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(54) **SEAMLESS STEEL PIPE, METHOD FOR MANUFACTURING SEAMLESS STEEL PIPE, PRESSURE VESSEL, PRESSURE VESSEL FOR HYDROGEN GAS, AND METHOD FOR MANUFACTURING PRESSURE VESSEL OR PRESSURE VESSEL FOR HYDROGEN GAS**

(57) The present invention has been made in view of the above circumstances, and an object thereof is to provide a seamless steel pipe having a high martensite fraction, being thick-walled and having high strength, and having excellent quench-crack resistance and delayed-fracture characteristics, which can be extremely suitably used as a member of a pressure vessel and the like. Further, an object thereof is to provide a method for manufacturing a seamless steel pipe, a pressure vessel, a pressure vessel for hydrogen gas, and a method for manufacturing a pressure vessel or a pressure vessel for hydrogen gas.

A seamless steel pipe has a specific component composition, satisfying formula (1), a degree of segregation of Mn at an inner surface of the steel pipe of less than 1.50, a metallic microstructure having an area fraction of martensite of 85% or more, and a cross-sectional hardness of 250 HV or more and less than 480 HV.

$$[P] \leq 0.042 - 0.002[C] - 0.024[Mn] - 0.001[Mo] - 0.001[Cr] - 0.002[Ni] \cdots (1) \quad (1)$$

(where [element] represents a content (mass%) of the element described in each set of brackets).

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Description

Technical Field

[0001] The present invention relates to a seamless steel pipe, and relates to a thick-walled and high-strength seamless steel pipe having a high martensite fraction, which is excellent in quench-crack resistance and delayed-fracture characteristics and, in particular, can be used extremely suitably as a member of a pressure vessel and the like, and a method for manufacturing the seamless steel pipe. Further, the present invention relates to a pressure vessel, a pressure vessel for hydrogen gas, and a method for manufacturing a pressure vessel or a pressure vessel for hydrogen gas.

Background Art

[0002] A seamless steel pipe (also simply referred to as a steel pipe) is used for various applications such as piping and structural members because it is excellent in strength and relatively inexpensive, and, in particular, is useful as a member used in a structure such as a pressure vessel that needs relaxation of stress concentration. The higher the pressure inside the steel pipe becomes, the more it is necessary to increase the strength of the steel pipe; in addition, in order to reduce the strength of fatigue caused by pressure fluctuation, a design in which the wall thickness of the steel pipe is increased is required. Further, for a pressure vessel, it is preferable to apply a steel pipe having a high martensite fraction that can ensure high strength against fatigue. However, for a steel pipe having a high martensite fraction and being thick-walled and high-strength, when quenching treatment indispensable for increasing strength is carried out, cracking occurs, and the problem of quench cracking becomes conspicuous.

[0003] Therefore, various techniques have been proposed in order to reduce the quench-cracking risk of a high-strength steel pipe.

[0004] For example, Patent Literature 1 proposes a technique of reducing quench-cracking risk by controlling heat treatment so as to optimize thermal stress and transformation stress, by cooling only from the inner surface of the steel pipe.

[0005] Further, Patent Literature 2 proposes a technique of reducing quench-cracking risk by reducing, among the component composition of the steel pipe, in particular, the concentration of P.

Citation List

Patent Literature

[0006]

PTL 1: Japanese Unexamined Patent Application Publication No. Hei 9-104925

PTL 2: International Publication No. WO 2018/055937

Summary of Invention

Technical Problem

[0007] In Patent Literature 1 above, quench-crack resistance in an actual steel-pipe shape is evaluated, but no view is shown regarding the P concentration, which is known to have a remarkable contribution to quench-crack resistance.

[0008] On the other hand, in Patent Literature 2 above, the influence of the P concentration is evaluated, but evaluation is performed using a test piece that is taken from a 1/4 thickness position of the steel pipe and that has a testpiece cross section in which a circular hole is provided in a disk, the wall thickness in the cross section being extremely inhomogeneous and the balance between thermal stress and transformation stress being intentionally deteriorated. In addition, contribution of segregation of P that inevitably occurs in a process using continuous casting technology cannot be considered.

[0009] Further, when manufacturing a steel pipe having a high martensite fraction and being thick-walled and high-strength, it is necessary to ensure hardenability, but ensuring hardenability by adding a large amount of alloying elements leads to an increase in cost. Therefore, it is more important to ensure hardenability by the cooling rate, and the cooling rate at the time of quenching is preferably as fast as possible. In addition, due to the seamless steel pipe being manufactured by rolling while forming a hole at the cross-section center of a solid cylindrical steel material cast or forged, unlike the segregation distribution of P in a plate-shaped steel material, segregation of P exists on the inner-surface side of the steel pipe. That is, it is important to consider the balance in a state where the highest point of the temperature distribution in the wall-thickness direction and the highest point of the segregation of P are different. Further, this effect appears more remarkably as the wall thickness of the steel pipe becomes thicker. Therefore, it is important to evaluate the presen-

ce/absence of quench cracking due to the balance between thermal stress and transformation stress in an actual shape, but in Patent Literature 1 and 2 above, evaluation in an actual shape is not performed. Further, delayed-fracture characteristics are also not particularly described.

[0010] The present invention has been made in view of the above circumstances, and an object thereof is to provide a seamless steel pipe that has a thick wall with a high martensite fraction and high strength, and that combines excellent quench-crack resistance and delayed-fracture characteristics, and that can be used extremely suitably as a member of a pressure vessel and the like. Further, an object thereof is to provide a method for manufacturing a seamless steel pipe, a pressure vessel, a pressure vessel for hydrogen gas, and a method for manufacturing a pressure vessel or a pressure vessel for hydrogen gas.

Solution to Problem

[0011] As a result of studies conducted by the present inventors in order to solve the above problems, it was found that, by optimizing the P concentration in the component composition of the seamless steel pipe, as well as rolling conditions in a pipe-forming process of the seamless steel pipe and heat-treatment conditions after the pipe-forming process, segregation of P on the inner-surface side of the seamless steel pipe can be controlled, and excellent quench-crack resistance and delayed-fracture characteristics can be obtained even in a thick-walled seamless steel pipe. On the other hand, since the P concentration in the seamless steel pipe is designed to be low in order to suppress segregation of P, there is also a problem that it is difficult to judge the degree of segregation of P. Therefore, focusing on Mn, which has high affinity with P, it was confirmed that a high correlation relationship is observed between the P concentration and the Mn concentration. Further, in the present invention, since the Mn concentration in the steel pipe is designed to be high, it is more reliable to evaluate the degree of segregation of Mn when evaluating the degree of segregation of P. Accordingly, it was found that quench-crack resistance and delayed-fracture characteristics can be improved by controlling the degree of segregation of Mn on the inner-surface side of the seamless steel pipe by optimizing the rolling conditions in the pipe-forming process of the seamless steel pipe and the heat-treatment conditions after the pipe-forming process. The gist of the present invention is described below.

[1] A seamless steel pipe which includes:

a component composition containing, in mass %, C: 0.20 to 0.60%,

Si: 0.01 to 2.0%,

Mn: 0.5 to 1.2%,

S: 0.010% or less,

O: 0.005% or less,

N: 0.010% or less,

Al: 0.01 to 0.08%,

Mo: 0.005 to 1.0%,

Cr: 0.005 to 3.0%, and

Ni: 0.005 to 3.0%,

optionally one or two or more selected from

Ti: 0.0001 to 0.1%,

Cu: 0.0001 to 5.0%,

Co: 0.0001 to 5.0%,

B: 0.0001 to 0.01%,

V: 0.0001 to 1.0%,

W: 0.0001 to 5.0%,

Nb: 0.0001 to 0.1%,

Zr: 0.0001 to 0.2%,

Hf: 0.0001 to 0.2%,

Ta: 0.0001 to 0.2%,

Sb: 0.0001 to 0.1%,

Sn: 0.0001 to 0.1%,

Ca: 0.0001 to 0.01%,

Mg: 0.0001 to 0.01%, and

REM: 0.0001 to 0.5%, and

the component composition further containing P so as to satisfy the following formula (1):

$$[P] \leq 0.042 - 0.002[C] - 0.024[Mn] - 0.001[Mo] - 0.001[Cr] - 0.002[Ni] \cdots (1) \quad (1)$$

(where [element] in formula (1) represents the content (mass %) of the element described in the brackets), the balance being Fe and unavoidable impurities;
a degree of segregation of Mn from an inner surface of the steel pipe to a 1/6 wall-thickness position of less than 1.50;
a metallic microstructure having an area fraction of martensite of 85% or more; and
a cross-sectional hardness of 250 HV or more and less than 480 HV.

[2] The seamless steel pipe according to [1], wherein the wall thickness of the steel pipe is 40 mm or more.

[3] The seamless steel pipe according to [1] or [2], wherein, from the inner surface of the steel pipe to a 1/6 wall-thickness position, the number of inclusions having an aspect ratio of 2 or less and a length of a long side of 10 μm or more is 10 pieces per 100 mm² or less.

[4] A method for manufacturing the seamless steel pipe according to any one of [1] to [3], the method includes:

a pipe-forming step of pipe-forming heated material such that a ratio of an inner diameter of the steel pipe divided by a wall thickness is 2.0 times or more;
a quenching step of heating the heated steel pipe to a temperature range of 860°C or more, holding in the temperature range for 30 min or more, water cooling under conditions such that an average cooling rate in a temperature range of 800 to 350°C is 3°C/s or more, wherein, in the water cooling, the steel pipe is cooled while bringing a cooling medium into contact with an inner surface of the steel pipe at a flow rate of 0.5 m³/min or more in a state that the steel pipe is rotated in a circumferential direction of the steel pipe; and
a tempering step of, after the quenching step, holding the steel pipe under conditions of 30 min or more in a temperature range in which the temperature is 400 to 680°C.

[5] The method for manufacturing the seamless steel pipe according to [4], wherein the pipe-forming step is performed such that a shape of the steel pipe satisfies the following formula (2).

$$(\text{EXP}(\text{coefficient } K \times \text{wall thickness}) / \text{area of circumferential cross section}) \times 10^6 < 210 \quad (2)$$

$$K = \{0.41([C] - 0.24) + 4.58[Mn] + 0.21[Cr] + 0.25[Ni]\} / 100$$

$$\dots (3)$$

(where [element] in formula (3) represents the content (mass %) of the element described in the brackets.)

[6] A pressure vessel wherein the seamless steel pipe according to any one of [1] to [3] is used as the pressure vessel.

[7] A pressure vessel for hydrogen gas wherein the seamless steel pipe according to any one of [1] to [3] is used as the pressure vessel.

[8] A method for manufacturing a pressure vessel or a pressure vessel for hydrogen gas, the method comprising processing the seamless steel pipe according to any one of [1] to [3].

Advantageous Effects of Invention

[0012] The seamless steel pipe of the present invention achieves high strength while having a high martensite fraction and a thick wall, and is excellent in quench-crack resistance and delayed-fracture characteristics.

Description of Embodiments

[0013] Hereinafter, the present invention will be described in detail. Note that the following description shows an example of a preferred embodiment of the present invention, and the present invention is not limited thereto. First, the component composition of a seamless steel pipe (also simply referred to as a steel pipe) will be described.

C: 0.20 to 0.60%

[0014] C is an element necessary for increasing the strength of the steel pipe. Strength is an important required characteristic as a structural material. It is preferable that the cross-sectional hardness of the steel pipe after quenching and tempering be 250 HV or more, and, in order to obtain such cross-sectional hardness, the C content is set to 0.20% or

more. The C content is preferably 0.25% or more, more preferably 0.30% or more, further preferably 0.33% or more, and most preferably 0.35% or more. On the other hand, if the C content exceeds 0.60%, quench cracking may occur when quenching is performed; therefore, the C content is set to 0.60% or less. In order to reduce the quench-cracking risk, the C content is preferably 0.50% or less, more preferably 0.45% or less, and further preferably 0.42% or less.

