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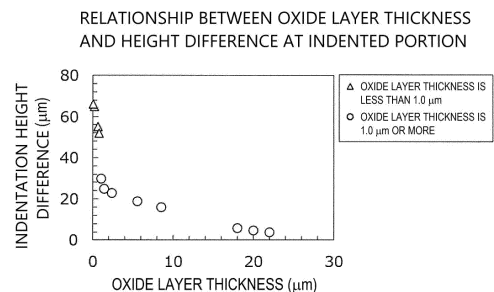
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(54) **DUPLEX STAINLESS STEEL PIPE AND METHOD FOR MANUFACTURING SAME**

(57) Provided herein is a duplex stainless steel pipe that is high in strength and has excellent abrasion resistance and indentation resistance on inner and outer surfaces of the steel pipe. A method for manufacturing such a stainless steel pipe is also provided. A duplex stainless steel pipe of the present invention has a composition that contains, in mass%, C: 0.005 to 0.150%, Si: 1.0% or less, Mn: 10.0% or less, Cr: 11.5 to 35.0%, Ni: 0.5 to 15.0%, Mo: 0.5 to 6.0%, N: less than 0.400%, and the balance being Fe and incidental impurities, and has a microstructure with a ferritic phase and an austenitic phase, the duplex stainless steel pipe having an axial tensile yield strength of 689 MPa or more, and having an outer surface and an inner surface each having an oxide layer having an average thickness of 1.0 μm or more.

[FIG. 1]



Description

Technical Field

5 **[0001]** The present invention relates to a stainless steel pipe having excellent axial tensile yield strength with excellent abrasion resistance and indentation resistance, and to a method for manufacturing such a stainless steel pipe. Here, "excellent axial tensile yield strength" means a yield strength of 689 MPa or more.

Background Art

10 **[0002]** Steel pipes used for extraction of oil and gas from oil wells and gas wells (hereinafter, also referred to simply as "steel pipes for oil wells") or steel pipes for geothermal wells are required to have corrosion resistance performance that can withstand use in highly corrosive high-temperature and high-pressure environments, and high strength characteristics that can withstand the tensile stress due to the weight of pipes joined to extend deep into the ground, and
15 the thermal stress and high pressure associated with high temperature. In order to have excellent corrosion resistance performance, steel needs to contain corrosion-resistance improving elements (e.g., Cr, Mo, W, and N) in adjusted amounts. In this connection, various duplex stainless steels are available, including, for example, SUS329J3L containing 22 mass% of Cr, SUS329J4L containing 25 mass% of Cr, and ISO S32750 and S32760 containing increased amounts of Mo.

20 **[0003]** In order to provide high strength characteristics, it is important to adjust the axial tensile yield strength, and a value of axial tensile yield strength represents the specified strength of the product. This is important because the pipe needs to withstand the tensile stress due to its own weight when joined to extend deep into the ground. With a sufficiently high axial tensile yield strength against the tensile stress due to its weight, the pipe undergoes less plastic deformation, and this prevents damage to the passive film that is important for keeping the pipe surface corrosion resistant.

25 **[0004]** In this respect, duplex stainless steels such as above have a duplex microstructure with a ferritic phase coexisting with an austenitic phase which is crystallographically low in yield strength. Because of this, hot forming and a heat treatment alone are not enough to provide the tensile strength needed for oil well or geothermal well applications.

[0005] The axial tensile yield strength of a duplex stainless steel pipe to be used for oil well or geothermal well applications is therefore provided by dislocation strengthening using various types of cold rolling. Cold drawing and cold
30 pilgering are two cold rolling techniques available for pipes to be used for oil well or geothermal well applications, as defined by NACE (The National Association of Corrosion Engineers), which provides international standards for use of oil well pipes. These cold rolling techniques both represent a longitudinal rolling process that reduces the wall thickness and the diameter of a pipe. A steel pipe to be subjected to these cold rolling processes needs to be cleaned with an acid, or a lubricant coating needs to be formed by chemical treatment before cold rolling, in order to reduce defects in
35 the product, or to protect the tools. When a lubricant coating is formed, the steel pipe needs to be cleaned with an acid after cold rolling.

[0006] Steel pipes intended for oil well or geothermal well applications are used outdoors, often in places that are not leveled. During extraction or passing of oil or hot water through the steel pipe, the steel pipe often collides with hard objects such as stones. Scraping or collision between steel pipes is also common when inserting a steel pipe into another
40 steel pipe, or when transporting steel pipes. When joining steel pipes, clamping with a fastening tool exerts a high contact pressure on steel pipe surface. Such collisions with hard objects, colliding and scraping of steel pipes, and contact pressure of a fastening tool cause scratch defects and indentations on inner and outer surfaces of a steel pipe.

[0007] These scratch defects and indentations become initiation points of corrosion. When excessively large, indentations also affect product dimensions. For example, the wall thickness decreases in proportion to the depth of a scratch defect or an indentation, causing a decrease of axial tensile strength, which is an important characteristic of a steel pipe.

45 **[0008]** As discussed above, duplex stainless steel pipes to be used for oil well or geothermal well applications require not only high strength and high corrosion resistance but the ability to reduce scratch defects and indentations on inner and outer surfaces of a steel pipe. That is, the inner and outer surfaces of steel pipes to be used for these applications need to have excellent abrasion resistance and indentation resistance.

50 **[0009]** In this regard, a duplex stainless steel pipe is produced through dislocation strengthening by cold rolling, in order to provide a high axial tensile yield strength, as described above. Before cold rolling, steel pipe surfaces are cleaned with an acid to remove the surface oxide layer, in order to reduce damage such as that experienced by a rolling tool during cold rolling. Alternatively, a highly lubricative chemical-treatment coating is formed to prevent galling during cold rolling. In this case, the surface oxide layer is removed with the chemical-treatment coating after cold rolling. Cold rolling
55 increases the surface area of a steel pipe by reducing the wall thickness and stretching the pipe along its axis. Accordingly, a steel pipe after cold rolling does not have the surface oxide layer, and, because of an increased surface area, the steel pipe has a bare metal surface with a metallic sheen.

[0010] However, with its metal surface exposed, the steel pipe is more susceptible to scratch defects and indentations

such as above. That is, a conventional duplex stainless steel pipe produced by cold rolling has a bare metal surface to provide high strength, and is susceptible to scratch defects and indentations.

[0011] Various techniques are available concerning steel pipes. For example, PTL 1 and PTL 2 disclose steel pipes having improved hardness and abrasion resistance of inner surfaces. PTL 3 discloses a clad steel pipe in which a material that is high in hardness and abrasion resistance is joined to a base material.

Citation List

Patent Literature

[0012]

PTL 1: Japanese Unexamined Patent Application Publication No. 57-194213

PTL 2: Japanese Unexamined Patent Application Publication No. 1-15323

PTL 3: Japanese Unexamined Patent Application Publication No. 63-290616

Summary of Invention

Technical Problem

[0013] However, the techniques described in PTL 1 to PTL 3 lack consideration with regard to improvement of all of strength characteristics, abrasion resistance, and indentation resistance, which are required for oil well or geothermal well applications described above, and further improvements are needed.

[0014] The present invention has been made under these circumstances, and it is an object of the present invention to provide a duplex stainless steel pipe that is high in strength and has excellent abrasion resistance and indentation resistance of inner and outer surfaces of the steel pipe. The invention is also intended to provide a method for manufacturing such a stainless steel pipe.

[0015] In the present invention, "high strength" means an axial tensile yield strength of 689 MPa or more as measured by a JIS Z2241 tensile test when a round-bar tensile test specimen taken parallel to the pipe axis at a middle portion of the wall thickness and having a diameter of 5.0 mm at a parallel portion is stretched to break at room temperature (25°C) with a crosshead speed of 1.0 mm/min.

[0016] In the present invention, abrasion resistance and indentation resistance are excellent when an indented portion created by a scratch test has an indentation height of 50 μm or less as measured in a middle portion of the length of the indented portion relative to an unindented raised portion after a pipe is scratched by sweeping a pipe surface over a distance of 30 mm at 3 mm/s along the pipe axis under a 59 N load of an indenter having a cemented carbide tip (a circular cone indenter having a tip angle of 60° (a point of contact with a steel pipe) in a triangular cross section perpendicular to the base of the circular cone).

Solution to Problem

[0017] In order to achieve the foregoing objects, the present inventors conducted intensive studies of a duplex stainless steel pipe.

[0018] To increase the corrosion resistance of a duplex stainless steel pipe, corrosion-resistant elements Cr and Mo must be added, and a corrosion resistance-reducing element C must be reduced. Addition of Cr and Mo and reduction of C increase the ferritic phase in the microstructure of the product. However, when the ferritic phase increases excessively, the duplex microstructure fails to provide excellent corrosion resistance performance, and low-temperature toughness decreases. In order to protect a duplex stainless steel pipe from various forms of corrosion, it is therefore important that elements such as Ni, N, and Mn, which increase the austenitic phase, are added in a well-balanced manner to produce an appropriate duplex ferritic and austenitic phase in the microstructure of the product.

[0019] In order to produce an appropriate duplex state in a duplex stainless steel pipe, a solid solution heat treatment is required, in addition to the appropriate addition of chemical components that form the ferritic phase and austenitic phase.

[0020] Stabilization of corrosion resistance performance is possible when a solid solution heat treatment produces appropriate fractions of the two phases, and when precipitates and an embrittlement phase that are formed during cooling and hot forming after solidification and are harmful to corrosion resistance are dissolved in steel and the corrosion-resistant elements are dispersed evenly in the steel.

[0021] A duplex stainless steel pipe can have high corrosion resistance performance by adjusting the chemical components and performing a solid solution heat treatment. However, the austenitic phase decreases the yield strength of the duplex stainless steel pipe. Accordingly, an axial tensile yield strength of 689 MPa or more required for steel pipes

to be used for oil well or geothermal well applications cannot be obtained by simply adjusting the chemical components and performing a solid solution heat treatment. For this reason, in manufacture of a duplex stainless steel pipe, the solid solution heat treatment is followed by cold-rolling dislocation strengthening to provide the desired strength.

[0022] Cold drawing or cold pilgering is a conventional method of cold rolling for increasing steel pipe strength. These rolling methods involve reduction of wall thickness or axial stretching of a steel pipe.

[0023] The solid solution heat treatment discussed above must be performed before these cold rolling processes. This is because the dislocation provided by cold rolling is annihilated, and the effect of cold rolling to improve yield strength cannot be obtained when a steel pipe is subjected to high temperature such as in a solid solution heat treatment after cold rolling. The solid solution heat treatment performed before cold rolling forms oxide layers on inner and outer surfaces of a steel pipe.

[0024] The oxide layers on inner and outer surfaces of a steel pipe before cold rolling are removed with an acid before a commonly performed cold drawing or pilger rolling because of a possibility of damaging tools used for cold rolling. An alternative way of protecting tools is to form a lubricative lubricant coating on a steel pipe surface by a chemical treatment, and remove the coating with the oxide layer by cleaning after cold rolling. Removal of oxide layers before or after cold rolling results in bare metal surfaces inside and outside of the steel pipe.

