02% or less

35 [0035] 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.

40 Nitrogen (N): 0.006% or less

45 [0036] Nitrogen (N) is an element 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%)

50 [0037] 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%.

[0038] On the other hand, when the content of 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%.

55 Molybdenum (Mo): 0.1 to 0.5%

[0039] 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 sufficiently obtain the effect described above, 0.1% or more of Mo may be included. Preferably, a lower limit of a content of molybdenum (Mo) may be 0.13%, and more preferably, the lower limit of the content of molybdenum (Mo) may be 0.15%. 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, an upper limit of the content of molybdenum (Mo) may be 0.48%, and more particularly, the upper limit of the content of molybdenum (Mo) may be 0.45%.

Niobium (Nb): 0.01 to 0.05%

[0040] 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 (Ni) may be included. However, when niobium (Ni) 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) may be 0.05%, and more preferably, the upper limit of the content of niobium (Nb) may be 0.04%.

Boron (B): 0.0002 to 0.005%

[0041] 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%.

Calcium (Ca): 0.0005 to 0.004%

[0042] 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%.

[0043] 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.

[0044] Specifically, the armored steel of the present disclosure may further include at least one of titanium (Ti) and vanadium (V).

Titanium (Ti): 0.005 to 0.025%

[0045] 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%.

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

[0046] 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.

[0047] 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.

[0048] The armored steel according to an aspect of the present disclosure may satisfy the following [Relational Expression 1].

[Relational Expression 1]

$$(A - 200) / 100 \leq 2.0$$

[0049] In Relational Expression 1, A refers to a value calculated by the following [Relational Expression 2].

[Relational Expression 2]

$$A = 539 - 423 * [C] - 30.4 * [Mn] - 17.7 * [Ni] - 12.1 * [Cr] - 7.5 * [Mo]$$

[0050] In Relational Expression 2, [C], [Mn], [Ni], [Cr], and [Mo] refer to contents (weight %) of carbon (C), manganese (Mn), nickel (Ni), chromium (Cr), and molybdenum (Mo) included in a steel sheet, and 0 is substituted if the corresponding component is not intentionally added.

[0051] 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), manganese (Mn), chromium (Cr), nickel (Ni), and molybdenum (Mo) is controlled to be within a certain range, as illustrated in [Relational Expression 1] and [Relational Expression 2], so that high hard characteristics and excellent low-temperature impact toughness may be effectively compatible.

[0052] The armored steel of the present disclosure having the above-described alloy composition may have a tempered martensite base structure including retained austenite as a microstructure, and may further include other inevitable structures. In this case, a preferred 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.

[0053] 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 armored 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 7% by area, and a lower limit of the fraction of the tempered martensite fraction may be 93% by area.

[0054] Meanwhile, the armored steel of the present disclosure may have the above-described microstructural configuration over the entire thickness.

[0055] The armored steel of the present disclosure having the suggested microstructure together with the alloy composition described above may have a thickness greater than 40 mm. An upper limit of the thickness thereof is not particularly limited, but a preferred thickness thereof may be 100 mm, and a more preferred thickness thereof may be 80 mm or less.

[0056] According to an aspect of the present disclosure, surface hardness of the armored steel may have a surface hardness of 360 to 440 HB, exhibiting high hardness, and may have an impact absorption energy of 27 J or more at -40 °C, exhibiting excellent low-temperature toughness.

[0057] 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).

[0058] Hereinafter, a manufacturing method for armored steel according to an aspect of the present disclosure will be described in more detail.

[0059] 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] and [Relational Expression 2]), 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.

[0060] 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- cooling - self tempering]. Hereinafter, each process condition will be described in detail.

[Steel slab heating process]

[0061] First, a steel slab having the alloy composition suggested in the present disclosure is prepared, which may be then heated in a temperature range of 1050 to 1250°C.

[0062] When the temperature is lower than 1050°C during 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.

[0063] Therefore, the steel slab may be heated in a temperature range of 1050 to 1250°C.

[Rolling process]

[0064] 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.

[0065] 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.

[0066] 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.

[0067] When the temperature is lower than 850°C in 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.

