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

(11) EP 3 901 303 A1

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

(43) Date of publication:
27.10.2021 Bulletin 2021/43

(21) Application number: **20749360.2**

(22) Date of filing: **14.01.2020**

(51) Int Cl.:
C22C 38/00 *(2006.01)* ***C21D 9/46*** *(2006.01)*
C22C 38/60 *(2006.01)*

(86) International application number:
PCT/JP2020/000783

(87) International publication number:
WO 2020/158357 (06.08.2020 Gazette 2020/32)

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

(30) Priority: **30.01.2019 JP 2019013957**

(71) Applicant: **JFE Steel Corporation**
Tokyo 100-0011 (JP)

(72) Inventors:
- **MIYAMOTO Yuka**
  Tokyo 100-0011 (JP)
- **SAKURAI Yasuhiro**
  Tokyo 100-0011 (JP)
- **ONO Yoshihiko**
  Tokyo 100-0011 (JP)

(74) Representative: **Haseltine Lake Kempner LLP**
Bürkleinstrasse 10
80538 München (DE)

(54) HIGH-CARBON HOT-ROLLED STEEL SHEET AND METHOD FOR MANUFACTURING SAME

(57) A high-carbon hot-rolled steel sheet and a method for manufacturing the high-carbon hot-rolled steel sheet are provided. The present invention is a high-carbon hot-rolled steel sheet having a particular chemical composition. The microstructure of the steel sheet includes ferrite, cementite, and pearlite that accounts for 6.5% or less of the entire microstructure by area fraction. Regarding the cementite, the proportion of the number of cementite grains having an equivalent circle diameter of 0.1 μm or less to the total number of cementite grains is 20% or less, the average cementite grain size is 2.5 μm or less, and the cementite accounts for 3.5% or more and 10.0% or less of the entire microstructure by area fraction. The average concentration of solute B in a region extending from a surface layer to a depth of 100 μm is 10 mass ppm or more. The average concentration of N present as AlN in the region extending from the surface layer to the depth of 100 μm is 70 mass ppm or less.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to a high-carbon hot-rolled steel sheet having high cold workability and high hardenability (immersion-quench hardenability and carburizing hardenability) and a method for manufacturing the high-carbon hot-rolled steel sheet.

Background Art

[0002] Currently, automotive parts such as transmissions and sheet recliners are often produced by processing hot-rolled steel sheets (high-carbon hot-rolled steel sheets) which are carbon steels for machine structural use specified in JIS G4051 and alloy steels for machine structural use into desired shapes through cold working and then subjecting the resultants to quenching treatment to ensure the desired hardness. Thus, the hot-rolled steel sheets used as materials are required to have high cold workability and high hardenability, and various steel sheets have previously been proposed.

[0003] For example, Patent Literature 1 discloses a high-carbon steel sheet for fine blanking. The steel sheet has a chemical composition containing, by wt%, C: 0.15% to 0.9%, Si: 0.4% or less, Mn: 0.3% to 1.0%, P: 0.03% or less, T. Al: 0.10% or less, and one or more of Cr: 1.2% or less, Mo: 0.3% or less, Cu: 0.3% or less, and Ni: 2.0% or less, or Ti: 0.01% to 0.05%, B: 0.0005% to 0.005%, and N: 0.01% or less and has a microstructure in which carbide grains having a spheroidization ratio of 80% or more and an average grain size of 0.4 to 1.0 μm are dispersed in ferrite.

[0004] Patent Literature 2 discloses a high-carbon steel sheet with improved workability. The steel sheet has a chemical composition containing, by mass%, C: 0.2% or more, Ti: 0.01% to 0.05%, and B: 0.0003% to 0.005% and has an average carbide grain size of 1.0 μm or less, with the proportion of carbide grains having a grain size of 0.3 μm or less being 20% or less.

[0005] Patent Literature 3 discloses a B-alloyed steel that contains, by mass%, C: 0.20% or more and 0.45% or less, Si: 0.05% or more and 0.8% or less, Mn: 0.5% or more and 2.0% or less, P: 0.001% or more and 0.04% or less, S: 0.0001% or more and 0.006% or less, Al: 0.005% or more and 0.1% or less, Ti: 0.005% or more and 0.2% or less, B: 0.001% or more and 0.01% or less, and N: 0.0001% or more and 0.01% or less, and, furthermore, one or more components selected from Cr: 0.05% or more and 0.35% or less, Ni: 0.01% or more and 1.0% or less, Cu: 0.05% or more and 0.5% or less, Mo: 0.01% or more and 1.0% or less, Nb: 0.01% or more and 0.5% or less, V: 0.01% or more and 0.5% or less, Ta: 0.01% or more and 0.5% or less, W: 0.01% or more and 0.5% or less, Sn: 0.003% or more and 0.03% or less, Sb: 0.003% or more and 0.03% or less, and As: 0.003% or more and 0.03% or less.

[0006] Patent Literature 4 discloses a steel for machine structural use with improved cold workability and improved low decarbonization properties. The steel has a chemical composition containing, by mass%, C: 0.10% to 1.2%, Si: 0.01% to 2.5%, Mn: 0.1% to 1.5%, P: 0.04% or less, S: 0.0005% to 0.05%, Al: 0.2% or less, Te: 0.0005% to 0.05%, and N: 0.0005% to 0.03%, furthermore, Sb: 0.001% to 0.05%, and, in addition, one or more of Cr: 0.2% to 2.0%, Mo: 0.1% to 1.0%, Ni: 0.3% to 1.5%, Cu: 1.0% or less, and B: 0.005% or less, and has a microstructure composed mainly of ferrite and pearlite, with the ferrite grain size number being 11 or more.

[0007] Patent Literature 5 discloses a high-carbon hot-rolled steel sheet with improved hardenability and improved workability. The steel sheet contains, by mass%, C: 0.20% to 0.40%, Si: 0.10% or less, Mn: 0.50% or less, P: 0.03% or less, S: 0.010% or less, sol. Al: 0.10% or less, N: 0.005% or less, and B: 0.0005% to 0.0050%, further contains one or more of Sb, Sn, Bi, Ge, Te, and Se in an amount of 0.002% to 0.03% in total, has a microstructure composed of ferrite and cementite, with the density of cementite in ferrite grains being 0.10/μm^2 or less, and has a hardness of 75 or less in terms of HRB and a total elongation of 38% or more.

[0008] Patent Literature 6 discloses a high-carbon hot-rolled steel sheet with improved hardenability and improved workability. The steel sheet contains, by mass%, C: 0.20% to 0.48%, Si: 0.10% or less, Mn: 0.50% or less, P: 0.03% or less, S: 0.010% or less, sol. Al: 0.10% or less, N: 0.005% or less, and B: 0.0005% to 0.0050%, further contains one or more of Sb, Sn, Bi, Ge, Te, and Se in an amount of 0.002% to 0.03% in total, has a microstructure composed of ferrite and cementite, with the density of cementite in ferrite grains being 0.10/μm^2 or less, and has a hardness of 65 or less in terms of HRB and a total elongation of 40% or more.

[0009] Patent Literature 7 discloses a high-carbon hot-rolled steel sheet that contains, by mass%, C: 0.20% to 0.40%, Si: 0.10% or less, Mn: 0.50% or less, P: 0.03% or less, S: 0.010% or less, sol. Al: 0.10% or less, N: 0.005% or less, and B: 0.0005% to 0.0050%, further contains one or more of Sb, Sn, Bi, Ge, Te, and Se in an amount of 0.002% to 0.03% in total, with the proportion of the amount of solute B to the B content being 70% or more, has a microstructure composed of ferrite and cementite, with the density of cementite in ferrite grains being 0.08/μm^2 or less, and has a hardness of 73 or less in terms of HRB and a total elongation of 39% or more.

[0010] Patent Literature 8 discloses a high-carbon hot-rolled steel sheet that has a composition containing, by mass%, C: 0.15% to 0.37%, Si: 1% or less, Mn: 2.5% or less, P: 0.1% or less, S: 0.03% or less, sol. Al: 0.10% or less, N: 0.0005%

to 0.0050%, B: 0.0010% to 0.0050%, and at least one of Sb and Sn in an amount of 0.003% to 0.10% in total and satisfying the relationship 0.50 ≤ (14[B])/(10.8[N]), with the balance being Fe and unavoidable impurities, has a microstructure composed of a ferrite phase and cementite, with the average grain size of the ferrite phase being 10 μm or less, the spheroidization ratio of cementite being 90% or more, and has a total elongation of 37% or more.

Citation List

Patent Literature

[0011]

PTL 1: Japanese Unexamined Patent ApplicationPublication No. 2009-299189
PTL 2: Japanese Unexamined Patent ApplicationPublication No. 2005-344194
PTL 3: Japanese Patent No. 4012475
PTL 4: Japanese Patent No. 4782243
PTL 5: Japanese Unexamined Patent ApplicationPublication No. 2015-017283
PTL 6: Japanese Unexamined Patent ApplicationPublication No. 2015-017284
PTL 7: International Publication No. 2015/146173
PTL 8: Japanese Patent No. 5458649

Summary of Invention

Technical Problem

[0012] The technique described in Patent Literature 1 relates to fine blanking properties, and the influence of the dispersion morphology of carbide on the fine blanking properties and hardenability is described. Specifically, Patent Literature 1 states that a steel sheet with improved fine blanking properties and improved hardenability can be obtained by controlling the average carbide grain size to 0.4 to 1.0 μm and the spheroidization ratio to 80% or more. However, Patent Literature 1 does not discuss cold workability and does not describe carburizing hardenability.

[0013] The technique described in Patent Literature 2 focuses on the fact that not only the average carbide grain size but fine carbide grains having a size of 0.3 μm or less have an influence on workability, and controls the average carbide grain size to 1.0 μm or less and also controls the proportion of carbide grains having a size of 0.3 μm or less to 20% or less. Patent Literature 2 states that this control provides a steel sheet with improved workability and discloses a steel sheet further containing Ti and B and having high hardenability. However, Patent Literature 2 does not describe, for example, solute B which influences hardenability and does not state that the quenching hardness is determined in what area of the steel sheet.

[0014] According to the technique described in Patent Literature 3, a steel with improved cold workability and improved decarbonization resistance can be obtained by adjusting the chemical composition. However, Patent Literature 3 does not describe immersion-quench hardenability or carburizing hardenability.

[0015] According to the technique described in Patent Literature 4, the incorporation of B and one or more components selected from Cr, Ni, Cu, Mo, Nb, V, Ta, W, Sn, Sb, and As and the presence of a predetermined amount of solute B in a surface layer provide a steel that achieves high hardenability. However, Patent Literature 4 specifies the hydrogen concentration in an atmosphere in the annealing step as 95% or more and does not describe whether nitrogen absorption can be suppressed to ensure solute B in an annealing step in a nitrogen atmosphere.

[0016] According to the techniques described in Patent Literatures 5 to 7, the incorporation of B and one or more of Sb, Sn, Bi, Ge, Te, and Se in an amount of 0.002% to 0.03% in total is highly effective in preventing nitrogen infiltration, and, for example, even when annealing is performed in a nitrogen atmosphere, nitrogen infiltration is prevented, and a predetermined amount of solute B is maintained, thus enhancing hardenability. However, none of Patent Literatures 5 to 7 describe the quenching hardness in a surface layer.

[0017] According to the technique described in Patent Literature 8, a steel that contains C: 0.15% to 0.37%, B, and at least one of Sb and Sn and hence has high hardenability is proposed. However, Patent Literature 8 does not discuss higher hardenability, such as carburizing hardenability.

[0018] The present invention has been made in view of the foregoing problems, and it is an object of the present invention to provide a high-carbon hot-rolled steel sheet having high cold workability and high hardenability (immersion-quench hardenability and carburizing hardenability) and a method for manufacturing the high-carbon hot-rolled steel sheet.