Si: 0.01 to 2.0%

[0015] Si is an element that contributes to increasing the strength of the steel pipe by solid-solution strengthening. In order to obtain the above effect, the Si content is set to 0.01% or more. The Si content is preferably 0.10% or more, more preferably 0.15% or more, further preferably 0.18% or more, and most preferably 0.20% or more. On the other hand, if the Si content exceeds 2.0%, the effect is saturated, and further the surface properties of the steel pipe deteriorate and rolling workability in the pipe-forming process also decreases. Therefore, the Si content is set to 2.0% or less. The Si content is preferably 1.5% or less, more preferably 1.0% or less, further preferably 0.5% or less, and most preferably 0.4% or less.

Mn: 0.5 to 1.2%

[0016] Mn is an element that contributes to the increase in strength of the steel pipe by solid-solution strengthening and improvement of hardenability. In order to obtain the above effect, the Mn content is set to 0.5% or more. The Mn content is preferably 0.55% or more, more preferably 0.6% or more, further preferably 0.65% or more, and most preferably 0.68% or more. On the other hand, if Mn is excessive, it becomes difficult to perform rolling in the pipe-forming process, and, in addition, austenite remains and fatigue characteristics deteriorate. Further, as described later, if Mn is excessively contained, the degree of segregation of Mn increases more, and the quench-cracking risk increases. Therefore, the Mn content is set to 1.2% or less. The Mn content is preferably 1.0% or less, more preferably 0.9% or less, and further preferably 0.88% or less.

S: 0.010% or less

[0017] Excessive S causes hot shortness and may cause manufacturing defects. Further, S forms an inclusion MnS and lowers toughness. Further, it also lowers delayed-fracture characteristics. These influences do not become a problem if the S content is 0.010% or less. Therefore, the S content is set to 0.010% or less. The S content is preferably 0.005% or less, more preferably 0.003% or less. On the other hand, an excessive reduction such that the S content is less than 0.0001% involves an increase in desulfurization cost in the steelmaking process. Therefore, the S content is preferably 0.0001% or more, more preferably 0.0002% or more, further preferably 0.0005% or more, and most preferably 0.001% or more.

O: 0.005% or less

[0018] O exists in the steel pipe as an impurity, and if the O content exceeds 0.005%, it forms coarse and high-hardness oxides and lowers mechanical characteristics such as toughness, and, in addition, increases the quench-cracking risk. Therefore, the O content is set to 0.005% or less. The O content is preferably as small as possible, preferably 0.004% or less, more preferably 0.003% or less, and further preferably 0.002% or less. On the other hand, an excessive reduction such that the O content is less than 0.0001% involves an increase in cost in the steelmaking process. Therefore, the O content is preferably 0.0001% or more, more preferably 0.0002% or more, further preferably 0.0005% or more, and most preferably 0.001% or more.

N: 0.010% or less

[0019] The influence of N on the strength of the steel pipe is small, and the effect of the present invention is not impaired if the N content is 0.010% or less. Therefore, the N content is set to 0.010% or less. The N content is preferably 0.008% or less, more preferably 0.005% or less, further preferably 0.0045% or less, and most preferably 0.004% or less. On the other hand, from the viewpoint of improving toughness, it is desirable that the N content be small, but excessive reduction increases cost in the steelmaking process; therefore, the N content is preferably 0.0001% or more, more preferably 0.001% or more.

Al: 0.01 to 0.08%

[0020] Al is an element effective as a deoxidizer in the steelmaking process. In order to obtain the effect, the Al content is set to 0.01% or more. The Al content is preferably 0.02% or more. On the other hand, if the Al content exceeds 0.08%, the

effect is saturated; therefore, the Al content is set to 0.08% or less. The Al content is preferably 0.06% or less, more preferably 0.05% or less, and further preferably 0.04% or less.

Mo: 0.005 to 1.0%

[0021] Mo is an element that improves hardenability, and contributes to increasing the strength of the steel pipe, and also has an action of increasing the ratio of microstructures other than ferrite (in particular, martensite) in the metallic microstructure by improving hardenability of the steel pipe, and is an element necessary for obtaining a high martensite fraction. Further, Mo improves quench-crack resistance by suppressing ferrite transformation. Further, by containing Mo, the cooling rate required for obtaining the above metallic microstructure is reduced, and the quench-cracking risk during heat treatment of the steel pipe can be lowered, and the effect of improving delayed-fracture characteristics is also high. In order to obtain the above effect, the Mo content is set to 0.005% or more. The Mo content is preferably 0.008% or more, more preferably 0.1% or more. On the other hand, if the Mo content exceeds 1.0%, the effect is saturated and becomes a factor of cost increase; therefore, the Mo content is set to 1.0% or less. The Mo content is preferably 0.8% or less, more preferably 0.5% or less, further preferably 0.3% or less, and most preferably 0.25% or less.

Cr: 0.005 to 3.0%

[0022] Cr is an element that improves hardenability, and contributes to increasing the strength of the steel pipe, and also has an action of increasing the ratio of microstructures other than ferrite (in particular, martensite) in the metallic microstructure by improving hardenability of the steel pipe, and is an element necessary for obtaining a high martensite fraction. Further, Cr improves quench-crack resistance by suppressing ferrite transformation. Further, by containing Cr, the cooling rate required for obtaining the above metallic microstructure can be reduced, and the quench-cracking risk during heat treatment of the steel pipe can be lowered. In order to obtain the above effect, the Cr content is set to 0.005% or more. The Cr content is preferably 0.1% or more, more preferably 0.5% or more, further preferably 0.7% or more, and most preferably 0.9% or more. On the other hand, if the Cr content exceeds 3.0%, the effect is saturated and, further, a predetermined degree of segregation of Mn cannot be obtained and quench-crack resistance deteriorates; therefore, the Cr content is set to 3.0% or less. The Cr content is preferably 2.0% or less, more preferably 1.5% or less, further preferably 1.3% or less, and most preferably 1.2% or less.

Ni: 0.005 to 3.0%

[0023] Ni is an element that improves hardenability and contributes to increasing the strength of the steel pipe. Further, as a result of improved hardenability, even in a steel pipe in which a portion where the cooling rate tends to be slow is likely to occur, such as one having a wall thickness of 40 mm or more, the strength can be increased. Further, Ni has an action of increasing the ratio of microstructures other than ferrite (in particular, martensite) in the metallic microstructure by improving hardenability of the steel pipe, and is an element necessary for obtaining a high martensite fraction. As a result, Ni improves quench-crack resistance by suppressing ferrite transformation. In order to obtain the above effect, the Ni content is set to 0.005% or more. The Ni content is preferably 0.01% or more, more preferably 0.5% or more, and further preferably 0.8% or more. On the other hand, excessive content increases cost; therefore, the Ni content is set to 3.0% or less. Preferably, the Ni content is set to 2.5% or less, more preferably 2.0% or less, and further preferably 1.8% or less.

[0024] P satisfies the following formula (1):

It is important that P satisfies the following formula (1).

$$[P] \leq 0.042 - 0.002[C] - 0.024[Mn] - 0.001[Mo] - 0.001[Cr] - 0.002[Ni] \cdots (1)$$

(However, in formula (1), the [element] represents content (mass %) of the element described in the brackets.)

[0025] P is an element that contributes to an increase in the strength of the steel pipe by solid-solution strengthening, and is also an element that lowers quench-crack resistance of the steel pipe.

[0026] As a mechanism of quench cracking, it is known that P trapped at grain boundaries lowers the bonding strength of the grain boundaries. Grain boundaries present in steel materials are planar lattice defects in which the crystal structure is disordered, and, compared with the density in the matrix in which atoms are arranged regularly and periodically, the density of lattice defects is lower. That is, the volume of gaps between atoms is large, and contained elements are easily trapped.

[0027] Trapping of P at grain boundaries can be broadly divided into two factors. The first is macro-segregation, which is a concentration distribution in a steel-material cross section that occurs due to differences in melting point for each element when the steel material is solidified from a liquid to a solid. The second is micro-segregation, which is a concentration distribution in a steel-material microstructure that occurs due to diffusion of contained elements from the matrix to grain boundaries during heat treatment of the steel material.

[0028] That is, by reducing each of macro-segregation of P and micro-segregation of P, the quench-cracking risk of the steel pipe finally obtained can be reduced. Hereinafter, in the present invention, the description "segregation" is defined as including both macro-segregation and micro-segregation, and each is also distinguished.

[0029] When manufacturing a thick-walled and high-strength seamless steel pipe, it is essential to contain elements that improve hardenability in order to ensure hardenability, but the quench-cracking risk increases. Further, the risk that delayed-fracture characteristics deteriorate also increases. P is an element that lowers bonding strength of grain boundaries, and, by reducing micro-segregation of P, grain-boundary cracking, which is an initiation point of delayed fracture, can be suppressed, and therefore improvement of delayed-fracture characteristics is expected. Therefore, it is important to reduce segregation of P in order to ensure quench-crack resistance and delayed-fracture characteristics of the seamless steel pipe.

[0030] In formula (1), which is a condition necessary for reducing segregation of P, the reasons why the P content has a relationship with the contents of C, Mn, Mo, Cr, and Ni are as follows.

[0031] C is a solid-solution-type atom that contributes to an increase in strength, and is a factor that strongly inhibits movement of dislocations within grains. By this effect, grain-interior strength increases, and the load on grain boundaries relatively increases. That is, when C is contained, the quench-cracking risk increases; therefore, it is preferable to lower the P content.

[0032] Mn has been conventionally known to have particularly high affinity with P, and reducing micro-segregation of Mn leads to reducing micro-segregation of P as a result. That is, when Mn is contained, the quench-cracking risk increases; therefore, it is preferable to lower the P content.

[0033] Further, Mo, Cr, and Ni are elements that improve hardenability, and when these elements are contained, the quench-cracking risk increases; therefore, it is preferable to lower the P content.

[0034] In addition, Cr and Ni are transition metals of the fourth period in the periodic table, similarly to Mn, and, compared with other contained elements, they do not easily inhibit diffusion of Mn atoms in the Fe matrix. In other words, Mn atoms become easier to diffuse. That is, Cr and Ni are elements having an effect of promoting micro-segregation of Mn, and when Cr and Ni are contained, the quench-cracking risk increases; therefore, it is preferable to lower the P content.

[0035] Note that, in the case of a seamless steel pipe in which macro-segregation exists on the inner-surface side of the steel pipe, by satisfying formula (1), it becomes possible to suppress cracking (quench cracking) that occurs on the inner surface of the steel pipe during quenching.

[0036] However, excessive reduction of the P content lowers production efficiency and causes an increase in refining cost; therefore, the P content is preferably set to 0.001% or more.

[0037] The above-described components are elements that are essential in the present invention.

[0038] In one embodiment of the present invention, the steel pipe has a component composition containing the above elements, and the balance being Fe and unavoidable impurity elements.

[0039] Here, "unavoidable impurities" are impurities unavoidably mixed in from raw materials, a manufacturing process, manufacturing equipment, or the like, and are permitted to be contained within a range that does not hinder the object of the present invention. As raw materials, iron ore, reduced iron, scrap, and the like can be mentioned. As impurities, for example, Zn, Pb, As, Bi, and the like can be mentioned.

[0040] Further, in another embodiment of the present invention, the component composition of the steel pipe can optionally contain one or more kinds of elements listed below. Elements to be contained as needed as appropriate are one or two or more kinds selected from Ti: 0.0001 to 0.1%, Cu: 0.0001 to 5.0%, Co: 0.0001 to 5.0%, B: 0.0001 to 0.01%, V: 0.0001 to 1.0%, W: 0.0001 to 5.0%, Nb: 0.0001 to 0.1%, Zr: 0.0001 to 0.2%, Hf: 0.0001 to 0.2%, Ta: 0.0001 to 0.2%, Sb: 0.0001 to 0.1%, Sn: 0.0001 to 0.1%, Ca: 0.0001 to 0.01%, Mg: 0.0001 to 0.01%, and REM: 0.0001 to 0.5%.

Ti: 0.0001 to 0.1%

[0041] Ti contributes to an increase in strength of the steel pipe. In order to obtain the above effect, in the case of containing Ti, the Ti content is set to 0.0001% or more. The Ti content is preferably 0.0010% or more, more preferably 0.0015% or more, further preferably 0.002% or more, and most preferably 0.01% or more. On the other hand, if the Ti content exceeds 0.1%, the effect is saturated and becomes a factor of cost increase. Therefore, in the case of containing Ti, the Ti content is set to 0.1% or less. For cost suppression, the Ti content is preferably 0.05% or less, more preferably 0.04% or less, and further preferably 0.03% or less.

