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**Miyata et al.**(10) **Pub. No.: US 2015/0101711 A1**(43) **Pub. Date: Apr. 16, 2015**(54) **HIGH-STRENGTH SEAMLESS STAINLESS  
STEEL TUBE FOR OIL COUNTRY TUBULAR  
GOODS AND METHOD OF  
MANUFACTURING THE SAME***C22C 38/00* (2006.01)*C22C 38/44* (2006.01)*C22C 38/42* (2006.01)*C22C 38/06* (2006.01)*C22C 38/04* (2006.01)*C22C 38/02* (2006.01)*C21D 8/10* (2006.01)*C22C 38/46* (2006.01)(71) Applicant: **JFE Steel Corporation**, Tokyo (JP)(72) Inventors: **Yukio Miyata**, Aichi (JP); **Yasuhide  
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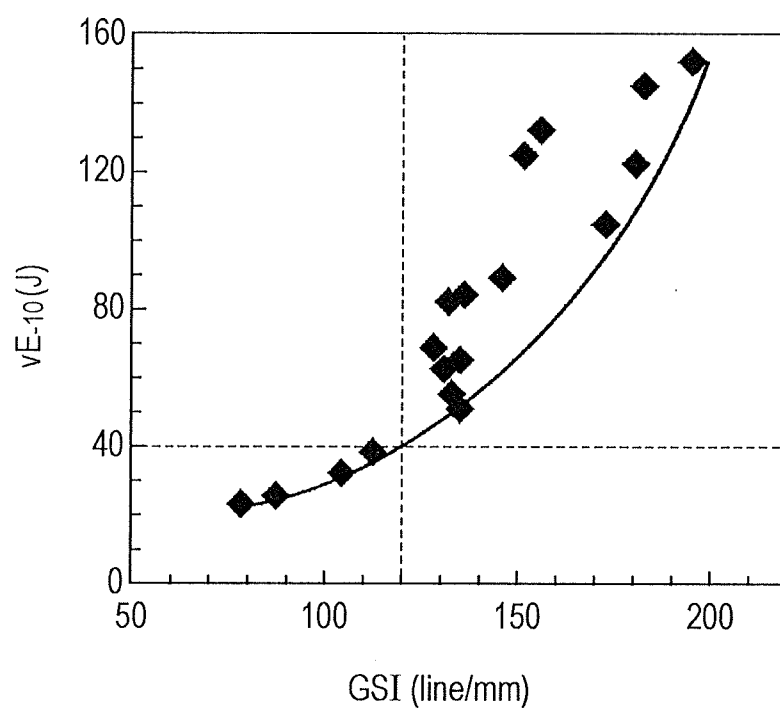
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**Publication Classification**(51) **Int. Cl.***C22C 38/54* (2006.01)*C21D 9/08* (2006.01)*C22C 38/50* (2006.01)*C22C 38/48* (2006.01)(57) **ABSTRACT**

A steel material has 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 contains 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  $Cr+0.65Ni+0.60Mo+0.30W+0.55Cu-20C \geq 19.5$  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.

FIG. 1



# **HIGH-STRENGTH SEAMLESS STAINLESS STEEL TUBE FOR OIL COUNTRY TUBULAR GOODS AND METHOD OF MANUFACTURING THE SAME**

## **TECHNICAL FIELD**

[0001] This disclosure 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**

[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 and so forth. Therefore, steel tubes for oil country tubular goods used 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 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.

[0005] To solve the problems described above, for example, Japanese Unexamined Patent Application Publication No. 2005-336595 describes a method of 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 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, 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:

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

[0006] (where Cr, Ni, Mo, W, Cu and C: contents (mass %) of chemical elements respectively represented by corresponding atomic symbols)

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

[0007] (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 Japanese Unexamined Patent Application Publication No. 2005-336595, 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.

[0008] In addition, Japanese Patent No. 4577457 describes a method of 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 Japanese Patent No. 4577457, a stainless steel tube for oil country tubular goods having not only 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.