Solution to Problem

[0019] To achieve the above object, the present inventors have conducted intensive studies on the relationship among conditions for the production of a high-carbon hot-rolled steel sheet having a steel chemical composition containing B and one or two selected from Sn and Sb, cold workability, and hardenability (immersion-quench hardenability and carburizing hardenability) and obtained the following findings.

[0020]

i) When annealing is performed in a nitrogen atmosphere, nitrogen in the atmosphere is infiltrated and concentrated into a steel sheet and binds to B and Al in the steel sheet to form boron nitride and aluminum nitride in a surface layer. This may reduce the amount of solute B in the steel sheet, or the presence of aluminum nitride may decrease the austenite grain size during heating in the austenite range before quenching, thus resulting in insufficient quenching. Thus, in the present invention, when annealing is performed in a nitrogen atmosphere, at least one of Sb and Sn is added in a predetermined amount into a steel sheet required to have higher hardenability (high carburizing hardenability). In addition, in the annealing, heating is performed at a predetermined heating rate in a temperature range from 450°C to 600°C, whereby the amount of nitrogen infiltration from the atmosphere into the steel can be reduced to a predetermined amount. As a result, the above nitrogen infiltration is prevented, and a decrease in the amount of solute B and an increase in aluminum nitride are suppressed, so that higher hardenability (high carburizing hardenability) can be ensured.

ii) The cold workability, and the degree of hardness (hardness) and the total elongation (hereinafter also referred to simply as elongation) of a high-carbon hot-rolled steel sheet before quenching are greatly influenced by cementite grains having an equivalent circle diameter of 0.1 μm or less. When the proportion of the number of cementite grains having an equivalent circle diameter of 0.1 μm or less to the total number of cementite grains is 20% or less, a tensile strength of 480 MPa or less and a total elongation (El) of 33% or more can be achieved.

iii) The degree of hardness (hardness) and the total elongation of a high-carbon hot-rolled steel sheet before quenching are greatly influenced by cementite grains having an equivalent circle diameter of 0.1 μm or less. When the proportion of the number of cementite grains having an equivalent circle diameter of 0.1 μm or less to the total number of cementite grains is 10% or less, a tensile strength of 440 MPa or less and a total elongation (El) of 36% or more can be achieved.

iv) A desired microstructure can be ensured as follows: after hot rough rolling, finish rolling is performed at a finishing temperature equal to or higher than an Ar_3 transformation temperature, and then cooling is performed to 650°C to 750°C at an average cooling rate of 20°C/sec to 100°C/sec; coiling is performed at a coiling temperature of 500°C to 700°C, and the coil is cooled to normal temperature to obtain a hot-rolled steel sheet; the hot-rolled steel sheet is then heated between 450°C and 600°C at an average heating rate of 15°C/h or more; and annealing that involves holding at an annealing temperature lower than an Ac_1 transformation temperature for 1.0 h or more is performed.

v) Alternatively, the desired microstructure can be ensured as follows: after hot rough rolling, finish rolling is performed at a finishing temperature equal to or higher than an Ar_3 transformation temperature, and then cooling is performed to 650°C to 750°C at an average cooling rate of 20°C/sec to 100°C/sec; coiling is performed at a coiling temperature of 500°C to 700°C, and the coil is cooled to normal temperature to obtain a hot-rolled steel sheet; the hot-rolled steel sheet is then heated between 450°C and 600°C at an average heating rate of 15°C/h or more; and two-stage annealing that involves holding at a temperature equal to or higher than an Ac_1 transformation temperature and equal to or lower than an Ac_3 transformation temperature for 0.5 h or more, followed by cooling to a temperature lower than an Ar_1 transformation temperature at an average cooling rate of 1°C/h to 20°C/h, and holding at a temperature lower than the Ar_1 transformation temperature for 20 h or more is performed.

[0021] The present invention is based on these findings, and the gist of the present invention is as follows.

[1] A high-carbon hot-rolled steel sheet has a chemical composition containing, by mass%, C: 0.20% or more and 0.50% or less, Si: 0.8% or less, Mn: 0.10% or more and 0.80% or less, P: 0.03% or less, S: 0.010% or less, sol. Al: 0.10% or less, N: 0.01% or less, Cr: 1.0% or less, B: 0.0005% or more and 0.005% or less, and one or two selected from Sb and Sn in an amount of 0.002% or more and 0.1% or less in total, with the balance being Fe and unavoidable impurities. The steel sheet has a microstructure including ferrite, cementite, and pearlite that accounts for 6.5% or less of the entire microstructure by area fraction. Regarding the cementite, the proportion of the number of cementite grains having an equivalent circle diameter of 0.1 μm or less to the total number of cementite grains is 20% or less, the average cementite grain size is 2.5 μm or less, and the cementite accounts for 3.5% or more and 10.0% or less of the entire microstructure by area fraction. The average concentration of solute B in a region extending from a surface layer to a depth of 100 μm is 10 mass ppm or more. The average concentration of N present as AlN in the region extending from the surface layer to the depth of 100 μm is 70 mass ppm or less.

[2] The high-carbon hot-rolled steel sheet according to [1] has a tensile strength of 480 MPa or less and a total elongation of 33% or more.
[3] In the high-carbon hot-rolled steel sheet according to [1] or [2], the ferrite has an average grain size of 4 to 25 μm.
[4] In the high-carbon hot-rolled steel sheet according to any one of [1] to [3], the chemical composition further contains, by mass%, one or two groups selected from Group A and Group B.

Group A: Ti: 0.06% or less
Group B: one or two or more selected from Nb, Mo, Ta, Ni, Cu, V, and W each in an amount of 0.0005% or more and 0.1% or less

[5] A method for manufacturing the high-carbon hot-rolled steel sheet according to any one of [1] to [4] includes subjecting a steel having the chemical composition to hot rough rolling and then performing finish rolling at a finishing temperature equal to or higher than an Ar_3 transformation temperature; then performing cooling to 650°C to 750°C at an average cooling rate of 20°C/sec to 100°C/sec; performing coiling at a coiling temperature of 500°C to 700°C to obtain a hot-rolled steel sheet; then heating the hot-rolled steel sheet in a temperature range from 450°C to 600°C at an average heating rate of 15°C/h or more; and performing annealing that involves holding at an annealing temperature lower than an Ac_1 transformation temperature for 1.0 h or more.
[6] A method for manufacturing the high-carbon hot-rolled steel sheet according to any one of [1] to [4] includes subjecting a steel having the chemical composition to hot rough rolling and then performing finish rolling at a finishing temperature equal to or higher than an Ar_3 transformation temperature; then performing cooling to 650°C to 750°C at an average cooling rate of 20°C/sec to 100°C/sec; performing coiling at a coiling temperature of 500°C to 700°C to obtain a hot-rolled steel sheet; then heating the hot-rolled steel sheet to a temperature range from 450°C to 600°C at an average heating rate of 15°C/h or more; and performing annealing that involves holding at a temperature equal to or higher than an Ac_1 transformation temperature and equal to or lower than an Ac_3 transformation temperature for 0.5 h or more, followed by cooling to a temperature lower than an Ar_1 transformation temperature at an average cooling rate of 1°C/h to 20°C/h, and holding at a temperature lower than the Ar_1 transformation temperature for 20 h or more. Advantageous Effects of Invention

[0022] According to the present invention, a high-carbon hot-rolled steel sheet having high cold workability and high hardenability (immersion-quench hardenability and carburizing hardenability) is provided. The use of the high-carbon hot-rolled steel sheet manufactured by the present invention as a material steel sheet required to have cold workability for automotive parts such as sheet recliners, door latches, and driving systems can contribute significantly to the production of automotive parts required to have stable quality, thus producing industrially excellent effects.

Description of Embodiments

[0023] Hereinafter, a high-carbon hot-rolled steel sheet according to the present invention and a method for manufacturing the high-carbon hot-rolled steel sheet will be described in detail. The present invention is not limited to the following embodiments.

1) Chemical composition

[0024] The chemical composition of the high-carbon hot-rolled steel sheet according to the present invention and the reason for the limitation will be described. Unless otherwise specified, "%", which is a unit of the content in the following chemical composition, means "mass%".

C: 0.20% or more and 0.50% or less

[0025] C is an element important to provide the strength after quenching. If the C content is less than 0.20%, a desired hardness is not provided by heat treatment after forming, and thus the C content needs to be 0.20% or more. However, a C content of more than 0.50% causes hardening, leading to deterioration of toughness and cold workability. Thus, the C content is 0.20% or more and 0.50% or less. When the steel sheet is used for cold working of a part having a complex shape and difficult to form by pressing, the C content is preferably 0.45% or less, more preferably 0.40% or less.

Si: 0.8% or less

[0026] Si is an element that increases strength through solid-solution strengthening. A higher Si content results in a higher hardness to deteriorate cold workability, and thus the Si content is 0.8% or less, preferably 0.65% or less, more

preferably 0.50% or less. When even higher cold workability is required in difficult-to-form part applications, the Si content is preferably 0.30% or less.
To ensure desired softening resistance in the tempering step after quenching, the Si content is preferably 0.1% or more, more preferably 0.2% or more.

Mn: 0.10% or more and 0.80% or less

[0027] Mn is an element that improves hardenability and increases strength through solid-solution strengthening. If the Mn content is less than 0.10%, both immersion-quench hardenability and carburizing hardenability begin to deteriorate, and thus the Mn content is 0.10% or more. When the inner portion of a thick material or the like is to be reliably quenched, the Mn content is preferably 0.25% or more, more preferably 0.30% or more. If the Mn content exceeds 0.80%, a banded structure due to Mn segregation develops, resulting in an inhomogeneous microstructure, and the steel becomes hard through solid-solution strengthening, resulting in low cold workability. Thus, the Mn content is 0.80% or less. In the case of a material for a part required to have formability, a certain level of cold workability is necessary, and thus the Mn content is preferably 0.65% or less, more preferably 0.55% or less.

P: 0.03% or less

[0028] P is an element that increases strength through solid-solution strengthening. If the P content exceeds 0.03%, grain boundary embrittlement is caused to deteriorate the toughness after quenching. The cold workability is also reduced. Thus, the P content is 0.03% or less. To provide high toughness after quenching, the P content is preferably 0.02% or less. Since P reduces the cold workability and the toughness after quenching, the P content is preferably as low as possible. However, an excessive reduction in P leads to an increase in refining cost, and thus the P content is preferably 0.005% or more, more preferably 0.007% or more.

S: 0.010% or less

[0029] S is an element that needs to be minimized because S forms sulfides and reduces the cold workability and the toughness after quenching of the high-carbon hot-rolled steel sheet. If the S content exceeds 0.010%, the cold workability and the toughness after quenching of the high-carbon hot-rolled steel sheet deteriorate significantly. Thus, the S content is 0.010% or less. To provide high cold workability and high toughness after quenching, the S content is preferably 0.005% or less. Since S reduces the cold workability and the toughness after quenching, the S content is preferably as low as possible. However, an excessive reduction in S leads to an increase in refining cost, and thus the S content is preferably 0.0005% or more.

sol. Al: 0.10% or less

[0030] If the sol. Al content exceeds 0.10%, AlN is formed during heating in quenching treatment, resulting in excessively fine austenite grains. This promotes the formation of a ferrite phase during cooling to form a microstructure composed of ferrite and martensite, resulting in low hardness after quenching. Thus, the sol. Al content is 0.10% or less, preferably 0.06% or less. sol. Al has a deoxidation effect, and to achieve sufficient deoxidation, the sol. Al content is preferably 0.005% or more.

N: 0.01% or less

[0031] If the N content exceeds 0.01%, the formation of AlN leads to the formation of excessively fine austenite grains during heating in quenching treatment, which promotes the formation of a ferrite phase during cooling, resulting in low hardness after quenching. Thus, the N content is 0.01% or less, preferably 0.0065% or less, more preferably 0.0050% or less. N is an element that forms AlN, Cr-based nitride, and B nitride and thus moderately inhibits the growth of austenite grains during heating in quenching treatment to improve the toughness after quenching. Thus, the N content is preferably 0.0005% or more, more preferably 0.0010% or more.

