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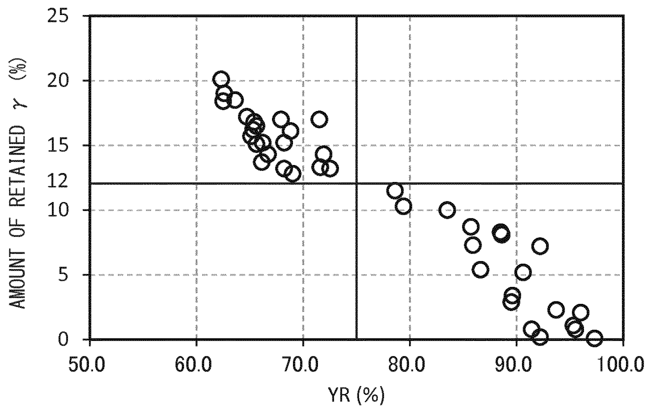
(54) **STAINLESS STEEL PIPE AND METHOD FOR PRODUCING SAME**

(57) A stainless steel pipe having a strength in a predetermined range and a low yield ratio is to be provided. A stainless steel pipe has a chemical composition of, in mass%: C: up to 0.02 %; Si: 0.05 to 1.00 %; Mn: 0.1 to 1.0 %; P: up to 0.030 %; S: up to 0.002 %; Ni: 5.5 to 8 %; Cr: 10 to 14 %; Mo: 2 to 4 %; V: 0.01 to 0.10 %; Ti: 0.05 to 0.3 %; Nb: up to 0.1 %; Al: 0.001 to 0.1 %; N: up to 0.05 %; Cu: up to 0.5 %; Ca: 0 to 0.008 %; Mg: 0 to 0.05 %; B: 0 to 0.005 %; and balance Fe and impurities, the stainless steel pipe having a microstructure including martensite and, by volume fraction, 12 to 18 % retained austenite. The martensite has prior austenite grains of a crystal grain size number lower than 8.0 in accordance with ASTM E112. The stainless steel pipe has a yield strength of 550 to 700 MPa.

Fig.5



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Description

TECHNICAL FIELD

[0001] The present invention relates to a stainless steel pipe and a method of manufacturing the same.

BACKGROUND ART

[0002] Steel pipe for use in extraction and transportation of petroleum, natural gas and other resources is required to have a corrosion resistance and strength that depend on its intended use environment.

[0003] In recent years, development of offshore oil fields has become increasingly large-scale, and flow lines are being installed by means of reeling more frequently. Reeling involves girth-welding steel pipes on land to provide a continuous pipe, winding it into a coil and placing it on a ship, and uncoiling it on the ship and placing it on the seabed. During reeling, the steel pipe experiences plastic deformation, and thus is required to have a low yield ratio.

[0004] JP Hei3(1991)-120337 A describes a martensitic stainless steel for an oil well with good sulfide stress corrosion cracking resistance which contains, in weight%, 8 to 15 % Cr, 2 to 8 % Ni and other elements.

[0005] JP Hei10(1998)-130785 A describes a martensitic stainless steel for an oil well with good sulfide stress corrosion cracking resistance and hot workability which contains, in weight%, 7 to 14 % Cr, 0 to 8 % Ni and other elements.

[0006] JP 2002-105604 A describes a high-Cr martensitic stainless steel pipe for line pipe with good corrosion resistance and weldability which contains 10 to 14 % Cr, 0.2 to 7.0 % Ni and other elements, where the main phase is martensite, and which contains, by area ratio, 5 % or more austenite.

[0007] JP 2001-107199 A describes a martensitic stainless steel with stable magnetic properties which contains 9 to 15 % Cr, 0.5 to 9 % Ni and other elements, where the sum of the proportion of retained austenite in the base material after tempering and the proportion of fresh martensite is not higher than 25 %.

[0008] JP 2001-107198 A describes a martensitic stainless steel mainly composed of tempered martensitic microstructure which contains, by volume fraction, 15 to 40 % retained austenite.

[0009] JP 2001-226749 A describes a low-yield-ratio martensitic stainless steel with good corrosion resistance which contains, by volume fraction, 4 % or more retained austenite and has a yield ratio of 90 % or lower.

[0010] JP 2001-303206 A describes a stainless steel for coiled tubing with good fatigue resistance and corrosion resistance which contains, by volume fraction, 2 % or more retained austenite.

[0011] JP 2000-226614 A describes a martensitic stainless steel in which the strength, stress-corrosion cracking resistance and toughness are improved at the same time while maintaining corrosion resistance.

[0012] JP 2001-107198 A, JP 2001-226749 A, JP 2001-303206 A and JP 2000-226614 listed above describe that tempering is performed on two-phase regions.

DISCLOSURE OF THE INVENTION

[0013] JP 2001-303206 A listed above describes a steel pipe with a yield ratio that is as low as 75 %. To perform reeling in a stable manner, it is preferable to further reduce yield ratio.

[0014] A transportation pipeline is made by girth-welding a plurality of steel pipes and is then put to use. For this purpose, it is preferable to use overmatch joints, in which the weld metal has a higher strength than the base material. As discussed above, a steel pipe for use in a transportation pipeline is required to have a strength that depends on its intended use environment. On the other hand, if the strength is too high, it is difficult to produce overmatch joints. Thus, in steel pipes that are to be welded together before being used, the strength must be adjusted to a predetermined range.

[0015] An object of the present invention is to provide a stainless steel pipe having a strength in a predetermined range and a low yield ratio, and a method of manufacturing such a stainless steel pipe.

[0016] A stainless steel pipe according to an embodiment of the present invention has a chemical composition of, in mass%: C: up to 0.02 %; Si: 0.05 to 1.00 %; Mn: 0.1 to 1.0 %; P: up to 0.030 %; S: up to 0.002 %; Ni: 5.5 to 8 %; Cr: 10 to 14 %; Mo: 2 to 4 %; V: 0.01 to 0.10 %; Ti: 0.05 to 0.3 %; Nb: up to 0.1 %; Al: 0.001 to 0.1 %; N: up to 0.05 %; Cu: up to 0.5 %; Ca: 0 to 0.008 %; Mg: 0 to 0.05 %; B: 0 to 0.005 %; and balance Fe and impurities, the stainless steel pipe having a microstructure including martensite and, by volume fraction, 12 to 18 % retained austenite. The martensite has prior austenite grains of a crystal grain size number lower than 8.0 in accordance with ASTM E112. The stainless steel pipe has a yield strength of 550 to 700 MPa.

