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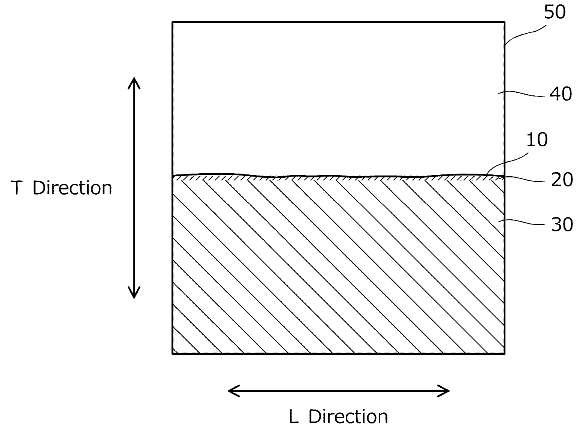
(54) **MARTENSITIC STAINLESS STEEL SEAMLESS PIPE AND METHOD FOR PRODUCING MARTENSITIC STAINLESS STEEL SEAMLESS PIPE**

(57) A martensitic stainless steel seamless pipe in which both a high yield strength, and excellent pitting resistance at the inner surface of the martensitic stainless steel seamless pipe are achieved is provided. A martensitic stainless steel seamless pipe according to the present disclosure has a chemical composition described in the description, the microstructure described in the description, and a yield strength of 862 MPa or more. An observation field of view region (50) which is 1.0 μm long in each of a pipe axis direction (L direction) and a pipe radius direction (T direction) and which includes an inner surface (10) extending in the L direction is composed of an inner surface vicinity region (20), an interior region (30) that is below contact with the inner surface vicinity region (20), and a hollow region (40). When the observation field of view region (50) is divided into sections by being divided equally into 256 sections in the L direction and divided equally into 256 sections in the T direction, an inner surface Cu occupancy OSc_u which is defined as the numerical proportion of sections in which a Cu concentration is more than 2.0% in the inner surface vicinity region (20), and an interior Cu occupancy OI_{Cu} which is defined as the numerical proportion of sections in which the Cu concentration is more than 2.0% in the interior region (30) satisfy Formula (2).

$$OS_{Cu}/OI_{Cu} \geq 1.20 \quad (2)$$

FIG.1



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Description

TECHNICAL FIELD

[0001] The present disclosure relates to a seamless steel pipe and a method for producing the seamless steel pipe, and more particularly relates to a martensitic stainless steel seamless pipe and a method for producing the martensitic stainless steel seamless pipe.

BACKGROUND ART

[0002] Oil wells or gas wells (hereinafter, oil wells and gas wells are collectively referred to simply as "oil wells") contain hydrogen sulfide (H_2S) or carbon dioxide gas (CO_2) or the like which are corrosive. Here, it is known that chromium (Cr) is effective for improving the carbonic-acid gas corrosion resistance of a steel material. Therefore, in oil wells in environments which contain a large amount of carbon dioxide gas, martensitic stainless steel materials containing about 13% by mass of Cr that are typified by API L80 13Cr steel material (normal 13Cr steel material) and Super 13Cr steel material in which the content of C is reduced are used according to the partial pressure and temperature of the carbon dioxide gas.

[0003] In recent years, oil wells are being made deeper, and consequently there is a need for steel materials to have not just corrosion resistance but to also have enhanced strength. For example, steel materials that have a yield strength of 110 ksi grade (110 to less than 125 ksi, that is, 758 to less than 862 MPa), and also of 125 ksi grade or more (that is, 862 MPa or more) are beginning to be demanded.

[0004] Here, in the present description, an environment containing hydrogen sulfide and carbon dioxide gas is referred to as a "sour environment". Oil-well steel materials to be used in a sour environment are also required to have excellent corrosion resistance. That is, in recent years, there is a growing demand for oil-well steel materials which achieve both high strength and excellent corrosion resistance.

[0005] International Application Publication No. WO2006/061881 (Patent Literature 1), International Application Publication No. WO2008/023702 (Patent Literature 2), and International Application Publication No. WO2015/178022 (Patent Literature 3) each proposes an oil-well steel material which achieves both high strength and excellent corrosion resistance.

[0006] Patent Literature 1 discloses an oil-well steel material that is a martensitic stainless steel pipe for oil wells that consists of, in mass%, C: 0.005 to 0.1%, Si: 0.05 to 1%, Mn: 1.5 to 5%, P: 0.05% or less, S: 0.01% or less, Cr: 9 to 13%, Ni: 0.5% or less, Mo: 2% or less, Cu: 2% or less, Al: 0.001 to 0.1%, and N: 0.001 to 0.1%, with the balance being Fe and impurities, and which has a Cr-depleted zone under the surface thereof. Patent Literature 1 discloses that, as a result, this oil-well steel material has a high strength of 655 MPa or more, and has high SCC resistance (stress corrosion cracking resistance) even though it has a Cr-depleted zone under the surface thereof.

[0007] Patent Literature 2 discloses an oil-well steel material that is a martensitic stainless steel that consists of, in mass%, C: 0.010 to 0.030%, Mn: 0.30 to 0.60%, P: 0.040% or less, S: 0.0100% or less, Cr: 10.00 to 15.00%, Ni: 2.50 to 8.00%, Mo: 1.00 to 5.00%, Ti: 0.050 to 0.250%, V: 0.25% or less, N: 0.07% or less, and one or more kinds of element among Si: 0.50% or less and Al: 0.10% or less, with the balance being Fe and impurities, and which satisfies the formula: ($6.0 \leq Ti/C \leq 10.1$). Patent Literature 2 discloses that this oil-well steel material has a yield strength of 758 to 862 MPa and, and with respect to corrosion resistance properties, is excellent in SSC resistance (sulfide stress cracking resistance).

[0008] Patent Literature 3 discloses an oil-well steel material that is a high-strength stainless steel seamless pipe for oil wells, which has a chemical composition that contains Cr and Ni and satisfies the formula: ($Cr/Ni \leq 5.3$), and has the microstructure mainly composed of tempered martensite phase. This oil-well steel material has a surface layer microstructure in which a phase which turns white in color upon etching with Vilella's reagent has a thickness of 10 to 100 μm in a wall thickness direction from the outer surface of the steel pipe and is dispersed with an area fraction of 50% or more at the outer surface of the steel pipe. Patent Literature 3 discloses that this oil-well steel material has a yield strength of 654 MPa or more and is excellent in corrosion resistance.

CITATION LIST

PATENT LITERATURE

[0009]

Patent Literature 1: International Application Publication No. WO2006/061881
Patent Literature 2: International Application Publication No. WO2008/023702
Patent Literature 3: International Application Publication No. WO2015/178022

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0010] The aforementioned Patent Literatures 1 to 3 propose techniques for achieving both high strength and excellent corrosion resistance. In this connection, when a martensitic stainless steel seamless pipe is used as an oil-well steel pipe, production fluid directly contacts the inner surface of the seamless steel pipe. Therefore, the inner surface of the seamless steel pipe, in particular, is required to have corrosion resistance against pitting and/or crevice corrosion (hereunder, referred to as "pitting resistance"). However, in the aforementioned Patent Literatures 1 to 3, no consideration is given to pitting resistance at the inner surface of a seamless steel pipe.

[0011] An objective of the present disclosure is to provide a martensitic stainless steel seamless pipe that can achieve both high strength and excellent pitting resistance at the inner surface of the seamless steel pipe, and a method for producing the martensitic stainless steel seamless pipe.

SOLUTION TO PROBLEM

[0012] A martensitic stainless steel seamless pipe according to the present disclosure consists of, in mass%,

C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cr: 11.00 to 14.00%,
Ni: 5.00 to 7.50%,
Mo: 1.50 to 4.50%,
Cu: 0.50 to 3.50%,
Co: 0.010 to 0.500%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Ca: 0.0005 to 0.0050%,
Al: 0.001 to 0.100%,
N: 0.0010 to 0.0500%,
O: 0.050% or less,
W: 0 to 2.00%,
Nb: 0 to 0.50%,
Mg: 0 to 0.0050%,
rare earth metal: 0 to 0.0050%,
B: 0 to 0.0050%, and
the balance: Fe and impurities,
and satisfies Formula (1),
wherein:

a microstructure is composed of, in volume percent, retained austenite in an amount of 0 to 15.0% and ferrite in an amount of 0 to 5.0%, with the balance being tempered martensite;
a yield strength is 862 MPa or more;
when a pipe axis direction of the martensitic stainless steel seamless pipe is defined as an L direction, and a pipe radius direction of the martensitic stainless steel seamless pipe is defined as a T direction,
with respect to a square observation field of view region that includes an inner surface of the martensitic stainless steel seamless pipe that extends in the L direction, and whose sides that extend in the L direction are 1.0 μm in length and whose sides that extend in the T direction are 1.0 μm in length,
when the observation field of view region is divided into 65,536 sections by being divided equally into 256 sections in the L direction and divided equally into 256 sections in the T direction,
the observation field of view region is composed of:

an inner surface vicinity region which is a rectangular region that has the inner surface of the martensitic stainless steel seamless pipe as a top edge and includes 256 sections in the L direction and six sections in the T direction,

an interior region which is below contact with the inner surface vicinity region, and
a hollow region which is above contact with the inner surface vicinity region; and
when, among all the sections in the inner surface vicinity region, a numerical proportion of sections in which a Cu concentration is more than 2.0% is defined as inner surface Cu occupancy OS_{Cu}, and
among all the sections in the interior region, a numerical proportion of sections in which a Cu concentration is more than 2.0% is defined as interior Cu occupancy OI_{Cu},
the inner surface Cu occupancy OS_{Cu} and the interior Cu occupancy OI_{Cu} satisfy Formula (2);

$$Mo + 0.5 \times W \geq 2.50 \quad (1)$$

$$OS_{Cu}/OI_{Cu} \geq 1.20 \quad (2)$$

where, a content of a corresponding element in mass% is substituted for each symbol of an element in Formula (1).

[0013] A method for producing a martensitic stainless steel seamless pipe according to the present disclosure is a method for producing the martensitic stainless steel seamless pipe described above, including:

a starting material preparation process of preparing a starting material which consists of, in mass%,
C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cr: 11.00 to 14.00%,
Ni: 5.00 to 7.50%,
Mo: 1.50 to 4.50%,
Cu: 0.50 to 3.50%,
Co: 0.010 to 0.500%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Ca: 0.0005 to 0.0050%,
Al: 0.001 to 0.100%,
N: 0.0010 to 0.0500%,
O: 0.050% or less,
W: 0 to 2.00%,
Nb: 0 to 0.50%,
Mg: 0 to 0.0050%,
rare earth metal: 0 to 0.0050%,
B: 0 to 0.0050%, and
the balance: Fe and impurities,
and which satisfies Formula (1);
a hot working process of heating, in a heating furnace, the starting material that is prepared, and thereafter performing hot working in which an area reduction ratio R defined by Formula (A) is 40% or more and a hot working time is 15 minutes or less to produce a hollow shell;
a quenching process of subjecting the hollow shell that is at a temperature not less than an A_3 point to quenching; and
a tempering process of performing tempering of the hollow shell subjected to the quenching, under conditions that satisfy Formula (B);

$$Mo + 0.5 \times W \geq 2.50 \quad (1)$$

$$R = \{1 - (\text{cross-sectional area perpendicular to pipe axis direction of the hollow shell after hot working/cross-sectional area perpendicular to axial direction of the starting material before hot working})\} \times 100 \quad (A)$$

$$(T + 273.15) \times (20 + \log_{10}(t/60)) \times (1 - [Cu]/100) \leq 17200 \quad (B)$$

where, a content of a corresponding element in mass% is substituted for each symbol of an element in Formula (1), and in Formula (B), a tempering temperature in °C is substituted for T, a tempering time in minutes is substituted for t, and a content of Cu in the hollow shell in mass% is substituted for [Cu].

ADVANTAGEOUS EFFECTS OF INVENTION

[0014] The martensitic stainless steel seamless pipe according to the present disclosure can achieve both high strength and excellent pitting resistance at an inner surface. According to the method for producing a martensitic stainless steel seamless pipe according to the present disclosure, a martensitic stainless steel seamless pipe that can achieve both high strength and excellent pitting resistance at an inner surface can be produced.

BRIEF DESCRIPTION OF DRAWINGS

[0015]

[FIG. 1] FIG. 1 is a schematic diagram illustrating one example of a manner of microstructure observation performed at a cross section including an inner surface of a martensitic stainless steel seamless pipe, that includes a pipe axis direction and a pipe radius direction.
[FIG. 2] FIG. 2 is a schematic diagram illustrating when an observation field of view region is divided into 65,536 sections by being divided equally into 256 sections in the pipe radius direction (L direction) and divided equally into 256 sections in the pipe axis direction (T direction).
[FIG. 3] FIG. 3 is a schematic diagram illustrating a relation between a position in the pipe radius direction (T direction) of each section in the observation field of view region and an average value of an Fe concentration in the pipe axis direction (L direction).

DESCRIPTION OF EMBODIMENTS

[0016] First, the present inventors conducted studies from the viewpoint of the chemical composition with respect to a martensitic stainless steel seamless pipe that can achieve both a high yield strength and excellent pitting resistance at an inner surface. As a result, the present inventors considered that if a martensitic stainless steel seamless pipe consists of, in mass%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, P: 0.030% or less, S: 0.0050% or less, Cr: 11.00 to 14.00%, Ni: 5.00 to 7.50%, Mo: 1.50 to 4.50%, Cu: 0.50 to 3.50%, Co: 0.010 to 0.500%, Ti: 0.050 to 0.300%, V: 0.01 to 1.00%, Ca: 0.0005 to 0.0050%, Al: 0.001 to 0.100%, N: 0.0010 to 0.0500%, O: 0.050% or less, W: 0 to 2.00%, Nb: 0 to 0.50%, Mg: 0 to 0.0050%, rare earth metal: 0 to 0.0050%, and B: 0 to 0.0050%, with the balance being Fe and impurities, there is a possibility that both a high yield strength of 125 ksi or more (862 MPa or more) and excellent pitting resistance at an inner surface can be achieved.
[0017] On the other hand, when the strength of a steel material is increased, there is a tendency for the corrosion resistance of the steel material to easily decrease. Therefore, even in the case of martensitic stainless steel seamless pipes having the chemical composition described above, there were some cases in which the pitting resistance decreased as a result of increasing the yield strength to 125 ksi or more. Therefore, the present inventors investigated various techniques for increasing the pitting resistance of a martensitic stainless steel seamless pipe having the chemical composition described above, while maintaining a yield strength of 125 ksi or more. As a result, the present inventors obtained the following finding.
[0018] With respect to a chemical composition for increasing the pitting resistance of a martensitic stainless steel seamless pipe, the present inventors focused on molybdenum (Mo) and tungsten (W). Mo dissolves and increases the pitting resistance of the seamless steel pipe. Further, W dissolves and increases the pitting resistance of the seamless steel pipe. That is, the present inventors considered that by increasing the content of Mo and the content of W, the pitting

resistance of the seamless steel pipe may be increased.

[0019] Here, let Fn1 be defined as Fn1 = Mo + 0.5 × W. If Fn1 is increased, the pitting resistance of the seamless steel pipe will be increased while maintaining the yield strength of the seamless steel pipe. Therefore, the martensitic stainless steel seamless pipe according to the present embodiment has the chemical composition and microstructure described above, and furthermore, the chemical composition satisfies the following Formula (1). As a result, on the condition that other requirements of the present embodiment are satisfied, the martensitic stainless steel seamless pipe according to the present embodiment can achieve both a yield strength of 125 ksi or more and excellent pitting resistance.

$$\mathrm{Mo} + 0.5 \times \mathrm{W} \geq 2.50 \qquad (1)$$

[0020] Where, a content of a corresponding element in mass% is substituted for each symbol of an element in Formula (1).

[0021] On the other hand, as a result of detailed studies conducted by the present inventors it was revealed that even in the case of martensitic stainless steel seamless pipes having the above chemical composition including Formula (1), when the yield strength is 125 ksi or more, excellent pitting resistance at the inner surface of the seamless steel pipe is not obtained in some cases. Therefore, with respect to a martensitic stainless steel seamless pipe having the above chemical composition including Formula (1), the present inventors conducted detailed studies regarding techniques for increasing the pitting resistance at the inner surface of the seamless steel pipe.