Cr: 1.0% or less

[0032] In the present invention, Cr is an important element that enhances hardenability. If the Cr content in the steel is 0%, ferrite is readily formed in a surface layer particularly during carburizing and quenching, and a completely quenched microstructure is not obtained, which may increase the likelihood of a decrease in hardness.
Thus, when the steel sheet is used in applications where hardenability is important, the Cr content is preferably 0.05%

or more, more preferably 0.10% or more, still more preferably 0.20% or more. If the Cr content exceeds 1.0%, the steel sheet before quenching becomes hard to have impaired cold workability. Thus, the Cr content is 1.0% or less. When a part difficult to form by pressing and requiring high workability is processed, even higher cold workability is required, and thus the Cr content is preferably 0.7% or less, more preferably 0.5% or less.

B: 0.0005% or more and 0.005% or less

[0033] In the present invention, B is an important element that enhances hardenability. If the B content is less than 0.0005%, the effect is not sufficiently produced. Thus, the B content needs to be 0.0005% or more, and is preferably 0.0010% or more. If the B content exceeds 0.005%, the recrystallization of austenite after finish rolling is retarded to develop a texture of the hot-rolled steel sheet, resulting in high anisotropy after annealing to increase the likelihood that an earing occurs in drawing. Thus, the B content is 0.005% or less, preferably 0.004% or less.

Total content of one or two selected from Sn and Sb: 0.002% or more and 0.1% or less

[0034] Sb and Sn are elements effective in suppressing nitrogen infiltration through the steel sheet surface layer. If the total content of one or more of these elements is less than 0.002%, the effect is not sufficiently produced. Thus, the total content of one or more of these elements is 0.002% or more, more preferably 0.005% or more. If one or more of these elements are contained in an amount of more than 0.1% in total, the nitrogen infiltration prevention effect plateaus. In addition, these elements tend to segregate at grain boundaries, and thus if these elements are contained in an amount of more than 0.1% in total, grain boundary embrittlement may occur due to the excessively high content. Thus, the total content of one or two selected from Sb and Sn is 0.1% or less, preferably 0.03% or less, still more preferably 0.02% or less.

[0035] In the present invention, since one or two selected from Sb and Sn is contained in an amount of 0.002% or more and 0.1% or less in total, nitrogen infiltration through the steel sheet surface layer is suppressed even when annealing is performed in a nitrogen atmosphere, and an increase in nitrogen concentration in the steel sheet surface layer is suppressed. Thus, according to the present invention, nitrogen infiltration through the steel sheet surface layer can be suppressed; therefore, even when annealing is performed in a nitrogen atmosphere, the amount of solute B in a region extending from the steel sheet surface layer to a depth of 100 μm after annealing can be appropriately ensured, and the formation of aluminum nitride (AlN) in the region extending from the steel sheet surface layer to the depth of 100 μm can be suppressed to allow austenite grains to grow during heating before quenching. As a result, the formation of ferrite and pearlite can be hindered during cooling, thus providing high hardenability.

[0036] In the present invention, the balance is Fe and unavoidable impurities.

[0037] The above-described essential elements provide the high-carbon hot-rolled steel sheet according to the present invention with the desired properties. To further improve, for example, hardenability, the high-carbon hot-rolled steel sheet according to the present invention may optionally contain the following elements.

Ti: 0.06% or less

[0038] Ti is an element effective in enhancing hardenability. When sufficient hardenability is not provided by the incorporation of B alone, the hardenability can be improved by the incorporation of Ti. This effect is not produced when the Ti content is less than 0.005%, and thus if Ti is contained, the Ti content is preferably 0.005% or more, more preferably 0.007% or more. When the Ti content exceeds 0.06%, the steel sheet before quenching becomes hard to have impaired cold workability, and thus if Ti is contained, the Ti content is 0.06% or less, preferably 0.04% or less.

[0039] Furthermore, to stabilize the mechanical properties and hardenability of the present invention, one or two or more selected from Nb, Mo, Ta, Ni, Cu, V, and W may be added each in a required amount.

Nb: 0.0005% or more and 0.1% or less

[0040] Nb is an element that forms a carbonitride and is effective in preventing exaggerated grain growth during heating before quenching, improving toughness, and improving temper softening resistance. When the Nb content is less than 0.0005%, the effect of addition is not sufficiently produced. Thus, if Nb is contained, the lower limit is preferably 0.0005%, more preferably 0.0010% or more. When the Nb content exceeds 0.1%, the effect of addition plateaus, and, in addition, a niobium carbide increases the tensile strength of the base metal to decrease elongation. Thus, if Nb is contained, the upper limit is preferably 0.1%, more preferably 0.05% or less, still more preferably less than 0.03%.

Mo: 0.0005% or more and 0.1% or less

[0041] Mo is an element effective in improving hardenability and temper softening resistance. When the Mo content is less than 0.0005%, the effect of addition is small. Thus, if Mo is contained, the lower limit is preferably 0.0005%, more preferably 0.0010% or more. When the Mo content exceeds 0.1%, the effect of addition plateaus, and the cost increases. Thus, if Mo is contained, the upper limit is preferably 0.1%, more preferably 0.05% or less, still more preferably less than 0.03%.

Ta: 0.0005% or more and 0.1% or less

[0042] Ta is an element that forms a carbonitride similarly to Nb and is effective in preventing exaggerated grain growth during heating before quenching, preventing coarsening of grains, and improving temper softening resistance. When the Ta content is less than 0.0005%, the effect of addition is small. Thus, if Ta is contained, the lower limit is preferably 0.0005%, more preferably 0.0010% or more. When the Ta content exceeds 0.1%, the effect of addition plateaus, the quenching hardness decreases due to excessive carbide formation, and the cost increases. Thus, if Ta is contained, the upper limit is preferably 0.1%, more preferably 0.05% or less, still more preferably less than 0.03%.

Ni: 0.0005% or more and 0.1% or less

[0043] Ni is an element highly effective in improving toughness and hardenability. When the Ni content is less than 0.0005%, the effect of addition is not produced. Thus, if Ni is contained, the lower limit is preferably 0.0005%, more preferably 0.0010% or more. When the Ni content exceeds 0.1%, the effect of addition plateaus, and, in addition, the cost increases. Thus, if Ni is contained, the upper limit is preferably 0.1%, more preferably 0.05% or less.

Cu: 0.0005% or more and 0.1% or less

[0044] Cu is an element effective in ensuring hardenability. When the Cu content is less than 0.0005%, the effect of addition is not sufficiently produced. Thus, if Cu is contained, the lower limit is preferably 0.0005%, more preferably 0.0010% or more. When the Cu content exceeds 0.1%, flaws are likely to occur during hot rolling, resulting in lower manufacturability, such as lower yields. Thus, if Cu is contained, the upper limit is preferably 0.1%, more preferably 0.05% or less.

V: 0.0005% or more and 0.1% or less

[0045] V is an element that forms a carbonitride similarly to Nb and Ta and is effective in preventing exaggerated grain growth during heating before quenching, improving toughness, and improving temper softening resistance. When the V content is less than 0.0005%, the effect of addition is not sufficiently produced. Thus, if V is contained, the lower limit is preferably 0.0005%, more preferably 0.0010% or more. When the V content exceeds 0.1%, the effect of addition plateaus, and, in addition, a niobium carbide increases the tensile strength of the base metal to decrease elongation. Thus, if V is contained, the upper limit is preferably 0.1%, more preferably 0.05% or less, still more preferably less than 0.03%.

W: 0.0005% or more and 0.1% or less

[0046] W is an element that forms a carbonitride similarly to Nb and V and is effective in preventing exaggerated growth of austenite grains during heating before quenching and improving tempering softening resistance. When the W content is less than 0.0005%, the effect of addition is small. Thus, if W is contained, the lower limit is preferably 0.0005%, more preferably 0.0010% or more. When the W content is more than 0.1%, the effect of addition plateaus, the quenching hardness decreases due to excessive carbide formation, and the cost increases. Thus, if W is contained, the upper limit is preferably 0.1%, more preferably 0.05% or less, still more preferably less than 0.03%.

[0047] In the present invention, when two or more selected from Nb, Mo, Ta, Ni, Cu, V, and W are contained, the total content thereof is preferably 0.001% or more and 0.1% or less.

2) Microstructure

[0048] The reason for the limitation of the microstructure of the high-carbon hot-rolled steel sheet according to the present invention will be described.

[0049] In the present invention, the microstructure includes ferrite and cementite. Regarding the cementite, the proportion of the number of cementite grains having an equivalent circle diameter of 0.1 μm or less to the total number of cementite grains is 20% or less, the average cementite grain size is 2.5 μm or less, and the cementite accounts for 3.5% or more and 10.0% or less of the entire microstructure by area fraction. The average concentration of solute B in a region extending from a surface layer to a depth of 100 μm is 10 mass ppm or more. The average concentration of N present as AlN in the region extending from the surface layer to the depth of 100 μm is 70 mass ppm or less.

[0050] In the present invention, the average grain size of the ferrite is preferably 4 to 25 μm, more preferably 5 μm or more.

2-1) Ferrite and cementite

[0051] The microstructure of the high-carbon hot-rolled steel sheet according to the present invention includes ferrite and cementite. In the present invention, the area fraction of the ferrite is preferably 90% or more. A ferrite area fraction of less than 90% may reduce formability, thus making it difficult to perform cold working in the case of a part requiring high workability. Thus, the ferrite area fraction is preferably 90% or more, more preferably 92% or more.

[0052] In the microstructure of the high-carbon hot-rolled steel sheet according to the present invention, pearlite may be formed in addition to the ferrite and cementite described above. Pearlite may be contained as long as the area fraction thereof in the entire microstructure is 6.5% or less because pearlite in such an amount does not impair the advantageous effects of the present invention.

2-2) Proportion of number of cementite grains having equivalent circle diameter of 0.1 μm or less to total number of cementite grains: 20% or less

[0053] If the number of cementite grains having an equivalent circle diameter of 0.1 μm or less is large, the hardness increases through dispersion strengthening to decrease elongation. To provide cold workability, in the present invention, the proportion of the number of cementite grains having an equivalent circle diameter of 0.1 μm or less to the total number of cementite grains is 20% or less. This can further achieve a tensile strength of 480 MPa or less and a total elongation (El) of 33% or more.

[0054] When the high-carbon hot-rolled steel sheet is used for a difficult-to-form part, high cold workability is required, and in this case, the proportion of the number of cementite grains having an equivalent circle diameter of 0.1 μm or less to the total number of cementite grains is preferably 10% or less. When the proportion the number of cementite grains having an equivalent circle diameter of 0.1 μm or less to the total number of cementite grains is 10% or less, a tensile strength of 440 MPa or less and a total elongation (El) of 36% or more can be achieved. The reason why the proportion of cementite grains having an equivalent circle diameter of 0.1 μm or less is specified is that cementite grains of 0.1 μm or less have a dispersion strengthening ability, and an increase in the number of cementite grains having such a size impairs cold workability.

[0055] To suppress exaggerated growth of ferrite grains during annealing, the proportion of the number of cementite grains having an equivalent circle diameter of 0.1 μm or less to the total number of cementite grains is preferably 3% or more.

[0056] Cementite grains present before quenching have an equivalent circle diameter of about 0.07 to 3.0 μm. Thus, the dispersion state of cementite grains before quenching having an equivalent circle diameter of more than 0.1 μm, which is a size not affecting precipitation strengthening much, is not particularly specified in the present invention.

2-3) Average cementite grain size: 2.5 μm or less

[0057] In quenching, the cementite needs to be wholly dissolved to ensure a desired amount of solute C in the ferrite. If the average cementite grain size exceeds 2.5 μm, the cementite cannot be completely dissolved during holding in the austenite range, and thus the average cementite grain size is 2.5 μm or less, more preferably 2.0 μm or less. If the cementite is excessively fine, precipitation strengthening of the cementite reduces cold workability, and thus the average cementite grain size is preferably 0.1 μm or more, more preferably 0.15 μm or more.