Cu: 0.0001 to 5.0%

[0042] Cu is an element that improves hardenability, and contributes to an increase in strength of the steel pipe, and also suppresses coarsening of prior-austenite grains and improves various characteristics of the steel pipe. In order to obtain the above effect, in the case of containing Cu, the Cu content is set to 0.0001% or more. The Cu content is preferably 0.001% or more, more preferably 0.1% or more, and further preferably 0.2% or more. On the other hand, if the Cu content

exceeds 5.0%, the effect is saturated and becomes a factor of cost increase. Therefore, in the case of containing Cu, the Cu content is set to 5.0% or less. The Cu content is preferably 4.3% or less, more preferably 4.0% or less, and further preferably 3.0% or less; for cost suppression, the Cu content is most preferably 2.0% or less.

5 Co: 0.0001 to 5.0%

[0043] Co is an element that improves hardenability, and contributes to an increase in strength of the steel pipe, and also suppresses coarsening of prior-austenite grains and improves various characteristics of the steel pipe. In order to obtain the above effect, in the case of containing Co, the Co content is set to 0.0001% or more. The Co content is preferably 0.001% or more, more preferably 0.1% or more, and further preferably 0.2% or more. On the other hand, if the Co content exceeds 5.0%, the effect is saturated and becomes a factor of cost increase. Therefore, in the case of containing Co, the Co content is set to 5.0% or less. The Co content is preferably 4.0% or less, more preferably 3.0% or less; for cost suppression, the Co content is further preferably 2.0% or less.

15 B: 0.0001 to 0.01%

[0044] B is an element that improves hardenability, and contributes to an increase in strength of the steel pipe, and also suppresses coarsening of prior-austenite grains and improves various characteristics of the steel pipe. In order to obtain the above effect, in the case of containing B, the B content is set to 0.0001% or more. The B content is preferably 0.0005% or more, more preferably 0.001% or more, and further preferably 0.002% or more. On the other hand, if the B content exceeds 0.01%, the effect is saturated and becomes a factor of cost increase. Therefore, in the case of containing B, the B content is set to 0.01% or less. The B content is preferably 0.008% or less, more preferably 0.006% or less; for cost suppression, the B content is further preferably 0.005% or less, and most preferably 0.004% or less.

25 V: 0.0001 to 1.0%

[0045] V contributes to an increase in strength of the steel pipe. Further, delayed-fracture characteristics can also be enhanced. In order to obtain the above effect, in the case of containing V, the V content is set to 0.0001% or more. The V content is preferably 0.0005% or more, more preferably 0.0010% or more, further preferably 0.0020% or more, and most preferably 0.01% or more. On the other hand, if the V content exceeds 1.0%, the effect is saturated and becomes a factor of cost increase. Therefore, in the case of containing V, the V content is set to 1.0% or less. The V content is preferably 0.8% or less; for cost suppression, the V content is more preferably 0.5% or less, and further preferably 0.4% or less.

35 W: 0.0001 to 5.0%

[0046] W contributes to an increase in strength of the steel pipe. In order to obtain the above effect, in the case of containing W, the W content is set to 0.0001% or more. The W content is preferably 0.0005% or more, more preferably 0.0010% or more, further preferably 0.0020% or more, and most preferably 0.1% or more. On the other hand, if the W content exceeds 5.0%, the effect is saturated and becomes a factor of cost increase. Therefore, in the case of containing W, the W content is set to 5.0% or less. The W content is preferably 4.0% or less, more preferably 3.0% or less, further preferably 2.0% or less, and most preferably 1.7% or less.

Nb: 0.0001 to 0.1%

[0047] Nb contributes to an increase in strength of the steel pipe. In order to obtain the above effect, in the case of containing Nb, the Nb content is set to 0.0001% or more. The Nb content is preferably 0.0005% or more, more preferably 0.0010% or more, and further preferably more than 0.001%. On the other hand, if the Nb content exceeds 0.1%, the effect is saturated and becomes a factor of cost increase. Therefore, in the case of containing Nb, the Nb content is set to 0.1% or less. The Nb content is preferably 0.08% or less; for cost suppression, the Nb content is more preferably 0.06% or less, further preferably 0.05% or less, and most preferably 0.045% or less.

Zr: 0.0001 to 0.2%, Hf: 0.0001 to 0.2%, Ta: 0.0001 to 0.2%

[0048] Zr, Hf, and Ta contribute to an increase in strength of the steel pipe. In order to obtain the above effect, in the case of containing Zr, Hf, and Ta respectively, the Zr content, the Hf content, and the Ta content are each set to 0.0001% or more. The Zr content, the Hf content, and the Ta content are each preferably 0.0002% or more, each more preferably 0.0005% or more, each further preferably 0.0010% or more, and each most preferably 0.01% or more. On the other hand, if the Zr content, the Hf content, and the Ta content each exceeds 0.2%, the effect is saturated and becomes a factor of cost

increase. Therefore, in the case of containing Zr, Hf, and Ta respectively, the Zr content, the Hf content, and the Ta content are each set to 0.2% or less. The Zr content, the Hf content, and the Ta content are each preferably 0.1% or less; for cost suppression, the Zr content, the Hf content, and the Ta content are each more preferably 0.09% or less, each further preferably 0.08% or less, and each most preferably 0.07% or less.

Sb: 0.0001 to 0.1%

[0049] Sb is an element effective for suppressing a decrease in strength of the steel pipe by suppressing denitrification, deboronization, and the like. In order to obtain the above effect, in the case of containing Sb, the Sb content is set to 0.0001% or more. The Sb content is preferably 0.002% or more, more preferably 0.005% or more, and further preferably 0.01% or more. If the Sb content exceeds 0.1%, embrittlement of the steel pipe may be caused. Therefore, in the case of containing Sb, the Sb content is set to 0.1% or less. The Sb content is preferably 0.08% or less, more preferably 0.07% or less, and further preferably 0.06% or less.

Sn: 0.0001 to 0.1%

[0050] Sn is an element effective for suppressing a decrease in strength of the steel pipe by suppressing pearlite. In order to obtain the above effect, in the case of containing Sn, the Sn content is set to 0.0001% or more. The Sn content is preferably 0.0002% or more, more preferably 0.005% or more, and further preferably 0.01% or more. If the Sn content exceeds 0.1%, embrittlement of the steel pipe may be caused. Therefore, in the case of containing Sn, the Sn content is set to 0.1% or less. The Sn content is preferably 0.08% or less, more preferably 0.05% or less, and further preferably 0.04% or less.

Ca: 0.0001 to 0.01%, Mg: 0.0001 to 0.01%

[0051] Ca and Mg contribute to improvement of inclusion state. In order to obtain the above effect, in the case of containing Ca and Mg respectively, the contents of Ca and Mg are each set to 0.0001% or more. Preferably, the Ca content and the Mg content are each 0.001% or more, and more preferably each set to 0.002% or more. On the other hand, if the Ca content and the Mg content each exceeds 0.01%, the effect is saturated and becomes a factor of cost increase. Therefore, in the case of containing Ca and Mg respectively, the Ca content and the Mg content are each set to 0.01% or less. The Ca content and the Mg content are each preferably 0.008% or less; for cost suppression, the Ca content and the Mg content are each more preferably 0.005% or less, and each further preferably 0.004% or less.

REM: 0.0001 to 0.5%

[0052] REM (Rare Earth Metals) contributes to improvement of inclusion state. In order to obtain the above effect, in the case of containing REM, the REM content is set to 0.0001% or more. The REM content is preferably 0.001% or more, more preferably 0.002% or more, and further preferably 0.01% or more. On the other hand, if the REM content exceeds 0.5%, the effect is saturated and becomes a factor of cost increase. Therefore, in the case of containing REM, the REM content is set to 0.5% or less. The REM content is preferably 0.3% or less; for cost suppression, the REM content is more preferably 0.28% or less, and further preferably 0.25% or less. Note that REM is a general term for Sc, Y, and 15 elements from lanthanum (La) of atomic number 57 to lutetium (Lu) of atomic number 71, and the REM content here is a total content of these elements.

[0053] Next, the degree of segregation of Mn in the seamless steel pipe will be described.

[0054] Degree of segregation of Mn from the inner surface of the steel pipe to a 1/6 wall-thickness position: less than 1.50

[0055] Mn, like P, is also an element that lowers the bonding strength of grain boundaries, and, by reducing micro-segregation of Mn, grain-boundary cracking, which is an initiation point of delayed fracture, can be suppressed, and improvement of delayed-fracture characteristics is expected. As described above, P has high affinity with Mn. And, P is a direct factor of quench-cracking risk; therefore, in the present invention, the P content (P concentration) is controlled to be low. Basically, suppression of segregation of P is required, but the concentration of Mn, which has high affinity with P, is higher than the concentration of P, and the reliability of analysis results by EPMA is high. Further, the P concentration and the Mn concentration have a high correlation relationship. Therefore, by suppressing segregation of Mn, segregation of P can also be surely suppressed. Accordingly, in evaluating the degree of segregation of P in the seamless steel pipe, the degree of segregation of Mn is used as an evaluation index.

[0056] Further, in the case of a plate-shaped steel material (steel plate) manufactured by rolling a continuously cast slab, macro-segregation exists in the plate thickness (wall thickness) central portion; therefore, the mitigating effect of macro-segregation by rolling becomes small compared with a seamless steel pipe. This is due to the following reason. In a pipe-forming process of the seamless steel pipe, a billet having a cylindrical shape is pierced by a piercing machine at the center,

and is rolled to form a pipe shape; therefore, the position of macro-segregation existing at the billet center is arranged on the inner-surface side of the seamless steel pipe in the pipe shape. That is, the inner-surface side of the seamless steel pipe, where macro-segregation of P is high, becomes the highest quench-cracking risk. On the other hand, because the billet center is pierced and rolled while pressing the billet outer surface, the amount of plastic deformation is higher on the inner-surface side of the steel pipe than on the outer-surface side of the steel pipe, and mitigation of macro-segregation of P on the inner-surface side of the steel pipe is expected by rolling. From this, it becomes important to control segregation of P, that is, segregation of Mn, on the inner-surface side of the seamless steel pipe.

[0057] Therefore, when evaluating the degree of segregation of Mn of the seamless steel pipe, it is important to manufacture the seamless steel pipe and evaluate it. At that time, it was found that, for the degree of segregation of Mn, it is sufficient to use, as a reference, a local concentration of Mn in the vicinity of a 1/4 wall-thickness position from the outer surface of the steel pipe, and to use a ratio of the segregation concentration of Mn in a segregation region on the inner-surface side of the steel pipe, that is, from the inner surface of the steel pipe to a 1/6 wall-thickness position. Here, the reason for using, as the reference local concentration of Mn, the local concentration of Mn in the vicinity of a 1/4 wall-thickness position from the outer surface of the steel pipe is that the vicinity of a 1/4 wall-thickness position from the outer surface of the steel pipe is a region having an average component composition without macro-segregation, and is a region that is distant in the wall-thickness direction also from the outer surface of the steel pipe where plastic deformation occurs due to a pressing load, and is a region where it is possible to increase the distance also from the inner surface of the steel pipe. On the other hand, as the segregation concentration of Mn, the segregation concentration of Mn in a segregation region on the inner-surface side of the steel pipe, that is, from the inner surface of the steel pipe to a 1/6 wall-thickness position, is used.

[0058] In order to reduce quench-cracking risk, the degree of segregation of Mn needs to be less than 1.50, and is more preferably 1.45 or less, further preferably 1.44 or less, and most preferably 1.43 or less. Further, the lower limit of the degree of segregation of Mn is not particularly limited, but from the viewpoint of cost suppression, it is preferably 1.00 or more, and more preferably 1.10 or more.

[0059] A method for calculating the degree of segregation of Mn is as shown below.

[0060] In order to quantitatively evaluate segregation of P on the inner-surface side of the seamless steel pipe, in the present invention, the degree of segregation of Mn is used. The degree of segregation of Mn is defined as a value obtained by dividing the segregation concentration of Mn from the inner surface of the seamless steel pipe to a 1/6 wall-thickness position by the local concentration of Mn in the vicinity of a 1/4 wall-thickness position from the outer surface of the steel pipe. A method for measuring the degree of segregation of Mn is as shown below.

