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(54) **HIGH-TENSILE STRENGTH STEEL AND MANUFACTURING METHOD THEREOF**

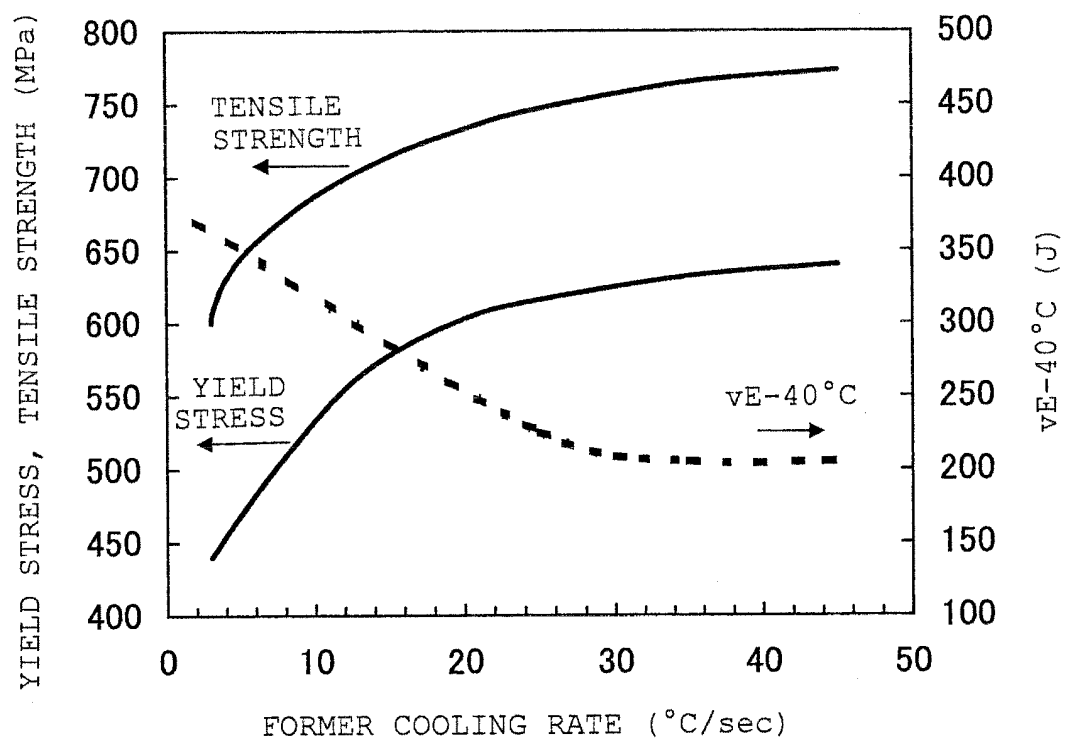
(57) Proposed are a high-tensile strength steel that is excellent in strength and toughness of the base material and also excellent in toughness of the weld heated zone, even if the steel has a large thick, and a method of advantageously manufacturing the steel. Specifically, the high-tensile strength steel has a component composition including, in mass%, C: 0.03 to 0.10%, Si: 0.30% or less, Mn: 1.60 to 2.30%, P: 0.015% or less, S: 0.005% or less, Al: 0.005 to 0.06%, Nb: 0.004 to 0.05%, Ti: 0.005 to 0.02%, N: 0.001 to 0.005%, Ca: 0.0005 to 0.003%, and the balance of Fe and inevitable impurities so that Ca, S, and O satisfy the following expression (1):

$$0 < (Ca - (0.18 + 130 \times Ca) \times O) / 1.25 / S < 1 \quad (1)$$

wherein, Ca, S, and O represent the respective contents (mass%) of the elements.

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FIG. 1



Description

Technical Field

[0001] The present invention relates to a high-tensile strength steel that is used in ships, marine structures, line pipes, pressure vessels, and so on and relates to a method of manufacturing the steel. Specifically, the present invention relates to a high-tensile strength steel that has a yield stress (YS) of 460 MPa or more and is not only excellent in strength and toughness of base material but also excellent in weld zone toughness (crack tip opening displacement (CTOD) properties) and relates to a method of manufacturing the steel.

Background Art

[0002] Steels used in ships, marine structures, and so on are usually formed into structures having desired shapes by welding joints. Therefore, from the viewpoint of ensuring safety of structures and so on, it is required not only that the base material itself is excellent in strength and toughness but also that the weld zone (weld metal and heat-affected zone) of a weld joint is excellent in toughness.

[0003] As evaluation standards of toughness of steels, conventionally, absorbed energy in a Charpy impact test has been mainly used. However, recently, in order to increase the reliability, a crack tip opening displacement test (hereinafter abbreviated to "CTOD test") is often used. In this test, a test piece having a fatigue precrack in a toughness-evaluating portion is subjected to three-point bending, and the value of opening displacement (value of plastic deformation) of the bottom of crack immediately before breaking is measured to evaluate occurrence resistance of brittle fracture.

[0004] Generally, steels having large thicknesses, as in those used in the above-mentioned purposes, are usually subjected to multi-pass welding. In such welding, since the heat-affected zone experiences a complicated thermal history, there are problems that local embrittlement tends to occur and that, in particular, the bond zone (boundary between a weld metal and a base material) and the inter-critically reheated zone (region that is coarse-grained in the first cycle of welding and is heated into a two-phase region of α and γ in the second cycle) are largely decreased in toughness. This is because that since the bond zone is exposed to a high temperature just below the melting point, austenite grains are coarsened and are, by subsequent cooling, transformed into a brittle upper bainitic structure. In addition, in the bond zone, embrittlement structures such as a Widmannstätten structure and island martensite (Martensite-Austenite constituent) are formed, and thereby the toughness is further deteriorated.

[0005] As a countermeasure against the problems mentioned above, for example, a technique of finely dispersing TiN in a steel in order to prevent the coarsening of austenite grains or to use as nuclei of ferrite transformation has been put into practical use. Furthermore, Japanese Examined Patent Application Publication No. 03-053367 and Japanese Unexamined Patent Application Publication No. 60-184663 disclose techniques of dispersing fine particles in a steel by combined addition of a rare-earth metal (REM) and Ti for preventing the growth of austenite grains and improving the toughness of the weld zone. In addition to the above, proposed are a technique of dispersing an oxide of Ti, a technique of combining ferrite nucleus-forming ability of BN with oxide dispersion, and also a technique of increasing toughness by controlling the shape of sulfide by adding Ca or REM.

[0006] The inter-critically reheated zone, that is, a region that is exposed to a high temperature just below the melting point in the first welding and is reheated to a two-phase region of ferrite and austenite in the subsequent welding is most embrittled. This is because that carbon is enriched in the austenite region by reheating to a two-phase region, and this allows the formation of a brittle bainitic structure containing island martensite during cooling, resulting in a decrease in toughness. Accordingly, as a countermeasure against the above, a technique of preventing the formation of island martensite by reducing the amounts of C and Si and also ensuring the base material strength by adding Cu is disclosed (for example, Japanese Unexamined Patent Application Publication No. 05-186823).

[0007] Furthermore, Japanese Unexamined Patent Application Publication No. 2007-231312 discloses, as a method for preventing the formation of an embrittlement structure due to reheating in welding, a technique of increasing the toughness of the welded heat-affected zone (CTOD properties) by adding Ni, while adjusting the amount of Ca added for controlling the shape of sulfide within an appropriate range.