[0058] In the present invention, the term "cementite grain size" refers to an equivalent circle diameter of a cementite grain, and the equivalent circle diameter of a cementite grain is a value obtained by measuring the major axis and the minor axis of the cementite grain and converting them into an equivalent circle diameter. The term "average cementite grain size" refers to a value determined by dividing the sum of equivalent circle diameters of all cementite grains by the total number of cementite grains.

2-4) Proportion (area fraction) of cementite relative to entire microstructure: 3.5% or more and 10.0% or less

[0059] If the proportion of the cementite to the entire microstructure exceeds 10.0%, the number of cementite grains of 0.1 μm or less contributing to precipitation strengthening is also increased, and the steel becomes hard. Thus, the proportion of the cementite is 10.0% or less, preferably 9.5% or less. On the other hand, if this proportion is less than 3.5%, the substantial C content does not reach 0.20%, and a desired hardness cannot be provided after heat treatment.

Thus, the proportion is 3.5% or more, more preferably 4.0% or more.

2-5) Average grain size of ferrite: 4 to 25 μm (suitable condition)

[0060] If the average grain size of the ferrite is less than 4 μm, the strength before cold working may increase to deteriorate press formability, and thus the average grain size of the ferrite is preferably 4 μm or more. If the average grain size of the ferrite exceeds 25 μm, the strength of the base metal may decrease. In the field where the steel sheet is formed into an intended product shape and then used without quenching, the base metal needs to have some degree of strength. Thus, the average grain size of the ferrite is preferably 25 μm or less. The average grain size of the ferrite is more preferably 5 μm or more, still more preferably 6 μm or more, and more preferably 20 μm or less, still more preferably 18 μm or less.

[0061] In the present invention, the equivalent circle diameter of a cementite grain, the average cementite grain size, the proportion of the cementite to the entire microstructure, the area fraction of the ferrite, the average grain size of the ferrite, etc. described above can be measured by methods described in EXAMPLES described later.

2-6) Average concentration of solute B in region extending from surface layer to depth of 100 μm: 10 mass ppm or more

[0062] In the high-carbon hot-rolled steel sheet according to the present invention, to prevent the formation of a quenched microstructure such as pearlite or sorbite, which is likely to be formed in a surface layer portion when the steel sheet is quenched, B in a region (portion) extending from the steel sheet surface layer to a 100 μm position in the thickness direction (surface layer 100 μm portion) needs to be present at an average concentration of 10 mass ppm or more in the form of solute B that is not nitrided or oxidized. Automotive parts that are subjected to quenching treatment for use and required to have wear resistance are required to have surface hardness. To provide a desired surface hardness, it is necessary to form a completely quenched microstructure in the surface layer 100 μm portion after quenching. The average concentration of the solute B is preferably 12 mass ppm or more, more preferably 15 mass ppm or more. An excessively high concentration of the solute B impedes the development of an aggregation texture of hot-rolled microstructures, and thus the average concentration of the solute B is 40 mass ppm or less, more preferably 35 mass ppm or less.

2-7) Average concentration of N present as AlN in region extending from surface layer to depth of 100 μm: 70 mass ppm or less

[0063] When the average concentration of N present as AlN in the region extending from the steel sheet surface layer to the 100 μm position in the thickness direction is 70 mass ppm or less, the growth of grains is promoted in the austenite range during heating before quenching. This reduces the likelihood of the formation of a microstructure such as pearlite or sorbite in the cooling stage and provides the desired surface hardness without causing insufficient quenching. The average concentration of N present as AlN in the region extending from the surface layer to the depth of 100 μm is preferably 50 mass ppm or less.

[0064] To inhibit the exaggerated grain growth during heating in the austenite range, the average concentration of N is preferably 10 mass ppm or more, more preferably 20 mass ppm or more.

[0065] In the present invention, it has been found that the amounts of solute B and N present as AlN in the steel sheet surface layer portion are closely related to the manufacturing conditions in each step including heating conditions, coiling conditions, and annealing conditions and that these manufacturing conditions need to be optimized. The reasons necessary for achieving the amounts of solute B and N present as AlN in each step will be described later.

3) Mechanical properties

[0066] The high-carbon hot-rolled steel sheet according to the present invention is used to form automotive parts such as gears, transmissions, and sheet recliners by cold pressing and thus is required to have high cold workability. In addition, it is necessary to impart wear resistance by increasing the hardness through quenching treatment. Thus, the high-carbon hot-rolled steel sheet according to the present invention has a reduced tensile strength (TS) of 480 MPa or less and an increased total elongation (El) of 33% or more and hence can achieve both high cold workability and high hardenability (immersion-quench hardenability and carburizing hardenability). More preferably, the TS is 460 MPa or less, and the El is 35% or more.

[0067] In the case where the steel sheet is used to form a difficult-to-form part required to have cold pressing properties, the tensile strength of the steel sheet is further reduced to a TS of 440 MPa or less, and the total elongation of the steel sheet is further increased to an El of 36% or more, whereby both high cold workability and high hardenability (immersion-quench hardenability and carburizing hardenability) can be achieved. More preferably, the TS is 410 MPa or less, and the El is 38% or more.

[0068] The tensile strength (TS) and the total elongation (El) described above can be measured by methods described in EXAMPLES described later.

4) Manufacturing method

[0069] The high-carbon hot-rolled steel sheet according to the present invention is manufactured in the following manner using, as a material, a steel having a chemical composition as described above. The material (steel material) is subjected to hot rough rolling, and then finish rolling is performed at a finishing temperature equal to or higher than an Ar_3 transformation temperature. Subsequently, cooling is performed to 650°C to 750°C at an average cooling rate of 20°C/sec to 100°C/sec. Coiling is performed at a coiling temperature of 500°C to 700°C, and the coil is cooled to normal temperature to obtain a hot-rolled steel sheet. The hot-rolled steel sheet is then heated in a temperature range from 450°C to 600°C at an average heating rate of 15°C/h or more. Annealing that involves holding at an annealing temperature lower than an Ac_1 transformation temperature for 1.0 h or more is performed.

[0070] Alternatively, the high-carbon hot-rolled steel sheet according to the present invention is manufactured in the following manner using, as a material, a steel having a chemical composition as described above. The material (steel material) is subjected to hot rough rolling, and then finish rolling is performed at a finishing temperature equal to or higher than an Ar_3 transformation temperature. Subsequently, cooling is performed to 650°C to 750°C at an average cooling rate of 20°C/sec to 100°C/sec. Coiling is performed at a coiling temperature of 500°C to 700°C, and the coil is cooled to normal temperature to obtain a hot-rolled steel sheet. The hot-rolled steel sheet is then heated in a temperature range from 450°C to 600°C at an average heating rate of 15°C/h or more. Two-stage annealing that involves holding at a temperature equal to or higher than an Ac_1 transformation temperature and equal to or lower than an Ac_3 transformation temperature for 0.5 h or more, followed by cooling to a temperature lower than an Ar_1 transformation temperature at an average cooling rate of 1°C/h to 20°C/h, and holding at a temperature lower than the Ar_1 transformation temperature for 20 h or more is performed.

[0071] Hereinafter, the reason for the limitation in the method for manufacturing the high-carbon hot-rolled steel sheet according to the present invention will be described. In the description, the expression "°C" regarding temperature indicates a temperature at a steel sheet surface or a surface of a steel material.

[0072] In the present invention, the steel material may be produced by any method. For example, to prepare a molten high-carbon steel of the present invention, either a converter or an electric furnace can be used. The molten high-carbon steel prepared by a known method, for example, using a converter is formed into, for example, a slab (steel material) by ingot making and blooming or continuous casting. Typically, the slab is heated and then subjected to hot rolling (hot rough rolling and finish rolling).

[0073] For example, in the case of a slab produced by continuous casting, direct rolling in which the slab is rolled as it is or while being kept hot for the purpose of suppressing temperature drop may be used. When the slab is heated and subjected to hot rolling, the heating temperature of the slab is preferably 1280°C or lower in order to avoid deterioration of the surface state due to scales. The lower limit of the heating temperature of the slab is preferably 1100°C, more preferably 1150°C, still more preferably 1200°C or higher. During the hot rolling, the material to be rolled may be heated by heating means such as a sheet bar heater in order to ensure the finishing temperature.

[0074] Finish rolling at finishing temperature equal to or higher than Ar_3 transformation temperature

[0075] If the finishing temperature is lower than the Ar_3 transformation temperature, coarse ferrite grains are formed after the hot rolling and after annealing to significantly decrease elongation. Thus, the finishing temperature is equal to or higher than the Ar_3 transformation temperature, preferably equal to or higher than (Ar_3 transformation temperature + 20°C). The upper limit of the finishing temperature need not be particularly specified, and is preferably 1000°C or lower to smoothly perform the cooling after the finish rolling.

[0076] The Ar_3 transformation temperature described above can be determined by actual measurement such as thermal expansion measurement or electrical resistance measurement during cooling using, for example, Formaster testing.

After finish rolling, cooling to 650°C to 750°C at average cooling rate of 20°C/sec to 100°C/sec

[0077] After the finish rolling, the average rate cooling to 650°C to 750°C greatly affects the size of spheroidized cementite grains after annealing. If the average cooling rate after the finish rolling is less than 20°C/sec, a microstructure before annealing is composed of an excessive ferrite microstructure and a pearlite microstructure, and thus a desired cementite dispersion state and a desired cementite size are not provided after annealing. Thus, the cooling needs to be performed at 20°C/sec or more. The average cooling rate is preferably 25°C/sec or more. If the average cooling rate exceeds 100°C/sec, cementite grains having a desired size are not readily formed after annealing, and thus the average cooling rate is 100°C/sec or less, preferably 75°C/sec or less.

Coiling temperature: 500°C to 700°C

[0078] The hot-rolled steel sheet after the finish rolling is wound into a coil shape. If the coiling temperature is excessively high, the hot-rolled steel sheet has excessively low strength and may be deformed by its own weight when wound into a coil shape. This is not preferable from the viewpoint of operation. Thus, the upper limit of the coiling temperature is 700°C, preferably 690°C or lower. If the coiling temperature is excessively low, the hot-rolled steel sheet disadvantageously becomes hard. Thus, the coiling temperature is 500°C, preferably 530°C or higher.

[0079] After being wound into a coil shape, the coil may be cooled to normal temperature and subjected to pickling treatment. After the pickling treatment, annealing is performed. For the pickling treatment, a known method can be used. Subsequently, the resulting hot-rolled steel sheet is subjected to the following annealing.

Average heating rate in temperature range from 450°C to 600°C: 15°C/h or more

[0080] The hot-rolled steel sheet obtained as described above is subjected to annealing (spheroidizing annealing of cementite). In the case of annealing in a nitrogen atmosphere, ammonia gas is likely to occur in a temperature range from 450°C to 600°C, and nitrogen decomposed from the ammonia gas enters the surface of the steel sheet and binds to B and Al in the steel to form nitrides. Thus, the heating time in the temperature range from 450°C to 600°C is set to be as short as possible. The average heating rate in this temperature range is 15°C/h or more. To reduce variation in temperature in the furnace for the purpose of improvement in productivity, the average heating rate is preferably 100°C/h or less, more preferably 70°C/h or less.