[0061] In evaluating the degree of segregation of Mn, attention was focused on mapping analysis by an electron probe microanalyzer (Electron Probe Micro Analyzer; EPMA), which can measure a local concentration of elements. First, a test piece for mapping analysis is taken such that a cross section in the C direction (rolling perpendicular direction) of the steel pipe is an observation surface, and the observation surface is mirror-finished. Subsequently, in the observation surface, when the wall thickness of the steel pipe is t , the local concentration of Mn to be used as a reference is obtained by performing mapping analysis of the Mn concentration in region 1 enclosed by a length of $t/6$ (mm) in the wall-thickness direction with the 1/4 wall-thickness position in the wall-thickness direction from the steel pipe outer surface as a center (a length in the wall-thickness direction of $\pm t/12$ (mm) with a 1/4 wall-thickness position in the wall-thickness direction from the outer surface of the steel pipe as a reference) and a length, in the circumferential direction, of 10 (mm), and by performing analysis described later, and calculating. Further, the segregation concentration of Mn is obtained by performing mapping analysis of the Mn concentration in region 2 enclosed by a length, in the wall-thickness direction, of $t/6$ (mm) ($t/6$ (mm) in the wall-thickness direction with the surface of the inner surface of the steel pipe as a reference) and a length, in the circumferential direction, of 10 (mm), and by performing analysis described later, and calculating. Here, in the mapping analysis of the Mn concentration, the mapping data may be acquired by determining an analysis pitch such that 40,000 points of mapping data are obtained for each of region 1 and region 2. Subsequently, the obtained 40,000 points of mapping data are statistically analyzed and the degree of segregation of Mn is calculated. The reference local concentration of Mn is taken as an average value of mapping data obtained by excluding outliers from all mapping data obtained in region 1. Outliers are mapping data less than 0.05 times and mapping data greater than 5 times the Mn concentration (Mn content) obtained from check analysis of the steel pipe. Further, the segregation concentration of Mn is taken as an average value of mapping data of the top 1% having a high Mn concentration, in mapping data obtained by excluding outliers from all mapping data obtained in region 2. At this time, mapping analysis of region 1 is performed in three fields of view, and the Mn local concentrations calculated in the three fields of view are summed and a value obtained by dividing by 3 is taken as the Mn local concentration. Similarly, mapping analysis of region 2 is also performed in three fields of view, and the Mn segregation concentrations calculated in the three fields of view are summed and a value obtained by dividing by 3 is taken as the Mn segregation concentration. A ratio of the Mn segregation concentration to the Mn local concentration obtained in this manner (a value obtained by dividing the Mn segregation concentration from the inner surface of the seamless steel pipe to a 1/6 wall-thickness position by the Mn local concentration in the vicinity of a 1/4 wall-thickness position from the outer surface of the steel pipe) is calculated as the degree of segregation of Mn.

[0062] Next, reasons for limitation of the metallic microstructure of the seamless steel pipe of the present invention will be described.

Area fraction of martensite: 85% or more

[0063] If the martensite occupying the metallic microstructure is less than 85% in terms of area fraction, the cross-sectional hardness of the seamless steel pipe is small and fatigue strength deteriorates. Therefore, in the present invention, from the viewpoint of securing cross-sectional hardness of the seamless steel pipe and improving fatigue strength, the total area fraction of martensite occupying the metallic microstructure of the seamless steel pipe is set to 85% or more. The total area fraction of martensite is preferably 88% or more, more preferably 90% or more, further preferably 92% or more, and most preferably 94% or more. On the other hand, the upper limit of the area fraction of martensite is not particularly limited, and may be 100% or less.

[0064] Note that the metallic microstructure in one embodiment of the present invention may be composed of martensite. Further, the metallic microstructure in another embodiment of the present invention may contain, in addition to martensite, other microstructures. The other microstructures are not particularly limited and may be any microstructure. Examples of the other microstructures include bainite, ferrite, pearlite, and retained austenite. When the metallic microstructure contains bainite, the area fraction of bainite is preferably 10% or less, and more preferably 5% or less. The area fraction of bainite may be 0% or more. When the metallic microstructure contains ferrite, the area fraction of ferrite is preferably 2% or less, and more preferably 1% or less. The area fraction of ferrite may be 0% or more. When the metallic microstructure contains pearlite, the area fraction of pearlite is preferably 2% or less, and more preferably 1% or less. The area fraction of pearlite may be 0% or more. When the metallic microstructure contains retained austenite, the retained austenite is preferably 1% or less. Note that, in the present invention, "high martensite fraction" means that martensite is 85% or more in terms of area fraction. Further, the area fraction of the metallic microstructure described above can be measured by the method described in the Examples.

[0065] From each of the obtained seamless steel pipes, a test piece is taken such that an observation position is at a central portion in the longitudinal direction of the seamless steel pipe and at a 1/4 wall-thickness position from the outer surface of the steel pipe. Here, a surface composed of a wall-thickness direction and a circumferential direction (so-called "C cross section") is taken as an observation surface. The observation surface is etched using a 3 vol.% nital solution. Thereafter, the observation surface is observed using a scanning electron microscope (SEM) at an appropriate magnification between 1,000 and 5,000 times, and a microstructure image is obtained. The obtained microstructure image is analyzed to evaluate types of metallic microstructures and area fractions of respective metallic microstructures. Further, the area fraction of retained austenite is obtained by chemically polishing the observation surface and performing X-ray diffraction. Co-K α radiation is used as an incident X-ray, and the area fraction of retained austenite is calculated from an intensity ratio of ferrite (200), (211), and (220) planes and austenite (200), (220), and (311) planes.

[0066] Next, the cross-sectional hardness of the seamless steel pipe will be described.

[0067] A steel pipe having an area fraction of martensite of 85% or more only by quenching treatment has high cross-sectional hardness, and has a high risk of so-called storage cracking, in which cracking occurs during storage of the steel pipe due to delayed fracture rather than cracking immediately after quenching, and is not excellent in delayed-fracture characteristics. Delayed fracture described in the present invention occurs due to penetration of a minute amount of hydrogen into the steel pipe, which is generated due to corrosion of the steel pipe. On the other hand, in an environment in which hydrogen constantly enters the steel pipe, there is also a risk of cracking due to so-called hydrogen embrittlement, in which hydrogen constantly enters the steel pipe and lowers material characteristics, and hydrogen-embrittlement resistance is not excellent. Further, crack susceptibility differs depending on tensile strength. Therefore, it is necessary to adjust cross-sectional hardness as needed. Note that tensile strength and cross-sectional hardness have a correlation relationship, and tensile strength can be adjusted by controlling cross-sectional hardness.

Cross-sectional hardness of 250 HV or more and less than 480 HV

[0068] Since storage cracking occurs with a smaller amount of hydrogen as strength becomes higher, it is effective to appropriately lower the strength of the steel pipe. In order to obtain excellent delayed-fracture characteristics, the cross-sectional hardness is set to less than 480 HV. On the other hand, for a pressure vessel, since it is required to increase the strength of the steel pipe and reduce the wall thickness in order to reduce the total weight of the vessel, the cross-sectional hardness is set to 250 HV or more.

[0069] The cross-sectional hardness of the seamless steel pipe of the present invention needs to be as described above, but it is preferable to select a preferable range of cross-sectional hardness depending on various uses. For example, when used for a pressure vessel, the cross-sectional hardness is preferably set to more than 350 HV and less than 480 HV, and when used for an application in which the steel pipe is intentionally used in an environment in which hydrogen constantly infiltrates into the steel pipe, the cross-sectional hardness is preferably set to 250 HV or more and 350 HV or less.

Cross-sectional hardness of more than 350 HV and less than 480 HV (preferred condition)

[0070] As described later, since cross-sectional hardness is lowered by tempering and delayed-fracture characteristics, toughness, and machinability are improved, cross-sectional hardness of the seamless steel pipe is adjusted according to specifications of various pressure vessels. For a pressure vessel for which strength of the steel pipe is required in order to reduce the weight of the vessel, or in order to secure a larger internal volume at the same outer diameter, it is preferable to set the cross-sectional hardness to more than 350 HV. The cross-sectional hardness is more preferably set to 360 HV or more, and further preferably 370 HV or more. As for the preferred upper limit, for the reasons described above, the cross-sectional hardness is set to less than 480 HV. The cross-sectional hardness is preferably set to 460 HV or less, more preferably 445 HV or less, and further preferably 440 HV or less.

Cross-sectional hardness of 250 HV or more and 350 HV or less (preferred condition)

[0071] Further, unlike a corrosion phenomenon that inevitably occurs, for example, when a steel pipe is intentionally used in an environment in which hydrogen constantly infiltrates into the steel pipe, such as an accumulator for a hydrogen station for fuel cell vehicles, cracking due to hydrogen embrittlement occurs, in which hydrogen infiltrates into the steel pipe and lowers material characteristics. In addition, a state in which a load is applied to the steel pipe promotes the amount of hydrogen infiltration. This hydrogen embrittlement, similarly to delayed fracture, is effective to appropriately lower the strength of the steel pipe; however, since the amount of infiltrated hydrogen is large, in order to obtain excellent hydrogen-embrittlement resistance, the cross-sectional hardness is preferably set to 350 HV or less, more preferably 345 HV or less, further preferably 315 HV or less, and most preferably 310 HV or less.

[0072] For the reasons described above, the cross-sectional hardness is set to 250 HV or more. It is preferable to set it to 260 HV or more, more preferably 265 HV or more, and further preferably 270 HV or more.

[0073] Next, the wall thickness of the seamless steel pipe of the present invention will be described.

[0074] Wall thickness of the steel pipe is 40 mm or more (preferred condition)

[0075] When the seamless steel pipe is used for a pressure vessel, the larger the wall thickness of the steel pipe is, the smaller the stress applied to the pressure vessel that is generated becomes, and therefore a pressure vessel that can withstand a higher pressure can be designed. Therefore, the wall thickness of the steel pipe of the present invention is preferably set to 40 mm or more. The wall thickness of the steel pipe is more preferably 45 mm or more, and 50 mm or more is further preferable.

[0076] On the other hand, when the wall thickness of the seamless steel pipe becomes large, the volume of the seamless steel pipe becomes large. That is, the total amount of heat that the seamless steel pipe itself can store increases. In the quenching process, since heat is removed from the inner surface and the outer surface of the steel pipe by a coolant, the temperature of the wall-thickness center of the steel pipe becomes higher than that of the inner surface and the outer surface of the steel pipe. On the other hand, the inner surface and the outer surface of the steel pipe always become a temperature equivalent to that of a medium such as water used in water cooling, and a temperature gradient occurs. This effect becomes remarkable with an increase in wall thickness. When the temperature gradient is large, the balance between thermal stress and transformation stress deteriorates and the quench-cracking risk increases. In addition, in a steel pipe having the same outer diameter, when the wall thickness increases, the inner diameter becomes small. Because the steel pipe is thick-walled, at the time of quenching, there exists a temperature distribution in which the temperature is lowest at the inner surface and the outer surface of the steel pipe and the temperature is highest at the wall-thickness center. When sufficiently cooling the inner surface and the outer surface of the steel pipe, since the heat exchange efficiencies at the inner surface and the outer surface of the steel pipe can be regarded as the same, a clear difference does not occur between the temperature gradient from the wall-thickness center to the outer surface and the temperature gradient from the wall-thickness center to the inner surface. On the other hand, when comparing the difference in circumferential length with the wall-thickness center as a reference, it is a positive value at the outer surface but becomes a negative value at the inner surface.

[0077] Even after transformation from a face-centered cubic structure to a body-centered cubic structure is completed at the time of quenching, a temperature gradient exists, and the side closer to the inner surface and the outer surface thermally shrinks first. That is, it changes in a direction in which the difference in circumferential-length from the wall-thickness center decreases. The outer surface has a positive circumferential-length difference, and since it changes in a direction in which the absolute value of the difference decreases, the thermal stress generated also decreases. On the other hand, since the inner surface has a negative circumferential-length difference, it changes in a direction in which the absolute value of the difference increases, and therefore the thermal stress generated increases. That is, when the wall thickness increases, the quench-cracking risk at the inner surface increases; therefore, the wall thickness is preferably smaller. Therefore, the wall thickness is preferably set to 70 mm or less, more preferably 65 mm or less, and further preferably 60 mm or less.

