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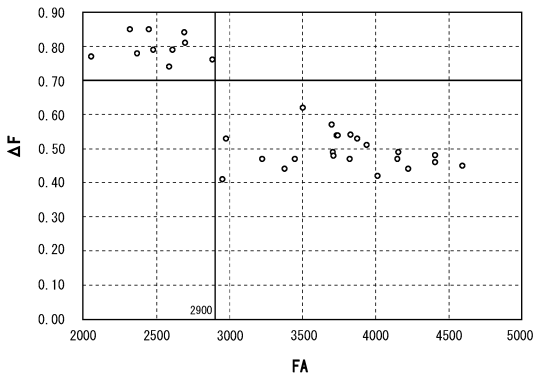
(54) MARTENSITIC STAINLESS STEEL MATERIAL

(57) A martensitic stainless steel material that has high strength and is excellent in SSC resistance is provided. A martensitic stainless steel material according to the present disclosure contains, in mass%, C: 0.030% or less, Ni: 5.00 to 7.00%, Cr: 10.00 to 14.00%, Mo: 1.50 to 3.00%, and Cu: more than 1.00 to 3.50%, and has a yield strength of 758 MPa or more. On two line segments LS of 1000 μm extending in a wall thickness direction with arbitrary two points as a center located at positions at a depth of 2 mm from the inner surface, respectively, a degree of Cr segregation ΔCr defined by Formula (1) described in the description, a degree of Mo segregation ΔMo defined by Formula (2) described in the description, and a degree of Cu segregation ΔCu defined by Formula (3) described in the description satisfy Formula (4):

$$\Delta Cr + \Delta Mo + \Delta Cu \leq A \quad (4)$$

where, when the yield strength is 758 to less than 862 MPa, A in Formula (4) is 0.70, and when the yield strength is 862 MPa or more, A in Formula (4) is 0.50.

FIG. 7A



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Description

TECHNICAL FIELD

[0001] The present disclosure relates to a steel material, and more particularly relates to a martensitic stainless steel material that is a seamless steel pipe or a round steel bar.

BACKGROUND ART

[0002] In oil wells and gas wells (hereunder, oil wells and gas wells are collectively referred to as "oil wells"), a steel material referred to as a downhole member is used that has been processed into a predetermined shape from a seamless steel pipe or a round steel bar. Oil wells are being made deeper in recent years, and consequently there is a demand to enhance the strength of steel materials to be used for oil wells. Specifically, steel materials for oil wells of 80 ksi grade (yield strength is 80 to less than 95 ksi, that is, 552 to less than 655 MPa) and 95 ksi grade (yield strength is 95 to less than 110 ksi, that is, 655 to less than 758 MPa) are being widely utilized. Furthermore, requests have also recently started to be made for steel materials for oil wells of 110 ksi grade (yield strength is 110 to less than 125 ksi, that is, 758 to less than 862 MPa).

[0003] In this connection, most deep wells are in sour environments that contain corrosive hydrogen sulfide. In the present description, the term "sour environment" means an acidified environment containing hydrogen sulfide, or hydrogen sulfide and carbon dioxide. Steel materials to be used in such sour environments are required to have not only the aforementioned high strength, but also to have excellent sulfide stress cracking resistance (hereunder, referred to as "SSC resistance").

[0004] The H_2S partial pressure in a sour environment differs depending on the region. In sour environments (mild sour environments) in which the H_2S partial pressure is 0.03 bar or less, martensitic stainless steel materials containing about 13% by mass of Cr that are typified by an API L80 13Cr steel material (normal 13Cr steel material) and a Super 13Cr steel material in which the content of C is reduced are used. However, in a sour environment (enhanced mild sour environment) in which the H_2S partial pressure is in the range of more than 0.03 to 0.10 bar or less that is higher than in a mild sour environment, SSC resistance that is higher than in the aforementioned normal 13Cr steel material and Super 13Cr steel material is required.

[0005] Steel materials having higher SSC resistance than the aforementioned normal 13Cr steel material and Super 13Cr steel material are proposed in Japanese Patent Application Publication No. 10-001755 (Patent Literature 1), Japanese Translation of PCT International Application Publication No. 10-503809 (Patent Literature 2), and Japanese Patent Application Publication No. 08-246107 (Patent Literature 3).

[0006] A martensitic stainless steel material according to Patent Literature 1 has a chemical composition consisting of, in mass%, C: 0.005 to 0.05%, Si: 0.05 to 0.5%, Mn: 0.1 to 1.0%, P: 0.025% or less, S: 0.015% or less, Cr: 10 to 15%, Ni: 4.0 to 9.0%, Cu: 0.5 to 3%, Mo: 1.0 to 3%, Al: 0.005 to 0.2%, and N: 0.005% to 0.1%, with the balance being Fe and unavoidable impurities, and satisfying $40C + 34N + Ni + 0.3Cu - 1.1Cr - 1.8Mo \geq -10$. The microstructure of the martensitic stainless steel material disclosed in this patent literature consists of a tempered martensite phase, a martensite phase, and a retained austenite phase. A total fraction of the tempered martensite phase and the martensite phase in the microstructure is 60% or more to 80% or less, and the balance is the retained austenite phase.

[0007] A martensitic stainless steel according to Patent Literature 2 consists of, in mass%, C: 0.005 to 0.05%, $Si \leq 0.50\%$, Mn: 0.1 to 1.0%, $P \leq 0.03\%$, $S \leq 0.005\%$, Mo: 1.0 to 3.0%, Cu: 1.0 to 4.0%, Ni: 5 to 8%, and $Al \leq 0.06\%$, with the balance being Fe and impurities. Further, the aforementioned chemical composition satisfies $Cr + 1.6Mo \geq 13$, and $40C + 34N + Ni + 0.3Cu - 1.1Cr - 1.8Mo \geq -10.5$. The microstructure of the martensitic stainless steel of this patent literature is a tempered martensite structure.

[0008] The chemical composition of a martensitic stainless steel according to Patent Literature 3 consists of, in mass%, C: 0.005% to 0.05%, Si: 0.05% to 0.5%, Mn: 0.1% to 1.0%, P: 0.025% or less, S: 0.015% or less, Cr: 12 to 15%, Ni: 4.5% to 9.0%, Cu: 1% to 3%, Mo: 2% to 3%, W: 0.1% to 3%, Al: 0.005 to 0.2%, and N: 0.005% to 0.1%, with the balance being Fe and unavoidable impurities. Further, the aforementioned chemical composition satisfies $40C + 34N + Ni + 0.3Cu + Co - 1.1Cr - 1.8Mo - 0.9W \geq -10$.

CITATION LIST

PATENT LITERATURE

[0009]

Patent Literature 1: Japanese Patent Application Publication No. 10-001755

Patent Literature 2: Japanese Translation of PCT International Application Publication No. 10-503809
Patent Literature 3: Japanese Patent Application Publication No. 08-246107

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0010] In the martensitic stainless steel materials for oil wells proposed in Patent Literature 1 to Patent Literature 3, adequate SSC resistance in a sour environment is obtained by adjusting the contents of the respective elements in the chemical composition based on a parameter formula. However, adequate SSC resistance in a sour environment together with high strength may be obtained by another means that is different from the means proposed in Patent Literature 1 to Patent Literature 3.

[0011] An objective of the present disclosure is to provide a martensitic stainless steel material that has high strength and is excellent in SSC resistance.

SOLUTION TO PROBLEM

[0012] A martensitic stainless steel material according to the present disclosure is as follows.

[0013] A martensitic stainless steel material that is a seamless steel pipe or a round steel bar, having a chemical composition 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,
Ni: 5.00 to 7.00%,
Cr: 10.00 to 14.00%,
Mo: 1.50 to 3.00%,
Al: 0.005 to 0.050%,
V: 0.01 to 0.30%,
N: 0.0030 to 0.0500%,
Ti: 0.020 to 0.150%,
Cu: more than 1.00 to 3.50%,
Co: 0.50% or less,
B: 0 to 0.0050%,
Ca: 0 to 0.0050%,
Mg: 0 to 0.0050%,
rare earth metal (REM): 0 to 0.0050%,
Nb: 0 to 0.15%,
W: 0 to 0.20%, and
the balance: Fe and impurities,
wherein:

a yield strength is 758 MPa or more;
in a case where the martensitic stainless steel material is the seamless steel pipe,
when, in a cross section including a rolling direction and a wall thickness direction of the seamless steel pipe, an arbitrary two points at positions at a depth of 2 mm from an inner surface are defined as two center points P1, and two line segments of 1000 μm extending in the wall thickness direction with each center point P1 as a center are defined as two line segments LS, energy dispersive X-ray spectroscopy is performed at measurement positions at a pitch of 1 μm on each line segment LS, and a Cr concentration, a Mo concentration, and a Cu concentration at each measurement position are determined;
in a case where the martensitic stainless steel material is the round steel bar,
when, in a cross section including a rolling direction and a radial direction of the round steel bar, an arbitrary two points on a central axis of the round steel bar are defined as two center points P1, and two line segments of 1000 μm extending in the radial direction with each center point P1 as a center are defined as two line segments LS, energy dispersive X-ray spectroscopy is performed at measurement positions at a pitch of 1 μm on each line segment LS, and a Cr concentration, a Mo concentration, and a Cu concentration at each meas-

urement position are determined; and
when:

an average value of all of the Cr concentrations determined at all of the measurement positions on the two line segments LS is defined as $[Cr]_{ave}$,
a sample standard deviation of all of the Cr concentrations determined at all of the measurement positions on the two line segments LS is defined as σ_{Cr},
among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ is defined as $[Cr^*]_{ave}$,
among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ is defined as $[Cr^*]_{max}$,
among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ is defined as [Cr*]min,
an average value of all of the Mo concentrations determined at all of the measurement positions on the two line segments LS is defined as $[Mo]_{ave}$,
a sample standard deviation of all of the Mo concentrations determined at all of the measurement positions on the two line segments LS is defined as σ_{Mo},
among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ is defined as $[Mo^*]_{ave}$,
among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ is defined as $[Mo^*]_{max}$,
among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ is defined as $[Mo^*]_{min}$,
an average value of all of the Cu concentrations determined at all of the measurement positions on the two line segments LS is defined as $[Cu]_{ave}$,
a sample standard deviation of all of the Cu concentrations determined at all of the measurement positions on the two line segments LS is defined as σ_{Cu},
among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ is defined as $[Cu^*]_{ave}$,
among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ is defined as [Cu*]max, and
among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ is defined as $[Cu^*]_{min}$,
a degree of Cr segregation ΔCr defined by Formula (1), a degree of Mo segregation ΔMo defined by Formula (2), and a degree of Cu segregation ΔCu defined by Formula (3) satisfy Formula (4):

$$\Delta Cr = ([Cr^*]_{max} - [Cr^*]_{min})/[Cr^*]_{ave} \quad (1)$$

$$\Delta Mo = ([Mo^*]_{max} - [Mo^*]_{min})/[Mo^*]_{ave} \quad (2)$$

$$\Delta Cu = ([Cu^*]_{max} - [Cu^*]_{min})/[Cu^*]_{ave} \quad (3)$$

$$\Delta Cr + \Delta Mo + \Delta Cu \leq A \quad (4)$$

where, in a case where the yield strength is 758 to less than 862 MPa, A in Formula (4) is 0.70, and in a case where the yield strength is 862 MPa or more, A in Formula (4) is 0.50.

ADVANTAGEOUS EFFECTS OF INVENTION

[0014] The martensitic stainless steel material according to the present disclosure has a high strength that is a yield

strength of 110 ksi or more (758 MPa or more), and is excellent in SSC resistance.

BRIEF DESCRIPTION OF DRAWINGS

[0015]

[FIG. 1] FIG. 1 is a cross-sectional diagram along a direction perpendicular to a longitudinal direction of a starting material of a martensitic stainless steel material of a present embodiment.
[FIG. 2] FIG. 2 is a cross-sectional diagram along a direction perpendicular to a rolling direction of a seamless steel pipe.
[FIG. 3] FIG. 3 is a cross-sectional diagram including the rolling direction and a wall thickness direction of the seamless steel pipe.
[FIG. 4] FIG. 4 is an enlarged view of a vicinity of center points P1 in FIG. 3.
[FIG. 5] FIG. 5 is a multiple view drawing including a cross-sectional diagram along a direction perpendicular to a rolling direction of a round steel bar, and a cross-sectional diagram along a direction parallel to the rolling direction of the round steel bar.
[FIG. 6] FIG. 6 is a schematic diagram of a heating furnace that is utilized in a process for producing the martensitic stainless steel material of the present embodiment.
[FIG. 7A] FIG. 7A is a view illustrating a relation between an FA value that is a heating condition and a total degree of segregation ΔF of the martensitic stainless steel material of the present embodiment in a case where a yield strength of the steel material is made 110 ksi grade (758 to less than 862 MPa).
[FIG. 7B] FIG. 7B is a view illustrating a relation between an FA value that is a heating condition and a total degree of segregation ΔF of the martensitic stainless steel material of the present embodiment in a case where the yield strength of the steel material is made 125 ksi or more (862 MPa or more).

DESCRIPTION OF EMBODIMENTS

[0016] The present inventors conducted studies regarding a steel material in which a yield strength of 110 ksi or more (758 MPa or more) and excellent SSC resistance in a sour environment can be compatibly obtained.

[0017] First, the present inventors conducted studies regarding a steel material in which a yield strength of 110 ksi or more and excellent SSC resistance can be compatibly obtained, from the viewpoint of the design of the chemical composition. As a result, the present inventors considered that if a steel material 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, Ni: 5.00 to 7.00%, Cr: 10.00 to 14.00%, Mo: 1.50 to 3.00%, Al: 0.005 to 0.050%, V: 0.01 to 0.30%, N: 0.0030 to 0.0500%, Ti: 0.020 to 0.150%, Cu: more than 1.00 to 3.50%, Co: 0.50% or less, B: 0 to 0.0050%, Ca: 0 to 0.0050%, Mg: 0 to 0.0050%, rare earth metal (REM): 0 to 0.0050%, Nb: 0 to 0.15%, and W: 0 to 0.20%, with the balance being Fe and impurities, there is a possibility that a yield strength of 110 ksi or more and excellent SSC resistance in a sour environment can be compatibly obtained.

[0018] Therefore, the present inventors produced a steel material having the aforementioned chemical composition by a well-known method, and evaluated the yield strength and SSC resistance in a sour environment. As a result, the present inventors found that, simply by adjusting the contents of the elements in the chemical composition, a yield strength of 110 ksi or more and excellent SSC resistance in a sour environment are not necessarily adequately obtained compatibly in some cases. Therefore, the present inventors conducted various studies to investigate the reason why, in some cases, a yield strength of 110 ksi or more and excellent SSC resistance in a sour environment cannot be compatibly obtained in a steel material having the aforementioned chemical composition. As a result, the present inventors obtained the following findings.

[0019] In the chemical composition described above, the SSC resistance of the steel material in a sour environment is improved by making the content of Cr 10.00 to 14.00%, the content of Mo 1.50 to 3.00%, and the content of Cu more than 1.00 to 3.50%, and setting the contents of the other elements to be within the aforementioned ranges. The aforementioned content of Cr forms a strong passivation film. By this means the SSC resistance of the steel material in a sour environment is enhanced. The aforementioned content of Mo forms Mo sulfides on the passivation film, and thereby inhibits contact between the passivation film and hydrogen sulfide ions (HS^-). As a result, the SSC resistance of the steel material in a sour environment is enhanced. The aforementioned content of Cu forms Cu sulfides on the passivation film, and thereby inhibits contact between the passivation film and hydrogen sulfide ions (HS^-). As a result, the SSC resistance of the steel material in a sour environment is enhanced.

[0020] However, Cr, Mo, and Cu are elements that easily segregate. In the aforementioned chemical composition, the content of Cr is 10.00 to 14.00% which is high, the content of Mo is 1.50 to 3.00% which is also high, and the content of Cu is more than 1.00 to 3.50% which is also high. Therefore, there is a possibility that Cr, Mo, and Cu will segregate. If Cr, Mo, and Cu segregate, there is a possibility that the SSC resistance in a sour environment will be low.

[0021] Thus the present inventors investigated the relation between the degree of segregation of Cr, Mo, and Cu and the SSC resistance in a sour environment with respect to a martensitic stainless steel material having the aforementioned chemical composition and having a yield strength of 110 ksi or more.

[0022] First, the present inventors conducted studies regarding locations where segregation is likely to occur in the steel material. FIG. 1 is a cross-sectional diagram (transverse cross-sectional diagram) along a direction perpendicular to a longitudinal direction (rolling direction) of a cylindrical billet (round billet) 100 that is the starting material for a seamless steel pipe. Referring to FIG. 1, it has been found that a segregation region SE is likely to be present at the center part in the transverse cross-section of the billet 100. In the segregation region SE, Cr, Mo, and Cu easily segregate. Therefore, it was more likely for Cr segregation, Mo segregation, and Cu segregation to occur in the segregation region SE than in regions other than the segregation region SE. In addition, when the billet 100 illustrated in FIG. 1 was subjected to piercing-rolling to be made into a martensitic stainless steel material that is a seamless steel pipe, a cross section perpendicular to the rolling direction of the seamless steel pipe was as illustrated in FIG. 2. Specifically, in a transverse cross-section of the seamless steel pipe, a segregation region SE was present that extended in a circumferential direction in a vicinity of an inner surface IS of the seamless steel pipe.

[0023] Based on the results of the studies described above, the present inventors initially considered that, in a martensitic stainless steel material having the aforementioned chemical composition, a yield strength of 110 ksi or more and excellent SSC resistance in a sour environment can be compatibly obtained if differences between a Cr concentration, a Mo concentration and a Cu concentration in the segregation region SE that exists in the vicinity of the inner surface IS of a seamless steel pipe and a Cr concentration, a Mo concentration and a Cu concentration in a region other than the segregation region SE, for example, a vicinity of an outer surface OS in FIG. 2 is made small. That is, the present inventors considered that if segregation within a macroscopic region in the steel material can be suppressed, a yield strength of 110 ksi or more and excellent SSC resistance in a sour environment can be compatibly obtained in a martensitic stainless steel material having the aforementioned chemical composition.

[0024] However, in a martensitic stainless steel material having the aforementioned chemical composition, even when differences between the Cr concentration, the Mo concentration and the Cu concentration in the segregation region SE and the Cr concentration, the Mo concentration and the Cu concentration in regions other than the segregation region SE were kept small, when the yield strength was made 110 ksi or more, in some cases the SSC resistance was still low.

[0025] Therefore, rather than attempting to reduce segregation within a macroscopic region consisting of the segregation region SE and the regions other than the segregation region SE, the present inventors focused their attention on microscopic regions within the segregation region SE, and investigated making the Cr concentration distribution, the Mo concentration distribution, and the Cu concentration distribution within the microscopic regions sufficiently uniform.