Holding at annealing temperature lower than Ac_1 transformation temperature for 1.0 h or more

[0081] If the annealing temperature is not lower than the Ac_1 transformation temperature, austenite is precipitated, and a coarse pearlite microstructure is formed during the cooling process after the annealing, resulting in an inhomogeneous microstructure. Thus, the annealing temperature is lower than the Ac_1 transformation temperature, preferably (Ac_1 transformation temperature - 10°C) or lower. The lower limit of the annealing temperature is not particularly specified, and to provide a desired cementite dispersion state, the annealing temperature is preferably 600°C or higher, more preferably 700°C or higher. As an atmospheric gas, any of nitrogen, hydrogen, and a gas mixture of nitrogen and hydrogen can be used. The holding time at the annealing temperature is 1.0 hour (h) or more. If the holding time at the annealing temperature is less than 1.0 hour, the effect of annealing is slight, and the target microstructure of the present invention is not formed, as a result of which the target hardness and elongation of the steel sheet of the present invention are not provided. Thus, the holding time at the annealing temperature is 1.0 hour or more, preferably 5 hours or more, more preferably more than 20 hours. If the holding time at the annealing temperature exceeds 40.0 hours, the productivity decreases, resulting in an excessively high manufacturing cost. Thus, the holding time at the annealing temperature is preferably 40.0 hours or less, more preferably 35 hours or less.

[0082] In the present invention, the following two-stage annealing may be performed instead of the above-described annealing. Specifically, the high-carbon hot-rolled steel sheet can also be manufactured as follows: after coiling and cooling to normal temperature are performed to obtain a hot-rolled steel sheet, the hot-rolled steel sheet is heated in a temperature range from 450°C to 600°C at an average heating rate of 15°C/h or more, and two-stage annealing that involves holding at a temperature equal to or higher than the Ac_1 transformation temperature and equal to or lower than the Ac_3 transformation temperature for 0.5 h or more (first-stage annealing), followed by cooling to a temperature lower than an Ar_1 transformation temperature at an average cooling rate of 1°C/h to 20°C/h, and holding at a temperature lower than the Ar_1 transformation temperature for 20 h or more (second-stage annealing) is performed.

[0083] In the present invention, the hot-rolled steel sheet is heated in a temperature range from 450°C to 600°C at an average heating rate of 15°C/h or more, held at a temperature equal to or higher than the Ac_1 transformation temperature for 0.5 h or more to dissolve relatively fine carbide precipitated in the hot-rolled steel sheet into a γ phase, and then cooled to a temperature lower than the Ar_1 transformation temperature at an average cooling rate of 1°C/h to 20°C/h and held at a temperature lower than the Ar_1 transformation temperature for 20 h or more. This allows solute C to precipitate with relatively coarse undissolved carbide and the like serving as nuclei to achieve a state in which the dispersion of carbide (cementite) is controlled such that the proportion of the number of cementite grains having an equivalent circle diameter of 0.1 μm or less to the total number of cementite grains is 20% or less. That is to say, in the present invention, the dispersion morphology of carbide is controlled by performing the two-stage annealing under the predetermined conditions, whereby the steel sheet is softened. For the softening of the high-carbon steel sheet of interest in the present invention, it is important to control the dispersion morphology of carbide after the annealing. In the present invention, the high-carbon hot-rolled steel sheet is held at a temperature equal to or higher than the Ac_1 transformation temperature and equal to or lower than the Ac_3 transformation temperature (first-stage annealing), whereby fine carbide is dissolved, and at the same time, C is dissolved in γ (austenite). In the subsequent cooling to a temperature lower than the Ar_1 transformation temperature and holding (second-stage annealing), the α/γ interface and undissolved carbide present in a temperature range of the Ac_1 transformation temperature or higher serve as nucleation sites to precipitate relatively coarse carbide. The conditions for the two-stage annealing will be described below. As an atmospheric gas during the annealing, any of nitrogen, hydrogen, and a gas mixture of nitrogen and hydrogen can be used.

Average heating rate in temperature range from 450°C to 600°C: 15°C/h or more

[0084] For the same reasons as above, ammonia gas is likely to occur in a temperature range from 450°C to 600°C, and nitrogen decomposed from the ammonia gas enters the surface of the steel sheet and binds to B and Al in the steel to form nitrides. Thus, the heating time in the temperature range from 450°C to 600°C is set to be as short as possible. The average heating rate in this temperature range is 15°C/h or more, preferably 20°C/h or more. The upper limit of the average heating rate is preferably 100°C/h, more preferably 90°C/h or less.

[0085] Holding at temperature equal to or higher than Ac_1 transformation temperature and equal to or lower than Ac_3 transformation temperature for 0.5 h or more (first-stage annealing)

[0086] By holding the hot-rolled steel sheet at a temperature equal to or higher than the Ac_1 transformation temperature, part of ferrite in the microstructure of the steel sheet is transformed into austenite, so that fine carbide precipitated in ferrite is dissolved, and C is dissolved in austenite. On the other hand, ferrite remained without being transformed into austenite is annealed at a high temperature, and as a result, the ferrite has a reduced dislocation density and softens. Undissolved relatively coarse carbide (undissolved carbide) remains in ferrite and becomes further coarsened through Ostwald ripening. If the annealing temperature is lower than the Ac_1 transformation temperature, austenite transformation does not occur, and thus carbide cannot be dissolved in austenite. If the first-stage annealing temperature is higher than the Ac_3 transformation temperature, a large number of rod-like cementite grains are formed after the annealing, and the desired elongation is not provided. Thus, the first-stage annealing temperature is equal to or lower than the Ac_3 transformation temperature. In the present invention, if the holding time at a temperature equal to or higher than the Ac_1 transformation temperature and equal to or lower than the Ac_3 transformation temperature is less than 0.5 h, fine carbide cannot be sufficiently dissolved. Thus, in the first-stage annealing, the steel sheet is held at a temperature equal to or higher than the Ac_1 transformation temperature and equal to or lower than the Ac_3 transformation temperature for 0.5 h or more. The holding time is preferably 1.0 h or more. The holding time is preferably 10 h or less. Even when the annealing is performed while holding the steel sheet at a temperature equal to or higher than the Ac_1 transformation temperature and equal to or lower than the Ac_3 transformation temperature, the heating rate is preferably such that the average heating rate in the temperature range from 450°C to 600°C is 15°C/h or more and the upper limit is 100°C/h or less.

Cooling to temperature lower than Ar_1 transformation temperature at average cooling rate of 1°C/h to 20°C/h

[0087] After the first-stage annealing described above, the steel sheet is cooled to a temperature lower than the Ar_1 transformation temperature within the temperature range of the second-stage annealing at an average cooling rate of 1°C/h to 20°C/h. During the cooling, C ejected from austenite as a result of transformation from austenite to ferrite is precipitated in the form of relatively coarse spherical carbide with the α/γ interface and undissolved carbide serving as nucleation sites. In this cooling, the cooling rate needs to be adjusted so as not to form pearlite. If the average cooling rate after the first-stage annealing and before the second-stage annealing is less than 1°C/h, the production efficiency is low. Thus, the average cooling rate is 1°C/h or more, preferably 5°C/h or more. If the average cooling rate exceeds 20°C/h, pearlite is precipitated to increase the hardness. Thus, the average cooling rate is 20°C/h or less, preferably 15°C/h or less.

Holding at temperature lower than Ar_1 transformation temperature for 20 h or more (second-stage annealing)

[0088] After the first-stage annealing described above, the steel sheet is cooled at a predetermined average cooling rate and held at a temperature lower than the Ar_1 transformation temperature to cause Ostwald ripening so that the coarse spherical carbide is further grown and fine carbide disappears. If the holding time at a temperature lower than the Ar_1 transformation temperature is less than 20 h, carbide cannot be sufficiently grown, resulting in an excessively high hardness after the annealing. Thus, in the second-stage annealing, the steel sheet is held at a temperature lower than the Ar_1 transformation temperature for 20 h or more. For sufficient growth of carbide, the second-stage annealing temperature is preferably, but not necessarily, 660°C or higher. From the viewpoint of production efficiency, the holding time is preferably, but not necessarily, 30 h or less.

[0089] The Ac_3 transformation temperature, the Ac_1 transformation temperature, the Ar_3 transformation temperature, and the Ar_1 transformation temperature described above can be determined by actual measurement such as thermal expansion measurement or electrical resistance measurement during heating or cooling using, for example, Formaster testing.

[0090] The average heating rates and the average cooling rates described above are determined by measuring temperatures with a thermocouple mounted in the furnace.

EXAMPLES

[0091] Molten steels having chemical compositions of steel Nos. A to T shown in Table 1 were cast into slab, and hot rolling was then performed under manufacturing conditions shown in Table 2-1 and Table 3-1. Subsequently, pickling was performed, and annealing (spheroidizing annealing) was performed in a nitrogen atmosphere (atmospheric gas: nitrogen) at annealing temperatures for annealing times (h) shown in Table 2-1 and Table 3-1 to manufacture hot-rolled annealed sheets having a thickness of 3.0 mm.

[0092] In Examples of the present invention, test pieces were taken from the hot-rolled annealed sheets thus obtained, and the microstructure, the amount of solute B, the amount of N in AlN, the tensile strength, the total elongation, and the quenching hardness (hardness of steel sheet after quenching and hardness of steel sheet after carburizing and quenching) were determined as described below. The Ac_3 transformation temperature, the Ac_1 transformation temperature, the Ar_1 transformation temperature, and the Ar_3 transformation temperature shown in Table 1 were determined by Formaster testing.

(1) Microstructure

[0093] The microstructure of each annealed steel sheet was determined as follows: a test piece (size: 3 mm thick × 10 mm × 10 mm) taken from a central portion in the width direction was cut, polished, and then subjected to nital etching. Images were captured with a scanning electron microscope (SEM) at a magnification of 3000 times at five points at 1/4 from a surface layer in the thickness direction. The captured microstructure images were subjected to image processing to identify phases (e.g., ferrite, cementite, and pearlite). In Table 2-2 and Table 3-2, "pearlite area fraction" is shown as a microstructure, and steels observed to have a pearlite area fraction of more than 6.5% are represented as Comparative Examples. Steels including pearlite with an area fraction of 6.5% or less, ferrite, and cementite are represented as Examples.

[0094] The SEM images were binarized into ferrite and a non-ferrite region using image analysis software to determine the area fraction (%) of ferrite. Also for cementite, the SEM images were binarized into cementite and a non-cementite region using image analysis software to determine the area fraction (%) of cementite. For pearlite, the area fractions (%) of ferrite and cementite were subtracted from 100 (%) to determine the area fraction (%) of pearlite.

[0095] In the captured microstructure images, the size of each cementite grain was determined. The cementite grain size was determined by measuring the major axis and the minor axis and converting them into an equivalent circle diameter. The average cementite grain size was determined by dividing the sum of equivalent circle diameters of all cementite grains by the total number of cementite grains. The number of cementite grains whose equivalent circle diameter values were 0.1 μm or less was determined and defined as the number of cementite grains having an equivalent circle diameter of 0.1 μm or less. The number of all cementite grains was determined and defined as the total number of cementite grains. The proportion of the number of cementite grains having an equivalent circle diameter of 0.1 μm or less to the total number of cementite grains ((the number of cementite grains having an equivalent circle diameter of 0.1 μm or less/the total number of cementite grains) × 100 (%)) was determined. "The proportion of cementite grains having an equivalent circle diameter of 0.1 μm or less" may also be referred to simply as cementite grains having an equivalent circle diameter of 0.1 μm or less.

[0096] In the captured microstructure images, the average grain size of ferrite was determined using a method for evaluation of crystal grain size (intercept method) specified in JIS G 0551.

(2) Measurement of average concentration of solute B

[0097] The same method as described in the following reference was used. Specifically, ground powder from a region extending from a surface layer to a depth of 100 μm was collected and measured three times, and the average value was determined as the average concentration of solute B. [Reference] Satoshi Kinoshiro, Tomoharu Ishida, Kunio Inose, and Kyoko Fujimoto, Tetsu-to-Hagane (Iron and Steel), vol. 99 (2013) No. 5, p. 362-365

(3) Measurement of average concentration of N present as AlN

[0098] Similarly to the above, the average concentration of N present as AlN was determined by the same method as described in the following reference.