[0009] Nowadays, since oil wells and gas fields 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 to prevent tubes for oil country tubular goods from being crushed due to pressure from the geological stratum. In the technique described in Japanese Patent No. 4577457, 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.

[0010] It could therefore be helpful 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<sub>-10</sub> determined by performing a Charpy impact test at a test temperature of -10° C., and, further, having excellent corrosion resistance and a method for manufacturing the steel tube. "Excellent corrosion resistance" refers to when a tube has excellent CO<sub>2</sub> corrosion resistance effective even in a corrosion environment having a high temperature of 230° C. or higher and containing CO<sub>2</sub> and Cl<sup>-</sup>.

## **SUMMARY**

[0011] We thus provide:

[0012] (1) A method of 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° 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:

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

[0013] (where Cr, Ni, Mo, W, Cu and C: contents (mass %) of chemical elements respectively represented by corresponding atomic symbols)

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

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

[0014] (2) The method of 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.

[0015] (3) The method of 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.

[0016] (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:

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

[0017] (where Cr, Ni, Mo, W, Cu and C: contents (mass %) of chemical elements respectively represented by corresponding atomic symbols)

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

[0018] (where Cr, Mo, W, Si, C, Mn, Ni, Cu and N: contents (mass %) of chemical elements respectively represented by corresponding atomic symbols).

[0019] (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.

[0020] (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.

[0021] 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 THE DRAWING

[0022] FIG. 1 is a graph illustrating the relationship between absorbed energy  $vE_{-10}$  in a Charpy impact test and a GSI value.

## DETAILED DESCRIPTION

[0023] We 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 to enhance the toughness of a stainless steel tube having a thick wall. In stainless steel having a chemical composition containing 16% to 18% of Cr and about 2% to 6% of Ni 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 the grain diameter even by performing a heat treatment afterward. Therefore, we 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 a stainless steel tube having a chemical composition containing 16% to 18% of Cr and about 2% to 6% of Ni, there is an enhancement in toughness by decreasing a GSI value, that is, by decreasing the spacing between various phases.

[0024] From the results of further investigations, we 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 enhancement in toughness.

[0025] First, experimental results will be described.

[0026] 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

mmφ 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.

[0027] FIG. 1 indicates that it is necessary to decrease the grain diameter of a microstructure to GSI: 120 or more to achieve toughness of  $vE_{-10}$ : 40 J or more. From the results of other experiments, we 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 of  $1100^{\circ}\text{C}$ . to  $900^{\circ}\text{C}$ . is 30% or more. In 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 of  $1100^{\circ}\text{C}$ . to  $900^{\circ}\text{C}$ . corresponds to rolling using an elongator mill and a plug mill or a mandrel mill. That is to say, we found that, to enhance the low-temperature toughness of a seamless steel tube, that is, 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.

[0028] The method of manufacturing a high-strength seamless stainless steel tube for oil country tubular goods will be described. A seamless steel tube is manufactured by heating a steel material and by performing hot rolling including piercing rolling.

[0029] The reasons for limitations on a chemical composition of a steel material will be described hereafter. Hereinafter, mass % used when describing a chemical composition is simply represented by %, unless otherwise noted.

[0030] The steel material 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 (1) and (2) are satisfied:

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

[0031] (where Cr, Ni, Mo, W, Cu and C: contents (mass %) of chemical elements respectively represented by corresponding atomic symbols)

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

[0032] (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

[0033] C is a chemical element 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, when the C content is more than 0.06%, there is a significant deterioration 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

[0034] Si is a chemical element which functions as a deoxidation agent, and Si is added in the amount of 0.05% or more. However, when the Si content is more than 0.5%, there is a deterioration in  $\text{CO}_2$  corrosion resistance and there is a deterioration 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

[0035] Mn is a chemical element which increases strength, and Mn is added in the amount of 0.2% or more to achieve the desired high strength. On the other hand, when 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

[0036] Since P is a chemical element which deteriorates corrosion resistance, it is preferable that the P content be as small as possible. However, since the P content is controlled at comparatively low cost without deteriorating corrosion resistance when 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 when the P content is excessively small, it is preferable that the P content be 0.005% or more.