[0017] A method of manufacturing a stainless steel pipe according to an embodiment of the present invention includes: hot-working a steel material having a chemical composition of, in mass%: C: up to 0.02 %; Si: 0.05 to 1.00 %; Mn: 0.1 to 1.0 %; P: up to 0.030 %; S: up to 0.002 %; Ni: 5.5 to 8 %; Cr: 10 to 14 %; Mo: 2 to 4 %; V: 0.01 to 0.10 %; Ti: 0.05 to 0.3 %; Nb: up to 0.1 %; Al: 0.001 to 0.1 %; N: up to 0.05 %; Cu: up to 0.5 %; Ca: 0 to 0.008 %; Mg: 0 to 0.05 %; B: 0 to 0.005 %; and balance Fe and impurities, to produce a hollow shell; after the hot-working, quenching the hollow shell from a temperature between 940 and 980 °C in an in-line manner with respect to the hot-working; and tempering the quenched hollow shell at a temperature between the Ac_1 point and Ac_3 point under the conditions described in Equation (1) below:

$$680 \leq T + 15.39 \ln(t) \leq 720 \ \ldots \ (1),$$

where T is a tempering temperature in °C, and t is a tempering time in minutes.

[0018] The present invention provides a stainless steel pipe having a strength in a predetermined range and a low yield ratio.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

[FIG. 1] FIG. 1 is a block diagram showing an exemplary manufacturing line.
[FIG. 2] FIG. 2 is a flow chart showing steps for manufacturing a stainless steel pipe.
[FIG. 3] FIG. 3 is a graph illustrating how the temperature of a workpiece being produced changes over time.
[FIG. 4] FIG. 4 is a scatterplot illustrating the relationship between the volume fraction of retained austenite and yield strength.
[FIG. 5] FIG. 5 is a scatterplot illustrating the relationship between the volume fraction of retained austenite and yield ratio.
[FIG. 6] FIG. 6 is a scatterplot illustrating the relationship between the value of T+15.39ln(t) and the volume fraction of retained austenite.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0020] The present inventors attempted to find out a way to achieve a low yield ratio with a yield strength in a predetermined range by adjusting heat treatment conditions for a stainless steel pipe containing 10 to 14 % Cr, 5.5 to 8 % Ni and other elements. The range of yield strength was set as follows: the lower limit was 550 MPa to provide a strength of grade 80 ksi, and the upper limit was 700 MPa to enable production of overmatch joints. Under these conditions, the inventors attempted to reduce the yield ratio to and below 75 %.

[0021] After an investigation, the inventors found that a stainless steel pipe containing 10 to 14 % Cr, 5.5 to 8 % Ni and other elements which contains, by volume fraction, 12 to 18 % retained austenite and a martensite having prior austenite grains of crystal grain size number lower than 8.0 in accordance with ASTM E112, provides a yield stress ranging from 550 to 700 MPa and a yield ratio not higher than 75 %.

[0022] Further, it was found that the above microstructure can be provided by quenching a post-hot-working hollow shell from a temperature of 940 to 980 °C in an in-line manner and then tempering the quenched steel pipe at a temperature ranging from the Ac_1 point to Ac_3 point under the conditions described in Equation (1) below:

$$680 \leq T + 15.39 \ln(t) \leq 720 \ \ldots \ (1),$$

where T is a tempering temperature in °C, and t is a tempering time in minutes.

[0023] The present invention was made based on the above findings. A stainless steel pipe according to an embodiment of the present invention will now be described in detail with reference to the drawings. The same or corresponding parts in the drawings are labeled with the same characters and their description will not be repeated.

[Chemical Composition]

[0024] The stainless steel pipe according to the present embodiment has the chemical composition described below. In the following description, "%" for the content of an element means mass percent.

C: up to 0.02 %

[0025] Carbon (C) improves the strength of steel. On the other hand, if the C content exceeds 0.02 %, the hardness of heat-affected zones increases and the toughness and sulfide stress corrosion cracking resistance (SSC resistance) decrease. In view of this, the C content should be not higher than 0.02 %. The upper limit of C content is preferably 0.015 %. The lower limit of C content is preferably 0.001 %.

Si: 0.05 to 1.00 %

[0026] Silicon (Si) deoxidizes steel. This effect is not sufficiently present if the Si content is lower than 0.05 %. On the other hand, if the Si content exceeds 1.00 %, this promotes the formation of δ ferrite, decreasing the SSC resistance, toughness and hot workability of the steel. In view of this, the Si content should be in the range of 0.05 to 1.00 %. The lower limit of Si content is preferably 0.10 %, and more preferably 0.15 %. The upper limit of Si content is preferably 0.50 %, and more preferably 0.40 %.

Mn: 0.1 to 1.0 %

[0027] Manganese (Mn) fixes S and improves the hot workability of the steel. Further, Mn stabilizes austenite and prevents production of δ ferrite. This effect is not sufficiently present if the Mn content is lower than 0.1 %. On the other hand, if the Mn content exceeds 1.0 %, Mn segregates in the steel, decreasing toughness. In view of this, the Mn content should be in the range of 0.1 to 1.0 %. The lower limit of Mn content is preferably 0.2 %, and more preferably 0.25 %. The upper limit of Mn content is preferably 0.8 %, and more preferably 0.7 %.

P: up to 0.030 %

[0028] Phosphorus (P) is an impurity. P segregates at grain boundaries and decreases the SSC resistance and toughness of the steel. Thus, the lower the P content, the better. In view of this, the P content should be not higher than 0.030 %. The P content is preferably not higher than 0.025 %.

S: up to 0.002 %

[0029] Sulphur (S) is an impurity. S decreases the hot workability of steel. Thus, the lower the S content, the better. In view of this, the S content should be not higher than 0.002 %. The S content is preferably not higher than 0.001 %.

Ni: 5.5 to 8 %

[0030] Nickel (Ni) improves the corrosion resistance of steel. Further, Ni is a powerful austenite-forming element that stabilizes austenite and prevents production of δ ferrite. This effect is not sufficiently present if the Ni content is lower than 5.5 %. On the other hand, if the Ni content exceeds 8 %, the hot workability of the steel decreases. In view of this, the Ni content should be in the range of 5.5 to 8 %. The Ni content is preferably higher than 6.0 %. The lower limit of the Ni content is preferably 6.1 %. The upper limit of the Ni content is preferably 7.5 %, and more preferably 7.0 %.

Cr: 10 to 14 %

[0031] Chromium (Cr) improves the corrosion resistance of steel. This effect is not sufficiently present if the Cr content is lower than 10 %. On the other hand, if the Cr content exceeds 14 %, this promotes the formation of δ ferrite, decreasing the SSC resistance, toughness and hot workability of the steel. In view of this, the Cr content should be in the range of 10 to 14 %. The lower limit of the Cr content is preferably 10.5 %, and more preferably 11 %. The upper limit of the Cr content is preferably 13 %, and more preferably 12.5 %.

Mo: 2 to 4 %

[0032] Molybdenum (Mo) improves the corrosion resistance of steel. Further, Mo prevents grain-boundary segregation of P, improving the toughness of the steel. Further, Mo is effective in producing retained austenite; however, this effect is not sufficiently present if the Mo content is lower than 2 %. On the other hand, if the Mo content exceeds 4 %, this promotes the formation of δ ferrite, decreasing the SSC resistance, toughness and hot workability of the steel. In view of this, the Mo content is in the range of 2 to 4 %. The lower limit of Mo content is preferably 2.2 %. The upper limit of the Mo content is preferably 3.5 %, and more preferably 3 %.