[0022] First, the present inventors focused on the state in the vicinity of the inner surface of a seamless steel pipe, and investigated techniques for increasing the pitting resistance of the inner surface. As a result, it was revealed that there is a possibility that copper (Cu) precipitates in the vicinity of the inner surface of a seamless steel pipe increase the pitting resistance of the inner surface of the seamless steel pipe. Therefore, the present inventors produced various martensitic stainless steel seamless pipes having the chemical composition described above and in which Cu precipitates were formed in the vicinity of the inner surface, and conducted detailed investigations and studies regarding the pitting resistance of the inner surface.

[0023] As a result of the detailed studies conducted by the present inventors it was revealed that in a martensitic stainless steel seamless pipe having the chemical composition described above, by not just simply causing Cu precipitates to precipitate, but rather by causing Cu precipitates to dominantly distribute in the vicinity of the inner surface, the pitting resistance of the inner surface is markedly increased. This point will be described specifically using the drawings.

[0024] FIG. 1 is a schematic diagram illustrating one example of a manner of performing microstructure observation performed at a cross section including an inner surface of a martensitic stainless steel seamless pipe having the chemical composition described above, that includes the pipe axis direction and the pipe radius direction. A horizontal direction in an observation field of view region 50 in FIG. 1 corresponds to the pipe axis direction, and a vertical direction corresponds to the pipe radius direction. In the present description, the pipe axis direction of the martensitic stainless steel seamless pipe is also referred to as an "L direction", and the pipe radius direction of the martensitic stainless steel seamless pipe is also referred to as a "T direction". In FIG. 1, the L-direction length of the observation field of view region 50 illustrated in the schematic diagram is 1.0 μm, and the T-direction length is also 1.0 μm.

[0025] In FIG. 1, an inner surface 10 of the seamless steel pipe can be confirmed as a line segment which is near the center in the T direction and which extends in the L direction. The inner surface 10 of the seamless steel pipe can be unambiguously identified by those skilled in the art by a method that is described later. Here, in FIG. 1, the area below the inner surface 10 is the martensitic stainless steel seamless pipe. In addition, the observation field of view region 50 shown in FIG. 1 is divided into 65,536 sections by being divided equally into 256 sections in the L direction and divided equally into 256 sections in the T direction.

[0026] Here, a region 20 in FIG. 1 is also referred to as an "inner surface vicinity region" of the seamless steel pipe. In the present embodiment, the inner surface vicinity region 20 is defined as a rectangular region which has the inner surface 10 as a top edge, and which is composed of 256 sections in the L direction and 6 sections in the T direction. In addition, a region 30 in FIG. 1 is also referred to as an "interior region" of the seamless steel pipe. In the present embodiment, the interior region 30 is a rectangular region that is below contact with the inner surface vicinity region 20. A region 40 in FIG. 1 is also referred to as a "hollow region". The hollow region 40 corresponds to a through-hole of the martensitic stainless steel seamless pipe. In short, the observation field of view region 50 in FIG. 1 is composed of the inner surface vicinity region 20, the interior region 30 that is below contact with the inner surface vicinity region 20, and the hollow region 40 that is above contact with the inner surface vicinity region 20.

[0027] Each of the 65,536 sections of the observation field of view region 50 is subjected to an element concentration analysis to identify the concentration of specific metal elements, which will be described in detail later, in each section. The proportion of Cu in the obtained specific metal elements is determined as a percentage, and is defined as the Cu concentration in each section. In the present description, in the observation field of view region 50, the numerical proportion of sections in which the Cu concentration is more than 2.0% among the sections which the inner surface vicinity region 20 includes is defined as "inner surface Cu occupancy OS_{Cu}". Similarly, in the present description, in the observation field of view region 50, the numerical proportion of sections in which the Cu concentration is more than 2.0% among the sections which the interior region 30 includes is defined as "interior Cu occupancy OIcu".

[0028] Let Fn2 be defined as Fn2 = OS_{Cu}/OI_{Cu}. Fn2 is an index that indicates the degree of dominant distribution of Cu precipitates to the inner surface vicinity region 20. The larger the value of Fn2 is, the greater the degree to which the Cu precipitates are dominantly distributed to the inner surface vicinity region 20 is, and the more the pitting resistance of the inner surface can be effectively increased. As a result of detailed studies, the present inventors discovered that in a martensitic stainless steel seamless pipe having the above chemical composition including Formula (1), when Fn2 is 1.20 or more, the pitting resistance at the inner surface of the seamless steel pipe markedly increases.

[0029] Therefore, the martensitic stainless steel seamless pipe according to the present embodiment has the above chemical composition including Formula (1), and in addition, the inner surface Cu occupancy OS_{Cu} and the interior Cu occupancy OI_{Cu} defined as described above satisfy the following Formula (2). As a result, the martensitic stainless steel seamless pipe according to the present embodiment can achieve both a high yield strength and excellent pitting resistance at the inner surface.

$$OS_{Cu}/OI_{Cu} \geq 1.20 \qquad (2)$$

[0030] Note that, the reason why the pitting resistance of the inner surface of a seamless steel pipe increases when Cu precipitates were caused to dominantly distribute in the inner surface vicinity region 20 has not been clarified in detail. However, the present inventors surmise that the reason is as follows. As described above, in a martensitic stainless steel seamless pipe for which use in an oil well environment is assumed, production fluid passes through the inside of the martensitic stainless steel seamless pipe. At such time, there is a possibility that H_2S gas contacts the inner surface of the seamless steel pipe and Cu sulfides are formed. In addition, there is a possibility that Cu precipitates strengthen a passive film formed on the surface of the martensitic stainless steel seamless pipe. Therefore, the present inventors surmise that, if Cu precipitates are dominantly distributed to the inner surface, it becomes easier for Cu sulfides to be formed and hence the pitting resistance of the inner surface increases.

[0031] The gist of the martensitic stainless steel seamless pipe according to the present embodiment, which has been completed based on the above findings, is as follows.

[0032]

[1]

A martensitic stainless steel seamless pipe consisting of, in mass%,
C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cr: 11.00 to 14.00%,
Ni: 5.00 to 7.50%,
Mo: 1.50 to 4.50%,
Cu: 0.50 to 3.50%,
Co: 0.010 to 0.500%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Ca: 0.0005 to 0.0050%,
Al: 0.001 to 0.100%,
N: 0.0010 to 0.0500%,
O: 0.050% or less,
W: 0 to 2.00%,
Nb: 0 to 0.50%,
Mg: 0 to 0.0050%, rare earth metal: 0 to 0.0050%,
B: 0 to 0.0050%, and
the balance: Fe and impurities,
and satisfying Formula (1),
wherein:
a microstructure is composed of, in volume percent, retained austenite in an amount of 0 to 15.0% and ferrite

in an amount of 0 to 5.0%, with the balance being tempered martensite;
a yield strength is 862 MPa or more;
when a pipe axis direction of the martensitic stainless steel seamless pipe is defined as an L direction, and a pipe radius direction of the martensitic stainless steel seamless pipe is defined as a T direction,
with respect to a square observation field of view region that includes an inner surface of the martensitic stainless steel seamless pipe that extends in the L direction, and whose sides that extend in the L direction are 1.0 μm in length and whose sides that extend in the T direction are 1.0 μm in length,
when the observation field of view region is divided into 65,536 sections by being divided equally into 256 sections in the L direction and divided equally into 256 sections in the T direction,
the observation field of view region is composed of:

an inner surface vicinity region which is a rectangular region that has the inner surface of the martensitic stainless steel seamless pipe as a top edge and includes 256 sections in the L direction and six sections in the T direction,
an interior region which is below contact with the inner surface vicinity region, and
a hollow region which is above contact with the inner surface vicinity region; and
when, among all the sections in the inner surface vicinity region, a numerical proportion of sections in which a Cu concentration is more than 2.0% is defined as inner surface Cu occupancy OS_{Cu}, and
among all the sections in the interior region, a numerical proportion of sections in which a Cu concentration is more than 2.0% is defined as interior Cu occupancy OI_{Cu},
the inner surface Cu occupancy OS_{Cu} and the interior Cu occupancy OI_{Cu} satisfy Formula (2);

$$\mathrm{Mo} + 0.5 \times \mathrm{W} \geq 2.50 \quad (1)$$

$$OS_{Cu}/OI_{Cu} \geq 1.20 \quad (2)$$

where, a content of a corresponding element in mass% is substituted for each symbol of an element in Formula (1).

[2]
The martensitic stainless steel seamless pipe according to [1], containing one or more elements selected from a group consisting of:

W: 0.01 to 2.00%,
Nb: 0.01 to 0.50%,
Mg: 0.0001 to 0.0050%,
rare earth metal: 0.0001 to 0.0050%, and
B: 0.0001 to 0.0050%.

[3]
A method for producing the martensitic stainless steel seamless pipe according to [1] or [2], including:

a starting material preparation process of preparing a starting material which consists of, in mass%,
C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cr: 11.00 to 14.00%,
Ni: 5.00 to 7.50%,
Mo: 1.50 to 4.50%,
Cu: 0.50 to 3.50%,
Co: 0.010 to 0.500%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Ca: 0.0005 to 0.0050%,

Al: 0.001 to 0.100%,
N: 0.0010 to 0.0500%,
O: 0.050% or less,
W: 0 to 2.00%,
Nb: 0 to 0.50%,
Mg: 0 to 0.0050%,
rare earth metal: 0 to 0.0050%,
B: 0 to 0.0050%, and
the balance: Fe and impurities,
and which satisfies Formula (1);
a hot working process of heating, in a heating furnace, the starting material that is prepared, and thereafter performing hot working in which an area reduction ratio R defined by Formula (A) is 40% or more and a hot working time is 15 minutes or less to produce a hollow shell;
a quenching process of subjecting the hollow shell that is at a temperature not less than an A_3 point to quenching; and
a tempering process of performing tempering of the hollow shell subjected to the quenching, under conditions that satisfy Formula (B);

$$\mathrm{Mo} + 0.5 \times \mathrm{W} \geq 2.50 \qquad (1)$$

R = {1 - (cross-sectional area perpendicular to pipe axis direction of the hollow shell after hot working/cross-sectional area perpendicular to axial direction of the starting material before hot working)} × 100 (A)

$$(T + 273.15) \times (20 + \log_{10}(t/60)) \times (1 - [\mathrm{Cu}]/100) \leq 17200 \qquad (B)$$

where, a content of a corresponding element in mass% is substituted for each symbol of an element in Formula (1) and
in Formula (B), a tempering temperature in °C is substituted for T, a tempering time in minutes is substituted for t, and a content of Cu in the hollow shell in mass% is substituted for [Cu].

[4]
The method for producing a martensitic stainless steel seamless pipe according to [3], wherein the starting material contains one or more elements selected from a group consisting of:

W: 0.01 to 2.00%,
Nb: 0.01 to 0.50%,
Mg: 0.0001 to 0.0050%,
rare earth metal: 0.0001 to 0.0050%, and
B: 0.0001 to 0.0050%.

The martensitic stainless steel seamless pipe according to the present embodiment is described in detail below. Note that, the symbol "%" relating to an element means "mass percent" unless otherwise noted.

[Chemical composition]

[0033] The chemical composition of the martensitic stainless steel seamless pipe according to the present embodiment contains the following elements.

C: 0.030% or less

[0034] Carbon (C) is unavoidably contained. That is, a lower limit of the content of C is more than 0%. C increases hardenability of the steel material and thus increases strength of the steel material. However, if the content of C is too high, it will become easy for C to combine with Cr to form Cr carbides. As a result, even if the contents of other elements are within the range of the present embodiment, toughness of the steel material will decrease. Therefore, the content of C is to be 0.030% or less. A preferable lower limit of the content of C is 0.001%, more preferably is 0.003%, and further preferably is 0.005%. A preferable upper limit of the content of C is 0.025%, more preferably is 0.020%, and further preferably is 0.015%. The content of C is preferably as low as possible.

Si: 1.00% or less

[0035] Silicon (Si) is unavoidably contained. That is, a lower limit of the content of Si is more than 0%. Si deoxidizes the steel. However, if the content of Si is too high, hot workability of the steel material will decrease even if the contents of other elements are within the range of the present embodiment. Therefore, the content of Si is to be 1.00% or less. A preferable lower limit of the content of Si is 0.05%, more preferably is 0.10%, further preferably is 0.15%, and further preferably is 0.20%. A preferable upper limit of the content of Si is 0.70%, more preferably is 0.50%, further preferably is 0.45%, and further preferably is 0.40%.

Mn: 1.00% or less

[0036] Manganese (Mn) is unavoidably contained. That is, a lower limit of the content of Mn is more than 0%. Mn increases hardenability of steel material and thus increases strength of the steel material. However, if the content of Mn is too high, even if the contents of other elements are within the range of the present embodiment, Mn will form coarse inclusions and reduce toughness of the steel material. Therefore, the content of Mn is to be 1.00% or less. A preferable lower limit of the content of Mn is 0.10%, more preferably is 0.20%, and further preferably is 0.25%. A preferable upper limit of the content of Mn is 0.80%, more preferably is 0.60%, and further preferably is 0.50%.

P: 0.030% or less

[0037] Phosphorus (P) is an impurity that is unavoidably contained. That is, a lower limit of the content of P is more than 0%. If the content of P is too high, even if the contents of other elements are within the range of the present embodiment, P will segregate to grain boundaries and cause toughness of the steel material to markedly decrease. Therefore, the content of P is to be 0.030% or less. A preferable upper limit of the content of P is 0.025%, and more preferably is 0.020%. The content of P is preferably as low as possible. However, excessively reducing the content of P will significantly increase the production cost. Therefore, when taking industrial production into consideration, a preferable lower limit of the content of P is 0.0001%, more preferably is 0.0005%, and further preferably is 0.001%.

S: 0.0050% or less

[0038] Sulfur (S) is an impurity that is unavoidably contained. That is, a lower limit of the content of S is more than 0%. If the content of S is too high, even if the contents of other elements are within the range of the present embodiment, S will segregate to grain boundaries and cause toughness of the steel material to markedly decrease. Therefore, the content of S is to be 0.0050% or less. A preferable upper limit of the content of S is 0.0040%, more preferably is 0.0030%, and further preferably is 0.0020%. The content of S is preferably as low as possible. However, excessively reducing the content of S will significantly increase the production cost. Therefore, when taking industrial production into consideration, a preferable lower limit of the content of S is 0.0001%, more preferably is 0.0002%, and further preferably is 0.0003%.

Cr: 11.00 to 14.00%

[0039] Chromium (Cr) increases the pitting resistance of the steel material. If the content of Cr is too low, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the content of Cr is too high, Cr carbides, intermetallic compounds containing Cr, and Cr oxides will be excessively formed. In such a case, corrosion resistance of the steel material will decrease even if the contents of other elements are within the range of the present embodiment. Therefore, the content of Cr is to be 11.00 to 14.00%. A preferable lower limit of the content of Cr is 11.05%, more preferably is 11.10%, further preferably is 11.50%, and further preferably is 11.80%. A preferable upper limit of the content of Cr is 13.70%, more preferably is 13.50%, further preferably is 13.40%, and further preferably is 13.30%.

Ni: 5.00 to 7.50%

[0040] Nickel (Ni) increases the pitting resistance of the steel material. Ni is also an austenite forming element, and causes the microstructure of the steel material after quenching to become martensitic. If the content of Ni is too low, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the content of Ni is too high, the aforementioned advantageous effects will be saturated and the production cost will increase. Therefore, the content of Ni is to be 5.00 to 7.50%. A preferable lower limit of the content of Ni is 5.10%, more preferably is 5.15%, and further preferably is 5.20%. A preferable upper limit of the content of Ni is 7.30%, more preferably is 7.00%, further preferably is 6.80%, further preferably is 6.60%, and further preferably is 6.40%.

Mo: 1.50 to 4.50%

[0041] Molybdenum (Mo) increases the pitting resistance of the steel material. If the content of Mo is too low, this advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the content of Mo is too high, the aforementioned advantageous effect will be saturated and the production cost will increase. Therefore, the content of Mo is to be 1.50 to 4.50%. A preferable lower limit of the content of Mo is 1.60%, more preferably is 1.70%, and further preferably is 1.80%. A preferable upper limit of the content of Mo is 4.30%, more preferably is 4.10%, further preferably is 3.90%, and further preferably is 3.70%.