S: 0.005% or Less

[0037] 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 when 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 when 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

[0038] Cr is a chemical element which enhances corrosion resistance as a result of forming a protective film and, in particular contributes to an enhancement in  $\text{CO}_2$  corrosion resistance. It is necessary that the Cr content be 15.5% or more to enhance corrosion resistance at a high temperature. On the other hand, when the Cr content is more than 18%, there is a deterioration 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

**[0039]** Ni is a chemical element effective in 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 when the Ni content is 1.5% or more. On the other hand, when 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

**[0040]** V contributes to an increase in strength through solid solution strengthening and is effective in increasing resistance to stress corrosion cracking. It is necessary that the V content be 0.02% or more to realize these effects. On the other hand, when 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

**[0041]** Al is a chemical element which functions as a deoxidation agent, and it is necessary that the Al content be 0.002% or more to realize this effect. On the other hand, when 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

**[0042]** N is a chemical element which markedly enhances pitting corrosion resistance, and it is necessary that the N content be 0.01% or more. On the other hand, when 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

**[0043]** 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, when 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.

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

**[0044]** 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.

**[0045]** Mo is a chemical element which contributes to an enhance in corrosion resistance by increasing resistance to pitting corrosion caused by and it is necessary that the Mo content be 1.0% or more. On the other hand, when the Mo content is more than 3.5%, there is a deterioration in strength and toughness and an increase in material cost. Therefore, when 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.

**[0046]** 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, when the W content is more than 3.0%, there is a deterioration in toughness and there is an increase in material cost. Therefore, when W is added, the W content is limited to 3.0% or less, preferably 0.5% or more and 2.5% or less.

**[0047]** Since Cu is effective in suppressing penetration of hydrogen into steel by strengthening a protective film, Cu contributes to an enhancement in corrosion resistance. It is preferable that the Cu content be 0.5% or more to realize these effects. However, when the Cu content is more than 3.5%, there is a deterioration in hot formability. Therefore, when Cu is added, the Cu content is limited to 3.5% or less, preferably 0.5% or more and 2.5% or less.

**[0048]** The contents of the constituent chemical elements described above are controlled to be within the ranges described above, in which expressions (1) and (2) are satisfied:

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

**[0049]** (where Cr, Ni, Mo, W, Cu and C: contents (mass %) of chemical elements respectively represented by corresponding atomic symbols)

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

**[0050]** (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 expressions (1) and (2) are calculated, a symbol is assigned a value of 0 when the corresponding chemical element is not contained.

**[0051]** By controlling the contents of Cr, Ni, Mo, W, Cu and C so that 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 expression (1) be 20.0 or more from the viewpoint of high-temperature corrosion resistance.

**[0052]** By controlling the contents of Cr, Mo, W, Si, C, Mn, Ni, Cu and N so that expression (2) is satisfied, there is an enhancement in hot workability, and hot workability necessary to manufacture a martensitic stainless steel tube can be achieved. It is preferable that the value of the left-hand side of expression (2) be 12.5 or more.

**[0053]** 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.

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

**[0054]** 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 to realize these effects. On the other hand, when 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 deterioration 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

**[0055]** 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 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 to realize this effect. On the other hand, when the Ca content is more than 0.01%, there is an increase in the amount of oxide containing inclusions, which deteriorates corrosion resistance. Therefore, when Ca is added, it is preferable that the Ca content be 0.01% or less.

**[0056]** 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.

**[0057]** There is no particular limitation on what method is used to manufacture 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, a cast material such as a billet may be manufactured using an ingot casting-blooming method.