[0008] However, though the problem of a reduction in toughness of the heat-affected zone is improved to a certain extent by the above-described conventional techniques, some problems to be solved are left. For example, in the technique using TiN, the effect is lost in the bond zone that is heated to a temperature range at which TiN is dissolved, and also a significant decrease in toughness may occur by embrittlement of the base structure due to a Ti solid solution and a N solid solution. The technique of using an oxide of Ti has a problem that the fine dispersion of the oxide cannot be sufficiently uniform. Furthermore, recently, along with an increase in size of ships and marine structures, steels used therein are required to have higher strengths and larger thicknesses. In order to correspond to these requirements, on the contrary to the technique of Japanese Unexamined Patent Application Publication No. 05-186823, it is effective to add large amounts of alloy elements. However, the addition of large amounts of alloy elements causes the formation of

an embrittlement structure and thus decrease in toughness of the welded heat-affected zone. Furthermore, in the technique disclosed in Japanese Unexamined Patent Application Publication No. 2007-231312, the addition of Ni, which is effective for increasing the toughness of a matrix (effect of a Ni solid solution), is indispensable as a measure for increasing the strength and the thickness, which causes a problem of an increase in cost.

[0009] Accordingly, it is an object of the present invention to solve the problems of the conventional techniques and thereby to propose a high-tensile strength steel that is not only excellent in strength and toughness of the base material but also excellent in toughness of the welded heat-affected zone, even in thick high-strength steel plate that are necessarily increased in the amounts of alloy elements, and to propose a method of properly manufacturing the steel.

Disclosure of Invention

[0010] The present invention provides a high-tensile strength steel having a component composition including C: 0.03 to 0.10 mass%, Si: 0.30 mass% or less, Mn: 1.60 to 2.30 mass%,

[0011] P: 0.015 mass% or less, S: 0.005 mass% or less, Al: 0.005 to 0.06 mass%, Nb: 0.004 to 0.05 mass%, Ti: 0.005 to 0.02 mass%, N: 0.001 to 0.005 mass%, Ca: 0.0005 to 0.003 mass%, and the balance of Fe and inevitable impurities so that Ca, S, and O satisfy the following expression (1):

$$0 < (Ca - (0.18 + 130 \times Ca) \times O) / 1.25 / S < 1 \quad (1)$$

wherein, Ca, S, and O represent the respective contents (mass%) of the elements.

[0012] The high-tensile strength steel of the present invention can further include one or more selected from the group consisting of B: 0.0003 to 0.0025 mass%, V: 0.2 mass% or less, Cu: 1 mass% or less, Ni: 2 mass% or less, Cr: 0.7 mass% or less, and Mo: 0.7 mass% or less, in addition to the above-mentioned component composition.

[0013] Furthermore, the present invention proposes a method of manufacturing the high-tensile strength steel. The method includes heating a steel slab having a component composition including C: 0.03 to 0.10 mass%, Si: 0.30 mass% or less, Mn: 1.60 to 2.30 mass%, P: 0.015 mass% or less, S: 0.005 mass% or less, Al: 0.005 to 0.06 mass%, Nb: 0.004 to 0.05 mass%, Ti: 0.005 to 0.02 mass%, N: 0.001 to 0.005 mass%, Ca: 0.0005 to 0.003 mass%, and the balance of Fe and inevitable impurities so that Ca, S, and O satisfy the following expression (1):

$$0 < (Ca - (0.18 + 130 \times Ca) \times O) / 1.25 / S < 1 \quad (1)$$

wherein, Ca, S, and O represent the respective contents (mass%) of the elements, to 1050 to 1200 °C; hot-rolling the slab in such a manner that the cumulative rolling reduction in the temperature range of 950°C or higher is 30% or more and the cumulative rolling reduction in the temperature range of lower than 950°C is 30 to 70%; then performing former cooling for cooling the steel from the finishing rolling temperature to a cooling termination temperature of 600 to 450°C at a cooling rate of 5 to 45°C/sec, more preferably, 5 to 20°C/sec, and latter cooling for cooling the steel from the former cooling termination temperature to a cooling termination temperature of 450°C or lower at a cooling rate of 1°C/sec or more and less than 5°C/sec.

[0014] Furthermore, in the manufacturing method of the present invention, the slab can further include one or more selected from the group consisting of B: 0.0003 to 0.0025 mass%, V: 0.2 mass% or less, Cu: 1 mass% or less, Ni: 2 mass% or less, Cr: 0.7 mass% or less, and Mo: 0.7 mass% or less, in addition to the above-mentioned component composition.

[0015] Furthermore, the manufacturing method of the present invention can subject the steel after the latter cooling to tempering at 450 to 650°C.

[0016] According to the present invention, a high-strength steel where the base material has a high strength with a yield stress of 460 MPa or more and is excellent in toughness and also the heat-affected zone after welding is excellent in toughness (CTOD properties) can be manufactured inexpensively. Therefore, the invention highly contributes to an increase in size of ships, marine structures, and so on.

Brief Description of Drawings

[0017]

[Fig. 1] Fig. 1 is a graph showing an effect of former cooling rate (cooling rate from the finishing rolling temperature

to a cooling termination temperature of 600 to 450°C) after hot-rolling on base material properties.

Best Modes for Carrying Out the Invention

[0018] The present inventors have intensively investigated methods that can increase the strength and toughness of the base material of a thick high-tensile strength steel and also improve the toughness of the welded heat-affected zone. As a result, it has been found that since a decrease in toughness of a welded heat-affected zone is caused by formation of an embrittlement structure, in order to increase the toughness of the welded heat-affected zone, prevention of coarsening of austenite grains in a region that is heated to a high temperature in welding and also uniform and fine dispersion of transformation nuclei for accelerating ferrite transformation in cooling after the welding are effective.

[0019] Accordingly, the present inventors have further investigated methods for preventing the formation of embrittlement structures and, as a result, have found the facts that adjustment of the amount of Ca added for controlling the shape of sulfide to an appropriate range is effective and that addition of Mn is effective for increasing the toughness (CTOD properties) of a welded heat-affected zone.

[0020] Furthermore, effects of rolling conditions on the strength and toughness of base materials have been investigated, and, as a result, it has been found that a steel plate of which main structure is an acicular ferrite structure can be obtained by conducting cooling after rolling by two-stage cooling consisting of former cooling at a high cooling rate and latter cooling at a low cooling rate and appropriately controlling both the cooling rates, and thereby a high-tensile strength steel excellent in strength and toughness of the base material can be manufactured. Furthermore, it has been found that, in order to further increase the strength and toughness of the base material, it is important to effectively use Nb, which is highly effective for forming a non-recrystallization zone in a low temperature range of austenite. Thus, the present invention has been finally accomplished by appropriately combining these techniques.

[0021] The basic technological concept of the present invention will be described.

[0022] A first aspect of the present invention is that, in order to increase the toughness of the welded heat-affected zone, crystallization of a compound (CaS) of Ca added for controlling the shape of sulfide is effectively utilized. Since the CaS is crystallized at a lower temperature compared to oxide, its uniform fine dispersion is possible. In addition, since a S solid solution is ensured even after crystallization of CaS by controlling the CaS addition amount and the dissolved oxygen amount in a molten steel when it is added to an appropriate ranges, MnS is precipitated on the surface of CaS to form complex sulfide. It is known that MnS has potential for ferrite nucleus, and a Mn depleted zone is formed in the periphery of precipitated MnS. Therefore, ferrite transformation is further accelerated. This effect of the Mn depleted zone can be further effectively exhibited by increasing the amount of Mn added to the steel. In addition, ferrite transformation nuclei such as TiN, BN, or AlN are precipitated on the precipitated MnS, which accelerates further ferrite transformation.