Cu: 0.50 to 3.50%

[0042] Copper (Cu) precipitates as Cu precipitates in the steel material. If the Cu precipitates are dominantly distributed to the inner surface vicinity region 20 of the seamless steel pipe, the pitting resistance of the inner surface of the seamless steel pipe will increase. The Cu precipitates also increase strength of the steel material. If the content of Cu is too low, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the content of Cu is too high, even if the contents of other elements are within the range of the present embodiment, strength of the steel material will be too high, and corrosion resistance and/or low-temperature toughness of the steel material will decrease. Therefore, the content of Cu is to be 0.50 to 3.50%. A preferable lower limit of the content of Cu is 0.60%, more preferably is 0.70%, and further preferably is 0.80%. A preferable upper limit of the content of Cu is less than 3.50%, more preferably is 3.45%, further preferably is 3.40%, and further preferably is 3.20%.

Co: 0.010 to 0.500%

[0043] Cobalt (Co) forms a coating on the surface of the steel material, and thereby increases the pitting resistance of the steel material. Co also increases hardenability of the steel material and stabilizes strength of the steel material. If the content of Co is too low, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the content of Co is too high, the aforementioned advantageous effects will be saturated and the production cost will increase. Therefore, the content of Co is to be 0.010 to 0.500%. A preferable lower limit of the content of Co is 0.015%, more preferably is 0.020%, and further preferably is 0.030%. A preferable upper limit of the content of Co is 0.450%, and more preferably is 0.400%.

Ti: 0.050 to 0.300%

[0044] Titanium (Ti) combines with C or N to form carbides or nitrides in the steel material. In this case, coarsening of grains is suppressed by the pinning effect, and strength of the steel material increases. In addition, by forming carbides or nitrides, Ti suppresses the occurrence of an excessive increase in strength caused by excessive formation of V precipitates (carbides, nitrides, and carbo-nitrides). As a result, the pitting resistance of the steel material increases. If the content of Ti is too low, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the content of Ti is too high, the aforementioned advantageous effects will be saturated and the production cost will increase. In addition, if the content of Ti is too high, Ti carbides or Ti nitrides will excessively form and toughness of the steel material will decrease. Therefore, the content of Ti is to be 0.050 to 0.300%. A preferable lower limit of the content of Ti is 0.060%, more preferably is 0.070%, and further preferably is 0.080%. A preferable upper limit of the content of Ti is 0.250%, and more preferably is 0.200%.

V: 0.01 to 1.00%

[0045] Vanadium (V) forms precipitates (V precipitates) such as carbides, nitrides, and carbo-nitrides in the steel material and thereby increases strength of the steel material. If the content of V is too low, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the content of V is too high, even if the contents of other elements are within the range of the present embodiment, V precipitates will excessively form and toughness of the steel material will decrease. Therefore, the content of V is to be 0.01 to 1.00%. A preferable lower limit of the content of V is 0.02%, and more preferably is 0.03%. A preferable upper limit of the content of V is 0.90%, more preferably is 0.80%, further preferably is 0.60%, and further preferably is 0.50%.

Ca: 0.0005 to 0.0050%

[0046] Calcium (Ca) renders S in the steel material harmless by forming sulfides, and thus increases hot workability of the steel material. If the content of Ca is too low, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the content of Ca is too high, even if the contents of other elements are within the range of the present embodiment, inclusions in the steel material will coarsen and toughness of the steel material will decrease. Therefore, the content of Ca is to be 0.0005 to 0.0050%. A preferable lower limit of the content of Ca is 0.0006%, more preferably is 0.0008%, and further preferably is 0.0010%. A preferable upper limit of the content of Ca is 0.0040%, and more preferably is 0.0030%.

Al: 0.001 to 0.100%

[0047] Aluminum (Al) deoxidizes the steel. If the content of Al is too low, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the content of Al is too high, even if the contents of other elements are within the range of the present embodiment, coarse Al oxides will form and toughness of the steel material will decrease. Therefore, the content of Al is to be 0.001 to 0.100%. A preferable lower limit of the content of Al is 0.002%, more preferably is 0.003%, and further preferably is 0.005%. A preferable upper limit of the content of Al is 0.095%, more preferably is 0.090%, and further preferably is 0.085%. Note that, as used in the present description, the term "content of Al" means the content of sol. Al (acid-soluble Al).

N: 0.0010 to 0.0500%

[0048] Nitrogen (N) increases corrosion resistance of the steel material. If the content of N is too low, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the content of N is too high, even if the contents of other elements are within the range of the present embodiment, coarse Ti nitrides will form and toughness of the steel material will decrease. Therefore, the content of N is to be 0.0010 to 0.0500%. A preferable lower limit of the content of N is 0.0015%, more preferably is 0.0020%, and further preferably is 0.0025%. A preferable upper limit of the content of N is 0.0450%, more preferably is 0.0400%, further preferably is 0.0350%, and further preferably is 0.0300%.

O: 0.050% or less

[0049] Oxygen (O) is an impurity that is unavoidably contained. That is, a lower limit of the content of O is more than 0%. O forms oxides, which reduces the pitting resistance of the steel material. Therefore, if the content of O is too high, the pitting resistance of the steel material will markedly decrease even if the contents of other elements are within the range of the present embodiment. Therefore, the content of O is to be 0.050% or less. A preferable upper limit of the content of O is 0.040%, more preferably is 0.030%, and further preferably is 0.020%. The content of O is preferably as low as possible. However, excessively reducing the content of O will increase the production cost. Therefore, when taking industrial production into consideration, a preferable lower limit of the content of O is 0.0005%, and more preferably is 0.001%.

[0050] The balance of the martensitic stainless steel seamless pipe according to the present embodiment is Fe and impurities. Here, the term "impurities" refers to substances which are mixed in from ore and scrap as the raw material or from the production environment or the like when industrially producing the steel material, and which are not intentionally contained, but are allowed within a range that does not adversely affect the martensitic stainless steel material according to the present embodiment.

[Optional elements]

[0051] The martensitic stainless steel seamless pipe according to the present embodiment may further contain W in lieu of a part of Fe.

W: 0 to 2.00%

[0052] Tungsten (W) is an optional element and does not have to be contained. That is, the content of W may be 0%. When contained, W stabilizes the passive film in a sour environment, and suppresses destruction of the passive film by chloride ions and hydrogen sulfide ions. As a result, the pitting resistance of the steel material increases. If even a small amount of W is contained, the aforementioned advantageous effect will be obtained to a certain extent. On the other hand, if the content of W is too high, W will combine with C and form coarse carbides. In such a case, the pitting resistance of the steel material will decrease even if the contents of other elements are within the range of the present embodiment. Therefore, the content of W is to be 0 to 2.00%. A preferable lower limit of the content of W is 0.01%, more preferably is 0.03%, and further preferably is 0.05%. A preferable upper limit of the content of W is 1.75%, more preferably is 1.50%, and further preferably is 1.20%.

[0053] The martensitic stainless steel seamless pipe according to the present embodiment may also contain Nb in lieu of a part of Fe.

Nb: 0 to 0.50%

[0054] Niobium (Nb) is an optional element, and does not have to be contained. That is, the content of Nb may be 0%. When contained, Nb combines with C and/or N to form Nb carbides and/or Nb carbo-nitrides. In such a case, coarsening of grains is suppressed by the pinning effect, and the yield strength of the steel material increases. If even a small amount of Nb is contained, the aforementioned advantageous effect will be obtained to a certain extent. On the other hand, if the content of Nb is too high, Nb carbides and/or Nb carbo-nitrides will excessively form even if the contents of other elements are within the range of the present embodiment. As a result, the pitting resistance of the steel material will decrease. Therefore, the content of Nb is to be 0 to 0.50%. A preferable lower limit of the content of Nb is 0.01%, more preferably is 0.02%, and further preferably is 0.03%. A preferable upper limit of the content of Nb is 0.45%, more preferably is 0.40%, and further preferably is 0.35%.

[0055] The martensitic stainless steel seamless pipe according to the present embodiment may further contain one or more elements selected from the group consisting of Mg, rare earth metal (REM), and B in lieu of a part of Fe. These elements are optional elements, and each of these elements increases hot workability of the steel material.

Mg: 0 to 0.0050%

[0056] Magnesium (Mg) is an optional element, and does not have to be contained. That is, the content of Mg may be 0%. When contained, Mg controls the morphology of inclusions and thereby increases hot workability of the steel material. If even a small amount of Mg is contained, the aforementioned advantageous effect will be obtained to a certain extent. However, if the content of Mg is too high, even if the contents of other elements are within the range of the present embodiment, coarse oxides will be formed and toughness of the steel material will decrease. Therefore, the content of Mg is to be 0 to 0.0050%. A preferable lower limit of the content of Mg is 0.0001%, more preferably is 0.0005%, and further preferably is 0.0010%. A preferable upper limit of the content of Mg is 0.0045%, more preferably is 0.0040%, and further preferably is 0.0035%.

Rare earth metal (REM): 0 to 0.0050%

[0057] Rare earth metal (REM) is an optional element, and does not have to be contained. That is, the content of REM may be 0%. When contained, similarly to Mg, REM controls the morphology of inclusions and thereby increases hot workability of the steel material. If even a small amount of REM is contained, the aforementioned advantageous effect will be obtained to a certain extent. However, if the content of REM is too high, even if the contents of other elements are within the range of the present embodiment, coarse oxides will be formed and toughness of the steel material will decrease. Therefore, the content of REM is to be 0 to 0.0050%. A preferable lower limit of the content of REM is 0.0001%, more preferably is 0.0005%, and further preferably is 0.0010%. A preferable upper limit of the content of REM is 0.0045%, more preferably is 0.0040%, and further preferably is 0.0035%.

[0058] Note that, in the present description the term "REM" means one or more types of element selected from the group consisting of scandium (Sc) which is the element with atomic number 21, yttrium (Y) which is the element with atomic number 39, and the elements from lanthanum (La) with atomic number 57 to lutetium (Lu) with atomic number

71 that are lanthanoids. Further, in the present description, the term "content of REM" refers to the total content of these elements.

B: 0 to 0.0050%

[0059] Boron (B) is an optional element, and does not have to be contained. That is, the content of B may be 0%. When contained, B segregates to austenite grain boundaries and thereby strengthens the grain boundaries and increases hot workability of the steel material. If even a small amount of B is contained, the aforementioned advantageous effect will be obtained to a certain extent. However, if the content of B is too high, even if the contents of other elements are within the range of the present embodiment, Cr carbo-borides will form and toughness of the steel material will decrease. Therefore, the content of B is to be 0 to 0.0050%. A preferable lower limit of the content of B is 0.0001%, and more preferably is 0.0002%. A preferable upper limit of the content of B is 0.0045%, more preferably is 0.0040%, further preferably is 0.0035%, and further preferably is 0.0030%.

[Formula (1)]

[0060] The martensitic stainless steel seamless pipe according to the present embodiment has the chemical composition described above, and also satisfies the following Formula (1).

$$\mathrm{Mo} + 0.5 \times \mathrm{W} \geq 2.50 \qquad (1)$$

[0061] Where, a content of a corresponding element in mass% is substituted for each symbol of an element in Formula (1).

[0062] When Fn1 (= Mo + 0.5 × W) is increased, the pitting resistance of the seamless steel pipe is increased while maintaining the yield strength of the seamless steel pipe. Therefore, the martensitic stainless steel seamless pipe according to the present embodiment has the chemical composition and the microstructure described above, and in addition, Fn1 is made 2.50 or more. As a result, on the condition that the other requirements of the present embodiment are satisfied, the martensitic stainless steel seamless pipe according to the present embodiment can achieve both a yield strength of 125 ksi or more and excellent pitting resistance. A preferable lower limit of Fn1 is 2.60, and more preferably is 2.70. In the present embodiment, an upper limit of Fn1 is not particularly limited, and for example is 4.50.

[Micro structure]

[0063] The microstructure of the martensitic stainless steel seamless pipe according to the present embodiment is composed of, in volume percent, retained austenite in an amount of 0 to 15.0% and ferrite in an amount of 0 to 5.0%, with the balance being tempered martensite. In the present description, the phrase "composed of retained austenite, ferrite, and tempered martensite" means that the amount of any phase other than retained austenite, ferrite, and tempered martensite is negligibly small. For example, in the chemical composition of the martensitic stainless steel seamless pipe according to the present embodiment, the volume ratios of precipitates and inclusions are negligibly small as compared with the volume ratios of retained austenite, ferrite, and tempered martensite. That is, the microstructure of the martensitic stainless steel seamless pipe according to the present embodiment may contain minute amounts of precipitates, inclusions and the like, in addition to retained austenite, ferrite, and tempered martensite.

[0064] As mentioned above, in the microstructure of the martensitic stainless steel seamless pipe according to the present embodiment, the volume ratio of retained austenite is 0 to 15.0% and the volume ratio of ferrite is 0 to 5.0%, with the balance being tempered martensite. That is, in the microstructure of the martensitic stainless steel seamless pipe according to the present embodiment, the volume ratio of tempered martensite is 80 to 100.0%. If the volume ratios of retained austenite and ferrite are too high, it will be difficult to control the mechanical properties of the steel material. On the other hand, a lower limit of the volume ratios of retained austenite and ferrite may be 0%. That is, the martensitic stainless steel seamless pipe according to the present embodiment may have the microstructure composed only of tempered martensite.

[0065] In the present embodiment, in the microstructure, the lower limit of the volume ratio of retained austenite may be 1.0% or may be 2.0%. Further, in the microstructure, an upper limit of the volume ratio of retained austenite may be 13.0% or may be 10.0%. In the present embodiment, in the microstructure, the lower limit of the volume ratio of ferrite may be 0.5%. Further, in the microstructure, an upper limit of the volume ratio of ferrite may be 3.0% or may be 2.0%.

[Method for measuring volume ratio of retained austenite]

[0066] The volume ratio (%) of retained austenite in the microstructure of the martensitic stainless steel seamless pipe according to the present embodiment can be determined by the method described hereunder.

[0067] The volume ratio of retained austenite is determined by an X-ray diffraction method. Specifically, a test specimen is prepared from a center portion of the wall thickness of the martensitic stainless steel seamless pipe. Although not particularly limited, the size of the test specimen is, for example, 15 mm × 15 mm × a thickness of 2 mm. In this case, the thickness direction of the test specimen is parallel to the wall thickness (pipe radius) direction. Using the prepared test specimen, the X-ray diffraction intensity of each of the (200) plane of α phase (ferrite and martensite), the (211) plane of α phase, the (200) plane of y phase (retained austenite), the (220) plane of y phase, and the (311) plane of y phase is measured to calculate an integrated intensity of each plane.

[0068] In the measurement of the X-ray diffraction intensity, the target of the X-ray diffraction apparatus is Mo (Mo Kα radiation). After the above calculation, the volume ratio Vy (%) of retained austenite is then calculated using Formula (I) for combinations (2 × 3 = 6 pairs) of each plane of the α phase and each plane of the y phase. Then, an average value of the volume ratios Vy of retained austenite of the six pairs is defined as the volume ratio (%) of retained austenite.

$$V\gamma = 100/\{1 + (I\alpha \times R\gamma)/(I\gamma \times R\alpha)\} \qquad (I)$$

[0069] Where, Iα represents the integrated intensity of α phase. Rα represents the crystallographic theoretical calculation value for α phase. Iy represents the integrated intensity of y phase. Ry represents the crystallographic theoretical calculation value for y phase. Note that, in the present description, Rα in the (200) plane of α phase is taken as 15.9, Rα in the (211) plane of α phase is taken as 29.2, Ry in the (200) plane of y phase is taken as 35.5, Ry in the (220) plane of y phase is taken as 20.8, and Ry in the (311) plane of y phase is taken as 21.8. Note that, a value determined by rounding off to the first decimal places of the obtained numerical value is adopted as the volume ratio of retained austenite.

[Method for measuring volume ratio of ferrite]

[0070] The volume ratio (%) of ferrite in the microstructure of the martensitic stainless steel seamless pipe according to the present embodiment can be determined by the method described hereunder.