[0025] Cold rolling is also a process that exposes metal on steel pipe surfaces. Specifically, cold drawing and cold pilgering are rolling methods that involve reduction of wall thickness and stretching of a steel pipe, and, accordingly, the metallic portion, which is the base material, increases its surface area. Unlike the base material, the oxide layer lacks ductility, and cannot follow the deformation. This results in even more exposure of metal on newly-formed surfaces of the steel pipe after cold rolling.

[0026] For the reasons discussed above, a current duplex stainless steel product inevitably has bare metal surfaces if it were to have high corrosion resistance and high axial tensile yield strength. When such a steel pipe is used in oil well or geothermal well applications, defects or indentations occur when the steel pipe scrapes or collides with hard objects or with other steel pipe, or when contact pressure is exerted upon by a joining tool. Such degradation of the product surface leads to damage or corrosion in the steel pipe, and the resulting decrease of dimensional accuracy causes a decrease of axial compressive yield strength and circumferential tensile yield strength.

[0027] By focusing on these points, the present inventors conducted investigation of a technique to produce a steel pipe without removing surface oxide layers. The investigation led to the finding that excellent abrasion resistance and indentation resistance can be achieved while ensuring high strength and high corrosion resistance when a solid solution heat treatment is performed under specific conditions, and when cold circumferential bending and reverse bending is performed without removing the oxide layers formed.

[0028] The present invention has been made on the basis of this finding, and the gist of the present invention is as follows.

[1] A duplex stainless steel pipe having a composition that contains, in mass%, C: 0.005 to 0.150%, Si: 1.0% or less, Mn: 10.0% or less, Cr: 11.5 to 35.0%, Ni: 0.5 to 15.0%, Mo: 0.5 to 6.0%, N: less than 0.400%, and the balance being Fe and incidental impurities, and having a microstructure with a ferritic phase and an austenitic phase, the duplex stainless steel pipe having an axial tensile yield strength of 689 MPa or more, and having an outer surface and an inner surface each having an oxide layer having an average thickness of 1.0 μm or more.

[2] The duplex stainless steel pipe according to [1], wherein the oxide layer covers at least 50% of the outer surface and at least 50% of the inner surface of the steel pipe in terms of an area percentage.

[3] The duplex stainless steel pipe according to [1] or [2], which has an axial compressive yield strength-to-axial tensile yield strength ratio of 0.85 to 1.15.

[4] The duplex stainless steel pipe according to any one of [1] to [3], wherein the composition further contains, in mass%, one or two or more selected from W: 6.0% or less, Cu: 4.0% or less, V: 1.0% or less, and Nb: 1.0% or less.

[5] The duplex stainless steel pipe according to any one of [1] to [4], wherein the composition further contains, in mass%, one or two selected from Ti: 0.30% or less and Al: 0.30% or less.

[6] The duplex stainless steel pipe according to any one of [1] to [5], wherein the composition further contains, in mass%, one or two or more selected from B: 0.010% or less, Zr: 0.010% or less, Ca: 0.010% or less, Ta: 0.30% or less, Sb: 0.30% or less, Sn: 0.30% or less, and REM: 0.010% or less.

[7] A method for manufacturing a duplex stainless steel pipe of any one of [1] to [6], the method including:

hot rolling a steel pipe material into a shape of a steel pipe;

subjecting the steel pipe material after the hot rolling to a solid solution heat treatment that satisfies the formula (1) below; and

performing cold circumferential bending and reverse bending without removing an oxide layer formed on the steel pipe material after the solid solution heat treatment,

$$T_{\max}^2 \times t / [\text{Cr}]^4 > 1,000 \quad (1),$$

wherein $T_{\max}$ is a highest heating temperature ($^{\circ}\text{C}$) of the solid solution heat treatment, t is a retention time (s) at the highest heating temperature of the solid solution heat treatment, and $[\text{Cr}]$ is the content of Cr (mass%) in the steel pipe.

[8] The method according to [7], wherein the highest heating temperature in the hot rolling is $1,150^{\circ}\text{C}$ or more.

[9] The method according to [7] or [8], wherein the cold bending and reverse bending reduces a diameter of the steel pipe material to $(D_i/D_o) \times 100 = 99\%$ or less, where D_i is an outside diameter of the steel pipe material after work, and D_o is an outside diameter of the steel pipe material before work.

[10] The method according to any one of [7] to [9], wherein $(L_i/L_o) \times 100 (\%)$ is 125% or less after the cold bending and reverse bending, where L_i is an axial length of the steel pipe material after work, and L_o is an axial length of the steel pipe material before work.

Advantageous Effects of Invention

[0029] With the present invention, high abrasion resistance and high indentation resistance can be achieved while ensuring excellent axial tensile yield strength. Scratch defects and indentations caused by collision and scraping can therefore be stably reduced even in oil well or geothermal well applications where temperature and pressure are high and the environment is highly corrosive.

Brief Description of Drawings

[0030]

FIG. 1 is a graph explaining the thickness of an oxide scale layer and its effect to reduce surface defect.

FIG. 2 shows schematic views representing circumferential bending and reverse bending.

Description of Embodiments

[0031] The present invention is described below.

[0032] A duplex stainless steel pipe of the present invention has a composition that contains, in mass%, C: 0.005 to 0.150%, Si: 1.0% or less, Mn: 10.0% or less, Cr: 11.5 to 35.0%, Ni: 0.5 to 15.0%, Mo: 0.5 to 6.0%, N: less than 0.400%, and the balance being Fe and incidental impurities, and has a microstructure with a ferritic phase and an austenitic phase. The duplex stainless steel pipe of the present invention has an axial tensile yield strength of 689 MPa or more, and has an outer surface and an inner surface each having an oxide layer having an average thickness of $1.0 \mu\text{m}$ or more.

[0033] The reasons for limiting the composition of the duplex stainless steel pipe of the present invention are described first. It is to be noted that "%" used in conjunction with the content of each component means "mass%".

C: 0.005 to 0.150%

[0034] C deteriorates corrosion resistance. Increasing the C content causes a transformation of austenitic phase into martensitic phase, and makes cold rolling and cold working difficult. The C content is therefore 0.150% or less to obtain appropriate corrosion resistance performance and an appropriate duplex structure. The C content is 0.005% or more because the decarburization cost of smelting increases when the C content is too low. The C content is preferably 0.080% or less.

Si: 1.0% or Less

[0035] Remaining Si in steel due to excess Si content has a possibility of impairing workability and low-temperature toughness. For this reason, the Si content is 1.0% or less. Preferably, the Si content is 0.8% or less. Si acts to deoxidize steel, and it is effective to add this element to the molten steel in appropriate amounts. To this end, the Si content is preferably 0.01% or more. In view of providing a sufficient deoxidizing effect while reducing the side effects of remaining excess Si in steel, the Si content is more preferably 0.2% or more.

Mn: 10.0% or Less

[0036] An excessively high Mn content decreases low-temperature toughness. For this reason, the Mn content is 10.0% or less. The Mn content is preferably less than 1.0% when low-temperature toughness needs to be increased. Mn is a strong austenitic phase-forming element, and is available at lower costs than other austenitic phase-forming elements. Mn is also effective at neutralizing the impurity element S that mixes into the molten steel, and Mn has the effect to fix S by forming MnS with S, which greatly impairs the corrosion resistance and toughness of steel even when added in trace amounts. From this viewpoint, the Mn content is preferably 0.01% or more. When there is a need to take advantage of Mn as an austenitic phase-forming element to achieve cost reduction while providing low-temperature toughness, the Mn content is more preferably 2.0% or more. The Mn content is more preferably 8.0% or less.

Cr: 11.5 to 35.0%

[0037] Cr is an element that increases the strength of the passive film of steel, and improves corrosion resistance. Cr is also an element that is needed to stabilize the ferritic phase and obtain an appropriate duplex structure. In the present invention, the Cr content needs to be 11.5% or more to obtain a duplex structure and high corrosion resistance. Cr is an underlying element that stabilizes the passive film, and the passive film becomes stronger as the Cr content increases. Accordingly, increasing the Cr content contributes to improving the corrosion resistance. However, with a Cr content of more than 35.0%, precipitation of embrittlement phase occurs in the process of solidification from the melt. This causes cracking throughout the steel, and makes the subsequent forming process difficult. For this reason, the upper limit of Cr content is 35.0%. Taken together, the Cr content is 11.5 to 35.0% in the present invention. From the viewpoint of ensuring corrosion resistance and manufacturability at the same time, the Cr content is preferably 20% or more. The Cr content is preferably 28% or less.

Ni: 0.5 to 15.0%

[0038] Ni is an expensive element compared to other austenitic phase-forming elements, and an increased Ni content leads to increased manufacturing costs. For this reason, the Ni content is 15.0% or less. Ni is a strong austenitic phase-forming element, and improves the low-temperature toughness of steel. It is therefore desirable to make active use of Ni when the use of Mn as an inexpensive austenitic phase-forming element is an issue for low-temperature toughness. To this end, the Ni content is 0.5% or more. When low-temperature toughness is not of concern, it is preferable to use Ni in combination with other elements with the Ni content of 0.5 to 5.0%. On the other hand, when high low-temperature toughness is needed, it is effective to actively add Ni, preferably in an amount of 5.0% or more. The Ni content is preferably 13.0% or less.

Mo: 0.5 to 6.0%

[0039] Mo increases the pitting corrosion resistance of steel in proportion to its content. To this end, Mo needs to be uniformly present on surfaces of steel material exposed to a corrosive environment. However, when Mo is added in excess amounts, precipitation of embrittlement phase occurs in the process of solidification from the melt. This causes large numbers of cracks in the solid microstructure, and greatly impairs stability in subsequent forming. For this reason, the Mo content is 6.0% or less. Mo increases the pitting corrosion resistance in proportion to its content. However, the Mo content needs to be 0.5% or more to maintain stable corrosion resistance in a sulfide environment. For these reasons, the Mo content is 0.5 to 6.0% in the present invention. From the viewpoint of satisfying both the corrosion resistance and production stability needed for the duplex stainless steel pipe, the Mo content is preferably 1.0% or more. The Mo content is preferably 5.0% or less.

N: Less than 0.400%

[0040] While N itself is inexpensive, excessive addition of N requires specialty equipment and time, and increases the manufacturing cost. For this reason, the N content is less than 0.400%. N is a strong austenitic phase-forming element, in addition to being inexpensive. In the form of a solid solution in steel, N is an element that is useful for improving corrosion resistance performance and strength. There is no particular need to set limits for N content, as long as the product can have an appropriate duplex fraction with N and other austenitic phase-forming elements. However, an overly low N content necessitates a high degree of vacuum for smelting and refining, and restricts the types of raw materials that can be used. For this reason, the N content is preferably 0.010% or more.

[0041] The balance in the composition above is Fe and incidental impurities.

[0042] Additionally, the following elements may be appropriately contained in the present invention, as needed.