[0078] Next, inclusions of the seamless steel pipe will be described.

[0079] Since inclusions have higher hardness than the Fe matrix and are difficult to deform, it is known that, when thermal stress occurs, they become a source of stress concentration. That is, they increase a risk of reducing quench-cracking risk and delayed-fracture characteristics.

[0080] In the range from the inner surface of the steel pipe to a 1/6 wall-thickness position, the number of inclusions having an aspect ratio of 2 or less and a length of a long side of 10 μm or more is 10 pieces per 100 mm^2 or less (preferred condition)

[0081] As inclusions, it is known that there are types such as sulfide-based inclusions, oxide-based inclusions, and nitride-based inclusions.

[0082] In rolling in the pipe-forming process, since inclusions having low hardness elongate during rolling, they can be characterized by the length of the long side and the length of the short side when the shape of inclusions is assumed to be an elliptical shape. A value obtained by dividing the length of the long side by the length of the short side is defined as an aspect ratio.

[0083] The higher the hardness of inclusions is, the smaller the elongation during rolling becomes, and the smaller the aspect ratio becomes. On the other hand, with respect to quench-crack resistance, the higher the hardness of inclusions is, the higher the quench-cracking risk becomes.

[0084] In particular, on the inner-surface side of the steel pipe, which is a region where segregation exists, that is, in the range from the inner surface of the steel pipe to a 1/6 wall-thickness position, inclusions that have an aspect ratio of 2 or less after rolling and have a length of the long side of 10 μm or more act as an initiation point of occurrence of quench cracking, and become a cause of increase in quench-cracking risk. That is, in order to reduce quench-cracking risk, the number of inclusions having a small aspect ratio is important. If the number of inclusions having an aspect ratio of 2 or less and a length of the long side of 10 μm or more is 10 pieces per 100 mm^2 or less, irregular quench cracking does not occur. For this reason, in the range from the inner surface of the steel pipe to a 1/6 wall-thickness position, it is preferable that the number of inclusions having an aspect ratio of 2 or less and a length of the long side of 10 μm or more be 10 pieces per 100 mm^2 or less. It is more preferable that the number of inclusions having an aspect ratio of 2 or less and a length of the long side of 10 μm or more be 8 pieces per 100 mm^2 or less; it is further preferable if it is 5 pieces per 100 mm^2 or less; and it is most preferable if it is 4.8 pieces per 100 mm^2 or less. The lower limit of the number of inclusions is not particularly limited, but from the viewpoint of cost suppression, it is preferable that it be 1 piece per 100 mm^2 or more. Further, the number of inclusions described above can be measured by the method described in the Examples.

[0085] Note that, similarly to macro-segregation, the amount of inclusions becomes larger at the billet center, which is a final solidification part. Therefore, in a seamless steel pipe obtained using a billet, inclusions become the most on the inner-surface side of the seamless steel pipe. As mentioned above, since the inner-surface side of the seamless steel pipe has a high quench-cracking risk due to the influence of segregation, it is preferable that there be fewer inclusions on the inner-surface side of the seamless steel pipe. Here, the "inner-surface side of the steel pipe" means a region from the inner surface of the steel pipe to a 1/6 wall-thickness position, where macro-segregation exists. Note that the size of inclusions can be controlled by controlling the reduction amount when manufacturing a seamless steel pipe from a material (billet).

[0086] Next, a method for manufacturing the seamless steel pipe of the present invention will be described.

Material (billet)

[0087] As the material (billet) to be used for pipe-forming of the seamless steel pipe, from the viewpoint of productivity, it is preferable to use a material manufactured by continuous casting. In continuous casting, when a mold becomes large, control of a solidification process becomes difficult; therefore, in order to stably mass-produce, the billet diameter is preferably 400 mm or less, more preferably 350 mm or less, and further preferably 345 mm or less. On the other hand, the lower limit of the billet diameter is not particularly limited, but it is preferably 320 mm or more, and more preferably 330 mm or more.

[0088] Further, since macro-segregation in a billet is improved by hot forging, for example, it is also effective to hot-forge a rectangular material manufactured by continuous casting into a circular material (billet).

(Pipe-forming step)

[0089] Pipe-forming such that a ratio of an inner diameter of the steel pipe divided by a wall thickness is 2.0 times or more

[0090] Macro-segregation at the billet center can be dissipated, in a piercing process when pipe-forming the seamless steel pipe, when plastically deforming by rolling from a solid billet to a hollow seamless steel pipe. In rolling, when it is assumed that the wall thickness is increased and the quench-cracking risk becomes high, the amount of plastic deformation when rolling and pipe-forming from the billet to the seamless steel pipe can be increased by increasing the inner diameter. It is good that the ratio of the inner diameter of the steel pipe divided by the wall thickness is 2.0 times or more. Since the larger this ratio is, the larger the amount of plastic deformation is, it is preferable to set it to 3.0 times or more, more preferably 4.0 times or more, further preferably 4.1 times or more, and most preferably 4.2 times or more.

Further, the upper limit of the above ratio is not particularly limited, but from the viewpoint of ensuring the amount of rolling, it is preferable to set it to 8.0 times or less, and more preferably 7.0 times or less.

[0091] Further, in order to increase the amount of plastic deformation, it is also effective to expand the pipe to an outer diameter larger than the billet diameter, and the outer diameter of the seamless steel pipe is preferably larger than 1.0 times the billet diameter, more preferably 1.1 times or more, and further preferably set to 1.2 times or more. Further, from the viewpoint of handling, it is preferable to set it to 2.0 times or less. Note that, in the pipe-forming step, piercing and rolling are essential requirements. Further, expansion is preferably carried out as needed.

[0092] In the pipe-forming step, the shape of the steel pipe satisfies formula (2) (preferred condition)

$$(EXP(\text{coefficient } K \times \text{wall thickness}) / \text{circumferential cross section area}) \times 10^6 < 210 \cdots (2) \quad (2)$$

$$K = \{0.41([C]-0.24) + 4.58[Mn] + 0.21[Cr] + 0.25[Ni]\} / 100 \cdots (3) \quad (3)$$

(In formula (3), [element] represents content (mass %) of the element described in the brackets.)

[0093] An increase in the wall thickness of the steel pipe increases the area of the circumferential cross section. That is, since the total amount of heat of the seamless steel pipe increases due to an increase in the volume of the seamless steel pipe, there also exists an effect of lowering the cooling rate at the time of quenching and lowering the quench-cracking risk.

[0094] As described above, an increase in wall thickness has both a positive factor and a negative factor with respect to quench-cracking risk, and it is preferable to optimize the balance thereof and consider productivity.

[0095] Further, since the temperature difference between the inner surface and the outer surface of the seamless steel pipe and the wall-thickness center is affected by thermal conductivity, it is affected by contribution of the component composition. Generally, physical property values (thermal conductivity) for carbon steel, manganese steel, chromium steel, nickel steel, and the like are measured, and C, Mn, Cr, and Ni contribute greatly.

[0096] Since quench-cracking risk is reduced by satisfying formula (2), it is preferable to make it satisfy formula (2). The right-hand side in formula (2) is more preferably set to 208 or less, and further preferably 205 or less. Further, from the viewpoint of pipe-forming efficiency, it is preferable that the left-hand side of formula (2) be 40 or more. The coefficient K in formula (2) is obtained by formula (3) above.

(Quenching step)

Heating to a temperature range of 860°C or more, and holding in the temperature range for 30 min or more

[0097] Hereinafter, unless otherwise stated, the temperature described refers to all the 1/4 position from the inner surface.

[0098] Immediately before quenching, it is held at a temperature in an austenite region. Since it is a temperature region in which it exists as a solid, dissipation of macro-segregation cannot be expected, but, because diffusion of atoms occurs actively, de-trapping of contained elements from grain boundaries is expected, and therefore it is effective for improvement of micro-segregation.

[0099] The frequency of diffusion depends on temperature and time, and when the temperature is less than 860°C, the de-trapping effect is weak; therefore, the temperature is set to 860°C or more. The temperature is preferably set to 865°C or more, more preferably 870°C or more, and further preferably 875°C or more. On the other hand, since an increase in temperature promotes coarsening of prior-austenite crystal grains and not only causes a decrease in fatigue strength but also causes a rise in heating cost, it is preferably set to 950°C or less, more preferably 930°C or less, further preferably 900°C or less, and most preferably 890°C or less. The holding time is set to 30 min or more for homogenization. The holding time is preferably set to 35 min or more, more preferably 40 min or more, and further preferably 45 min or more. Further, since an increase in holding time causes a decrease in productivity, it is preferably set to 90 min or less, more preferably 60 min or less, and further preferably 55 min or less.

[0100] Water cooling under conditions such that an average cooling rate in a temperature range of 800 to 350°C is 3°C/s or more

[0101] The water cooling after the above heating and holding is essential for ensuring an area fraction of martensite of 85% or more. In addition, the average cooling rate in the temperature range of 800 to 350°C is set to 3°C/s or more. Since a faster average cooling rate is expected to increase the area fraction of martensite, it is preferably 4°C/s or more, more preferably 5°C/s or more, further preferably set to 5.5°C/s or more, and most preferably 6°C/s or more. On the other hand, the upper limit of the average cooling rate is not particularly limited, but it is preferably set to 15°C/s or less, and more preferably 10°C/s or less. Note that the average cooling rate is obtained by dividing a temperature difference in the temperature range of 800 to 350°C by the time required to cool in this temperature range.

[0102] In the water cooling, bringing a cooling medium into contact with the inner surface of the steel pipe at a flow rate of

0.5 m³/min or more in a state that steel pipe is rotated in a circumferential direction of the pipe

[0103] It is important to remove a vapor film generated during water cooling. The outer surface of the seamless steel pipe has a high degree of freedom in equipment, and removal of a vapor film can be realized even with an apparatus having a simple structure, but there are many restrictions on equipment for removal of a vapor film on the inner surface of the steel pipe. Therefore, it is necessary to bring a cooling medium into contact with the inner surface of the steel pipe, and, for example, an appropriate method such as a method of running a jet flow of the cooling medium may be used, and the flow rate is set to 0.5 m³/min or more. The flow rate is preferably set to 0.55 m³/min or more, more preferably 0.58 m³/min or more, further preferably 0.6 m³/min or more, and most preferably 0.65 m³/min or more. The upper limit of the flow rate is not particularly limited, but from the viewpoint of reducing equipment load, it is preferably set to 1.5 m³/min or less.

[0104] In addition, in order to shorten the time during which thermal stress occurs, it is important to remove heat remaining in the steel pipe even after martensitic transformation is completed, and the jet-flow injection time is preferably 3 min or more, more preferably 5 min or more, further preferably 5.5 min or more, and most preferably 6 min or more. Note that, since a vapor film is generated in an initial stage of injection, after 90 s from injection, the flow rate may be reduced to less than 0.5 m³/min and 0.05 m³/min or more. In addition, it is preferable that the steel-pipe surface temperature after completion of injection be 50°C or less. Since the cooling medium needs to have a function of sufficiently cooling, water of 50°C or less may be used. The temperature of the water is more preferably 45°C or less, and further preferably 40°C or less. The temperature of the water is preferably 2°C or more.

[0105] Further, in order to mitigate a thermal distribution caused by rolling thickness deviation, at the time of jet-flow injection, it is preferable to rotate the seamless steel pipe in the circumferential direction at a rotational speed of 10 rpm or more. The rotational speed is more preferably set to 12 rpm or more, and further preferably 15 rpm or more. On the other hand, the upper limit of the rotational speed is not particularly limited, but it is preferable to set it to 1200 rpm or less.

[0106] Note that the quenching step refers to a series of processes of heating, holding, and water cooling after the pipe-forming step.

[0107] Since the seamless steel pipe is cooled while rotating at high speed, it is difficult to directly measure the temperature using a general temperature measurement method in which a thermocouple is attached and calculate an average cooling rate at the time of quenching. Therefore, a CCT diagram may be prepared, and the average cooling rate may be determined by corresponding it to hardness measured in the steel pipe after quenching.