[0023] In addition, an increase in the Mn addition amount can effectively increase the base material strength in such a manner that island martensite, which is an embrittlement structure, is not formed as far as possible in the welded heat-affected zone. This is because that the island martensite formed during the cooling after welding tends to be decomposed to cementite by increasing the Mn addition amount thereby to reduce the island martensite in the heat-affected zone structure. As a result of these effects, the toughness of the welded heat-affected zone can be ensured without requiring addition of Ni.

[0024] According to the technique described above, ferrite transformation nuclei that are not dissolved even at high temperature can be finely dispersed thereby to reduce the welded heat-affected zone structure in size, and also high toughness can be obtained by preventing the formation of island martensite (M-A constituent) as far as possible. In addition, since the first welded heat-affected zone structure is reduced in size, even in the region reheated into two-phase region by a heat cycle in multilayer welding, the toughness of the untransformed region is increased. Furthermore, since the austenite grains that are retransformed are also reduced in size, the degree of a decrease in toughness can be controlled to be small.

[0025] A second aspect of the present invention is that the cooling after rolling of a steel is performed by two-stage cooling of former cooling and latter cooling, wherein the cooling rate of the former cooling is higher than that of the latter cooling. This point will be described on the basis of experimental results.

[0026] A steel slab including C: 0.08 mass%, Si: 0.2 mass%, and Mn: 1.8 mass% as basic components was heated to 1150°C and then hot-rolled in such a manner that the cumulative rolling reduction in the temperature range of 950°C or higher was 40%, the cumulative rolling reduction in the temperature range of lower than 950°C was 50%, and the finishing rolling temperature was 850°C, and then former cooling for cooling the steel from the rolling completion temperature to 500°C at a cooling rate of 5 to 45°C/sec, more preferably, 5 to 20°C/sec, and latter cooling for cooling the steel to 350°C at a cooling rate of 3°C/sec were performed, followed by air cooling to give a thick steel sheet having a thickness of 10 to 50 mm. The thick steel plate was examined for tensile strength properties and toughness properties at -40°C (Charpy impact absorbed energy).

[0027] Regarding the results of the measurement, Fig. 1 shows an effect of former cooling rate on the strength and

toughness of the base material. It is confirmed that a steel excellent in strength-toughness balance such that the strength is high so as to have a yield stress of 460 MPa or more and the $vE-40^{\circ}C$ is 200 J or more can be obtained by controlling the cooling rate of the former cooling from the finishing rolling temperature to $500^{\circ}C$ to the range of 5 to $45^{\circ}C/sec$.

[0028] Furthermore, it was confirmed that the main microstructure of the steel plate thus cooled at the above-mentioned cooling rate is acicular ferrite. In general, when a high strength steel is tried to be obtained, a relatively coarse upper bainitic microstructure that contains, for example, island martensite between laths is formed, resulting in a large decrease in toughness. Accordingly, in order to achieve both high strength and high toughness, it is necessary to form a finer acicular ferrite microstructure by, for example, adjusting the rolling conditions. However, the present inventors have found the fact that a steel sheet excellent in strength-toughness balance can be obtained by performing the cooling after rolling by two steps of former cooling and latter cooling, wherein the cooling rate of the latter cooling is lower than that of the former cooling and both the cooling rates are appropriately controlled, thereby to form a structure of mainly acicular ferrite. This is because that the microstructure after transformation can become a dense acicular ferrite instead of a coarse bainitic microstructure by performing the former cooling at a higher cooling rate than that of the latter cooling to increase the transformation nucleation density. Furthermore, it has been found that the cooling rate of the latter cooling is required to be controlled in an appropriate range because that when the cooling rate is too higher than that of the former cooling, island martensite is formed to decrease the toughness of the base material and, in contrast, that when the cooling rate of the latter cooling is too low, the strength of the base material is decreased.

[0029] The present invention has been thus accomplished based on the above-described findings.

[0030] Next, the chemical composition that should be possessed by the high-tensile strength steel according to the present invention will be described.

C: 0.03 to 0.10 mass%

[0031] C is an element that most largely affects the strength of a steel and is necessary to be contained in an amount of 0.03 mass% or more for ensuring strength ($YS \geq 460$ MPa) required in structural steels. However, conversely, when the amount is too large, a decrease in toughness of the base material and cold cracking during welding are caused. Therefore, the upper limit is determined to be 0.10 mass%.

Si: 0.30 mass% or less

[0032] Si is a component that is added as a deoxidizing material and also for highly strengthening a steel. In order to obtain such effects, it is preferable that the addition amount be 0.01 mass% or more. However, when the amount is higher than 0.30 mass%, the toughness of the base material and the weld zone is reduced. Therefore, the amount has to be 0.30 mass% or less and is preferably in the range of 0.01 to 0.20 mass%.

Mn: 1.60 to 2.30 mass%

[0033] Mn is an element effective for ensuring the strength of the base material, but, in the present invention, Mn is an important element that is added for accelerating the reduction of a welded heat-affected zone structure in size and also preventing the formation of an embrittlement structure as far as possible thereby to increase the toughness of the welded heat-affected zone (CTOD properties). In order to achieve these effects, an addition amount of 1.60 mass% or more is necessary. Conversely, since an amount larger than 2.30 mass% significantly decreases the toughness of the base material and the weld zone, the amount is 2.30 mass% or less and is preferably in the range of 1.65 to 2.15 mass%.

P: 0.015 mass% or less

[0034] P is an impurity that is inevitably contained. When the amount is larger than 0.015 mass%, the toughness of the base material and the weld zone is decreased, and therefore the amount is limited to 0.015 mass% or less and preferably 0.010 mass% or less.

S: 0.005 mass% or less

[0035] S is an impurity that is inevitably contained. When the amount is larger than 0.005 mass%, the toughness of the base material and the weld zone is decreased, and therefore the amount is limited to 0.005 mass% or less and preferably 0.0035 mass% or less.

Al: 0.005 to 0.06 mass%

[0036] Al is an element to be added for deoxidizing the molten steel and is required to be contained in an amount of 0.005 mass% or more. On the other hand, an amount larger than 0.06 mass% decreases the toughness of the base material and also causes interfusion with a weld metal by dilution due to welding, which decreases the toughness. Therefore, the amount is necessarily limited to 0.06 mass% or less and preferably 0.010 to 0.055 mass%.

Nb: 0.004 to 0.05 mass%

[0037] Nb enlarges a non-recrystallization zone in a low temperature range of austenite. Therefore, the base material structure can be reduced in size and increased in toughness by conducting rolling in such a temperature range. In addition, precipitation strengthening can be achieved by conducting tempering after the rolling and cooling. Therefore, Nb is an important element from the viewpoint of strengthening the steel. In order to obtain the above-described effects, Nb is necessarily contained in an amount of 0.004 mass% or more. However, when Nb is added in an excessive amount of higher than 0.05 mass%, the toughness of the weld zone is decreased. Therefore, the upper limit is determined to be 0.05 mass%.