[Cooling and Self tempering process]

[0068] The hot rolled steel sheet manufactured through the rolling process described above is cooled to 50 to 250°C at a rate of 3°C/s and then air-cooled to room temperature.

[0069] The cooling is performed to obtain a martensite base structure to satisfy high hardness, and when a cooling end temperature is higher than 250°C, phase transformation from austenite particles produced by hot rolling into martensite may not be completed, and thus hardness of a final product may be deteriorated. On the other hand, when the cooling end temperature is lower than 50°C, the phase transformation therefrom into martensite is completely completed, which is favorable in terms of securing hardness, but latent heat in a material decreases, so that a self-tempering effect cannot be obtained. Self-tempering is a method that can produce an effect similar to that of normal tempering through latent heat of a material, which is rapidly cooled without a separate subsequent process. Therefore, an end of the cooling of the hot-rolled steel sheet is preferably performed in a range of 50 to 250 °C. A lower limit of the cooling end temperature is more preferably 60 °C, even more preferably 70 °C, and most preferably 80 °C. In addition, an upper limit of the cooling end temperature is more preferably 240 °C, even more preferably 230°C, and most preferably 220°C.

[0070] Meanwhile, when the cooling rate is less than 3°C/s during the cooling, bainite and ferrite, which are relatively soft phases, are generated, so that phase transformation by rapid cooling, that is, a martensite structure cannot be sufficiently obtained. However, as a thickness of the steel sheet increases, the cooling rate inevitably decreases physically, so there is no separate upper limit. Therefore, the cooling rate is preferably 3 °C/s or more. The cooling rate is more preferably 3.2 °C/s or more, more preferably 3.5°C/s or more, and most preferably 4°C/s or more.

[0071] In a process of cooling the steel sheet to a temperature range of 50 to 250 °C, and then air cooling the same to room temperature, self-tempering may be performed by latent heat in a central portion thereof, and martensite introduced during cooling may be softened through self-tempering, thereby effectively securing low-temperature impact toughness. In the present disclosure, the thickness of the hot-rolled steel sheet manufactured through a series of manufacturing processes does not be specifically limited, but a lower limit of the thickness thereof may be limited to be more

than 40 mm in terms of securing a self-tempering effect. Preferably, the hot-rolled steel sheet may have a thickness of 41 mm or more, and an upper limit of the thickness thereof is also not limited, but the hot-rolled steel sheet may preferably have a thickness of 100 mm or less, more preferably 80 mm or less.

5 Mode for Invention

10 **[0072]** 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.

(Example)

15 **[0073]** A steel slab having alloy compositions shown in the following Table 1 was prepared, and then was subjected to [heating - rolling - cooling - self-tempering] according to process conditions shown in the following Table 2 to manufacture each hot-rolled steel sheet. In this case, water cooling was performed to a cooling end temperature, and then air cooling was applied to room temperature. Alloy compositions not listed in Table 1 refers to inevitable 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.

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[Table 1]

Steel type	Alloy composition(weight%)													[Relatio nal Expressi on 1]			
	C	Si	Mn	P*	S*	Ni	Cr	Mo	Nb	V	Al	Ca*	Ti	B*	N*		
A	0.31	1.62	1.25	73	20	0.71	0.87	0.43	0.03	0.04	0.04	20	-	19	46	1.44	
B	0.12	1.33	0.89	74	19	0.43	0.51	0.15	0.01	-	0.03	17	0.012	20	48	2.46	
C	0.19	1.49	1.02	72	21	0.85	1.24	0.34	0.02	-	0.04	18	-	21	49	1.95	
D	0.22	1.23	1.16	78	23	0.69	0.81	0.42	0.04	0.03	0.03	20	-	18	47	1.86	
E	0.24	1.38	0.95	73	20	1.04	0.66	0.39	0.03	-	0.03	21	0.017	22	45	1.79	
F	0.18	1.06	0.61	75	22	0.62	0.43	0.27	0.02	-	0.03	20	0.014	20	43	2.26	

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

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[Table 2]