One or Two or More Selected from W: 6.0% or Less, Cu: 4.0% or Less, V: 1.0% or Less, and Nb: 1.0% or Less W: 6.0% or Less

[0043] As is Mo, W is an element that increases the pitting corrosion resistance in proportion to its content. However, when contained in excess amounts, W impairs the workability of hot working, and damages production stability. For this reason, W, when contained, is contained in an amount of 6.0% or less. W improves pitting corrosion resistance in proportion to its content, and the W content does not particularly require a lower limit. It is, however, preferable to add W in an amount of 0.1% or more, in order to stabilize the corrosion resistance performance of the duplex stainless steel pipe. From the viewpoint of the corrosion resistance and production stability needed for the duplex stainless steel pipe, the W content is more preferably 1.0% or more. The W content is more preferably 5.0% or less.

Cu: 4.0% or Less

[0044] Cu is a strong austenitic phase-forming element, and improves the corrosion resistance of steel. It is therefore desirable to make active use of Cu when sufficient corrosion resistance cannot be provided by other austenitic phase-forming elements Mn and Ni. On the other hand, when contained in excessively large amounts, Cu leads to decrease of hot workability, and forming becomes difficult. For this reason, Cu, when contained, is contained in an amount of 4.0% or less. The Cu content does not particularly require a lower limit. However, the corrosion resistance improving effect can be obtained when the Cu content is 0.1% or more. From the viewpoint of satisfying both improvement of corrosion resistance and hot workability, the Cu content is more preferably 1.0% or more. The Cu content is more preferably 3.0% or less.

V: 1.0% or Less

[0045] Excess addition of V impairs low-temperature toughness, and the V content is preferably 1.0% or less when V is contained. Because V is also effective for improving strength, this element can be contained when higher strength is required. The strength improving effect can be obtained with a V content of 0.01% or more. For this reason, the V content is preferably 0.01% or more when V is contained. Because V is an expensive element, the V content is preferably 0.40% or less from the view point of its strength improving effect and cost. The V content is more preferably 0.10% or less, even more preferably 0.06% or less. The V content is more preferably 0.05% or more.

Nb: 1.0% or Less

[0046] Excess addition of Nb impairs low-temperature toughness, and the Nb content is preferably 1.0% or less. Because Nb is also effective for improving strength, this element can be contained when higher strength is required. The strength improving effect can be obtained with a Nb content of 0.01% or more. For this reason, the Nb content is preferably 0.01% or more when Nb is contained. As is V, Nb is an expensive element, and the Nb content is preferably 0.40% or less from the view point of its strength improving effect and cost. The Nb content is more preferably 0.10% or less, even more preferably 0.06% or less. The Nb content is more preferably 0.05% or more.

[0047] The following elements may also be appropriately contained in the present invention, as needed.

One or Two Selected from Ti: 0.30% or Less and Al: 0.30% or Less

Ti: 0.30% or Less

[0048] The Ti content is preferably 0.30% or less because increasing the Ti content decreases the low-temperature toughness of steel pipe. Ti is capable of refining the solidified microstructure and fixing the excess C and N, and may be appropriately contained when control of microstructure or adjustments of chemical components are needed. When containing Ti, these effects can be obtained with a Ti content of 0.0001% or more. The Ti content is more preferably 0.001% or more. The Ti content is more preferably 0.10% or less.

Al: 0.30% or Less

[0049] Al impairs toughness when this element remains in large amounts in steel pipe. For this reason, the Al content is preferably 0.30% or less when Al is contained. The Al content is more preferably 0.10% or less, even more preferably 0.02% or less.

[0050] Al is also effective as a deoxidizing agent in refining. To obtain this effect, the Al content is preferably 0.01% or more.

[0051] The following elements may also be appropriately contained in the present invention, as needed.

One or Two or More Selected from B: 0.010% or less, Zr: 0.010% or less, Ca: 0.010% or less, Ta: 0.30% or less, Sb: 0.30% or less, Sn: 0.30% or less, and REM: 0.010% or less

[0052] B, Zr, Ca, and REM impair hot workability when contained in excessively large amounts, and, because these are rare elements, B, Zr, Ca, and REM raise the alloying cost when the content is excessively high. For this reason, the content is preferably 0.010% or less for each of B, Zr, Ca, and REM. The content is more preferably 0.0015% or less for each of Ca and REM.

[0053] When contained in trace amounts, B, Zr, Ca, and REM improve bonding at grain boundaries, and improve hot workability and formability by altering the form of surface oxide. A duplex stainless steel pipe is typically a difficult-to-process material, and is susceptible to roll marks and shape defects attributed to amounts and form of work. B, Zr, Ca, and REM are effective when the forming conditions involve this issue. The lower limit is not particularly required for the content of each element. However, when these elements are contained, the workability and formability improving effect can be obtained when the content of each element is 0.0001% or more.

[0054] When Ta is contained, the Ta content is preferably 0.30% or less because an excessively high Ta content increases the alloying cost. When added in small amounts, Ta reduces the transformation into the embrittlement phase, and improves hot workability and corrosion resistance at the same time. Ta is effective when the embrittlement phase persists for a long time period in a stable temperature region in hot working or in subsequent cooling. For these reasons, the Ta content is preferably 0.0001% or more when Ta is contained.

[0055] Formability decreases when the content of Sb and Sn is overly high. For this reason, when Sb and Sn are contained, the content is preferably 0.30% or less for each of these elements. Sb and Sn improve corrosion resistance when contained in small amounts. For this reason, the content is preferably 0.0003% or more for each of Sb and Sn when Sb and Sn are contained.

Duplex Ferritic and Austenitic Phase

[0056] The following describes the ferritic phase and austenitic phase, which affect corrosion resistance. The ferritic phase and austenitic phase of the duplex stainless steel pipe act differently on corrosion resistance, and provide high corrosion resistance by being present in a duplex state in steel. That is, the duplex stainless steel must have both austenitic phase and ferritic phase. Because the present invention provides a duplex stainless steel pipe used in applications requiring corrosion resistance, it is preferable that the fractions of the two phases is controlled from the viewpoint of corrosion resistance. In the present invention, the fraction (volume fraction) of the ferritic phase in the microstructure of the duplex stainless steel pipe is preferably 20% to 80%. For use in environments requiring even higher corrosion resistance, the ferritic phase is preferably 35% to 65%, in compliance with ISO 15156-3. The remainder is preferably the austenitic phase.

[0057] A microstructure containing a martensitic phase or an embrittlement phase cannot be used because hot workability and cold workability decrease, and the stainless steel cannot be formed into the shape of the product. When the microstructure is not a duplex structure but is a single-phase structure of ferritic or austenitic phase, it is not possible to obtain corrosion resistance performance, and cold working fails to produce a high axial tensile strength. In the present invention, the microstructure is required to contain both ferritic phase and austenitic phase.

[0058] Specifically, the microstructure of the present invention is a microstructure with a ferritic phase and an austenitic phase, preferably a microstructure consisting of a ferritic phase and an austenitic phase.

[0059] For observation of the microstructure, a test specimen for microstructure observation is taken to observe an axial plane section. The volume fractions of ferritic phase and austenitic phase can be determined by observing the surface with a scanning electron microscope. Specifically, the test specimen for microstructure observation is etched with a Vilella's solution (a reagent prepared by mixing 2 g of picric acid, 10 ml of hydrochloric acid, and 100 ml of ethanol), and a microstructure image is captured with a scanning electron microscope (SEM; 1,000 times). From the micrograph of microstructure, the average area percentage is calculated for the ferritic phase and the austenitic phase to determine the volume fraction (volume%) of each phase, using an image analyzer.

[0060] In a captured image, the ferritic phase, which is less likely to be etched, appears white in color after binarization, whereas the easier to be etched austenitic phase appears black in the binarized image. The image is binarized for a $600\ \mu\text{m} \times 800\ \mu\text{m}$ measurement area ($1,920\ \text{pixels} \times 2,560\ \text{pixels}$) after the captured image is transformed into a grayscale image with 256 intensities. For binarization, the minimum brightness between two peaks observed in a histogram plotting brightness (256 intensities) on the horizontal axis is set as the threshold.

Axial Tensile Yield Strength: 689 MPa or More

[0061] For extraction of oil from oil wells or extraction of hot water, steel pipes are joined to extend down from the ground, and experience a high axial tensile stress. This makes the adjustment of axial tensile yield strength important from among different types of strengths. An ordinary duplex stainless steel pipe cannot achieve an axial tensile yield strength of 689 MPa or more after a solid solution heat treatment performed to provide excellent corrosion resistance performance. The yield strength is therefore increased by cold-rolling dislocation strengthening. The axial tensile yield strength is preferably 757.9 MPa or more because material can be saved by reducing the pipe thickness needed for strength improvement. The axial tensile yield strength is more preferably 861.25 MPa or more. There is no upper limit; however, the axial tensile yield strength is preferably 1033.5 MPa or less because the effect to reduce the wall thickness of steel pipe becomes lost when the axial tensile yield strength exceeds 1033.5 MPa.

Axial Compressive Yield Strength/Axial Tensile Yield Strength: 0.85 to 1.15

[0062] Adjustment of axial tensile yield strength is important for the strength characteristics of a steel pipe. However, a steel pipe also undergoes axial bending deformation or experiences axial compressive stress during fastened with threads or the like, though the extent of such deformation or stress is small. It is therefore preferable that the ratio of axial compressive yield strength to axial tensile yield strength is 0.85 to 1.15, more preferably 0.90 or more. The ratio is more preferably 1.10 or less. When the ratio of axial compressive yield strength to axial tensile yield strength is 0.90 to 1.10, the steel pipe can withstand an even higher compressive yield stress when joined with threads.

[0063] For the measurement of axial compressive yield strength and axial tensile yield strength, a round-bar tensile test specimen and a cylindrical compression test specimen, each measuring 5.0 mm in outside diameter, are taken from a middle portion of the wall thickness at an end of a pipe prepared for pressure test. These are compressed or stretched at a rate of 1.0 mm/min, and a stress-strain curve is calculated in a tensile or compression test at room temperature.

The axial tensile yield strength and axial compressive yield strength are then calculated from the stress-strain curve.

[0064] Specifically, a cylinder compression test is performed for the measurement of axial compressive yield strength. A cylindrical test specimen to be compressed is taken from a middle portion of the wall thickness, parallel to the pipe axis. The cylindrical test specimen cut out from a middle portion of the pipe wall thickness has dimensions with an outside diameter d of 5.0 mm, and a height h of 8.0 mm. In the compression test, a load is applied to the test specimen placed between flat plates at room temperature (25°C), and the compressive yield strength is calculated from a stress-strain curve obtained as a result of compression. The stress-strain curve is obtained by compressing the test specimen 30% at a crosshead speed of 1.0 mm/min, using a compression testing machine.

[0065] For the measurement of axial tensile yield strength, a round-bar tensile test specimen, measuring 5.0 mm in diameter at a parallel portion, is taken from a middle portion of the pipe wall thickness, parallel to the pipe axis in accordance with JIS Z2241. In a tensile test, the test specimen is stretched to break at room temperature (25°C) with a crosshead speed of 1.0 mm/min. The tensile yield strength is then calculated from a stress-strain curve obtained as a result of the tensile test.