Ti: 0.005 to 0.02 mass%

[0038] Ti is precipitated as TiN when molten steel is solidified thereby to prevent the austenite in the weld zone from being coarsened and also acts as ferrite transformation nuclei thereby to contribute to an increase in toughness of the weld zone. In order to obtain the effects, Ti is necessarily contained in an amount of 0.005 mass% or more. When the amount is less than 0.005 mass%, the effect is small, but an amount larger than 0.02 mass% causes coarsening of TiN grains, and, thereby, the effect increasing the toughness of the base material and the weld zone cannot be obtained. Therefore, the Ti addition amount is determined to be in the range of 0.005 to 0.02 mass%.

N: 0.001 to 0.005 mass%

[0039] N is an element necessary for forming TiN that prevents the weld zone structure from being coarsened and is contained in an amount of 0.001 mass% or more. On the other hand, when the amount is larger than 0.005 mass%, the N solid solution significantly decreases the toughness of the base material and the weld zone. Therefore, the upper limit is determined to be 0.005 mass%. Incidentally, in order to form TiN in an amount sufficient for pinning to prevent the structure from being coarsened, the N amount is preferably in the range of 0.003 to 0.005 mass%.

Ca: 0.0005 to 0.003 mass%

[0040] Ca is an element that increases the toughness by fixing S. In order to realize this effect, it is necessary to be contained in an amount of at least 0.0005 mass%. However, in an amount larger than 0.003 mass%, the effect is saturated. Therefore, Ca is contained in the range of 0.0005 to 0.003 mass%.

$$0 < (Ca - (0.18 + 130 \times Ca) \times O) / 1.25 / S < 1$$

[0041] In order to finely disperse CaS serving as a ferrite transformation nucleus that is not dissolved even at high temperature, Ca, S, and O are necessarily contained so as to satisfy the following expression (1):

$$0 < (Ca - (0.18 + 130 \times Ca) \times O) / 1.25 / S < 1 \quad (1)$$

wherein, Ca, S, and O represent the respective contents (mass%) of the elements. In the expression, $(Ca - (0.18 + 130 \times Ca) \times O) / 1.25 / S$ is a value showing the ratio of atomic concentrations of Ca and S for effectively controlling the shape of sulfide and suggests the shape of the sulfide (Mochida, et al., "Tetsu to Hagane (Iron and Steel)", The Iron and Steel Institute of Japan, vol. 66 (1980), No. 3, pp. 354-362).

[0042] That is, when the value of $((Ca - (0.18 + 130 \times Ca) \times O) / 1.25 / S)$ is 0 or less, CaS is not crystallized. Therefore, since S is precipitated in a MnS form alone, fine dispersion of ferrite transformation nuclei in the welded heat-affected zone, which is the focus of the present invention, cannot be achieved. Furthermore, MnS precipitated alone is elongated

in rolling process, resulting in a decrease in toughness of the base material.

[0043] On the other hand, when the value of $((Ca - (0.18 + 130 \times Ca) \times O) / 1.25 / S)$ is 1 or more, S is completely fixed with Ca, and MnS that acts as a ferrite transformation nucleus is not precipitated on CaS. Therefore, complex sulfide cannot sufficiently act as a ferrite transformation nucleus.

[0044] Compared with the above, when Ca, S, and O satisfy the expression (1), MnS is precipitated on CaS to form complex sulfide and can effectively function as a ferrite transformation nucleus. Incidentally, the value of $((Ca - (0.18 + 130 \times Ca) \times O) / 1.25 / S)$ is preferably in the range of 0.2 to 0.8.

[0045] The high-tensile strength steel of the present invention can contain one or more selected from the group consisting of B, V, Cu, Ni, Cr, and Mo for further increasing strength and toughness, in addition to the above-described essential components.

B: 0.0003 to 0.0025 mass%

[0046] B segregates in an austenite grain boundary and thereby to prevent ferrite transformation that occurs from the grain boundary, which increases the fraction of a bainitic structure thereby to achieve an effect of strengthening the steel. Such an effect can be achieved when the addition amount is 0.0003 mass% or more. However, when the amount is larger than 0.0025 mass%, conversely, the toughness is decreased. The amount of B is more preferably in the range of 0.0005 to 0.002 mass%.

V: 0.2 mass% or less

[0047] V is an element effective for increasing the strength and toughness of the base material and is precipitated as VN, which also acts as a ferrite transformation nucleus. In order to obtain the effects, the amount to be added is preferably 0.01 mass% or more. However, when the addition amount is larger than 0.2 mass%, contrarily, a decrease in toughness is caused. Therefore, the amount to be added is preferably 0.2 mass% or less, and more preferably 0.15 mass% or less.

Cu: 1 mass% or less

[0048] Cu is an element having an effect of increasing the strength of a steel. In order to obtain the effect, it is preferably to be contained in an amount of 0.05 mass% or more. However, when the amount is larger than 1 mass%, hot brittleness causes surface defects of the steel plate. Therefore, the addition amount is preferably in the range of 1 mass% or less and more preferably 0.8 mass% or less.

Ni: 2 mass% or less

[0049] Ni is an element effective for increasing the strength of a steel and the CTOD properties of the welded heat-affected zone. In order to obtain the effects, the addition amount is preferably 0.05 mass% or more. However, since Ni is an expensive element, it is preferably to determine the upper limit to be 2.0 mass%. When the Mn addition amount is 1.6 % or more as in this application, the amount of Ni is further preferably less than 0.3% from the viewpoint of a reduction in cost.

Cr: 0.7 mass% or less

[0050] Cr is an element effective for strengthening the base material. In order to obtain the effect, the addition amount is preferably 0.05 mass% or more. However, since a large amount of Cr, adversely affects the toughness, the upper limit is preferably determined to be 0.7 mass%, more preferably, 0.5 mass% or less.

Mo: 0.7 mass% or less

[0051] Mo is an element effective for strengthening the base material as in Cr. In order to obtain the effect, the addition amount is preferably 0.05 mass% or more. However, since a large amount of Mo, adversely affects the toughness, the upper limit is preferably determined to be 0.7 mass%, more preferably, 0.5 mass% or less.

[0052] Next, the high-tensile strength steel structure of the present invention will be described.

[0053] Microstructure of the high-tensile strength steel of the present invention is mainly composed of an acicular ferrite, and its area ratio is preferably 60% or more and more preferably 70% or more. If the area ratio of the acicular ferrite is less than 60% and a coarse upper bainite is increased, the toughness is decreased. Incidentally, the upper limit of the area ratio is not particularly limited. The acicular ferrite microstructure of the high-tensile steel of the present invention is bainitic ferrite with a high dislocation density having morphology of fine needle-like or lath-like shape and is

different from a polygonal ferrite or coarse upper bainite.

[0054] Next, the method of manufacturing the high-tensile strength steel of the present invention will be described.

[0055] It is preferable that the high-tensile strength steel of the present invention be manufactured as a high-tensile strength steel having a large thickness by ingoting a molten steel having the above-described component composition of the present invention by a common method using a converter furnace, an electric furnace, a vacuum melting furnace, or the like, making a steel material such as a slab by a common step such as continuous-casting or ingot-casting-blooming, and then hot-rolling the steel material. On this occasion, it is necessary to adjust the heating temperature of the steel material to the range of 1050 to 1200°C in advance the hot-rolling. A heating temperature of not lower than 1050°C is necessary for certainly pressure-bonding cast defects, which are present in the as-cast steel material, by the hot-rolling. However, since heating to a temperature higher than 1200°C coarsens TiN that has been precipitated during solidification and decreases the toughness of the base material and the weld zone, the heating temperature is necessarily regulated to 1200°C or less.

