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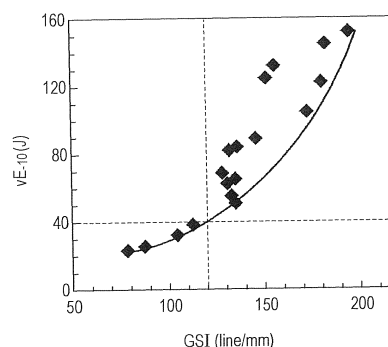
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(54) **HIGH-STRENGTH STAINLESS STEEL SEAMLESS PIPE FOR USE AS OIL WELL PIPING, AND  
MANUFACTURING METHOD THEREFOR**

(57) Provided is a high-strength stainless steel tube for oil country tubular goods having a wall thickness of more than 25.4 mm and a high strength of a 110 ksi (758 MPa) grade yield stress or more with excellent toughness and excellent corrosion resistance. A steel material having a chemical composition containing, by mass%, C: 0.005% or more and 0.06% or less, Si: 0.05% or more and 0.5% or less, Mn: 0.2% or more and 1.8% or less, Cr: 15.5% or more and 18.0% or less, Ni: 1.5% or more and 5.0% or less, V: 0.02% or more and 0.2% or less, Al: 0.002% or more and 0.05% or less, N: 0.01% or more and 0.15% or less, O: 0.006% or less, and further containing one or more of Mo: 1.0% or more and 3.5% or less, W: 3.0% or less and Cu: 3.5% or less, in which the relational expressions  
 $Cr+0.65Ni+0.60Mo+0.30W+0.55Cu-20C \geq 19.5$  and  
 $Cr+Mo+0.50W+0.30Si-43.5C-0.4Mn-Ni-0.3Cu-9N \geq 11.5$   
are satisfied, is made into a seamless steel tube by performing heating and hot rolling. The hot rolling is performed under conditions such that the total rolling reduction in a temperature range of 1100°C to 900°C is 30% or more. After the hot rolling has been performed, cooling is performed at a cooling rate equal to or more than an air-cooling rate, and, further, quenching-tempering is

performed. With this method, a high-strength and high-toughness seamless steel tube having a strength of 110 ksi (758 MPa) or more and a toughness of 40 J or more in terms of  $vE_{-10}$  despite having a thick wall and excellent corrosion resistance even in a high-temperature corrosion environment having a temperature of 230°C and containing  $CO_2$  and  $Cl^-$  can be stably manufactured.

FIG. 1



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## Description

[Technical Field]

5 **[0001]** The present invention relates to a seamless steel tube for oil country tubular goods, in particular, to a high-strength seamless stainless steel tube with both excellent low-temperature toughness and excellent corrosion resistance.

[Background Art]

10 **[0002]** Nowadays, deep oil wells to which consideration has never been given and sour gas fields whose development was abandoned due to their intense corrosion environment and so forth are being actively developed on a global scale from the viewpoint of a sharp rise in the price of crude oil and the exhaustion of oil resources which is anticipated in the near future. Such oil wells and gas fields are generally found very deep in the ground and in an intense corrosion environment in which the atmosphere has a high temperature and contains CO<sub>2</sub>, Cl<sup>-</sup> and so forth. Therefore, steel tubes  
15 for oil country tubular goods which are used in order to drill such oil wells and gas fields have been required to have not only high strength but also excellent corrosion resistance.

**[0003]** For oil wells and gas fields in an intense corrosion environment containing CO<sub>2</sub>, Cl<sup>-</sup> and so forth, 13%Cr martensitic stainless steel tubes have been used as steel tubes for oil country tubular goods in the past. However, there has been a problem in that ordinary 13%Cr martensitic stainless steel cannot be used in an environment containing a  
20 large amount of Cl<sup>-</sup> and having a high temperature of higher than 100°C.

**[0004]** Therefore, in such a high-temperature corrosion environment, duplex stainless tubes have been used. However, there is a problem in that, since duplex stainless tubes contain a large amount of alloying chemical elements and are poor in terms of hot formability, duplex stainless tubes can be manufactured by only using particular kinds of hot processing and are expensive.

25 **[0005]** In order to solve the problems described above, for example, Patent Literature 1 describes a method for manufacturing a high-strength stainless steel tube for oil country tubular goods with excellent corrosion resistance, the method including making a steel tube material having a chemical composition including, by mass%, C: 0.005% to 0.05%, Si: 0.05% to 0.5%, Mn: 0.2% to 1.8%, Cr: 15.5% to 18%, Ni: 1.5% to 5%, Mo: 1% to 3.5%, V: 0.02% to 0.2%, N: 0.01% to 0.15%, and O: 0.006% or less, in which relational expressions (1) and (2) below are satisfied, into a steel tube having  
30 a specified size by performing hot processing for tube making, cooling the tube down to room temperature at a cooling rate equal to or more than an air-cooling rate after tube making has been performed and performing quenching-tempering on the tube by reheating the tube up to a temperature of 850°C or higher, by subsequently cooling the heated tube down to a temperature of 100°C or lower at a cooling rate equal to or more than an air-cooling rate and then heating the cooled tube up to a temperature of 700°C or lower:

35

$$\text{Cr} + 0.65\text{Ni} + 0.60\text{Mo} + 0.30\text{W} + 0.55\text{Cu} - 20\text{C} \geq 19.5 \quad \cdots (1),$$

40 (where Cr, Ni, Mo, W, Cu and C: contents (mass%) of chemical elements respectively represented by corresponding atomic symbols)

$$\text{Cr} + \text{Mo} + 0.50\text{W} + 0.30\text{Si} - 43.5\text{C} - 0.4\text{Mn} - \text{Ni} - 0.3\text{Cu} - 9\text{N} \geq 11.5 \quad \cdots (2),$$

(where Cr, Mo, W, Si, C, Mn, Ni, Cu and N: contents (mass%) of chemical elements respectively represented by corresponding atomic symbols). According to the technique described in Patent Literature 1, a high-strength stainless steel tube for oil country tubular goods having sufficient corrosion resistance effective even in an intense corrosion environment having increased concentrations of CO<sub>2</sub>, Cl<sup>-</sup> and so forth and an increased temperature of up to about 200°C in which 13%Cr martensitic stainless steel cannot be used can be stably manufactured.

45 **[0006]** In addition, Patent Literature 2 describes a method for manufacturing a stainless steel tube, the method including making a billet having a chemical composition containing, by mass%, C: 0.001% to 0.05%, Si: 0.05% to 1%, Mn: 2% or less, Cr: 16% to 18%, Ni: 3.5% to 7%, Mo: more than 2% and 4% or less, Cu: 1.5% to 4%, rare-earth element: 0.001% to 0.3%, sol.Al: 0.001% to 0.1%, Ca: 0.0001% to 0.3%, N: 0.05% or less and O: 0.05% or less, or further containing one or more selected from the group consisting of Ti: 0.5% or less, Zr: 0.5% or less, Hf: 0.5% or less and V: 0.5% or less into a steel tube by performing hot processing and then performing quenching-tempering on the steel tube. According to the technique described in Patent Literature 2, a stainless steel tube for oil country tubular goods having not only  
50 sufficient corrosion resistance effective even in an intense corrosion environment having a high temperature of up to about 230°C but also high strength can be manufactured.

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[Citation List]

[Patent Literature]

**[0007]**

[PTL 1] Japanese Unexamined Patent Application Publication No. 2005-336595

[PTL 2] Japanese Patent No. 4577457

[Summary of Invention]

[Technical Problem]

**[0008]** Nowadays, since oil wells and gas fields which are found very deep in the ground are being drilled more often than ever before, tubes for oil country tubular goods having a thick wall are demanded in order to prevent tubes for oil country tubular goods from being crushed due to pressure from a geological stratum. In the case of the technique described in Patent Literature 2, there is a problem in that, when a tube has a wall thickness of more than 25.4 mm, toughness deteriorates and thus the desired high toughness and high strength cannot be achieved at the same time.

**[0009]** An object of the present invention is, by solving the problems in conventional techniques described above, to provide a high-strength seamless stainless steel tube for oil country tubular goods having a wall thickness of more than 25.4 mm, having not only a high strength of a 110 ksi (758 MPa) grade yield stress or more but also a high toughness of 40 J or more in terms of absorbed energy  $vE_{10}$  determined by performing a Charpy impact test at a test temperature of  $-10^{\circ}\text{C}$ , and, further, having excellent corrosion resistance and a method for manufacturing the steel tube. Here, "excellent corrosion resistance" refers to a case where a tube has excellent  $\text{CO}_2$  corrosion resistance effective even in a corrosion environment having a high temperature of  $230^{\circ}\text{C}$  or higher and containing  $\text{CO}_2$  and  $\text{Cl}^-$ .