V: 0.01 to 0.10 %

[0033] Vanadium (V) forms a carbide and improves the strength of the steel. These effects are not sufficiently present if the V content is lower than 0.01 %. On the other hand, if the V content exceeds 0.10 %, the weld cracking sensitivity of the steel increases. In view of this, the V content should be in the range of 0.01 to 0.10 %. The lower limit of V content is preferably 0.02 %, and more preferably 0.03 %. The upper limit of V content is preferably 0.08 %, and more preferably 0.07 %.

Ti: 0.05 to 0.3 %

[0034] Titanium (Ti) forms a carbide and improves the strength of the steel. These effects are not sufficiently present if the Ti content is lower than 0.05 %. On the other hand, if the Ti content exceeds 0.3 %, the weld cracking sensitivity of the steel increases. In view of this, the Ti content should be in the range of 0.05 to 0.3 %. The lower limit of Ti content is preferably 0.06 %, and more preferably 0.08 %. The upper limit of Ti content is preferably 0.25 %, and more preferably 0.20 %.

Nb: up to 0.1 %

[0035] Niobium (Nb) forms a carbide and improves the strength of the steel. This effect is present if a small amount of Nb is contained. On the other hand, if the Nb content exceeds 0.1 %, the weld cracking sensitivity of the steel increases. In view of this, the Nb content should be not higher than 0.1 %. The lower limit of Nb content is preferably 0.001 %. The upper limit of Nb content is preferably 0.08 %, and more preferably 0.05 %.

Al: 0.001 to 0.1 %

[0036] Aluminum (Al) deoxidizes steel. This effect is not sufficiently present if the Al content is lower than 0.001 %. On the other hand, if the Al content exceeds 0.1 %, this leads to more inclusions, decreasing the toughness of the steel. In view of this, the Al content should be in the range of 0.001 to 0.1 %. The lower limit of Al content is preferably 0.01 %. The upper limit of Al content is preferably 0.08 %, and more preferably 0.06 %.

N: up to 0.05 %

[0037] Nitrogen (N) increases the hardness of welding heat-affected zones and decreases toughness and sulfide stress corrosion cracking resistance (SSC resistance). Thus, the lower the N content, the better. In view of this, the N content should be not higher than 0.05 %. The upper limit of N content is preferably 0.03 %, and more preferably 0.02 %. From a cost viewpoint, the lower limit of N content is preferably 0.001 %.

Cu: up to 0.5 %

[0038] It is not necessary to intentionally include copper (Cu). Since Cu is effective in improving corrosion resistance in an acidic environment containing both carbon dioxide gas and hydrogen sulfide, an appropriate amount of Cu may be included. In order that this effect be present, it is preferable to include 0.05 % or more Cu. On the other hand, if the Cu content exceeds 0.5 %, the hardness of heat-affected zones increases. In view of this, the Cu content should be not higher than 0.5 %. The lower limit of Cu content is more preferably 0.08 %. The upper limit of Cu content is preferably 0.4 %.

[0039] The balance of the chemical composition of the stainless steel pipe according to the present embodiment is made of Fe and impurities. Impurity in this context means an element originating from ore or scraps used as a raw material of steel or an element that has entered from the environment or the like during the manufacturing process.

[0040] Further, in the chemical composition of the stainless steel pipe according to the present embodiment, some Fe may be replaced by one or more elements selected from the group consisting of Ca, Mg and B. Each of these elements improves the hot workability of the steel. Ca, Mg and B are optional elements. That is, the chemical composition of the stainless steel pipe according to the present embodiment may not contain one or more or all of these elements.

Ca: 0 to 0.008 %

[0041] Calcium (Ca) improves the hot workability of steel. This effect is present if a small amount of Ca is contained. On the other hand, if the Ca content exceeds 0.008 %, coarse particles of oxides are formed, decreasing the toughness of the steel. In view of this, the Ca content should be in the range of 0 to 0.008 %. The lower limit of Ca content is preferably 0.001 %. The upper limit of Ca content is preferably 0.005 %.

Mg: 0 to 0.05 %

[0042] Magnesium (Mg) improves the hot workability of steel. This effect is present if a small amount of Mg is contained. On the other hand, if the Mg content exceeds 0.05 %, coarse particles of oxides are formed, decreasing the toughness of the steel. In view of this, the Mg content should be in the range of 0 to 0.05 %. The lower limit of Mg content is preferably 0.001 %. The upper limit of Mg content is preferably 0.03 %.

B: 0 to 0.005 %

[0043] Boron (B) improves the hot workability of steel. This effect is present if a small amount of B is contained. On the other hand, if the B content exceeds 0.005 %, the weld cracking sensitivity of the steel increases. In view of this, the B content should be in the range of 0 to 0.005 %. The lower limit of B content is preferably 0.0005 %. The upper limit of B content is preferably 0.003 %.

[Microstructure and Yield Strength]

[0044] The microstructure of the stainless steel pipe according to the present embodiment is mainly composed of martensite and includes, by volume fraction, 12 to 18 % retained austenite. The martensite includes prior austenite grains of a crystal grain size number lower than 8.0 in accordance with ASTM E112.

[0045] With the chemical composition of the stainless steel pipe according to the present embodiment, the volume fraction of retained austenite may be 12 % or higher and the crystal grain size number of prior austenite grains in the martensite may be lower than 8.0 to achieve a yield ratio not higher than 75 %.

[0046] The volume fraction of retained austenite may be adjusted by heat treatment, as discussed further below. The volume fraction of retained austenite also depends on the balance between the contents of austenite-forming elements such as C, Mn, Ni and Cu, and the contents of ferrite-forming elements such as Si, Cr, Mo and V. Particularly, it is significantly affected by the Ni content.

[0047] The volume fraction of retained austenite may be measured by X-ray diffraction in the following manner: Stainless steel pipes are tempered, and samples each including a central portion as measured in wall thickness of the stainless steel pipe are extracted from the stainless steel pipes. The surfaces of the extracted samples are polished. X-ray diffraction is performed on the polished surfaces using the CoKa line as an incident X ray. The volume fraction of retained austenite is calculated quantitatively from the integrated intensities of the (211) plane, (200) plane and (110) plane of the ferrite (bcc structure) and the integrated intensities of the (220) plane, (200) plane and (111) plane of the austenite (fcc structure).

[0048] If the volume fraction of retained austenite is lower than 12 %, it is difficult to achieve a yield ratio not higher than 75 %. On the other hand, if the volume fraction of retained austenite is higher than 18 %, it is difficult to provide a yield strength of 550 MPa or higher. In view of this, the volume fraction of retained austenite should be in the range of 12 to 18 %. The lower limit of the volume fraction of retained austenite is preferably 13 %. The upper limit of the volume fraction of retained austenite is preferably 17 %.