[0056] Then, the steel material heated to the above-mentioned temperature is subjected to hot-rolling in such a manner that the cumulative rolling reduction in the temperature range of 950°C or higher is 30% or more and the cumulative rolling reduction in the temperature range of lower than 950°C is 30 to 70% to obtain a high-tensile strength steel having a set thickness. The hot-rolling is performed at a cumulative rolling reduction of 30% in the temperature range of 950°C or higher because that the austenite grains are recrystallized to make the microstructure fine by regulating the cumulative rolling reduction in this temperature range to 30% or more, but the abnormally coarsened grains produced in the heating are left when the cumulative rolling reduction is lower than 30% to adversely affect the toughness of the base material.

[0057] In addition, the hot-rolling is performed at a cumulative rolling reduction of 30 to 70% in the temperature range of lower than 950°C because that since the austenite grains rolled in this temperature range are not sufficiently recrystallized thereby to hold the elongated shape after the rolling, a large amount of defects such as deformation bands are introduced, and thereby the internal strain becomes high. In addition, the cumulative internal energy works as a driving force for the subsequent ferrite transformation to accelerate the ferrite transformation. However, when the cumulative rolling reduction is lower than 30%, the cumulative internal energy is not sufficient. Therefore, the ferrite transformation hardly occurs thereby to decrease the toughness of the base material. On the other hand, a cumulative rolling reduction of higher than 70% accelerates the formation of polygonal ferrite and prevents the formation of acicular ferrite, and, therefore, high strength and high toughness cannot be simultaneously achieved.

[0058] The subsequent cooling after the completion of the hot-rolling is performed by former cooling and latter cooling, and the cooling rate of the former cooling is relatively higher than that of the latter cooling. That is, it is necessary that the former cooling is performed from the finishing rolling temperature to a cooling termination temperature of 600 to 450°C, preferably, from the finishing rolling temperature to a cooling termination temperature of 580 to 480°C at a cooling rate of 5 to 45°C/sec, preferably 5 to 20°C/sec, and further preferably 6 to 16°C/sec, and then the latter cooling is performed from the former cooling termination temperature to the latter cooling termination temperature of 450°C or less, preferably, from the former cooling termination temperature to the cooling termination temperature of 400 to 250°C at a cooling rate of 1°C/sec or more and less than 5°C/sec, more preferably, 2 to 4.5°C/sec.

[0059] When the cooling termination temperature of the former cooling is higher than the above-mentioned temperature range, the strength is hardly increased. Conversely, when the temperature is lower than the above-mentioned temperature range, the toughness is deteriorated. In addition, when the former cooling rate is lower than the lower limit of the above-mentioned range, the dominant microstructure is polygonal ferrite, and therefore an increase in the strength is not obtained. Conversely, when the rate is higher than the upper limit of the above-mentioned range, the toughness is decreased. Furthermore, when the cooling termination temperature of the latter cooling is higher than the upper limit of the above-mentioned temperature range, the increase of the strength is insufficient. In addition, the latter cooling rate is lower than the lower limit of the above-mentioned range, the base material suffers from a shortage of strength. Conversely, when the rate is higher than the upper limit of the above-mentioned range, the toughness of the base material is decreased. In addition, when the latter cooling rate is too higher than that of the former cooling rate, island martensite is formed thereby to decrease the toughness of the base material.

[0060] Incidentally, in the present invention, in order to reduce the residual internal stress, the steel material after the cooling may be subjected to tempering in the temperature range of 450 to 650°C. When the temperature of the tempering is lower than 450°C, the effect removing the residual stress is small. On the other hand, when the temperature is higher than 650°C, various types of carbonitrides are precipitated thereby to cause precipitation strengthening and decrease the toughness, which is undesirable.

[0061] As described above, in the method of manufacturing a high-tensile strength steel of the present invention, it is important to appropriately control the cumulative rolling reduction according to the rolling temperature in the hot-rolling and to appropriately control the two-stage cooling conditions after the completion of the rolling. In particular, by setting the cooling rate of the former cooling to be larger than that of the latter cooling, the main structure of the base material becomes acicular ferrite, and thereby a steel material excellent in strength-toughness balance can be obtained.

[0062] Furthermore, in the present invention, a high strength steel in which the base material has a high strength of

a yield stress of 550 MPa or more and is excellent in toughness and also the heat-affected zone after welding is excellent in toughness (CTOD properties) can be inexpensively manufactured by controlling the amount of N in the chemical components to be higher than 0.0030%, the cooling rate in the former cooling to higher than 20°C/sec and not higher than 45°C/sec, the cooling termination temperature of the former cooling to 450°C or higher and lower than 500°C.

Example

[0063] Thick steel sheets having thicknesses of 25 to 80 mm were manufactured using steel slabs Nos. 1 to 31 having component compositions shown in Tables 1-1 and 1-2 as materials by performing hot-rolling, former cooling, and latter cooling under conditions shown in Tables 2-1 and 2-2. Incidentally, the temperatures shown in Tables 2-1 and 2-2 are each that of one-fourth thickness portion calculated from the steel plate surface temperature measured with a radiation thermometer. Samples prepared from the thus obtained thick steel plates were subjected to a tensile test and a Charpy impact test. In the tensile test, JIS #4 tensile test pieces were sampled from one-fourth thickness portions of the thick steel plates in such a manner that the longitudinal axis direction of each test piece was parallel to the rolling direction, and the yield stress (YS) and tensile strength (TS) of the test pieces were measured. In the Charpy impact test, JIS #4 impact test pieces were sampled from one-fourth thickness portions of the thick steel plates parallel to transverse direction, and the absorbed energy at -40°C (vE-40°C) was measured. A test piece satisfying all of $YS \geq 460$ MPa, $TS \geq 570$ MPa, and $vE-40^\circ C \geq 200$ J was determined to have satisfactory base material properties.

[0064] Furthermore, test plates prepared from the thick steel plates that satisfy all the above-mentioned criteria of YS, TS, and vE-40°C as the base material properties were each provided with a single bevel groove (bevel angle: 30°). The test plate was subjected to CO₂ arc welding at a heat input amount of 25 kJ/cm to produce a weld joint. A CTOD test piece provided with a notch in the straight bond zone of the single bevel groove was prepared from each weld joint and subjected to a CTOD test at -10°C. Incidentally, the preparation of the CTOD test pieces and the test conditions were in accordance with British standard BS 7448. In addition, JIS #4 impact test pieces having notches in the bond zones were prepared and were each subjected to the Charpy impact test at -40°C and measured for the absorbed energy (vE-40°C).

[0065] The test results are also shown in Tables 2-1 and 2-2. These results confirm that in the steel plates of the present invention, the base material has a yield stress (YS) of 460 MPa or more and a Charpy absorbed energy (vE-40°C) of 200 J or more and is thus excellent in both the strength and the toughness, and also the welded heat-affected zone is excellent in toughness such that the bond zone of a CO₂ arc welding joint has a vE-40°C of 200 J or more and a CTOD value of 0.10 mm or more. On the other hand, in Comparative Examples that are out of the scope of the present invention, the resulting steel plates are unsatisfactory in any one or more of the above-mentioned characteristics.

[0066] Furthermore, the steel plates of Nos. 11 to 17, which are steel plates according to the present invention and contain N in amounts of larger than 0.0030 mass%, are excellent such that all the CTOD values of weld zones are 0.45 mm or more due to the pinning effect of TiN.