[Solution to Problem]

**[0010]** In order to achieve the object described above, first, the present inventors diligently conducted investigations regarding various factors having an influence on toughness, and, as a result, found that it is necessary to form a microstructure having a decreased grain diameter in order to enhance the toughness of a stainless steel tube having a thick wall. In the case of stainless steel having a chemical composition containing 16% to 18% of Cr and about 2% to 6% of Ni in order to enhance corrosion resistance, a ferrite phase crystallizes at a time of solidification, and some of the ferrite phase transforms into an austenite phase when the stainless steel is cooled down to room temperature. However, since the ferrite phase is not completely eliminated and some of the ferrite phase is retained, it is almost impossible to decrease a grain diameter even by performing a heat treatment afterward. Therefore, the present inventors thought of using a spacing GSI (grain size index) value between various phases such as a ferrite phase and an austenite phase (or a martensite phase) as an index expressing the degree of a decrease in the grain diameter of a microstructure and found that, in the case of a stainless steel tube having a chemical composition containing 16% to 18% of Cr and about 2% to 6% of Ni, there is an enhance in toughness by decreasing a GSI value, that is, by decreasing the spacing between various phases.

**[0011]** From the results of further investigations by the present inventors, it was found that, when hot processing including piercing rolling is performed, there is a decrease in spacing GSI between various phases by performing hot processing under conditions such that rolling reduction in a specified temperature range is equal to or more than a certain value, which results in a significant enhance in toughness.

**[0012]** First, experimental results which became the basis of the present invention will be described. Steel materials (billets) having a chemical composition containing, by mass%, 0.026%C-0.20%Si-0.24%Mn-0.01%P-0.001%S-16.7%Cr-4.11%Ni-0.027%V-2.13%Mo-1.06%W-0.51%Cu-0.02%Al-0.051%N and the balance being Fe and inevitable impurities were heated at various heating temperatures. Moreover, by performing hot rolling using a piercer mill, an elongator mill, a plug mill and so forth at various temperatures with various rolling reductions, seamless steel tubes having an outer diameter of 297 mm $\phi$  and a wall thickness of 26 to 34 mm were made and cooled down to room temperature by performing air-cooling. Using a test piece for microstructure observation which had been cut out of the obtained steel tube, polished and etched with a vilella's reagent, a microstructure was observed using an optical microscope (at a magnification of 400 times). By performing image analysis on the taken microstructure photograph, a GSI value was determined as an index representing the degree of a decrease in the grain diameter of a microstructure. The GSI value was determined by counting the number of ferrite-martensite grain boundaries per unit length (line/mm) in the wall thickness direction using the obtained microstructure photograph. In addition, using a Charpy impact test piece (having a thickness of 10 mm) cut out of the obtained steel tube in the longitudinal direction of the steel tube, absorbed

energy  $vE_{-10}$  (J) at a test temperature of  $-10^{\circ}\text{C}$  was determined. The obtained results are illustrated in the form of the relationship between  $vE_{-10}$  and a GSI value in Fig. 1.

**[0013]** Fig. 1 indicates that it is necessary to decrease the grain diameter of a microstructure to GSI: 120 or more in order to achieve toughness of  $vE_{-10}$ : 40 J or more. Incidentally, from the results of other experiments, the present inventors confirmed that a decrease in the grain diameter of a microstructure to GSI: 120 or more can be achieved by performing hot rolling under conditions such that the total rolling reduction in a temperature range of  $1100^{\circ}\text{C}$  to  $900^{\circ}\text{C}$  is 30% or more. In the case of hot rolling including piercing rolling where a slab is heated at an ordinary heating temperature ( $1100^{\circ}\text{C}$  to  $1250^{\circ}\text{C}$ ), a temperature range of  $1100^{\circ}\text{C}$  to  $900^{\circ}\text{C}$  corresponds to rolling using an elongator mill and a plug mill or an mandrel mill. That is to say, it was found that, in order to enhance the low-temperature toughness of a seamless steel tube, that is, in order to decrease the grain diameter of a microstructure, it is necessary that rolling using an elongator mill, a plug mill and so forth be performed under conditions such that the temperature is low and the rolling reduction is high, that is, the total rolling reduction is 30% or more.

**[0014]** The present invention has been completed on the basis of the knowledge described above and further investigations. That is to say, the subject matter of the present invention is as follows.

(1) A method for manufacturing a high-strength seamless stainless steel tube for oil country tubular goods having a wall thickness of more than 25.4 mm, the method including heating a steel material; hot rolling including piercing rolling the steel material into a seamless steel tube; and cooling the seamless steel tube down to room temperature at a cooling rate equal to or more than an air-cooling rate, the steel material having a chemical composition containing, by mass%, C: 0.005% or more and 0.06% or less, Si: 0.05% or more and 0.5% or less, Mn: 0.2% or more and 1.8% or less, P: 0.03% or less, S: 0.005% or less, Cr: 15.5% or more and 18.0% or less, Ni: 1.5% or more and 5.0% or less, V: 0.02% or more and 0.2% or less, Al: 0.002% or more and 0.05% or less, N: 0.01% or more and 0.15% or less, O: 0.006% or less, and further containing one, two or more selected from among Mo: 1.0% or more and 3.5% or less, W: 3.0% or less and Cu: 3.5% or less and the balance being Fe and inevitable impurities, in which relational expressions (1) and (2) below are satisfied, the hot rolling including piercing rolling is performed under conditions such that the total rolling reduction in a temperature range of  $1100^{\circ}\text{C}$  to  $900^{\circ}\text{C}$  is 30% or more, and after the rolled steel tube is cooled down to the room temperature, quenching-tempering or tempering is performed:

$$\text{Cr} + 0.65\text{Ni} + 0.60\text{Mo} + 0.30\text{W} + 0.55\text{Cu} - 20\text{C} \geq 19.5 \quad \dots (1),$$

(where Cr, Ni, Mo, W, Cu and C: contents (mass%) of chemical elements respectively represented by corresponding atomic symbols)

$$\text{Cr} + \text{Mo} + 0.50\text{W} + 0.30\text{Si} - 43.5\text{C} - 0.4\text{Mn} - \text{Ni} - 0.3\text{Cu} - 9\text{N} \geq 11.5 \quad \dots$$

(2),

(where Cr, Mo, W, Si, C, Mn, Ni, Cu and N: contents (mass%) of chemical elements respectively represented by corresponding atomic symbols).

(2) The method for manufacturing a high-strength seamless stainless steel tube for oil country tubular goods according to item (1), in which the chemical composition further contains, by mass%, one or more selected from among Nb: 0.2% or less, Ti: 0.3% or less, Zr: 0.2% or less and B: 0.01% or less.

(3) The method for manufacturing a high-strength seamless stainless steel tube for oil country tubular goods according to item (1) or (2), in which the chemical composition further contains, by mass%, Ca: 0.01% or less.

(4) A high-strength seamless stainless steel tube for oil country tubular goods having a wall thickness of more than 25.4 mm, the steel tube having a chemical composition containing, by mass%, C: 0.005% or more and 0.06% or less, Si: 0.05% or more and 0.5% or less, Mn: 0.2% or more and 1.8% or less, P: 0.03% or less, S: 0.005% or less, Cr: 15.5% or more and 18.0% or less, Ni: 1.5% or more and 5.0% or less, V: 0.02% or more and 0.2% or less, Al: 0.002% or more and 0.05% or less, N: 0.01% or more and 0.15% or less, O: 0.006% or less, and further containing one, two or more selected from among Mo: 1.0% or more and 3.5% or less, W: 3.0% or less and Cu: 3.5% or less and the balance being Fe and inevitable impurities, in which relational expressions (1) and (2) below are satisfied, having a microstructure including a martensite phase as a main phase and a second phase consisting of, at volume ratio, 10% or more and 60% or less of a ferrite phase and 0% or more and 10% or less of an austenite phase, in which a GSI value, which is defined as the number of ferrite-martensite grain boundaries per unit length of a line segment drawn in the wall thickness direction, is 120 or more in the central portion in the wall thickness direction,

and having excellent low-temperature toughness and excellent corrosion resistance:

$$\text{Cr} + 0.65\text{Ni} + 0.60\text{Mo} + 0.30\text{W} + 0.55\text{Cu} - 20\text{C} \geq 19.5 \quad \dots (1),$$

(where Cr, Ni, Mo, W, Cu and C: contents (mass%) of chemical elements respectively represented by corresponding atomic symbols)

$$\text{Cr} + \text{Mo} + 0.50\text{W} + 0.30\text{Si} - 43.5\text{C} - 0.4\text{Mn} - \text{Ni} - 0.3\text{Cu} - 9\text{N} \geq 11.5 \quad \dots (2),$$

(where Cr, Mo, W, Si, C, Mn, Ni, Cu and N: contents (mass%) of chemical elements respectively represented by corresponding atomic symbols).