[0066] In order to ensure that the ratio of axial compressive yield strength to axial tensile yield strength stably falls in the 0.85 to 1.15 range, it is preferable that the average aspect ratio of austenite grains separated by a crystal orientation angle difference of 15° or more in an axial wall-thickness plane section is preferably 9 or less.

[0067] It is also preferable that austenite grains with an aspect ratio of 9 or less have an area fraction of 50% or more.

[0068] Specifically, the average aspect ratio is preferably 9 or less for austenite grains having a grain size (diameter) of 10 μm or more by assuming that the grains are true circles (true circles created without changing the area).

[0069] It is also preferable that austenite grains having an aspect ratio of 9 or less have an area fraction of 50% or more in austenite grains having a grain diameter of 10 μm or more. That is, it is preferable to satisfy $((2)/(1)) \times 100 (\%) = 50\%$ or more, where (1) represents the total area of austenite grains having a grain diameter of 10 μm or more, and (2) represents the area of austenite grains having a grain diameter of 10 μm or more and an aspect ratio of 9 or less.

[0070] A duplex stainless steel pipe of the present invention is adjusted to have appropriate fractions of two phases by a solid solution heat treatment.

[0071] Here, the austenitic phase is a microstructure having a plurality of crystal grains separated by an orientation angle of 15° or more after recrystallization. This makes the aspect ratio of austenite grains smaller. In this state, the duplex stainless steel pipe does not have the axial tensile yield strength required for oil well or geothermal well applications. However, the ratio of axial compressive yield strength to axial tensile yield strength is close to an ideal value of 1. The duplex stainless steel pipe is then subjected to cold working to provide the axial tensile yield strength required for oil well or geothermal well applications. However, a notable characteristic of metals, including duplex stainless steels, is that the yield strength of the direction opposite the direction stretched by cold working decreases because of the Bauschinger effect. That is, the relationship between axial compressive strength and axial yield strength tends to become unstable when the aspect ratio increases as a result of stretching of microstructure by cold rolling.

[0072] For these reasons, in the present invention, a duplex stainless steel pipe having an axial compressive yield strength-to-axial tensile yield strength ratio of 0.85 to 1.15 can easily be obtained when austenite grains having a grain diameter of 10 μm or more have an average aspect ratio of 9 or less. A stable steel pipe with a small strength anisotropy can also be obtained when austenite grains having an aspect ratio of 9 or less have an area fraction of 50% or more. A duplex stainless steel pipe with a desirable relationship between axial compressive yield strength and axial tensile yield strength can be obtained even more stably when the average aspect ratio is 5 or less. Smaller aspect ratios mean smaller strength anisotropies, and, accordingly, the aspect ratio should be brought closer to 1, with no lower limit.

[0073] The aspect ratio of austenite grains is determined, for example, as a ratio of the longer side and shorter side of a rectangular enclosure containing grains having a crystal orientation angle of 15° or more observed in the austenitic phase in a crystal orientation analysis of an axial wall-thickness plane section. Specifically, for the measurement of aspect ratio, the aspect ratio of austenite grains separated by a crystal orientation angle of 15° is measured by an EBSD crystal orientation analysis of an axial plane section of the steel pipe at a middle portion of the wall thickness. The aspect ratio is measured for austenite grains having a grain size (diameter) of 10 μm or more in a 1.2 mm $\times$ 1.2 mm measurement area by assuming that the grains are true circles (true circles created without changing the area).

[0074] Here, austenite grains of small grain diameters are prone to producing large measurement errors, and the presence of such austenite grains of small grain diameters may cause errors in the aspect ratio. It is therefore preferable that the aspect ratio is measured for austenite grains having a grain diameter of 10 μm or more by assuming that the grains are true circles.

[0075] The aspect ratio of ferritic phase is not particularly limited. This is because the austenitic phase has a lower yield strength, and, unlike the aspect ratio of austenite grains that easily affects the Bauschinger effect after work, the aspect ratio of ferrite grains has no effect on the Bauschinger effect.

Oxide layers (Surface Oxide Coatings) on Outer and Inner Surfaces of Steel Pipe Have Average Thickness of 1.0 μm or More

[0076] The surface of stainless steel has a passive film that improves corrosion resistance. The passive film is different from the surface oxide layer of interest in the present invention. The passive film is a thin film with a thickness of 0.01 μm or less. In contrast, the oxide layer of interest in the present invention is a layer of primarily Cr, Fe, and O (oxygen) that is formed by heating at 600°C or more, and contains ferrioxides containing O and Cr.

[0077] In the case of a duplex stainless steel, the oxides that form the oxide layer are usually of a spinel form rich in Fe, O, Cr, and Si ((Fe,Cr,Si)₃O₄, (Fe,Cr)₃O₄, Fe₃O₄).

[0078] A Si-rich oxide layer may occur in regions closer to the base material different from the oxide layer. The outer surface of oxide layer has a low Cr content, and hematite may be present that is composed of Fe and O (OH). Regardless of its composition, the oxide layer is harder than the base material, and produces the desired effect, provided that the oxide layer is an oxide with a composition containing O diffused by heating. In the present invention, it is preferable to form a spinel-type oxide layer, which has good adhesion to the base material, in a thickness of 1.0 μm or more (average thickness).

[0079] In the present invention, the composition of oxide layer is not particularly limited, as discussed above. However, the thickness of oxide layer needs to be adjusted. The present inventors have elucidated the effect of the chemical components in steel and the heat treatment conditions (highest heating temperature and the retention time at the highest heating temperature) on the thickness of oxide layer, and how the thickness of oxide layer, surface abrasion resistance, and indentation resistance are related to one another, as follows.

[0080] First, the present inventors prepared sets of five duplex stainless steel pipes containing 22.0 to 28.0 mass% of Cr, and investigated the thickness of the oxide layer on steel pipe surface by performing a solid solution heat treatment with varying highest heating temperature and varying retention time at the highest heating temperature. It was confirmed after this and other investigations that the oxide layer can stably have a thickness (average thickness) of 1.0 μm or more by satisfying the following formula (1).

$$T_{\text{max}}^2 \times t / [\text{Cr}]^4 > 1,000 \quad (1)$$

[0081] In the formula (1), T_{max} is the highest heating temperature (°C) of a solid solution heat treatment, t is the retention time (s) at the highest heating temperature in the solid solution heat treatment, and $[\text{Cr}]$ is the content of Cr (mass%) in the steel pipe.

[0082] Solid solution heat treatments were performed under different conditions satisfying values calculated from formula (1), and steel pipes (steel pipe materials) having 1.0 to 45.0 μm -thick surface oxide layers were obtained. A steel pipe selected from each set of steel pipes sharing the same components was cleaned with an acid or polished to remove and reduce the thickness of the surface oxide layer to less than 1.0 μm . At this stage, the steel pipe materials

had an axial tensile yield strength of 689 MPa or less.

[0083] The steel pipe materials with the oxide layers, and the steel pipe materials with oxide layers less than 1.0 μm thick after cleaning with an acid or polishing were all subjected to cold bending and reverse bending that reduced the outside diameter 10% and stretched the pipe 8% along the axis, in order to increase the axial tensile yield strength of steel pipe from 861 MPa to 931 MPa. The oxide layer thickness measured after cold bending and reverse bending was no different from that before the cold working.

[0084] The high-strength steel pipes so obtained were subjected to a scratch test, in which the steel pipe surface was scratched over a distance of 30 mm along the pipe axis with an indenter (a stylus with a cemented carbide tip) under a 59 N load. The oxide layer on steel pipe surface was then evaluated with regard to abrasion resistance and indentation resistance by measuring the oxide layer thickness and the height difference after the scratch test (the height of the indented portion in the scratched surface relative to the raised portion occurring after making the indentation).

[0085] The results are shown in FIG. 1. Steel pipes having oxide layers with a thickness of 1.0 μm or more had significantly reduced height differences in the surfaces, and showed improvement of abrasion resistance and indentation resistance characteristics. In contrast, in steel pipes that had the oxide layers removed by cleaning with an acid, large height differences were observed after the scratch test, and the dimensional accuracy was poor because of defects and irregularities. The indented portions created by scratching are portions where stress concentrates, and it was confirmed that such indentations have a possibility of adversely affecting corrosion resistance performance against such as stress corrosion cracking.

[0086] From these results, it was found that excellent abrasion resistance and indentation resistance can be achieved when the oxide layer has an average thickness of 1.0 μm or more. It can also be seen from FIG. 1 that the height difference decreases as the oxide layer becomes thicker. It is therefore preferable that the average thickness of the oxide layer is 3.0 μm or more, more preferably 5.0 μm or more, provided that the conditions for the temperature and retention time of the solid solution heat treatment that provides the oxide layer are satisfied. There is no upper limit for the thickness of oxide layer. However, the preferred thickness of oxide layer is 200.0 μm or less because the oxide layer may exfoliate when it is too thick.

[0087] In the present invention, the oxide layer is a region in a cross section of a sliced steel pipe where the oxygen concentration is at least two times higher than in the base metal when measured from the inner and outer sides of the pipe by energy dispersive x-ray analysis after polishing the cross-sectional surface to a mirror finish. The oxide layer thickness (average thickness) is the average of measured values from arbitrarily chosen 5 points (preferably, equally spaced apart along the circumferential direction) (oxide layer thickness = a value obtained by dividing a total of thicknesses from 5 points by 5).

[0088] It is preferable not to perform pickling before the solid solution heat treatment and cold working (so that the oxide layer from hot rolling remains on steel pipe surface) because it allows the oxide layer to have a thickness that effectively provides abrasion resistance and indentation resistance.

Coverage of Oxide Layer on Outer and Inner Surfaces of Steel Pipe is 50% or More in Terms of Area Percentage in Each Surface

[0089] The steel pipe is protected from abrasion, scratch defects, and indentations in areas covered by the oxide layer. Preferably, the oxide layer covers at least 50% of the total surface area of the steel pipe. Preferably, the coverage is 80% or more when larger outer surface areas need to be protected. Preferably, the oxide layer covers at least 90% of the inner surface because the inner surface is more susceptible to collision damage caused by hard objects traveling inside the steel pipe.

[0090] The coverage of a steel pipe surface by oxide layer is a percentage determined from the pipe surface area of a region with no oxide layer (uncoated area) divided by the total surface area of pipe calculated from the outside diameter, wall thickness, and length of the pipe. The surface area of a region with no oxide layer is easily measurable because these regions show a metallic sheen after abrasive polishing or pickling.

[0091] Specifically, an enclosure (a rectangle) that is parallel to circumferential and axial directions is drawn so as to include a region that, upon visual inspection, appears to have been polished or pickled. The uncoated area can then be calculated from the circumferential length (the longer side of the rectangle) and the axial length (the shorter side of the rectangle). Here, the area is calculated as the product of the circumferential length (the longer side of the rectangle) and the axial length (the shorter side of the rectangle), and the sum of these areas from the same steel pipe is determined.