[0026] If the Cr concentration distribution, the Mo concentration distribution, and the Cu concentration distribution within microscopic regions can be made sufficiently uniform, the Cr concentration distribution, the Mo concentration distribution, and the Cu concentration distribution of the steel material as a whole will also be sufficiently uniform. As a result, there is a possibility that a yield strength of 110 ksi or more and excellent SSC resistance in a sour environment can be compatibly obtained.

[0027] Therefore, instead of focusing their attention on segregation in the macroscopic region, the present inventors focused on microscopic regions within the segregation region SE and conducted further studies regarding the relation between the SSC resistance of the steel material having a yield strength of 110 ksi or more and the Cr concentration distribution, Mo concentration distribution, and Cu concentration distribution.

[0028] Specifically, referring to FIG. 3, in a case where the martensitic stainless steel material was a seamless steel pipe, in a cross section including a rolling direction L and a wall thickness direction T of the seamless steel pipe, an arbitrary two points at positions at a depth of 2 mm from the inner surface IS were defined as two center points P1. The two center points P1 were positions which corresponded to the segregation region SE illustrated in FIG. 2.

[0029] FIG. 4 is an enlarged view of a vicinity of the two center points P1 in FIG. 3. Referring to FIG. 4, two line segments of 1000 μm extending in the wall thickness direction T that centered on the respective center points P1 were defined as line segments LS. The two line segments LS corresponded to the interior of the segregation region SE, and were microscopic regions. On each line segment LS, point analysis using energy dispersive X-ray spectroscopy (EDS) was performed at measurement positions at a pitch of 1 μm, and the Cr concentration (mass%), Mo concentration (mass%), and Cu concentration (mass%) at each measurement position were determined. In the point analysis, the accelerating voltage was set to 20 kV.

[0030] The following items were defined based on the determined Cr concentrations.

(A) An average value of all of the Cr concentrations determined at all of the measurement positions on the two line segments LS was defined as $[Cr]_{ave}$.

(B) A sample standard deviation of all of the Cr concentrations determined at all of the measurement positions on the two line segments LS was defined as σ_{Cr}.

(C) Based on the so-called three sigma rule, among all of the Cr concentrations determined at all of the measurement

positions on the two line segments LS, an average value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ was defined as $[Cr^*]_{ave}$.

(D) Among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ was defined as $[Cr^*]_{max}$.

(E) Among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ was defined as $[Cr^*]_{min}$.

Similarly, the following items were defined based on the determined Mo concentrations.

(F) An average value of all of the Mo concentrations determined at all of the measurement positions on the two line segments LS was defined as $[Mo]_{ave}$.

(G) A sample standard deviation of all of the Mo concentrations determined at all of the measurement positions on the two line segments LS was defined as σ_{Mo}.

(H) Based on the three sigma rule, among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ was defined as $[Mo^*]_{ave}$.

(I) Among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ was defined as $[Mo^*]_{max}$.

(J) Among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ was defined as $[Mo^*]_{min}$.

Similarly, the following items were defined based on the determined Cu concentrations.

(K) An average value of all of the Cu concentrations determined at all of the measurement positions on the two line segments LS was defined as $[Cu]_{ave}$.

(L) A sample standard deviation of all of the Cu concentrations determined at all of the measurement positions on the two line segments LS was defined as σ_{Cu}.

(M) Based on the three sigma rule, among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ was defined as $[Cu^*]_{ave}$.

(N) Among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ was defined as $[Cu^*]_{max}$.

(O) Among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ was defined as $[Cu^*]_{min}$.

[0031] Based on the items determined in the above (A) to (O), a degree of Cr segregation ΔCr defined by Formula (1) was determined, a degree of Mo segregation ΔMo defined by Formula (2) was determined, and a degree of Cu segregation ΔCu defined by Formula (3) was determined.

$$\Delta Cr = ([Cr^*]_{max} - [Cr^*]_{min})/[Cr^*]_{ave} \quad (1)$$

$$\Delta Mo = ([Mo^*]_{max} - [Mo^*]_{min})/[Mo^*]_{ave} \quad (2)$$

$$\Delta Cu = ([Cu^*]_{max} - [Cu^*]_{min})/[Cu^*]_{ave} \quad (3)$$

[0032] The degree of Cr segregation ΔCr defined by Formula (1) means the degree of Cr segregation within microscopic regions in the segregation region SE. The degree of Mo segregation ΔMo defined by Formula (2) means the degree of Mo segregation within microscopic regions in the segregation region SE. The degree of Cu segregation ΔCu defined by Formula (3) means the degree of Cu segregation within microscopic regions in the segregation region SE.

[0033] The present inventors considered that if the degree of Cr segregation ΔCr, the degree of Mo segregation ΔMo, and the degree of Cu segregation ΔCu in these microscopic regions can be reduced, the Cr concentration distribution, the Mo concentration distribution, and the Cu concentration distribution in the steel material as a whole will be close to being sufficiently uniform. Further, the present inventors considered that if the total value of the degree of Cr segregation ΔCr, the degree of Mo segregation ΔMo, and the degree of Cu segregation ΔCu is kept sufficiently low, excellent SSC resistance in a sour environment will be obtained even when the steel material has a yield strength of 110 ksi or more.

[0034] Based on the technical idea described above, on the premise that the steel material has the aforementioned chemical composition, the present inventors investigated the relation between the SSC resistance and the total value of the degree of Cr segregation ΔCr, the degree of Mo segregation ΔMo, and the degree of Cu segregation ΔCu in microscopic regions within the segregation region SE in the steel material. As a result, the present inventors discovered

that in a martensitic stainless steel material having the aforementioned chemical composition, in a case where the degree of Cr segregation ΔCr defined by Formula (1), the degree of Mo segregation ΔMo defined by Formula (2), and the degree of Cu segregation ΔCu defined by Formula (3) satisfy Formula (4), a yield strength of 110 ksi grade and excellent SSC resistance in a sour environment can be compatibly obtained.

$$\Delta Cr + \Delta Mo + \Delta Cu \leq A \qquad (4)$$

[0035] Here, in a case where the yield strength is 758 to less than 862 MPa, A in Formula (4) is 0.70, and in a case where the yield strength is 862 MPa or more, A in Formula (4) is 0.50.

[0036] The martensitic stainless steel material according to the present disclosure was completed based on the technical idea described above, and is as follows.

[1] A martensitic stainless steel material that is a seamless steel pipe or a round steel bar, having a chemical composition 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,
Ni: 5.00 to 7.00%,
Cr: 10.00 to 14.00%,
Mo: 1.50 to 3.00%,
Al: 0.005 to 0.050%,
V: 0.01 to 0.30%,
N: 0.0030 to 0.0500%,
Ti: 0.020 to 0.150%,
Cu: more than 1.00 to 3.50%,
Co: 0.50% or less,
B: 0 to 0.0050%,
Ca: 0 to 0.0050%,
Mg: 0 to 0.0050%,
rare earth metal (REM): 0 to 0.0050%,
Nb: 0 to 0.15%,
W: 0 to 0.20%, and
the balance: Fe and impurities,
wherein:

a yield strength is 758 MPa or more;
in a case where the martensitic stainless steel material is the seamless steel pipe,
when, in a cross section including a rolling direction and a wall thickness direction of the seamless steel pipe, an arbitrary two points at positions at a depth of 2 mm from an inner surface are defined as two center points P1, and two line segments of 1000 μm extending in the wall thickness direction with each center point P1 as a center are defined as two line segments LS, energy dispersive X-ray spectroscopy is performed at measurement positions at a pitch of 1 μm on each line segment LS, and a Cr concentration, a Mo concentration, and a Cu concentration at each measurement position are determined;
in a case where the martensitic stainless steel material is the round steel bar, when, in a cross section including a rolling direction and a radial direction of the round steel bar, an arbitrary two points on a central axis of the round steel bar are defined as two center points P1, and two line segments of 1000 μm extending in the radial direction with each center point P1 as a center are defined as two line segments LS, energy dispersive X-ray spectroscopy is performed at measurement positions at a pitch of 1 μm on each line segment LS, and a Cr concentration, a Mo concentration, and a Cu concentration at each measurement position are determined; and
when:

an average value of all of the Cr concentrations determined at all of the measurement positions on the two line segments LS is defined as $[Cr]_{ave}$,

a sample standard deviation of all of the Cr concentrations determined at all of the measurement positions on the two line segments LS is defined as σ_{Cr},
among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ is defined as $[Cr^*]_{ave}$,
among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ is defined as $[Cr^*]_{max}$,
among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ is defined as $[Cr^*]_{min}$,
an average value of all of the Mo concentrations determined at all of the measurement positions on the two line segments LS is defined as $[Mo]_{ave}$,
a sample standard deviation of all of the Mo concentrations determined at all of the measurement positions on the two line segments LS is defined as σ_{Mo},
among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ is defined as $[Mo^*]_{ave}$,
among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ is defined as $[Mo^*]_{max}$,
among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ is defined as $[Mo^*]_{min}$,
an average value of all of the Cu concentrations determined at all of the measurement positions on the two line segments LS is defined as $[Cu]_{ave}$,
a sample standard deviation of all of the Cu concentrations determined at all of the measurement positions on the two line segments LS is defined as σ_{Cu},
among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ is defined as $[Cu^*]_{ave}$,
among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ is defined as $[Cu^*]_{max}$, and
among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ is defined as $[Cu^*]_{min}$,
a degree of Cr segregation ΔCr defined by Formula (1), a degree of Mo segregation ΔMo defined by Formula (2), and a degree of Cu segregation ΔCu defined by Formula (3) satisfy Formula (4):

$$\Delta Cr = ([Cr^*]_{max} - [Cr^*]_{min})/[Cr^*]_{ave} \quad (1)$$

$$\Delta Mo = ([Mo^*]_{max} - [Mo^*]_{min})/[Mo^*]_{ave} \quad (2)$$

$$\Delta Cu = ([Cu^*]_{max} - [Cu^*]_{min})/[Cu^*]_{ave} \quad (3)$$

$$\Delta Cr + \Delta Mo + \Delta Cu \leq A \quad (4)$$

where, in a case where the yield strength is 758 to less than 862 MPa, A in Formula (4) is 0.70, and in a case where the yield strength is 862 MPa or more, A in Formula (4) is 0.50.

Here, the term "round steel bar" means a steel bar in which a cross section perpendicular to a longitudinal direction is a circular shape.

[2] The martensitic stainless steel material according to [1], wherein the chemical composition contains one or more elements selected from the group consisting of:

B: 0.0001 to 0.0050%,
Ca: 0.0001 to 0.0050%,
Mg: 0.0001 to 0.0050%,
rare earth metal (REM): 0.0001 to 0.0050%,
Nb: 0.01 to 0.15%, and
W: 0.01 to 0.20%.

[0037] Hereunder, the martensitic stainless steel material of the present embodiment is described in detail. The symbol "%" in relation to an element means mass% unless otherwise stated.

[Chemical composition]

[0038] The chemical composition of the martensitic stainless steel material of the present embodiment contains the following elements.

C: 0.030% or less

[0039] Carbon (C) is unavoidably contained. That is, the content of C is more than 0%. C increases hardenability of the steel material and thus increases the strength of the steel material. However, if the content of C is more than 0.030%, C will easily 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, the SSC resistance of the steel material will be likely to decrease.

[0040] Accordingly, 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%.

Si: 1.00% or less

[0041] Silicon (Si) is unavoidably contained. That is, the content of Si is more than 0%. Si deoxidizes steel. However, if the content of Si is more than 1.00%, the hot workability of the steel material will decrease even if the contents of other elements are within the range of the present embodiment.

[0042] Accordingly, 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

[0043] Manganese (Mn) is unavoidably contained. That is, the content of Mn is more than 0%. Mn increases hardenability of steel material and thus increases the strength of the steel material. However, if the content of Mn is more than 1.00%, even if the contents of other elements are within the range of the present embodiment, Mn will form coarse inclusions and cause toughness of the steel material to decrease.

[0044] Accordingly, 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

[0045] Phosphorus (P) is an impurity that is unavoidably contained. That is, the content of P is more than 0%. If the content of P is more than 0.030%, even if the contents of other elements are within the range of the present embodiment, P will segregate at grain boundaries and cause toughness of the steel material to markedly decrease.

[0046] Accordingly, 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 0.001%, more preferably is 0.002%, and further preferably is 0.005%.

S: 0.0050% or less

[0047] Sulfur (S) is an impurity that is unavoidably contained. That is, the content of S is more than 0%. If the content of S is more than 0.0050%, S will excessively segregate at grain boundaries, and an excessively large amount of MnS that is an inclusion will form. In such a case, toughness and hot workability of the steel material will markedly decrease even if the contents of other elements are within the range of the present embodiment.

[0048] Accordingly, the content of S is to be 0.0050% or less. A preferable upper limit of the content of S is 0.0030%, more preferably is 0.0020%, and further preferably is 0.0015%. 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 0.0004%.

Ni: 5.00 to 7.00%

[0049] Nickel (Ni) forms sulfides on a passivation film in a sour environment. The Ni sulfides inhibit chloride ions (Cl^-) and hydrogen sulfide ions (HS^-) from coming into contact with the passivation film. Consequently, it is difficult for the passivation film to be destroyed by chloride ions and hydrogen sulfide ions. As a result, Ni increases the SSC resistance of the steel material in a sour environment. Ni is also an austenite-forming element. Therefore, Ni causes the microstructure of the steel material after quenching to become martensitic. If the content of Ni is less than 5.00%, even if the contents of other elements are within the range of the present embodiment, the aforementioned effects will not be sufficiently obtained. On the other hand, if the content of Ni is more than 7.00%, the aforementioned effects will be saturated and the production cost will increase.

[0050] Accordingly, the content of Ni is to be 5.00 to 7.00%. 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 6.50%, more preferably is 6.40%, further preferably is 6.30%, and further preferably is 6.20%.

Cr: 10.00 to 14.00%

[0051] Chromium (Cr) forms a passivation film on the surface of the steel material in a sour environment, and thereby improves the SSC resistance of the steel material.

[0052] If the content of Cr is less than 10.00%, the aforementioned 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 more than 14.00%, Cr carbides, intermetallic compounds containing Cr, and Cr oxides will excessively form. In such a case the SSC resistance of the steel material will decrease even if the contents of other elements are within the range of the present embodiment.

[0053] Accordingly, the content of Cr is to be 10.00 to 14.00%. A preferable lower limit of the content of Cr is 10.05%, more preferably is 10.10%, further preferably is 10.50%, and further preferably is 11.00%. 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%.

Mo: 1.50 to 3.00%

[0054] Molybdenum (Mo) forms sulfides on a passivation film in a sour environment. The Mo sulfides inhibit chloride ions (Cl^-) and hydrogen sulfide ions (HS^-) from coming into contact with the passivation film. Consequently, it is difficult for the passivation film to be destroyed by chloride ions and hydrogen sulfide ions. As a result, Mo increases the SSC resistance of the steel material in a sour environment. If the content of Mo is less than 1.50%, this 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 more than 3.00%, the aforementioned effect will be saturated and the production cost will increase.

[0055] Accordingly, the content of Mo is to be 1.50 to 3.00%. A preferable lower limit of the content of Mo is 1.70%, more preferably is 1.80%, further preferably is 1.90%, and further preferably is 2.00%. A preferable upper limit of the content of Mo is 2.95%, more preferably is 2.90%, further preferably is 2.85%, and further preferably is 2.80%.

Al: 0.005 to 0.050%

[0056] Aluminum (Al) deoxidizes steel. If the content of Al is less than 0.005%, the aforementioned 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 more than 0.050%, even if the contents of other elements are within the range of the present embodiment, coarse Al oxides will form and the toughness of the steel material will decrease.

[0057] Accordingly, the content of Al is to be 0.005 to 0.050%. A preferable lower limit of the content of Al is 0.007%, more preferably is 0.010%, and further preferably is 0.015%. A preferable upper limit of the content of Al is 0.047%, more preferably is 0.043%, and further preferably is 0.040%. In the present description, the term "content of Al" means the content of sol. Al (acid-soluble Al).

V: 0.01 to 0.30%

[0058] Vanadium (V) forms V precipitates such as carbides, nitrides, and carbo-nitrides in the steel material. The V precipitates increase the strength of the steel material. If the content of V is less than 0.01%, the aforementioned 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 more than 0.30%, V precipitates will excessively form and the strength of the steel material will become excessively high. In such a case, the SSC resistance of the steel material will decrease even if the contents of other elements are within the range of the present embodiment.

[0059] Accordingly, the content of V is to be 0.01 to 0.30%. 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 0.25%, more preferably is 0.20%, further preferably is 0.15%, further preferably is 0.10%, and further preferably is 0.08%.

N: 0.0030 to 0.0500%

[0060] Nitrogen (N) improves pitting resistance of the steel material and increases the SSC resistance of the steel material. If the content of N is less than 0.0030%, the aforementioned 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 more than 0.0500%, coarse TiN will form. In such a case, the SSC resistance of the steel material will decrease even if the contents of other elements are within the range of the present embodiment.

[0061] Accordingly, the content of N is to be 0.0030 to 0.0500%. A preferable lower limit of the content of N is 0.0033%, more preferably is 0.0035%, and further preferably is 0.0038%. A preferable upper limit of the content of N is 0.0400%, more preferably is 0.0300%, further preferably is 0.0200%, further preferably is 0.0100%, further preferably is 0.0080%, and further preferably is 0.0070%.

Ti: 0.020 to 0.150%

[0062] Titanium (Ti) combines with C or N to form Ti precipitates that are carbides or nitrides. The Ti precipitates suppress coarsening of grains by the pinning effect. As a result, the strength of the steel material increases. In addition, an excessive increase in strength due to excessive formation of V precipitates is suppressed by formation of the Ti precipitates. As a result, the SSC resistance of the steel material increases. Here, the term "V precipitates" refers to carbides, nitrides, carbo-nitrides and the like. If the content of Ti is less than 0.020%, the aforementioned 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 more than 0.150%, the aforementioned effects will be saturated. Furthermore, if the content of Ti is more than 0.150%, Ti carbides or Ti nitrides will excessively form, and toughness of the steel material will decrease.

[0063] Accordingly, the content of Ti is to be 0.020 to 0.150%. A preferable lower limit of the content of Ti is 0.030%, more preferably is 0.040%, and further preferably is 0.050%. A preferable upper limit of the content of Ti is 0.140%, and more preferably is 0.130%.

Cu: more than 1.00 to 3.50%

[0064] Copper (Cu) forms sulfides on a passivation film in a sour environment. The Cu sulfides inhibit chloride ions (Cl^-) and hydrogen sulfide ions (HS^-) from coming into contact with the passivation film. Consequently, it is difficult for the passivation film to be destroyed by chloride ions and hydrogen sulfide ions. As a result, Cu increases the SSC resistance of the steel material in a sour environment. If the content of Cu is less than 1.00%, this 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 Cu is more than 3.50%, hot workability of the steel material will decrease even if the contents of other elements are within the range of the present embodiment.