[0071] The volume ratio of ferrite is determined by a point counting method in accordance with ASTM E562 (2019). Specifically, a test specimen is prepared from a center portion of the wall thickness of the martensitic stainless steel seamless pipe. The test specimen is not particularly limited as long as the test specimen has an observation surface that is perpendicular to the rolling elongation (pipe axis) direction. The test specimen is embedded in resin, and the observation surface that has been polished to obtain a mirror surface is immersed in Vilella's reagent (a mixed solution of ethanol, hydrochloric acid, and picric acid) for about 60 seconds to reveal the microstructure by etching. Thirty visual fields on the etched observation surface are observed using an optical microscope. Although not particularly limited, the visual field area is, for example, 0.03 mm^2 per visual field (magnification of ×400).

[0072] Those skilled in the art are able to distinguish ferrite from the other phases (retained austenite and tempered martensite) based on contrast in each observation visual field. Therefore, the ferrite in each observation visual field is identified based on contrast. The area fraction of the identified ferrite is determined by a point counting method in accordance with ASTM E562 (2019). The arithmetic average value of the area fractions of ferrite determined in the 30 visual fields is defined as the volume ratio (%) of ferrite. Note that, a value determined by rounding off to the first decimal places of the obtained numerical value is adopted as the volume ratio of ferrite.

[Method for measuring volume ratio of tempered martensite]

[0073] The volume ratio (%) of tempered martensite can be determined by the following method. Specifically, using the volume ratio (%) of retained austenite obtained by the aforementioned X-ray diffraction method, and the volume ratio (%) of ferrite obtained by the aforementioned point counting method, the volume ratio (%) of tempered martensite in the microstructure of the martensitic stainless steel seamless pipe is determined by the following formula.

Volume ratio (%) of tempered martensite = 100 - {volume ratio (%) of retained austenite + volume ratio (%) of ferrite}

[Yield strength]

[0074] The martensitic stainless steel seamless pipe according to the present embodiment has a yield strength of 862 MPa or more (125 ksi or more). As used in the present description, the term "yield strength" means 0.2% offset proof stress obtained in a tensile test. Even though the martensitic stainless steel seamless pipe according to the present embodiment has a yield strength of 125 ksi or more, by having the above chemical composition including Formula (1), and satisfying Formula (2) which is described later, excellent pitting resistance is exhibited at the inner surface of the seamless steel pipe. In the martensitic stainless steel seamless pipe according to the present embodiment, although not particularly limited, an upper limit of the yield strength is, for example, 1172 MPa.

[0075] The yield strength of the martensitic stainless steel seamless pipe according to the present embodiment can be determined by the following method. A tensile test specimen is prepared in accordance with ASTM E8/E8M (2021) from the martensitic stainless steel seamless pipe according to the present embodiment. Specifically, a round bar specimen is prepared from a center portion of the wall thickness of the seamless steel pipe. The size of the round bar test specimen is, for example, as follows: the diameter of the parallel portion is 8.9 mm and the gage length is 35.6 mm. In a case where a round bar specimen cannot be prepared from the seamless steel pipe, an arc-shaped test specimen is to be prepared. The size of the arc-shaped test specimen is, for example, as follows: the thickness is the same as the wall thickness of the seamless steel pipe, the width is 25.4 mm, and the gage length is 50.8 mm. Note that, the axial direction of the tensile test specimen is parallel to the pipe axis direction of the seamless steel pipe. A tensile test is carried out at normal temperature (24 ± 3°C) in accordance with ASTM E8/E8M (2021) using the tensile test specimen, and the obtained 0.2% offset proof stress (MPa) is defined as the yield strength (MPa). Note that, in the present description, a value determined by rounding off the decimals of the obtained numerical value is adopted as the yield strength.

[Formula (2)]

[0076] In the martensitic stainless steel seamless pipe according to the present embodiment, with respect to a square observation field of view region that includes an inner surface of the seamless steel pipe and whose sides extending in the L direction are 1.0 μm in length and whose sides extending in the T direction are 1.0 μm in length, in a case where the observation field of view region has been divided into 65,536 sections by being divided equally into 256 sections in the L direction and divided equally into 256 sections in the T direction, when the numerical proportion of sections in which the Cu concentration is more than 2.0% in the inner surface vicinity region 20 of the martensitic stainless steel seamless pipe is defined as "inner surface Cu occupancy OS_{Cu}" and the numerical proportion of sections in which the Cu concentration is more than 2.0% in the interior region 30 of the martensitic stainless steel seamless pipe is defined as "interior Cu occupancy OI_{Cu}", the inner surface Cu occupancy OS_{Cu} and the interior Cu occupancy OI_{Cu} satisfy Formula (2).

$$OS_{Cu}/OI_{Cu} \geq 1.20 \qquad (2)$$

[0077] Fn2 (= OS_{Cu}/OI_{Cu}) is an index that indicates the degree of dominant distribution of Cu precipitates to the inner surface vicinity region 20. The larger the value of Fn2 is, the greater the degree to which the Cu precipitates are dominantly distributed to the inner surface vicinity region 20 is, and the more the pitting resistance of the inner surface can be effectively increased. Therefore, the martensitic stainless steel seamless pipe according to the present embodiment has the above chemical composition including Formula (1), has a yield strength of 125 ksi or more, and in addition, Fn2 is 1.20 or more. As a result, the martensitic stainless steel seamless pipe according to the present embodiment can achieve both a high yield strength, and excellent pitting resistance at the inner surface of the martensitic stainless steel seamless pipe.

[0078] Accordingly, the martensitic stainless steel seamless pipe according to the present embodiment has a chemical composition satisfying Formula (1) and a yield strength of 862 MPa or more, and in addition, Fn2 is made 1.20 or more. In the martensitic stainless steel seamless pipe according to the present embodiment, a preferable lower limit of Fn2 is 1.25, and more preferably is 1.30. In the present embodiment, although not particularly limited, an upper limit of Fn2 is, for example, 5.00.

[0079] In the martensitic stainless steel seamless pipe according to the present embodiment, the inner surface Cu occupancy OS_{Cu} and the interior Cu occupancy OI_{Cu} can be determined by the following method. A thin film test specimen for inner surface observation is prepared from the martensitic stainless steel seamless pipe according to the present embodiment. The thin film test specimen is prepared by focused ion beam (hereunder, also referred to as "FIB") processing. The shape of the thin film test specimen is not particularly limited as long as an observation surface that is described later is obtained. The size of the observation surface of the thin film test specimen is, for example, 10 μm × 10 μm, and the thickness of the thin film test specimen is, for example, 150 nm. In the FIB processing, in addition, a protective film (a so-called "deposition film") that protects the inner surface is to be formed on the inner surface.

[0080] On the observation surface of the obtained thin film test specimen, an observation field of view region of 1.0 μm in the L direction × 1.0 μm in the T direction = 1.0 μm^2 is specified. The observation field of view region is adjusted so that the inner surface of the seamless steel pipe is included therein. Preferably, as illustrated in FIG. 1, an observation field of view region 50 is specified so that the inner surface 10 of the seamless steel pipe is located in the vicinity of the center in the T direction of the observation field of view region 50, and extends in the L direction. Here, the description "the inner surface 10 of the seamless steel pipe is located in the vicinity of the center in the T direction of the observation field of view region 50" means that, when specifying the observation field of view region 50, the inner surface 10 of the seamless steel pipe that can be confirmed by observation is located approximately at the center in the T direction of the observation field of view region 50. For example, in a case where the observation field of view region 50 is equally divided into five regions in the T direction, if the inner surface 10 of the seamless steel pipe is within the third region from the top in the T direction over the overall length in the L direction, it can be said that the inner surface 10 of the seamless steel pipe is located in the vicinity of the center in the T direction of the observation field of view region 50. Further, the description "the inner surface 10 of the seamless steel pipe extends in the L direction of the observation field of view region 50" means that, when specifying the observation field of view region 50, the inner surface 10 of the seamless steel pipe that can be confirmed by observation is approximately parallel to the L direction of the observation field of view region 50. Note that, in the present embodiment, an arbitrary four observation field of view regions are specified from the observation surface of the thin film test specimen.

[0081] The four observation field of view regions that are specified are subjected to microstructural observation using a transmission electron microscope (hereinafter, also referred to as a "TEM"). The conditions for the microstructural observation are not particularly limited, and for example the accelerating voltage is set to 200 kV.

[0082] Each observation field of view region that is subjected to microstructural observation using a TEM is divided into 65,536 sections by being divided equally into 256 sections in the L direction and divided equally into 256 sections in the T direction. Note that, each section is a square with dimensions of 4 nm in the L direction × 4 nm in the T direction = 16 nm^2. In the present description, each section is denoted by (n, m), with the upper left corner of the observation field of view region as the origin. Here, n (integer) means the L-direction position in the observation field of view region, with 1 denoting the left edge of the observation field of view region, and 256 denoting the right edge. Similarly, m (integer) means the T-direction position in the observation field of view region, with 1 denoting the top edge of the observation field of view region, and 256 denoting the bottom edge. Hereunder, the observation field of view region is described specifically using the drawings.

[0083] FIG. 2 is a schematic diagram illustrating when the observation field of view region 50 has been divided into 65,536 sections by being divided equally into 256 sections in the L direction and divided equally into 256 sections in the T direction. Referring to FIG. 2, a section that is the n-th section from the left edge of the observation field of view region 50 and is the m-th section from the top edge of the observation field of view region 50 is denoted by (n, m). Further, referring to FIG. 2, the section located at the top left corner of the observation field of view region 50 is denoted by (1, 1), the section located at the top right corner of the observation field of view region 50 is denoted by (256, 1), the section located at the bottom left corner of the observation field of view region 50 is denoted by (1, 256), and the section located at the bottom right corner of the observation field of view region 50 is denoted by (256, 256).

[0084] Note that, as described above, in the seamless steel pipe according to the present embodiment, the inner surface 10 extends in the L direction of the observation field of view region 50. In short, in the seamless steel pipe according to the present embodiment, the observation field of view region 50 is specified in a manner so that the inner surface 10 of the seamless steel pipe that can be confirmed in the observation is approximately parallel to the L direction of the observation field of view region 50. Therefore, the observation field of view region 50 is specified in a manner so that sections in the T direction including the inner surface 10 of the seamless steel pipe that can be confirmed in the observation are as few as possible over the overall length in the L direction. For example, the inner surface 10 of the seamless steel pipe according to the present embodiment may be included in five sections in the T direction over the overall length in the L direction, and more preferably may be included in three sections in the T direction over the overall length in the L direction. Most preferably, the inner surface 10 of the seamless steel pipe according to the present embodiment is included in one section in the T direction over the overall length in the L direction.

[0085] Next, each section of the observation field of view region is subjected to element concentration analysis by an EDS (energy dispersive X-ray spectroscopy) using an energy dispersive X-ray spectrometer attached to the TEM. Note that, the EDS analysis is conducted for Fe, Cr, Ni, Mo, and Cu as elements to be analyzed. Based on the EDS analysis results, for each section (n, m), an Fe concentration $C_{Fe}(n, m)$ and a Cu concentration $C_{Cu}(n, m)$ are identified in terms of relative intensity. Specifically, the Fe concentration $C_{Fe}(n, m)$ and the Cu concentration $C_{Cu}(n, m)$ are defined by the following Formulae (3) and (4).

$$C_{Fe}(n,m) = 100 \times [Fe]_{(n,m)}/([Fe]_{(n,m)}+[Cr]_{(n,m)}+[Ni]_{(n,m)}+[Mo]_{(n,m)}+[Cu]_{(n,m)} \quad (3)$$

$$C_{Cu}(n,m) = 100 \times [Cu]_{(n,m)}/([Fe]_{(n,m)}+[Cr]_{(n,m)}+[Ni]_{(n,m)}+[Mo]_{(n,m)}+[Cu]_{(n,m)} \quad (4)$$

[0086] Where, the detected intensities of Fe, Cr, Ni, Mo, and Cu in section (n, m) determined by the EDS analysis are substituted for $[Fe]_{(n, m)}$, $[Cr]_{(n, m)}$, $[Ni]_{(n, m)}$, $[Mo]_{(n, m)}$, and $[Cu]_{(n, m)}$ in Formulae (3) and (4).

[0087] The inner surface of the seamless steel pipe in the observation field of view region can be identified using the determined Fe concentration $C_{Fe}(n, m)$ in each section. Specifically, for example, L-direction average values of the Fe concentration $C_{Fe}(n, m)$ can be determined, and the inner surface of the seamless steel pipe can be determined based on a plot of the L-direction average values that are determined. More specifically, with respect to a T-direction position m, the arithmetic average value of Fe concentrations $C_{Fe}(1, m)$ to $C_{Fe}(256, m)$ is determined, and is defined as an L-direction average value $A_{Fe}(m)$ of the Fe concentration. The obtained 256 L-direction average values $A_{Fe}(m)$ of the Fe concentration are plotted with respect to the T-direction position m.

[0088] FIG. 3 is a schematic diagram illustrating a relation between the position m in the pipe radius direction (T direction) of each section in the observation field of view region, and the average value $A_{Fe}(m)$ of the Fe concentration in the pipe axis direction (L direction). Referring to FIG. 3, the L-direction average value $A_{Fe}(m)$ of the Fe concentration changes sharply in a region 100. In addition, referring to FIG. 3, on the right side of the region 100 (that is, in the positive direction of the T-direction position m), the L-direction average value $A_{Fe}(m)$ of the Fe concentration is comparatively stable. This is because, in the observation field of view region, the Fe concentration differs greatly between the hollow region 40 and the inner surface vicinity region 20, and furthermore, the content of Fe in the interior region 30 is comparatively stable.

[0089] In this way, the inner surface of the seamless steel pipe can be identified from the shape of the plot of the L-direction average value $A_{Fe}(m)$ of the Fe concentration with respect to the T-direction position m. Specifically, the region 100 in which the L-direction average value $A_{Fe}(m)$ of the Fe concentration changes sharply is identified as illustrated in FIG. 3. Those skilled in the art are fully capable of identifying the region 100 in which the L-direction average value $A_{Fe}(m)$ of the Fe concentration changes sharply. Next, the maximum value and the minimum value of the L-direction average value $A_{Fe}(m)$ of the Fe concentration in the region 100 are determined, and an arithmetic average value $A_{Fe\text{-}ave}$ of those two values is determined. In addition, when the value of the L-direction average value $A_{Fe}(m)$ of the Fe concentration first exceeds $A_{Fe\text{-}ave}$ in the region 100, the m of the relevant L-direction average value $A_{Fe}(m)$ of the Fe concentration is identified as the T-direction position of the inner surface. More specifically, when the T-direction position of the inner surface is taken as "k (integer)", the following Formulae (5) and (6) hold between the L-direction average value $A_{Fe}(m)$ of the Fe concentration and $A_{Fe\text{-}ave}$.

$$A_{Fe}(k-1) \le A_{Fe\text{-}ave} \quad (5)$$

$$A_{Fe}(k) > A_{Fe\text{-}ave} \quad (6)$$

[0090] In the present embodiment, the inner surface vicinity region 20 is defined as a rectangular region which includes the inner surface of the martensitic stainless steel seamless pipe as a top edge, and which is composed of 256 sections in the L direction and 6 sections in the T direction. To express this another way using the T-direction position k of the inner surface, in the present embodiment, the rectangular region whose top left corner is the section (1, k), whose top right corner is the section (256, k), whose bottom left corner is the section (1, k + 5), and whose bottom right corner is the section (256, k + 5) is defined as the inner surface vicinity region 20.

[0091] In addition, the observation field of view region 50 is composed of the inner surface vicinity region 20, the interior region 30, and the hollow region 40. Here, the interior region 30 is below contact with the inner surface vicinity region 20. That is, expressed another way using the T-direction position k of the inner surface, in the present embodiment, the rectangular region whose top left corner is the section (1, k + 6), whose top right corner is the section (256, k + 6), whose bottom left corner is the section (1, 256), and whose bottom right corner is the section (256, 256) is defined as the interior region 30.

[0092] Similarly, the hollow region 40 is above contact with the inner surface vicinity region 20. That is, expressed another way using the T-direction position k of the inner surface, in the present embodiment, the rectangular region whose top left corner is the section (1, 1), whose top right corner is the section (256, 1), whose bottom left corner is the section (1, k-1), and whose bottom right corner is the section (256, k-1) is defined as the hollow region 40. Note that, as mentioned above, the hollow region 40 corresponds to the through-hole of the martensitic stainless steel seamless pipe.