[0092] In order to find the total surface area of a steel pipe (the total surface area is the surface area excluding the end portions where the pipe is cut), the outer circumferential length and inner circumferential length of the steel pipe are determined from its outside diameter and wall thickness, and the outer circumferential length and inner circumferential length are separately multiplied by the axial length, and the products of these multiplications are added to determine the total surface area. Here, the outside diameter, wall thickness, and length are average values. The coverage of a steel pipe surface by oxide layer can then be determined as a percentage (%) by dividing the uncoated area by the total

surface area of the steel pipe.

[0093] In view of uniformity of properties along the circumferential direction, the duplex stainless steel pipe is preferably a seamless steel pipe with no seams along the circumferential direction.

[0094] The following describes a method for manufacturing a duplex stainless steel pipe of the present invention.

[0095] First, a steel material of the foregoing duplex stainless steel composition is produced. The process for smelting the duplex stainless steel may use a variety of melting processes, and is not limited. For example, a vacuum melting furnace or an atmospheric melting furnace may be used when making the steel by electric melting of iron scrap or a mass of various elements. As another example, a bottom-blown decarburization furnace using an Ar-O₂ mixed gas, or a vacuum decarburization furnace may be used when using hot metal from a blast furnace. The molten material is solidified by static casting or continuous casting, and formed into ingots or slabs before being hot rolled into a sheet- or round billet-shaped material.

[0096] In the case of a welded steel pipe produced by forming a sheet-shaped steel material into a cylindrical shape and welding the end portions, the steel pipe may be a UOE steel pipe using a steel sheet, or an electric resistance welded steel pipe produced by roll forming. In the case of a seamless steel pipe using a round billet, a round billet is heated with a heating furnace, and formed into a steel pipe through hot pierce rolling and subsequent wall thickness reduction sizing. The process used to form a round billet into a hollow pipe by hot forming (piercing) may be, for example, the Mannesmann process or extrusion pipe-making process. For wall thickness reduction and outside diameter sizing, it is possible to use, for example, an elongator, an assel mill, a mandrel mill, a plug mill, a sizer, or a stretch reducer.

[0097] The highest heating temperature in the hot rolling is preferably 1,150°C or more.

[0098] A thicker oxide layer can be obtained when the oxide layer after the solid solution heat treatment and cold working is not removed by, for example, pickling or surface polishing, and when the highest heating temperature of hot rolling is 1,150°C or more, as described below.

Solid Solution Heat Treatment

[0099] A solid solution heat treatment is performed because after the steel is hot-formed into a steel pipe, various carbonitrides and intermetallic compounds are formed in steel upon air cooling. Specifically, a duplex stainless steel in hot rolling undergoes a gradual temperature decrease while being hot rolled from the high-temperature state of heating. The steel pipe is typically air cooled after hot forming, and temperature control is not achievable because the temperature history varies with the size and type of product. This may lead to decrease of corrosion resistance as a result of the corrosion-resistant elements being consumed in the form of thermochemically stable precipitates that form in various temperature regions in the course of temperature decrease. There is also a possibility of a phase transformation into the embrittlement phase, which leads to serious decrease of low-temperature toughness. A duplex stainless steel needs to withstand a variety of corrosive environments, and it is important that the austenitic phase and ferritic phase are in an appropriate duplex state in use. However, because the rate of cooling from the heating temperature is not controllable, it is difficult to control the fractions of the two phases consecutively varying with retention temperature.

[0100] To address these issues, a solid solution heat treatment is often performed that involves rapid cooling after hot forming, so as to form a solid solution of precipitates in steel, and to initiate a reverse transformation of embrittlement phase to non-embrittlement phase, and bring the phase fractions to an appropriate duplex state.

[0101] The solid solution heat treatment is a process that heat-decomposes the carbonitrides and embrittlement phase without decomposing the duplex ferritic and austenitic phase (for example, by heating at a heating temperature of 1,000°C or more), and quenches the heated steel to prevent reprecipitation.

[0102] This process dissolves the precipitates and embrittlement phase into steel, and controls the phase fractions to achieve an appropriate duplex state. The solid solution heat treatment is typically performed at a high temperature of 900°C or more, though the temperature that dissolves the precipitates, the temperature that initiates a reverse transformation of embrittlement phase, and the temperature that brings the phase fractions to an appropriate duplex state slightly vary with the types of elements added. In the present invention, the solid solution heat treatment temperature is preferably 900°C or more, even more preferably 1,000°C or more. The solid solution heat treatment temperature is preferably 1,150°C or less.

[0103] The heating is followed by quenching to maintain the solid-solution state. This may be achieved by compressed-air cooling, or by using various coolants, such as mist, oil, and water. In the present invention, the surface oxide layer important for abrasion resistance and indentation resistance can occur after the hot rolling and after the solid solution heat treatment, and the oxide layer is not removed before or after cold working.

[0104] The oxide layer after the solid solution heat treatment is not removed by pickling, and the way this is achieved is not particularly limited, as long as the steel pipe produced has an oxide layer having an average thickness of 1.0 μm or more. For example, the oxide layer may be removed over the smallest possible area by, for example, polishing surfaces in areas affected by defects or galling, instead of removing the oxide layer throughout the pipe. Alternatively, the oxide layer in areas affected by defects or galling may be removed by, for example, polishing the surface before the

solid solution heat treatment in which growth of an oxide layer (oxide coating) takes place, without removing the oxide layer by pickling after the solid solution heat treatment.

$$T_{\max}^2 \times t / [\text{Cr}]^4 > 1,000 \quad (1)$$

[0105] In the formula (1), $T_{\max}$ is the highest heating temperature ($^{\circ}\text{C}$) of the solid solution heat treatment, t is the retention time (s) at the highest heating temperature of the solid solution heat treatment, and $[\text{Cr}]$ is the content (mass%) of Cr in the steel pipe.

[0106] Preferably, $T_{\max}$ is 900 to 1,150 $^{\circ}\text{C}$. Preferably, t is 600 to 3,600 s.

[0107] The solid solution heat treatment is performed so as to satisfy the formula (1), as noted above. In this way, the oxide layers formed on the outer and inner surfaces of the steel pipe can have an average thickness of 1.0 μm or more. In order to provide a thicker oxide layer, the left-hand side of the formula (1) is preferably more than 2,000, more preferably 2,500 or more, even more preferably 3,000 or more. The left-hand side of the formula (1) is preferably 8,000 or less, even more preferably 6,000 or less because the oxide layer may fall off in the furnace when there is excessive growth of oxide layer.

Cold Circumferential Bending and Reverse Bending (hereinafter, also referred to as "bending and reverse bending")

[0108] A steel pipe material after the solid solution heat treatment contains the low-yield-strength austenitic phase, and, with its as-processed form, the axial tensile yield strength required for oil well or gas well applications and for extraction of hot water cannot be obtained. To increase strength, dislocation strengthening is performed using various cold working techniques.

[0109] In the present invention, the yield strength of pipe is increased by circumferential bending and reverse bending. This enables formation of the surface oxide layer required for abrasion resistance and indentation resistance while stably improving axial tensile yield strength, as described below.

[0110] The cold working technique of the present invention is a novel method that makes use of dislocation strengthening by circumferential bending and reverse bending. This technique is described below, with reference to FIG. 2. Unlike cold drawing and cold pilgering that improve the tensile yield strength of a steel pipe by rolling that reduces the wall thickness and stretches the pipe along the axis, the foregoing technique produces strain by a bending process by flattening of a pipe (first flattening), and a reverse bending process that restores the full roundness (second flattening), as shown in FIG. 2. In this technique, the amount of strain is adjusted by repeating bending and reverse bending, or by varying the amount of bend, without greatly changing the initial shape of the steel pipe. That is, in contrast to the conventional cold rolling method that uses the axial elongation strain, the cold working method of the present invention that hardens the steel and increases steel pipe strength takes advantage of circumferential bending strain, and does not impart a large change in the shape of steel pipe after bending and reverse bending. That is, unlike cold drawing and cold pilgering that involve a newly-formed surface that occurs as a result of stretching that reduces the wall thickness, the method of the present invention, in principle, does not usually form such a new surface, and the steel pipe can have high yield strength while maintaining the surface oxide layers. The method of the present invention also differs from cold drawing and cold pilgering in that the method does not involve deformation occurring as a result of wall thickness reduction or stretching but involves bending that uses shear deformation. Bending is a form of deformation that requires a smaller force to provide the same deformation, and causes less damage to tools used for cold bending and reverse bending. Bending also does not require cleaning of the oxide layer with an acid before cold bending and reverse bending. There is also no need for a chemical-treatment coating process for lubrication because the extent of sliding against the tool is small. Another characteristic is that a tool does not need to be disposed on the inner side of the steel pipe. This makes it easier to maintain the oxide layer provided by the solid solution heat treatment.

[0111] In FIG. 2, (a) and (b) show cross-sectional views illustrating a tool with two points of contact. In FIG. 2, (c) is a cross-sectional view showing a tool with three points of contact. Thick arrows in FIG. 2 indicate the direction of an exerted force flattening the steel pipe. As shown in FIG. 2, for second flattening, the tool may be moved or shifted in such a manner as to rotate the steel pipe and make contact with portions of pipe that were not flattened by the first flattening (portions flattened by the first flattening are indicated by shadow shown in FIG. 2).

[0112] As illustrated in FIG. 2, the circumferential bending and reverse bending that flattens the steel pipe, when intermittently or continuously applied throughout the pipe circumference, produces strain in the pipe, with bending strain occurring in portions where the curvature becomes the largest, and reverse bending strain occurring toward portions where the curvature is the smallest. The strain needed to improve the strength of the steel pipe (dislocation strengthening) accumulates after the deformation due to bending and reverse bending. Unlike the working that achieves reduced wall thickness and reduced outside diameter by compression, a characteristic feature of the foregoing method is that the pipe is deformed by being flattened, and, because this is achieved without requiring large power, it is possible to minimize

the shape change before and after work.

[0113] A tool used to flatten the steel pipe, such as that shown in FIG. 2, may have a form of a roll. In this case, two or more rolls may be disposed around the circumference of a steel pipe. Deformation and strain due to repeated bending and reverse bending can be produced with ease by flattening the pipe and rotating the pipe between the rolls. The rotational axis of the roll may be tilted within 90° with respect to the rotational axis of the pipe. In this way, the steel pipe moves in a direction of its rotational axis while being flattened, and can be continuously worked with ease. When using such rolls for continuous working, for example, the distance between the rolls may be appropriately varied in such a manner as to change the extent of flattening of a moving steel pipe. This makes it easy to vary the curvature (extent of flattening) of the steel pipe in the first and second runs of flattening. That is, by varying the roll distance, the moving path of the neutral line can be changed to uniformly produce strain in a wall thickness direction. The same effect can be obtained when the extent of flattening is varied by varying the roll diameter, instead of roll distance. It is also possible to vary both roll distance and roll diameter. With three or more rolls, the pipe can be prevented from whirling around during work, and this makes the procedure more stable, though the system becomes more complex.