[0108] Note that, as cooling equipment, appropriate equipment such as immersion equipment, mist cooling equipment, shower cooling equipment, and the like may be used, but basically, since cooling is performed most uniformly by immersing the entire steel pipe in water, rotating it, and running a jet flow on the inner surface of the steel pipe, it is preferable to use immersion equipment.

(Tempering step)

Tempering at a temperature range of 400 to 680°C for 30 min or more

[0109] Note that, since cross-sectional hardness is lowered by tempering and delayed-fracture characteristics, toughness, and machinability are improved, cross-sectional hardness of the seamless steel pipe is adjusted according to specifications of various pressure vessels. For a pressure vessel for which strength of the steel pipe is required in order to reduce the weight of the vessel, or in order to secure a larger internal volume at the same outer diameter, it is desirable to obtain a cross-sectional hardness of less than 480 HV and more than 350 HV, and the temperature for the tempering is set to 400°C or more, preferably 405°C or more, more preferably 410°C or more, and further preferably 415°C or more. Further, the temperature is preferably less than 620°C. For a pressure vessel that stores hydrogen gas (pressure vessel for hydrogen gas), it is desirable to obtain a cross-sectional hardness of 350 HV or less and 250 HV or more, and the temperature is set to 680°C or less, preferably 675°C or less, and more preferably 660°C or less. Further, the temperature is preferably set to 620°C or more.

[0110] Further, regarding the tempering time, in order to uniformly temper in the wall-thickness direction, it is necessary to hold for 30 min or more in the above temperature range. The holding time at the above temperature is preferably 35 min or more, more preferably 40 min or more, and further preferably 45 min or more. Further, the holding time at the above temperature is preferably set to 90 min or less, and more preferably 80 min or less.

[0111] In another embodiment of the present invention, processing described later can be further performed.

[0112] A decarburized layer generated on the surface of the steel pipe during quenching and tempering is more brittle than the base phase of the steel pipe and cracking is likely to occur. Further, rolling defects also become an initiation point of cracking. Therefore, it is also effective to perform machining such as cutting and polishing, and shot blasting, or both thereof, to remove the decarburized layer and the rolling defects.

[0113] Further, in order to suppress corrosion of the inner surface of the seamless steel pipe, it is also effective to apply rust-preventive oil or perform coating.

[0114] When cooling the seamless steel pipe, since transfer of heat at the inner surface and the outer surface becomes

dominant, the outer surface, which has a larger surface area of the steel pipe, is cooled more efficiently. Therefore, in the temperature distribution with respect to the wall-thickness direction, the position having the highest temperature moves from the wall-thickness center toward the inner-surface side. In that case, the load at the outer surface becomes large, and the risk that quench cracking occurs at the outer surface becomes high. Although the outer surface does not have macro-segregation like the inner surface, it is affected by micro-segregation; therefore, an extremely large wall thickness is not desirable. Therefore, as a relationship between the inner diameter and the outer diameter, it is preferable that a value obtained by dividing a difference between an outer circumferential length and an inner circumferential length by a circumferential length at the wall-thickness center be 0.45 or less, and more preferably 0.40 or less. The lower limit is not particularly limited, but it is preferable to set it to 0.10 or more.

[0115] Next, a pressure vessel and a method for manufacturing a pressure vessel will be described.

[0116] The seamless steel pipe of the present invention can be used as a pressure vessel having high pressure, such as a pressure vessel for compressed fluid or a pressure vessel for high-pressure gas, and having specifications in which, for example, compared with an electric-resistance-welded pipe and the like, a requirement for roundness is high.

[0117] For example, when using the seamless steel pipe of the present invention for a pressure vessel, a pressure vessel can be manufactured by performing necessary processing on the seamless steel pipe. The processing is not particularly limited, but examples thereof include processing for rendering defects on the inner surface of the steel pipe harmless, and processing for attaching a lid to an end portion of the steel pipe. Examples of processing for rendering defects on the inner surface of the steel pipe harmless include cutting the inner surface of the steel pipe with a tool, grinding with a grindstone, and shot blasting. Further, examples of processing for attaching a lid include providing a screw thread for screwing a lid to an end portion of the steel pipe, and forming a flange for tightening a lid with bolts.

[0118] Further, the seamless steel pipe of the present invention can be used for any use in which it is used in a state of being in contact with hydrogen gas, such as a pressure vessel for hydrogen gas and piping for hydrogen gas. Among these, it can be used suitably as a seamless steel pipe excellent in hydrogen-embrittlement resistance used under a high-pressure hydrogen-gas environment.

[0119] For example, when using the seamless steel pipe of the present invention for a pressure vessel for hydrogen gas, a pressure vessel for hydrogen gas can be manufactured by performing necessary processing on the seamless steel pipe. The above-described processing is not particularly limited, but examples thereof include processing for rendering defects on the inner surface of the steel pipe harmless, and processing for attaching a lid to an end portion of the steel pipe. Examples of processing for rendering defects on the inner surface of the steel pipe harmless include cutting the inner surface of the steel pipe with a tool, grinding with a grindstone, and shot blasting. Further, examples of processing for attaching a lid include providing a screw thread for screwing a lid to an end portion of the steel pipe, and forming a flange for tightening a lid with bolts.

[0120] The seamless steel pipe of the present invention can be used without performing heat treatment such as additionally adjusting strength, even when used as a pressure vessel other than for hydrogen gas, or when used as a pressure vessel for hydrogen gas.

[0121] Note that, since the seamless steel pipe of the present invention is excellent in quench-crack resistance and delayed-fracture characteristics, it can be used as a pressure vessel. Further, a seamless steel pipe that is excellent also in hydrogen-embrittlement resistance in addition to the above characteristics can be used as a vessel for hydrogen gas.

EXAMPLES

[0122] Next, Examples will be described.

[0123] A heated material (billet) having a component composition shown in Table 1 was subjected to piercing, pipe expansion, and rolling as shown in Table 2 to form into a pipe such that a ratio of an inner diameter of the steel pipe divided by a wall thickness was 2.0 times or more. A quenching step and a tempering step under conditions shown in Table 2 were carried out, and a seamless steel pipe having an outer diameter and a wall thickness shown in Table 2 was produced. Cooling in the quenching step was carried out while immersing the steel pipe in water and, in a state that the steel pipe was rotated in the circumferential direction of the steel pipe, by bringing a cooling medium into contact with the inner surface of the steel pipe at a flow rate of 0.5 m³/min or more. From a central portion in the longitudinal direction of each obtained seamless steel pipe, test pieces for microstructure observation, Mn segregation-degree evaluation (EPMA observation), and inclusion investigation were taken.

Average cooling rate in the quenching step:

[0124] Since it is difficult to directly measure an average cooling rate of a rotating steel pipe by a thermocouple or the like, evaluation was performed by using test pieces of the same wall thickness, obtained by dividing, in the circumferential direction into four, a steel pipe having a length of 500 mm taken from an end portion of the obtained steel pipe, and by attaching a thermocouple at the center of the wall thickness and performing actual measurement. Based on the idea that, in

a water-cooling process of the steel pipe, in addition to the fact that a cooling-rate difference in the wall-thickness direction of the steel pipe becomes small by continuously bringing a cooling medium into contact with the inner surface of the steel pipe, a cooling-rate difference in the circumferential direction becomes small by rotation of the steel pipe, the water-cooling process of the steel pipe can be simulated only by immersing the test pieces in water at room temperature, measurement was performed by the above method. For each steel type described in Table 2, four test pieces were produced, and an average value of cooling rates in a temperature range of 800 to 350°C was taken as the average cooling rate of the steel pipe. The average cooling rate is as shown in Table 2.

Microstructure observation:

[0125] From each of the seamless steel pipes, a test piece was taken such that an observation position was a 1/4 wall-thickness position from the outer surface of the steel pipe at a central portion in the longitudinal direction of the seamless steel pipe. Here, a surface composed of a wall-thickness direction and a circumferential direction (so-called "C cross section") was taken as an observation surface (10 mm × 10 mm). First, for the observation surface, an area fraction of retained austenite was calculated by the following method. The area fraction of retained austenite was obtained by chemically polishing the observation surface and performing X-ray diffraction. Co-K α radiation was used as an incident X-ray, and the area fraction of retained austenite was calculated from an intensity ratio of ferrite (200), (211), and (220) planes and austenite (200), (220), and (311) planes.

[0126] Next, after mirror-polishing the observation surface, etching was performed using an aqueous picric acid solution, and polishing was performed such that a prior γ grain boundary remained, and the size and morphology of the prior γ grain boundary were grasped using an optical microscope at an appropriate magnification between 100 and 500 times. These are indices of martensite, that is, the size and morphology of martensite were grasped. Further, after mirror-polishing the observation surface, etching was performed using a 3 vol.% nital solution, and, from comparison of images by nital etching and picric-acid etching, it was confirmed that the morphology of the prior γ grain boundary was not extremely flattened and, in addition, the inside of the prior γ grain was in a fine lath-like state, and that the microstructure was predominantly martensitic (85% or more). Thereafter, using an optical microscope at an appropriate magnification between 100 and 500 times for the structure etched with the nital, coarse grains were judged as ferrite, and an area fraction of ferrite was calculated. Thereafter, by observing the cross section etched with the nital using a scanning electron microscope (SEM) at an appropriate magnification between 1,000 and 10,000 times, a region in which lamellar carbides were confirmed was judged as pearlite, and an area fraction of pearlite was calculated. An area fraction obtained by subtracting the area fractions of retained austenite, ferrite, and pearlite from the whole (taken as 100%) was taken as an area fraction of martensite.

Inclusions

[0127] Investigation of inclusions was performed for a region from the inner surface of the steel pipe to a 1/6 wall-thickness position, which is a segregation region on the inner-surface side of the steel pipe. Specifically, it was performed by taking, from the inner surface of the obtained steel pipe, a test piece for inclusion measurement having dimensions of 20 mm in the longitudinal direction of the steel pipe, 5 mm in the circumferential direction, and 15 mm in the wall-thickness direction. The test piece was resin-embedded such that a surface composed of the longitudinal direction and the wall-thickness direction of the steel pipe (so-called "L cross section") became an observation surface, and after mirror polishing, an optical microscope observation was performed to measure a number density of inclusions having an aspect ratio of 2 or less and a length of a long side of 10 μ m or more in an area of 10 mm × 10 mm (100 mm²). Note that, for each level steel pipe, ten test pieces for inclusion investigation were taken, and a total number of inclusions having an aspect ratio of 2 or less and a length of a long side of 10 μ m or more measured in the above manner using these ten test pieces was arithmetically averaged and taken as an inclusion number (inclusion number density) of the steel pipe of that level. Note that the aspect ratio and the long-side length of inclusions are values obtained in conformity with JIS G 0555:2020 (Microscopic testing method for nonmetallic inclusions in steel).

Degree of segregation of Mn

[0128] For evaluation of the degree of segregation of Mn, a test piece taken such that a cross section in the C direction (rolling perpendicular direction) of the steel pipe became an observation surface and the observation surface was mirror-finished was used. In the observation surface, when the wall thickness of the steel pipe was t , a local concentration of Mn to be used as a reference was calculated by performing mapping analysis of the Mn concentration in region 1 enclosed by a length, in the wall-thickness direction, of $t/6$ (mm) with the 1/4 wall-thickness position in the wall-thickness direction from the steel pipe outer surface as a center (a length in the wall-thickness direction of $\pm t/12$ (mm) with a 1/4 wall-thickness position in the wall-thickness direction from the outer surface of the steel pipe as a reference) and a length, in the

circumferential direction, of 10 (mm), and by performing analysis described later. Further, a segregation concentration of Mn was calculated by performing mapping analysis of the Mn concentration in region 2 enclosed by a length, in the wall-thickness direction, of $t/6$ (mm) and a length, in the circumferential direction, of 10 (mm), and by performing analysis described later. Here, mapping analysis of the Mn concentration was performed such that mapping data were acquired by determining an analysis pitch such that 40,000 points of mapping data were obtained for each of region 1 and region 2. Subsequently, the obtained 40,000 points of mapping data were statistically analyzed and the degree of segregation of Mn was calculated. The reference local concentration of Mn was taken as an average value of mapping data obtained by excluding outliers from all mapping data obtained in region 1. Outliers were taken as mapping data less than 0.05 times and mapping data greater than 5 times the Mn concentration (Mn content) obtained from check analysis of the steel pipe. Further, the segregation concentration of Mn was taken as an average value of mapping data of the top 1% having a high Mn concentration, in mapping data obtained by excluding outliers from all mapping data obtained in region 2. At this time, mapping analysis of region 1 was performed in three fields of view, and the Mn local concentrations calculated in the three fields of view were summed and a value obtained by dividing by 3 was taken as the Mn local concentration. Similarly, mapping analysis of region 2 was also performed in three fields of view, and the Mn segregation concentrations calculated in the three fields of view were summed and a value obtained by dividing by 3 was taken as the Mn segregation concentration. A ratio of the Mn segregation concentration to the Mn local concentration obtained in this manner was calculated as the degree of segregation of Mn. *Note that the above mapping analysis was performed by EPMA as described in the embodiment.*

Cross-sectional hardness

[0129] For cross-sectional hardness, a test piece was taken such that a 1/4 wall-thickness position from the outer surface of the steel pipe became an evaluation position, and, in conformity with JIS 2244 "Vickers hardness test-Test method," hardness was measured at five points using a load of 10 kgf at the 1/4 wall-thickness position from the outer surface of the steel pipe, and an average value thereof was taken.