[0093] The numerical proportion of sections in which the Cu concentration is more than 2.0% among all the sections of the inner surface vicinity region 20 defined as described above is defined as "inner surface Cu occupancy OS_{Cu}". Here, the phrase "all the sections of the inner surface vicinity region 20" means 256 sections in the L direction × 6 sections in the T direction, which equals a total of 1,536 sections. Among all the sections of the rectangular region having the section (1, k) as a top left corner and having the section (256, k + 5) as a bottom right corner, the number of sections in which the Cu concentration $C_{Cu}(n, m)$ is more than 2.0% are counted, and the numerical proportion with respect to the total number of sections 1,536 is determined. As mentioned above, in the present embodiment an arbitrary four observation field of view regions are specified from the observation surface of the thin film test specimen. Therefore, an arithmetic average value of the numerical proportions determined in the four observation field of view regions is defined as the inner surface Cu occupancy OS_{Cu}. Note that, in the present description, a value determined by rounding off to the second decimal places of the obtained numerical value is adopted as the inner surface Cu occupancy OS_{Cu}.

[0094] Similarly, the numerical proportion of sections in which the Cu concentration is more than 2.0% among all the sections of the interior region 30 defined as described above is defined as "interior Cu occupancy OI_{Cu}". Here, as described above, in the interior region 30, among all the sections of the rectangular region having the section (1, k + 6) as a top left corner and having the section (256, 256) as a bottom right corner, the number of sections in which the Cu concentration $C_{Cu}(n, m)$ is more than 2.0% are counted, and the numerical proportion with respect to the total number of sections is determined. As mentioned above, in the present embodiment an arbitrary four observation field of view regions are specified from the observation surface of the thin film test specimen. Therefore, an arithmetic average value of the numerical proportions determined in the four observation field of view regions is defined as the interior Cu occupancy OI_{Cu}. Note that, in the present description, a value determined by rounding off to the second decimal places of the obtained numerical value is adopted as the interior Cu occupancy OI_{Cu}.

[0095] Here, as mentioned above, a protective film is formed on the inner surface in the FIB processing. On the other hand, in the present embodiment, the inner surface 10 of the seamless steel pipe is identified using the Fe concentration C_{Fe} as described above. Therefore, it is preferable that an element constituting the protective film formed in the FIB processing is an element other than Fe (for example, carbon: C, tungsten: W, or platinum: Pt). These elements are used as ordinary deposition elements for thin film test specimens on which microstructural observation is performed by a TEM, and those skilled in the art are, as a matter of course, fully capable of selecting and using these elements.

[Pitting resistance]

[0096] The martensitic stainless steel seamless pipe according to the present embodiment has excellent pitting resistance at the inner surface thereof. In the present embodiment, "excellent pitting resistance at the inner surface" is defined as follows.

[0097] In the present embodiment, the pitting potential at the inner surface of the seamless steel pipe is measured to evaluate the pitting resistance. Specifically, a test specimen for measuring pitting potential is prepared from the seamless steel pipe according to the present embodiment. The test specimen includes an area of 1.0 cm^2 of the inner surface of the seamless steel pipe as a test surface. The shape of the test specimen is not particularly limited as long as the test specimen includes the aforementioned test surface. For example, the test specimen may have an area of 1.0 cm^2 or more of the inner surface, and the thickness of the test specimen may be the same as the wall thickness of the seamless steel pipe. In the test specimen, a region other than the test surface is covered with an insulator. Here, the insulator is not particularly limited, and it suffices to use a well-known insulator that can be used in a test environment which is described later. For example, resin may be used as the insulator.

[0098] An electrochemical test is performed using the test specimen for measuring pitting potential to thereby measure the anodic polarization curve. Specifically, a 25% by mass sodium chloride aqueous solution whose pH is adjusted to 4.5 with 0.08 g/L sodium hydrogen carbonate is adopted as the test solution. The test solution is degassed before use. The test specimen is then enclosed in an autoclave. In the autoclave, the test specimen is immersed in the test solution so that the solution volume to specimen area ratio is 500 mL/cm^2 or more, and this is adopted as the test bath. After the test bath has been degassed, a gaseous mixture of H_2S gas at 0.03 atm and CO_2 gas at 10 atm is charged under pressurization into the autoclave, and the test bath is stirred to create a corrosive environment.

[0099] The test bath is heated to 175°C. In the electrochemical test, a saturated KCl silver-silver chloride electrode is used as a reference electrode. In addition, a platinum electrode is used as a counter electrode. After the open circuit potential stabilizes, the anodic polarization curve is measured at a potential sweep rate of 20 mV/min in the anode direction from the open circuit potential using a potentiostat. Note that, measurement of the anodic polarization curve is performed until the anodic current density reaches 1000 μA/cm^2.

[0100] The potential when the anodic current density reaches 1000 μA/cm^2 is determined from the obtained anodic polarization curve. The same measurement is performed three times, and an arithmetic average value of the obtained potentials is defined as a pitting potential V'c1000 (mV). In the present embodiment, if the pitting potential V'c1000 according to the above definition is -230 mV or more, it is determined that the seamless steel pipe has excellent pitting resistance at the inner surface thereof.

[Uses of seamless steel pipe]

[0101] The uses of the martensitic stainless steel seamless pipe according to the present embodiment are not particularly limited. The martensitic stainless steel seamless pipe according to the present embodiment is suitable as a seamless steel pipe for oil wells. Examples of a seamless steel pipe for oil wells include a casing steel pipe, a tubing steel pipe, and a drilling steel pipe which are used for drilling oil wells or gas wells, collection of crude oil or natural gas, and the like.

[Production method]

[0102] One example of a method for producing the martensitic stainless steel seamless pipe according to the present embodiment will now be described. Note that, the production method described hereunder is an example, and a method for producing the martensitic stainless steel seamless pipe of the present embodiment is not limited to this production method. That is, as long as the martensitic stainless steel seamless pipe of the present embodiment that is composed as described above can be produced, a method for producing the martensitic stainless steel seamless pipe is not limited to the production method described hereunder, and the martensitic stainless steel seamless pipe may be produced by another production method. Preferably, the method for producing the martensitic stainless steel seamless pipe according to the present embodiment includes a starting material preparation process, a hot working process, and a heat treatment process (quenching process and tempering process). Hereunder, a case where the production method includes a starting material preparation process, a hot working process, and a heat treatment process is described in detail.

[Starting material preparation process]

[0103] In the starting material preparation process, a starting material having the chemical composition described above is prepared. Here, the chemical composition of the starting material is the same as the chemical composition of the martensitic stainless steel seamless pipe according to the present embodiment. Specifically, the starting material according to the present embodiment consists of, in mass%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, P: 0.030% or less, S: 0.0050% or less, Cr: 11.00 to 14.00%, Ni: 5.00 to 7.50%, Mo: 1.50 to 4.50%, Cu: 0.50 to 3.50%, Co: 0.010 to 0.500%, Ti: 0.050 to 0.300%, V: 0.01 to 1.00%, Ca: 0.0005 to 0.0050%, Al: 0.001 to 0.100%, N: 0.0010 to 0.0500%, O: 0.050% or less, W: 0 to 2.00%, Nb: 0 to 0.50%, Mg: 0 to 0.0050%, rare earth metal: 0 to 0.0050%, and B: 0 to 0.0050%, with the balance being Fe and impurities. As long as the starting material has the above chemical composition, the production method is not particularly limited. The starting material may be prepared by producing the starting material, or may be prepared by purchasing the starting material from a third party. That is, the method for preparing the starting material is not limited.

[0104] In the case of preparing the starting material by producing the starting material, for example, the starting material is produced by the following method. A molten steel having the above chemical composition is produced by a well-known refining method. The produced molten steel is used to produce a cast piece through a continuous casting process. Here, the cast piece is a slab, a bloom, or a billet. In place of the cast piece, an ingot may be produced by an ingot-making process using the aforementioned molten steel. As needed, the slab, the bloom, or the ingot may be subjected to hot rolling to produce a billet. The starting material (slab, bloom, or billet) is produced by the above described production process.

[Hot working process]

[0105] In the hot working process, the prepared starting material is subjected to hot working. First, the starting material is heated in a heating furnace. Although not particularly limited, the heating temperature is, for example, 1100 to 1300°C. The starting material extracted from the heating furnace is subjected to hot working to produce a hollow shell (seamless steel pipe). Specifically, in the present embodiment, piercing-rolling is performed as hot working to produce a hollow shell. The piercing-rolling is not particularly limited, and a well-known method can be used. For example, when performing piercing-rolling, the piercing ratio is not particularly limited.

[0106] In the hot working process according to the present embodiment, as necessary, hot rolling may also be performed on the hollow shell after the piercing-rolling. Specifically, after the hollow shell after the piercing-rolling has been subjected to tube drawing, the hollow shell may be subjected to sizing. In such a case, for the tube drawing, a mandrel mill may be used or a plug mill may be used. Further, as necessary, tube drawing using an elongator mill may be performed. In addition, tube drawing in which a plurality of these mills is used in combination may be performed. For example, the hollow shell after piercing-rolling may be subjected to tube drawing using an elongator mill, and thereafter may be subjected to tube drawing using a plug mill. In the sizing performed on the hollow shell after the tube drawing, a stretch reducer may be used, a sizing mill may be used, or a plurality of these apparatuses may be used in combination. A hollow shell is produced by the above process.

[0107] Preferably, in the hot working process according to the present embodiment, a cumulative area reduction ratio R in the hot working is 40% or more. The area reduction ratio R is defined by the following Formula (A).

R = {1 - (cross-sectional area perpendicular to pipe axis direction of the hollow shell after hot working/ cross-sectional area perpendicular to axial direction of the starting material before hot working)} $\times$ 100 (A)

[0108] Note that, the phrase "hollow shell after hot working" in Formula (A) means the hollow shell after the final hot working ended. The phrase "starting material before hot working" in Formula (A) means the starting material before performing hot working. That is, in the hot working process according to the present embodiment, the area reduction ratio R is defined by the cross-sectional area perpendicular to the axial direction of the starting material that is changed by the hot working.

[0109] If the area reduction ratio R in the hot working process is large, a shearing force will be strongly applied to the inner surface of the hollow shell during working, and a large number of precipitation sites for Cu precipitates will be formed on the inner surface of the hollow shell. As a result, it will be easy for Cu precipitates to be dominantly distributed at the inner surface of the produced martensitic stainless steel seamless pipe. Specifically, after satisfying the other preferable production conditions, if the area reduction ratio R is made 40% or more, Fn2 can be made 1.20 or more in the produced martensitic stainless steel seamless pipe.

[0110] Therefore, in the hot working process according to the present embodiment, preferably the area reduction ratio R is made 40% or more. In the hot working process according to the present embodiment, although not particularly limited, an upper limit of the area reduction ratio R is, for example, 80%.

[0111] Preferably, in the hot working process according to the present embodiment, the working time is set to 15 minutes or less. The term "working time (min)" means the time period from when the starting material is extracted from the heating furnace until the final hot working ends. If the working time is too long, precipitation sites for Cu precipitates on the inner surface of the hollow shell will decrease during the hot working. As a result, it will be difficult for Cu precipitates to be dominantly distributed at the inner surface of the produced martensitic stainless steel seamless pipe. On the other hand, after satisfying the other preferable production conditions, if the working time is set to 15 minutes or less, Fn2 can be made 1.20 or more in the produced martensitic stainless steel seamless pipe.

[0112] Therefore, in the hot working process according to the present embodiment, preferably the working time is set to 15 minutes or less. A more preferable upper limit of the working time is 13 minutes, and further preferably is 10 minutes. In the hot working process according to the present embodiment, although not particularly limited, a lower limit of the working time is, for example, 5 minutes.

[0113] As described above, in the hot working process according to the present embodiment, after the starting material has been subjected to piercing-rolling, as necessary, hot rolling is performed. Specifically, after subjecting the starting material to piercing-rolling, tube drawing may be performed, and in addition, sizing may be performed. Further, since the hot working process according to the present embodiment is carried out by combining a plurality of hot rolling operations, the hot working process also includes a conveying process between the hot rolling operations. In addition, as necessary, the hollow shell may be heated using a holding furnace or a heating furnace. That is, in the hot working process according to the present embodiment, the term "working time" means a total time period that includes not only the time taken to perform a plurality of hot rolling operations, but also the time required for conveying the starting material between the hot rolling operations and for heating and the like. In short, it means that in the hot working process according to the present embodiment, the total time taken for piercing-rolling, tube drawing, sizing, as well as conveying and heating and the like is 15 minutes or less.

[Heat treatment process]

[0114] The heat treatment process includes a quenching process and a tempering process. In the heat treatment process, first, the hollow shell produced in the hot working process is subjected to quenching (quenching process). The hollow shell after quenching is subjected to tempering (tempering process). Hereunder, the quenching process and the tempering process are each described.

[Quenching process]

[0115] In the quenching process, quenching is performed by a well-known method. In the present description, the term "quenching" means rapidly cooling a hollow shell which is at a temperature that is not lower than the A_3 point. Quenching may be performed immediately after hot working without cooling the hollow shell to normal temperature after the hot working (direct quenching), or quenching may be performed after loading the hollow shell into a heat treatment furnace or holding furnace before the temperature of the hollow shell after hot working decreases and bringing the hollow shell to a quenching temperature.

[0116] The quenching temperature is not lower than the Acs transformation point, and for example is 900 to 1000°C. Here, the term "quenching temperature" means the furnace temperature in the case of using a heat treatment furnace or a holding furnace, and means the temperature of the outer surface of the hollow shell in the case of direct quenching. When using a heat treatment furnace or a holding furnace, furthermore, although not particularly limited, the time for which the hollow shell is held at the quenching temperature is, for example, 10 to 120 minutes.

[0117] Although not particularly limited, the quenching method is, for example, water cooling. As a method for quenching the hollow shell by water cooling, specifically, the hollow shell may be rapidly cooled by immersing the hollow shell in a water bath or an oil bath. Alternatively, the hollow shell may be rapidly cooled by pouring or jetting cooling water onto the outer surface and/or the inner surface of the hollow shell by shower cooling or mist cooling.

[Tempering process]

[0118] In the tempering process, the hollow shell that has been quenched is subjected to tempering to adjust the yield strength. In the present description, the term "tempering" means reheating the hollow shell after quenching to a temperature that is not more than the A_{c1} point and holding the hollow shell at that temperature. In the tempering process according to the present embodiment, the tempering temperature is set within the range of 500°C to the A_{c1} transformation point. In the tempering process according to the present embodiment, the tempering time is 10 to 180 minutes. In the present description, the term "tempering temperature" means the furnace temperature (°C) in the heat treatment furnace. In the present description, the term "tempering time" means the time for which the hollow shell is held at the tempering temperature.

[0119] Preferably, in the tempering process according to the present embodiment, a tempering temperature T (°C) and a tempering time t (min) are adjusted so as to satisfy the following Formula (B).

$$(T + 273.15) \times (20 + \log_{10}(t/60)) \times (1 - [Cu]/100) \leq 17200 \quad (B)$$

[0120] Where, in Formula (B), a tempering temperature (°C) is substituted for T, a tempering time (min) is substituted for t, and the content (mass%) of Cu in the hollow shell is substituted for [Cu].

[0121] Let FnB be defined as FnB = $(T + 273.15) \times (20 + \log_{10}(t/60)) \times (1 - [Cu]/100)$. FnB is an index indicating the yield strength of the produced martensitic stainless steel seamless pipe. If FnB is too large, the desired yield strength may not be obtained in some cases. On the other hand, after satisfying the other preferable production conditions, if FnB is made 17200 or less, the yield strength of the produced martensitic stainless steel seamless pipe can be stably made 862 MPa or more.

[0122] Therefore, in the tempering process according to the present embodiment, it is preferable to make FnB 17200 or less. A more preferable upper limit of FnB is 17100, and further preferably is 17000. A preferable upper limit of FnB when it is desired to stably obtain a yield strength of 965 MPa or more is 16700. Although not particularly limited, a lower limit of FnB is, for example, 14350.