[0065] Accordingly, the content of Cu is to be more than 1.00 to 3.50%. A preferable lower limit of the content of Cu is 1.40%, more preferably is 1.50%, further preferably is 1.60%, further preferably is 1.70%, and further preferably is 1.80%. A preferable upper limit of the content of Cu is 3.30%, more preferably is 3.10%, and further preferably is 3.00%.

Co: 0.50% or less

[0066] Cobalt (Co) is unavoidably contained. That is, the content of Co is more than 0%. In a sour environment, Co forms sulfides on a passivation film. The Co sulfides inhibit chloride ions (Cl^-) and hydrogen sulfide ions (HS^-) from coming into contact with the passivation film. Consequently, it is difficult for the passivation film to be destroyed by chloride ions and hydrogen sulfide ions. As a result, Co increases the SSC resistance of the steel material. Co also suppresses the formation of retained austenite, and suppresses the occurrence of variations in the strength of the steel material. However, if the content of Co is more than 0.50%, toughness of the steel material will decrease even if the contents of other elements are within the range of the present embodiment.

[0067] Accordingly, the content of Co is to be 0.50% or less. A preferable lower limit of the content of Co is 0.01%, more preferably is 0.05%, further preferably is 0.10%, and further preferably is 0.15%. A preferable upper limit of the content of Co is 0.45%, more preferably is 0.40%, further preferably is 0.35%, and further preferably is 0.30%.

[0068] The balance of the chemical composition of the martensitic stainless steel material according to the present embodiment is Fe and impurities. Here, the term "impurities" refers to elements which, during industrial production of the martensitic stainless steel material, are mixed in from ore or scrap that is used as the raw material, or from the production environment or the like, and which are not intentionally contained but are allowed within a range that does not adversely influence the advantageous effects of the martensitic stainless steel material of the present embodiment.

[Regarding optional elements]

[0069] The chemical composition of the martensitic stainless steel material according to the present embodiment may further contain, in lieu of a part of Fe, one or more optional elements selected from the following group.

B: 0 to 0.0050%
Ca: 0 to 0.0050%
Mg: 0 to 0.0050%
Rare earth metal (REM): 0 to 0.0050%
Nb: 0 to 0.15%
W: 0 to 0.20%

[0070] Hereunder, these optional elements are described.

[First group: B, Ca, Mg, and rare earth metal (REM)]

[0071] The chemical composition of the martensitic stainless steel material according to the present embodiment may further contain one or more elements selected from the group consisting of B, Ca, Mg, and rare earth metal (REM) in lieu of a part of Fe. These elements are optional elements, and each of these elements increases the hot workability of the steel material.

B: 0 to 0.0050%

[0072] Boron (B) is an optional element, and need not be contained. That is, the content of B may be 0%. When contained, B segregates at austenite grain boundaries and strengthens the grain boundaries. As a result, hot workability of the steel material is increased. If even a small amount of B is contained, the aforementioned effect will be obtained to a certain extent. However, if the content of B is more than 0.0050%, Cr carbo-borides will form even if the contents of other elements are within the range of the present embodiment. In such a case, toughness of the steel material will decrease.

[0073] Accordingly, 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 0.0040%, more preferably is 0.0030%, further preferably is 0.0020%, further preferably is 0.0010%, further preferably is 0.0008%, and further preferably is 0.0007%.

Ca: 0 to 0.0050%

[0074] Calcium (Ca) is an optional element, and need not be contained. That is, the content of Ca may be 0%. When contained, Ca spheroidizes and/or refines inclusions, and thereby increases hot workability of the steel material. If even a small amount of Ca is contained, this effect will be obtained to a certain extent. However, if the content of Ca is more than 0.0050%, coarse oxides will form. In such a case, toughness of the steel material will decrease even if the contents of other elements are within the range of the present embodiment.

[0075] Accordingly, the content of Ca is to be 0 to 0.0050%. A preferable lower limit of the content of Ca is 0.0001%, more preferably is 0.0005%, further preferably is 0.0010%, and further preferably is 0.0015%. A preferable upper limit of the content of Ca is 0.0045%, more preferably is 0.0040%, and further preferably is 0.0035%.

Mg: 0 to 0.0050%

[0076] Magnesium (Mg) is an optional element, and need not be contained. That is, the content of Mg may be 0%. When contained, similarly to Ca, Mg spheroidizes and/or refines inclusions, and thereby increases hot workability of the steel material. If even a small amount of Mg is contained, the aforementioned effect will be obtained to a certain extent. However, if the content of Mg is more than 0.0050%, coarse oxides will form. In such a case, toughness of the steel material will decrease even if the contents of other elements are within the range of the present embodiment.

[0077] Accordingly, 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 0.0035%, and further preferably is 0.0025%.

Rare earth metal (REM): 0 to 0.0050%

[0078] Rare earth metal (REM) is an optional element, and need not be contained. That is, the content of REM may be 0%. When contained, similarly to Ca, REM spheroidizes and/or refines inclusions, and thereby increases hot workability of the steel material. If even a small amount of REM is contained, the aforementioned effect will be obtained to a certain extent. However, if the content of REM is more than 0.0050%, coarse oxides will form. In such a case, toughness of the steel material will decrease even if the contents of other elements are within the range of the present embodiment.

[0079] Accordingly, 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 0.0035%, and further preferably is 0.0025%.

[0080] Note that, in the present description the term "REM" means one or more elements 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.

[Second group: Nb and W]

[0081] The chemical composition of the martensitic stainless steel material according to the present embodiment may further contain one or more elements selected from the group consisting of Nb and W in lieu of a part of Fe. These elements are optional elements, and each of these elements increases the SSC resistance of the steel material.

Nb: 0 to 0.15%

[0082] Niobium (Nb) is an optional element, and need not be contained. That is, the content of Nb may be 0%. When contained, Nb forms Nb precipitates that are fine carbides, nitrides, or carbo-nitrides. The Nb precipitates refine the substructure of the steel material by the pinning effect. As a result, the SSC resistance of the steel material increases. If even a small amount of Nb is contained, the aforementioned effect will be obtained to a certain extent. However, if the content of Nb is more than 0.15%, Nb precipitates will excessively form. In such a case, the SSC resistance of the steel material will decrease even if the contents of other elements are within the range of the present embodiment.

[0083] Accordingly, the content of Nb is to be 0 to 0.15%. 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 0.14%, more preferably is 0.13%, and further preferably is 0.10%.

W: 0 to 0.20%

[0084] Tungsten (W) is an optional element, and need not be contained. That is, the content of W may be 0%. When contained, W stabilizes the passivation film in a sour environment. Consequently, it is difficult for the passivation film to be destroyed by chloride ions and hydrogen sulfide ions. As a result, the SSC resistance of the steel material increases. If even a small amount of W is contained, the aforementioned effect will be obtained to a certain extent. However, if the content of W is more than 0.20%, W will combine with C, and coarse W carbides will be formed. In such a case, toughness of the steel material will decrease even if the contents of other elements are within the range of the present embodiment.

[0085] Accordingly, the content of W is to be 0 to 0.20%. 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 0.18%, and more

preferably is 0.16%.

[Regarding Cr concentration distribution, Mo concentration distribution, and Cu concentration distribution in steel material]

[0086] In the martensitic stainless steel material of the present embodiment, in addition, a degree of Cr segregation ΔCr defined by Formula (1), a degree of Mo segregation ΔMo defined by Formula (2), and a degree of Cu segregation ΔCu defined by Formula (3) satisfy Formula (4):

$$\Delta Cr = ([Cr^*]_{max} - [Cr^*]_{min})/[Cr^*]_{ave} \quad (1)$$

$$\Delta Mo = ([Mo^*]_{max} - [Mo^*]_{min})/[Mo^*]_{ave} \quad (2)$$

$$\Delta Cu = ([Cu^*]_{max} - [Cu^*]_{min})/[Cu^*]_{ave} \quad (3)$$

$$\Delta Cr + \Delta Mo + \Delta Cu \leq A \quad (4)$$

where, in a case where the yield strength is 758 to less than 862 MPa, A in Formula (4) is 0.70, and in a case where the yield strength is 862 MPa or more, A in Formula (4) is 0.50.

[0087] The degree of Cr segregation ΔCr defined by Formula (1), the degree of Mo segregation ΔMo defined by Formula (2), and the degree of Cu segregation ΔCu defined by Formula (3) are determined by the following method.

[Method for measuring degree of Cr segregation ΔCr, degree of Mo segregation ΔMo, and degree of Cu segregation ΔCu]

[0088] Referring to FIG. 3, in a case where the martensitic stainless steel material is a seamless steel pipe, in a cross section including a rolling direction L and a wall thickness direction T of the seamless steel pipe, an arbitrary two points at positions at a depth of 2 mm from an inner surface IS are defined as two center points P1. Referring to FIG. 4, two line segments of 1000 μm extending in the wall thickness direction T with each center point P1 as a center are defined as two line segments LS. On each line segment LS, point analysis using energy dispersive X-ray spectroscopy (EDS) is performed at measurement positions at a pitch of 1 μm, and the Cr concentration (mass%), the Mo concentration (mass%), and the Cu concentration (mass%) at each measurement position are determined. In the point analysis, the accelerating voltage is set to 20 kV.

[0089] Similarly, in a case where the martensitic stainless steel material is a round steel bar, referring to FIG. 5, in a cross section including a rolling direction L and a radial direction D of the round steel bar, an arbitrary two points on a central axis C1 of the round steel bar are defined as two center points P1. Two line segments of 1000 μm extending in the radial direction D with each center point P1 as a center are defined as two line segments LS. On each line segment LS, point analysis using EDS is performed at measurement positions at a pitch of 1 μm, and the Cr concentration (mass%), the Mo concentration (mass%), and the Cu concentration (mass%) at each measurement position are determined. In the point analysis, the accelerating voltage is set to 20 kV.

[0090] The following items are defined based on the determined Cr concentrations.

(A) An average value of all of the Cr concentrations determined at all of the measurement positions on the two line segments LS is defined as $[Cr]_{ave}$.

(B) A sample standard deviation of all of the Cr concentrations determined at all of the measurement positions on the two line segments LS is defined as σ_{Cr}.

(C) Based on the so-called three sigma rule, among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ is defined as $[Cr^*]_{ave}$.

(D) Among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ is defined as $[Cr^*]_{max}$.

(E) Among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ is defined as $[Cr^*]_{min}$.

Similarly, the following items are defined based on the determined Mo concentrations.

(F) An average value of all of the Mo concentrations determined at all of the measurement positions on the two line segments LS is defined as $[Mo]_{ave}$.

(G) A sample standard deviation of all of the Mo concentrations determined at all of the measurement positions on the two line segments LS is defined as σ_{Mo}.

(H) Based on the three sigma rule, among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ is defined as $[Mo^*]_{ave}$.

(I) Among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ is defined as $[Mo^*]_{max}$.

(J) Among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ is defined as $[Mo^*]_{min}$.

Similarly, the following items are defined based on the determined Cu concentrations.

(K) An average value of all of the Cu concentrations determined at all of the measurement positions on the two line segments LS is defined as $[Cu]_{ave}$.

(L) A sample standard deviation of all of the Cu concentrations determined at all of the measurement positions on the two line segments LS is defined as σ_{Cu}.

(M) Based on the three sigma rule, among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ is defined as $[Cu^*]_{ave}$.

(N) Among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ is defined as $[Cu^*]_{max}$.

(O) Among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ is defined as $[Cu^*]_{min}$.

[0091] Based on the items determined in the above (A) to (O), the degree of Cr segregation ΔCr defined by Formula (1) is determined, the degree of Mo segregation ΔMo defined by Formula (2) is determined, and the degree of Cu segregation ΔCu defined by Formula (3) is determined.

$$\Delta Cr = ([Cr^*]_{max} - [Cr^*]_{min})/[Cr^*]_{ave} \quad (1)$$

$$\Delta Mo = ([Mo^*]_{max} - [Mo^*]_{min})/[Mo^*]_{ave} \quad (2)$$

$$\Delta Cu = ([Cu^*]_{max} - [Cu^*]_{min})/[Cu^*]_{ave} \quad (3)$$

[0092] In the martensitic stainless steel material of the present embodiment, the degree of Cr segregation ΔCr defined by Formula (1), the degree of Mo segregation ΔMo defined by Formula (2), and the degree of Cu segregation ΔCu defined by Formula (3) satisfy Formula (4):

$$\Delta Cr + \Delta Mo + \Delta Cu \leq A \quad (4)$$

where, in a case where the yield strength is 758 to less than 862 MPa, A in Formula (4) is 0.70, and in a case where the yield strength is 862 MPa or more, A in Formula (4) is 0.50.

[0093] Let a total degree of segregation ΔF be defined as $\Delta F = \Delta Cr + \Delta Mo + \Delta Cu$. Each line segment LS that is a measurement region for measuring the Cr concentration, the Mo concentration, and the Cu concentration, in other words, each line segment LS which extends in the wall thickness direction T or the radial direction D and has the center point P1 as its center is a region where Cr, Mo, and Cu segregate the most in the steel material. The line segments LS are microscopic regions in the steel material.

[0094] Here, a case in which the yield strength of the steel material of the present embodiment is 110 ksi grade (758 to less than 862 MPa) will be assumed. In this case, if the total degree of segregation ΔF that is the total sum of the degree of Cr segregation ΔCr, the degree of Mo segregation ΔMo, and the degree of Cu segregation ΔCu on the line segments LS is 0.70 or less, segregation of the Cr concentration, the Mo concentration, and the Cu concentration is sufficiently suppressed even in the microscopic regions in which the Cr concentration, the Mo concentration, and the Cu concentration are segregated the most. This means that in the entire steel material also, in other words, the macroscopic region of the steel material, the Cr concentration, the Mo concentration, and the Cu concentration are each distributed in a sufficiently uniform manner.

[0095] Similarly, a case in which the yield strength of the steel material of the present embodiment is 125 ksi or more

(862 MPa or more) will be assumed. In this case, if the total degree of segregation ΔF that is the total sum of the degree of Cr segregation ΔCr, the degree of Mo segregation ΔMo, and the degree of Cu segregation ΔCu on the line segments LS is 0.50 or less, segregation of the Cr concentration, the Mo concentration, and the Cu concentration is sufficiently suppressed even in the microscopic regions in which the Cr concentration, the Mo concentration, and the Cu concentration are segregated the most. This means that in the entire steel material also, in other words, the macroscopic region of the steel material, the Cr concentration, the Mo concentration, and the Cu concentration are each distributed in a sufficiently uniform manner.

[0096] Accordingly, the total degree of segregation ΔF is to be 0.70 or less in a case where the yield strength of the steel material is 110 ksi grade, and is to be 0.50 or less in a case where the yield strength of the steel material is 125 ksi or more.

[0097] By being composed as described above, the martensitic stainless steel material of the present embodiment can obtain excellent SSC resistance in a sour environment while also having a yield strength of 110 ksi or more.

[0098] When the yield strength of the steel material is 110 ksi grade (758 to less than 862 MPa), a preferable upper limit of ΔF is 0.65, more preferably is 0.63, further preferably is 0.61, further preferably is 0.59, further preferably is 0.57, and further preferably is 0.55.

[0099] When the yield strength of the steel material is 125 ksi or more (862 MPa or more), a preferable upper limit of ΔF is 0.49, more preferably is 0.48, and further preferably is 0.47.

[Microstructure]

[0100] The microstructure of the martensitic stainless steel material according to the present embodiment is mainly composed of martensite. In the present description, the term "martensite" includes not only fresh martensite but also tempered martensite. Moreover, in the present description, the phrase "mainly composed of martensite" means that the volume ratio of martensite is 80.0% or more in the microstructure.

[0101] In the microstructure of the martensitic stainless steel material according to the present embodiment, a preferable lower limit of the volume ratio of martensite is 85.0%, and more preferably is 90.0%. Further preferably, the microstructure of the steel material is composed of single-phase martensite.

[0102] The balance of the microstructure is retained austenite. That is, the volume ratio of retained austenite is 0 to 20.0% in the martensitic stainless steel material of the present embodiment. The volume ratio of retained austenite is preferably as low as possible.

[0103] On the other hand, in the microstructure, a small amount of retained austenite significantly increases the toughness of steel material while suppressing the occurrence of a significant decrease in strength. Accordingly, when it is desired to increase toughness, a microstructure that includes retained austenite may be adopted. However, if the volume ratio of retained austenite is too high, the strength of the steel material will markedly decrease. Accordingly, in a case where the microstructure of the steel material includes retained austenite, a preferable upper limit of the volume ratio of retained austenite is 15.0%, and further preferably is 10.0%.

[Method for measuring volume ratio of martensite]

[0104] The volume ratio (%) of martensite in the microstructure of the martensitic stainless steel material of the present embodiment can be obtained by subtracting the volume ratio (%) of retained austenite, which is obtained by the following method, from 100.0%.

[0105] The volume ratio of retained austenite can be obtained by an X-ray diffraction method. Specifically, a test specimen is taken from the martensitic stainless steel material. In a case where the martensitic stainless steel material is a seamless steel pipe, the test specimen is taken from a center portion of the wall thickness of the steel pipe. In a case where the martensitic stainless steel material is a round steel bar, the test specimen is taken from an R/2 portion, that is, a center portion of a radius R in a cross section perpendicular to the longitudinal direction of the round steel bar. 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 the wall thickness direction in a case where the martensitic stainless steel material is a seamless steel pipe, and is the radial direction in a case where the martensitic stainless steel material is a round steel bar.

[0106] Using the obtained test specimen, the X-ray diffraction intensity of each of the (200) plane of α phase, the (211) plane of α phase, the (200) plane of γ phase, the (220) plane of γ phase, and the (311) plane of γ phase is measured to calculate an integrated intensity of each plane. In the measurement of the X-ray diffraction intensity, the target of the X-ray diffraction apparatus is Mo (MoKα ray), and the output is 50 kV and 40 mA.

[0107] After calculation, the volume ratio Vy (%) of retained austenite is calculated using Formula (I) for combinations (2 × 3 = 6 pairs) of each plane of the α phase and each plane of the γ 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.

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

[0108] Where, $I\alpha$ is an integrated intensity of α phase. $R\alpha$ is a crystallographic theoretical calculation value of α phase. $I\gamma$ is an integrated intensity of γ phase. $R\gamma$ is a crystallographic theoretical calculation value of γ phase. Note that, in the present description, $R\alpha$ in the (200) plane of α phase is 15.9, $R\alpha$ in the (211) plane of α phase is 29.2, $R\gamma$ in the (200) plane of γ phase is 35.5, $R\gamma$ in the (220) plane of γ phase is 20.8, and $R\gamma$ in the (311) plane of γ phase is 21.8. Note that the volume ratio of retained austenite is obtained by rounding off the second decimal place of an obtained numerical value.