[0114] In the cold bending and reverse bending of the present invention, it is preferable that $(D_i/D_o) \times 100$ is 99% or less, where D_i is the outside diameter after working of the steel pipe material (the steel pipe diameter after work), and D_o is the outside diameter before working of the steel pipe material (the initial diameter of steel pipe), regardless of the form of working. In this way, a circumferential increase in the areas of inner and outer surfaces can be reduced, and, accordingly, there is less exposure of a newly-formed surface after deformation, enabling the whole steel pipe to be stably coated with the oxide layer that provides excellent abrasion resistance and indentation resistance. In view of stably providing strength characteristics and oxide layers for the steel pipe, the range of $(D_i/D_o) \times 100$ is more preferably 80 to 95%.

[0115] In the cold bending and reverse bending of the present invention, it is preferable that $(L_i/L_o) \times 100$ (%) is 125% or less, where L_i is the axial length of the steel pipe material after work, and L_o is the axial length of the steel pipe material before work (a rate of elongational change).

[0116] In this way, an axial increase in the areas of inner and outer surfaces can be reduced, and, accordingly, there is less exposure of a newly-formed surface after deformation, enabling the whole steel pipe to be stably coated with the oxide layer that provides excellent abrasion resistance and indentation resistance. In view of stably providing strength characteristics and oxide layers for the steel pipe, the rate of elongational change is preferably 105 to 115%.

[0117] A duplex stainless steel pipe of the present invention can be produced by using the manufacturing method described above.

[0118] As described above, the present invention employs the cold bending and reverse bending method that enables the oxide layers to be maintained, and the duplex stainless steel produced can have high yield strength characteristics, and excellent abrasion resistance and indentation resistance provided by the oxide layers. This makes it possible to reduce defects and indentations that occur in a steel pipe used in oil well or gas well applications or in extraction of hot water (geothermal well applications), and provide a duplex stainless steel pipe having excellent corrosion resistance and dimensional accuracy.

Examples

[0119] The present invention is described below through Examples.

[0120] Steel materials of the compositions represented by steels A to O in Table 1 were smelted with a vacuum melting furnace, and each steel was hot rolled into a round billet having an outside diameter $\varnothing$ of 80 mm. In steels L, M, and N, the microstructure did not have an appropriate duplex state because the elements added to these steels were outside of the ranges of the present invention. In steel O in which Cr and Mo were added beyond the range of the present invention, cracking occurred in the process of solidification from the melt or during hot rolling.

[0121] A seamless steel pipe was formed by hot rolling, and subjected to a solid solution heat treatment.

[0122] The solid solution heat treatment was performed at the highest heating temperatures T_{max} (°C) and with the retention times t (s) at highest heating temperatures shown in Table 2.

[0123] The axial tensile yield strength of steel pipe was increased by dislocation strengthening using various types of cold rolling and cold working. Strength was increased by cold circumferential bending and reverse bending, which represents the cold working method of the present invention. For comparison, draw rolling and pilger rolling were also performed. Before cold drawing and cold pilgering, the surface oxide layer was removed by cleaning with an acid. For pickling, a mixture of nitric acid and hydrofluoric acid was used, and the oxide layers on inner and outer surfaces of steel pipe were removed by immersing the steel pipe in a bath. The steel pipe was immersed until the oxide layers were no longer observable by visual inspection.

[0124] Circumferential bending and reverse bending was performed with two oppositely disposed mill rolls, and with three mill rolls circumferentially disposed 120° apart from one another. The steel pipe was measured for $(D_i/D_o) \times 100$ (%), where D_i is the outside diameter of the steel pipe material after work (the outside diameter of pipe after cold working),

and D_o is the outside diameter of the steel pipe material before work (the initial outside diameter of the base pipe). The steel pipe was also measured for L_o , which is the axial length of the steel pipe material before work (initial axial length), and L_i , which is the axial length after work (the axial length after cold working). In table 2, these are presented as D_i/D_o and L_i/L_o . In draw rolling and pilger rolling, the steel pipe was stretched by rolling to reduce the wall thickness by 15 to 60%.

[0125] The microstructure was observed in the following fashion. First, a test specimen for microstructure observation was taken to observe an axial plane section. The volume fractions of ferritic phase and austenitic phase were determined by observing the surface with a scanning electron microscope. Specifically, the test specimen for microstructure observation was etched with a Vilella's solution (a reagent prepared by mixing 2 g of picric acid, 10 ml of hydrochloric acid, and 100 ml of ethanol), and a microstructure image was captured with a scanning electron microscope (SEM; 1,000 times). From the micrograph of microstructure, the average area percentage was calculated for the ferritic phase and the austenitic phase to determine the volume fraction (volume%) of each phase, using an image analyzer.

[0126] In a captured image, the ferritic phase, which is less likely to be etched, appears white in color after binarization, whereas the easier to be etched austenitic phase appears black in the binarized image. The image was binarized for a $600\text{ }\mu\text{m} \times 800\text{ }\mu\text{m}$ measurement area ($1,920\text{ pixels} \times 2,560\text{ pixels}$) after the captured image was transformed into a grayscale image with 256 intensities. For binarization, the minimum brightness between two peaks observed in a histogram plotting brightness (256 intensities) on the horizontal axis was set as the threshold. The martensitic phase is easy to be etched, and appears gray in a captured image before binarization. Unlike the austenitic phase that also appears gray, the martensitic phase can be recognized by the shades of gray due to the substructure including blocks and laths. The martensitic phase was therefore determined by measuring the area of regions where such substructures were observable in the gray portions of the captured image. When present, the embrittlement phase occurs at its grain boundary with the ferritic phase, and appears black after being etched. Accordingly, the embrittlement phase was determined by measuring the area of black portions.

[0127] Table 1 shows the observed duplex state of the microstructure in each steel pipe, along with the measured fractions of ferritic phase.

[0128] The oxide layer is a region in a cross section of a sliced steel pipe where the oxygen concentration was at least two times higher than in the base metal when measured from the inner and outer sides of pipe by energy dispersive x-ray analysis after polishing the cross-sectional surface to a mirror finish. The oxide layer thickness (average thickness) is the average of measured values from arbitrarily chosen 5 points (equally spaced apart along the circumferential direction) (oxide layer thickness = a value obtained by dividing a total of thicknesses from 5 points by 5). Table 2 shows the thickness of the oxide layer of each steel pipe.

[0129] The coverage of a steel pipe surface by oxide layer is a percentage determined from the pipe surface area of a region with no oxide layer (uncoated area) divided by the total surface area of pipe calculated from the outside diameter, wall thickness, and length of the pipe. The surface area of a region with no oxide layer is easily measurable because these regions show a metallic sheen after abrasive polishing or pickling.

[0130] Specifically, an enclosure (a rectangle) that is parallel to circumferential and axial directions was drawn so as to include a region that, upon visual inspection, appeared to have been polished or pickled. The uncoated area was then calculated from the circumferential length (the longer side of the rectangle) and the axial length (the shorter side of the rectangle). Here, the area was calculated as the product of the circumferential length (the longer side of the rectangle) and the axial length (the shorter side of the rectangle), and the sum of these areas from the same steel pipe was determined.

[0131] In order to find the total surface area of a steel pipe (the total surface area is the surface area excluding the end portions where the pipe is cut), the outer circumferential length and inner circumferential length of the steel pipe were determined from its outside diameter and wall thickness. The outer circumferential length and inner circumferential length were separately multiplied by the axial length, and the products of these multiplications were added to determine the total surface area. Here, the outside diameter, wall thickness, and length are average values. The coverage of a steel pipe surface by oxide layer was then determined as a percentage (%) by dividing the uncoated area by the total surface area of the steel pipe.

[0132] Table 2 shows the coverage of pipe surface by oxide layer for each steel pipe.

[0133] For the measurement of axial compressive yield strength and axial tensile yield strength, a round-bar tensile test specimen and a cylindrical compression test specimen, each measuring 5.0 mm in outside diameter, were taken from a middle portion of the wall thickness at an end of a pipe prepared for pressure test. These were compressed or stretched at a rate of 1.0 mm/min and a stress-strain curve was calculated in a tensile or compression test at room temperature. The axial tensile yield strength and axial compressive yield strength were then calculated from the stress-strain curve.

[0134] Specifically, a cylinder compression test was performed for the measurement of axial compressive yield strength. A cylindrical test specimen to be compressed was taken from a middle portion of the wall thickness, parallel to the pipe axis. The cylindrical test specimen cut out from a middle portion of the pipe wall thickness had dimensions with an outside diameter d of 5.0 mm, and a height h of 8.0 mm. In the compression test, a load was applied to the test specimen placed

between flat plates at room temperature (25°C), and the compressive yield strength was calculated from a stress-strain curve obtained as a result of compression. The stress-strain curve was obtained by compressing the test specimen 30% at a crosshead speed of 1.0 mm/min, using a compression testing machine.

[0135] For the measurement of axial tensile yield strength, a round-bar tensile test specimen having a diameter of 5.0 mm at a parallel portion was taken parallel to the pipe axis at a middle portion of the wall thickness, according to JIS Z2241. In a tensile test, the test specimen was stretched to break at room temperature (25°C) with a crosshead speed of 1.0 mm/min. The tensile yield strength was calculated from a stress-strain curve obtained in the test.

[0136] In a scratch test, the pipe was scratched by sweeping a pipe surface over a distance of 30 mm at 3 mm/s along the pipe axis under a 59 N load of an indenter provided as a stylus having a cemented carbide tip (a circular cone indenter having a tip angle of 60° (a point of contact with a steel pipe) in a triangular cross section taken perpendicular to the base of the circular cone). The height of the indented portion relative to the raised portion was then measured at a lengthwise middle portion of the indented portion scratched in the metallic base material portion (the maximum height of the indented portion along the wall thickness relative to the raised portion formed by scratching). Steel pipes were determined as having excellent abrasion resistance and indentation resistance and having passed the test when the indentation height was 50 μm or less.

[0137] The aspect ratio of austenite grains separated by a crystal orientation angle of 15° was measured by an EBSD crystal orientation analysis of an axial plane section of the steel pipe at a middle portion of the wall thickness. The aspect ratio was measured for austenite grains having a grain diameter of 10 μm or more in a 1.2 mm × 1.2 mm measurement area by assuming that the grains are true circles having the same area. The area fraction of austenite grains having an aspect ratio of 9 or less was also calculated. The area fraction was measured for austenite grains having a grain diameter of 10 μm or more by calculating the percentage of the total area of austenite grains with an aspect ratio of 9 or less with respect to the area of all austenite grains.