[0123] The martensitic stainless steel seamless pipe according to the present embodiment can be produced by the processes described above. Note that, as mentioned above, the martensitic stainless steel seamless pipe may be produced by a method other than the production method described above. In addition, as needed, the produced martensitic stainless steel seamless pipe may be subjected to a post-treatment. The post-treatment is, for example, descaling that removes oxide scale formed on the surface of the steel material. Hereunder, the present invention is described more specifically by way of examples.

EXAMPLES

[0124] Molten steels having the chemical compositions shown in Table 1 were produced. Note that, the symbol "-" in Table 1 means that the content of the corresponding element was 0% when a fraction of the numerical value described in Table 1 was rounded off. Specifically, the symbol "-" means that the content of W in Steel No. 3 was 0% when rounded off to the second decimal places. The symbol "-" means that the content of Nb in Steel No. 1 was 0% when rounded off to the second decimal places. The symbol "-" means that the content of Mg, the content of REM, and the content of B in Steel No. 1 were each 0% when rounded off to the fourth decimal places. Further, Fn1 that was determined based on the chemical composition described in Table 1 and the above definition is shown in Table 1.

[Table 1]

TABLE 1

Steel Number	Chemical Composition (unit is mass%; balance is Fe and impurities)																				Fn1
	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Co	Ti	V	Ca	Al	N	O	W	Nb	Mg	REM	B	
1	0.015	0.23	0.39	0.015	0.0007	13.22	6.18	2.65	2.15	0.188	0.125	0.05	0.0018	0.038	0.0082	0.002	0.18	-	-	-	-	2.74
2	0.010	0.21	0.41	0.017	0.0006	13.09	6.05	2.74	2.03	0.205	0.105	0.05	0.0011	0.022	0.0088	0.004	0.19	-	-	-	-	2.84
3	0.010	0.22	0.41	0.015	0.0005	13.06	7.28	2.61	2.01	0.168	0.102	0.05	0.0012	0.024	0.0078	0.003	-	-	-	-	-	2.61
4	0.011	0.23	0.41	0.014	0.0004	13.54	7.02	2.81	2.29	0.198	0.112	0.05	0.0016	0.027	0.0072	0.004	-	-	-	-	0.0002	2.81
5	0.008	0.24	0.42	0.016	0.0008	13.02	6.01	2.51	2.04	0.088	0.095	0.06	0.0021	0.018	0.0068	0.005	0.18	-	-	-	-	2.60
6	0.007	0.24	0.41	0.016	0.0003	12.98	6.04	2.52	2.02	0.114	0.102	0.05	0.0023	0.022	0.0075	0.004	-	-	-	-	-	2.52
7	0.011	0.22	0.43	0.017	0.0006	13.52	6.12	2.72	2.12	0.175	0.106	0.05	0.0019	0.027	0.0087	0.004	-	-	-	-	-	2.72
8	0.012	0.25	0.39	0.014	0.0005	13.02	5.99	2.52	3.01	0.092	0.108	0.05	0.0008	0.021	0.0092	0.003	0.19	-	-	-	-	2.62
9	0.012	0.23	0.40	0.016	0.0005	13.55	6.03	2.53	2.03	0.094	0.097	0.05	0.0024	0.026	0.0086	0.003	-	-	-	Y:0.0010	-	2.53
10	0.018	0.22	0.35	0.015	0.0008	13.08	7.06	3.06	1.88	0.194	0.108	0.04	0.0022	0.031	0.0083	0.003	-	-	-	-	-	3.06
11	0.011	0.22	0.41	0.016	0.0006	13.58	6.03	2.72	2.01	0.146	0.112	0.04	0.0025	0.032	0.0071	0.003	0.28	0.01	-	-	-	2.86
12	0.011	0.22	0.41	0.016	0.0003	13.01	6.01	2.60	1.50	0.186	0.106	0.05	0.0022	0.031	0.0080	0.004	-	-	0.0003	-	-	2.60
13	0.012	0.24	0.41	0.015	0.0006	12.78	6.18	2.61	2.23	-	0.114	0.05	0.0033	0.035	0.0121	0.005	0.20	-	-	-	-	2.71
14	0.013	0.25	0.43	0.016	0.0005	12.02	7.00	2.96	-	0.230	0.087	0.05	0.0020	0.025	0.0110	0.003	-	0.01	-	-	0.0003	2.96
15	0.012	0.24	0.42	0.015	0.0010	13.12	6.06	2.12	2.13	0.156	0.102	0.04	0.0024	0.032	0.0074	0.005	0.15	-	-	-	-	2.20
16	0.010	0.23	0.40	0.015	0.0005	12.88	6.15	2.48	1.98	0.122	0.112	0.05	0.0022	0.028	0.0086	0.003	-	-	-	-	-	2.48

[0125] An ingot was produced by the ingot-making process using the produced molten steel of each steel number. The ingot of each steel number was heated for three hours at 1250°C, and subjected to hot forging to produce a round billet with a diameter of 200 mm.

[0126] After heating the round billet of each test number to 1230°C, each round billet was subjected to hot rolling as hot working to produce a hollow shell (seamless steel pipe). The area reduction ratio R of the hot working (hot rolling) performed for each test number is shown in Table 2 to Table 4. Note that, in the column "Area Reduction Ratio R" in Table 2 to Table 4, "A (Acceptable)" means that the area reduction ratio R was 40% or more. Further, a numerical value described in the column "Area Reduction Ratio R" in Table 2 to Table 4 means the numerical value (%) of the area reduction ratio R. In addition, the time period (working time) from when the round billet was extracted from the heating furnace until the final hot working (hot rolling) ended is shown in Table 2 to Table 4. Note that, in the column "Hot Working Time" in Table 2 to Table 4, "A (Acceptable)" means that the hot working time was 15 minutes or less. Further, in the column "Hot Working Time" in Table 2 to Table 4, "NA (Not Acceptable)" means that the hot working time was more than 15 minutes.

[Table 2]

[0127]

TABLE 2

Test Number	Steel Number	Fn1	Hot Working Process		Tempering Process		FnB	YS (MPa)	Microstructure		Inner Surface Observation Results			Pitting Potential V'c1000 (mV)
			Area Reduction Ratio R	Hot Working Time	Tempering Temperature T (°C)	Tempering Time t (min)			Retained γ (%)	Ferrite (%)	OS_{Cu}	OI_{Cu}	Fn2	
1	1	2.74	A	A	540	30	15674	1088	3.5	0.0	0.63	0.25	2.52	-186
2	1	2.74	A	A	560	30	16059	1056	3.5	0.0	0.57	0.23	2.48	-188
3	1	2.74	A	A	580	30	16445	1004	3.6	0.0	0.56	0.21	2.67	-188
4	1	2.74	A	A	590	30	16638	990	3.6	0.1	0.52	0.20	2.60	-189
5	1	2.74	A	A	605	30	16927	963	3.7	0.5	0.48	0.16	3.00	-207
6	1	2.74	A	A	560	60	16305	1020	3.6	0.0	0.55	0.22	2.50	-192
7	1	2.74	A	A	590	60	16892	915	3.8	0.3	0.48	0.20	2.40	-202
8	2	2.84	A	A	540	30	15693	1056	3.6	0.0	0.55	0.23	2.39	-167
9	2	2.84	A	A	560	30	16079	1030	3.6	0.0	0.49	0.20	2.45	-171
10	2	2.84	A	A	580	30	16465	994	3.6	0.0	0.47	0.20	2.35	-172
11	2	2.84	A	A	590	30	16658	973	3.7	0.2	0.38	0.18	2.11	-172
12	2	2.84	A	A	620	30	17237	799	10.7	0.4	0.28	0.15	1.87	-189
13	3	2.61	A	A	540	30	15696	1058	3.6	0.0	0.61	0.26	2.35	-184
14	3	2.61	A	A	580	30	16468	983	4.6	0.0	0.54	0.24	2.25	-185
15	3	2.61	A	A	620	30	17240	727	12.4	1.3	0.32	0.15	2.13	-215
16	4	2.81	A	A	540	30	15651	1087	3.7	0.0	0.63	0.32	1.97	-195
17	4	2.81	A	A	560	30	16036	1056	3.8	0.0	0.58	0.30	1.93	-195
18	4	2.81	A	A	600	30	16806	927	4.6	0.6	0.49	0.24	2.04	-198
19	5	2.60	A	A	520	30	15306	1079	1.9	0.0	0.72	0.31	2.32	-185
20	5	2.60	A	A	560	30	16077	1039	1.9	0.0	0.65	0.28	2.32	-187
21	5	2.60	A	A	580	30	16463	999	2.0	0.0	0.57	0.25	2.28	-195

(continued)

Test Number	Steel Number	Fn1	Hot Working Process		Tempering Process		FnB	YS (MPa)	Microstructure		Inner Surface Observation Results			Pitting Potential V'c1000 (mV)
			Area Reduction Ratio R	Hot Working Time	Tempering Temperature T (°C)	Tempering Time t (min)			Retained γ (%)	Ferrite (%)	OS_{Cu}	OI_{Cu}	Fn2	
22	5	2.60	A	A	600	30	16849	961	2.1	0.3	0.31	0.20	1.55	-198
23	5	2.60	A	A	620	45	17389	712	12.8	1.7	0.28	0.16	1.75	-218
24	6	2.52	A	A	540	30	15695	1053	1.8	0.0	0.52	0.28	1.86	-217
25	6	2.52	A	A	560	30	16081	1029	1.8	0.0	0.47	0.24	1.96	-216

[Table 3]

[0128]

TABLE 3

Test Number	Steel Number	Fn1	Hot Working Process		Tempering Process		FnB	YS (MPa)	Microstructure		Inner Surface Observation Results			Pitting Potential V'c1000 (mV)
			Area Reduction Ratio R	Hot Working Time	Tempering Temperature T (°C)	Tempering Time t (min)			Retained γ (%)	Ferrite (%)	OS_{Cu}	OI_{Cu}	Fn2	
26	6	2.52	A	A	580	30	16467	998	1.9	0.0	0.47	0.22	2.14	-222
27	6	2.52	A	A	600	30	16853	956	2.1	0.0	0.41	0.21	1.95	-225
28	6	2.52	A	A	600	60	17110	925	2.7	0.5	0.35	0.19	1.84	-225
29	7	2.72	A	A	560	30	16064	1025	1.3	0.0	0.72	0.45	1.60	-189
30	7	2.72	A	A	585	30	16546	989	1.4	0.5	0.64	0.38	1.68	-187
31	7	2.72	A	A	600	30	16836	947	1.3	0.7	0.61	0.35	1.74	-205
32	7	2.72	A	A	600	60	17093	930	1.4	1.3	0.52	0.32	1.63	-208
33	7	2.72	A	A	620	30	17221	790	8.8	2.3	0.27	0.16	1.69	-212
34	8	2.62	A	A	520	30	15154	1123	7.9	0.0	0.67	0.48	1.40	-165
35	8	2.62	A	A	540	30	15536	1094	7.9	0.0	0.68	0.45	1.51	-172
36	8	2.62	A	A	560	30	15918	1063	7.9	0.0	0.68	0.42	1.62	-175
37	8	2.62	A	A	580	30	16300	1028	8.0	0.0	0.67	0.36	1.86	-175
38	8	2.62	A	A	600	30	16682	981	8.1	0.0	0.60	0.35	1.71	-178
39	8	2.62	A	A	615	30	16969	929	8.4	0.4	0.48	0.33	1.45	-205
40	8	2.62	A	A	615	60	17228	820	11.6	0.7	0.47	0.35	1.34	-207
41	8	2.62	A	A	615	90	17380	750	13.5	0.9	0.52	0.37	1.41	-212
42	9	2.53	A	A	540	30	15693	1056	2.6	0.0	0.38	0.25	1.52	-185
43	9	2.53	A	A	560	30	16079	1029	2.6	0.0	0.34	0.22	1.55	-188
44	9	2.53	A	A	585	30	16562	989	2.7	0.7	0.33	0.18	1.83	-189
45	9	2.53	A	A	600	30	16851	937	2.9	1.7	0.25	0.15	1.67	-195
46	9	2.53	A	A	600	60	17109	942	2.8	3.5	0.20	0.12	1.67	-193

(continued)

Test Number	Steel Number	Fn1	Hot Working Process		Tempering Process		FnB	YS (MPa)	Microstructure		Inner Surface Observation Results			Pitting Potential V'c1000 (mV)
			Area Reduction Ratio R	Hot Working Time	Tempering Temperature T (°C)	Tempering Time t (min)			Retained γ (%)	Ferrite (%)	OS_{Cu}	OI_{Cu}	Fn2	
47	9	2.53	A	A	620	30	17237	774	7.4	6.7	0.17	0.10	1.70	-205
48	10	3.06	A	A	560	30	16104	1060	6.9	0.2	0.54	0.27	2.00	-197
49	10	3.06	A	A	585	30	16587	967	8.8	1.8	0.53	0.24	2.21	-198
50	10	3.06	A	A	600	30	16877	945	9.4	1.2	0.50	0.18	2.77	-197

TABLE [Table 4]

Test Number	Steel Number	Fn1	Hot Working Process		Tempering Process		FnB	YS (MPa)	Microstructure		Inner Surface Observation Results			Pitting Potential V'c1000 (mV)
			Area Reduction Ratio R	Hot Working Time	Tempering Temperature T (°C)	Tempering Time t (min)			Retained γ (%)	Ferrite (%)	OS_{Cu}	OI_{Cu}	Fn2	
51	10	3.06	A	A	600	60	17135	898	9.5	2.1	0.42	0.15	2.80	-205
52	10	3.06	A	A	600	75	17218	854	12.5	4.5	0.25	0.10	2.50	-208
53	10	3.06	A	A	620	30	17263	750	11.8	7.8	0.28	0.14	2.00	-203
54	11	2.86	A	A	540	30	15696	1053	2.8	0.0	0.68	0.28	2.43	-210
55	11	2.86	A	A	560	30	16082	1032	2.8	0.0	0.70	0.26	2.69	-212
56	11	2.86	A	A	580	30	16468	999	2.9	0.0	0.51	0.26	1.96	-215
57	11	2.86	A	A	600	30	16854	961	3.7	0.1	0.38	0.20	1.90	-223
58	12	2.60	A	A	560	30	16166	1007	1.4	0.0	0.56	0.25	2.24	-225
59	12	2.60	A	A	580	30	16554	971	1.5	0.0	0.54	0.24	2.25	-224
60	12	2.60	A	A	600	30	16942	934	1.9	0.3	0.46	0.22	2.09	-228
61	13	2.81	A	A	600	30	16817	832	4.8	0.0	0.64	0.36	1.78	-225
62	14	2.96	A	A	540	30	16018	930	0.4	0.0	-	-	-	-252
63	14	2.96	A	A	560	30	16412	929	0.5	0.0	-	-	-	-263
64	14	2.96	A	A	580	30	16806	885	1.0	0.1	-	-	-	-275
65	15	2.20	A	A	540	30	15677	987	2.4	0.0	0.55	0.40	1.38	-248
66	16	2.48	A	A	600	30	16860	934	2.3	0.1	0.53	0.42	1.26	-253
67	1	2.74	20	A	540	30	15674	952	3.6	0.0	0.15	0.13	1.15	-256
68	1	2.74	30	A	540	30	15674	986	3.6	0.0	0.20	0.18	1.11	-255
69	1	2.74	35	A	540	30	15674	1012	3.6	0.0	0.22	0.20	1.10	-248
70	7	2.72	20	A	560	30	16064	924	1.6	0.0	0.21	0.18	1.17	-247
71	7	2.72	30	A	560	30	16064	948	1.5	0.0	0.29	0.25	1.16	-255
72	7	2.72	35	A	560	30	16064	980	1.5	0.0	0.38	0.33	1.15	-252

(continued)

Test Number	Steel Number	Fn1	Hot Working Process		Tempering Process		FnB	YS (MPa)	Microstructure		Inner Surface Observation Results			Pitting Potential V'c1000 (mV)
			Area Reduction Ratio R	Hot Working Time	Tempering Temperature T (°C)	Tempering Time t (min)			Retained γ (%)	Ferrite (%)	OS_{Cu}	OI_{Cu}	Fn2	
73	1	2.74	A	NA	540	30	15674	978	3.4	0.0	0.19	0.21	0.90	-248
74	1	2.74	A	NA	560	30	16059	915	3.5	0.0	0.08	0.12	0.67	-246
75	7	2.72	A	NA	560	30	16064	915	1.4	0.0	0.10	0.09	1.11	-250
76	7	2.72	A	NA	585	30	16546	889	1.6	0.2	0.08	0.07	1.14	-255

[0129] The hollow shell of each test number was subjected to quenching. The quenching was performed by reheating the hollow shell in a heat treatment furnace, and then immersing the hollow shell in a water bath. For the hollow shell of each test number, the quenching temperature (furnace temperature of the heat treatment furnace) was 900°C, and the time for which the hollow shell was held at the quenching temperature was 15 minutes. After being quenched, the hollow shell of each test number was subjected to tempering. The tempering was performed by reheating each hollow shell after quenching in a tempering furnace, and holding the hollow shell at the tempering temperature. For each test number, the tempering temperature T (°C) and the tempering time t (min) during tempering, as well as FnB which was determined based on the tempering temperature T (°C), the tempering time t (min), the content of Cu (mass%), and the definition described above are shown in Table 2 to Table 4. A martensitic stainless steel seamless pipe of each test number was produced by the above production process.