[0109] Using the volume ratio (%) of retained austenite obtained by the above described X-ray diffraction method, the volume ratio (vol.%) of martensite of the microstructure of the martensitic stainless steel material is obtained by the following Formula.

$$\text{Volume ratio of martensite} = 100.0 - \text{volume ratio of retained austenite (\%)}$$

[Yield strength]

[0110] The yield strength of the martensitic stainless steel material of the present embodiment is 110 ksi or more, that is, 758 MPa or more.

[0111] In the present description, the yield strength means 0.2% offset proof stress (MPa) which is obtained by a tensile test at normal temperature (24 ± 3°C) in conformity with ASTM E8/E8M (2013). Specifically, the yield strength is obtained by the following method.

[0112] In a case where the martensitic stainless steel material is a seamless steel pipe, a tensile test specimen is taken from the center portion of the wall thickness of the steel pipe. In a case where the martensitic stainless steel material is a round steel bar, a tensile test specimen is taken from the R/2 portion. The tensile test specimen is, for example, a round bar tensile test specimen having a parallel portion diameter of 6.0 mm and a parallel portion length of 40.0 mm. The longitudinal direction of the parallel portion of the round bar tensile test specimen is made parallel with the rolling direction (longitudinal direction) of the martensitic stainless steel material.

[0113] A tensile test is conducted at normal temperature (24 ± 3°C) in conformity with ASTM E8/E8M (2013) using the round bar tensile test specimen to obtain 0.2% offset proof stress (MPa). The obtained 0.2% offset proof stress is defined as the yield strength (MPa).

[0114] Although an upper limit of the yield strength of the martensitic stainless steel material of the present embodiment is not particularly limited, when the contents of the elements are within the ranges of the chemical composition described above, the upper limit of the yield strength is, for example, 1000 MPa (145 ksi), and preferably is 965 MPa (140 ksi).

[0115] The yield strength of the martensitic stainless steel material of the present embodiment may be 110 ksi grade (758 to less than 862 MPa), or may be 125 ksi or more (862 MPa or more).

[0116] In a case where the yield strength of the martensitic stainless steel material of the present embodiment is made 110 ksi grade, a preferable lower limit of the yield strength is 765 MPa, more preferably is 770 MPa, further preferably is 775 MPa, and further preferably is 780 MPa. A preferable upper limit of the yield strength of the martensitic stainless steel material of the present embodiment is 860 MPa, and more preferably is 855 MPa.

[0117] In a case where the yield strength of the martensitic stainless steel material of the present embodiment is made 125 ksi or more, a preferable lower limit of the yield strength is 870 MPa, more preferably is 880 MPa, further preferably is 890 MPa, and further preferably is 900 MPa.

[SSC resistance of steel material]

[0118] The SSC resistance of the steel material according to the present embodiment can be evaluated by a SSC resistance evaluation test conducted in accordance with NACE TM0177-2005 Method A.

[0119] An SSC resistance evaluation test method that is in accordance with NACE TM0177-2005 Method A is as follows. A round bar specimen is taken from the martensitic stainless steel material according to the present embodiment. If the martensitic stainless steel material is a steel pipe, the round bar specimen is taken from the center portion of the wall thickness. If the martensitic stainless steel material is a round steel bar, the round bar specimen is taken from the R/2 portion. The size of the round bar specimen is not particularly limited. The round bar specimen, for example, has a size in which the diameter of the parallel portion is 6.35 mm, and the length of the parallel portion is 25.4 mm. Note that, the longitudinal direction of the round bar specimen is made parallel with the rolling direction (longitudinal direction) of the martensitic stainless steel material.

[0120] An aqueous solution containing 20 mass% of sodium chloride in which the pH is 4.0 is adopted as the test solution. A stress equivalent to 90% of the actual yield stress is applied to the round bar specimen. The test solution at

24°C is poured into a test vessel so that the round bar specimen to which the stress has been applied is immersed therein, and this is adopted as a test bath. After degassing the test bath, a gaseous mixture consisting of H_2S at 0.10 bar and CO_2 at 0.90 bar is blown into the test bath so that the test bath is saturated with H_2S gas. The test bath in which the H_2S gas is saturated is held at 24°C for 720 hours. After the test specimen has been held for 720 hours, the surface of the test specimen is observed with a magnifying glass with a magnification of × 10 to check for the presence of cracking. If a place is found where cracking is suspected in the observation with a magnifying glass, a cross section at the place where cracking is suspected is observed with an optical microscope with a magnification of × 100 to confirm whether or not there is cracking.

[0121] The martensitic stainless steel material of the present embodiment has excellent SSC resistance. Specifically, in the martensitic stainless steel material of the present embodiment, in the aforementioned SSC resistance evaluation test conducted in accordance with NACE TM0177-2005 Method A, cracking is not confirmed after 720 hours elapses. In the present description, the phrase "cracking is not confirmed" means that cracking is not confirmed as a result of observing the test specimen after the test with a magnifying glass with a magnification of × 10 and an optical microscope with a magnification of × 100.

[Shape and uses of martensitic stainless steel material]

[0122] The martensitic stainless steel material according to the present embodiment is a seamless steel pipe or a round steel bar (solid material). In a case where the martensitic stainless steel material is a seamless steel pipe, the martensitic stainless steel material is a steel pipe for oil country tubular goods. The term "steel pipe for oil country tubular goods" means a steel pipe that is to be used in oil country tubular goods. Oil country tubular goods are, for example, a casing pipe, a tubing pipe, and a drilling pipe which are used for drilling of an oil well or a gas well, collection of crude oil or natural gas, and the like.

[0123] In a case where the martensitic stainless steel material is a round steel bar, for example, the martensitic stainless steel material is to be used for a downhole member.

[0124] As described above, in the martensitic stainless steel material of the present embodiment, the content of each element in the chemical composition is within the range of the present embodiment, and in a microscopic segregation region (line segment LS), a degree of Cr segregation ΔCr defined by Formula (1), a degree of Mo segregation ΔMo defined by Formula (2), and a degree of Cu segregation ΔCu defined by Formula (3) satisfy Formula (4). That is, in a microscopic segregation region (line segment LS) in the steel material also, the Cr concentration distribution, the Mo concentration distribution, and the Cu concentration distribution are sufficiently uniform. Therefore, the martensitic stainless steel material of the present embodiment can obtain excellent SSC resistance in a sour environment while also having a yield strength of 110 ksi grade.

[Production method]

[0125] An example of a method for producing the martensitic stainless steel material of 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 material of the present embodiment is not limited to this production method. That is, as long as the martensitic stainless steel material of the present embodiment that is composed as described above can be produced, a method for producing the martensitic stainless steel material is not limited to the production method described hereunder. However, the production method described hereunder is a favorable method for producing the martensitic stainless steel material of the present embodiment.

[0126] One example of a method for producing the martensitic stainless steel material of the present embodiment includes the following processes.

(1) Starting material preparation process
(2) Blooming process
(3) Steel material production process
(4) Heat treatment process

[0127] Hereunder, each process is described in detail.

[(1) Starting material preparation process]

[0128] In the starting material preparation process, molten steel in which the content of each element in the chemical composition is within the range of the present embodiment is produced by a well-known steel-making method. A cast piece is produced by a continuous casting process using the produced molten steel. Here, the cast piece is a bloom or

a billet. Instead of the cast piece, an ingot may be produced by an ingot-making process using the aforementioned molten steel. The starting material (bloom or ingot) is produced by the above described production process.

[(2) Blooming process]

[0129] In the blooming process, the starting material (bloom or ingot) is subjected to hot rolling using a blooming mill to thereby produce a billet. The blooming process includes the following processes.

(21) Starting material heating process
(22) Hot working process

[0130] Hereunder, each process is described in detail.

[(21) Starting material heating process]

[0131] In the starting material heating process, the starting material is heated in a bloom reheating furnace. The in-furnace temperature of the bloom reheating furnace and the residence time of the starting material in the bloom reheating furnace are as follows.

In-furnace temperature of bloom reheating furnace: 1200 to 1350°C

Holding time in bloom reheating furnace: 200 to 400 minutes

[0132] Here, the term "holding time" refers to the in-furnace residence time from a time point at which the in-furnace temperature of the heating furnace reaches a predetermined temperature.

[0133] The aforementioned range of the in-furnace temperature (°C) of the bloom reheating furnace is a well-known range. The aforementioned range of the holding time (minutes) at the bloom reheating furnace is also a well-known range. If the in-furnace temperature of the bloom reheating furnace is 1200 to 1350°C, and the holding time in the bloom reheating furnace is 200 to 400 minutes, the hot workability of the starting material will sufficiently increase. Therefore, in the hot working process in the next process, the starting material can be made into a billet.

[0134] Note that, a thermometer (thermocouple) is disposed in the bloom reheating furnace, and it is possible to measure the in-furnace temperature. Further, the holding time (minutes) in the bloom reheating furnace can be determined based on the time point at which the starting material is charged into the bloom reheating furnace and the time point at which the starting material is extracted from the bloom reheating furnace.

[(22) Hot working process]

[0135] In the hot working process, the starting material that was heated in the starting material heating process is subjected to hot rolling to produce a billet. Specifically, the heated starting material is subjected to hot rolling using a blooming mill to thereby produce a billet. After hot rolling by the blooming mill, as necessary, the starting material may be subjected to further hot rolling using a continuous mill arranged downstream of the blooming mill to produce a billet. The total reduction of area in the blooming process is not particularly limited, and for example is 20 to 70%. The billet produced in the hot working process is cooled to normal temperature before the steel material production process.

[(3) Steel material production process]

[0136] In the steel material production process, the billet produced in the blooming process is subjected to hot working to produce a steel material. The steel material production process includes the following processes.

(31) Steel material heating process
(32) Hot working process

[0137] Hereunder, each process is described in detail.

[(31) Steel material heating process]

[0138] In the steel material heating process, the billet produced in the blooming process is charged into a continuous heating furnace and heated. The heating furnace may be a rotary hearth heating furnace or may be a walking beam

heating furnace. In the following description, the use of a rotary hearth heating furnace is described as one example of a continuous heating furnace.

[0139] FIG. 6 is a schematic diagram (plan view) illustrating a rotary hearth heating furnace that is one example of a continuous heating furnace. Referring to FIG. 6, a heating furnace 10 includes a furnace main body 13 having a charging port 11 and an extraction port 12. A billet B1 which is the object to be heated is charged into the heating furnace 10 from the charging port 11. In FIG. 6, the billet B1 is heated while moving through the inside of the heating furnace. In FIG. 6, the billet B1 that was charged into the heating furnace 10 from the charging port 11 moves in the clockwise direction. When the billet B1 which has been heated while moving arrives at the extraction port 12, the billet B1 is extracted to outside from the extraction port 12.

[0140] The furnace main body 13 is divided into a preheating zone Z1, a heating zone Z2, and a holding zone Z3 in that order in the direction from the charging port 11 toward the extraction port 12. The preheating zone Z1 is a zone that has the charging port 11. The preheating zone Z1 is the zone in which the in-furnace temperature is lowest among the three zones (preheating zone Z1, heating zone Z2 and holding zone Z3). The heating zone Z2 is a zone arranged between the preheating zone Z1 and the holding zone Z3. The holding zone Z3 is a zone that follows the heating zone Z2, and has the extraction port 12 at the rear end thereof. The heating zone Z2 and the holding zone Z3 are maintained at approximately the same temperature. Specifically, although the temperature in the holding zone Z3 is somewhat higher than the temperature in the heating zone Z2, the temperature difference between the holding zone Z3 and the heating zone Z2 is 20°C or less. One or a plurality of burners is provided in each of the zones. In each zone, the temperature is adjusted by means of the burner(s).

[0141] In the present embodiment the in-furnace temperature and the residence time in the preheating zone Z1, the heating zone Z2, and the holding zone Z3 are as follows.

[Preheating zone Z1]

[0142] The in-furnace temperature and the residence time in the preheating zone Z1 are as follows.

[0143] In-furnace temperature: a temperature from 1000 to less than 1275°C, and which is a temperature that is lower than an in-furnace temperature T in the heating zone Z2 and the holding zone Z3

Residence time: 100 minutes or more

[0144] In the preheating zone Z1, the in-furnace temperature is 1000 to less than 1275°C, and is set to a lower temperature than an in-furnace temperature T (°C) in the heating zone Z2 and the holding zone Z3. In addition, the residence time of the billet in the preheating zone Z1 is set to 100 minutes or more. The preheating zone Z1 mainly fulfills a role of increasing the temperature of the billet that is at normal temperature. Preferably, the residence time in the preheating zone Z1 is set to 120 minutes or more, and more preferably is set to 130 minutes or more.

[Heating zone Z2 and holding zone Z3]

[0145] The conditions in the heating zone Z2 and the holding zone Z3 are as follows.

In-furnace temperature T: a temperature from 1225 to 1275°C, and which is a temperature that is higher than the in-furnace temperature in the preheating zone Z1

Total residence time t: time that satisfies Formula (A)

These conditions are described hereunder.

(Regarding in-furnace temperature T)

[0146] With regard to the heating zone Z2 and the holding zone Z3, the in-furnace temperature T in the heating zone Z2 and the holding zone Z3 is set in the range of 1225 to 1275°C, and is set to a temperature that is higher than the in-furnace temperature in the preheating zone Z1. If the in-furnace temperature T in the heating zone Z2 and the holding zone Z3 is less than 1225°C, the Cr concentration distribution, the Mo concentration distribution, and the Cu concentration distribution within the segregation region SE will not be uniform, and variations will occur. Consequently, in the produced martensitic stainless steel material, the degree of Cr segregation ΔCr, the degree of Mo segregation ΔMo, and the degree of Cu segregation ΔCu will not satisfy Formula (4). On the other hand, if the in-furnace temperature T in the heating zone Z2 and the holding zone Z3 is more than 1275°C, δ-ferrite will be formed in the steel material having the aforementioned chemical composition. The δ-ferrite will decrease the hot workability of the steel material. Accordingly, the in-furnace temperature T in the heating zone Z2 and the holding zone Z3 is to be within the range of 1225 to 1275°C.

(Regarding total residence time t)

[0147] Let the total residence time in the heating zone Z2 and the holding zone Z3 be defined as t (minute). The term "total residence time t" means the time (minutes) from when the billet produced in the blooming process enters the heating zone Z2 until the billet is discharged to outside from the extraction port 12. The in-furnace temperature T and the total residence time t in the heating zone Z2 and the holding zone Z3 are set so as to satisfy the following Formula (A):

$$B \leq (t/60)^{0.5} \times (T + 273) \quad (A)$$

where, when the yield strength is 110 ksi grade (758 to less than 862 MPa), B in Formula (A) is 2900, and when the yield strength is 862 MPa or more, B in Formula (A) is 3900.

[0148] In Formula (A), the total residence time t (minutes) of the billet in the heating zone Z2 and the holding zone Z3 is substituted for "t". Further, the in-furnace temperature T (°C) in the heating zone Z2 and the holding zone Z3 is substituted for "T". Note that, an arithmetic average value of the in-furnace temperature (°C) in the heating zone Z2 obtained with a thermometer and the in-furnace temperature (°C) in the holding zone Z3 obtained with a thermometer is adopted as the in-furnace temperature T (°C) in the heating zone Z2 and the holding zone Z3.

[0149] Let FA be defined as FA = $(t/60)^{0.5} \times (T + 273)$. FIG. 7A is a view illustrating the relation between FA and a total degree of segregation ΔF (= $\Delta Cr + \Delta Mo + \Delta Cu$) of Cr, Mo, and Cu in a microscopic segregation region (line segment LS) in a case where the yield strength of the steel material is made 110 ksi grade (758 to less than 862 MPa). FIG. 7B is a view illustrating the relation between FA and the total degree of segregation ΔF in a case where the yield strength of the steel material is made 125 ksi or more (862 MPa or more).

[Case where yield strength of steel material is made 110 ksi grade]

[0150] Referring to FIG. 7A, in a case where the yield strength of the steel material is made 110 ksi grade, if FA is less than 2900, the billet is not sufficiently held in a temperature range of 1225°C or more. In this case, at least one kind among variations in the Cr concentration distribution, variations in the Mo concentration distribution, and variations in the Cu concentration distribution in the segregation region SE in the billet cannot be sufficiently reduced. Therefore, as illustrated in FIG. 7A, in the produced martensitic stainless steel material, the total degree of segregation ΔF is more than 0.70.

[0151] On the other hand, if FA is 2900 or more, the billet is sufficiently held in a temperature range of 1225°C or more. In this case, in the segregation region SE in the billet, variations in the Cr concentration distribution are sufficiently reduced, variations in the Mo concentration distribution are sufficiently reduced, and variations in the Cu concentration distribution are sufficiently reduced. As a result, as illustrated in FIG. 7A, in comparison to when FA is less than 2900, the total degree of segregation ΔF in the produced martensitic stainless steel material markedly decreases, and becomes 0.70 or less. That is, variations in the Cr concentration, the Mo concentration, and the Cu concentration in the segregation region SE can be markedly suppressed.

[0152] A preferable lower limit of FA in a case where the yield strength of the steel material is made 110 ksi grade is 3000, more preferably is 3100, further preferably is 3150, further preferably is 3200, and further preferably is 3250. An upper limit of FA is not particularly limited. However, taking into consideration the productivity during normal industrial production, the total residence time t is preferably 600 minutes or less. Accordingly, the upper limit of FA is, for example, 4890.

[0153] Note that, a preferable lower limit of the total residence time t (minutes) in the heating zone Z2 and the holding zone Z3 in a case where the yield strength of the steel material is made 110 ksi grade is 220 minutes, more preferably is 230 minutes, further preferably is 240 minutes, and further preferably is 250 minutes.

[0154] In a case where the yield strength of the steel material is made 110 ksi grade, in the steel material heating process, the billet is heated using a continuous heating furnace so that, in particular, FA is 2900 or more in the temperature range of 1225 to 1275°C in the heating zone Z2 and the holding zone Z3. Taking into consideration the residence time in the preheating zone Z1, in the present embodiment a preferable furnace time of the billet in the heating furnace is 320 minutes or more, and further preferably is 330 minutes or more.

[Case where yield strength of steel material is made 125 ksi or more]

[0155] Referring to FIG. 7B, in a case where the yield strength of the steel material is made 125 ksi or more, if FA is less than 3900, the billet is not sufficiently held in a temperature range of 1225°C or more. In this case, at least one kind among variations in the Cr concentration distribution, variations in the Mo concentration distribution, and variations in the Cu concentration distribution in the segregation region SE in the billet cannot be sufficiently reduced. Therefore, as

illustrated in FIG. 7B, in the produced martensitic stainless steel material, the total degree of segregation ΔF is more than 0.50.