[Table 1]

Steel grades	Composition (mass%)														Microstructure	Fraction of ferritic phase (volume%)	Remarks
	C	Si	Mn	Cr	Ni	Mo	N	W	Cu	V	Nb	Ti	Al	B, Zr, Ca, Ta, Sb, Sn, REM			
A	0.008	0.1	0.1	22.4	5.3	3.1	0.183	-	-	-	-	-	-	-	Ferritic + austenitic phase	43	Present Example
B	0.022	0.4	0.5	22.1	4.1	3.5	0.235	0.8	1.5	-	-	-	-	-	Ferritic + austenitic phase	43	Present Example
C	0.025	0.5	1.2	22.4	4.8	3.8	0.185	1.2	1.2	-	-	0.001	0.012	Zr:0.003, REM: 0.0005	Ferritic + austenitic phase	43	Present Example
D	0.028	0.1	0.2	22.3	5.1	2.7	0.192	-	-	0.031	0.033	0.002	0.015	Sn:0.003, Sb:0.003, Ca: 0.0008, B: 0.004	Ferritic + austenitic phase	43	Present Example
E	0.075	0.1	5.0	22.2	1.0	0.8	0.081	-	-	-	-	-	-	-	Ferritic + austenitic phase	43	Present Example
F	0.018	0.2	0.2	25.1	7.9	3.6	0.185	-	-	-	-	-	-	-	Ferritic + austenitic phase	43	Present Example
G	0.021	0.6	1.2	25.3	7.1	3.2	0.245	-	-	-	-	0.001	0.012	Zr:0.002, REM: 0.0003, Ta: 0.15	Ferritic + austenitic phase	43	Present Example
H	0.028	0.1	0.8	25.4	6.8	3.6	0.305	0.8	1.2	0.033	0.025	0.002	0.011	Sn:0.003, Sb:0.003, Ca: 0.0006, B: 0.003	Ferritic + austenitic phase	43	Present Example

(continued)

Steel grades	Composition (mass%)													Microstructure	Fraction of ferritic phase (volume%)	Remarks	
	C	Si	Mn	Cr	Ni	Mo	N	W	Cu	V	Nb	Ti	Al				B, Zr, Ca, Ta, Sb, Sn, REM
I	0.028	0.2	0.6	25.3	7.3	3.4	0.235	1.5	1.3	-	-	-	-	Sn: 0.012, Sb: 0.017, Ca: 0.0005, B: 0.003	Ferritic + austenitic phase	43	Present Example
J	0.008	0.1	0.3	29.7	9.9	4.6	0.303	-	-	-	-	0.001	0.010	Sn: 0.26, Sb: 0.26	Ferritic + austenitic phase	43	Present Example
K	0.110	0.1	0.1	12.0	6.0	3.6	0.010	-	-	-	-	-	-	-	Ferritic + austenitic phase	10	Present Example
L	<u>0.160</u>	0.4	0.1	<u>11.1</u>	<u>0.4</u>	2.1	0.008	-	-	-	-	-	-	-	Ferritic + <u>martensitic phase</u>	5	<u>Comparative Example</u>
<u>M</u>	0.010	0.3	0.3	25.4	<u>0.4</u>	2.8	0.080	-	-	-	-	-	-	-	<u>Ferritic phase</u>	100	<u>Comparative Example</u>
N	0.030	0.3	0.3	<u>11.1</u>	10.0	<u>0.4</u>	0.220	-	0.6	-	-	-	-	-	<u>Austenitic phase</u>	0	Comparative Example
<u>O</u>	0.030	0.3	0.3	<u>36.5</u>	12.0	<u>6.5</u>	0.330	-	-	-	-	-	-	-	<u>Cracking due to formation of embrittlement phase</u>	-	<u>Comparative Example</u>
Underline means outside of the range of the present invention. The balance in the composition is Fe and incidental impurities.																	

[Table 2]

No.	Steel grades	Highest heating temp. of hot rolling (°C)	Presence or absence of pickling after hot rolling	Solid solution heat treatment			Presence or absence of oxide layer removal after solid solution heat treatment	Working method	Runs (passes)	Number of rolls	DiDo (%)	Li/Lo (%)
				Left-hand value of formula (1) (*1)	Tmax (°C)	t(s)						
1	A	1230	Absent	7585	1030	1800	<u>Present</u>	<u>Draw rolling</u>	1	-	96	135
2	A	1230	Absent	7585	1030	1800	<u>Present</u>	<u>Pilger rolling</u>	1	-	85	225
3	A	1230	Present	1264	1030	300	Absent	Bending and reverse bending	1	2	96	104
4	A	1230	Present	<u>965</u>	900	300	Absent	Bending and reverse bending	1	2	96	104
5	A	1230	Present	7585	1030	1800	<u>Present</u>	Bending and reverse bending	1	2	96	104
6	A	1230	Absent	7585	1030	1800	Absent	Bending and reverse bending	1	3	96	103
7	B	1200	Absent	5546	1050	1200	<u>Present</u>	<u>Draw rolling</u>	1	-	88	140
8	B	1200	Absent	5546	1050	1200	Absent	Bending and reverse bending	2	3	82	113

(continued)

No.	Steel grades	Highest heating temp. of hot rolling (°C)	Presence or absence of pickling after hot rolling	Solid solution heat treatment			Presence or absence of oxide layer removal after solid solution heat treatment	Working method	Runs (passes)	Number of rolls	DiDo (%)	Li/Lo (%)
				Left-hand value of formula (1) (*1)	Tmax (°C)	t(s)						
9	C	1100	Absent	4214	1030	1000	Absent	Bending and reverse bending	1	3	88	110
10	D	1150	Absent	3432	1030	800	Absent	Bending and reverse bending	1	3	87	111
11	E	1200	Absent	7411	1000	1800	Absent	<u>Bending and reverse bending</u>	1	2	82	118
12	F	1200	Absent	5290	1080	1800	<u>Present</u>	<u>Draw rolling</u>	1	-	87	145
13	F	1200	Present	5290	1080	1800	Absent	Bending and reverse bending	2	2	95	103
14	F	1200	Present	1008	1000	400	Absent	Bending and reverse bending	2	2	95	103
15	F	1200	Present	<u>756</u>	1000	300	Absent	Bending and reverse bending	2	2	95	103

(continued)

No.	Steel grades	Highest heating temp. of hot rolling (°C)	Presence or absence of pickling after hot rolling	Solid solution heat treatment			Presence or absence of oxide layer removal after solid solution heat treatment	Working method	Runs (passes)	Number of rolls	DiDo (%)	Li/Lo (%)
				Left-hand value of formula (1) (*1)	Tmax (°C)	t(s)						
16	F	1200	Absent	5290	1080	1800	Absent	Bending and reverse bending	1	3	87	105
17	G	1200	Absent	4036	1050	1500	Absent	Bending and reverse bending	1	3	87	104
18	H	1200	Absent	3179	1050	1200	Absent	Bending and reverse bending	2	3	82	115
19	I	1200	Absent	3229	1050	1200	Absent	Bending and reverse bending	1	3	85	108
20	J	1230	Present	4249	1150	2500	Absent	Bending and reverse bending	1	3	92	111
21	K	1100	Absent	26114	950	600	Absent	Bending and reverse bending	3	3	82	124

(continued)

No.	Steel grades	Highest heating temp. of hot rolling (°C)	Presence or absence of pickling after hot rolling	Solid solution heat treatment			Presence or absence of oxide layer removal after solid solution heat treatment	Working method	Runs (passes)	Number of rolls	Di/Do (%)	Li/Lo (%)
				Left-hand value of formula (1) (*1)	Tmax (°C)	t(s)						
22	<u>L</u>	1200	Absent	79048	1000	1200	Absent	Bending and reverse bending	<u>Unworkable</u>	3	-	-
23	<u>M</u>	1200	Absent	2883	1000	1200	Absent	Bending and reverse bending	1	3	83	114
24	<u>N</u>	1200	Absent	79048	1000	1200	Absent	Bending and reverse bending	1	3	83	115
25	<u>O</u>	1200	Unformable	-	-	-	-	-	-	-	-	-
No.	Thickness of oxide layer (μm)		Surface coverage by oxide layer (%)	Axial strength characteristics		Outer surface	Inner surface	Average aspect ratio of austenite grains	Area fraction of austenite grains with aspect ratio of 9 or less (%)	Indentation height (μm)		Remarks
	Inner surface	Outer surface		Tensile yield strength (MPa)	Compressive/tensile (yield strength)					Inner surface	Outer surface	
1	<u>0.0</u>	<u>0.0</u>	0	875	0.82	0	0	10.2	20	<u>75.2</u>	<u>76.2</u>	<u>Comparative example</u>
2	<u>0.0</u>	<u>0.0</u>	0	880	0.84	0	0	12.5	10	<u>74.2</u>	<u>74.0</u>	<u>Comparative example</u>
3	1.4	1.6	100	882	1.04	100	100	4.8	80	38.0	35.0	Present example

(continued)

No.	Thickness of oxide layer (μm)		Surface coverage by oxide layer (%)		Axial strength characteristics		Average aspect ratio of austenite grains	Area fraction of austenite grains with aspect ratio of 9 or less (%)	Indentation height (μm)		Remarks
	Inner surface	Outer surface	Inner surface	Outer surface	Tensile yield strength (MPa)	Compressive/tensile (yield strength)			Inner surface	Outer surface	
4	<u>0.8</u>	<u>0.8</u>	85	75	881	1.03	4.8	80	<u>55.0</u>	<u>52.0</u>	<u>Comparative example</u>
5	<u>0.0</u>	<u>0.0</u>	0	0	883	1.04	4.7	80	<u>63.6</u>	<u>64.2</u>	<u>Comparative example</u>
6	28.0	27.0	100	80	887	1.02	3.3	90	9.9	10.0	Present example
7	<u>0.0</u>	<u>0.0</u>	0	0	877	0.82	11.1	20	<u>85.2</u>	<u>86.0</u>	<u>Comparative example</u>
8	21.0	20.0	100	100	889	1.02	3.9	85	9.9	10.0	Present example
9	16.0	17.0	80	100	886	1.02	3.6	90	11.9	12.2	Present example
10	14.0	14.0	100	100	899	1.03	3.9	85	10.9	11.2	Present example
11	63.0	60.0	100	100	712	1.02	2.2	95	8.3	8.9	Present example
12	<u>0.0</u>	<u>0.0</u>	0	0	895	0.82	11.9	15	<u>69.5</u>	<u>70.3</u>	<u>Comparative example</u>
13	5.0	5.0	100	100	912	0.97	4.8	75	24.9	25.5	Present example
14	1.3	1.4	90	90	910	0.98	4.8	75	33.0	32.0	Present example
15	<u>0.8</u>	<u>0.8</u>	70	70	908	0.98	4.9	70	<u>51.0</u>	<u>53.0</u>	<u>Comparative example</u>

(continued)