[Evaluation tests]

[0130] The produced seamless steel pipe of each test number was subjected to a tensile test, a microstructure observation test, an inner surface observation test, and a pitting resistance test.

[Tensile test]

[0131] The seamless steel pipe of each test number was subjected to a tensile test in accordance with ASTM E8/E8M (2021). Specifically, a round bar tensile test specimen was prepared from a center portion of the wall thickness of the seamless steel pipe of each test number. In each round bar tensile test specimen, the diameter of the parallel portion was 8.9 mm and the gage length was 35.6 mm. The longitudinal direction of the round bar tensile test specimen was parallel to the rolling elongation direction (pipe axis direction) of the seamless steel pipe. A tensile test was carried out at normal temperature (25°C) in air using the round bar tensile test specimen of each test number, and the 0.2% offset proof stress (MPa) was determined. The determined 0.2% offset proof stress was defined as the yield strength (MPa). The obtained yield strength of each test number is shown in the column "YS (MPa)" in Table 2 to Table 4.

[Microstructure observation test]

[0132] The seamless steel pipe of each test number was subjected to a microstructure volume ratio measurement test, and the volume ratios of retained austenite and ferrite were determined. For the seamless steel pipe of each test number, the volume ratio (%) of retained austenite was determined by the X-ray diffraction method described above. The obtained volume ratio (%) of retained austenite in the seamless steel pipe of each test number is shown in the column "Retained γ (%)" in Table 2 to Table 4. In addition, for the seamless steel pipe of each test number, the volume ratio (%) of ferrite was determined by the aforementioned point counting method in accordance with ASTM E562 (2019). The obtained volume ratio (%) of ferrite for each test number is shown in the column "Ferrite (%)" in Table 2 to Table 4.

[Inner surface observation test]

[0133] The seamless steel pipe of each test number other than Test Nos. 62 to 64 was subjected to an inner surface observation test, and the inner surface Cu occupancy OS_{Cu}, the interior Cu occupancy OI_{Cu}, and Fn2 were determined. For the seamless steel pipe of the respective test numbers, a thin film test specimen was prepared by the method described above, and TEM observation was performed. The thin film test specimen used for the TEM observation was prepared by FIB processing. Gallium (Ga) ions were used for the FIB processing. When performing the FIB processing, a protective film of carbon was formed on the inner surface in order to protect the inner surface. The size of the observation surface of the thin film test specimen was 10 μm $\times$ 10 μm, and the thickness of the thin film test specimen was 150 nm. In addition, an observation field of view region with dimensions of 1.0 μm in the L direction and 1.0 μm in the T direction was divided into 65,536 sections by being divided equally into 256 sections in the L direction and divided equally into 256 sections in the T direction, and each section was subjected to EDS analysis. holding furnaceThe method described above was used to identify the T-direction position of the inner surface and to also identify the inner surface vicinity region and the interior region in the observation field of view region. Among the sections included in the identified inner surface vicinity region and in the identified interior region, respectively, the numerical proportion of sections having a Cu concentration of more than 2.0% were determined, and the determined numerical proportions were defined as the inner surface Cu occupancy OS_{Cu} and the interior Cu occupancy OI_{Cu}, respectively. Fn2 was determined based on the determined inner surface Cu occupancy OS_{Cu} and interior Cu occupancy OI_{Cu}, and Formula (2) that is described above. The determined inner surface Cu occupancy OS_{Cu}, interior Cu occupancy OI_{Cu}, and Fn2 are shown in Table 2 to Table 4. Note that, because the seamless steel pipes of Test Nos. 62 to 64 did not contain Cu, the seamless steel pipes of Test Nos. 62 to 64 were not subjected to an inner surface observation test.

[Pitting resistance test]

[0134] The seamless steel pipe of each test number was subjected to a pitting resistance test, and the pitting potential V'c1000 (mV) was determined. Specifically, from the seamless steel pipe of each test number, a test specimen for measuring pitting potential was prepared which included an area of 1.0 cm^2 or more of the inner surface as a test surface, and whose thickness was the same as the wall thickness of the seamless steel pipe. A 25% by mass sodium chloride aqueous solution whose pH was adjusted to 4.5 with 0.08 g/L sodium hydrogen carbonate and which was degassed before use was adopted as the test solution. In an autoclave, the test specimen was immersed in a test solution so that the solution volume to specimen area ratio was 500 mL/cm^2 or more, and this was adopted as the test bath. After degassing the test bath, a gaseous mixture of H_2S gas at 0.03 atm and CO_2 gas at 10 atm was charged under pressurization into the autoclave, and the test bath was stirred.

[0135] The test bath was heated to 175°C. In an electrochemical test, a saturated KCl silver-silver chloride electrode was used as a reference electrode, and a platinum electrode was used as a counter electrode. After the open circuit potential stabilized, the anodic polarization curve was measured at a potential sweep rate of 20 mV/min in the anode direction from the open circuit potential using a potentiostat. The potential when the anodic current density reached 1000 $\mu A/cm^2$ was determined from the obtained anodic polarization curve. The same measurement was performed three times, and the arithmetic average value of the obtained potentials was defined as the pitting potential V'c1000 (mV). The pitting potential V'c1000 (mV) determined for each test number is shown in Table 2 to Table 4.

[Test results]

[0136] Referring to Table 1 to Table 4, for the seamless steel pipes of Test Nos. 1 to 11, 13, 14, 16 to 22, 24 to 32, 34 to 39, 42 to 46, 48 to 51, and 54 to 60, the chemical composition was appropriate, Fn1 was 2.50 or more, and the production method was the preferable production method described in the description. As a result, in each of these seamless steel pipes the yield strength was 862 MPa or more, and in the microstructure, the volume ratio of retained austenite was 0 to 15.0%, and the volume ratio of ferrite was 0 to 5.0%. In addition, in each of these seamless steel pipes, Fn2 was 1.20 or more. As a result, for these seamless steel pipes, the pitting potential V'c1000 in the pitting resistance test was -230 mV or more. That is, these seamless steel pipes had a high strength of 862 MPa or more, and excellent pitting resistance at the inner surface.

[0137] On the other hand, for the seamless steel pipes of Test Nos. 12, 15, 23, 33, 40, 41, and 52, in the production method, FnB was more than 17200. As a result, these seamless steel pipes had a yield strength of less than 862 MPa, and the desired strength was not obtained.

[0138] For the seamless steel pipes of Test Nos. 47 and 53, in the production method, FnB was more than 17200. As a result, in these seamless steel pipes the volume ratio of ferrite was more than 5.0%, and the yield strength was less than 862 MPa. That is, in these seamless steel pipes, the desired strength was not obtained.

[0139] In the seamless steel pipe of Test No. 61, the content of Co was too low. As a result, in this seamless steel pipe the yield strength was less than 862 MPa, and the desired strength was not obtained.

[0140] In the seamless steel pipes of Test Nos. 62 to 64, the content of Cu was too low. As a result, for these seamless steel pipes, the pitting potential V'c1000 was less than -230 mV in the pitting resistance test. That is, these seamless steel pipes did not have excellent pitting resistance at the inner surface.

[0141] In the seamless steel pipes of Test Nos. 65 and 66, Fn1 was too low. As a result, in the pitting resistance test, the pitting potential V'c1000 was less than -230 mV. That is, these seamless steel pipes did not have excellent pitting resistance at the inner surface.

[0142] For the seamless steel pipes of Test Nos. 67 to 72, in the production method, the area reduction ratio R was less than 40%. Consequently, in these seamless steel pipes, Fn2 was less than 1.20. As a result, in the pitting resistance test, the pitting potential V'c1000 was less than -230 mV. That is, these seamless steel pipes did not have excellent pitting resistance at the inner surface.

[0143] For the seamless steel pipes of Test Nos. 73 to 76, in the production method, the hot working time was more than 15 minutes. Consequently, in these seamless steel pipes, Fn2 was less than 1.20. As a result, in the pitting resistance test, the pitting potential V'c1000 was less than -230 mV. That is, these seamless steel pipes did not have excellent pitting resistance at the inner surface.

[0144] An embodiment of the present disclosure has been described above. However, the embodiment described above is merely an example for carrying out the present disclosure. Therefore, the present disclosure is not limited to the above-described embodiment, and can be implemented by appropriately modifying the above embodiment within a range that does not depart from the gist of the present disclosure.

REFERENCE SIGNS LIST

[0145]

10 Inner surface
20 Inner surface vicinity region
30 Interior region
40 Hollow region
50 Observation field of view region

[0146] Note that, the gist of the martensitic stainless steel seamless pipe according to the present embodiment can also be described as follows.

[0147]

[1]

A martensitic stainless steel seamless pipe consisting of, in mass%,
C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cr: 11.00 to 14.00%,
Ni: 5.00 to 7.50%,
Mo: 1.50 to 4.50%,
Cu: 0.50 to 3.50%,
Co: 0.010 to 0.500%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Ca: 0.0005 to 0.0050%,
Al: 0.001 to 0.100%,
N: 0.0010 to 0.0500%,
O: 0.050% or less, and
the balance: Fe and impurities,
and satisfies Formula (IA),
wherein:
a microstructure is composed of, in volume percent, retained austenite in an amount of 0 to 15.0% and ferrite in an amount of 0 to 5.0%, with the balance being tempered martensite;
a yield strength is 862 MPa or more;
when a pipe axis direction of the martensitic stainless steel seamless pipe is defined as an L direction, and a pipe radius direction of the martensitic stainless steel seamless pipe is defined as a T direction,
with respect to a square observation field of view region that includes an inner surface of the martensitic stainless steel seamless pipe that extends in the L direction, and whose sides that extend in the L direction are 1.0 μm in length and whose sides that extend in the T direction are 1.0 μm in length,
when the observation field of view region is divided into 65,536 sections by being divided equally into 256 sections in the L direction and divided equally into 256 sections in the T direction,
the observation field of view region is composed of:

an inner surface vicinity region which is a rectangular region that has the inner surface of the martensitic stainless steel seamless pipe as a top edge and includes 256 sections in the L direction and six sections in the T direction,
an interior region which is below contact with the inner surface vicinity region, and
a hollow region which is above contact with the inner surface vicinity region; and
when, among all the sections in the inner surface vicinity region, a numerical proportion of sections in which a Cu concentration is more than 2.0% is defined as inner surface Cu occupancy OS_{Cu}, and
among all the sections in the interior region, a numerical proportion of sections in which a Cu concentration is more than 2.0% is defined as interior Cu occupancy OI_{Cu},
the inner surface Cu occupancy OS_{Cu} and the interior Cu occupancy OI_{Cu} satisfy Formula (2);

$$Mo \geq 2.50 \quad (1A)$$

$$OS_{Cu}/OI_{Cu} \geq 1.20 \quad (2)$$

where, a content of a corresponding element in mass% is substituted for each symbol of an element in Formula (IA).

[2]

A martensitic stainless steel seamless pipe consisting of, in mass%,
C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cr: 11.00 to 14.00%,
Ni: 5.00 to 7.50%,
Mo: 1.50 to 4.50%,
Cu: 0.50 to 3.50%,
Co: 0.010 to 0.500%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Ca: 0.0005 to 0.0050%,
Al: 0.001 to 0.100%,
N: 0.0010 to 0.0500%, and
O: 0.050% or less,
and also containing one or more elements selected from a group consisting of:
W: 2.00% or less,
Nb: 0.50% or less,
Mg: 0.0050% or less,
rare earth metal: 0.0050% or less, and
B: 0.0050% or less,
with the balance being Fe and impurities,
and satisfying Formula (1B),
wherein:

a microstructure is composed of, in volume percent, retained austenite in an amount of 0 to 15.0% and ferrite in an amount of 0 to 5.0%, with the balance being tempered martensite;
a yield strength is 862 MPa or more;
when a pipe axis direction of the martensitic stainless steel seamless pipe is defined as an L direction, and a pipe radius direction of the martensitic stainless steel seamless pipe is defined as a T direction,
with respect to a square observation field of view region that includes an inner surface of the martensitic stainless steel seamless pipe that extends in the L direction, and whose sides that extend in the L direction are 1.0 μm in length and whose sides that extend in the T direction are 1.0 μm in length,
when the observation field of view region is divided into 65,536 sections by being divided equally into 256 sections in the L direction and divided equally into 256 sections in the T direction,
the observation field of view region is composed of:

an inner surface vicinity region which is a rectangular region that has the inner surface of the martensitic stainless steel seamless pipe as a top edge and includes 256 sections in the L direction and six sections in the T direction,
an interior region which is below contact with the inner surface vicinity region, and
a hollow region which is above contact with the inner surface vicinity region; and
when, among all the sections in the inner surface vicinity region, a numerical proportion of sections in which a Cu concentration is more than 2.0% is defined as inner surface Cu occupancy OS_{Cu}, and among all the sections in the interior region, a numerical proportion of sections in which a Cu concen-

tration is more than 2.0% is defined as interior Cu occupancy OI_{Cu},
the inner surface Cu occupancy OS_{Cu} and the interior Cu occupancy OI_{Cu} satisfy Formula (2);

$$Mo + 0.5 \times W \geq 2.50 \quad (1B)$$

$$OS_{Cu}/OI_{Cu} \geq 1.20 \quad (2)$$

where, a content of a corresponding element in mass% is substituted for each symbol of an element in Formula (1B).

[3]
A method for producing the martensitic stainless steel seamless pipe according to [1], including:

a starting material preparation process of preparing a starting material which consists of, in mass%,
C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cr: 11.00 to 14.00%,
Ni: 5.00 to 7.50%,
Mo: 1.50 to 4.50%,
Cu: 0.50 to 3.50%,
Co: 0.010 to 0.500%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Ca: 0.0005 to 0.0050%,
Al: 0.001 to 0.100%,
N: 0.0010 to 0.0500%, and
O: 0.050% or less,
with the balance being Fe and impurities,
and which satisfies Formula (1A);
a hot working process of heating, in a heating furnace, the starting material that is prepared, and thereafter performing hot working in which an area reduction ratio R defined by Formula (A) is 40% or more and a hot working time is 15 minutes or less to produce a hollow shell;
a quenching process of subjecting the hollow shell that is at a temperature not less than an A_3 point to quenching; and
a tempering process of performing tempering of the hollow shell subjected to the quenching, under conditions that satisfy Formula (B);

$$Mo \geq 2.50 \quad (1A)$$

R = {1 - (cross-sectional area perpendicular to pipe axis direction of the hollow shell after hot working/cross-sectional area perpendicular to axial direction of the starting material before hot working)} × 100 (A)

$$(T + 273.15) \times (20 + \log_{10}(t/60)) \times (1 - [Cu]/100) \leq 17200 \quad (B)$$

where, a content of a corresponding element in mass% is substituted for each symbol of an element in Formula

(IA); and
in Formula (B), a tempering temperature in °C is substituted for T, a tempering time in minutes is substituted for t, and a content of Cu in the hollow shell in mass% is substituted for [Cu].