[0067] Furthermore, in both the steel plates of Nos. 15 and 16, which are steel plates of the present invention and contain N in amounts of larger than 0.0030 mass% and of which manufacturing conditions are that the cooling rate of the former cooling after hot-rolling is higher than 20°C/sec and not higher than 45°C/sec and the former cooling termination temperature is 450°C or higher and lower than 500°C, the base materials have high strength such that the yield stresses are 550 MPa or more.

Industrial Applicability

[0068] The high-tensile strength steels of the present invention can be properly used not only in ships, marine structures, line pipes, and pressure vessels but also in steel structures that are assembled by welding in the fields of constructions, civil works, and so on.

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No.	Chemical Component (mass%)																			Notes
	C	Si	Mn	P	S	Al	Nb	Ti	N	Ca	O	B	V	Cu	Ni	Cr	Mo	Ceq *1	ACR *2	
1	0.056	0.10	2.05	0.005	0.0018	0.026	0.030	0.01	0.001	0.0030	0.0035	-	-	0.22	0.23	-	-	0.428	0.447	Example
2	0.055	0.08	2.15	0.009	0.0015	0.044	0.029	0.01	0.0038	0.0024	0.0017	-	-	-	-	0.11	-	0.435	0.834	Example
3	0.076	0.13	2.02	0.010	0.0021	0.027	0.022	0.014	0.0028	0.0014	0.0024	-	-	-	-	-	0.20	0.453	0.202	Example
4	0.077	0.08	1.99	0.009	0.0034	0.050	0.025	0.011	0.0047	0.0023	0.0028	-	-	0.34	0.19	-	-	0.444	0.226	Example
5	0.063	0.18	2.12	0.005	0.0016	0.047	0.021	0.014	0.0019	0.0019	0.0016	-	-	-	-	0.21	-	0.458	0.608	Example
6	0.052	0.06	2.14	0.004	0.0026	0.016	0.034	0.018	0.0019	0.0011	0.0012	0.0019	-	-	-	-	-	0.409	0.219	Example
7	0.085	0.16	2.14	0.008	0.0019	0.030	0.033	0.017	0.0024	0.0013	0.0022	-	0.016	-	-	-	0.12	0.469	0.224	Example
8	0.036	0.19	1.78	0.005	0.0026	0.017	0.019	0.015	0.0031	0.0011	0.0012	-	0.022	-	-	0.32	0.28	0.457	0.219	Example
9	0.053	0.20	1.66	0.008	0.0028	0.029	0.037	0.015	0.0033	0.0030	0.0032	-	-	-	-	0.29	0.17	0.422	0.336	Example
10	0.066	0.19	2.11	0.006	0.0011	0.024	0.039	0.016	0.0022	0.0008	0.0012	-	-	-	-	-	-	0.418	0.334	Example
11	0.048	0.05	1.88	0.007	0.0026	0.033	0.008	0.012	0.0037	0.0022	0.0018	-	-	0.15	0.18	-	-	0.383	0.419	Example
12	0.062	0.03	1.75	0.009	0.0035	0.028	0.026	0.014	0.0048	0.001	0.0021	-	-	-	-	0.20	0.10	0.414	0.096	Example
13	0.071	0.16	2.12	0.005	0.0015	0.043	0.016	0.008	0.0043	0.0008	0.0028	-	-	-	-	-	-	0.424	0.003	Example
14	0.055	0.12	2.06	0.012	0.0019	0.035	0.012	0.016	0.0045	0.0016	0.0024	0.0011	-	-	-	-	-	0.398	0.282	Example
15	0.050	0.08	1.98	0.011	0.0031	0.038	0.015	0.010	0.0034	0.0022	0.0015	-	-	0.33	0.75	-	-	0.452	0.387	Example
*1: Ceq=C+Mn/6+(Cr+Mo+V)/5+-(Cu+Ni)/15 *2: ACR=(Ca-(0.18+18+130×Ca)×O)/1.25/S In expressions *1 and *2, the element symbols represent the respective contents (mass%) of the elements.																				

Table 1-2

No.	Chemical Component (mass%)																			Notes
	C	Si	Mn	P	S	Al	Nb	Ti	N	Ca	O	B	V	Cu	Ni	Cr	Mo	Ceq *1	ACR *2	
16	0.015	0.18	1.72	0.006	0.0034	0.035	0.038	0.009	0.0027	0.0015	0.0010	-	-	-	-	-	0.19	0.340	0.265	Comparative Example
17	<u>0.130</u>	0.13	2.07	0.007	0.0016	0.053	0.029	0.018	0.0043	0.0022	0.0015	-	-	-	-	-	-	0.475	0.751	Comparative Example
18	0.080	<u>0.42</u>	2.06	0.010	0.0029	0.048	0.043	0.014	0.0024	0.0027	0.0012	-	-	-	-	-	-	0.423	0.569	Comparative Example
19	0.064	0.09	<u>1.36</u>	0.006	0.0025	0.028	0.016	0.012	0.0049	0.0030	0.0023	-	-	-	-	0.12	0.12	0.339	0.540	Comparative Example
20	0.067	0.23	<u>2.63</u>	0.010	0.0023	0.037	0.023	0.015	0.0021	0.0020	0.0025	-	-	-	-	-	-	0.505	0.313	Comparative Example
21	0.072	0.23	2.12	<u>0.027</u>	0.0013	0.029	0.030	0.008	0.0049	0.0020	0.0030	-	0.016	-	-	-	-	0.429	0.418	Comparative Example
22	0.074	0.14	2.14	0.006	<u>0.0062</u>	0.053	0.039	0.016	0.0036	0.0021	0.0022	0.0011	-	-	-	0.11	-	0.453	0.142	Comparative Example
23	0.051	0.26	2.13	0.007	0.0025	0.050	<u>0.063</u>	0.010	0.0034	0.0016	0.0026	-	-	-	-	-	-	0.406	0.189	Comparative Example
24	0.087	0.08	2.11	0.010	0.0032	0.041	0.032	<u>0.033</u>	0.0023	0.0024	0.0033	-	-	-	-	-	-	0.439	0.194	Comparative Example
25	0.075	0.18	2.07	0.007	0.0018	0.054	0.033	0.017	<u>0.0076</u>	0.0022	0.0036	-	-	-	-	-	-	0.420	0.232	Comparative Example
26	0.089	0.12	2.09	0.011	0.0020	0.034	0.015	0.016	0.0017	0.0028	0.0017	<u>0.0047</u>	-	-	-	0.16	-	0.469	0.750	Comparative Example
27	0.034	0.16	1.88	0.005	0.0027	0.049	0.033	0.014	0.0016	0.0009	0.0013	-	-	-	-	-	<u>0.91</u>	<u>0.529</u>	0.152	Comparative Example
28	0.087	0.22	1.91	0.004	0.0036	0.046	0.038	0.008	0.0029	0.0021	0.0026	-	<u>0.220</u>	-	-	-	-	0.449	0.205	Comparative Example

(continued)

No.	Chemical Component (mass%)																			Notes
	C	Si	Mn	P	S	Al	Nb	Ti	N	Ca	O	B	V	Cu	Ni	Cr	Mo	Ceq *1	ACR *2	
29	0.041	0.08	1.66	0.009	0.0017	0.026	0.042	0.008	0.0025	0.0012	0.0020	-	-	-	-	<u>0.94</u>	-	0.506	0.248	Comparative Example
30	0.088	0.25	2.08	0.005	0.0029	0.023	0.021	0.013	0.0031	0.0011	0.0038	-	-	0.34	0.24	-	-	0.473	<u>-0.035</u>	Comparative Example
31	0.051	0.25	2.12	0.007	0.0012	0.021	0.017	0.014	0.0040	0.0028	0.0011	-	-	0.30	0.19	-	0.11	0.459	<u>1.468</u>	Comparative Example
*1: $Ceq = C + Mn/6 + (Cr + Mo + V)/5 + (Cu + Ni)/15$ *2: $ACR = (Ca - (0.18 + 130 \times O) \times O) / 1.25 / S$ In expressions *1 and *2, the element symbols represent the respective contents (mass%) of the elements.																				