(5) The high-strength seamless stainless steel tube for oil country tubular goods according to item (4), in which the chemical composition further contains, by mass%, one or more selected from among Nb: 0.2% or less, Ti: 0.3% or less, Zr: 0.2% or less and B: 0.01% or less.

(6) The high-strength seamless stainless steel tube for oil country tubular goods according to item (4) or (5), in which the chemical composition further contains, by mass%, Ca: 0.01% or less.

#### [Advantageous Effects of Invention]

**[0015]** According to the present invention, a high-strength seamless stainless steel tube for oil country tubular goods having a wall thickness of more than 25.4 mm, having not only a high strength of a 110 ksi (758 MPa) grade yield stress or more but also a high toughness of 40 J or more in terms of absorbed energy  $vE_{-10}$  in a Charpy impact test, and, further, having excellent corrosion resistance can be manufactured easily and at low cost, which results in a significant industrial effect.

#### [Brief Description of Drawing]

**[0016]** [Fig. 1] Fig. 1 is a graph illustrating the relationship between absorbed energy  $vE_{-10}$  in a Charpy impact test and a GSI value.

#### Description of Embodiments

**[0017]** First, the method for manufacturing a high-strength seamless stainless steel tube for oil country tubular goods according to the present invention will be described. In the present invention, a seamless steel tube is manufactured by heating a steel material and by performing hot rolling including piercing rolling.

**[0018]** The reasons for limitations on a chemical composition of a steel material used in the present invention will be described hereafter. Hereinafter, mass% used when describing a chemical composition is simply represented by %, unless otherwise noted.

**[0019]** The steel material used in the present invention has a chemical composition containing C: 0.005% or more and 0.06% or less, Si: 0.05% or more and 0.5% or less, Mn: 0.2% or more and 1.8% or less, P: 0.03% or less, S: 0.005% or less, Cr: 15.5% or more and 18.0% or less, Ni: 1.5% or more and 5.0% or less, V: 0.02% or more and 0.2% or less, Al: 0.002% or more and 0.05% or less, N: 0.01% or more and 0.15% or less, O: 0.006% or less, and further containing one, two or more selected from among Mo: 1.0% or more and 3.5% or less, W: 3.0% or less and Cu: 3.5% or less and the balance being Fe and inevitable impurities, in which relational expressions (1) and (2) below are satisfied:

$$\text{Cr} + 0.65\text{Ni} + 0.60\text{Mo} + 0.30\text{W} + 0.55\text{Cu} - 20\text{C} \geq 19.5 \quad \dots (1),$$

(where Cr, Ni, Mo, W, Cu and C: contents (mass%) of chemical elements respectively represented by corresponding atomic symbols)

$$\text{Cr} + \text{Mo} + 0.50\text{W} + 0.30\text{Si} - 43.5\text{C} - 0.4\text{Mn} - \text{Ni} - 0.3\text{Cu} - 9\text{N} \geq 11.5 \quad \dots$$

(2),

(where Cr, Mo, W, Si, C, Mn, Ni, Cu and N: contents (mass%) of chemical elements respectively represented by corresponding atomic symbols).

C: 0.005% or more and 0.06% or less

**[0020]** C is a chemical element which is related to an increase in the strength of martensitic stainless steel. It is necessary that the C content be 0.005% or more in the present invention. On the other hand, in the case where the C content is more than 0.06%, there is a significant deteriorate in corrosion resistance. Therefore, the C content is limited to 0.005% or more and 0.06% or less, preferably 0.01% or more and 0.04% or less.

Si: 0.05% or more and 0.5% or less

**[0021]** Si is a chemical element which functions as a deoxidation agent, and Si is added in the amount of 0.05% or more in the present invention. However, in the case where the Si content is more than 0.5%, there is a deteriorate in CO<sub>2</sub> corrosion resistance and there is a deteriorate in hot formability. Therefore, the Si content is limited to 0.05% or more and 0.5% or less, preferably 0.1% or more and 0.4% or less.

Mn: 0.2% or more and 1.8% or less

**[0022]** Mn is a chemical element which increases strength, and Mn is added in the amount of 0.2% or more in order to achieve the desired high strength in the present invention. On the other hand, in the case where the Mn content is more than 1.8%, there is a negative influence on toughness. Therefore, the Mn content is limited to 0.2% or more and 1.8% or less, preferably 0.2% or more and 0.8% or less.

P: 0.03% or less

**[0023]** Since P is a chemical element which deteriorates corrosion resistance, it is preferable that the P content be as small as possible in the present invention. However, since the P content is controlled at comparatively low cost without deteriorating corrosion resistance in the case where the P content is 0.03% or less, it is acceptable that the P content is about 0.03% or less. Therefore the P content is limited to 0.03% or less. Since there is an increase in manufacturing cost in the case where the P content is excessively small, it is preferable that the P content be 0.005% or more.

S: 0.005% or less

**[0024]** Since S is a chemical element which significantly deteriorates hot formability, it is preferable that the S content be as small as possible. However, it is acceptable that the S content is 0.005% or less, because it is possible to manufacture a pipe using normal processes in the case where the S content is 0.005% or less. Therefore, the S content is limited to 0.005% or less. Since there is an increase in manufacturing cost in the case where the S content is excessively small, it is preferable that the S content be 0.0005% or more.

Cr: 15.5% or more and 18.0% or less

**[0025]** Cr is a chemical element which enhances corrosion resistance as a result of forming a protective film, and, in particular contributes to an enhance in CO<sub>2</sub> corrosion resistance. It is necessary that the Cr content be 15.5% or more in order to enhance corrosion resistance at a high temperature. On the other hand, in the case where the Cr content is more than 18%, there is a deteriorate in hot formability and there is a decrease in strength. Therefore, the Cr content is limited to 15.5% or more and 18.0% or less, preferably 16.0% or more and 17.5% or less, more preferably 16.5% or more and 17.0% or less.

Ni: 1.5% or more and 5.0% or less

**[0026]** Ni is a chemical element which is effective for increasing corrosion resistance by strengthening a protective film and which increases the strength of steel as a result of forming a solid solution. These effects become noticeable

in the case where the Ni content is 1.5% or more. On the other hand, in the case where the Ni content is more than 5.0%, since there is a decrease in the stability of a martensite phase, there is a decrease in strength. Therefore, the Ni content is limited to 1.5% or more and 5.0% or less, preferably 3.0% or more and 4.5% or less.

V: 0.02% or more and 0.2% or less

**[0027]** V contributes to an increase in strength through solid solution strengthening and is effective for increasing resistance to stress corrosion cracking. It is necessary that the V content be 0.02% or more in order to realize these effects. On the other hand, in the case where the V content is more than 0.2%, there is a deterioration in toughness. Therefore, the V content is limited to 0.02% or more and 0.2% or less, preferably 0.03% or more and 0.08% or less.

Al: 0.002% or more and 0.05% or less

**[0028]** Al is a chemical element which functions as a deoxidation agent, and it is necessary that the Al content be 0.002% or more in order to realize this effect. On the other hand, in the case where the Al content is more than 0.05%, since there is an increase in the amount of alumina containing inclusions, there is a deterioration in ductility and toughness. Therefore, the Al content is limited to 0.002% or more and 0.05% or less, preferably 0.01% or more and 0.04% or less.

N: 0.01% or more and 0.15% or less

**[0029]** N is a chemical element which markedly enhances pitting corrosion resistance, and it is necessary that the N content be 0.01% or more in the present invention. On the other hand, in the case where the N content is more than 0.15%, various nitrides are formed and there is a deterioration in toughness. Therefore, the N content is limited to 0.01% or more and 0.15% or less, preferably 0.02% or more and 0.08% or less.