[0049] The crystal grain size number of prior austenite grains in the martensite may be measured by electron beam backward scattering diffraction (EBSD) in the following manner: Stainless steel pipes are tempered, and a sample is extracted from a central portion as measured in wall thickness of a cross section of each of the stainless steel pipes (i.e. a section perpendicular to the axial direction of the steel pipe). The extracted samples are used to identify prior austenite grain boundaries by EBSD in an observed range of $90 \times 90\ \mu m^2$, and the crystal grain size number is determined in accordance with ASTM E112.

[0050] If the crystal grain size number of prior austenite grains in the martensite is 8.0 or higher, the amount of retained austenite produced can easily increase. In view of this, the crystal grain size number of prior austenite grains in the martensite should be lower than 8.0. The upper limit of the crystal grain size number of prior austenite grains in the martensite is preferably 7.8.

[0051] The stainless steel according to the present embodiment has a yield strength of 550 to 700 MPa. The upper limit of the yield strength should be 700 MPa because a yield strength higher than 700 MPa will make it difficult to make overmatch joints.

[Manufacturing Method]

[0052] An exemplary method of manufacturing the stainless steel pipe according to the present embodiment will now be described. However, the method of manufacturing the stainless steel pipe according to the present embodiment is not limited thereto.

[0053] FIG. 1 is a block diagram showing an exemplary manufacturing line. The manufacturing line includes a heating furnace 1, a piercing machine 2, an elongation-rolling mill 3, a sizing mill 4, a supplementary-heating furnace 5, a water-cooling apparatus 6, and a tempering apparatus 7. Transportation rollers 10 are positioned between these units. In the manufacturing method of the implementation of FIG. 1, hot working, quenching and tempering are all performed in an in-line manner.

[0054] FIG. 2 is a flow chart showing steps for manufacturing the stainless steel pipe according to the present embodiment. FIG. 3 is a graph illustrating how the temperature of a workpiece being produced (steel material or hollow shell) changes over time. "A1" in the graph indicates the Ac_1 point when the workpiece is being heated, and the An point when the workpiece is being cooled. Further, "A3" in the graph indicates the Ac_3 point when the workpiece is being heated, and the Ar_3 point when the workpiece is being cooled.

[0055] First, the steel material is heated by the heating furnace 1 (heating step: S1). The heating furnace 1 may be a walking-beam furnace or rotary furnace, for example. The steel material may be a round billet, for example. The steel material may be produced by continuous-casting equipment, such as a round CC, or may be produced by hot-working (forging or blooming, for example) an ingot or slab. The preferable heating temperature is 1100 to 1300 °C.

[0056] The heated steel material is hot-worked to produce a hollow shell (S2 and S3). More specifically, the round billet is piercing-rolled by a piercing machine to produce a hollow shell (piercing-rolling step: S2). Further, the piercing-rolled hollow shell is rolled by the elongation-rolling mill 3 and sizing mill 4 (elongation-rolling and sizing step: S3).

[0057] The hollow shell produced by hot working is continuously quenched in an in-line manner (quenching step: S5). If necessary, a reheating step (S4) may be performed between the elongation-rolling and sizing step (S3) and quenching step (S5).

[0058] During the reheating step (S4), the hot-worked hollow shell is heated by the supplementary-heating furnace to a predetermined temperature that is not lower than 940 °C. The reheating step (S4) may be omitted if quenching at the following quenching step is possible without such a reheating step. Nevertheless, even if this is the case, performing the reheating step (S4) is preferable to make the temperature in the hollow shell uniform.

[0059] The hollow shell produced by hot working, or the hollow shell that has been reheated, is quenched by the water-cooling apparatus 6 in an in-line manner (quenching step: S5). As used herein, "quenching in an in-line manner" means both quenching immediately after hot working and quenching after reheating by the supplementary-heating apparatus 5 after hot working.

[0060] The water-cooling apparatus 6 may be a laminar water-flow device and/or jet water-flow device, for example. The cooling rate is preferably 5 °C/second or higher.

[0061] The microstructure of the hollow shell immediately before water cooling is substantially a single phase of austenite. If the temperature in the hollow shell immediately before water cooling (quenching temperature) is increased, the grain diameter of such austenite increases. When water-cooled, the austenite becomes martensite and, when further tempered, becomes martensite. The size of prior austenite grains is hardly affected by tempering. Thus, the size of prior austenite grains in the martensite is mostly determined by the quenching conditions. That is, the quenching conditions control the size of prior austenite grains in the martensite contained in the microstructure of the tempered stainless steel pipe.

[0062] Further, quenching in an in-line manner can increase the size of prior austenite grains more easily than quenching in an off-line manner (i.e. after hot working, leaving the temperature of the hollow shell to go down to room temperature and then heating it again to a predetermined temperature for quenching; typically, heat treatment equipment independent of the unit for hot working is used).

[0063] If the quenching temperature is lower than 940 °C, it is difficult to make the crystal grain size number of prior austenite grains lower than 8.0. On the other hand, if the quenching temperature is higher than 980 °C, it is difficult to provide a yield strength not lower than 550 MPa. In view of this, the quenching temperature should be in the range of 940 to 980 °C.

[0064] The quenched hollow shell is tempered by the tempering apparatus 7 (tempering step: S6). More specifically, the quenched hollow shell is loaded into the furnace at a temperature between the Ac_1 point and Ac_3 point (hereinafter tempering temperature) and is held for a predetermined period of time (hereinafter tempering time) that satisfies Equation (1) below. As used herein, tempering temperature means the average temperature in the furnace. Tempering time means the time between the time point at which a hollow shell is loaded into the furnace and the time point at which it is removed therefrom (i.e. in-furnace time). The tempered hollow shell is typically cooled by air cooling.

$$680 \leq T + 15.39 \ln(t) \leq 720 \quad \ldots (1),$$

where T is a tempering temperature in °C, and t is a tempering time in minutes. ln(t) is the natural logarithm of t.

[0065] As the tempering temperature is between the Ac_1 point and Ac_3 point, some of the martensite is reverse-transformed into austenite. While the hollow shell is held at the tempering temperature, austenite-stabilizing elements are concentrated in the reverse-transformed austenite. Much of the reverse-transformed austenite maintains the austenitic phase after cooling and becomes retained austenite.

[0066] The higher the tempering temperature, the higher the volume fraction of retained austenite. Further, the longer the tempering time, the higher the volume fraction of retained austenite. With the chemical composition of the stainless steel pipe according to the present embodiment, the volume fraction of retained austenite is in the range of 12 to 18 % if the tempering temperature and tempering time satisfy Equation (1).

[0067] The above manufacturing process provides a stainless steel pipe with a yield strength of 550 MPa or higher and a yield ratio that is as low as 75 % or lower.

[0068] A stainless steel pipe according to an embodiment of the present invention and a method of manufacturing such a stainless steel pipe have been described. The present embodiment provides a stainless steel pipe having a strength in a predetermined range and a low yield ratio.