Table 2-1

Steel plate No.	Steel No.	Rolling Condition					Former Cooling		Latter Cooling		Tempering Temp. (°C)	Base Material Property			Weld Zone Toughness		Notes
		Thickness (mm)	Slab heating temp. (°C)	Cumulative rolling reduction (%) at 950°C or higher	Cumulative rolling reduction (%) at lower than 950°C	Finishing temp. (°C)	Cooling rate (°C/s)	Termination temp. (°C)	Cooling rate (°C/s)	Termination temp. (°C)		YS (MPa)	TS (MPa)	vE-40°C (J)	vE-40°C (J)	CTOD-10°C (mm)	
1	1	50	1093	50	60	728	12	580	4.5	350	-	525	635	267	292	0.68	Example
2	2	50	1125	50	60	761	12	580	4.5	350	-	517	642	260	293	0.30	Example
3	3	65	1130	48	50	700	10	550	4.0	300	-	513	623	278	218	0.38	Example
4	4	65	1100	48	50	784	10	550	4.0	320	-	509	617	283	202	0.67	Example
5	5	70	1135	44	50	766	9	560	3.5	250	550	510	617	283	263	0.34	Example
6	6	70	1157	44	50	773	9	550	3.5	350	-	483	579	317	240	0.19	Example
7	7	70	1107	44	50	741	9	550	3.5	380	-	538	649	254	296	0.25	Example
8	8	80	1088	36	50	738	7	550	3.0	360	-	496	594	303	234	0.30	Example
9	9	80	1112	36	50	723	7	540	3.0	250	580	487	577	319	246	0.33	Example
10	10	80	1179	36	50	791	7	540	3.0	350	-	487	576	319	230	0.49	Example
11	11	65	1120	48.0	50	745	10	550	4.0	320	-	486	582	303	280	0.45	Example
12	12	65	1140	48.0	50	738	10	550	4.0	320	-	503	611	281	243	0.58	Example
13	13	65	1080	48.0	50	722	10	550	4.0	320	-	525	618	284	218	0.51	Example
14	14	65	1080	48.0	50	752	10	550	4.0	320	-	468	579	286	249	0.62	Example
15	14	35	1080	65.0	60	744	27	470	4.5	350	-	620	734	245	205	0.65	Example
16	14	25	1080	75.0	60	735	37	470	4.5	350	-	628	741	221	216	0.51	Example
17	15	65	1130	48.0	50	747	10	550	4.0	320	-	531	643	276	254	0.53	Example

Table 2-2

Steel plate No.	Steel No.	Rolling Condition					Former Cooling		Latter Cooling		Tempering Temp. (°C)	Base Material Property			Weld Zone Toughness		Notes
		Thickness (mm)	Slab heating temp. (°C)	Cumulative rolling reduction (%) at 950°C or higher	Cumulative rolling reduction (%) at lower than 950°C	Finishing temp. (°C)	Cooling rate (°C/s)	Termination temp. (°C)	Cooling rate (°C/S)	Termination temp. (°C)		YS (MPa)	TS (MPa)	vE-40°C (J)	vE-40°C (J)	CTOD-10°C (mm)	
18	1	50	1240	50	60	715	12	570	4.5	330	-	525	635	26	-	-	Comparative Example
19	2	65	1129	26	65	708	12	570	4.5	310	-	501	612	38	-	-	Comparative Example
20	3	65	1162	65	25	738	10	570	4.0	260	-	508	623	59	-	-	Comparative Example
21	4	65	1119	48	50	709	4	560	3.0	340	-	443	549	344	-	-	Comparative Example
22	5	70	1091	44	50	764	9	660	3.5	350	-	457	561	333	-	-	Comparative Example
23	6	50	1163	60	50	704	12	558	6.0	430	-	451	559	171	-	-	Comparative Example
24	7	70	1115	44	50	703	9	580	3.5	520	-	452	561	274	-	-	Comparative Example
25	16	50	1163	50	60	720	12	546	4.5	370	-	450	541	351	-	-	Comparative Example
26	17	50	1099	50	60	744	12	565	4.5	260	-	571	690	49	-	-	Comparative Example
27	18	50	1107	50	60	768	12	575	4.5	360	550	541	650	253	35	0.06	Comparative Example
28	19	50	1153	50	60	733	12	553	4.5	350	-	416	508	381	-	-	Comparative Example

(continued)

Steel plate No.	Steel No.	Rolling Condition					Former Cooling		Latter Cooling		Tempering Temp. (°C)	Base Material Property			Weld Zone Toughness		Notes
		Thickness (mm)	Slab heating temp. (°C)	Cumulative rolling reduction (%) at 950°C or higher	Cumulative rolling reduction (%) at lower than 950°C	Finishing temp. (°C)	Cooling rate (°C/s)	Termination temp. (°C)	Cooling rate (°C/S)	Termination temp. (°C)		YS (MPa)	TS (MPa)	vE-40°C (J)	vE-40°C (J)	CTOD-10°C (mm)	
29	<u>20</u>	50	1152	50	60	732	12	552	4.5	280	-	592	717	36	-	-	Comparative Example
30	<u>21</u>	65	1142	48	50	796	10	566	4.0	320	550	497	606	162	32	0.04	Comparative Example
31	<u>22</u>	65	1118	48	50	701	10	579	4.0	280	-	535	649	51	-	-	Comparative Example
32	<u>23</u>	65	1140	48	50	787	10	551	4.0	340	-	523	628	273	26	0.05	Comparative Example
33	<u>24</u>	65	1146	48	50	750	10	567	4.0	350	-	509	621	19	-	-	Comparative Example
34	<u>25</u>	65	1153	48	50	764	10	575	4.0	270	550	492	600	34	-	-	Comparative Example
35	<u>26</u>	65	1126	48	50	750	10	552	4.0	370	-	515	633	22	-	-	Comparative Example
36	<u>27</u>	65	1106	48	50	772	10	540	4.0	270	-	602	732	33	-	-	Comparative Example
37	<u>28</u>	80	1152	36	50	742	7	553	3.0	260	-	499	613	21	-	-	Comparative Example
38	<u>29</u>	80	1129	36	50	779	7	542	3.0	380	-	561	686	41	-	-	Comparative Example
39	<u>30</u>	80	1161	36	50	790	7	555	3.0	290	-	498	616	154	39	0.09	Comparative Example
40	<u>31</u>	80	1126	36	50	702	7	553	3.0	340	-	477	592	305	28	0.07	Comparative Example

Claims

1. A high-tensile strength steel having a component composition comprising:

C: 0.03 to 0.10 mass%, Si: 0.30 mass% or less, Mn: 1.60 to 2.30 mass%, P: 0.015 mass% or less, S: 0.005 mass% or less, Al: 0.005 to 0.06 mass%, Nb: 0.004 to 0.05 mass%, Ti: 0.005 to 0.02 mass%, N: 0.001 to 0.005 mass%, Ca: 0.0005 to 0.003 mass%, and the balance of Fe and inevitable impurities so that Ca, S, and O satisfy the following expression (1):

$$0 < (Ca - (0.18 + 130 \times Ca) \times O) / 1.25 / S < 1 \quad (1)$$

wherein, Ca, S, and O represent the respective contents (mass%) of the elements.