[0156] On the other hand, if FA is 3900 or more, the billet is sufficiently held in the temperature range of 1225°C or more. In this case, in the segregation region SE in the billet, variations in the Cr concentration distribution are sufficiently reduced, variations in the Mo concentration distribution are sufficiently reduced, and variations in the Cu concentration distribution are sufficiently reduced. As a result, as illustrated in FIG. 7B, in comparison to when FA is less than 3900, the total degree of segregation ΔF in the produced martensitic stainless steel material markedly decreases, and becomes 0.50 or less. That is, variations in the Cr concentration, the Mo concentration, and the Cu concentration in the segregation region SE can be markedly suppressed.

[0157] A preferable lower limit of FA in a case where the yield strength of the steel material is made 125 ksi or more is 3950, more preferably is 3980, and further preferably is 4000. An upper limit of FA is not particularly limited. However, taking into consideration the productivity during normal industrial production, the total residence time t is preferably 600 minutes or less. Accordingly, the upper limit of FA is, for example, 4890.

[0158] Note that, a preferable lower limit of the total residence time t (minutes) in the heating zone Z2 and the holding zone Z3 in a case where the yield strength of the steel material is made 125 ksi or more is 350 minutes, more preferably is 380 minutes, and further preferably is 400 minutes.

[0159] In a case where the yield strength of the steel material is made 125 ksi or more, in the steel material heating process, the billet is heated using a continuous heating furnace so that, in particular, FA is 3900 or more in the temperature range of 1225 to 1275°C in the heating zone Z2 and the holding zone Z3. Taking into consideration the residence time in the preheating zone Z1, in the present embodiment a preferable furnace time of the billet in the heating furnace is 450 minutes or more, and further preferably is 500 minutes or more.

[0160] Note that, a thermometer (thermocouple) is arranged in each of the preheating zone Z1, the heating zone Z2, and the holding zone Z3, and thus the in-furnace temperature in the respective zones can be measured. An arithmetic average value of the in-furnace temperature (°C) in the heating zone Z2 obtained with a thermometer and the in-furnace temperature (°C) in the holding zone Z3 obtained with a thermometer is defined as the in-furnace temperature T (°C) in the heating zone Z2 and the holding zone Z3. Further, the residence time of the billet in each zone (preheating zone Z1, heating zone Z2, and holding zone Z3) can be determined based on the order and feeding speed of the billets charged into the heating furnace.

[0161] In the above description, a rotary hearth heating furnace has been described as the heating furnace. However, the structure of a walking beam heating furnace is the same as the structure of a rotary hearth heating furnace. Specifically, a walking beam heating furnace includes a main body that has a charging port and an extraction port. The main body is divided into a preheating zone, a heating zone, and a holding zone in that order in the direction from the charging port toward the extraction port. Accordingly, in a walking beam heating furnace also, the conditions of the heating process are as described above.

[0162] In FIG. 6, the preheating zone Z1, the heating zone Z2, and the holding zone Z3 are divided equally inside the furnace main body 13. However, the preheating zone Z1, the heating zone Z2, and the holding zone Z3 do not have to be divided equally.

[0163] In the production process of the present embodiment, an important point is that heating for a long time period is not performed with respect to the as-solidified starting material (bloom or billet), and instead the billet subjected to hot working by the blooming process is subjected to heating for a long time period. The microstructure of the as-solidified starting material includes dendrite (a tree-like structure). Dendrite inhibits diffusion of Cr, Mo, and Cu during heating. By performing hot rolling on the starting material in the blooming process, dendrite is physically or mechanically destroyed. Therefore, in comparison to the microstructure of the starting material in the starting material preparation process, almost no dendritic structure is present in the microstructure of the billet produced in the blooming process, and the microstructure of the billet is a fine microstructure. By subjecting such a billet in which the amount of dendritic structure is small to heating under the aforementioned conditions, Cr, Mo, and Cu within the billet can be adequately diffused. As a result, in the produced martensitic stainless steel material, the degree of Cr segregation ΔCr defined by Formula (1), the degree of Mo segregation ΔMo defined by Formula (2), and the degree of Cu segregation ΔCu defined by Formula (3) satisfy Formula (4).

[(32) Hot working process]

[0164] In the hot working process, the billet heated under the aforementioned conditions by the heating process is subjected to hot working. If the end product is a seamless steel pipe, the heated billet is subjected to hot working to produce a hollow shell (seamless steel pipe). For example, hot rolling by the Mannesmann-mandrel process is performed as the hot working to produce a hollow shell. In this case, the billet is subjected to piercing-rolling by a piercing machine. When performing piercing-rolling, although not particularly limited, the piercing ratio is, for example, 1.0 to 4.0. The billet after piercing-rolling is subjected to elongating and rolling using a mandrel mill. In addition, as needed, the billet after

elongating and rolling is subjected to diameter adjusting rolling using a reducer or a sizing mill. A hollow shell is produced by the above process. Although not particularly limited, the cumulative reduction of area in the hot working process is, for example, 20 to 70%.

[0165] If the end product is a round steel bar, for example, the heated billet is subjected to hot forging to produce a round steel bar.

[(4) Heat treatment process]

[0166] The heat treatment process includes the following processes.

(41) Quenching process
(42) Tempering process

[0167] Each process is described hereunder.

[(41) Quenching process]

[0168] In the heat treatment process, first, the steel material (hollow shell or round steel bar) produced in the hot working process is subjected to quenching (quenching process). The quenching is performed by a well-known method. Specifically, the steel material after the hot working process is charged into a heat treatment furnace and held at a quenching temperature. The quenching temperature is equal to or higher than the Acs transformation point and, for example, is 900 to 1000°C. After being held at the quenching temperature, the steel material is rapidly cooled (quenched). Although not particularly limited, the holding time at the quenching temperature is for example, 10 to 60 minutes. The quenching method is, for example, water cooling or oil cooling. The quenching method is not particularly limited. For example, the hollow shell may be rapidly cooled by immersing the hollow shell in a water bath or an oil bath, or the hollow shell may be rapidly cooled by pouring or jetting cooling water onto the outer surface and/or inner surface of the hollow shell by shower cooling or mist cooling.

[0169] In a case where the martensitic stainless steel material is a seamless steel pipe, after the hot working process, quenching (direct quenching) may be performed immediately after the hot working, without cooling the hollow shell to normal temperature. Further, quenching may be performed after the hollow shell after hot working has been held at the quenching temperature after being charged into a supplementary heating furnace before the temperature of the hollow shell decreased after the hot working.

[(42) Tempering process]

[0170] The hollow shell after quenching is also subjected to a tempering process. In the tempering process, the yield strength of the steel material is adjusted. For the martensitic stainless steel material of the present embodiment, the tempering temperature is set in the range of 550°C to the Aci transformation point.

[0171] In a case where the yield strength of the steel material is to be made 110 ksi grade (758 to less than 862 MPa), a preferable lower limit of the tempering temperature is 610°C, and more preferably is 620°C. A preferable upper limit of the tempering temperature is 640°C, and more preferably is 635°C.

[0172] In a case where the yield strength of the steel material is to be made 125 ksi or more (862 MPa or more), a preferable lower limit of the tempering temperature is 575°C, and more preferably is 580°C. A preferable upper limit of the tempering temperature is less than 610°C, and more preferably is 605°C.

[0173] Although not particularly limited, the holding time at the tempering temperature is, for example, 20 to 60 minutes. A preferable upper limit of the holding time is 50 minutes, and more preferably is 45 minutes. By appropriately adjusting the tempering temperature according to the chemical composition, the yield strength of the martensitic stainless steel material can be adjusted. Specifically, the tempering conditions are adjusted so that the yield strength of the martensitic stainless steel material becomes 110 ksi or more (758 MPa or more).

[0174] The martensitic stainless steel material of the present embodiment can be produced by the processes described above.

EXAMPLE 1

[0175] The advantageous effect of one aspect of the steel material of the present embodiment will be described more specifically by way of examples. The conditions adopted in the following examples are one example of conditions employed for confirming the workability and advantageous effects of the steel material of the present embodiment. Accordingly, the steel material of the present embodiment is not limited to this one example of the conditions.

[0176] In Example 1, steel materials having a yield strength of 110 ksi grade (758 to less than 862 MPa) were produced, and various evaluation tests were performed. The details are described hereunder.

[Production of steel material]

[Starting material preparation process]

[0177] Molten steels having the chemical compositions shown in Table 1 were produced.

[Table 1]

[0178]

TABLE1

Test No.	Chemical Composition Values (mass%; balance: Fe and impurities)																			
	C	Si	Mn	P	S	Ni	Cr	Mo	Al	V	N	Ti	Cu	Co	B	Ca	Mg	REM	Nb	W
1	0.008	0.23	0.44	0.015	0.0007	5.80	13.20	2.34	0.040	0.04	0.0054	0.110	1.92	0.34	-	-	-	-	-	-
2	0.027	0.33	0.39	0.013	0.0004	5.21	13.02	2.15	0.027	0.05	0.0038	0.060	2.10	0.15	-	-	-	-	-	-
3	0.012	0.23	0.38	0.016	0.0009	5.30	13.40	2.57	0.037	0.03	0.0059	0.090	1.96	0.13	-	-	-	-	-	-
4	0.012	0.30	0.40	0.014	0.0005	5.99	10.10	2.51	0.037	0.04	0.0065	0.120	1.86	0.33	-	-	-	-	-	-
5	0.008	0.37	0.48	0.016	0.0005	5.87	13.30	2.34	0.037	0.04	0.0065	0.100	2.71	0.36	-	-	-	-	-	-
6	0.010	0.24	0.40	0.011	0.0009	5.33	13.00	2.00	0.037	0.04	0.0065	0.090	2.89	0.23	-	-	-	-	-	-
7	0.009	0.31	0.41	0.017	0.0006	5.67	12.70	2.89	0.037	0.04	0.0065	0.100	2.65	0.18	-	-	-	-	-	-
8	0.008	0.27	0.46	0.016	0.0008	5.60	13.30	2.68	0.037	0.04	0.0065	0.070	1.87	0.33	-	-	-	-	-	-
9	0.009	0.34	0.43	0.013	0.0007	6.06	11.30	2.32	0.037	0.04	0.0065	0.080	3.24	0.28	-	-	-	-	-	-
10	0.011	0.36	0.34	0.011	0.0008	5.56	12.70	2.50	0.029	0.05	0.0062	0.080	2.91	0.18	0.0001	-	-	-	-	-
11	0.012	0.26	0.40	0.011	0.0008	5.43	13.10	2.36	0.027	0.03	0.0051	0.050	2.66	0.28	-	0.0033	-	-	-	-
12	0.029	0.25	0.41	0.013	0.0006	5.38	12.89	2.00	0.026	0.05	0.0047	0.066	2.11	0.18	-	-	0.0043	-	-	-
13	0.026	0.27	0.40	0.015	0.0006	5.40	12.86	2.02	0.031	0.05	0.0048	0.068	2.08	0.21	-	-	-	0.0045	-	-
14	0.009	0.25	0.39	0.013	0.0007	6.15	12.50	2.54	0.029	0.04	0.0055	0.050	2.92	0.10	-	-	-	-	0.02	-
15	0.011	0.32	0.30	0.010	0.0007	6.00	12.50	2.44	0.037	0.05	0.0051	0.060	3.06	0.29	-	-	-	-	-	0.12
16	0.009	0.25	0.30	0.011	0.0006	5.60	13.20	2.70	0.036	0.04	0.0063	0.090	2.04	0.22	-	-	-	-	0.03	0.15
17	0.010	0.26	0.38	0.013	0.0008	5.74	11.30	2.11	0.030	0.06	0.0071	0.080	2.07	0.20	0.0003	-	-	-	0.03	0.12
18	0.009	0.31	0.37	0.017	0.0005	5.89	11.90	2.35	0.031	0.04	0.0063	0.050	1.96	0.38	0.0001	-	-	-	0.04	0.14
19	0.011	0.35	0.41	0.012	0.0008	5.49	12.40	2.31	0.038	0.06	0.0055	0.080	2.84	0.20	0.0001	0.0030	-	-	0.09	0.11
20	0.009	0.30	0.35	0.010	0.0008	5.53	12.30	2.64	0.041	0.06	0.0043	0.100	2.88	0.25	0.0002	-	-	0.0010	0.06	0.08
21	0.008	0.36	0.40	0.013	0.0010	5.74	12.30	2.40	0.025	0.06	0.0064	0.090	2.90	0.12	0.0004	-	0.0010	0.0015	0.02	0.19
22	0.008	0.31	0.37	0.017	0.0006	5.28	11.40	2.57	0.034	0.06	0.0035	0.110	2.89	0.25	0.0001	-	0.0017	0.0017	0.04	0.14

23	0.009	0.35	0.44	0.014	0.0009	6.11	11.60	2.48	0.031	0.06	0.0050	0.090	2.48	0.31	0.0004	0.0027	0.0016	0.0014	0.02	0.18
24	0.012	0.37	0.42	0.014	0.0009	5.86	9.50	2.43	0.041	0.03	0.0053	0.100	2.88	0.13	-	-	-	-	-	-
25	0.010	0.30	0.42	0.015	0.0006	6.07	15.50	2.32	0.029	0.04	0.0048	0.050	2.45	0.24	-	-	-	-	-	-
26	0.009	0.32	0.41	0.011	0.0005	5.67	12.70	1.41	0.041	0.06	0.0044	0.070	2.03	0.22	-	-	-	-	-	-
27	0.008	0.33	0.38	0.011	0.0009	5.72	13.10	3.12	0.037	0.07	0.0048	0.090	2.28	0.36	-	-	-	-	-	-
28	0.009	0.30	0.40	0.013	0.0008	5.88	12.00	2.44	0.039	0.04	0.0055	0.080	0.92	0.20	-	-	-	-	-	-
29	0.009	0.27	0.40	0.016	0.0009	5.57	13.20	2.47	0.030	0.05	0.0045	0.130	3.81	0.31	-	-	-	-	-	-
30	0.009	0.21	0.48	0.014	0.0010	5.57	12.28	1.93	0.029	0.05	0.0065	0.091	2.01	0.12	-	-	-	-	-	-
31	0.009	0.25	0.40	0.015	0.0010	6.01	13.40	2.26	0.044	0.05	0.0066	0.090	2.09	0.24	-	-	-	-	-	-
32	0.008	0.28	0.36	0.011	0.0008	5.23	11.20	2.70	0.036	0.03	0.0058	0.070	1.98	0.23	-	-	-	-	0.02	-
33	0.012	0.38	0.31	0.014	0.0011	5.54	12.80	2.68	0.031	0.07	0.0049	0.120	2.64	0.29	-	-	-	-	-	0.05
34	0.011	0.31	0.44	0.016	0.0011	6.05	11.20	2.68	0.041	0.03	0.0040	0.080	2.99	0.26	-	-	-	-	0.02	0.14
35	0.012	0.32	0.47	0.013	0.0011	6.07	11.70	2.64	0.041	0.03	0.0038	0.050	2.42	0.17	0.0001	-	-	-	-	-
36	0.011	0.37	0.43	0.014	0.0011	5.29	11.10	2.57	0.042	0.06	0.0051	0.120	1.89	0.19	-	0.0015	-	-	-	-
37	0.011	0.37	0.46	0.017	0.0009	6.12	11.20	2.52	0.026	0.04	0.0049	0.080	2.89	0.18	0.0004	0.0027	-	-	-	-
38	0.009	0.38	0.45	0.017	0.0008	6.00	12.10	2.68	0.037	0.04	0.0065	0.080	2.40	0.25	0.0001	0.0009	0.0005	0.0005	0.04	0.11
39	0.010	0.24	0.40	0.015	0.0010	6.05	12.50	2.60	0.035	0.05	0.0042	0.110	2.47	0.17	-	-	-	-	-	-

[0179] In Table 1, the "-" symbol means that the content of the corresponding element was less than the detection limit. Specifically, for example, with regard to Test Number 1 in Table 1, the "-" symbol means that the content of Nb was 0% (0.00%) when rounded off to the second decimal place, and that the content of W was 0% (0.00%) when rounded off to the second decimal place.

[0180] Each of the produced molten steels was used to produce a bloom by continuous casting.

[Blooming process]

[0181] Next, in a blooming process, each bloom was subjected to hot rolling to produce a cylindrical billet (round billet) having a diameter of 310 mm. Specifically, first, the bloom was heated in a bloom reheating furnace. The in-furnace temperature (°C) of the bloom reheating furnace and the holding time (minutes) in the bloom reheating furnace for each test number were as shown in Table 2.