Specimen No.	Steel type	Thickness (mm)	Slab heating (°C)	Rolling		Cooling	
				Rough rolling (°C)	Finish hot rolling (°C)	Cooling end temperature (°C)	Cooling rate (°C/s)
1	A	45	1146	1045	917	153	16.2
2	A	60	1127	987	905	134	7.1
3	A	80	1143	954	901	147	3.6
4	B	60	1131	1022	905	256	10.2
5	B	70	1124	1001	920	145	4.9
6	C	45	1165	1024	914	205	19.1
7	C	50	1164	988	901	19	9.5
8	C	65	1152	985	913	197	7.4
9	D	50	1148	1004	896	286	12.6
10	D	60	1150	996	900	192	11.5
11	D	75	1153	952	916	173	4.7
12	E	50	1137	1032	907	189	13.4
13	E	50	1140	992	909	145	2.6
14	E	65	1135	988	897	151	7.7
15	E	80	1151	960	882	164	3.8
16	F	60	1138	992	905	202	10.6

[0074] Thereafter, a microstructure and mechanical properties were of each hot-rolled steel sheet were measured, and the results thereof were shown in Table 3.

[0075] 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 part. In this case, a fraction of the microstructure was measured by electron back-scattered diffraction (EBSD) analysis.

[0076] 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.

[0077]

[Table 3]

Specimen No.	Steel type	Microstructure (area %)			Surface hardness (HB)	Impact toughness (J, @-40°C)
		TM	F or B	R-γ		
1	A	96	-	4	512	29
2	A	98	-	2	523	22
3	A	96	-	4	509	25
4	B	98	-	2	317	56
5	B	97	-	3	339	47
6	C	96	-	4	425	45

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(continued)

Specimen No.	Steel type	Microstructure (area %)			Surface hardness (HB)	Impact toughness (J, @-40°C)
		TM	F or B	R-γ		
7	C	99	-	1	464	19
8	C	95	-	5	406	58
9	D	54	B: 46	0	312	93
10	D	97	-	3	419	44
11	D	97	-	3	422	40
12	E	94	-	6	387	53
13	E	0	B: 81, F: 19	0	296	107
14	E	97	-	3	400	41
15	E	96	-	4	395	47
16	F	95	-	5	351	52

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

[0078] As shown in Tables 1 to 3, it can be seen that specimens satisfying both the alloy compositions and the process conditions of the present disclosure have a surface hardness of 360 to 440 HB and impact absorption energy of 27J 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 360 to 440 HB or impact absorption energy of 27 J or more at -40°C at the same time.

[0079] 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: 0.18 to 0.25% 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]

$$(A-200) / 100 \leq 2.0$$

in the Relational Expression 1, A refers to a value calculated by the following Relational Expression 2,

[Relational Expression 2]

$$A = 539 - 423*[C] - 30.4*[Mn] - 17.7*[Ni] - 12.1*[Cr] - 7.5*[Mo]$$

in the Relational Expression 2, [C], [Mn], [Ni], [Cr], and [Mo] refer to contents (weight %) of carbon (C), manganese

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(Mn), nickel (Ni), chromium (Cr), and molybdenum (Mo) included in the steel sheet, 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).
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.
4. The high-hardness armored steel having excellent low-temperature impact toughness of claim 1, wherein the armored steel has a surface hardness of 360 to 440 HB and an impact absorption energy of 27 J or more at -40°C.
5. The high-hardness armored steel having excellent low-temperature impact toughness of claim 1, wherein the armored steel has a thickness greater than 40 mm.
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: 0.18 to 0.25% 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];

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; and

cooling the hot-rolled steel sheet to a cooling end temperature of 50 to 250 °C at a cooling rate of 3 °C/s or more and then air cooling the same to room temperature,

[Relational Expression 1]

$$(A-200) / 100 \leq 2.0$$

in the Relational Expression 1, A refers to a value calculated by the following Relational Expression 2,

[Relational Expression 2]

$$A = 539 - 423*[C] - 30.4*[Mn] - 17.7*[Ni] - 12.1*[Cr] - 7.5*[Mo]$$

in the Relational Expression 2, [C], [Mn], [Ni], [Cr], and [Mo] refer to contents (weight %) of carbon (C), manganese (Mn), nickel (Ni), chromium (Cr), and molybdenum (Mo) included in the steel slab, and 0 is substituted when the corresponding element is not intentionally added.