EXAMPLES

[0069] The present invention will now be described in more detail by means of Examples. The present invention is not limited to these Examples.

[0070] A plurality of stainless steel pipes having various chemical compositions were produced and the relationship between their mechanical properties and amount of retained austenite were measured.

[Investigation Method]

[0071] A plurality of steel melts having the chemical compositions shown in Table 1 were produced by an electric furnace. Ingots were produced from the steel melts. The ingots were hot-forged to produce round billets. "-" in Table 1 indicates that the content was at an impurity level.

[Table 1]

[0072]

TABLE 1

Steel	Chemical composition (in mass%; balance Fe and impurities)																
	C	Si	Mn	P	S	Ni	Cr	Mo	V	Ti	Nb	Al	Cu	B	Ca	Mg	N
1	0.01	0.25	0.34	0.013	0.001	6.51	12.04	2.42	0.044	0.11	0.006	0.038	0.07	0.001	0.0014	-	0.007
2	0.01	0.12	0.55	0.020	0.001	6.20	11.89	2.28	0.050	0.13	0.012	0.022	0.06	-	-	-	0.009
3	0.01	0.27	0.50	0.015	0.001	6.59	12.07	2.45	0.050	0.10	0.002	0.034	0.07	0.001	-	0.001	0.008
4	0.01	0.20	0.44	0.015	0.001	**5.42**	11.88	**1.89**	0.050	0.09	0.001	0.029	0.06	0.001	0.0012	-	0.006
5	0.02	0.30	0.42	0.020	0.001	6.41	12.66	2.71	0.060	0.12	0.001	0.050	0.10	0.001	-	-	0.007

[0073] For all of these steels, the Ac_1 point was about 570 °C and the Ac_3 point was about 660 °C.

[0074] The round billets produced were heated by a heating furnace to a temperature between 1100 to 1300 °C. Subsequently, the round billets were subjected to piercing-rolling by a piercing machine to produce hollow shells. Subsequently, these hollow shells were subjected to elongation-rolling by a mandrel mill. Subsequently, the hollow shells were subjected to reduction-rolling (i.e. sizing) in a sizer to produce stainless steel pipes with an outer diameter of 273.1 mm and a wall thickness of 14.3 mm.

[0075] The stainless steel pipes that have undergone sizing are heated by a supplementary heating furnace to the quenching temperatures shown in Table 2, and were then quenched by a water-cooling apparatus to cool them to room temperature at a cooling rate that is not lower than 5 °C/second. After quenching, tempering was performed on the stainless steel pipes at the tempering temperatures and tempering times shown in Table 2. The column labeled "Eq. (1)" in Table 2 lists values of T+15.39ln(t) from Equation (1).

[Table 2]

[0076]

TABLE 2

Steel	Test No.	Heat treatment conditions				Mechanical properties			Amount of retained γ	Prior austenite grain size number	Remarks
		quenching	tempering conditions		Eq. (1)	YS	TS	Y.R			
		temp. (°C)	temp. (°C)	time (min.)		(MPa)	(MPa)	(%)	(%)		
1	A1	950°C	580	40	**637**	**877**	959	**91.4**	**0.8**	-	comparative steel
	B1		600	40	**657**	**847**	904	**93.7**	**2.3**	-	
	C1		620	40	**677**	**775**	875	**88.6**	**8.1**	-	
	D1		625	30	**677**	679	855	**79.4**	**10.3**	-	
	E1		625	70	690	618	853	72.5	13.2	-	inventive steel
	F1		625	150	702	569	860	66.2	15.2	-	
	G1		625	720	**726**	**535**	859	62.3	**20.1**	-	comparative steel
	H1		630	2.5	**644**	**749**	865	**86.6**	**5.4**	-	comparative steel
	I1		630	10	**665**	**745**	867	**85.9**	**7.3**	-	
	J1		630	70	695	589	867	67.9	17	-	inventive steel
	K1		630	150	707	571	874	65.3	16.2	-	
	L1		630	720	**731**	**544**	856	63.6	**18.5**	-	comparative steel
	M1		640	30	692	616	860	71.6	13.3	7.5	inventive steel
	N1		640	40	697	593	862	68.8	16.1	6.4	
	O1		640	70	705	575	876	65.6	15.1	7.8	
	P1		640	150	717	571	877	65.1	15.7	7.5	
	Q1	**900°C**	640	150	717	**545**	856	63.7	**19.2**	**8.8**	comparative steel
	A2		580	40	**637**	**876**	950	**92.2**	**0.2**	-	comparative steel
	B2		600	40	**657**	**808**	903	**89.5**	**2.9**	-	
	C2		620	40	**677**	**774**	875	**88.5**	**8.3**	-	
	D2		625	30	**677**	669	851	**78.6**	**11.5**	-	

(continued)

Steel	Test No.	Heat treatment conditions				Mechanical properties			Amount of retained γ	Prior austenite grain size number	Remarks
		quenching	tempering conditions		Eq. (1)	YS	TS	Y.R			
		temp. (°C)	temp. (°C)	time (min.)		(MPa)	(MPa)	(%)	(%)		
2	E2	950°C	625	70	690	584	846	69.0	12.8	-	inventive steel
	F2		625	150	702	561	858	65.4	16.8	-	
	G2		625	720	**726**	**540**	863	62.6	**19**	-	comparative steel
	H2		630	2.5	**644**	**784**	875	**89.6**	**3.4**	-	comparative steel
	I2		630	10	**665**	**724**	867	**83.5**	**10**	-	
	J2		630	70	695	585	858	68.2	15.2	-	inventive steel
	K2		630	150	707	558	862	64.7	17.2	-	
	L2		630	720	**731**	**539**	863	62.5	**18.4**	-	comparative steel
	M2		640	30	692	621	864	71.9	14.3	7.4	inventive steel
	N2		640	40	697	611	855	71.5	17	6.9	
	O2		640	70	705	580	869	66.7	14.3	7.1	
	P2		640	150	717	576	878	65.6	16.5	7.6	
	Q2	**900°C**	640	150	717	**543**	871	62.3	**19.2**	**8.4**	comparative steel

(continued)

Steel	Test No.	Heat treatment conditions			Eq. (1)	Mechanical properties			Amount of retained γ	Prior austenite grain size number	Remarks
		quenching	tempering conditions			YS	TS	Y.R			
		temp. (°C)	temp. (°C)	time (min.)		(MPa)	(MPa)	(%)	(%)		
3	A3	950°C	630	60	693	585	858	68.2	13.2	-	inventive steel
	B3		610	60	**673**	**779**	859	**90.6**	**5.2**	-	comparative steel
	C3		615	60	678	**723**	844	**85.7**	**8.7**	-	
	D3		590	60	**653**	**844**	879	**96.0**	**2.1**	-	
	E3		595	60	**658**	**824**	864	**95.3**	**1.1**	-	
4	A4		620	35	**675**	**786**	841	**93.5**	**0.7**	-	comparative steel
	B4		630	35	685	**728**	829	**87.8**	**1.8**	-	
	C4		650	35	705	659	817	**80.7**	**4.1**	-	
5	A5		580	30	**632**	**929**	955	**97.3**	**0.1**	-	comparative steel
	B5		600	30	**652**	**872**	913	**95.5**	**0.8**	-	
	C5		620	30	**672**	**827**	897	**92.2**	**7.2**	-	
	D5		640	30	692	588	889	66.1	13.7	-	inventive steel

[0077] The yield strength and tensile strength of each of the stainless steel pipes were measured in accordance with ASTM A370. The value of yield strength was divided by the value of tensile strength to determine the yield ratio. Further, the volume fraction of retained austenite of each of the stainless steel pipes was measured by X-ray diffraction. The results are shown in Table 2 above. In Table 2, "YS" means yield strength (MPa), "TS" means tensile strength (MPa), "YR" means yield ratio (%), "Amount of retained γ" means the volume fraction of retained austenite (%).