[0099] [Reference] Satoshi Kinoshiro, Tomoharu Ishida, Kunio Inose, and Kyoko Fujimoto, Tetsu-to-Hagane (Iron and Steel), vol. 99 (2013) No. 5, p. 362-365

(4) Tensile strength and elongation of steel sheet

[0100] Using a JIS No. 5 tensile test piece cut out from each annealed steel sheet (original sheet) in a direction at 0° with respect to the rolling direction (L direction), a tensile test was performed at 10 mm/min. A nominal stress-nominal strain curve was determined, and the maximum stress was used as a tensile strength. The broken samples were butted against each other to determine the total elongation. The result was used as an elongation (El).

(5) Hardness of steel sheet after quenching (immersion-quench hardenability)

[0101] A flat test piece (15 mm wide × 40 mm long × 3 mm thick) was taken from a central portion in the width direction of each annealed steel sheet, and subjected to quenching treatment with oil cooling at 70°C as described below to determine the quenching hardness (immersion-quench hardenability). The quenching treatment was performed in a manner that the flat test piece was held at 900°C for 600 s and immediately cooled with oil at 70°C (70°C oil cooling). The quenching hardness was determined as follows: in a cut surface of the quenching-treated test piece, the hardness was measured in an inner region 70 μm from the surface layer in the width direction and at 1/4 from the surface layer in the width direction each at five points with a Vickers hardness tester under a load to 0.2 kgf, and the average hardness was determined as the quenching hardness (HV). The above-described inner region 70 μm from the surface layer in the thickness direction is expressed as "surface layer" in Table 2-2 and Table 3-2.

(6) Hardness of steel sheet after carburizing and quenching (carburizing hardenability)

[0102] Each annealed steel sheet was subjected to a carburizing and quenching treatment including steel soaking, carburizing treatment, and diffusion treatment at 930°C for 4 hours in total, held at 850°C for 30 minutes, and then cooled in oil (oil cooling temperature: 60°C). The hardness was measured under a load of 1 kgf from a position 0.1 mm deep from the steel sheet surface to a position 1.2 mm deep at intervals of 0.1 mm to determine the hardness (HV) at 0.1 mm from the surface layer and the effective case depth (mm) after carburizing and quenching. The effective case depth is defined as a depth at which the hardness measured from the surface after the heat treatment reaches 550 HV or more.

[0103] From the results obtained from the above (5) and (6), the hardenability was evaluated under conditions shown in Table 4. Table 4 presents acceptance criteria of hardenability depending on the C content, in which the hardenability can be evaluated as sufficient. When all of the hardness (HV) after 70°C oil cooling, the hardness (HV) at 0.1 mm deep from the surface layer after carburizing and quenching, and the effective case depth after carburizing and quenching satisfied the criteria in Table 4, the steel sheet was judged as acceptable (denoted by the symbol O) and evaluated as having high hardenability. When any of the values did not satisfy the criteria shown in Table 4, the steel sheet was judged as unacceptable (denoted by the symbol ×) and evaluated as having poor hardenability.

[Table 1]

Steel No.	Chemical composition (mass%)																			Ac_1 transformation temperature (°C)	Ar_1 transformation temperature (°C)	Ac_3 transformation temperature (°C)	Ar_3 transformation temperature (°C)	Remarks
	C	Si	Mn	P	S	sol. Al	N	Cr	B	Sb, Sn	Ti	Nb	Mo	Ta	Ni	Cu	V	W					
A	0.20	0.01	0.55	0.02	0.004	0.030	0.0044	0.50	0.0030	Sb+Sn:0.010	-	-	-	-	-	-	-	-	726	716	836	824	Inventive Steel
B	0.22	0.03	0.45	0.01	0.003	0.050	0.0041	0.40	0.0030	Sb:0.012	-	-	-	-	-	-	-	-	726	716	835	825	Inventive Steel
C	0.28	0.79	0.50	0.02	0.004	0.010	0.0044	0.12	0.0020	Sb:0.025	-	-	-	-	-	-	-	-	743	737	852	840	Inventive Steel
D	0.24	0.64	0.60	0.02	0.004	0.010	0.0044	0.65	0.0015	Sb+Sn:0.020	-	0.001	-	-	-	-	-	-	746	736	842	832	Inventive Steel
E	0.23	0.85	0.40	0.02	0.004	0.010	0.0044	0.50	0.0025	Sb:0.010	-	0.001	-	-	-	-	-	-	752	742	861	851	Comparative Steel
F	0.22	0.15	0.85	0.02	0.004	0.050	0.0050	0.30	0.0035	Sb+Sn:0.010	-	-	-	-	-	-	-	-	723	713	829	827	Comparative Steel
G	0.22	0.30	0.40	0.01	0.003	0.006	0.0045	0.02	0.0030	Sb:0.012	-	-	-	-	-	-	-	-	728	718	835	825	Inventive Steel
H	0.23	0.35	0.45	0.01	0.003	0.030	0.0050	0.40	0.0032	Sb:0.008	0.02	-	-	-	-	-	-	-	735	725	839	829	Inventive Steel
I	0.22	0.01	0.35	0.01	0.003	0.050	0.0050	1.05	0.0020	Sb+Sn:0.010	-	-	-	-	-	-	-	-	737	727	832	820	Comparative Steel
J	0.23	0.01	0.45	0.01	0.003	0.030	0.0050	0.40	0.0032	0.000	-	-	-	-	-	-	-	-	725	727	824	814	Comparative Steel
K	0.35	0.01	0.35	0.02	0.004	0.010	0.0044	0.01	0.0020	Sb:0.009	-	-	0.0015	-	0.001	-	-	-	720	716	810	798	Inventive Steel
L	0.33	0.15	0.31	0.01	0.003	0.120	0.0110	0.10	0.0015	Sb:0.025	0.01	-	-	-	-	-	-	-	726	716	855	845	Comparative Example
M	0.35	0.05	0.35	0.02	0.004	0.020	0.0044	0.20	0.0001	Sb+Sn:0.012	-	-	-	-	-	-	-	-	724	714	811	801	Comparative Steel
N	0.36	0.01	0.04	0.02	0.003	0.050	0.0047	0.20	0.0030	Sb+Sn:0.011	-	-	-	-	-	0.0150	-	-	726	717	830	819	Comparative Steel
O	0.45	0.03	0.35	0.02	0.004	0.030	0.0050	0.02	0.0026	Sb+Sn:0.100	-	-	-	0.0020	-	0.0015	-	-	720	723	801	790	Inventive Steel
P	0.48	0.25	0.31	0.01	0.004	0.010	0.0044	0.06	0.0025	Sb:0.009	-	-	-	-	0.025	-	0.0015	-	728	718	794	782	Inventive Steel
Q	0.48	0.03	0.28	0.01	0.002	0.035	0.0052	0.45	0.0010	Sb+Sn:0.012	-	-	-	-	-	-	-	0.0015	728	716	788	778	Inventive Steel
R	0.44	0.10	0.32	0.01	0.003	0.040	0.0047	0.05	0.0048	Sb:0.011	0.04	-	-	0.0015	-	-	-	-	723	713	803	793	Inventive Steel
S	0.18	0.05	0.45	0.01	0.004	0.035	0.0050	0.40	0.0030	Sb:0.010	0.04	-	-	-	-	-	-	-	726	715	840	829	Comparative Steel
T	0.55	0.25	0.45	0.01	0.003	0.040	0.0050	0.45	0.0020	Sb+Sn:0.008	-	-	0.0012	-	-	-	-	-	733	722	785	775	Comparative Steel

[Table 2-1]

Sample No.	Steel No.	Hot rolling conditions			Annealing conditions	
		Finishing temperature (°C)	Average cooling rate to 650°C to 750°C after finish rolling (°C/sec)	Coiling temperature (°C)	Average heating rate in temperature range from 450°C to 600°C (°C/h)	Annealing (annealing temperature-holding time)
1	A	850	40	550	45	715°C-30 h
2	A	850	55	480	60	715°C-30 h
3	A	850	55	680	15	715°C-30 h
4	A	850	55	620	15	710°C-15 h
5	B	845	30	550	30	715°C-30 h
6	B	845	30	550	30	770°C-25 h
7	B	845	30	510	15	715°C-30 h
8	B	845	30	620	5	715°C-30 h
9	C	860	40	620	35	715°C-22 h
10	D	860	60	680	90	710°C-25 h
11	E	880	50	580	20	715°C-30 h
12	F	840	50	620	30	710°C-25 h
13	G	850	50	600	30	680°C-25 h
14	H	850	40	580	50	715°C-30 h
15	H	850	40	510	40	715°C-0.25 h
16	I	840	50	600	40	715°C-30 h
17	J	830	80	700	20	715°C-30 h
18	K	830	60	700	40	715°C-30 h
19	L	860	40	700	50	715°C-30 h
20	M	880	50	680	60	715°C-30 h
21	N	840	50	660	40	715°C-30 h
22	O	830	50	590	40	715°C-30 h
23	P	830	25	550	40	715°C-30 h
24	Q	830	25	560	30	715°C-30 h
25	R	820	40	650	45	715°C-30 h
26	S	860	40	650	40	715°C-30 h
27	T	810	40	650	40	710°C-25 h

[Table 2-2]

Sample No.	Steel No.	Microstructure	[(Number of cementite grains with equivalent circle diameter of 0.1 μm or less)/(total number of cementite grains)] × 100 (%)	Average cementite grain size (μm)	Ferrite average grain size (μm)	Ferrite area fraction (%)	Proportion of cementite to entire microstructure (area%)	Pearlite area fraction (%)	Average concentration of solute B in portion 100 μm from surface layer (mass ppm)	Average concentration of N present as AlN in portion 100 μm from surface layer (mass ppm)	TS (MPa)	Total elongation (%)	Immersion-quench hardenability (HV)		Carburizing hardenability		Evaluation of hardenability	Remarks
													70°C oil cooling (surface layer)	70°C oil cooling (1/4 thickness)	Hardness at 0.1 mm from surface layer after carburizing and quenching (HV)	Effective case depth after carburizing and quenching (mm)		
1	A	ferrite + cementite	15	0.40	7	95	3.5	1.5	15	35	460	37	360	390	670	0.70	○	Example
2	A	ferrite + cementite	22	0.18	6	91	3.9	5.1	14	40	490	32	355	385	665	0.68	O	Comparative Example
3	A	ferrite + cementite	12	0.45	8	95	3.5	1.5	16	60	450	38	360	395	675	0.65	O	Example
4	A	ferrite + cementite	18	0.35	4	94	3.6	2.4	15	60	470	34	360	395	675	0.65	O	Example
5	B	ferrite + cementite	11	0.55	8	94	3.6	2.4	15	35	450	38	380	420	655	0.65	O	Example
6	B	ferrite + cementite + pearlite	4	0.65	11	80	0.5	19.5	15	40	460	31	370	420	655	0.64	O	Comparative Example

(continued)

Sample No.	Steel No.	Microstructure	[(Number of cementite grains with equivalent circle diameter of 0.1 μm or less)/(total number of cementite grains)] × 100 (%)	Average cementite grain size (μm)	Ferrite average grain size (μm)	Ferrite area fraction (%)	Proportion of cementite to entire microstructure (area%)	Pearlite area fraction (%)	Average concentration of solute B in portion 100 μm from surface layer (mass ppm)	Average concentration of N present as AlN in portion 100 μm from surface layer (mass ppm)	TS (MPa)	Total elongation (%)	Immersion-quench hardenability (HV)		Carburizing hardenability		Evaluation of hardenability	Remarks
													70°C oil cooling (surface layer)	70°C oil cooling (1/4 thickness)	Hardness at 0.1 mm from surface layer after carburizing and quenching (HV)	Effective case depth after carburizing and quenching (mm)		
7	B	ferrite + cementite	1	0.50	7	94	3.6	2.4	10	70	460	36	360	425	600	0.62	○	Example
8	B	ferrite + cementite	13	0.52	7	93	3.7	3.3	9	80	395	41	340	415	580	0.60	×	Comparative Example
9	C	ferrite + cementite	14	0.45	7	93	4.7	2.3	17	40	460	35	390	470	680	0.62	○	Example
10	D	ferrite + cementite	12	0.50	8	94	4.0	2.0	15	30	480	33	380	430	690	0.70	○	Example
11	E	ferrite + cementite	14	0.38	7	93	3.8	3.2	14	40	490	32	370	425	670	0.70	○	Comparative Example
12	F	ferrite + cementite	14	0.40	6	92	3.7	4.3	14	40	490	32	390	425	700	0.80	○	Comparative Example