**[0058]** 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. The size of a steel material which is a starting material is controlled to be within an appropriate range to achieve a seamless steel tube having such a wall thickness. Heating temperature of a steel material: 1100° C. or higher and 1300° C. or lower

**[0059]** When the heating temperature of a steel material is lower than 1100° C., there is an enhancement 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, when the heating temperature is higher than 1300° C., there is a deterioration 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.

**[0060]** 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 reeler 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 to perform piercing rolling, a subsequent mandrel mill and reducer mill in this order, may be used.

**[0061]** 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 enhancement in toughness. Even when rolling reduction is controlled in a temperature range out 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 cannot be achieved. When the total rolling reduction in this temperature range is less than 30%, it is difficult to achieve a decrease in grain diameter, 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 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 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.

**[0062]** 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.

**[0063]** 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 a steel tube having the range of chemical composition, 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.

**[0064]** After tube making has been performed, the cooled steel tube is subsequently subjected to a heat treatment including quenching-tempering.

**[0065]** In quenching, the steel tube is heated up to a heating temperature for quenching at 850° C. or higher and 1000° C. or lower, and then cooled with water. When 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, when 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.

**[0066]** 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. When the tempering temperature is lower than 400° C., a sufficient tempering effect cannot be realized. On the other hand, when 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.

[0067] Further, only tempering described above may be performed without performing quenching on the steel tube which has been subjected to tube making.

[0068] The seamless steel tube 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.

[0069] 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.

[0070] When the volume ratio of a ferrite phase is less than 10%, there is a deterioration in hot formability. On the other hand, when 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%, to achieve sufficient strength. When the volume ratio of an austenite phase is more than 10%, it is difficult to achieve the desired high strength.

[0071] The steel tube 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. When 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.

[0072] 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).

[0073] Our steel tubes and methods will be further described on the basis of EXAMPLES hereafter.

## EXAMPLES

[0074] 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 mmφ 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 reeler 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.

[0075] 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

[0076] 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.

[0077] 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:

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

[0078] where  $I\alpha$ : integrated intensity of a  $\alpha$  phase

[0079]  $I\gamma$ : integrated intensity of a  $\gamma$  phase

[0080]  $R\alpha$ : theoretically calculated value of  $\alpha$  on the basis of crystallography

[0081]  $R\gamma$ : 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.

[0082] 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

[0083] 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 El) were determined.

### (3) Toughness

[0084] 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  $-10^{\circ}\text{C}$ . in order to determine absorbed energy  $vE_{-10}$  (J). 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

**[0085]** 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.

**[0086]** In the corrosion test, the test specimen was immersed in a 20% NaCl aqueous solution (having a temperature of  $230^{\circ}\text{C}$ . 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 to observe whether or not pitting corrosion occurred. Pitting corrosion of a diameter of 0.2 mm or more was observed and evaluated.

**[0087]** The obtained results are given in Table 3.

TABLE 1

	Chemical Composition (mass %)										
Steel No.	C	Si	Mn	P	S	Cr	Ni	V	Al	N	O
A	0.026	0.2	0.24	0.01	0.001	16.7	4.11	0.027	0.02	0.051	0.0025
B	0.019	0.18	0.49	0.01	0.001	17	3.88	0.045	0.02	0.049	0.0033
C	0.034	0.26	0.77	0.01	0.001	17.2	4.31	0.036	0.02	0.057	0.0029
D	0.023	0.33	0.66	0.01	0.001	16.1	3.59	0.054	0.02	0.047	0.0041
E	0.018	0.23	0.31	0.02	0.001	17.5	4	0.046	0.01	0.05	0.0019
F	0.012	0.27	0.45	0.02	0.001	16.7	2.6	0.46	0.01	0.056	0.0028
G	0.035	0.28	0.39	0.02	0.001	16.1	4.6	0.043	0.02	0.042	0.0024