[0078] For some of the stainless steel pipes, prior austenite grains in the martensite were measured by EBSD. The results are shown in the column labeled "Prior austenite grain size number" in Table 2. "-" in this column means that the crystal grain size number was not measured. For all the "inventive steel" stainless steel pipes, the crystal grain size number of prior austenite grains was lower than 8.0.

[0079] As shown in Table 2, for each of test Nos. E1, F1, J1, K1, M1 to P1, E2, F2, J2, K2, M2 to P2, A3 and D5, the quenching conditions were appropriate and the tempering temperature and tempering time satisfied Equation (1). For each of these stainless steel pipes, the volume fraction of retained austenite was in the range of 12 to 18 %. For each of these stainless steel pipes, the yield strength was in the range of 550 to 700 MPa and the yield ratio was lower than 75 %.

[0080] Each of the stainless steel pipes of test Nos. A1 to D1, H1, I1, A2 to D2, H2, I2, B3 to E3, A4 to C4 and A5 to C5 had a yield ratio higher than 75 %. This is presumably because the tempering temperature and tempering time did not satisfy Equation (1) or the chemical composition was not in the specified range and thus the volume fraction of retained austenite was lower than 12 %.

[0081] Each of the stainless steel pipes of test Nos. Q1 and Q2 had a yield strength lower than 550 MPa. This is presumably because the quenching temperature was low and thus the prior austenite grain size became finer, increasing the amount of retained austenite produced.

[0082] Each of the stainless steel pipes of test Nos. G1, L1, G2 and L2 had a yield strength lower than 550 MPa. This is presumably because the volume fraction of retained austenite was higher than 18 %. The volume fraction of retained austenite was higher than 18 % presumably because the tempering temperature and tempering time did not satisfy Equation (1).

[0083] FIG. 4 is a scatterplot illustrating the relationship between the volume fraction of retained austenite and yield strength in steels whose chemical composition and quenching temperature were in the predetermined ranges. This graph demonstrates that a yield strength of 550 to 700 MPa can be achieved if the volume fraction of retained austenite is higher than 10 % and not higher than 18 %.

[0084] FIG. 5 is a scatterplot illustrating the relationship between the volume fraction of retained austenite and yield ratio in steels whose chemical composition and quenching temperature were in the predetermined ranges. This graph demonstrates that a yield ratio not higher than 75 % can be achieved if the volume fraction of retained austenite is not lower than 12 %.

[0085] FIGS. 4 and 5 demonstrate that a yield strength in the range of 550 to 700 MPa and a yield ratio that is as low as 75 % or lower can be achieved if the volume fraction of retained austenite is in the range of 12 to 18 %.

[0086] FIG. 6 is a scatterplot illustrating the relationship between the value of T+15.39ln(t) and the volume fraction of retained austenite in steels whose chemical composition and quenching temperature were in the predetermined ranges. FIG. 6 demonstrates that the volume fraction of retained austenite is in the range of 12 to 18 % if the value of T+15.39ln(t) is in the range of 680 to 720.

[0087] Although embodiments of the present invention have been described, the above embodiments are merely examples for carrying out the present invention. Therefore, the present invention is not limited to the above embodiments and the above embodiments may be modified as necessary without departing from the spirit of the invention.

Claims

1. A stainless steel pipe having a chemical composition of, in mass%:

C: up to 0.02 %;
Si: 0.05 to 1.00 %;
Mn: 0.1 to 1.0 %;
P: up to 0.030 %;
S: up to 0.002 %;
Ni: 5.5 to 8 %;
Cr: 10 to 14 %;
Mo: 2 to 4 %;
V: 0.01 to 0.10 %;
Ti: 0.05 to 0.3 %;
Nb: up to 0.1 %;

Al: 0.001 to 0.1 %;
N: up to 0.05 %;
Cu: up to 0.5 %;
Ca: 0 to 0.008 %;
Mg: 0 to 0.05 %;
B: 0 to 0.005 %; and
balance Fe and impurities,
the stainless steel pipe having a microstructure including martensite and, by volume fraction, 12 to 18 % retained austenite,
the martensite having prior austenite grains of a crystal grain size number lower than 8.0 in accordance with ASTM E112,
the stainless steel pipe having a yield strength of 550 to 700 MPa.

2. The stainless steel pipe according to claim 1, wherein the chemical composition includes one or more elements selected from the group consisting of, in mass%:

Ca: 0.001 to 0.008 %;
Mg: 0.001 to 0.05 %; and
B: 0.0005 to 0.005 %.

3. A method of manufacturing a stainless steel pipe comprising:

hot-working a steel material having a chemical composition of, in mass%: C: up to 0.02 %; Si: 0.05 to 1.00 %; Mn: 0.1 to 1.0 %; P: up to 0.030 %; S: up to 0.002 %; Ni: 5.5 to 8 %; Cr: 10 to 14 %; Mo: 2 to 4 %; V: 0.01 to 0.10 %; Ti: 0.05 to 0.3 %; Nb: up to 0.1 %; Al: 0.001 to 0.1 %; N: up to 0.05 %; Cu: up to 0.5 %; Ca: 0 to 0.008 %; Mg: 0 to 0.05 %; B: 0 to 0.005 %; and balance Fe and impurities, to produce a hollow shell;
after the hot-working, quenching the hollow shell from a temperature between 940 and 980 °C in an in-line manner with respect to the hot-working; and
tempering the quenched hollow shell at a temperature between the Ac_1 point and Ac_3 point under the conditions described in Equation (1) below:

$$680 \leq T + 15.39 \ln(t) \leq 720 \quad \dots (1),$$

where T is a tempering temperature in °C, and t is a tempering time in minutes.