2. The high-tensile strength steel according to Claim 1, further comprising one or more selected from the group consisting of B: 0.0003 to 0.0025 mass%, V: 0.2 mass% or less, Cu: 1 mass% or less, Ni: 2 mass% or less, Cr: 0.7 mass% or less, and Mo: 0.7 mass% or less, in addition to the component composition.

3. A method of manufacturing a high-tensile strength steel comprising:

heating a steel slab having a component composition including C: 0.03 to 0.10 mass%, Si: 0.30 mass% or less, Mn: 1.60 to 2.30 mass%, P: 0.015 mass% or less, S: 0.005 mass% or less, Al: 0.005 to 0.06 mass%, Nb: 0.004 to 0.05 mass%, Ti: 0.005 to 0.02 mass%, N: 0.001 to 0.005 mass%, Ca: 0.0005 to 0.003 mass%, and the balance of Fe and inevitable impurities so that Ca, S, and O satisfy the following expression (1):

$$0 < (Ca - (0.18 + 130 \times Ca) \times O) / 1.25 / S < 1 \quad (1)$$

wherein, Ca, S, and O represent the respective contents (mass%) of the elements, to 1050 to 1200°C; hot-rolling the steel in such a manner that the cumulative rolling reduction in the temperature range of 950°C or higher is 30% or more and the cumulative rolling reduction in the temperature range of lower than 950°C is 30 to 70%; and then

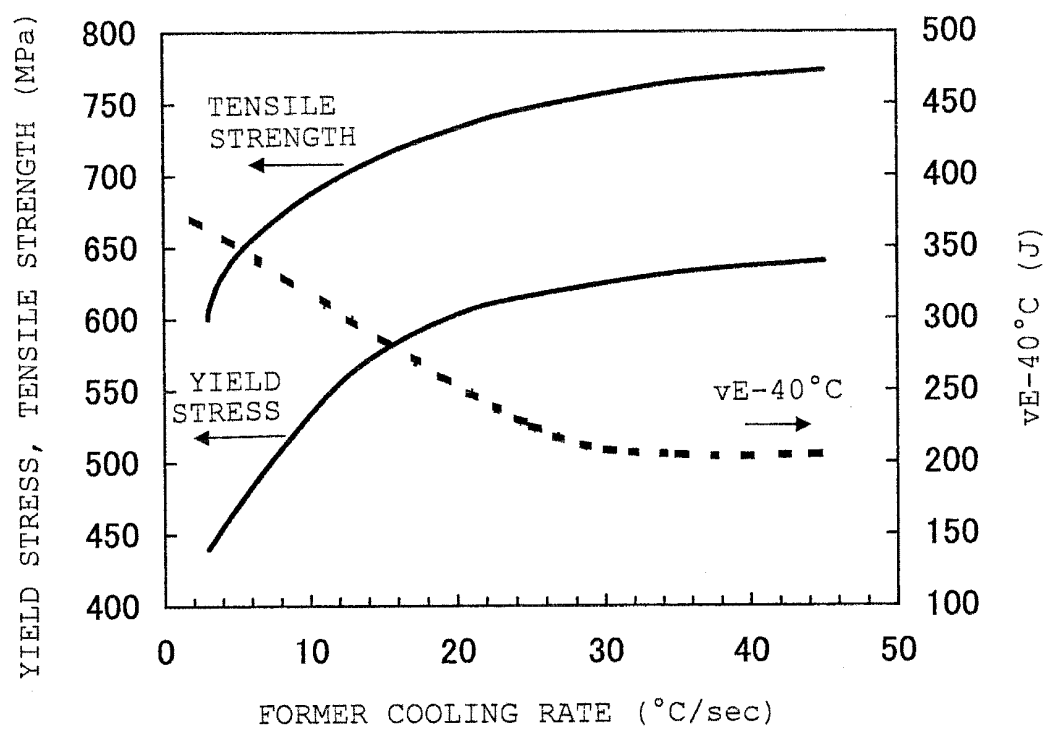
performing former cooling for cooling the steel from the hot-rolling finishing temperature to a cooling termination temperature of 600 to 450°C at a cooling rate of 5 to 45°C/sec and latter cooling for cooling the steel from the former cooling termination temperature to a cooling termination temperature of 450°C or lower at a cooling rate of 1°C/sec or more and less than 5°C/sec.

4. The method of manufacturing a high-tensile strength steel according to Claim 3, wherein the steel slab further includes one or more selected from the group consisting of B: 0.0003 to 0.0025 mass%, V: 0.2 mass% or less, Cu: 1 mass% or less, Ni: 2 mass% or less, Cr: 0.7 mass% or less, and Mo: 0.7 mass% or less, in addition to the component composition.

5. The method of manufacturing a high-tensile strength steel according to Claim 3 or 4, wherein the steel after the latter cooling is subjected to tempering at 450 to 650°C.

6. The method of manufacturing a high-tensile strength steel according to any one of Claims 3 to 5, wherein the former cooling is performed at a cooling rate of 5 to 20°C/sec.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/056906

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/14 (2006.01) i, C22C38/58 (2006.01) i, C21D8/02 (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)

C22C38/00-38/60, C21D8/00-8/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2007-231312 A (JFE Steel Corp.), 13 September, 2007 (13.09.07), Claims; Par. No. [0001] (Family: none)	2, 4-6 1, 3
Y A	JP 2002-235114 A (Kawasaki Steel Corp.), 23 August, 2002 (23.08.02), Claims; Par. No. [0001] (Family: none)	1, 3 2, 4-6
Y A	JP 2002-212670 A (Nippon Steel Corp.), 31 July, 2002 (31.07.02), Claims; Par. No. [0001] & EP 1221493 A1 & WO 2001/086013 A1	1, 3 2, 4-6

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

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
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"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)	"&" document member of the same patent family
"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	

 Date of the actual completion of the international search
 22 June, 2009 (22.06.09)

 Date of mailing of the international search report
 30 June, 2009 (30.06.09)

 Name and mailing address of the ISA/
 Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/056906

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 2002-317242 A (NKK Corp.), 31 October, 2002 (31.10.02), Claims; Par. No. [0001] (Family: none)	1, 3 2, 4-6
A	JP 2007-277681 A (Nippon Steel Corp.), 25 October, 2007 (25.10.07), Claims; Par. No. [0001] (Family: none)	1-6
A	JP 63-210235 A (Nippon Steel Corp.), 31 August, 1988 (31.08.88), Claims (Family: none)	1-6
A	JP 58-077529 A (Nippon Steel Corp.), 10 May, 1983 (10.05.83), Claims (Family: none)	1-6

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 3053367 A [0005]
- JP 60184663 A [0005]
- JP 5186823 A [0006] [0008]
- JP 2007231312 A [0007] [0008]

Non-patent literature cited in the description

- **Mochida et al.** Tetsu to Hagane (Iron and Steel). *The Iron and Steel Institute of Japan*, 1980, vol. 66 (3), 354-362 [0041]