Quench-crack resistance:

[0130] Presence/absence of occurrence of quench cracking was evaluated in conformity with JIS G 0582 "Automatic ultrasonic testing method for steel pipes." A threshold used as a criterion for judging presence/absence of occurrence of quench cracking was set to 5% of the wall thickness, and a steel pipe satisfying this criterion was judged to have no quench cracking. First, 20 steel pipes of each level shown in Table 2 were prepared and quench-crack resistance was evaluated. That is, presence/absence of occurrence of quench cracking in the obtained steel pipes was confirmed, and a proportion of a number of those in which quench cracking did not occur among the 20 steel pipes, that is, (number of steel pipes in which quench cracking has not occurred/20) $\times$ 100 (%) was taken as a quench-cracking pass rate. Quench-crack resistance was judged to pass when the quench-cracking pass rate was 90% or more.

Delayed-fracture characteristics:

[0131] Delayed-fracture characteristics were evaluated by carrying out a storage-cracking resistance evaluation test. The storage-cracking resistance evaluation test was performed by the following procedure. First, in the evaluation of quench-crack resistance described above, after storing steel pipes in which quench cracking did not occur for 30 days outdoors where rain does not directly fall, presence/absence of occurrence of storage cracking was evaluated in conformity with JIS G 0582 "Automatic ultrasonic testing method for steel pipes," similarly to evaluation of presence/absence of occurrence of quench cracking. A threshold used as a criterion for judging occurrence of storage cracking was set to 5% of the wall thickness, and a steel pipe satisfying this criterion was judged to have no occurrence of storage cracking. Presence/absence of occurrence of storage cracking in steel pipes after storage for 30 days was confirmed, and a proportion of a number of steel pipes in which storage cracking did not occur, that is, (number of steel pipes in which storage cracking has not occurred / number of steel pipes in which quench cracking has not occurred) $\times$ 100 (%) was taken as a storage-cracking pass rate. Note that the storage-cracking resistance evaluation test was carried out only for levels whose quench-cracking pass rate in quench-crack resistance was 90% or more. Then, it was judged that a storage-cracking pass rate of 80% or more is excellent in delayed-fracture characteristics.

Hydrogen-embrittlement resistance:

[0132] Hydrogen-embrittlement resistance was evaluated by performing a tensile test in high-pressure hydrogen gas (105 MPa) at room temperature in conformity with ASTM G142, and obtaining RTS ((tensile strength in hydrogen) / tensile strength in air). A test piece was taken, in a cross section perpendicular to the pipe axis of the steel pipe (C direction:

circumferential direction), with a 1/4 wall-thickness position from the outer surface of the steel pipe as a center, such that a longitudinal direction of the test piece became a circumferential direction, as a test piece for a tensile test piece. The taken test piece was processed into a rod-shaped test piece prescribed in JIS Z 2201 "Metallic materials tensile test pieces." A tensile test was performed using the rod-shaped test piece, and it was judged that obtained RTS of 0.98 or more is excellent in hydrogen-embrittlement resistance.

[0133] As can be understood from the results shown in Table 2, the seamless steel pipes satisfying the conditions of the present invention had a metallic microstructure sufficient to realize high strength, that is, a high martensite fraction was obtained, and, as a result of obtaining a prescribed degree of segregation of Mn, satisfied a quench-cracking pass rate of 90% or more in heat treatment, a storage-cracking pass rate of 80% or more, and a cross-sectional hardness of 250 HV or more and less than 480 HV, and were excellent in quench-crack resistance and delayed-fracture characteristics. Further, the seamless steel pipes at levels at which RTS was 0.98 or more were also excellent in hydrogen-embrittlement resistance.

[0134] As described above, the seamless steel pipe of the present invention has sufficient quench-crack resistance and delayed-fracture characteristics despite having a high martensite fraction, and also has a prescribed cross-sectional hardness. In addition, it can be judged that, since the martensite fraction is high, fatigue strength is excellent. As a result, it becomes possible to supply a thick-walled and high-strength seamless steel pipe.

[Table 1]

Steel type	Component composition (mass %)										Right-hand side of Equation (1)	Satisfaction of Equation (1)	Remarks
	C	Si	Mn	S	O	N	Al	Mo	Cr	Ni	P	Others	
A	0.38	0.23	0.79	0.005	0.002	0.0034	0.03	0.25	1.05	0.01	0.018	-	Inventive steel
B	0.43	0.24	0.76	0.003	0.001	0.0062	0.03	0.22	0.80	2.04	0.015	-	Inventive steel
C	0.38	0.23	0.82	0.005	0.002	0.0034	0.03	0.25	0.65	2.95	0.013	-	Inventive steel
D	0.33	0.25	0.61	0.004	0.001	0.0051	0.03	0.30	0.91	0.02	0.023	-	Inventive steel
E	0.38	0.21	1.06	0.004	0.001	0.0041	0.03	0.28	1.04	0.04	0.013	-	Inventive steel
F	0.41	0.22	0.56	0.005	0.002	0.0042	0.04	0.21	1.09	0.01	0.024	-	Inventive steel
G	0.55	0.93	0.82	0.005	0.001	0.0035	0.03	0.16	2.84	0.01	0.009	-	Inventive steel
H	0.21	0.25	0.84	0.004	0.002	0.0028	0.03	0.19	0.99	0.01	0.016	-	Inventive steel
I	0.35	0.27	0.80	0.004	0.001	0.0036	0.04	0.48	1.04	0.01	0.018	-	Inventive steel
J	0.37	0.20	0.81	0.003	0.001	0.0039	0.03	0.23	1.02	0.03	0.022	-	Comparative steel
K	0.37	0.23	0.81	0.005	0.002	0.0031	0.04	0.28	1.07	0.01	0.021	-	Comparative steel
L	0.42	0.23	0.83	0.004	0.001	0.0049	0.03	0.24	0.95	1.91	0.017	-	Comparative steel
M	0.33	0.24	0.81	0.004	0.001	0.0031	0.03	0.22	0.92	0.02	0.022	-	Comparative steel
N	0.36	0.29	1.25	0.004	0.002	0.0032	0.03	0.19	0.99	0.01	0.012	-	Comparative steel
O	0.38	0.23	0.75	0.005	0.002	0.0034	0.03	0.25	0.35	3.51	0.017	-	Comparative steel
P	0.38	0.23	0.85	0.005	0.002	0.0034	0.03	0.25	3.21	0.01	0.018	-	Comparative steel
Q	0.63	0.27	0.67	0.004	0.001	0.0036	0.04	0.28	0.72	1.02	0.023	-	Comparative steel

(continued)

Steel type	Component composition (mass %)										Right-hand side of Equation (1)	Satisfaction of Equation (1)	Remarks
	C	Si	Mn	S	O	N	Al	Mo	Cr	Ni	P	Others	
<u>R</u>	<u>0.19</u>	0.26	<u>0.44</u>	0.004	0.002	0.0036	0.04	0.31	1.12	0.02	0.024	-	Comparative steel
<u>S</u>	0.35	0.27	0.54	0.004	0.001	0.0036	0.04	0.28	1.04	0.01	0.029	-	Comparative steel
T	0.37	0.25	0.81	0.004	0.001	0.0036	0.04	0.29	1.02	1.53	0.015	B:0.002, Ti:0.02	Inventive steel
U	0.36	0.29	0.87	0.004	0.001	0.0050	0.04	0.28	1.01	0.02	0.013	Cu:1.05, Co:0.99	Inventive steel
V	0.39	0.21	0.73	0.005	0.002	0.0036	0.03	0.34	0.98	0.01	0.017	V:0.38, Nb:0.041	Inventive steel
W	0.34	0.56	0.67	0.006	0.003	0.0036	0.04	0.15	1.07	0.02	0.016	W:1.7, Zr:0.02, Ta:0.05	Inventive steel
X	0.41	0.31	0.81	0.004	0.001	0.0036	0.03	0.27	0.78	0.01	0.008	Hf:0.07, Sb:0.06, Sn:0.04	Inventive steel
Y	0.38	0.46	0.75	0.006	0.002	0.0030	0.04	0.25	1.09	0.01	0.020	Ca:0.002, Mg:0.003, REM:0.25	Inventive steel
Z	0.37	0.23	0.81	0.005	0.002	0.0034	0.03	0.25	1.05	0.01	0.014	Cu:0.06	Inventive steel
AA	0.35	0.24	0.78	0.006	0.002	0.0035	0.03	0.25	1.04	2.05	0.012	Cu:0.43, Sn:0.03	Inventive steel
AB	0.36	0.25	0.75	0.003	0.001	0.0031	0.04	0.17	0.98	1.98	0.009	Cu:4.10	Inventive steel
Those underlined are outside the scope of the present invention.													

[0135]

[Table 2]