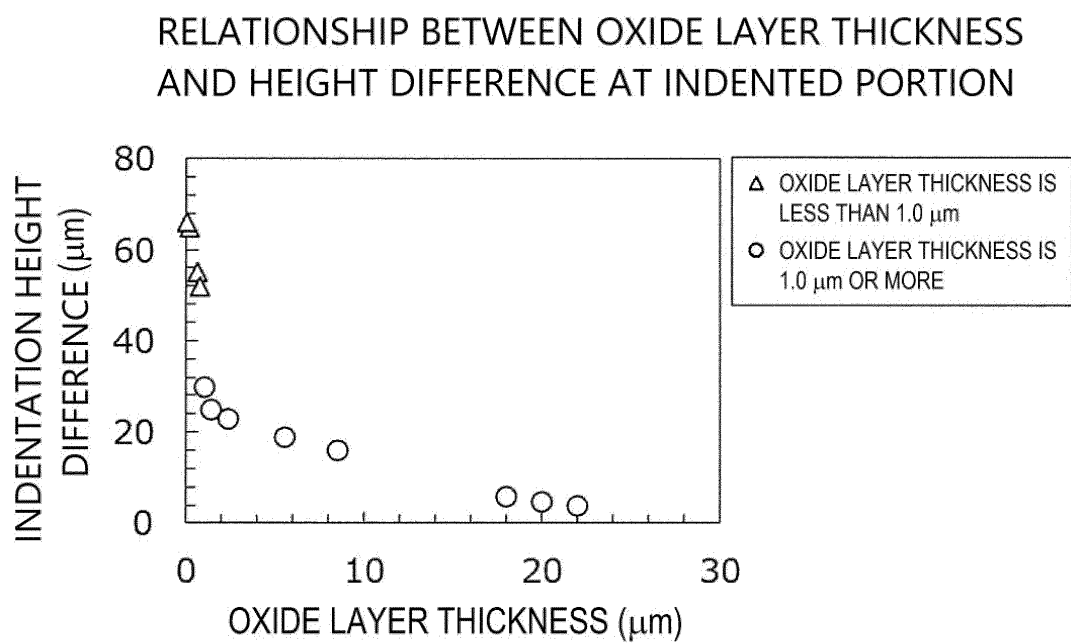
No.	Thickness of oxide layer (μm)		Surface coverage by oxide layer (%)		Axial strength characteristics		Average aspect ratio of austenite grains	Area fraction of austenite grains with aspect ratio of 9 or less (%)	Indentation height (μm)		Remarks
	Inner surface	Outer surface	Inner surface	Outer surface	Tensile yield strength (MPa)	Compressive/tensile (yield strength)			Inner surface	Outer surface	
16	22.0	22.0	100	100	912	1.02	3.2	85	9.4	9.6	Present example
17	17.0	17.0	100	100	922	1.02	2.8	90	10.5	10.7	Present example
18	14.0	13.0	55	100	932	1.04	3.9	85	11.8	12.2	Present example
19	12.0	12.0	100	55	933	1.02	2.8	90	11.9	12.3	Present example
20	4.0	2.0	100	100	936	1.09	4.6	65	27.3	28.2	Present example
21	45.0	43.0	100	100	762	0.91	2.2	90	8.4	8.8	Present example
22	55.0	56.0	100	100	-	-	-	-	-	-	Comparative example
23	18.0	18.0	100	100	<u>475</u>	1.00	-	-	<u>102.5</u>	<u>105.2</u>	Comparative example
24	48.0	50.0	100	100	<u>600</u>	1.02	2.5	85	<u>65.7</u>	<u>70.2</u>	Comparative example
25	-	-	-	-	-	-	-	-	-	-	Comparative example
(*1) Left-hand side: $T_{\text{max}}^2 \times t/[\text{Cr}]^4$ (T_{max} : Highest heating temperature of solid solution heat treatment ($^{\circ}\text{C}$); t : Retention time at highest heating temperature of solid solution heat treatment (s); [Cr]: Content of Cr in steel pipe (mass%) Underline means outside of the range of the present invention.											

[0138] As can be seen from the results presented in Table 2, the present examples all had a high axial tensile yield strength of 689 MPa or more, and formation of oxide layer was confirmed. The scratch test showed that the abrasion resistance and indentation resistance were excellent in the present examples. In contrast, it was not possible to obtain high yield strength and oxide layers in steel pipes produced by cold drawing and cold pilgering representing conventional cold rolling methods. Accordingly, the scratch test showed inferior results, suggesting that the steel pipes will have inferior abrasion resistance and indentation resistance when used in oil well applications or in geothermal well applications (collection of hot water).

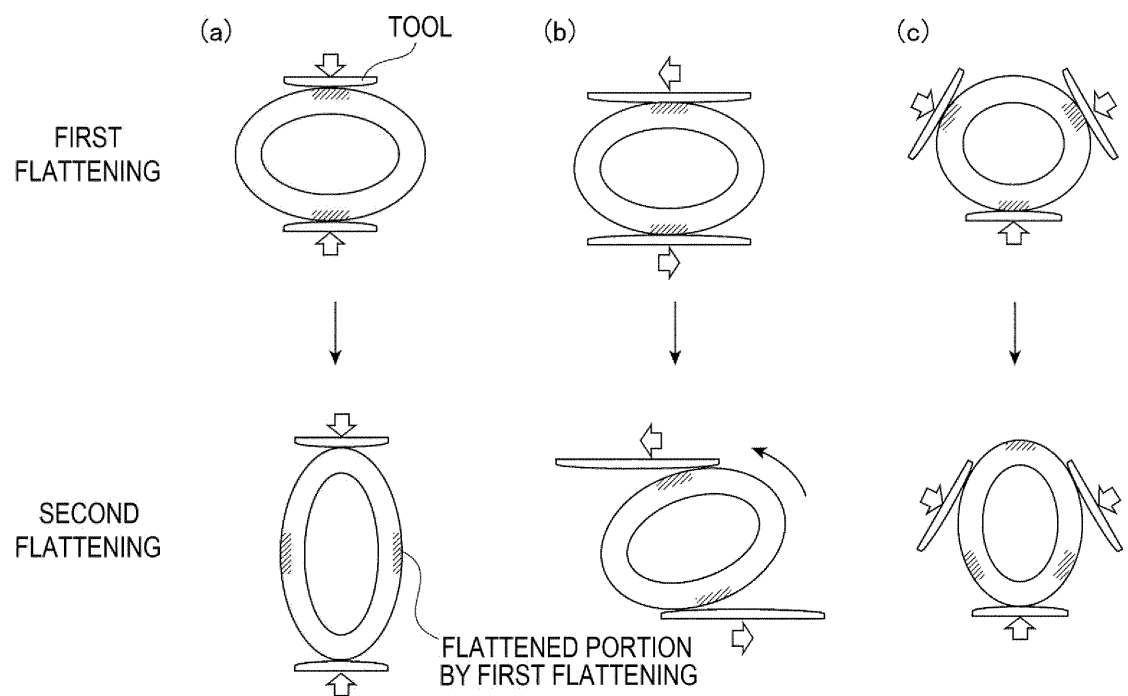
Claims

1. A duplex stainless steel pipe having a composition that comprises, in mass%, C: 0.005 to 0.150%, Si: 1.0% or less, Mn: 10.0% or less, Cr: 11.5 to 35.0%, Ni: 0.5 to 15.0%, Mo: 0.5 to 6.0%, N: less than 0.400%, and the balance being Fe and incidental impurities, and having a microstructure with a ferritic phase and an austenitic phase, the duplex stainless steel pipe having an axial tensile yield strength of 689 MPa or more, and having an outer surface and an inner surface each having an oxide layer having an average thickness of 1.0 μm or more.
2. The duplex stainless steel pipe according to claim 1, wherein the oxide layer covers at least 50% of the outer surface and at least 50% of the inner surface of the steel pipe in terms of an area percentage.
3. The duplex stainless steel pipe according to claim 1 or 2, which has an axial compressive yield strength-to-axial tensile yield strength ratio of 0.85 to 1.15.
4. The duplex stainless steel pipe according to any one of claims 1 to 3, wherein the composition further comprises, in mass%, one or two or more selected from W: 6.0% or less, Cu: 4.0% or less, V: 1.0% or less, and Nb: 1.0% or less.
5. The duplex stainless steel pipe according to any one of claims 1 to 4, wherein the composition further comprises, in mass%, one or two selected from Ti: 0.30% or less and Al: 0.30% or less.
6. The duplex stainless steel pipe according to any one of claims 1 to 5, wherein the composition further comprises, in mass%, one or two or more selected from B: 0.010% or less, Zr: 0.010% or less, Ca: 0.010% or less, Ta: 0.30% or less, Sb: 0.30% or less, Sn: 0.30% or less, and REM: 0.010% or less.
7. A method for manufacturing a duplex stainless steel pipe of any one of claims 1 to 6, the method comprising:
 - hot rolling a steel pipe material into a shape of a steel pipe;
 - subjecting the steel pipe material after the hot rolling to a solid solution heat treatment that satisfies the formula (1) below; and
 - performing cold circumferential bending and reverse bending without removing an oxide layer formed on the steel pipe material after the solid solution heat treatment,
$$T_{\text{max}}^2 \times t / [\text{Cr}]^4 > 1,000 \quad (1),$$
 - wherein T_{max} is a highest heating temperature ($^{\circ}\text{C}$) of the solid solution heat treatment, t is a retention time (s) at the highest heating temperature of the solid solution heat treatment, and $[\text{Cr}]$ is the content of Cr (mass%) in the steel pipe.
8. The method according to claim 7, wherein the highest heating temperature in the hot rolling is 1,150 $^{\circ}\text{C}$ or more.
9. The method according to claim 7 or 8, wherein the cold bending and reverse bending reduces a diameter of the steel pipe material to $(D_i/D_o) \times 100 = 99\%$ or less, where D_i is an outside diameter of the steel pipe material after work, and D_o is an outside diameter of the steel pipe material before work.
10. The method according to any one of claims 7 to 9, wherein $(L_i/L_o) \times 100 (\%)$ is 125% or less after the cold bending and reverse bending, where L_i is an axial length of the steel pipe material after work, and L_o is an axial length of the steel pipe material before work.

[FIG. 1]



[FIG. 2]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/005176

A. CLASSIFICATION OF SUBJECT MATTER

C21D 7/10(2006.01)i; **C21D 9/08**(2006.01)i; **C22C 38/00**(2006.01)i; **C22C 38/58**(2006.01)i; **C22C 38/60**(2006.01)i
 FI: C22C38/00 302H; C21D9/08 E; C22C38/58; C22C38/60; C21D7/10 E

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)

C21D7/10; C21D9/08; C22C38/00; C22C38/58; C22C38/60

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2020/044988 A1 (JFE STEEL CORP.) 05 March 2020 (2020-03-05)	1-10
A	JP 11-80904 A (KAWASAKI STEEL CORP.) 26 March 1999 (1999-03-26)	1-10
A	JP 2017-20105 A (NIPPON STEEL & SUMITOMO METAL CORP.) 26 January 2017 (2017-01-26)	1-10
A	WO 2018/003941 A1 (NIPPON STEEL & SUMITOMO METAL CORP.) 04 January 2018 (2018-01-04)	1-10
A	JP 2016-191149 A (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORP.) 10 November 2016 (2016-11-10)	1-10

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

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INTERNATIONAL SEARCH REPORT
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PCT/JP2022/005176

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