[Table 2]

[0182]

TABLE2

Test No.	Blooming Process		Steel Material Production Process						ΔCr	ΔMo	ΔCu	ΔF	Tempering Process		Yield Strength (MPa)	SSC Resistance
	In-furnace Temperature in Bloom Reheating Furnace (°C)	Holding Time in Bloom Reheating Furnace (min)	In-furnace Temperature in Preheating Zone (°C)	Residence Time in Preheating Zone (min)	In-furnace Temperature T (°C) in Heating Zone and Holding Zone	Total Residence Time t (min) in Heating Zone and Holding Zone	FA	Furnace Time in Heating Furnace (min)					Temperature (°C)	Holding Time (min)		
1	1250	233	1100	157	1250	401	3937	558	0.07	0.25	0.19	0.51	640	20	818	P
2	1270	202	1100	152	1250	378	3823	530	0.05	0.28	0.14	0.47	620	43	851	P
3	1270	220	1050	148	1275	260	3222	408	0.06	0.27	0.14	0.47	639	37	794	P
4	1270	280	1060	180	1250	354	3699	534	0.05	0.42	0.1	0.57	637	32	832	P
5	1260	269	1090	153	1250	379	3828	532	0.07	0.33	0.14	0.54	636	26	818	P
6	1250	269	1100	171	1250	388	3873	559	0.06	0.25	0.22	0.53	636	41	788	P
7	1260	218	1130	173	1250	317	3501	490	0.07	0.31	0.24	0.62	639	21	805	P
8	1260	240	1140	139	1250	229	2975	368	0.06	0.32	0.15	0.53	634	34	790	P
9	1270	380	1080	186	1250	446	4152	632	0.05	0.27	0.17	0.49	639	38	825	P
10	1260	255	1130	172	1250	546	4594	718	0.06	0.2	0.19	0.45	632	23	798	P
11	1270	256	1060	160	1250	417	4015	577	0.06	0.18	0.18	0.42	639	34	778	P
12	1250	320	1100	147	1250	360	3731	507	0.06	0.29	0.19	0.54	620	40	853	P
13	1250	209	1100	150	1250	362	3741	512	0.06	0.29	0.19	0.54	620	40	857	P
14	1260	271	1140	176	1250	355	3705	531	0.05	0.3	0.14	0.49	632	21	823	P
15	1270	260	1150	181	1250	502	4405	683	0.06	0.28	0.14	0.48	637	23	801	P
16	1250	239	1120	165	1250	307	3445	472	0.06	0.25	0.16	0.47	637	26	823	P
17	1260	238	1060	160	1250	225	2949	385	0.04	0.29	0.08	0.41	632	34	783	P
18	1260	222	1130	165	1250	356	3710	521	0.06	0.33	0.09	0.48	633	26	803	P

(continued)

Test No.	Blooming Process		Steel Material Production Process						ΔCr	ΔMo	ΔCu	ΔF	Tempering Process		Yield Strength (MPa)	SSC Resistance
	In-furnace Temperature in Bloom Reheating Furnace (°C)	Holding Time in Bloom Reheating Furnace (min)	In-furnace Temperature in Preheating Zone (°C)	Residence Time in Preheating Zone (min)	In-furnace Temperature T (°C) in Heating Zone and Holding Zone	Total Residence Time t (min) in Heating Zone and Holding Zone	FA	Furnace Time in Heating Furnace (min)					Temperature (°C)	Holding Time (min)		
19	1260	301	1100	202	1250	546	4594	748	0.06	0.25	0.14	0.45	639	43	785	P
20	1250	235	1100	178	1250	502	4405	680	0.06	0.26	0.14	0.46	633	43	826	P
21	1270	245	1100	180	1250	461	4222	641	0.05	0.25	0.14	0.44	639	37	814	P
22	1270	254	1130	186	1250	445	4148	631	0.05	0.29	0.13	0.47	632	36	815	P
23	1250	295	1060	168	1225	305	3377	473	0.04	0.29	0.11	0.44	631	33	839	P
24	1250	238	1100	170	1250	458	4208	628	0.05	0.26	0.23	0.54	632	23	788	F
25	1270	268	1070	160	1250	263	3189	423	0.14	0.27	0.39	0.80	630	39	858	F
26	1260	279	1120	142	1250	257	3152	399	0.07	0.23	0.20	0.50	638	24	762	F
27	1260	283	1060	166	1250	381	3838	547	0.10	0.39	0.33	0.82	639	32	835	F
28	1250	315	1120	161	1250	374	3802	535	0.07	0.43	0.10	0.60	635	28	798	F
29	1260	340	1110	181	1250	398	3923	579	0.11	0.26	0.39	0.76	636	41	857	F
30	1250	206	1090	136	1250	173	2586	309	0.08	0.36	0.30	0.74	636	22	833	F
31	1250	229	1070	140	1250	109	2053	249	0.10	0.45	0.22	0.77	639	28	834	F
32	1270	284	1110	160	1250	188	2696	348	0.09	0.48	0.24	0.81	633	23	817	F
33	1250	280	1130	151	1250	176	2608	327	0.10	0.27	0.42	0.79	633	35	840	F
34	1260	305	1150	155	1250	187	2689	342	0.11	0.28	0.45	0.84	638	27	831	F
35	1250	223	1070	154	1250	139	2318	293	0.09	0.35	0.41	0.85	637	32	781	F
36	1260	237	1120	154	1250	155	2448	309	0.11	0.42	0.32	0.85	635	31	787	F
37	1250	237	1090	151	1250	159	2479	310	0.09	0.24	0.46	0.79	637	26	807	F

(continued)

Test No.	Blooming Process		Steel Material Production Process										Tempering Process		Yield Strength (MPa)	SSC Resistance
	In-furnace Temperature in Bloom Reheating Furnace (°C)	Holding Time in Bloom Reheating Furnace (min)	In-furnace Temperature in Preheating Zone (°C)	Residence Time in Preheating Zone (min)	In-furnace Temperature T (°C) in Heating Zone and Holding Zone	Total Residence Time t (min) in Heating Zone and Holding Zone	FA	Fumace Time in Heating Furnace (min)	ΔCr	ΔMo	ΔCu	ΔF	Temperature (°C)	Holding Time (min)		
38	1250	282	1060	146	1250	145	2368	291	0.09	0.32	0.37	0.78	635	24	793	F
39	1260	267	1080	155	1225	222	2881	377	0.11	0.40	0.25	0.76	632	25	826	F

[0183] After the bloom was heated in the bloom reheating furnace, the heated bloom was subjected to hot rolling using a blooming mill to produce a round billet having a diameter of 310 mm.

[Steel material production process]

[0184] The round billet of each test number was subjected to a steel material heating process. Specifically, the round billet of each test number was loaded into a rotary hearth heating furnace. The in-furnace temperature (°C) of the preheating zone, the residence time (minutes) in the preheating zone, the in-furnace temperature T (°C) in the heating zone and the holding zone, and the total residence time t (minutes) in the heating zone and the holding zone in the heating furnace were as shown in Table 2. Further, $FA = (t/60)^{0.5} \times (T + 273)$ was as shown in Table 2. Note that, an arithmetic average value of an in-furnace temperature (°C) in the heating zone Z2 obtained with a thermometer and an in-furnace temperature (°C) in the holding zone Z3 obtained with a thermometer was adopted as the in-furnace temperature T (°C) in the heating zone and the holding zone.

[0185] Each of the round billets heated by the steel material heating process was subjected to a hot working process. Specifically, each round billet was subjected to hot rolling by the Mannesmann-mandrel process to thereby produce a hollow shell (seamless steel pipe) of each test number. At such time, the piercing ratio was within the range of 1.0 to 4.0, and the cumulative reduction of area in the hot working process was within the range of 20 to 70%.

[Heat treatment process]

[0186] Each of the produced hollow shells was subjected to a heat treatment process (quenching process and tempering process). In the quenching process, the quenching temperature was set to 910°C, and the holding time at the quenching temperature was set to 15 minutes. In the tempering process, the tempering temperature (°C) was set as shown in Table 2, and the holding time (minutes) at the tempering temperature was set as shown in Table 2. The yield strength was adjusted to 110 ksi grade (758 to less than 862 MPa) by the heat treatment process. Martensitic stainless steel materials (seamless steel pipes) were produced by the above production process.

[Evaluation test]

[0187] The seamless steel pipe of each test number was subjected to the following evaluation tests.

(1) Microstructure observation test
(2) Cr concentration, Mo concentration, and Cu concentration measurement test
(3) Tensile test
(4) SSC resistance evaluation test

[(1) Microstructure observation test]

[0188] The volume ratio of martensite of the seamless steel pipe of each test number was measured by the following method. Specifically, the volume ratio (%) of retained austenite was determined, and the determined value was subtracted from 100.0% to determine the martensite volume ratio.

[0189] The volume ratio of retained austenite was determined by an X-ray diffraction method. Specifically, a test specimen was taken from the center portion of the wall thickness of the seamless steel pipe. The size of the test specimen was 15 mm × 15 mm × a thickness of 2 mm. The thickness direction of the test specimen was the wall thickness direction of the seamless steel pipe. Using the obtained test specimen, the X-ray diffraction intensity of each of the (200) plane of α phase, the (211) plane of α phase, the (200) plane of γ phase, the (220) plane of γ phase, and the (311) plane of γ phase was measured, and the integrated intensity of each plane was calculated. In the measurement of the X-ray diffraction intensity, the target of the X-ray diffraction apparatus was Mo (MoKα ray), and the output was set to 50 kV and 40 mA. After calculation, the volume ratio $V\gamma$ (%) of retained austenite was calculated using Formula (I) for combinations ($2 \times 3 = 6$ pairs) of each plane of the α phase and each plane of the γ phase. Then, an average value of the volume ratios $V\gamma$ of retained austenite of the six pairs was defined as the volume ratio (%) of retained austenite.

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

[0190] Where, $I\alpha$ is an integrated intensity of α phase. $R\alpha$ is a crystallographic theoretical calculation value of α phase. $I\gamma$ is an integrated intensity of γ phase. $R\gamma$ is a crystallographic theoretical calculation value of γ phase. Note that, $R\alpha$ in the (200) plane of α phase was set to 15.9, $R\alpha$ in the (211) plane of α phase was set to 29.2, $R\gamma$ in the (200) plane of γ

phase was set to 35.5, Rγ in the (220) plane of γ phase was set to 20.8, and Rγ in the (311) plane of γ phase was set to 21.8. The volume ratio of retained austenite was obtained by rounding off the second decimal place of the obtained numerical value.

[0191] The volume ratio (%) of retained austenite obtained by the X-ray diffraction method described above was used to obtain the volume ratio (%) of martensite in the microstructure of the seamless steel pipe by the following Formula.

$$\text{Volume ratio of martensite} = 100.0 - \text{volume ratio of retained austenite (\%)}$$

[0192] The measurement results showed that in each test number the volume ratio of martensite was 80.0% or more.

[(2) Cr concentration, Mo concentration, and Cu concentration measurement test]

[0193] The degree of Cr segregation ΔCr, the degree of Mo segregation ΔMo, and the degree of Cu segregation ΔCu of each test number were determined by the following method.

[0194] In a cross section including a rolling direction L and a wall thickness direction T of the seamless steel pipe, an arbitrary two points at positions at a depth of 2 mm from the inner surface were defined as two center points P1. Two line segments of 1000 μm extending in the wall thickness direction T with each center point P1 as a center were defined as two line segments LS. On each line segment LS, point analysis using energy dispersive X-ray spectroscopy (EDS) was performed at measurement positions at a pitch of 1 μm, and the Cr concentration (mass%), the Mo concentration (mass%), and the Cu concentration (mass%) at each measurement position were determined. In the point analysis, the accelerating voltage was set to 20 kV.

[0195] The following items were defined based on the measured Cr concentration, Mo concentration, and Cu concentration.

(A) An average value of all of the Cr concentrations determined at all of the measurement positions on the two line segments LS was defined as $[Cr]_{ave}$.

(B) A sample standard deviation of all of the Cr concentrations determined at all of the measurement positions on the two line segments LS was defined as σ_{Cr}.

(C) Based on the three sigma rule, among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ was defined as $[Cr^*]_{ave}$.

(D) Among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ was defined as $[Cr^*]_{max}$.

(E) Among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ was defined as $[Cr^*]_{min}$.

(F) An average value of all of the Mo concentrations determined at all of the measurement positions on the two line segments LS was defined as $[Mo]_{ave}$.

(G) A sample standard deviation of all of the Mo concentrations determined at all of the measurement positions on the two line segments LS was defined as σ_{Mo}.

(H) Based on the three sigma rule, among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ was defined as $[Mo^*]_{ave}$.

(I) Among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ was defined as $[Mo^*]_{max}$.

(J) Among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ was defined as $[Mo^*]_{min}$.

(K) An average value of all of the Cu concentrations determined at all of the measurement positions on the two line segments LS was defined as $[Cu]_{ave}$.

(L) A sample standard deviation of all of the Cu concentrations determined at all of the measurement positions on the two line segments LS was defined as σ_{Cu}.

(M) Based on the three sigma rule, among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ was defined as $[Cu^*]_{ave}$.

(N) Among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ was defined as $[Cu^*]_{max}$.

(O) Among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ was defined as $[Cu^*]_{min}$.

[0196] Based on the items determined in the above (A) to (O), a degree of Cr segregation ΔCr defined by Formula (1) was determined, a degree of Mo segregation ΔMo defined by Formula (2) was determined, and a degree of Cu segregation ΔCu defined by Formula (3) was determined.

$$\Delta Cr = ([Cr^*]_{max} - [Cr^*]_{min})/[Cr^*]_{ave} \quad (1)$$

$$\Delta Mo = ([Mo^*]_{max} - [Mo^*]_{min})/[Mo^*]_{ave} \quad (2)$$

$$\Delta Cu = ([Cu^*]_{max} - [Cu^*]_{min})/[Cu^*]_{ave} \quad (3)$$

[0197] Based on the obtained degree of Cr segregation ΔCr, degree of Mo segregation ΔMo, and degree of Cu segregation ΔCu, a total degree of segregation ΔF defined by the following formula was determined.

$$\Delta F = \Delta Cr + \Delta Mo + \Delta Cu$$

[0198] The degree of Cr segregation ΔCr, the degree of Mo segregation ΔMo, the degree of Cu segregation ΔCu, and ΔF are shown in Table 2.

[(3) Tensile test]

[0199] The yield strength of the seamless steel pipe of each test number was determined by the following method. A tensile test specimen was taken from the center portion of the wall thickness of the seamless steel pipe. The tensile test specimen was a round bar tensile test specimen in which the diameter of the parallel portion was 6.0 mm, and the length of the parallel portion was 40.0 mm. The longitudinal direction of the parallel portion of the round bar tensile test specimen was parallel to the rolling direction (longitudinal direction) of the seamless steel pipe. A tensile test was conducted at 24°C in conformity with ASTM E8/E8M (2013) using the round bar tensile test specimen, 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 is shown in Table 2.

[(4) SSC resistance evaluation test]

[0200] The seamless steel pipe of each test number was subjected to an SSC resistance evaluation test in accordance with NACE TM0177-2005 Method A. A round bar specimen was taken from the center portion of the wall thickness of the seamless steel pipe. The round bar specimen had a size in which the diameter of the parallel portion was 6.35 mm, and the length of the parallel portion was 25.4 mm. The longitudinal direction of the parallel portion of the round bar specimen was parallel to the rolling direction (longitudinal direction) of the seamless steel pipe.

[0201] An aqueous solution containing 20 mass% of sodium chloride in which the pH was 4.0 was adopted as the test solution. A stress equivalent to 90% of the actual yield stress was applied to the round bar specimen. The test solution at 24°C was poured into a test vessel so that the round bar specimen to which the stress had been applied was immersed therein, and this was adopted as the test bath. After degassing the test bath, a gaseous mixture consisting of H_2S at 0.10 bar and CO_2 at 0.90 bar was blown into the test bath so that the test bath was saturated with H_2S gas. The test bath in which the H_2S gas was saturated was held at 24°C for 720 hours. After the test specimen had been held for 720 hours, the surface of the test specimen was observed with a magnifying glass with a magnification of ×10 to check for the presence of cracking. If a place where cracking was suspected was found in the observation with the magnifying glass, a cross section at the place where cracking was suspected was observed with an optical microscope with a magnification of ×100 to confirm whether cracking was present.

[0202] If the result of confirming whether cracking was present was that cracking was not confirmed even when observed with the magnifying glass with a magnification of ×10 and the optical microscope with a magnification of ×100, the relevant seamless steel pipe was evaluated as being excellent in SSC resistance (described as "P" (Pass) in the column "SSC resistance" in Table 2). On the other hand, if cracking was confirmed when the surface of the test specimen was observed with the magnifying glass with a magnification of ×10 or the optical microscope with a magnification of ×100, the relevant seamless steel pipe was evaluated as having low SSC resistance (described as "F" (Fail) in the column "SSC resistance" in Table 2).

[Evaluation results]

[0203] Referring to Table 2, in Test Numbers 1 to 23, the content of each element in the chemical composition was within the range of the present embodiment. In addition, in the heating process, the in-furnace temperature and residence time in the preheating zone were appropriate, the in-furnace temperature T in the heating zone and the holding zone was 1225 to 1275°C, and FA was 2900 or more. Therefore, the total degree of segregation ΔF was 0.70 or less, and the Cr concentration distribution, the Mo concentration distribution, and the Cu concentration distribution in a microscopic segregation region in the steel material were sufficiently uniform. As a result, the yield strength was 110 ksi grade (758 to less than 862 MPa), and excellent SSC resistance was obtained.

[0204] In Test Number 24, the content of Cr was too low. Therefore, the SSC resistance was low.

[0205] In Test Number 25, the content of Cr was too high. Therefore, the total degree of segregation ΔF was more than 0.70. As a result, the SSC resistance was low.

[0206] In Test Number 26, the content of Mo was too low. Therefore, the SSC resistance was low.

[0207] In Test Number 27, the content of Mo was too high. Therefore, the total degree of segregation ΔF was more than 0.70. As a result, the SSC resistance was low.

[0208] In Test Number 28, the content of Cu was too low. Therefore, the SSC resistance was low.

[0209] In Test Number 29, the content of Cu was too high. Therefore, the total degree of segregation ΔF was more than 0.70. As a result, the SSC resistance was low.

[0210] On the other hand, in Test Numbers 30 to 39, although the content of each element in the chemical composition was within the range of the present embodiment, FA was less than 2900 and Formula (A) was not satisfied. Therefore, the total degree of segregation ΔF in these test numbers was more than 0.70. As a result, in these test numbers the SSC resistance was low.

EXAMPLE 2

[0211] Steel materials (seamless steel pipes) having a yield strength of 125 ksi or more (862 MPa or more) were produced by the same production method as the method used in Example 1. The produced steel materials were subjected to the same evaluation tests as in Example 1.

[Production of steel material]

[Starting material preparation process]

[0212] Molten steels having the chemical compositions shown in Table 3 were produced.