(continued)

Sample No.	Steel No.	Microstructure	[(Number of cementite grains with equivalent circle diameter of 0.1 μm or less)/(total number of cementite grains)] × 100 (%)	Average cementite grain size (μm)	Ferrite average grain size (μm)	Ferrite area fraction (%)	Proportion of cementite to entire microstructure (area%)	Pearlite area fraction (%)	Average concentration of solute B in portion 100 μm from surface layer (mass ppm)	Average concentration of N present as AlN in portion 100 μm from surface layer (mass ppm)	TS (MPa)	Total elongation (%)	Immersion-quench hardenability (HV)		Carburizing hardenability		Evaluation of hardenability	Remarks
													70°C oil cooling (surface layer)	70°C oil cooling (1/4 thickness)	Hardness at 0.1 mm from surface layer after carburizing and quenching (HV)	Effective case depth after carburizing and quenching (mm)		
13	G	ferrite + cementite	17	0.30	5	94	3.7	2.3	15	40	430	40	370	425	650	0.65	○	Example
14	H	ferrite + cementite	12	0.50	8	92	3.8	4.2	12	35	430	40	370	430	700	0.70	○	Example
15	H	ferrite + cementite + pearlite	30	0.20	4	90	3.3	6.7	15	40	480	32	370	430	700	0.65	○	Comparative Example
16	I	ferrite + cementite	10	0.30	8	94	3.7	2.3	15	35	490	30	400	425	710	0.80	○	Comparative Example
17	J	ferrite + cementite	15	0.50	7	93	3.7	3.3	5	50	430	39	300	430	580	0.65	×	Comparative Example
18	K	ferrite + cementite	12	0.40	8	94	5.9	0.1	12	60	420	40	510	570	680	0.65	○	Example

(continued)

Sample No.	Steel No.	Microstructure	[(Number of cementite grains with equivalent circle diameter of 0.1 μm or less)/(total number of cementite grains)] × 100 (%)	Average cementite grain size (μm)	Ferrite average grain size (μm)	Ferrite area fraction (%)	Proportion of cementite to entire microstructure (area%)	Pearlite area fraction (%)	Average concentration of solute B in portion 100 μm from surface layer (mass ppm)	Average concentration of N present as AlN in portion 100 μm from surface layer (mass ppm)	TS (MPa)	Total elongation (%)	Immersion-quench hardenability (HV)		Carburizing hardenability		Evaluation of hardenability	Remarks
													70°C oil cooling (surface layer)	70°C oil cooling (1/4 thickness)	Hardness at 0.1 mm from surface layer after carburizing and quenching (HV)	Effective case depth after carburizing and quenching (mm)		
19	L	ferrite + cementite	12	0.41	8	94	5.5	0.5	12	200	420	38	380	480	580	0.65	×	Comparative Steel
20	M	ferrite + cementite	12	0.35	8	93	5.9	1.1	0	70	430	41	470	530	570	0.55	×	Comparative Steel
21	N	ferrite + cementite	11	0.40	7	94	6.0	0.0	15	50	410	42	470	490	590	0.50	×	Comparative Example
22	O	ferrite + cementite	7	0.40	9	92	7.5	0.5	17	40	460	35	670	680	700	0.70	○	Example
23	P	ferrite + cementite	13	0.45	10	92	8.0	0.0	15	35	460	36	680	700	675	0.70	○	Example
24	Q	ferrite + cementite	12	0.48	9	91	8.1	0.9	14	34	450	37	680	710	675	0.70	○	Example

(continued)

Sample No.	Steel No.	Microstructure	[(Number of cementite grains with equivalent circle diameter of 0.1 µm or less)/(total number of cementite grains)] × 100 (%)	Average cementite grain size (µm)	Ferrite average grain size (µm)	Ferrite area fraction (%)	Proportion of cementite to entire microstructure (area%)	Pearlite area fraction (%)	Average concentration of solute B in portion 100 µm from surface layer (mass ppm)	Average concentration of N present as AlN in portion 100 µm from surface layer (mass ppm)	TS (MPa)	Total elongation (%)	Immersion-quench hardenability (HV)		Carburizing hardenability		Evaluation of hardenability	Remarks
													70°C oil cooling (surface layer)	70°C oil cooling (1/4 thickness)	Hardness at 0.1 mm from surface layer after carburizing and quenching (HV)	Effective case depth after carburizing and quenching (mm)		
25	R	ferrite + cementite	9	0.50	9	92	7.4	0.6	14	38	440	37	580	620	695	0.70	○	Example
26	S	ferrite + cementite	12	0.40	7	95	2.7	2.3	15	40	400	42	310	380	700	0.60	×	Comparative Example
27	T	ferrite + cementite	25	0.35	6	90	9.2	0.8	15	40	520	28	680	720	700	0.68	○	Comparative Example

[Table 3-1]

Sample No.	Steel No.	Hot rolling conditions			Annealing conditions			
		Finishing temperature (°C)	Average cooling rate to 650°C to 750°C after finish rolling (°C/sec)	Coiling temperature (°C)	Average heating rate in temperature range from 450°C to 600°C (°C/h)	First-stage annealing (annealing temperature-holding time)	Average cooling rate from first stage to second stage (°C/h)	Second-stage annealing (annealing temperature-holding time)
28	A	850	40	680	50	790°C-8 h	10	710°C-30 h
29	A	850	55	680	50	790°C-8 h	10	710°C-15 h
30	A	850	55	680	10	790°C-8 h	10	710°C-30 h
31	A	850	40	680	50	820°C-0.1 h	10	710°C-30 h
32	B	845	30	620	40	780°C-10 h	12	710°C-20 h
33	B	845	30	620	40	860°C-8 h	10	710°C-30 h
34	B	845	30	670	15	800°C-6 h	50	710°C-30 h
35	C	860	40	680	35	790°C-7 h	12	710°C-25 h
36	D	860	60	620	90	750°C-8 h	10	715°C-20 h
37	E	880	50	480	30	755°C-4 h	10	690°C-30 h
38	F	840	50	510	30	750°C-4 h	10	690°C-20 h
39	G	850	50	550	60	790°C-8 h	10	710°C-30 h
40	H	850	40	510	50	760°C-8 h	10	710°C-25 h
41	I	840	50	600	40	770°C-6 h	10	710°C-30 h
42	J	830	80	700	20	800°C-6 h	10	710°C-25 h
43	K	830	60	700	15	800°C-6 h	10	710°C-25 h
44	L	860	40	700	50	800°C-6 h	10	710°C-25 h
45	M	880	50	680	50	800°C-6 h	10	710°C-20 h
46	N	840	50	660	40	790°C-8 h	15	705°C-30 h
47	O	830	50	590	40	790°C-4 h	8	710°C-25 h
48	Q	830	25	610	30	770°C-8 h	10	710°C-20 h

(continued)

Sample No.	Steel No.	Hot rolling conditions			Annealing conditions			
		Finishing temperature (°C)	Average cooling rate to 650°C to 750°C after finish rolling (°C/sec)	Coiling temperature (°C)	Average heating rate in temperature range from 450°C to 600°C (°C/h)	First-stage annealing (annealing temperature-holding time)	Average cooling rate from first stage to second stage (°C/h)	Second-stage annealing (annealing temperature-holding time)
49	R	820	40	700	45	800°C-8 h	10	710°C-30 h
50	S	860	40	650	40	810°C-4 h	10	710°C-21 h
51	T	810	40	650	40	800°C-6 h	10	710°C-25 h

[Table 3-2]

Sample No.	Steel No.	Microstructure	[(Number of cementite grains with equivalent circle diameter of 0.1 μm or less)/(total number of cementite grains)] × 100 (%)	Average cementite grain size (μm)	Ferrite average grain size (μm)	Ferrite area fraction (%)	Proportion of cementite to entire microstructure (area%)	Pearlite area fraction (%)	Average concentration of solute B (mass ppm)	Average concentration of N present as AlN (mass ppm)	TS (MPa)	Total elongation (%)	Immersion-quench hardenability (HV)		Carburizing hardenability		Evaluation of hardenability	Remarks
													70°C oil cooling (surface layer)	70°C oil cooling (1/4 thickness)	Hardness at 0.1 mm from surface layer after carburizing and quenching (HV)	Effective case depth after carburizing and quenching (mm)		
28	A	ferrite + cementite	1	1.5	15	95	3.8	1.2	15	30	400	42	360	395	670	0.72	○	Example
29	A	ferrite + cementite + pearlite	5	1.3	13	83	3.9	13.1	15	30	400	32	360	400	670	0.73	○	Comparative Example
30	A	ferrite + cementite	1	1.5	16	94	3.7	2.3	10	80	390	43	340	395	590	0.60	×	Comparative Example
31	A	ferrite + cementite	25	0.4	10	92	3.5	4.5	15	30	480	32	365	398	671	0.72	○	Comparative Example
32	B	ferrite + cementite	1	1.5	17	94	4.2	1.8	17	35	370	44	375	410	655	0.65	○	Example

(continued)

Sample No.	Steel No.	Microstructure	[(Number of cementite grains with equivalent circle diameter of 0.1 μm or less)/(total number of cementite grains)] × 100 (%)	Average cementite grain size (μm)	Ferrite average grain size (μm)	Ferrite area fraction (%)	Proportion of cementite to entire microstructure (area%)	Pearlite area fraction (%)	Average concentration of solute B (mass ppm)	Average concentration of N present as AlN (mass ppm)	TS (MPa)	Total elongation (%)	Immersion-quench hardenability (HV)		Carburizing hardenability		Evaluation of hardenability	Remarks
													70°C oil cooling (surface layer)	70°C oil cooling (1/4 thickness)	Hardness at 0.1 mm from surface layer after carburizing and quenching (HV)	Effective case depth after carburizing and quenching (mm)		
33	B	ferrite + cementite + pearlite	5	1.1	17	80	0.5	19.5	13	35	370	32	375	410	655	0.67	○	Comparative Example
34	B	ferrite + cementite + pearlite	3	1.2	15	83	4.2	12.8	14	36	371	32	375	405	655	0.65	○	Comparative Example
35	C	ferrite + cementite	1	1.3	14	94	5.2	0.8	15	70	410	40	390	465	680	0.63	○	Example
36	D	ferrite + cementite	1	2.0	17	94	4.5	1.5	10	50	385	41	380	415	675	0.70	○	Example
37	E	ferrite + cementite	1	1.1	12	93	4.3	2.7	16	30	485	32	370	425	671	0.70	○	Comparative Example

(continued)

Sample No.	Steel No.	Microstructure	[(Number of cementite grains with equivalent circle diameter of 0.1 μm or less)/(total number of cementite grains)] × 100 (%)	Average cementite grain size (μm)	Ferrite average grain size (μm)	Ferrite area fraction (%)	Proportion of cementite to entire microstructure (area%)	Pearlite area fraction (%)	Average concentration of solute B (mass ppm)	Average concentration of N present as AlN (mass ppm)	TS (MPa)	Total elongation (%)	Immersion-quench hardenability (HV)		Carburizing hardenability		Evaluation of hardenability	Remarks
													70°C oil cooling (surface layer)	70°C oil cooling (1/4 thickness)	Hardness at 0.1 mm from surface layer after carburizing and quenching (HV)	Effective case depth after carburizing and quenching (mm)		
38	F	ferrite + cementite	1	1.1	12	92	4.1	3.9	16	30	485	32	370	430	698	0.68	○	Comparative Example
39	G	ferrite + cementite	1	1.5	15	93	4.1	2.9	14	30	370	45	370	430	690	0.65	○	Example
40	H	ferrite + cementite	1	1.5	14	92	4.4	3.6	15	35	380	44	370	420	702	0.85	○	Example
41	I	ferrite + cementite	1	1.1	10	91	4.1	4.9	13	45	490	32	370	420	710	0.80	○	Comparative Example
42	J	ferrite + cementite	1	1.3	14	93	4.3	2.7	16	35	365	45	340	420	590	0.55	×	Comparative Example
43	K	ferrite + cementite	1	1.8	15	93	6.5	0.5	14	60	370	42	510	570	680	0.65	○	Example