Fig.1

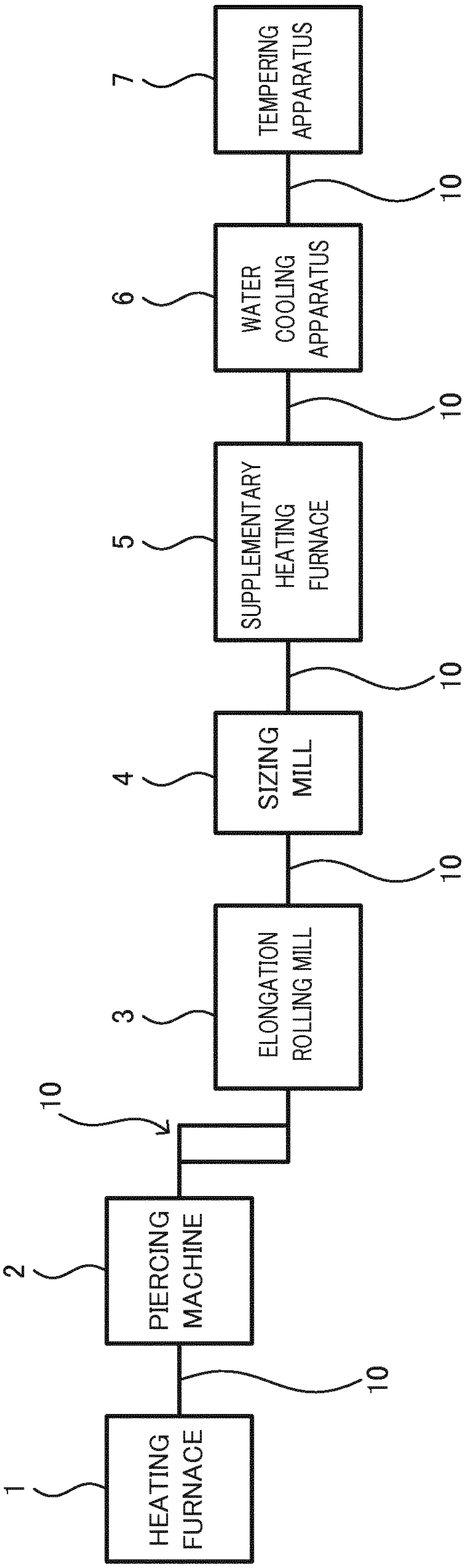

HEATING FURNACE
1
PIERCING MACHINE
2
10
ELONGATION ROLLING MILL
3
SIZING MILL
4
SUPPLEMENTARY HEATING FURNACE
5
WATER COOLING APPARATUS
6
TEMPERING APPARATUS
7
10