[4]
A method for producing the martensitic stainless steel seamless pipe according to [2], including:

a starting material preparation process of preparing a starting material consisting of, in mass%,
C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cr: 11.00 to 14.00%,
Ni: 5.00 to 7.50%,
Mo: 1.50 to 4.50%,
Cu: 0.50 to 3.50%,
Co: 0.010 to 0.500%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Ca: 0.0005 to 0.0050%,
Al: 0.001 to 0.100%,
N: 0.0010 to 0.0500%, and
O: 0.050% or less,
and also containing one or more elements selected from a group consisting of:

W: 2.00% or less,
Nb: 0.50% or less,
Mg: 0.0050% or less,
rare earth metal: 0.0050% or less, and
B: 0.0050% or less,
with the balance being Fe and impurities,
and satisfying Formula (1B);
a hot working process of heating, in a heating furnace, the starting material that is prepared, and thereafter performing hot working in which an area reduction ratio R defined by Formula (A) is 40% or more and a hot working time is 15 minutes or less to produce a hollow shell;
a quenching process of subjecting the hollow shell that is at a temperature not less than an A_3 point to quenching; and
a tempering process of performing tempering of the hollow shell subjected to the quenching, under conditions that satisfy Formula (B);

$$\mathrm{Mo} + 0.5 \times \mathrm{W} \geq 2.50 \qquad (1\mathrm{B})$$

R = {1 - (cross-sectional area perpendicular to pipe axis direction of the hollow shell after hot working/cross-sectional area perpendicular to axial direction of the starting material before hot working)} × 100 (A)

$$(\mathrm{T} + 273.15) \times (20 + \log_{10}(\mathrm{t}/60)) \times (1 - [\mathrm{Cu}]/100) \leq 17200 \qquad (\mathrm{B})$$

where, a content of a corresponding element in mass% is substituted for each symbol of an element in Formula (1B); and
in Formula (B), a tempering temperature in °C is substituted for T, a tempering time in minutes is substituted

for t, and a content of Cu in the hollow shell in mass% is substituted for [Cu].

Claims

1. A martensitic stainless steel seamless pipe consisting of, in mass%,

C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cr: 11.00 to 14.00%,
Ni: 5.00 to 7.50%,
Mo: 1.50 to 4.50%,
Cu: 0.50 to 3.50%,
Co: 0.010 to 0.500%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Ca: 0.0005 to 0.0050%,
Al: 0.001 to 0.100%,
N: 0.0010 to 0.0500%,
O: 0.050% or less,
W: 0 to 2.00%,
Nb: 0 to 0.50%,
Mg: 0 to 0.0050%,
rare earth metal: 0 to 0.0050%, and
B: 0 to 0.0050%,
with the balance being Fe and impurities,
and satisfying Formula (1),
wherein:

a microstructure is composed of, in volume percent, retained austenite in an amount of 0 to 15.0% and ferrite in an amount of 0 to 5.0%, with the balance being tempered martensite;
a yield strength is 862 MPa or more;
when a pipe axis direction of the martensitic stainless steel seamless pipe is defined as an L direction, and a pipe radius direction of the martensitic stainless steel seamless pipe is defined as a T direction,
with respect to a square observation field of view region that includes an inner surface of the martensitic stainless steel seamless pipe that extends in the L direction, and whose sides that extend in the L direction are 1.0 μm in length and whose sides that extend in the T direction are 1.0 μm in length,
when the observation field of view region is divided into 65,536 sections by being divided equally into 256 sections in the L direction and divided equally into 256 sections in the T direction,
the observation field of view region is composed of:

an inner surface vicinity region which is a rectangular region that has the inner surface of the martensitic stainless steel seamless pipe as a top edge and includes 256 sections in the L direction and six sections in the T direction,
an interior region which is below contact with the inner surface vicinity region, and
a hollow region which is above contact with the inner surface vicinity region; and
when, among all the sections in the inner surface vicinity region, a numerical proportion of sections in which a Cu concentration is more than 2.0% is defined as inner surface Cu occupancy OS_{Cu}, and among all the sections in the interior region, a numerical proportion of sections in which a Cu concentration is more than 2.0% is defined as interior Cu occupancy OI_{Cu},
the inner surface Cu occupancy OS_{Cu} and the interior Cu occupancy OI_{Cu} satisfy Formula (2);

$$\mathrm{Mo} + 0.5 \times \mathrm{W} \geq 2.50 \qquad (1)$$

$$OS_{Cu}/OI_{Cu} \geq 1.20 \quad (2)$$

where, a content of a corresponding element in mass% is substituted for each symbol of an element in Formula (1).

2. The martensitic stainless steel seamless pipe according to claim 1, containing one or more elements selected from a group consisting of:

W: 0.01 to 2.00%,
Nb: 0.01 to 0.50%,
Mg: 0.0001 to 0.0050%,
rare earth metal: 0.0001 to 0.0050%, and
B: 0.0001 to 0.0050%.

3. A method for producing the martensitic stainless steel seamless pipe according to claim 1 or claim 2, including:

a starting material preparation process of preparing a starting material which consists of, in mass%,
C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cr: 11.00 to 14.00%,
Ni: 5.00 to 7.50%,
Mo: 1.50 to 4.50%,
Cu: 0.50 to 3.50%,
Co: 0.010 to 0.500%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Ca: 0.0005 to 0.0050%,
Al: 0.001 to 0.100%,
N: 0.0010 to 0.0500%,
O: 0.050% or less,
W: 0 to 2.00%,
Nb: 0 to 0.50%,
Mg: 0 to 0.0050%,
rare earth metal: 0 to 0.0050%, and
B: 0 to 0.0050%,
with the balance being Fe and impurities,
and which satisfies Formula (1);
a hot working process of heating, in a heating furnace, the starting material that is prepared, and thereafter performing hot working in which an area reduction ratio R defined by Formula (A) is 40% or more and a hot working time is 15 minutes or less to produce a hollow shell;
a quenching process of subjecting the hollow shell that is at a temperature not less than an A_3 point to quenching; and
a tempering process of performing tempering of the hollow shell subjected to the quenching, under conditions that satisfy Formula (B);

$$Mo + 0.5 \times W \geq 2.50 \quad (1)$$

R = {1 - (cross-sectional area perpendicular to pipe axis direction of the hollow shell after hot working/cross-sectional area perpendicular to axial direction of the starting material before hot working)} × 100 (A)

$$(T + 273.15) \times (20 + \log_{10}(t/60)) \times (1 - [Cu]/100) \leq 17200 \qquad (B)$$

where, a content of a corresponding element in mass% is substituted for each symbol of an element in Formula (1), and
in Formula (B), a tempering temperature in °C is substituted for T, a tempering time in minutes is substituted for t, and a content of Cu in the hollow shell in mass% is substituted for [Cu].

4. The method for producing a martensitic stainless steel seamless pipe according to claim 3, wherein the starting material contains one or more elements selected from a group consisting of:

W: 0.01 to 2.00%,
Nb: 0.01 to 0.50%,
Mg: 0.0001 to 0.0050%,
rare earth metal: 0.0001 to 0.0050%, and
B: 0.0001 to 0.0050%.

FIG.1

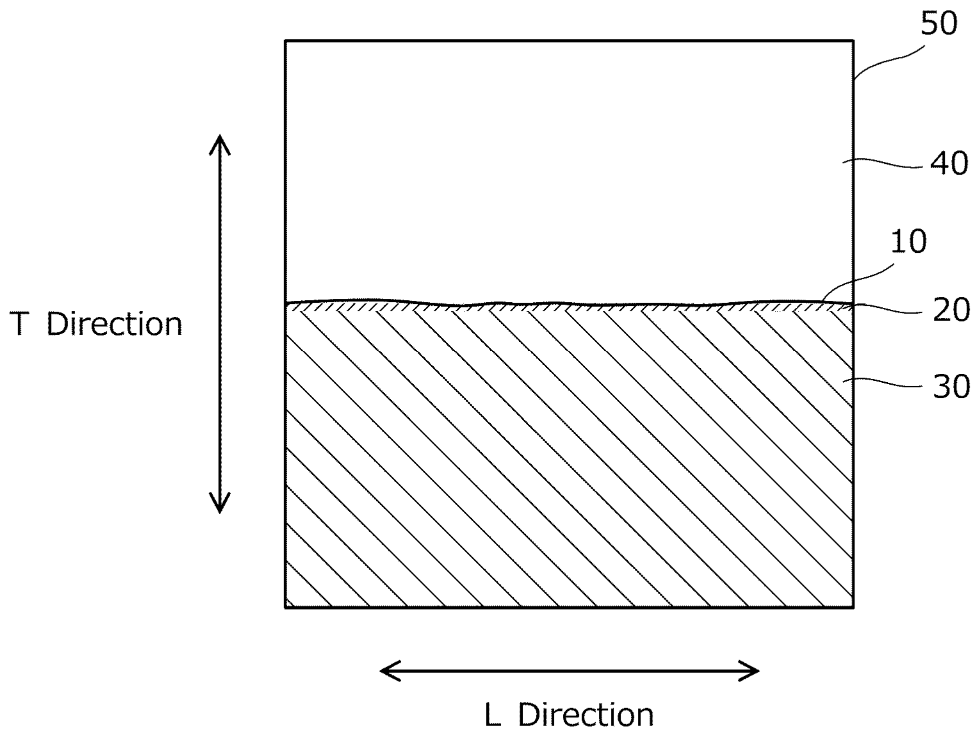

50
40
10
20
30
T Direction
L Direction

FIG.2

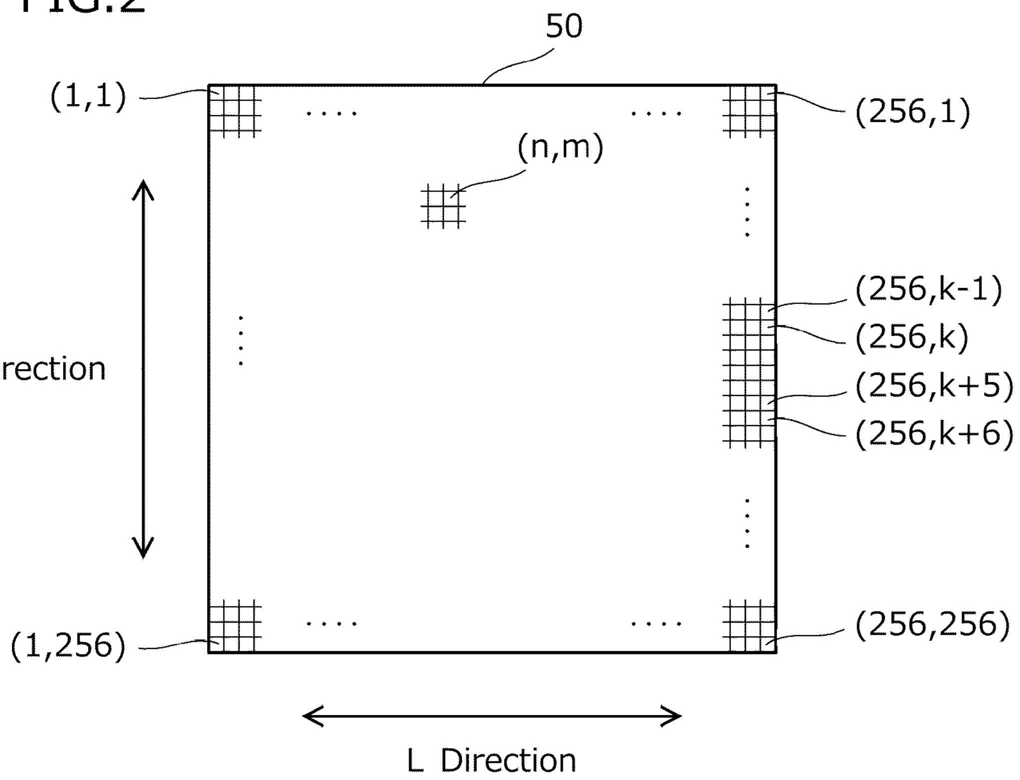
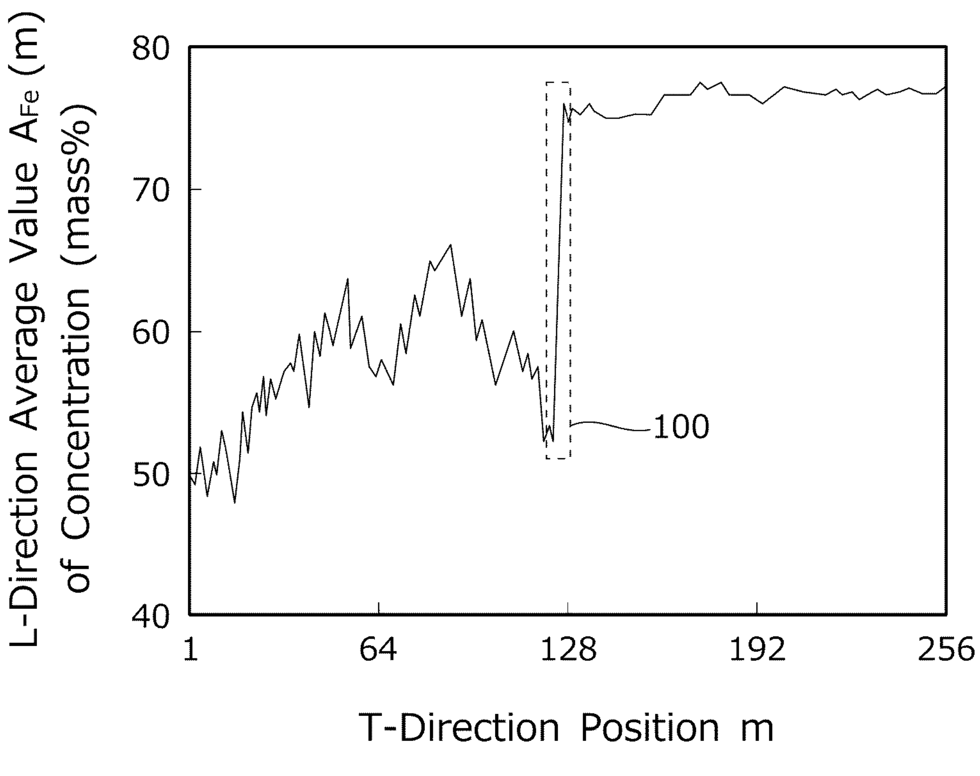

50
(1,1)
(256,1)
(n,m)
(256,k-1)
(256,k)
(256,k+5)
(256,k+6)
T Direction
(1,256)
(256,256)
L Direction

FIG.3


L-Direction Average Value A_{Fe} (m) of Concentration (mass%)
80
70
60
50
40
100
1
64
128
192
256
T-Direction Position m

INTERNATIONAL SEARCH REPORT

International application No. **PCT/JP2022/040601**

A. CLASSIFICATION OF SUBJECT MATTER

C21D 8/10(2006.01)i; ***C22C 38/00***(2006.01)i; ***C22C 38/54***(2006.01)i
FI: C22C38/00 302Z; C22C38/54; C21D8/10 D

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)

C21D8/10; C22C38/00-38/60; B21C37/00-37/30

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 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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	WO 2021/206080 A1 (NIPPON STEEL CORP.) 14 October 2021 (2021-10-14) entire text	1-4
A	WO 2021/210564 A1 (NIPPON STEEL CORP.) 21 October 2021 (2021-10-21) entire text	1-4
A	WO 2020/071344 A1 (NIPPON STEEL CORP.) 09 April 2020 (2020-04-09) entire text	1-4
A	WO 2020/067247 A1 (NIPPON STEEL CORP.) 02 April 2020 (2020-04-02) entire text	1-4
P, A	WO 2022/075406 A1 (NIPPON STEEL CORP.) 14 April 2022 (2022-04-14) entire text	1-4

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

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

Date of the actual completion of the international search	Date of mailing of the international search report
13 December 2022	**27 December 2022**

Name and mailing address of the ISA/JP	Authorized officer
Japan Patent Office (ISA/JP) **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	 Telephone No.

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/040601

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2021/206080 A1	14 October 2021	(Family: none)	
WO 2021/210564 A1	21 October 2021	BR 112022019494 A2 entire text	
WO 2020/071344 A1	09 April 2020	US 2021/0317556 A1 entire text EP 3862451 A1	
WO 2020/067247 A1	02 April 2020	US 2021/0238705 A1 entire text EP 3859031 A1	
WO 2022/075406 A1	14 April 2022	JP 713405 B2 entire text	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2006061881 A **[0005] [0009]**
- WO 2008023702 A **[0005] [0009]**
- WO 2015178022 A **[0005] [0009]**