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).
8. The manufacturing method for a high-hardness armored steel having excellent low-temperature impact toughness of claim 6, wherein the hot-rolled steel sheet has a thickness greater than 40 mm.

INTERNATIONAL SEARCH REPORT

International application No.
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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		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C22C 38/58(2006.01); B21B 1/26(2006.01); C21D 6/00(2006.01); C21D 8/02(2006.01); C21D 9/46(2006.01); C22C 38/00(2006.01); C22C 38/04(2006.01); C22C 38/14(2006.01); C22C 38/60(2006.01)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models: IPC as above Japanese utility models and applications for utility models: IPC as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS (KIPO internal) & keywords: 템퍼드 마르텐사이트(tempered martensite), 오스테나이트(austenite), 냉각(cooling), 템퍼링(tempering), 니켈(Ni), 크롬(Cr), 몰리브덴(Mo), 니오븀(Nb), 보론(B), 칼슘(Ca)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2010-0116608 A (JFE STEEL CORPORATION) 01 November 2010 (2010-11-01) See paragraphs [0105] and [0115] and claims 1-4 and 8.	1-8
X	WO 2020-170681 A1 (NIPPON STEEL CORPORATION) 27 August 2020 (2020-08-27) See paragraph [0046] and claims 1, 4 and 7.	1-8
X	KR 10-1766567 B1 (NIPPON STEEL & SUMITOMO METAL CORPORATION) 08 August 2017 (2017-08-08) See paragraphs [0061] and [0071] and claim 1.	1-5
X	KR 10-2014-0074981 A (JFE STEEL CORPORATION) 18 June 2014 (2014-06-18) See claims 1 and 3-5.	1-5
A	JP 08-295990 A (CREUSOT LOIRE IND.) 12 November 1996 (1996-11-12) See paragraph [0013] and claim 1.	1-8
<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 "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
Date of the actual completion of the international search 31 March 2022		Date of mailing of the international search report 31 March 2022
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208 Facsimile No. +82-42-481-8578		Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2021/015870

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10
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20
25
30
35
40
45
50
55

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
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
WO 2020-170681 A1	27 August 2020	CN 113383095 A	10 September 2021
		EP 3929315 A1	29 December 2021
		JP WO2020-170681 A1	27 August 2020
		KR 10-2021-0110356 A	07 September 2021
KR 10-1766567 B1	08 August 2017	BR 112015021149 A2	18 July 2017
		BR 112015021149 B1	10 March 2020
		CN 105143488 A	09 December 2015
		CN 105143488 B	17 May 2017
		EP 3000905 A1	30 March 2016
		EP 3000905 B1	30 October 2019
		ES 2759051 T3	07 May 2020
		JP 6048580 B2	21 December 2016
		JP WO2014-188966 A1	23 February 2017
		KR 10-2015-0114540 A	12 October 2015
		MX 2015011027 A	22 October 2015
		PL 3000905 T3	30 April 2020
		TW 201502287 A	16 January 2015
		TW 1510649 B	01 December 2015
		US 10023929 B2	17 July 2018
US 2015-0376730 A1	31 December 2015		
WO 2014-188966 A1	27 November 2014		
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		
JP 08-295990 A	12 November 1996	AT 187207 T	15 December 1999
		AU 5064896 A	07 November 1996

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No. PCT/KR2021/015870

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Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
		AU 692377 B2	04 June 1998
		BR 9602054 A	13 October 1999
		DE 69605350 T2	24 August 2000
		DE 69605350 T3	27 July 2006
		EP 0739993 A1	30 October 1996
		EP 0739993 B1	01 December 1999
		EP 0739993 B2	23 November 2005
		EP 0739993 B8	08 March 2006
		ES 2141446 T3	16 March 2000
		ES 2141446 T5	01 June 2006
		FR 2733516 A1	31 October 1996
		FR 2733516 B1	30 May 1997
		JP 08-295990 A	12 November 1996
		JP 4058562 B2	12 March 2008
		KR 10-0204545 B1	15 June 1999
		KR 10-1996-0037857 A	19 November 1996
		US 5714116 A	03 February 1998
		ZA 963295 B	06 November 1996

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- KR 1020180043788 [0005]