Fig.2

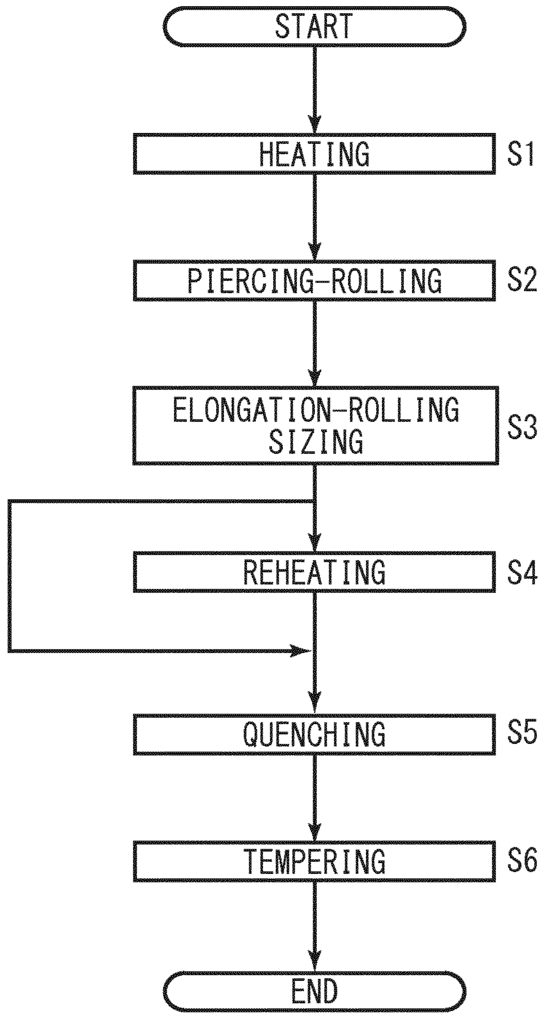

START
HEATING
S1
PIERCING-ROLLING
S2
ELONGATION-ROLLING
SIZING
S3
REHEATING
S4
QUENCHING
S5
TEMPERING
S6
END

Fig.3

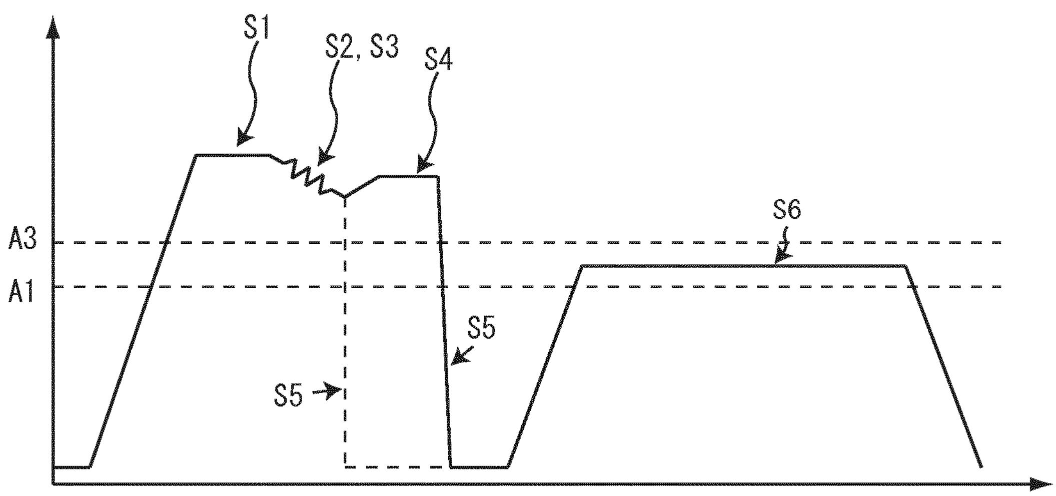

S1
S2, S3
S4
A3
A1
S6
S5
S5

Fig.4

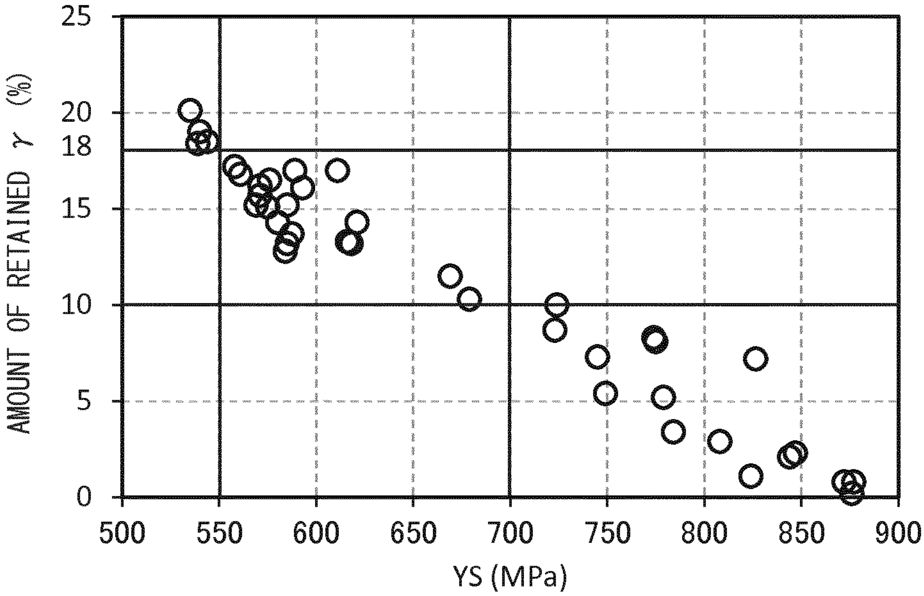

25
20
18
15
10
5
0
AMOUNT OF RETAINED γ (%)
500
550
600
650
700
750
800
850
900
YS (MPa)

Fig.5

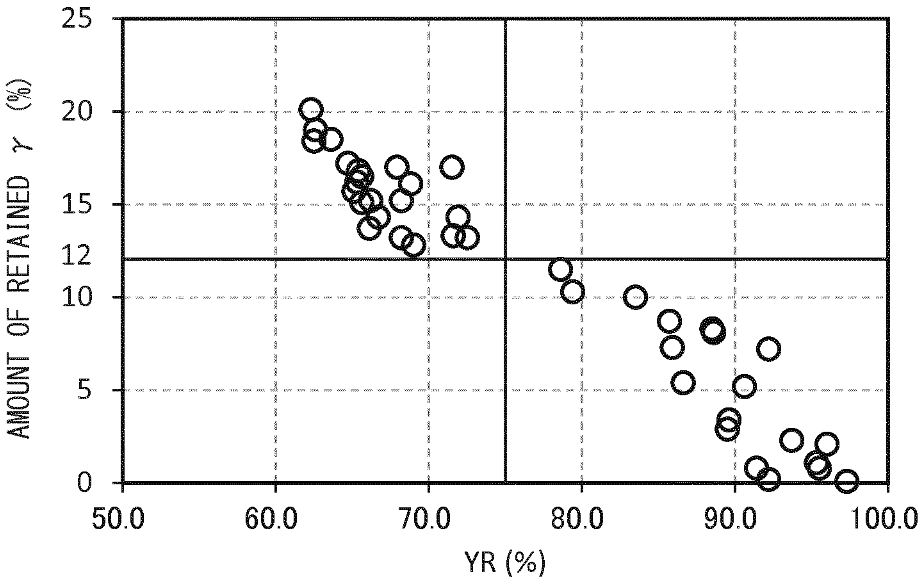
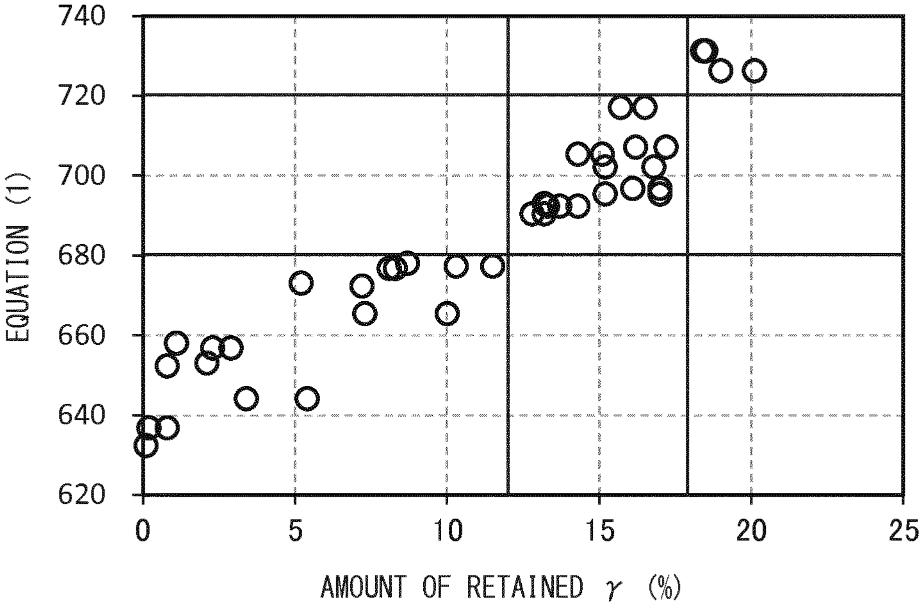

25
20
15
12
10
5
0
AMOUNT OF RETAINED γ (%)
50.0
60.0
70.0
80.0
90.0
100.0
YR (%)

Fig.6



740
720
700
680
660
640
620
EQUATION (1)
0
5
10
15
20
25
AMOUNT OF RETAINED γ (%)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/066277

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21D8/10*(2006.01)i, *C21D9/08*(2006.01)i, *C22C38/54* (2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00, C21D8/10, C21D9/08, C22C38/54

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2016
Kokai Jitsuyo Shinan Koho	1971-2016	Toroku Jitsuyo Shinan Koho	1994-2016

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.
P,A	JP 2015-161010 A (JFE Steel Corp.), 07 September 2015 (07.09.2015), tables 1, 2; claims (Family: none)	1-3
A	JP 2002-212684 A (Sumitomo Metal Industries, Ltd.), 31 July 2002 (31.07.2002), paragraphs [0017], [0018] (Family: none)	1-3
A	JP 2007-332442 A (JFE Steel Corp.), 27 December 2007 (27.12.2007), claims; tables 1, 2 (Family: none)	1-3

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

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Date of the actual completion of the international search	Date of mailing of the international search report
10 August 2016 (10.08.16)	23 August 2016 (23.08.16)

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

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/066277

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/001082 A1 (JFE Steel Corp.), 31 December 2003 (31.12.2003), claims; tables 1 to 6 & US 2004/0238079 A1 claims; tables 1 to 6 & EP 1514950 A1	1-3
A	JP 2003-129190 A (Sumitomo Metal Industries, Ltd.), 08 May 2003 (08.05.2003), claims; tables 1 to 3 & US 2003/217789 A1 claims; tables 1 to 3 & WO 03/035921 A1 & EP 1446512 A1 & CN 1571859 A	1-3
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A	JP 2015-71822 A (JFE Steel Corp.), 16 April 2015 (16.04.2015), claims; tables 1 to 2-2 & WO 2015/033518 A1 & EP 3042968 A1 claims; tables 1, 2-1, 2-2 & CN 105579597 A	1-3

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2001226749 A **[0009] [0012]**
- JP 2001303206 A **[0010] [0012] [0013]**
- JP 2000226614 A **[0011] [0012]**