O: 0.006% or less

**[0030]** O is present in the form of an oxide in steel and has a negative effect on ductility, toughness and so forth. Therefore, it is preferable that the O content be as small as possible. In particular, in the case where the O content is more than 0.006%, there is a significant deterioration in hot formability, toughness and corrosion resistance. Therefore, the O content is limited to 0.006% or less.

**[0031]** One, two or more selected from Mo: 1.0% or more and 3.5% or less, W: 3.0% or less and Cu: 3.5% or less

**[0032]** Since Mo, W and Cu are all chemical elements which enhance corrosion resistance, one, two or more selected from among these chemical elements are added.

**[0033]** Mo is a chemical element which contributes to an enhance in corrosion resistance by increasing resistance to pitting corrosion caused by Cl<sup>-</sup>, and it is necessary that the Mo content be 1.0% or more. On the other hand, in the case where the Mo content is more than 3.5%, there is a deterioration in strength and toughness and there is an increase in material cost. Therefore, in the case where Mo is added, the Mo content is limited to 1.0% or more and 3.5% or less, preferably 1.5% or more and 3.0% or less.

**[0034]** W is a chemical element which contributes to an enhance in corrosion resistance like Mo, and it is preferable that the W content be 0.5% or more. However, in the case where the W content is more than 3.0%, there is a deterioration in toughness and there is an increase in material cost. Therefore, in the case where W is added, the W content is limited to 3.0% or less, preferably 0.5% or more and 2.5% or less.

**[0035]** Since Cu is effective for suppressing penetration of hydrogen into steel by strengthening a protective film, Cu contributes to an enhance in corrosion resistance. It is preferable that the Cu content be 0.5% or more in order to realize these effects. However, in the case where the Cu content is more than 3.5%, there is a deterioration in hot formability. Therefore, in the case where Cu is added, the Cu content is limited to 3.5% or less, preferably 0.5% or more and 2.5% or less.

**[0036]** The contents of the constituent chemical elements described above are controlled to be within the ranges described above, in which relational expressions (1) and (2) below are satisfied:

$$\text{Cr} + 0.65\text{Ni} + 0.60\text{Mo} + 0.30\text{W} + 0.55\text{Cu} - 20\text{C} \geq 19.5 \quad \cdots (1),$$

(where Cr, Ni, Mo, W, Cu and C: contents (mass%) of chemical elements respectively represented by corresponding atomic symbols)

$$\text{Cr} + \text{Mo} + 0.50\text{W} + 0.30\text{Si} - 43.5\text{C} - 0.4\text{Mn} - \text{Ni} - 0.3\text{Cu} - 9\text{N} \geq 11.5 \quad \dots$$

(2),

(where Cr, Mo, W, Si, C, Mn, Ni, Cu and N: contents (mass%) of chemical elements respectively represented by corresponding atomic symbols). Note that, when the values of the left-hand sides of relational expressions (1) and (2) are calculated, a symbol is assigned a value of 0 in the case where the corresponding chemical element is not contained.

**[0037]** By controlling the contents of Cr, Ni, Mo, W, Cu and C so that relational expression (1) is satisfied, there is a significant enhance in corrosion resistance (CO<sub>2</sub> corrosion resistance) at a high temperature (up to 230°C) in a corrosion environment containing CO<sub>2</sub> and Cl<sup>-</sup>. It is preferable that the value of the left-hand side of relational expression (1) be 20.0 or more from the viewpoint of high-temperature corrosion resistance.

**[0038]** By controlling the contents of Cr, Mo, W, Si, C, Mn, Ni, Cu and N so that relational expression (2) is satisfied, there is an enhance in hot workability, and hot workability which is necessary to manufacture a martensitic stainless steel tube can be achieved. It is preferable that the value of the left-hand side of relational expression (2) be 12.5 or more.

**[0039]** The chemical composition described above is a base chemical composition, and, in addition to the base chemical composition, one or more selected from among Nb: 0.2% or less, Ti: 0.3% or less, Zr: 0.2% or less and B: 0.01% or less and/or Ca: 0.01% or less may be added.

**[0040]** One or more selected from among Nb: 0.2% or less, Ti: 0.3% or less, Zr: 0.2% or less and B: 0.01% or less

**[0041]** Since Nb, Ti, Zr and B are all chemical elements which increase the strength of steel and enhance resistance to stress corrosion cracking, one or more selected from among these chemical elements may be added as needed. It is preferable that the contents of these chemical elements be respectively Nb: 0.02% or more, Ti: 0.04% or more, Zr: 0.02% or more and B: 0.001% or more in order to realize these effects. On the other hand, in the case where the contents of these chemical elements are respectively Nb: more than 0.2%, Ti: more than 0.3%, Zr: more than 0.2% and B: more than 0.01%, there is a deteriorate in toughness. Therefore, the contents of these chemical elements are respectively limited to Nb: 0.2% or less, Ti: 0.3% or less, Zr: 0.2% or less and B: 0.01% or less.

Ca: 0.01% or less

**[0042]** Since Ca is a chemical element which contributes to a morphology control function of sulfides as a result of spheroidizing sulfide containing inclusions, Ca may be added as needed. By spheroidizing sulfide containing inclusions, there is a decrease in the lattice distortion in a matrix in the vicinity of the inclusions so as to obtain an effect of decreasing the hydrogen trapping capability of the inclusions. It is preferable that the Ca content be 0.0005% or more in order to realize this effect. On the other hand, in the case where the Ca content is more than 0.01%, there is an increase in the amount of oxide containing inclusions, which deteriorates corrosion resistance. Therefore, in the case where Ca is added, it is preferable that the Ca content be 0.01% or less.

**[0043]** The remainder of the chemical composition other than the constituent chemical elements described above consists of Fe and inevitable impurities. As an inevitable impurity, O: 0.010% or less is acceptable.

**[0044]** There is no particular limitation on what method is used for manufacturing a steel tube material. However, it is preferable that molten steel having a specified chemical composition be smelted using a common refining method such as one using a steel converter and that the smelted steel be made into a cast material such as a billet using a common casting method such as a continuous casting method. Note that, other than a continuous casting method, it is needless to say that a cast material such as a billet may be manufactured using an ingot casting-blooming method.

**[0045]** In the present invention, a seamless steel tube is manufactured by heating a steel material having the chemical composition described above, by performing ordinary hot rolling including piercing rolling using a Mannesmann-plug mill method or a Mannesmann-mandrel mill method, and further performing cooling down to room temperature at a cooling rate equal to or more than an air-cooling rate. Herein, the wall thickness of the seamless steel tube is set to be more than 25.4 mm. It is needless to say that the size of a steel material which is a starting material is controlled to be within an appropriate range in order to achieve a seamless steel tube having such a wall thickness.

**[0046]** Heating temperature of a steel material: 1100°C or higher and 1300°C or lower

**[0047]** In the case where the heating temperature of a steel material is lower than 1100°C, there is an enhance in deformation resistance due to the heating temperature being excessively low and it is difficult to perform hot rolling due to a load on rolling mills being excessively large. On the other hand, in the case where the heating temperature is higher than 1300°C, there is a deteriorate in toughness due to an increase in crystal grain diameter and there is a decrease in yield due to an increase in the amount of scale loss. Therefore, it is preferable that the heating temperature of a steel material be 1100°C or higher and 1300°C or lower, more preferably 1200°C or higher and 1280°C or lower.

**[0048]** The steel material which has been heated up to the heating temperature described above is subjected to hot rolling including piercing rolling. Regarding hot rolling, any of an ordinary Mannesmann-plug mill method, in which the

steel material is subjected to processing using a piercer mill for performing piercing rolling, a subsequent elongator mill, a plug mill and a realer mill, or, further, a sizing mill in this order, and an ordinary Mannesmann-mandrel mill method, in which the steel material is subjected to processing using a piercer mill for performing piercing rolling, a subsequent mandrel mill and reducer mill in this order, may be used.