(continued)

Sample No.	Steel No.	Microstructure	[(Number of cementite grains with equivalent circle diameter of 0.1 µm or less)/(total number of cementite grains)] × 100 (%)	Average cementite grain size (µm)	Ferrite average grain size (µm)	Ferrite area fraction (%)	Proportion of cementite to entire microstructure (area%)	Pearlite area fraction (%)	Average concentration of solute B (mass ppm)	Average concentration of N present as AlN (mass ppm)	TS (MPa)	Total elongation (%)	Immersion-quench hardenability (HV)		Carburizing hardenability		Evaluation of hardenability	Remarks
													70°C oil cooling (surface layer)	70°C oil cooling (1/4 thickness)	Hardness at 0.1 mm from surface layer after carburizing and quenching (HV)	Effective case depth after carburizing and quenching (mm)		
44	L	ferrite + cementite	1	1.5	13	93	6.2	0.8	12	200	370	43	380	480	580	0.65	×	Comparative Example
45	M	ferrite + cementite	1	1.3	15	93	6.7	0.3	0	70	390	43	470	530	570	0.55	×	Comparative Example
46	N	ferrite + cementite	1	2.5	20	93	6.8	0.2	15	35	365	44	470	490	590	0.50	×	Comparative Example
47	O	ferrite + cementite	1	1.9	18	91	8.4	0.6	16	30	410	38	670	680	705	0.68	○	Example
48	Q	ferrite + cementite	1	1.3	13	91	8.9	0.1	14	35	400	40	680	710	675	0.70	○	Example
49	R	ferrite + cementite	1	1.4	13	91	8.2	0.8	15	40	400	39	685	705	670	0.67	O	Example

(continued)

Sample No.	Steel No.	Microstructure	[(Number of cementite grains with equivalent circle diameter of 0.1 μm or less)/(total number of cementite grains)] × 100 (%)	Average cementite grain size (μm)	Ferrite average grain size (μm)	Ferrite area fraction (%)	Proportion of cementite to entire microstructure (area%)	Pearlite area fraction (%)	Average concentration of solute B (mass ppm)	Average concentration of N present as AlN (mass ppm)	TS (MPa)	Total elongation (%)	Immersion-quench hardenability (HV)		Carburizing hardenability		Evaluation of hardenability	Remarks
													70°C oil cooling (surface layer)	70°C oil cooling (1/4 thickness)	Hardness at 0.1 mm from surface layer after carburizing and quenching (HV)	Effective case depth after carburizing and quenching (mm)		
50	S	ferrite + cementite	1	1.4	15	94	3.0	3.0	14	35	360	45	310	380	700	0.60	×	Comparative Example
51	T	ferrite + cementite + pearl ite	25	1.5	12	50	10.5	39.5	14	35	490	32	680	720	700	0.68	○	Comparative Example

[Table 4]

C content	Hardness after 70°C oil cooling (HV)	Hardness at 0.1 mm deep from surface layer after carburizing and quenching (HV)	Effective case depth after carburizing and quenching (mm)
C < 0.20%	≥ 340	≥ 600	≥ 0.60
0.20% ≤ C < 0.30%	≥ 350	≥ 600	≥ 0.60
0.30% ≤ C < 0.35%	≥ 400	≥ 600	≥ 0.60
0.35% ≤ C < 0.40%	≥ 490	≥ 600	≥ 0.60
0.40% ≤ C < 0.45%	≥ 580	≥ 600	≥ 0.60
0.45% ≤ C < 0.50%	≥ 670	≥ 600	≥ 0.60
0.50% ≤ C	≥ 700	≥ 650	≥ 0.60

[0104] The results in Table 2-2 and Table 3-2 show that the high-carbon hot-rolled steel sheets of Examples each have a microstructure including ferrite and cementite, the proportion of the number of cementite grains having an equivalent circle diameter of 0.1 μm or less to the total number of cementite grains being 20% or less, the average cementite grain size being 2.5 μm or less, the cementite accounting for 3.5% or more and 10.0% or less of the entire microstructure, and have both high cold workability and high hardenability. In addition, the high-carbon hot-rolled steel sheets of Examples were provided with excellent mechanical properties, i.e., a tensile strength of 480 MPa or less and a total elongation (El) of 33% or more.

[0105] In contrast, in Comparative Examples outside the scope of the present invention, any one or more of the chemical composition, the microstructure, the amount of solute B, and the amount of N in AlN do not satisfy the scope of the present invention, and as a result, the target performance described above cannot be satisfied in any one or more of the cold workability and the hardenability. In some Comparative Examples, the target properties were not satisfied in one or more of the tensile strength (TS) and the total elongation (El). For example, in Table 2-2 and Table 3-2, Steel S has a C content lower than the range of the present invention and thus does not satisfy the immersion-quench hardenability. Steel T has a C content higher than the range of the present invention and thus does not satisfy the TS and total elongation of the steel sheet.

Claims

1. A high-carbon hot-rolled steel sheet having a chemical composition comprising, by mass%,

C: 0.20% or more and 0.50% or less,
Si: 0.8% or less,
Mn: 0.10% or more and 0.80% or less,
P: 0.03% or less,
S: 0.010% or less,
sol. Al: 0.10% or less,
N: 0.01% or less,
Cr: 1.0% or less,
B: 0.0005% or more and 0.005% or less, and
one or two selected from Sb and Sn in an amount of 0.002% or more and 0.1% or less in total, with the balance being Fe and unavoidable impurities,
the steel sheet having a microstructure including ferrite, cementite, and pearlite that accounts for 6.5% or less of the entire microstructure by area fraction,
wherein regarding the cementite, a proportion of a number of cementite grains having an equivalent circle diameter of 0.1 μm or less to a total number of cementite grains is 20% or less, an average cementite grain

size is 2.5 μm or less, and the cementite accounts for 3.5% or more and 10.0% or less of the entire microstructure by area fraction,
an average concentration of solute B in a region extending from a surface layer to a depth of 100 μm is 10 mass ppm or more, and
an average concentration of N present as AlN in the region extending from the surface layer to the depth of 100 μm is 70 mass ppm or less.

2. The high-carbon hot-rolled steel sheet according to Claim 1, having a tensile strength of 480 MPa or less and a total elongation of 33% or more.

3. The high-carbon hot-rolled steel sheet according to Claim 1 or 2, wherein the ferrite has an average grain size of 4 to 25 μm.

4. The high-carbon hot-rolled steel sheet according to any one of Claims 1 to 3, wherein the chemical composition further comprises, by mass%, one or two groups selected from Group A and Group B:

Group A: Ti: 0.06% or less, and
Group B: one or two or more selected from Nb, Mo, Ta, Ni, Cu, V, and W each in an amount of 0.0005% or more and 0.1% or less.

5. A method for manufacturing the high-carbon hot-rolled steel sheet according to any one of Claims 1 to 4, the method comprising:

subjecting a steel having the chemical composition to hot rough rolling, then performing finish rolling at a finishing temperature equal to or higher than an Ar_3 transformation temperature, and then performing cooling to 650°C to 750°C at an average cooling rate of 20°C/sec to 100°C/sec;
performing coiling at a coiling temperature of 500°C to 700°C to obtain a hot-rolled steel sheet; and
then heating the hot-rolled steel sheet in a temperature range from 450°C to 600°C at an average heating rate of 15°C/h or more and performing annealing that involves holding at an annealing temperature lower than an Ac_1 transformation temperature for 1.0 h or more.

6. A method for manufacturing the high-carbon hot-rolled steel sheet according to any one of Claims 1 to 4, the method comprising:

subjecting a steel having the chemical composition to hot rough rolling, then performing finish rolling at a finishing temperature equal to or higher than an Ar_3 transformation temperature, and then performing cooling to 650°C to 750°C at an average cooling rate of 20°C/sec to 100°C/sec;
performing coiling at a coiling temperature of 500°C to 700°C to obtain a hot-rolled steel sheet; and
then heating the hot-rolled steel sheet in a temperature range from 450°C to 600°C at an average heating rate of 15°C/h or more and performing annealing that involves holding at a temperature equal to or higher than an Ac_1 transformation temperature and equal to or lower than an Ac_3 transformation temperature for 0.5 h or more, followed by cooling to a temperature lower than an Ar_1 transformation temperature at an average cooling rate of 1°C/h to 20°C/h, and holding at a temperature lower than the Ar_1 transformation temperature for 20 h or more.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2020/000783

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl. C22C38/00(2006.01)i, C21D9/46(2006.01)i, C22C38/60(2006.01)i
FI: C22C38/00 301W, C21D9/46 T, C22C38/60

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)
Int. Cl. C22C38/00-38/60, C21D9/46

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2020
Registered utility model specifications of Japan	1996-2020
Published registered utility model applications of Japan	1994-2020

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 A	WO 2010/106748 A1 (NIPPON STEEL CORP.) 23 September 2010, claims, paragraphs [0077], [0096]-[0099], tables 5, 6, 11, 12	4-5 1-3, 6
A	WO 2015/146173 A1 (JFE STEEL CORP.) 01 October 2015	1-6
A	WO 2015/146174 A1 (JFE STEEL CORP.) 01 October 2015	1-6
A	WO 2016/190396 A1 (NIPPON STEEL & SUMITOMO METAL CORP.) 01 December 2016	1-6
A	JP 2004-250767 A (NIPPON STEEL CORP.) 09 September 2004	1-6

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

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance
"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 19.03.2020	Date of mailing of the international search report 31.03.2020
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2020/000783

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	WO 2019/131099 A1 (JFE STEEL CORP.) 04 July 2019	1-6

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/JP2020/000783

Patent Documents referred to in the Report	Publication Date	Patent Family	Publication Date
WO 2010/106748 A1	23.09.2010	KR 10-2011-0115608 A CN 102348822 A TW 201038751 A	
WO 2015/146173 A1	01.10.2015	US 2017/0121787 A1 EP 3091098 A1 CN 106133170 A KR 10-2016-0138230 A TW 201538744 A	
WO 2015/146174 A1	01.10.2015	US 2017/0121786 A1 EP 3091097 A1 CN 106133169 A KR 10-2016-0138231 A TW 201538745 A	
WO 2016/190396 A1	01.12.2016	US 2018/0135146 A1 EP 3305930 A1 KR 10-2017-0138510 A CN 107614726 A MX 2017014938 A BR 112017024957 A2 TW 201704501 A	
JP 2004-250767 A	09.09.2004	(Family: none)	
WO 2019/131099 A1	04.07.2019	(Family: none)	

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2009299189 A **[0011]**
- JP 2005344194 A **[0011]**
- JP 4012475 B **[0011]**
- JP 4782243 B **[0011]**
- JP 2015017283 A **[0011]**
- JP 2015017284 A **[0011]**
- WO 2015146173 A **[0011]**
- JP 5458649 B **[0011]**

Non-patent literature cited in the description

- **SATOSHI KINOSHIRO ; TOMOHARU ISHIDA ; KUNIO INOSE ; KYOKO FUJIMOTO.** *Tetsu-to-Hagane (Iron and Steel),* 2013, vol. 99 (5), 362-365 **[0097] [0099]**