[Table 3]

[0213]

TABLE3

Test No.	Chemical Composition Values (mass%; balance: Fe and impurities)																		
	C	Si	Mn	P	S	Ni	Cr	Mo	Al	V	N	Ti	Cu	Co	B	Ca	Mg	REM	Nb	W
1	0.008	0.38	0.30	0.012	0.0011	6.03	12.40	2.33	0.034	0.04	0.0043	0.110	1.85	0.19	-	-	-	-	-	-
2	0.028	0.33	0.41	0.012	0.0005	5.89	13.00	2.50	0.031	0.06	0.0051	0.120	2.21	0.24	-	-	-	-	-	-
3	0.009	0.33	0.46	0.013	0.0005	5.72	12.00	2.49	0.029	0.07	0.0066	0.120	2.89	0.10	-	-	-	-	-	-
4	0.010	0.27	0.35	0.010	0.0006	5.87	12.90	2.37	0.038	0.05	0.0062	0.100	2.61	0.20	-	-	-	-	-	-
5	0.010	0.30	0.41	0.011	0.0009	5.98	13.00	2.55	0.038	0.05	0.0044	0.080	2.70	0.25	-	-	-	-	-	-
6	0.008	0.28	0.45	0.014	0.0008	5.62	10.30	2.37	0.037	0.04	0.0065	0.050	2.10	0.22	-	-	-	-	-	-
7	0.012	0.25	0.34	0.016	0.0007	5.95	13.30	2.11	0.037	0.04	0.0065	0.110	2.21	0.10	-	-	-	-	-	-
8	0.012	0.33	0.36	0.016	0.0005	5.70	13.20	2.01	0.037	0.04	0.0065	0.090	1.99	0.17	-	-	-	-	-	-
9	0.010	0.27	0.43	0.017	0.0005	5.45	12.20	2.66	0.037	0.04	0.0065	0.120	2.21	0.38	-	-	-	-	-	-
10	0.011	0.29	0.34	0.016	0.0005	5.30	11.10	2.52	0.037	0.04	0.0065	0.050	1.61	0.12	-	-	-	-	-	-
11	0.010	0.28	0.32	0.013	0.0006	5.48	11.10	2.38	0.037	0.04	0.0065	0.070	3.13	0.35	-	-	-	-	-	-
12	0.012	0.36	0.35	0.011	0.0011	5.73	12.20	2.54	0.030	0.05	0.0037	0.060	2.48	0.21	0.0004	-	-	-	-	-
13	0.011	0.26	0.49	0.017	0.0008	6.01	12.50	2.32	0.038	0.04	0.0045	0.060	2.80	0.19	-	0.0030	-	-	-	-
14	0.029	0.29	0.37	0.011	0.0005	6.08	12.70	2.47	0.034	0.05	0.0053	0.110	2.18	0.32	-	-	0.0037	-	-	-
15	0.029	0.27	0.35	0.013	0.0005	6.05	12.80	2.48	0.034	0.04	0.0058	0.110	2.23	0.28	-	-	-	0.0035	-	-
16	0.008	0.38	0.37	0.017	0.0007	6.03	12.60	2.40	0.036	0.04	0.0062	0.130	2.92	0.35	-	-	-	-	0.11	-
17	0.010	0.24	0.42	0.011	0.0006	5.76	13.10	2.51	0.035	0.05	0.0036	0.060	1.81	0.21	-	-	-	-	-	0.07
18	0.012	0.22	0.37	0.016	0.0011	5.50	11.20	2.62	0.027	0.07	0.0050	0.100	2.94	0.26	-	-	-	-	0.04	0.07
19	0.009	0.27	0.40	0.012	0.0010	6.14	12.70	2.40	0.034	0.04	0.0040	0.110	2.80	0.34	0.0003	-	-	-	0.04	0.09
20	0.010	0.22	0.32	0.011	0.0009	5.62	11.70	2.53	0.033	0.04	0.0052	0.090	1.81	0.13	0.0003	0.0033	-	-	0.04	0.12
21	0.011	0.23	0.42	0.012	0.0009	5.94	12.80	2.32	0.035	0.03	0.0037	0.070	2.85	0.27	0.0002	-	-	0.0012	0.05	0.08

22	0.010	0.27	0.48	0.013	0.0005	5.83	11.60	2.40	0.034	0.04	0.0054	0.050	2.40	0.29	0.0003	-	0.0010	0.0012	0.11	0.12
23	0.011	0.26	0.49	0.012	0.0007	5.22	11.50	2.68	0.029	0.06	0.0043	0.060	2.83	0.13	0.0004	-	0.0017	0.0014	0.01	0.05
24	0.012	0.37	0.47	0.011	0.0009	5.98	11.80	2.46	0.035	0.04	0.0036	0.100	2.99	0.24	0.0005	0.0029	0.0015	0.0010	0.06	0.05
25	0.011	0.37	0.49	0.012	0.0006	5.80	9.50	2.70	0.031	0.05	0.0042	0.090	2.70	0.35	-	-	-	-	-	-
26	0.010	0.24	0.49	0.011	0.0006	5.49	15.50	2.68	0.026	0.05	0.0033	0.060	2.43	0.17	-	-	-	-	-	-
27	0.012	0.37	0.32	0.012	0.0006	5.62	11.70	1.41	0.025	0.07	0.0063	0.120	2.15	0.21	-	-	-	-	-	-
28	0.009	0.25	0.32	0.011	0.0006	5.71	13.40	3.12	0.032	0.04	0.0048	0.090	2.88	0.10	-	-	-	-	-	-
29	0.012	0.32	0.37	0.017	0.0009	5.64	12.30	2.33	0.029	0.06	0.0060	0.090	0.95	0.21	-	-	-	-	-	-
30	0.012	0.32	0.47	0.017	0.0005	5.80	13.30	2.68	0.038	0.07	0.0064	0.090	3.81	0.17	-	-	-	-	-	-
31	0.009	0.21	0.48	0.014	0.0010	5.57	12.28	1.93	0.029	0.05	0.0065	0.091	2.01	0.12	-	-	-	-	-	-
32	0.010	0.33	0.38	0.012	0.0010	6.04	13.20	2.29	0.030	0.05	0.0049	0.090	2.11	0.25	-	-	-	-	-	-
33	0.010	0.29	0.36	0.016	0.0005	5.39	13.30	2.60	0.025	0.05	0.0034	0.110	2.61	0.29	-	-	-	-	0.14	-
34	0.010	0.22	0.48	0.013	0.0011	5.78	11.20	2.56	0.033	0.06	0.0057	0.060	2.33	0.12	-	-	-	-	-	0.06
35	0.011	0.25	0.45	0.016	0.0007	6.13	12.50	2.38	0.034	0.05	0.0066	0.130	1.92	0.26	-	-	-	-	0.02	0.15
36	0.012	0.26	0.49	0.017	0.0005	6.06	12.30	2.70	0.029	0.05	0.0033	0.060	2.13	0.26	0.0005	-	-	-	-	-
37	0.008	0.25	0.40	0.016	0.0008	5.68	11.60	2.50	0.026	0.05	0.0053	0.120	2.29	0.35	-	0.0015	-	-	-	-
38	0.012	0.28	0.31	0.014	0.0006	5.85	11.60	2.68	0.035	0.06	0.0055	0.080	2.82	0.23	0.0003	0.0032	-	-	-	-
39	0.008	0.26	0.48	0.015	0.0008	6.14	12.40	2.37	0.037	0.04	0.0065	0.080	2.24	0.11	0.0003	0.0009	0.0005	0.0005	0.15	0.20
40	0.009	0.26	0.40	0.012	0.0009	5.84	12.80	2.50	0.033	0.05	0.0050	0.099	2.33	0.19	-	-	-	-	-	-

[0214] The produced molten steels were used to produce blooms by continuous casting. Next, similarly to Example 1, a blooming process was performed to produce round billets having a diameter of 310 mm. The in-furnace temperature (°C) and holding time (minutes) in the bloom reheating furnace were as shown in Table 4.

[Table 4]

[0215]

TABLE4

Test No.	Blooming Process		Steel Material Production Process						ΔCr	ΔMo	ΔCu	ΔF	Tempering Process		Yield Strength (MPa)	SSC Resistance
	In-furnace Temperature in Bloom Reheating Furnace (°C)	Holding Time in Bloom Reheating Furnace (min)	In-furnace Temperature in Preheating Zone (°C)	Residence Time in Preheating Zone (nun)	In-furnace Temperature T (°C) in Heating Zone and Holding Zone	Total Residence Time t (min) in Heating Zone and Holding Zone	FA	Furnace Time in Heating Furnace (nun)					Temperature (°C)	Holding Time (min)		
1	1260	255	1080	190	1250	447	4157	637	0.05	0.22	0.18	0.45	606	23	915	P
2	1250	241	1090	170	1250	484	4326	654	0.05	0.26	0.12	0.43	580	25	938	P
3	1250	238	1070	178	1275	400	3997	578	0.05	0.23	0.19	0.47	602	40	881	P
4	1250	220	1120	180	1250	401	3937	581	0.05	0.23	0.17	0.45	605	39	885	P
5	1250	203	1150	157	1250	405	3957	562	0.05	0.26	0.11	0.42	592	40	902	P
6	1250	235	1050	188	1250	446	4152	634	0.05	0.28	0.14	0.47	606	26	903	P
7	1260	267	1130	170	1250	485	4330	655	0.05	0.26	0.14	0.45	587	31	920	P
8	1250	268	1060	176	1250	526	4509	702	0.04	0.26	0.12	0.42	590	35	893	P
9	1260	386	1140	184	1250	514	4458	698	0.04	0.24	0.13	0.41	599	20	919	P
10	1250	254	1100	187	1250	492	4361	679	0.05	0.27	0.11	0.43	599	34	901	P
11	1260	301	1060	189	1250	436	4106	625	0.06	0.11	0.27	0.44	610	22	890	P
12	1260	330	1140	170	1250	443	4138	613	0.05	0.22	0.19	0.46	605	25	916	P
13	1270	233	1070	164	1250	475	4285	639	0.05	0.20	0.17	0.42	599	22	938	P
14	1250	251	1090	160	1250	510	4440	670	0.05	0.29	0.13	0.47	585	27	941	P
15	1250	277	1080	172	1250	509	4436	681	0.04	0.29	0.13	0.46	580	24	946	P
16	1260	280	1060	180	1250	489	4348	669	0.05	0.26	0.12	0.43	591	29	912	P
17	1260	312	1110	180	1250	490	4352	670	0.06	0.29	0.08	0.43	591	36	937	P
18	1260	326	1130	191	1250	544	4586	735	0.04	0.20	0.18	0.42	588	22	939	P

(continued)

Test No.	Blooming Process		Steel Material Production Process						ΔCr	ΔMo	ΔCu	ΔF	Tempering Process		Yield Strength (MPa)	SSC Resistance
	In-furnace Temperature in Bloom Reheating Furnace (°C)	Holding Time in Bloom Reheating Furnace (min)	In-furnace Temperature in Preheating Zone (°C)	Residence Time in Preheating Zone (nun)	In-furnace Temperature T (°C) in Heating Zone and Holding Zone	Total Residence Time t (min) in Heating Zone and Holding Zone	FA	Furnace Time in Heating Furnace (nun)					Temperature (°C)	Holding Time (min)		
19	1260	299	1070	185	1250	443	4138	628	0.05	0.20	0.20	0.45	605	42	914	P
20	1270	204	1070	170	1250	423	4044	593	0.06	0.34	0.08	0.48	609	36	890	P
21	1250	256	1120	184	1250	439	4120	623	0.05	0.23	0.19	0.47	610	35	904	P
22	1250	245	1110	174	1250	520	4484	694	0.04	0.29	0.10	0.43	586	21	904	P
23	1260	212	1070	166	1250	428	4068	594	0.05	0.25	0.14	0.44	607	43	883	P
24	1270	294	1080	169	1225	474	4210	643	0.04	0.24	0.15	0.43	610	43	873	P
25	1250	344	1110	200	1250	531	4531	731	0.04	0.26	0.17	0.47	605	31	874	F
26	1250	360	1060	185	1250	488	4343	673	0.09	0.34	0.26	0.69	589	43	978	F
27	1260	221	1110	175	1250	544	4586	719	0.06	0.19	0.19	0.44	604	38	891	F
28	1250	238	1100	182	1250	447	4157	629	0.11	0.31	0.32	0.74	588	23	963	F
29	1270	262	1130	191	1250	484	4326	675	0.05	0.30	0.08	0.43	590	40	914	F
30	1260	300	1120	175	1250	422	4039	597	0.09	0.24	0.45	0.78	606	25	988	F
31	1260	257	1090	160	1250	341	3631	501	0.07	0.28	0.23	0.58	598	26	927	F
32	1250	226	1090	170	1250	288	3337	458	0.06	0.25	0.22	0.53	590	43	907	F
33	1270	300	1070	176	1250	317	3501	493	0.07	0.21	0.25	0.53	600	32	915	F
34	1270	208	1150	165	1250	304	3428	469	0.05	0.26	0.22	0.53	590	41	909	F
35	1260	240	1140	168	1250	313	3479	481	0.08	0.32	0.14	0.54	585	32	938	F
36	1250	354	1090	174	1250	326	3550	500	0.07	0.35	0.17	0.59	585	22	950	F
37	1250	288	1110	158	1250	316	3495	474	0.05	0.25	0.22	0.52	610	26	881	F

(continued)

Test No.	Blooming Process		Steel Material Production Process									Tempering Process		Yield Strength (MPa)	SSC Resistance
	In-furnace Temperature in Bloom Reheating Furnace (°C)	Holding Time in Bloom Reheating Furnace (min)	In-furnace Temperature in Preheating Zone (°C)	Residence Time in Preheating Zone (nun)	In-furnace Temperature T (°C) in Heating Zone and Holding Zone	Total Residence Time t (min) in Heating Zone and Holding Zone	FA	Fumace Time in Heating Fumace (nun)	ΔCr	ΔMo	ΔCu	ΔF	Temperature (°C)	Holding Time (min)		
38	1250	303	1120	158	1250	344	3647	502	0.07	0.29	0.21	0.57	600	34	880	F
39	1250	290	1150	154	1250	328	3561	482	0.06	0.25	0.21	0.52	593	22	905	F
40	1260	266	1060	156	1225	403	3882	559	0.06	0.32	0.17	0.55	595	39	902	F

[0216] Next, similarly to Example 1, the round billet of each test number was subjected to a steel material production process. In the steel material heating process, the in-furnace temperature (°C) in the preheating zone, the residence time (minutes) in the preheating zone, the in-furnace temperature T (°C) in the heating zone and the holding zone, and the total residence time t (minutes) in the heating zone and the holding zone were as shown in Table 4. Further, FA = $(t/60)^{0.5} \times (T + 273)$ was as shown in Table 4.

[0217] Each heated round billet was subjected to hot working under the same conditions as in Example 1 to thereby produce a hollow shell for each test number. In addition, each produced hollow shell was subjected to a heat treatment process (quenching process and tempering process). In the quenching process, the quenching temperature was set to 910°C, and the holding time at the quenching temperature was set to 15 minutes. In the tempering process, the tempering temperature (°C) was set as shown in Table 4, and the holding time (minutes) at the tempering temperature was set as shown in Table 4. The yield strength was adjusted to 125 ksi or more (862 MPa or more) by the heat treatment process. Martensitic stainless steel materials (seamless steel pipes) were produced by the above production process.

[Evaluation tests]

[0218] The seamless steel pipe of each test number was subjected to the following evaluation tests by the same methods as the methods employed in Example 1.

(1) Microstructure observation test
(2) Cr concentration, Mo concentration, and Cu concentration measurement test
(3) Tensile test
(4) SSC resistance evaluation test

[0219] The result of the microstructure observation test showed that, in each test number, the volume ratio of martensite was 80.0% or more. The results for degree of Cr segregation ΔCr, degree of Mo segregation ΔMo, degree of Cu segregation ΔCu, ΔF, yield strength, and SSC resistance evaluation obtained in the evaluation tests of (2) to (4) mentioned above are shown in Table 4.

[Evaluation results]

[0220] Referring to Table 4, in Test Numbers 1 to 24, the content of each element in the chemical composition was within the range of the present embodiment. In addition, in the heating process, the in-furnace temperature and residence time in the preheating zone were appropriate, the in-furnace temperature T in the heating zone and the holding zone was 1225 to 1275°C, and FA was 3900 or more. Therefore, the total degree of segregation ΔF was 0.50 or less, and the Cr concentration distribution, the Mo concentration distribution, and the Cu concentration distribution in a microscopic segregation region in the steel material were sufficiently uniform. As a result, the yield strength was 125 ksi grade or more (862 MPa or more), and excellent SSC resistance was obtained.

[0221] On the other hand, in Test Number 25 the content of Cr was too low. Therefore, the SSC resistance was low.

[0222] In Test Number 26 the content of Cr was too high. Therefore, the total degree of segregation ΔF was more than 0.50. As a result, the SSC resistance was low.

[0223] In Test Number 27 the content of Mo was too low. Therefore, the SSC resistance was low.

[0224] In Test Number 28 the content of Mo was too high. Therefore, the total degree of segregation ΔF was more than 0.50. As a result, the SSC resistance was low.

[0225] In Test Number 29 the content of Cu was too low. Therefore, the SSC resistance was low.

[0226] In Test Number 30, the content of Cu was too high. Therefore, the total degree of segregation ΔF was more than 0.50. As a result, the SSC resistance was low.

[0227] In Test Numbers 31 to 40, although the content of each element in the chemical composition was within the range of the present embodiment, FA was less than 3900 and Formula (A) was not satisfied. Therefore, the total degree of segregation ΔF in these test numbers was more than 0.50. As a result, in these test numbers the SSC resistance was low.

[0228] An embodiment of the present disclosure has been described above. However, the foregoing embodiment is merely an example for implementing the present disclosure. Accordingly, the present disclosure is not limited to the above embodiment, and the above embodiment can be appropriately modified and implemented within a range which does not deviate from the gist of the present disclosure.

REFERENCE SIGNS LIST

[0229]

10 Heating furnace
100 Billet
SE Segregation region
Z1 Preheating zone
Z2 Heating zone
Z3 Holding zone

Claims

1. A martensitic stainless steel material that is a seamless steel pipe or a round steel bar, having a chemical composition 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,
Ni: 5.00 to 7.00%,
Cr: 10.00 to 14.00%,
Mo: 1.50 to 3.00%,
Al: 0.005 to 0.050%,
V: 0.01 to 0.30%,
N: 0.0030 to 0.0500%,
Ti: 0.020 to 0.150%,
Cu: more than 1.00 to 3.50%,
Co: 0.50% or less,
B: 0 to 0.0050%,
Ca: 0 to 0.0050%,
Mg: 0 to 0.0050%,
rare earth metal (REM): 0 to 0.0050%,
Nb: 0 to 0.15%, and
W: 0 to 0.20%,
with the balance being Fe and impurities,
wherein:

a yield strength is 758 MPa or more;
in a case where the martensitic stainless steel material is the seamless steel pipe,
when, in a cross section including a rolling direction and a wall thickness direction of the seamless steel pipe, an arbitrary two points at positions at a depth of 2 mm from an inner surface are defined as two center points P1, and two line segments of 1000 μm extending in the wall thickness direction with each center point P1 as a center are defined as two line segments LS, energy dispersive X-ray spectroscopy is performed at measurement positions at a pitch of 1 μm on each line segment LS, and a Cr concentration, a Mo concentration, and a Cu concentration at each measurement position are determined;
in a case where the martensitic stainless steel material is the round steel bar, when, in a cross section including a rolling direction and a radial direction of the round steel bar, an arbitrary two points on a central axis of the round steel bar are defined as two center points P1, and two line segments of 1000 μm extending in the radial direction with each center point P1 as a center are defined as two line segments LS, energy dispersive X-ray spectroscopy is performed at measurement positions at a pitch of 1 μm on each line segment LS, and a Cr concentration, a Mo concentration, and a Cu concentration at each measurement position are determined; and
when:

an average value of all of the Cr concentrations determined at all of the measurement positions on the two line segments LS is defined as $[Cr]_{ave}$,
a sample standard deviation of all of the Cr concentrations determined at all of the measurement positions on the two line segments LS is defined as σ_{Cr},
among all of the Cr concentrations determined at all of the measurement positions on the two line

segments LS, an average value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ is defined as $[Cr^*]_{ave}$,
among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ is defined as $[Cr^*]_{max}$,
among all of the Cr concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Cr concentrations included within a range of $[Cr]_{ave} \pm 3\sigma_{Cr}$ is defined as $[Cr^*]_{min}$,
an average value of all of the Mo concentrations determined at all of the measurement positions on the two line segments LS is defined as $[Mo]_{ave}$,
a sample standard deviation of all of the Mo concentrations determined at all of the measurement positions on the two line segments LS is defined as σ_{Mo},
among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ is defined as $[Mo^*]_{ave}$,
among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ is defined as $[Mo^*]_{max}$,
among all of the Mo concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Mo concentrations included within a range of $[Mo]_{ave} \pm 3\sigma_{Mo}$ is defined as $[Mo^*]_{min}$,
an average value of all of the Cu concentrations determined at all of the measurement positions on the two line segments LS is defined as $[Cu]_{ave}$,
a sample standard deviation of all of the Cu concentrations determined at all of the measurement positions on the two line segments LS is defined as σ_{Cu},
among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, an average value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ is defined as $[Cu^*]_{ave}$,
among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, a maximum value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ is defined as $[Cu^*]_{max}$, and
among all of the Cu concentrations determined at all of the measurement positions on the two line segments LS, a minimum value of the Cu concentrations included within a range of $[Cu]_{ave} \pm 3\sigma_{Cu}$ is defined as $[Cu^*]_{min}$,
a degree of Cr segregation ΔCr defined by Formula (1), a degree of Mo segregation ΔMo defined by Formula (2), and a degree of Cu segregation ΔCu defined by Formula (3) satisfy Formula (4):

$$\Delta Cr = ([Cr^*]_{max} - [Cr^*]_{min})/[Cr^*]_{ave} \quad (1)$$

$$\Delta Mo = ([Mo^*]_{max} - [Mo^*]_{min})/[Mo^*]_{ave} \quad (2)$$

$$\Delta Cu = ([Cu^*]_{max} - [Cu^*]_{min})/[Cu^*]_{ave} \quad (3)$$

$$\Delta Cr + \Delta Mo + \Delta Cu \leq A \quad (4)$$

where, in a case where the yield strength is 758 to less than 862 MPa, A in Formula (4) is 0.70, and in a case where the yield strength is 862 MPa or more, A in Formula (4) is 0.50.