**[0049]** In the present invention, the hot rolling including piercing rolling described above is performed under conditions such that the total rolling reduction in a temperature range of 1100°C to 900°C is 30% or more. By controlling rolling reduction in this temperature range to be within an appropriate range, the spacing between ferrite-austenite (martensite) grain boundaries can be controlled to be small and a decrease in grain diameter can be achieved, which results in an enhance in toughness. Even in the case where rolling reduction is controlled in a temperature range out of the range of 1100°C to 900°C, if rolling reduction in the temperature range of 1100°C to 900°C is out of the appropriate range described above, a decrease in grain diameter according to the present invention cannot be achieved. In the case where the total rolling reduction in this temperature range is less than 30%, it is difficult to achieve a decrease in grain diameter according to the present invention, that is, it is difficult to control the number GSI of ferrite-austenite (martensite) grain boundaries per unit length in the wall thickness direction to be 120 or more. Therefore, the rolling reduction in the temperature range of 1100°C to 900°C is set to be 30% or more. With this method, since it is possible to control the spacing between ferrite-austenite (martensite) grain boundaries to be equal to or less than the specified value, a decrease in grain diameter can be realized even in the case of a steel tube having a thick wall, which results in an enhance in toughness. Note that there is no particular limitation on the upper limit of rolling reduction in this temperature range.

**[0050]** In addition, there is no particular limitation on what rolling conditions are used out of the temperature range of 1100°C to 900°C as long as a seamless steel tube having a specified size and shape can be manufactured.

**[0051]** The seamless steel tube which has been manufactured by performing hot rolling for tube making as described above is subsequently subjected to cooling down to room temperature at a cooling rate equal to or more than an air-cooling rate. In the case of a steel tube having the range of chemical composition according to the present invention, a microstructure including a martensite phase as a main phase can be achieved by performing cooling at a cooling rate equal to or more than an air-cooling rate.

**[0052]** After tube making has been performed, the cooled steel tube is subsequently subjected to a heat treatment including quenching-tempering.

**[0053]** In quenching, the steel tube is heated up to a heating temperature for quenching of 850°C or higher and 1000°C or lower, and then cooled with water. In the case where the heating temperature for quenching is lower than 850°C, transformation into a martensite does not sufficiently progress, and the desired high strength cannot be achieved. Further, there is concern that intermetallic compounds may be formed and toughness and corrosion resistance may deteriorate. On the other hand, in the case where the heating temperature for quenching is higher than 1000°C, the fraction of a martensite formed becomes excessively high, and strength becomes excessively high. Therefore, it is preferable that the heating temperature for quenching be 850°C or higher and 1000°C or lower. There is no particular limitation on a holding time when heating is performed for quenching. However, it is preferable that the holding time be 10 to 30 minutes from the viewpoint of productivity. Further, it is more preferable that the heating temperature for quenching be 920°C or higher and 980°C or lower.

**[0054]** After quenching has been performed, tempering is further performed. In tempering, the steel tube is heated up to a tempering temperature of 400°C or higher and 700°C or lower, and then cooled at a cooling rate equal to or more than an air-cooling rate. In the case where the tempering temperature is lower than 400°C, a sufficient tempering effect cannot be realized. On the other hand, in the case where the tempering temperature is higher than 700°C, there is a tendency for intermetallic compounds to precipitate, which may deteriorate toughness and corrosion resistance. Therefore, it is preferable that the tempering temperature be 400°C or higher and 700°C or lower. Note that there is no particular limitation on a holding time when heating for tempering is performed. However, it is preferable that the holding time be 20 to 60 minutes from the viewpoint of productivity. Further, it is more preferable that the tempering temperature be 550°C or higher and 650°C or lower.

**[0055]** Further, only tempering described above may be performed without performing quenching on the steel tube which has been subjected to tube making.

**[0056]** The seamless steel tube which is manufactured using the manufacturing method described above has a chemical composition described above and a microstructure including a martensite phase as a main phase and a second phase consisting of, at volume ratio, 10% or more and 60% or less of a ferrite phase and 0% or more and 10% or less of an austenite phase. Also, the steel tube is a thick high-strength seamless stainless steel tube for oil country tubular goods having a wall thickness of more than 25.4 mm and having a microstructure in which a GSI value, which is defined as the number of ferrite-martensite grain boundaries per unit length of a line segment drawn in the wall thickness direction, is 120 or more in the central portion in the wall thickness direction.

**[0057]** In the present invention, a microstructure includes a martensite phase as a main phase and a second phase consisting of, at volume ratio, 10% or more and 60% or less of a ferrite phase and 0% or more and 10% or less of an austenite phase in order to achieve the desired high strength.

**[0058]** In the case where the volume ratio of a ferrite phase is less than 10%, there is a deterioration in hot formability. On the other hand, in the case where the volume ratio of a ferrite phase is more than 60%, there is a deterioration in strength and toughness. In addition, although the second phase may include 10% or less of an austenite phase other than a ferrite phase, it is preferable that the volume ratio of an austenite phase be as small as possible, including 0%, in order to achieve sufficient strength. In the case where the volume ratio of an austenite phase is more than 10%, it is difficult to achieve the desired high strength.

**[0059]** The steel tube according to the present invention has a microstructure including a martensite and a ferrite phase, and, further, a retained austenite phase as described above, in which a GSI value, which is defined as the number of ferrite-martensite grain boundaries per unit length of a line segment drawn in the wall thickness direction, is 120 or more in the central portion in the wall thickness direction. In the case where the GSI value is less than 120, since it is difficult to achieve a decrease in the grain diameter of a microstructure, it is difficult to stably achieve the desired toughness.

**[0060]** Note that a GSI value (line/mm) is a value which can be determined by counting the number (line/mm) of ferrite-martensite grain boundaries in the wall thickness direction using a microstructure photograph taken through the observation of a sample, which has been etched with a vilella's reagent, using an optical microscope (magnification of 100 to 1000 times).

**[0061]** The present invention will be further described on the basis of EXAMPLES hereafter.

#### [EXAMPLES]

**[0062]** Molten steels having the chemical compositions given in Table 1 were smelted using a steel converter, and then cast into billets (steel materials having an outer diameter of 260 mm) using a continuous casting method. The obtained steel materials were heated at the temperatures given in Table 2, and then made into seamless steel tubes (having an outer diameter of 168.3 to 297 mm $\phi$  and a wall thickness of 26 to 34 mm) by performing hot rolling using an ordinary Mannesmann-plug mill method in which the steel material is subjected to hot processing using a piercing mill, an elongator mill, a plug mill and realer mill, or, further, a sizing mill in this order under conditions such that the rolling reduction in a temperature range of 1100°C to 900°C satisfied the conditions given in Table 2. Further, after hot rolling had been performed, cooling was performed under the conditions given in Table 2. The obtained seamless steel tubes were subjected to quenching-tempering under the conditions given in Table 2.

**[0063]** Using test pieces cut out of the obtained steel tubes, a microstructure was observed, and tensile properties, toughness and corrosion resistance were investigated. Investigation methods will be described hereafter.

#### (1) Microstructure observation

**[0064]** Using a test piece for microstructure observation cut out of the central portion in the wall thickness direction of the obtained steel tube, a microstructure in a cross section in the wall thickness direction, which had been polished and etched with a vilella's reagent, was observed using an optical microscope (at a magnification of 100 to 1000 times). Using the taken photograph, the kinds of microstructures were identified, and the fraction (volume ratio) of a ferrite phase was calculated by performing image analysis.

**[0065]** Here, that of an austenite phase ( $\gamma$ ) was determined using an X-ray diffraction method. The integrated intensities of diffracted X-ray for the (220) plane of a  $\gamma$  phase and the (211) plane of a ferrite phase ( $\alpha$ ) were determined, and conversion was performed using the following equation:

$$\gamma \text{ (volume ratio)} = 100 / (1 + (I_{\alpha}R_{\gamma} / I_{\gamma}R_{\alpha})),$$

where  $I_{\alpha}$ : integrated intensity of a  $\alpha$  phase

$I_{\gamma}$ : integrated intensity of a  $\gamma$  phase

$R_{\alpha}$ : theoretically calculated value of  $\alpha$  on the basis of crystallography

$R_{\gamma}$ : theoretically calculated value of  $\gamma$  on the basis of crystallography. Here, the phase fraction of a martensite phase was derived as the remainder other than these phases.

**[0066]** In addition, the test piece for microstructure observation was etched with a vilella's reagent and observed using an optical microscope (at a magnification of 400 times). Using the taken photograph, the number (line/mm) of ferrite-martensite grain boundaries was counted in the wall thickness direction in order to calculate a GSI value.