5	Level	Steel type	Dimensions of the steel pipe					Manufacturing step					Material properties of the seamless steel pipe							Quench-cracking resistance	Delayed-fracture resistance	Hydrogen-embrittlement resistance	Remarks	
								Quenching			Tempering													
			Outer diameter (mm)	Wall thickness (mm)	Inner diameter (mm)	Left-hand side of Formula (2)	Whether Equation (2) is satisfied	Temperature (°C)	Time (min)	Average cooling rate in the temperature range of 800 to 350°C (°C/s)	Yes or No	Temperature (°C)	Time (min)	Segregation degree of Mn	Segregation degree evaluation	Number of inclusions (/100mm ²)	Inclusion evaluation	Area fraction of Martensite (%)	Area fraction evaluation	Cross-sectional Hardness (HV)	Quench cracking pass rate (%)	Storage cracking pass rate (%)		RTS
10	1	A	406	42	322	107	○	820	30	7	Yes	640	30	1.55	×	5.2	○	90.0	○	280	75	—	—	Comparative Example
	2	A	406	42	322	107	○	860	15	7	Yes	640	30	1.53	×	5.3	○	95.0	○	281	80	—	—	Comparative Example
	3	A	406	42	322	107	○	860	30	7	Yes	640	30	1.47	○	5.4	○	100.0	○	283	95	100	1.00	Inventive Example
	4	A	406	42	322	107	○	860	30	7	No	—	—	1.47	○	5.4	○	100.0	○	552	60	—	—	Comparative Example
	5	A	406	60	286	159	○	860	15	5	Yes	640	30	1.52	×	7.2	○	85.0	○	274	85	—	—	Comparative Example
15	6	A	406	60	286	159	○	860	30	5	Yes	640	30	1.45	○	7.3	○	85.0	○	272	95	100	1.00	Inventive Example
	7	A	406	60	286	159	○	860	60	5	Yes	640	60	1.42	○	7.9	○	90.0	○	278	100	100	1.01	Inventive Example
	8	A	406	60	286	159	○	900	15	5	Yes	640	30	1.51	×	7.6	○	85.0	○	275	80	—	—	Comparative Example
	9	A	406	60	286	159	○	900	30	5	Yes	640	30	1.42	○	7.8	○	85.0	○	276	100	100	0.99	Inventive Example
	10	A	406	60	286	159	○	900	30	5	Yes	440	30	1.42	○	7.8	○	85.0	○	467	100	100	0.85	Inventive Example
20	11	A	406	60	286	159	○	900	30	5	Yes	500	30	1.45	○	3.5	○	100.0	○	389	100	95	0.93	Inventive Example
	12	A	406	60	286	159	○	900	30	5	Yes	610	30	1.47	○	4.1	○	100.0	○	305	100	100	0.99	Inventive Example
	13	A	406	71	264	213	×	860	30	3	Yes	640	30	1.49	○	10.6	×	85.0	○	274	90	83	—	Inventive Example
	14	A	356	60	236	186	○	860	30	5	Yes	640	30	1.47	○	8.7	○	85.0	○	272	95	100	1.00	Inventive Example
	15	A	356	70	216	244	×	860	30	4	Yes	640	30	1.49	○	9.5	○	85.0	○	254	90	94	—	Inventive Example
25	16	A	306	55	196	197	○	860	30	5	Yes	640	30	1.45	○	8.9	○	85.0	○	275	95	100	1.01	Inventive Example
	17	A	306	70	166	295	×	860	30	4	Yes	640	30	1.49	○	9.6	○	85.0	○	268	90	89	—	Inventive Example
	18	B	406	61	284	200	○	860	30	5	Yes	640	30	1.48	○	8.2	○	95.0	○	282	95	100	1.01	Inventive Example
	19	C	406	42	322	149	○	860	30	5	Yes	640	30	1.41	○	8.6	○	100.0	○	284	90	100	1.00	Inventive Example
	20	D	406	40	326	73	○	860	30	7	Yes	640	30	1.42	○	4.3	○	90.0	○	277	100	100	0.99	Inventive Example
	21	E	406	40	326	170	○	860	30	7	Yes	640	30	1.48	○	6.7	○	100.0	○	287	100	100	1.00	Inventive Example
	22	F	406	40	326	68	○	860	30	8	Yes	640	30	1.42	○	3.5	○	95.0	○	291	100	100	0.99	Inventive Example
	23	G	406	42	322	137	○	860	30	6	Yes	640	30	1.46	○	5.6	○	95.0	○	328	100	90	1.00	Inventive Example
	24	H	406	41	324	112	○	860	30	7	Yes	640	30	1.47	○	8.2	○	95.0	○	261	95	100	1.00	Inventive Example
	25	I	406	40	326	105	○	860	30	7	Yes	640	30	1.39	○	2.4	○	95.0	○	271	100	100	1.02	Inventive Example

30	Level	Steel type	Dimensions of the steel pipe					Manufacturing step					Material properties of the seamless steel pipe							Quench-cracking resistance	Delayed-fracture resistance	Hydrogen-embrittlement resistance	Remarks	
								Quenching			Tempering													
			Outer diameter (mm)	Wall thickness (mm)	Inner diameter (mm)	Left-hand side of Formula (2)	Whether Equation (2) is satisfied	Temperature (°C)	Time (min)	Average cooling rate in the temperature range of 800 to 350°C (°C/s)	Yes or No	Temperature (°C)	Time (min)	Segregation degree of Mn	Segregation degree evaluation	Number of inclusions (/100mm ²)	Inclusion evaluation	Area fraction of Martensite (%)	Area fraction evaluation	Cross-sectional Hardness (HV)	Quench cracking pass rate (%)	Storage cracking pass rate (%)		RTS
35	26	J	406	42	322	111	○	860	30	7	Yes	640	30	1.43	○	1.4	○	95.0	○	278	80	—	—	Comparative Example
	27	K	406	61	284	173	○	860	30	5	Yes	640	30	1.47	○	4.4	○	95.0	○	280	70	—	—	Comparative Example
	28	L	406	61	284	243	×	860	30	5	Yes	640	30	1.50	×	6.1	○	100.0	○	284	40	—	—	Comparative Example
	29	M	406	40	326	105	○	860	30	8	Yes	640	30	1.46	○	5.9	○	95.0	○	273	75	—	—	Comparative Example
	30	N	406	41	324	247	×	860	30	7	Yes	640	30	1.61	×	7.3	○	100.0	○	279	25	—	—	Comparative Example
40	31	O	406	41	324	132	○	860	30	7	Yes	640	30	1.48	○	6.7	○	100.0	○	284	65	—	—	Comparative Example
	32	P	406	42	322	145	○	860	30	6	Yes	640	30	1.53	×	5.3	○	95.0	○	277	55	—	—	Comparative Example
	33	Q	406	40	326	93	○	860	30	7	Yes	640	60	1.43	○	4.3	○	95.0	○	301	35	—	—	Comparative Example
	34	R	406	41	324	53	○	860	30	7	Yes	640	30	1.38	○	4.3	○	75.0	×	248	100	100	—	Comparative Example
	35	S	406	41	324	65	○	860	30	7	Yes	640	30	1.41	○	10.8	×	95.0	○	272	45	—	—	Comparative Example
	36	T	406	42	322	130	○	860	30	7	Yes	640	30	1.43	○	7.2	○	95.0	○	272	100	100	1.00	Inventive Example
	37	U	406	43	320	127	○	860	30	6	Yes	640	30	1.47	○	6.9	○	100.0	○	272	100	100	1.01	Inventive Example
	38	V	406	41	324	94	○	860	30	7	Yes	640	30	1.37	○	5.4	○	95.0	○	276	100	100	1.00	Inventive Example
	39	W	406	40	326	83	○	860	30	7	Yes	640	60	1.35	○	7.3	○	90.0	○	265	100	100	1.00	Inventive Example
	40	X	406	41	324	107	○	860	30	7	Yes	640	30	1.42	○	6.5	○	100.0	○	288	95	100	0.99	Inventive Example
45	41	Y	406	42	322	99	○	860	30	6	Yes	640	30	1.44	○	5.7	○	95.0	○	282	100	100	1.00	Inventive Example
	42	Z	406	60	286	168	○	860	30	6	Yes	640	30	1.45	○	5.5	○	95.0	○	291	95	95	1.00	Inventive Example
	43	AA	406	60	286	208	○	860	30	6	Yes	640	30	1.43	○	4.1	○	100.0	○	288	100	100	1.00	Inventive Example
	44	AB	406	60	286	189	○	860	30	7	Yes	600	30	1.41	○	2.7	○	100.0	○	351	100	100	1.00	Inventive Example

Those underlined are outside the scope of the present invention

50 Claims

1. A seamless steel pipe comprising:

a component composition containing, in mass%,
 C: 0.20 to 0.60%,
 Si: 0.01 to 2.0%,
 Mn: 0.5 to 1.2%,
 S: 0.010% or less,

O: 0.005% or less,
 N: 0.010% or less,
 Al: 0.01 to 0.08%,
 Mo: 0.005 to 1.0%,
 Cr: 0.005 to 3.0%, and
 Ni: 0.005 to 3.0%,
 optionally one or two or more selected from
 Ti: 0.0001 to 0.1%,
 Cu: 0.0001 to 5.0%,
 Co: 0.0001 to 5.0%,
 B: 0.0001 to 0.01%,
 V: 0.0001 to 1.0%,
 W: 0.0001 to 5.0%,
 Nb: 0.0001 to 0.1%,
 Zr: 0.0001 to 0.2%,
 Hf: 0.0001 to 0.2%,
 Ta: 0.0001 to 0.2%,
 Sb: 0.0001 to 0.1%,
 Sn: 0.0001 to 0.1%,
 Ca: 0.0001 to 0.01%,
 Mg: 0.0001 to 0.01%, and
 REM: 0.0001 to 0.5%, and
 the component composition further containing P so as to satisfy the following formula (1):

$$[P] \leq 0.042 - 0.002[C] - 0.024[Mn] - 0.001[Mo] - 0.001[Cr] - 0.002[Ni] \cdots (1) \quad (1)$$

(where [element] in formula (1) represents a content (mass%) of the element described in the brackets),
 the balance being Fe and unavoidable impurities;
 a degree of segregation of Mn from an inner surface of the steel pipe to a 1/6 wall-thickness position of less than 1.50;
 a metallic microstructure having an area fraction of martensite of 85% or more; and
 a cross-sectional hardness of 250 HV or more and less than 480 HV.

2. The seamless steel pipe according to claim 1, wherein a wall thickness of the steel pipe is 40 mm or more.
3. The seamless steel pipe according to claim 1 or 2, wherein, in a region from the inner surface of the steel pipe to a 1/6 wall-thickness position, a number of inclusions having an aspect ratio of 2 or less and a length of a long side of 10 μm or more is 10 pieces per 100 mm^2 or less.
4. A method for manufacturing a seamless steel pipe according to any one of claims 1 to 3, the method comprising:
 - a pipe-forming step of pipe-forming a heated material such that a ratio of an inner diameter of the steel pipe divided by a wall thickness is 2.0 times or more;
 - a quenching step of heating the formed steel pipe to a temperature range of 860°C or more, holding in the temperature range for 30 min or more, and water cooling under conditions such that an average cooling rate in a temperature range of 800 to 350°C is 3°C/s or more, wherein, in the water cooling, the steel pipe is cooled while bringing a cooling medium into contact with an inner surface of the steel pipe at a flow rate of 0.5 m^3/min or more in a state that the steel pipe is rotated in a circumferential direction of the steel pipe; and
 - a tempering step of, after the quenching step, holding the steel pipe under conditions of 30 min or more in a temperature range in which the temperature is 400 to 680°C.
5. The method for manufacturing a seamless steel pipe according to claim 4, wherein the pipe-forming step is performed such that a shape of the steel pipe satisfies the following formula (2):

$$(\text{EXP}(\text{coefficient } K \times \text{wall thickness}) / \text{circumferential cross section area}) \times 10^6 < 210 \cdots (2) \quad (2)$$

$$K = \{0.41([C] - 0.24) + 4.58[Mn] + 0.21[Cr] + 0.25[Ni]\} / 100$$

... (3)

(where [element] in formula (3) represents a content (mass%) of the element described in the brackets).

6. A pressure vessel wherein the seamless steel pipe according to any one of claims 1 to 3 is used as the pressure vessel.
7. A pressure vessel for hydrogen gas wherein the seamless steel pipe according to any one of claims 1 to 3 is used as the pressure vessel.
8. A method for manufacturing a pressure vessel or a pressure vessel for hydrogen gas, the method comprising processing the seamless steel pipe according to any one of claims 1 to 3.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2025/004596

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/00(2006.01)i; *C21D 7/06*(2006.01)i; *C21D 8/10*(2006.01)i; *C21D 9/08*(2006.01)i; *C22C 38/60*(2006.01)i
FI: C22C38/00 301Z; C21D8/10 C; C21D9/08 E; C22C38/60; C21D7/06 A

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C38/00-38/60; C21D7/06; C21D8/10; C21D9/08

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 1971-2025
Registered utility model specifications of Japan 1996-2025
Published registered utility model applications of Japan 1994-2025

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.
A	JP 2014-012890 A (JFE STEEL CORPORATION) 23 January 2014 (2014-01-23) entire text, all drawings	1-8
A	JP 2018-070970 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 10 May 2018 (2018-05-10) entire text, all drawings	1-8
A	JP 2019-183218 A (NIPPON STEEL CORPORATION) 24 October 2019 (2019-10-24) entire text, all drawings	1-8
A	WO 2016/038810 A1 (JFE STEEL CORPORATION) 17 March 2016 (2016-03-17) entire text	1-8
A	WO 2018/025778 A1 (NIPPON STEEL & SUMITOMO METAL CORPORATION) 08 February 2018 (2018-02-08) entire text, all drawings	1-8

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

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“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

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“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

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Date of the actual completion of the international search

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Name and mailing address of the ISA/JP

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2025/004596

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JP	2014-012890	A	23 January 2014	(Family: none)		
JP	2018-070970	A	10 May 2018	(Family: none)		
JP	2019-183218	A	24 October 2019	(Family: none)		
WO	2016/038810	A1	17 March 2016	US	2017/0283918	A1
				whole document		
WO	2018/025778	A1	08 February 2018	US	2019/0177813	A1
				whole document		

REFERENCES CITED IN THE DESCRIPTION

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- WO 2018055937 A [0006]