2. The martensitic stainless steel material according to claim 1, wherein the chemical composition contains one or more elements selected from the group consisting of:

B: 0.0001 to 0.0050%,
Ca: 0.0001 to 0.0050%,
Mg: 0.0001 to 0.0050%,

rare earth metal (REM): 0.0001 to 0.0050%,
Nb: 0.01 to 0.15%, and
W: 0.01 to 0.20%.

FIG. 1

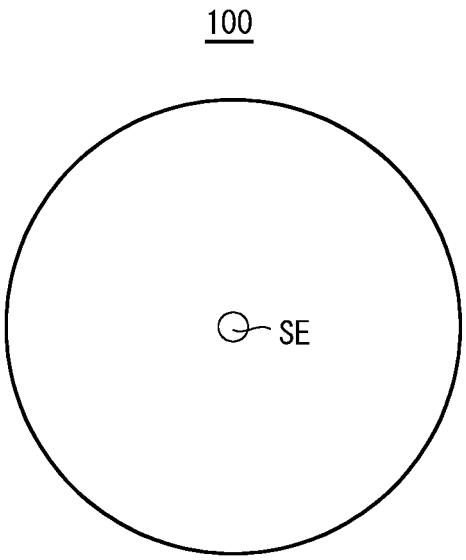


FIG. 2

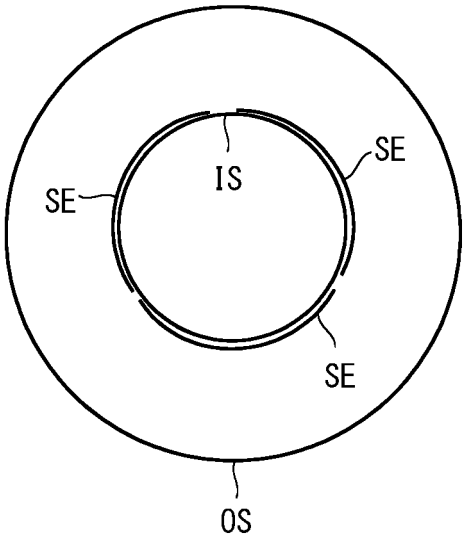


FIG. 3

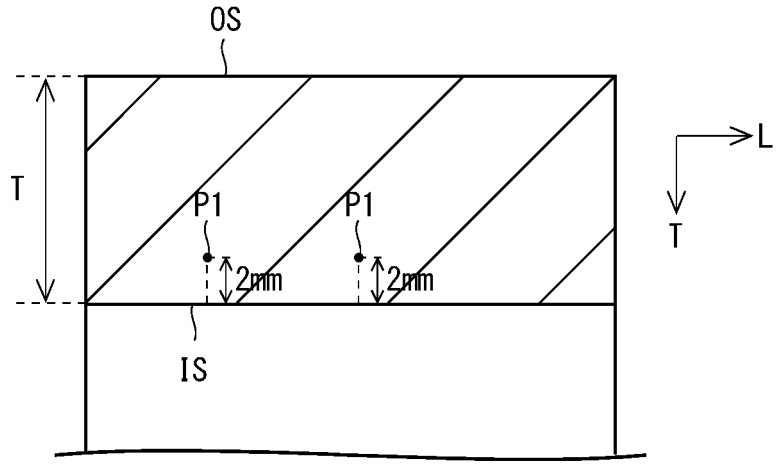


FIG. 4

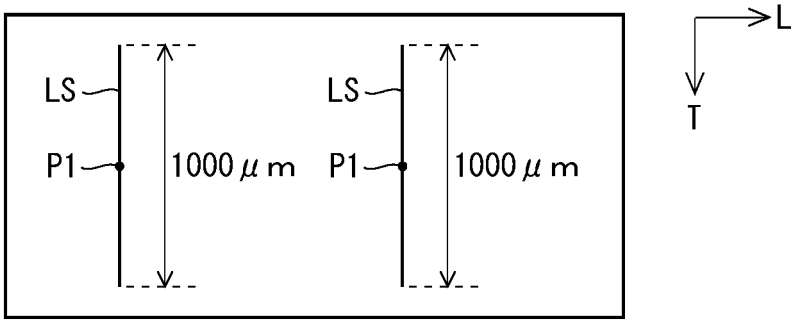


FIG. 5

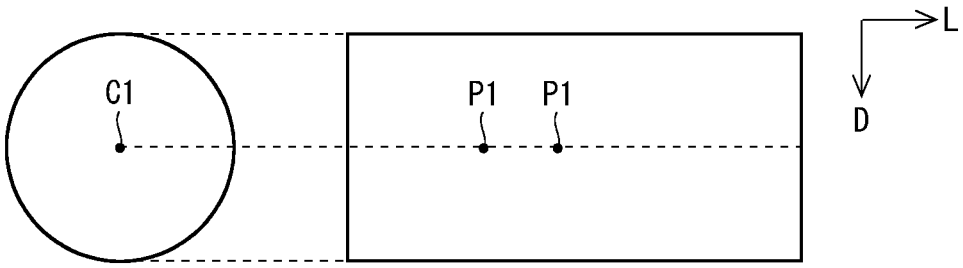


FIG. 6

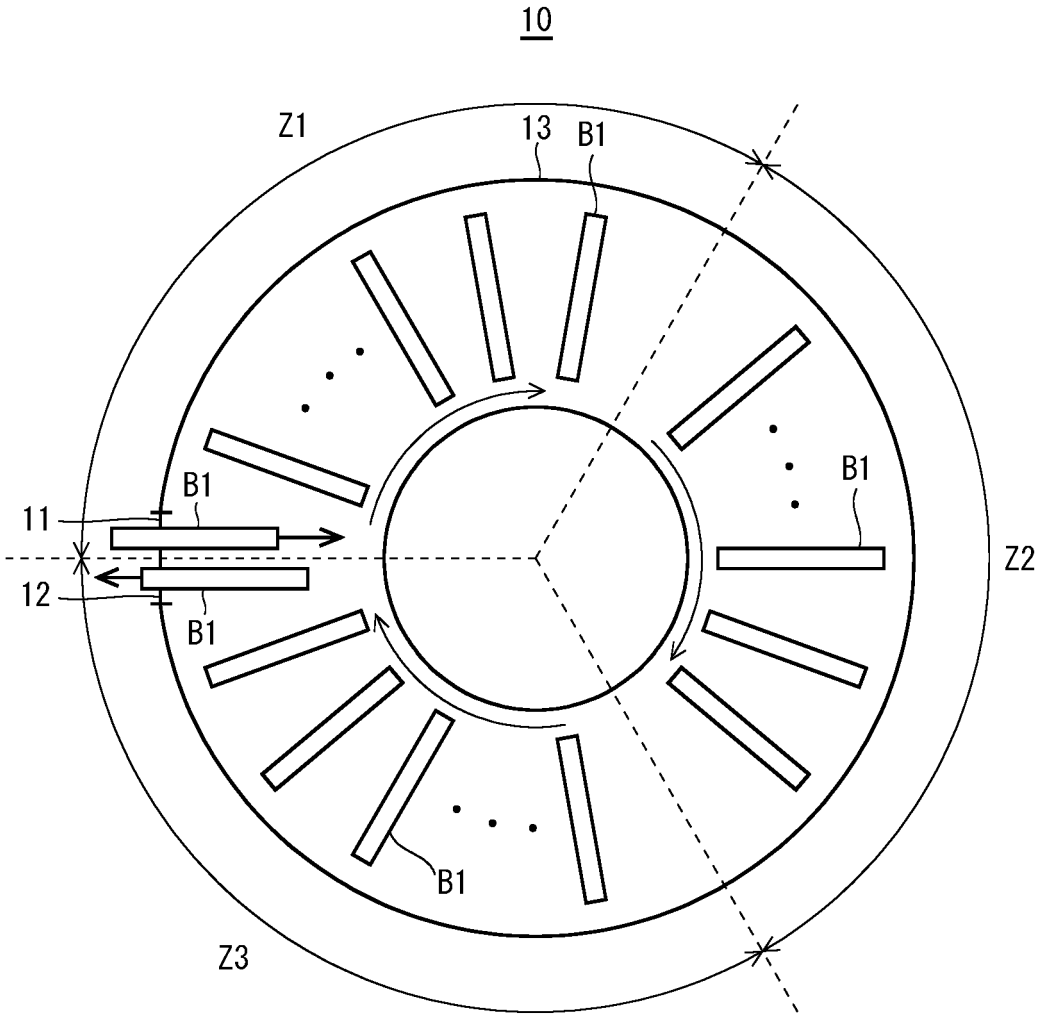
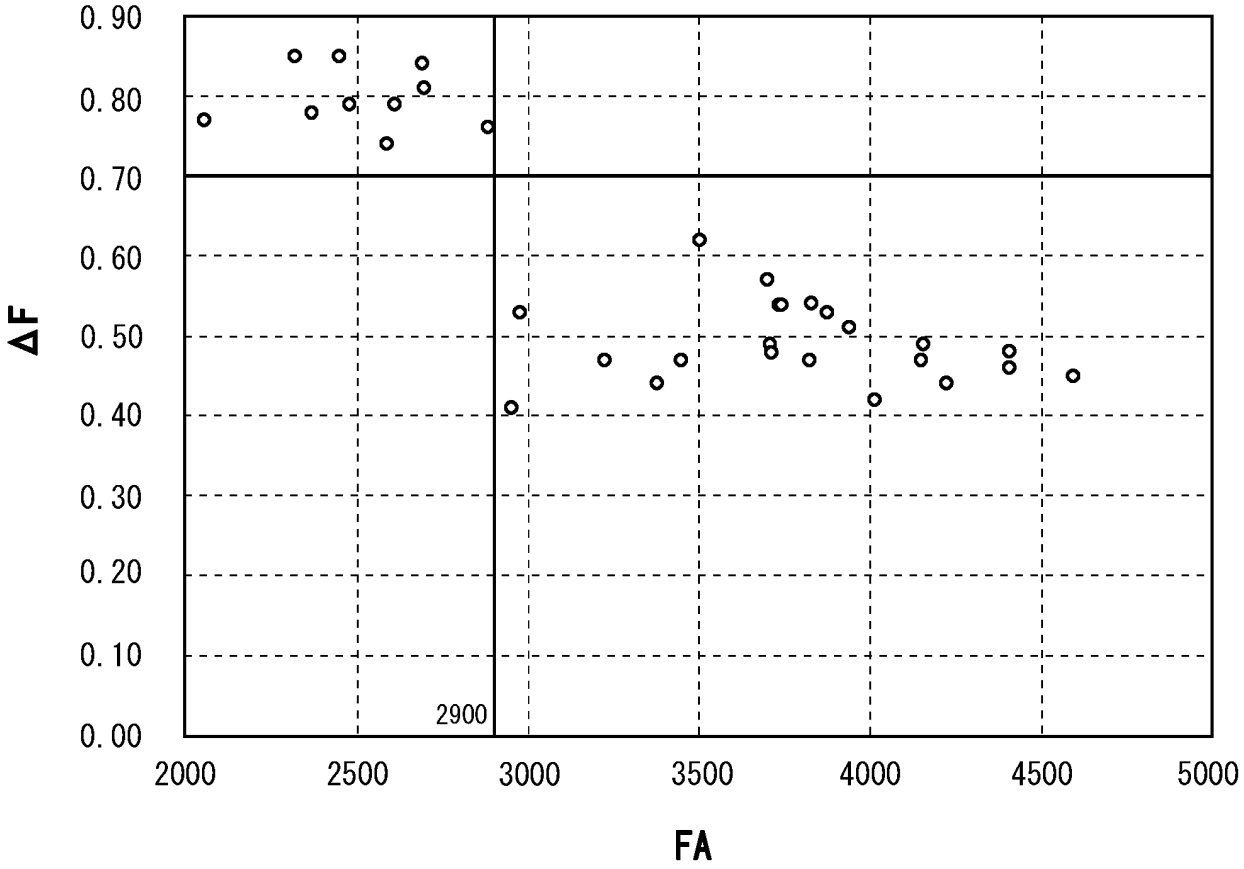


FIG. 7A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0.50
0.40
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0.00
ΔF
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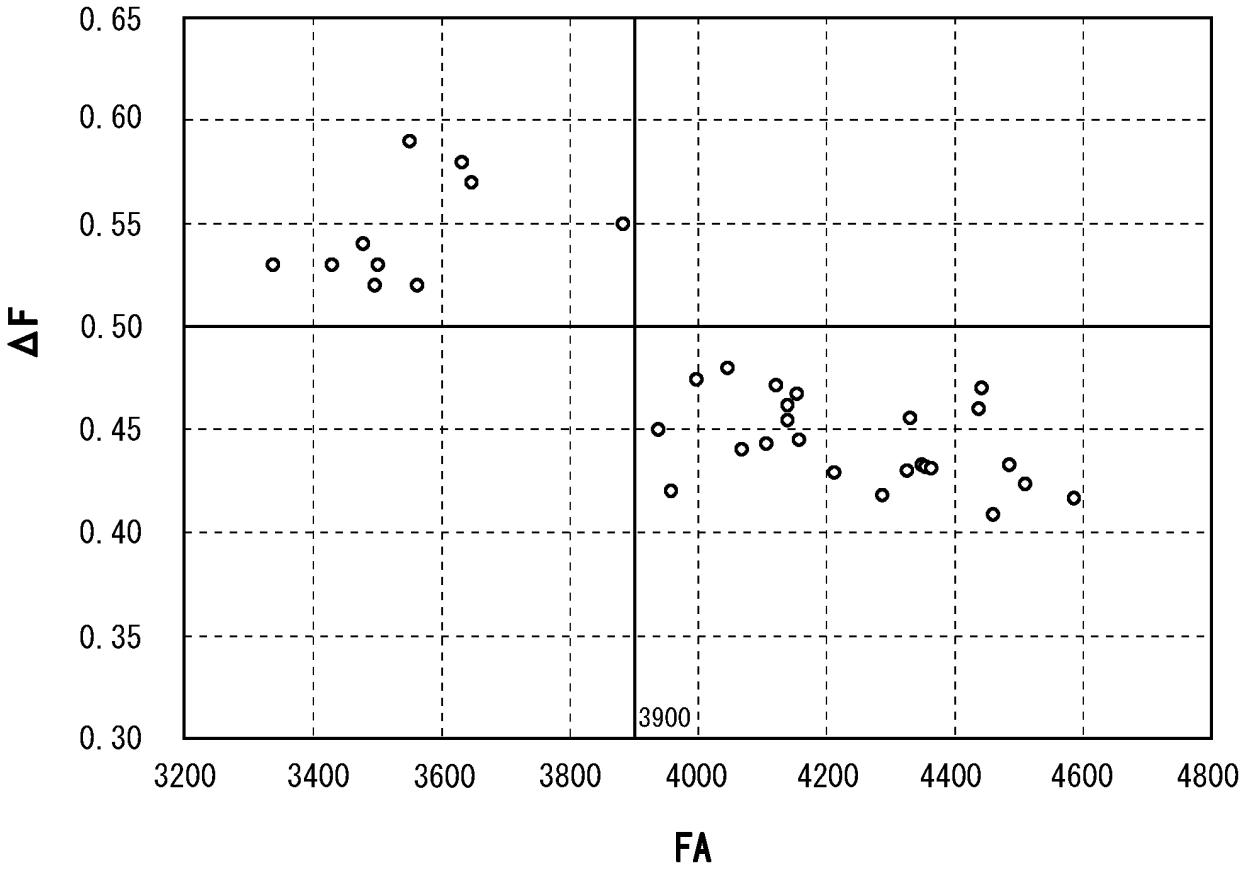
2500
3000
3500
4000
4500
5000
FA

FIG. 7B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4000
4200
4400
4600
4800
FA

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2021/037135

A. CLASSIFICATION OF SUBJECT MATTER

C21D 8/06(2006.01)i; ***C21D 8/10***(2006.01)i; ***C21D 9/00***(2006.01)i; ***C21D 9/08***(2006.01)i; ***C22C 38/00***(2006.01)i; ***C22C 38/54***(2006.01)i
FI: C22C38/00 302Z; C22C38/54; C21D9/08 E; C21D9/00 101A; C21D9/00 101F; C21D8/06 B; 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)

C21D8/00-8/12; C21D9/00-9/70; C22C38/00-38/60

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 1971-2021
Registered utility model specifications of Japan 1996-2021
Published registered utility model applications of Japan 1994-2021

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 2020/071344 A1 (NIPPON STEEL CORP) 09 April 2020 (2020-04-09) entire text	1-2
A	WO 2020/067247 A1 (NIPPON STEEL CORP) 02 April 2020 (2020-04-02) entire text	1-2
A	JP 10-237604 A (NIPPON STEEL CORP) 08 September 1998 (1998-09-08) entire text	1-2

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 December 2021	**21 December 2021**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2021/037135

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2020/071344 A1	09 April 2020	(Family: none)	
WO 2020/067247 A1	02 April 2020	(Family: none)	
JP 10-237604 A	08 September 1998	(Family: none)	

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

REFERENCES CITED IN THE DESCRIPTION

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- JP 8246107 A **[0005] [0009]**