#### (2) Tensile properties

**[0067]** A strip specimen specified by API standard (having a gage length of 50.8 mm) was cut out of the central portion

in the wall thickness direction of the obtained steel tube in accordance with API standard so that the tensile direction is the direction of the tube axis. By performing a tensile test based on API standard, tensile properties (yield strength YS, tensile strength TS and elongation EI) were determined.

5 (3) Toughness

10 **[0068]** Using a V-notch test piece (having a thickness of 10 mm) which was cut out of the central portion in the wall thickness direction of the obtained steel tube in accordance with ISO standard so that the longitudinal direction of the test piece was the circumferential direction of the tube, a Charpy impact test was performed under a condition of a test temperature of -10°C in order to determine absorbed energy  $vE_{-10}$  (J). Here, the number of the test pieces was 3 for each steel tube, the average value of the three was used as the value for the steel tube.

(4) Corrosion resistance

15 **[0069]** A test specimen for a corrosion test (having a thickness of 3 mm, a width of 25 mm and a length of 50 mm) was cut out of the central portion in the wall thickness direction of the obtained steel tube and used for a corrosion test.

20 **[0070]** In the corrosion test, the test specimen was immersed in a 20% NaCl aqueous solution (having a temperature of 230°C with carbon dioxide gas of 3.0 MPa being dissolved in the saturated state) which was contained in an autoclave, for 14 days. After the corrosion test had been performed, by determining the weight of the test specimen, a corrosion rate was calculated from a decrease in weight. In addition, after the corrosion test had been performed, the test specimen was observed using a loupe at a magnification ratio of 50 times in order to observe whether or not pitting corrosion occurred. A case where pitting corrosion of a diameter of 0.2 mm or more was observed was evaluated as a case where pitting corrosion occurred.

**[0071]** The obtained results are given in Table 3.

25 **[0072]** [Table 1]

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[Table 1]

| Steel No. | Chemical Composition (mass%) |      |      |      |       |      |      |       |      |       |        |                                   |                                                   |    | Satisfaction of Relational Expression (1) | Left-Hand Side Value of Relational Expression (1) *) | Satisfaction of Relational Expression (2) | Left-Hand Side Value of Relational Expression (2) **) | Note                |
|-----------|------------------------------|------|------|------|-------|------|------|-------|------|-------|--------|-----------------------------------|---------------------------------------------------|----|-------------------------------------------|------------------------------------------------------|-------------------------------------------|-------------------------------------------------------|---------------------|
|           | C                            | Si   | Mn   | P    | S     | Cr   | Ni   | V     | Al   | N     | O      | Mo,W,Cu                           | Nb,Ti,Zr,B                                        | Ca |                                           |                                                      |                                           |                                                       |                     |
| A         | 0.026                        | 0.2  | 0.24 | 0.01 | 0.001 | 16.7 | 4.11 | 0.027 | 0.02 | 0.051 | 0.0025 | Mo: 2.13,<br>W: 1.05,<br>Cu: 0.51 | Nb: 0.043                                         | —  | 20.73                                     | Yes                                                  | 13.47                                     | Yes                                                   | Example             |
| B         | 0.019                        | 0.18 | 0.49 | 0.01 | 0.001 | 17   | 3.88 | 0.045 | 0.02 | 0.049 | 0.0033 | Mo: 2.59                          | —                                                 | —  | 20.7                                      | Yes                                                  | 14.3                                      | Yes                                                   | Example             |
| C         | 0.034                        | 0.26 | 0.77 | 0.01 | 0.001 | 17.2 | 4.31 | 0.036 | 0.02 | 0.057 | 0.0029 | Mo: 2.34,<br>Cu: 0.56             | Nb: 0.035,<br>Ti: 0.075,<br>Zr: 0.0087, B: 0.0013 | —  | 21.33                                     | Yes                                                  | 12.84                                     | Yes                                                   | Example             |
| D         | 0.023                        | 0.33 | 0.66 | 0.01 | 0.001 | 16.1 | 3.59 | 0.054 | 0.02 | 0.047 | 0.0041 | Mo: 2.01,<br>W: 1.21,<br>Cu: 2.02 | Ti: 0.076                                         | —  | 20.65                                     | Yes                                                  | 12.95                                     | Yes                                                   | Example             |
| E         | 0.018                        | 0.23 | 0.31 | 0.02 | 0.001 | 17.5 | 4    | 0.046 | 0.01 | 0.05  | 0.0019 | Mo: 2.40,<br>Cu: 0.75             | Nb: 0.044                                         | —  | 21.59                                     | Yes                                                  | 14.39                                     | Yes                                                   | Example             |
| F         | 0.012                        | 0.27 | 0.45 | 0.02 | 0.001 | 16.7 | 2.6  | 0.46  | 0.01 | 0.056 | 0.0028 | Mo: 1.90                          | —                                                 | —  | 19.22                                     | No                                                   | 14.83                                     | Yes                                                   | Comparative Example |
| G         | 0.035                        | 0.28 | 0.39 | 0.02 | 0.001 | 16.1 | 4.6  | 0.043 | 0.02 | 0.042 | 0.0024 | Mo: 1.90,<br>Cu: 0.62             | Ti: 0.025                                         | —  | 19.87                                     | Yes                                                  | 11.24                                     | No                                                    | Comparative Example |

\*)  $\text{Cr} + 0.65\text{Ni} + 0.60\text{Mo} + 0.30\text{W} + 0.55\text{Cu} - 20\text{C} \geq 19.5$  ... (1)

\*\*)  $\text{Cr} + \text{Mo} + 0.50\text{W} + 0.30\text{Si} - 43.5\text{C} - 0.4\text{Mu} - \text{Ni} - 0.3\text{Cu} - 9\text{Nb} \geq 11.5$  ... (2)

Underlined value is out of the range according to the present invention.

[Table 2]

| Steel Tube No. | Steel No. | Hot Rolling              |                                            |                       |                           | Seamless Steel Tube | Heat Treatment           |                    |               |                               |                          |                    | Note                |
|----------------|-----------|--------------------------|--------------------------------------------|-----------------------|---------------------------|---------------------|--------------------------|--------------------|---------------|-------------------------------|--------------------------|--------------------|---------------------|
|                |           | Heating Temperature (°C) | Rolling Reduction from 1100°C to 900°C (%) | Hot Rolling Method *) | Cooling after Tube Making |                     | Heating Temperature (°C) | Holding Time (min) | Cooling       | Cooling Stop Temperature (°C) | Heating Temperature (°C) | Holding Time (min) |                     |
| 1              | A         | 1250                     | 21                                         | a                     | Water Cooling             | 297φ×34             | 960                      | 30                 | Water Cooling | 25                            | 620                      | 60                 | Comparative Example |
| 2              | A         | 1250                     | 26                                         | a                     | Water Cooling             | 297φ×34             | 960                      | 30                 | Water Cooling | 25                            | 620                      | 60                 | Comparative Example |
| 3              | A         | 1250                     | 34                                         | a                     | Water Cooling             | 297φ×34             | 960                      | 30                 | Water Cooling | 25                            | 620                      | 60                 | Example             |
| 4              | A         | 1250                     | 40                                         | a                     | Water Cooling             | 297φ×34             | 960                      | 30                 | Water Cooling | 25                            | 620                      | 60                 | Example             |
| 5              | A         | 1250                     | 38                                         | a                     | Water Cooling             | 297φ×26             | 960                      | 30                 | Water Cooling | 25                            | 620                      | 60                 | Example             |
| 6              | A         | 1250                     | 45                                         | a                     | Water Cooling             | 297φ×26             | 960                      | 30                 | Water Cooling | 25                            | 620                      | 60                 | Example             |
| 7              | B         | 1250                     | 23                                         | a                     | Water Cooling             | 297φ×32             | 1000                     | 30                 | Water Cooling | 25                            | 630                      | 60                 | Comparative Example |
| 8              | B         | 1250                     | 29                                         | a                     | Water Cooling             | 297φ×32             | 1000                     | 30                 | Water Cooling | 25                            | 630                      | 60                 | Comparative Example |
| 9              | B         | 1250                     | 33                                         | a                     | Water Cooling             | 297φ×32             | 1000                     | 30                 | Water Cooling | 25                            | 630                      | 60                 | Example             |
| 10             | B         | 1250                     | 37                                         | a                     | Water Cooling             | 297φ×32             | 1000                     | 30                 | Water Cooling | 25                            | 630                      | 60                 | Example             |
| 11             | C         | 1260                     | 35                                         | a                     | Water Cooling             | 297φ×32             | 980                      | 30                 | Water Cooling | 25                            | 600                      | 60                 | Example             |
| 12             | C         | 1260                     | 40                                         | b                     | Water Cooling             | 168.3φ×26           | 980                      | 30                 | Water Cooling | 25                            | 600                      | 60                 | Example             |

(continued)

| Steel Tube No. | Steel No. | Hot Rolling              |                                            |                       |                           | Seamless Steel Tube | Heat Treatment           |                    |               |                               |                          |                    | Note                |
|----------------|-----------|--------------------------|--------------------------------------------|-----------------------|---------------------------|---------------------|--------------------------|--------------------|---------------|-------------------------------|--------------------------|--------------------|---------------------|
|                |           | Heating Temperature (°C) | Rolling Reduction from 1100°C to 900°C (%) | Hot Rolling Method *) | Cooling after Tube Making |                     | Quenching                |                    |               | Tempering                     |                          |                    |                     |
|                |           |                          |                                            |                       |                           |                     | Heating Temperature (°C) | Holding Time (min) | Cooling       | Cooling Stop Temperature (°C) | Heating Temperature (°C) | Holding Time (min) |                     |
| 13             | D         | 1240                     | 33                                         | a                     | Water Cooling             | 297φ×32             | 980                      | 30                 | Water Cooling | 25                            | 600                      | 60                 | Example             |
| 14             | E         | 1240                     | 36                                         | a                     | Water Cooling             | 297φ×32             | 980                      | 30                 | Water Cooling | 25                            | 590                      | 60                 | Example             |
| 15             | E         | 1240                     | 32                                         | b                     | Water Cooling             | 168.3φ×26           | 980                      | 30                 | Water Cooling | 25                            | 600                      | 60                 | Example             |
| 16             | E         | 1240                     | 28                                         | a                     | Water Cooling             | 297φ×62             | 980                      | 30                 | Water Cooling | 25                            | 610                      | 60                 | Example             |
| 17             | E         | 1240                     | 33                                         | a                     | Water Cooling             | 297φ×32             | 980                      | 30                 | Water Cooling | 25                            | 610                      | 60                 | Example             |
| 18             | F         | 1240                     | 35                                         | a                     | Water Cooling             | 297φ×32             | 980                      | 30                 | Water Cooling | 25                            | 600                      | 60                 | Comparative Example |
| 19             | G         | 1260                     | 34                                         | a                     | Water Cooling             | 297φ×26             | 980                      | 30                 | Water Cooling | 25                            | 600                      | 60                 | Comparative Example |

\*) a: Mannesmann-Plug mill method, b: Mannesmann-mandrel mill method

\*) a: Mannesmann-Plug mill method, b: Mannesmann-mandrel mill method

[0074] [Table 3]

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[Table 3]

| Steel Tube No. | Steel No. | Microstructure |             |             |             |                  |             | Tensile Property |           |                             | Toughness | Corrosion Resistance           |                     | Note  |
|----------------|-----------|----------------|-------------|-------------|-------------|------------------|-------------|------------------|-----------|-----------------------------|-----------|--------------------------------|---------------------|-------|
|                |           | Kind*          | M<br>(vol%) | F<br>(vol%) | γ<br>(vol%) | GSI<br>(line/mm) | YS<br>(MPa) | TS<br>(MPa)      | El<br>(%) | Corrosion Rate<br>(mm/year) |           | Existence of Pitting Corrosion |                     |       |
| 1              | A         |                | M+F+γ       | 58          | 35          | 7                | 88          | 812              | 987       |                             | 25.4      |                                | 25                  | 0.105 |
| 2              | A         | M+F+γ          | 58          | 34          | 8           | 113              | 833         | 974              | 23        | 38                          | 0.098     | No                             | Comparative Example |       |
| 3              | A         | M+F+γ          | 59          | 33          | 8           | 131              | 786         | 913              | 24.1      | 62                          | 0.102     | No                             | Example             |       |
| 4              | A         | M+F+γ          | 55          | 37          | 8           | 145              | 823         | 952              | 22.8      | 105                         | 0.978     | No                             | Example             |       |
| 5              | A         | M+F+γ          | 57          | 38          | 5           | 182              | 811         | 965              | 23.4      | 145                         | 0.965     | No                             | Example             |       |
| 6              | A         | M+F+γ          | 59          | 33          | 8           | 194              | 798         | 987              | 24.4      | 152                         | 0.104     | No                             | Example             |       |
| 7              | B         | M+F+γ          | 63          | 29          | 8           | 79               | 799         | 944              | 24.1      | 23                          | 0.108     | No                             | Comparative Example |       |
| 8              | B         | M+F+γ          | 55          | 39          | 6           | 105              | 783         | 916              | 23.6      | 32                          | 0.093     | No                             | Comparative Example |       |
| 9              | B         | M+F+γ          | 57          | 41          | 2           | 132              | 800         | 933              | 21.5      | 82                          | 0.078     | No                             | Example             |       |
| 10             | B         | M+F+γ          | 60          | 32          | 8           | 140              | 812         | 945              | 25.4      | 125                         | 0.069     | No                             | Example             |       |
| 11             | C         | M+F+γ          | 65          | 28          | 7           | 135              | 868         | 1025             | 22.9      | 45                          | 0.099     | No                             | Example             |       |
| 12             | C         | M+F+γ          | 62          | 31          | 7           | 142              | 876         | 1033             | 22        | 79                          | 0.087     | No                             | Example             |       |
| 13             | D         | M+F+γ          | 59          | 36          | 5           | 136              | 796         | 987              | 23.2      | 84                          | 0.082     | No                             | Example             |       |
| 14             | E         | M+F+γ          | 59          | 33          | 8           | 140              | 823         | 976              | 29.4      | 105                         | 0.093     | No                             | Example             |       |
| 15             | E         | M+F+γ          | 61          | 33          | 6           | 133              | 856         | 1001             | 23        | 55                          | 0.103     | No                             | Example             |       |
| 16             | E         | M+F+γ          | 59          | 33          | 8           | 137              | 889         | 1052             | 23.5      | 69                          | 0.11      | No                             | Example             |       |
| 17             | E         | M+F+γ          | 61          | 31          | 8           | 141              | 901         | 1085             | 23.2      | 89                          | 0.09      | No                             | Example             |       |
| 18             | F         | M+F+γ          | 47          | 49          | 4           | 132              | 812         | 974              | 24.9      | 29                          | 0.101     | No                             | Comparative Example |       |

(continued)

| Steel<br>Tube<br>No.                                                                                                          | Steel<br>No. | Microstructure |             |             |             |                  | Tensile Property |             |           | Toughness | Corrosion Resistance           |                                   | Note                   |
|-------------------------------------------------------------------------------------------------------------------------------|--------------|----------------|-------------|-------------|-------------|------------------|------------------|-------------|-----------|-----------|--------------------------------|-----------------------------------|------------------------|
|                                                                                                                               |              | Kind*          | M<br>(vol%) | F<br>(vol%) | γ<br>(vol%) | GSI<br>(line/mm) | YS<br>(MPa)      | TS<br>(MPa) | El<br>(%) |           | Corrosion<br>Rate<br>(mm/year) | Existence of Pitting<br>Corrosion |                        |
| 19                                                                                                                            | G            | M+F+γ          | 62          | 31          | 7           | 135              | 796              | 966         | 23.9      | 65        | 0.179                          | Yes                               | Comparative<br>Example |
| *) M; martensite, F: ferrite, γ: austenite<br><u>Underlined value</u> is out of the range according to the present invention. |              |                |             |             |             |                  |                  |             |           |           |                                |                                   |                        |

**[0075]** All of the examples of the present invention had a high strength of 758 MPa (110 ksi) or more and a high toughness of  $vE_{10}(J)$ : 40 J or more despite having a large wall thickness. In addition, even in the intense corrosion environment having a high temperature and containing  $CO_2$  and  $Cl^-$ , a decrease in weight due to corrosion was 0.127 mm/year or less and pitting corrosion did not occur, which means these steel tubes were excellent in terms of corrosion resistance.

**[0076]** On the other hand, in the case of the comparative examples which were out of the range according to the present invention, corresponded to one or more of a case where the desired high strength was not achieved, a case where a GSI value was less than 120 and  $vE_{10}(J)$  was less than 40 J, which means high toughness was not stably achieved, and a case where a decrease in weight due to corrosion was more than 0.127 mm/year, which means there was a deterioration in corrosion resistance.

## Claims

1. A method for manufacturing a high-strength seamless stainless steel tube for oil country tubular goods having a wall thickness of more than 25.4 mm, the method comprising heating a steel material; hot rolling including piercing rolling the steel material into a seamless steel tube; and cooling the seamless steel tube down to room temperature at a cooling rate equal to or more than an air-cooling rate, the steel material having a chemical composition containing, by mass%,  
C: 0.005% or more and 0.06% or less, Si: 0.05% or more and 0.5% or less,  
Mn: 0.2% or more and 1.8% or less, P: 0.03% or less,  
S: 0.005% or less, Cr: 15.5% or more and 18.0% or less,  
Ni: 1.5% or more and 5.0% or less, V: 0.02% or more and 0.2% or less,  
Al: 0.002% or more and 0.05% or less, N: 0.01% or more and 0.15% or less, O: 0.006% or less, and further containing one, two or more selected from among Mo: 1.0% or more and 3.5% or less, W: 3.0% or less and Cu: 3.5% or less and the balance being Fe and inevitable impurities, wherein relational expressions (1) and (2) below are satisfied, the hot rolling including piercing rolling is performed under conditions such that the total rolling reduction in a temperature range of 1100°C to 900°C is 30% or more, and after the rolled steel tube is cooled down to the room temperature, quenching-tempering or tempering is performed:

$$Cr + 0.65Ni + 0.60Mo + 0.30W + 0.55Cu - 20C \geq 19.5 \quad \cdots (1),$$

$$Cr + Mo + 0.50W + 0.30Si - 43.5C - 0.4Mn - Ni - 0.3Cu - 9N \geq 11.5 \quad \cdots$$

(2),

where Cr, Mo, W, Si, C, Mn, Ni, Cu and N: contents (mass%) of chemical elements respectively represented by corresponding atomic symbols.

2. The method for manufacturing a high-strength seamless stainless steel tube for oil country tubular goods according to Claim 1, wherein the chemical composition further contains, by mass%, one or more selected from among Nb: 0.2% or less, Ti: 0.3% or less, Zr: 0.2% or less and B: 0.01% or less.
3. The method for manufacturing a high-strength seamless stainless steel tube for oil country tubular goods according to Claim 1 or 2, wherein the chemical composition further contains, by mass%, Ca: 0.01% or less.
4. A high-strength seamless stainless steel tube for oil country tubular goods having a wall thickness of more than 25.4 mm, the steel tube having a chemical composition containing, by mass%,  
C: 0.005% or more and 0.06% or less, Si: 0.05% or more and 0.5% or less,  
Mn: 0.2% or more and 1.8% or less, P: 0.03% or less,  
S: 0.005% or less, Cr: 15.5% or more and 18.0% or less,  
Ni: 1.5% or more and 5.0% or less, V: 0.02% or more and 0.2% or less,  
Al: 0.002% or more and 0.05% or less, N: 0.01% or more and 0.15% or less, O: 0.006% or less, and further containing one, two or more selected from among Mo: 1.0% or more and 3.5% or less, W: 3.0% or less and Cu: 3.5% or less and the balance being Fe and inevitable impurities, in which relational expressions (1) and (2)

below are satisfied, having a microstructure including a martensite phase as a main phase and a second phase consisting of, at volume ratio, 10% or more and 60% or less of a ferrite phase and 0% or more and 10% or less of an austenite phase, in which a GSI value, which is defined as the number of ferrite-martensite grain boundaries per unit length of a line segment drawn in the wall thickness direction, is 120 or more in the central portion in the wall thickness direction, and having excellent low-temperature toughness and excellent corrosion resistance:

$$\text{Cr} + 0.65\text{Ni} + 0.60\text{Mo} + 0.30\text{W} + 0.55\text{Cu} - 20\text{C} \geq 19.5 \quad \cdots (1),$$

$$\text{Cr} + \text{Mo} + 0.50\text{W} + 0.30\text{Si} - 43.5\text{C} - 0.4\text{Mn} - \text{Ni} - 0.3\text{Cu} - 9\text{N} \geq 11.5 \quad \cdots$$

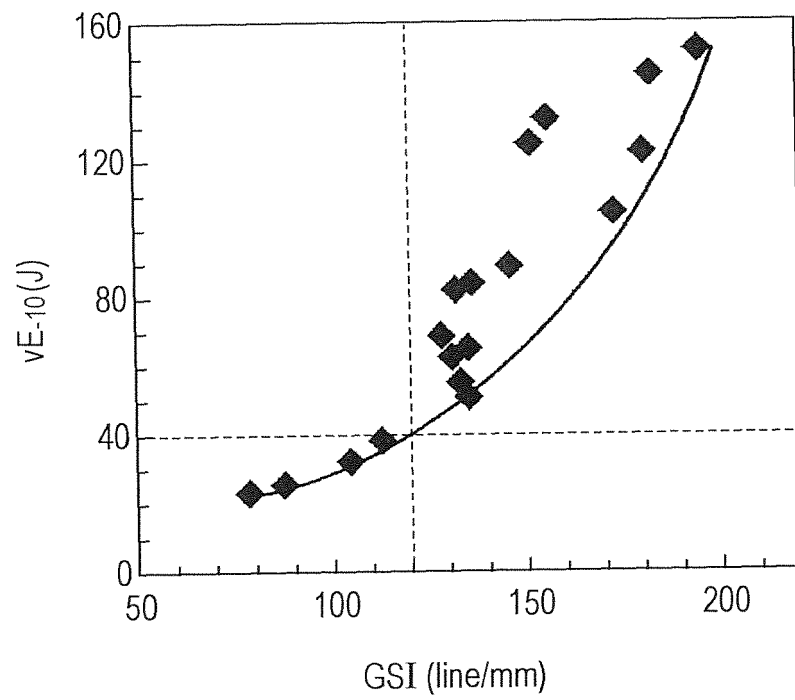
(2),

where Cr, Mo, W, Si, C, Mn, Ni, Cu and N: contents (mass%) of chemical elements respectively represented by corresponding atomic symbols.

5. The high-strength seamless stainless steel tube for oil country tubular goods according to Claim 4, wherein the chemical composition further contains, by mass%, one or more selected from among Nb: 0.2% or less, Ti: 0.3% or less, Zr: 0.2% or less and B: 0.01% or less.

6. The high-strength seamless stainless steel tube for oil country tubular goods according to Claim 4 or 5, wherein the chemical composition further contains, by mass%, Ca: 0.01% or less.

FIG. 1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/003411

## A. CLASSIFICATION OF SUBJECT MATTER

C21D8/10(2006.01)i, C21D9/08(2006.01)i, C22C38/00(2006.01)i, C22C38/58(2006.01)i

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C21D8/10, C21D9/08, C22C38/00, C22C38/58

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2013  
 Kokai Jitsuyo Shinan Koho 1971-2013 Toroku Jitsuyo Shinan Koho 1994-2013

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 2011/136175 A1 (Sumitomo Metal Industries, Ltd.),<br>03 November 2011 (03.11.2011),<br>claims; paragraphs [0058], [0064], [0065];<br>tables 1, 3 to 4 | 1-6                   |
| A         | WO 2010/134498 A1 (Sumitomo Metal Industries, Ltd.),<br>25 November 2010 (25.11.2010),<br>claims; paragraph [0071]; tables 1 to 2                        | 1-6                   |
| A         | WO 2010/050519 A1 (Sumitomo Metal Industries, Ltd.),<br>06 May 2010 (06.05.2010),<br>claims; paragraph [0042]; tables 1 to 2                             | 1-6                   |

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

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search  
24 July, 2013 (24.07.13)Date of mailing of the international search report  
06 August, 2013 (06.08.13)Name and mailing address of the ISA/  
Japanese Patent Office

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/003411

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                           | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | JP 2008-81793 A (JFE Steel Corp.),<br>10 April 2008 (10.04.2008),<br>claims; paragraph [0039]; tables 1 to 3 | 1-6                   |
| A         | WO 2005/042793 A1 (JFE Steel Corp.),<br>12 May 2005 (12.05.2005),<br>claims; examples                        | 1-6                   |

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## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/JP2013/003411

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**REFERENCES CITED IN THE DESCRIPTION**

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