	Chemical Composition (mass %)								
Steel No.	Mo, W, Cu	Nb, Ti, Zr, B	Ca	Left-Hand Side Value of Relational Expression (1) *	Satisfaction of Relational Expression (1)	Left-Hand Side Value of Relational Expression (2) **	Satisfaction of Relational Expression (2)	Note	
A	Mo: 2.13, W: 1.05, Cu: 0.51	Nb: 0.043	—	20.73	Yes	13.47	Yes	Example	
B	Mo: 2.59	—	—	20.7	Yes	14.3	Yes	Example	
C	Mo: 2.34, Cu: 0.56	Nb: 0.035, Ti: 0.075, Zr: 0.0087, B: 0.0013	—	21.33	Yes	12.84	Yes	Example	
D	Mo: 2.01, W: 1.21, Cu: 2.02	Ti: 0.076	—	20.65	Yes	12.95	Yes	Example	
E	Mo: 2.40, Cu: 0.75	Nb: 0.044	—	21.59	Yes	14.39	Yes	Example	
F	Mo: 1.90	—	—	<u>19.29</u>	No	14.83	Yes	Comparative Example	
G	Mo: 1.90, Cu: 0.62	Ti: 0.025	—	19.87	Yes	<u>11.24</u>	No	Comparative Example	

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

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

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

TABLE 2

		Hot Rolling				Seamless	
			Rolling Reduction			Steel Tube Size	Heat Treatment
			from	Hot	Cooling	(Outer	Quenching
Steel Tube No.	Steel No.	Heating Temperature (° C.)	1100° C. to 900° C. (%)	Rolling Method *)	after Tube Making	diameter mmφ × Wall Thickness mm)	Heating Temperature (° C.)
1	A	1250	21	a	Water Cooling	297φ × 34	960
2	A	1250	26	a	Water Cooling	297φ × 34	960
3	A	1250	34	a	Water Cooling	297φ × 34	960

TABLE 2-continued

4	A	1250	40	a	Water Cooling	297 $\phi$ × 34	960
5	A	1250	38	a	Water Cooling	297 $\phi$ × 26	960
6	A	1250	45	a	Water Cooling	297 $\phi$ × 26	960
7	B	1250	23	a	Water Cooling	297 $\phi$ × 32	1000
8	B	1250	29	a	Water Cooling	297 $\phi$ × 32	1000
9	B	1250	33	a	Water Cooling	297 $\phi$ × 32	1000
10	B	1250	37	a	Water Cooling	297 $\phi$ × 32	1000
11	C	1260	35	a	Water Cooling	297 $\phi$ × 32	980
12	C	1260	40	b	Water Cooling	168.3 $\phi$ × 26	980
13	D	1240	33	a	Water Cooling	297 $\phi$ × 32	980
14	E	1240	36	a	Water Cooling	297 $\phi$ × 32	980
15	E	1240	32	b	Water Cooling	168.3 $\phi$ × 26	980
16	E	1240	28	a	Water Cooling	297 $\phi$ × 32	980
17	E	1240	33	a	Water Cooling	297 $\phi$ × 32	980
18	F	1240	35	a	Water Cooling	297 $\phi$ × 32	980
19	G	1260	34	a	Water Cooling	297 $\phi$ × 26	980

## Heat Treatment

## Quenching

## Cooling

## Tempering

Steel Tube No.	Steel No.	Holding Time (min)	Cooling	Stop Temperature (° C.)	Heating Temperature (° C.)	Holding Time (min)	Note
1	A	30	Water Cooling	25	620	60	Comparative Example
2	A	30	Water Cooling	25	620	60	Comparative Example
3	A	30	Water Cooling	25	620	60	Example
4	A	30	Water Cooling	25	620	60	Example
5	A	30	Water Cooling	25	620	60	Example
6	A	30	Water Cooling	25	620	60	Example
7	B	30	Water Cooling	25	630	60	Comparative Example
8	B	30	Water Cooling	25	630	60	Comparative Example
9	B	30	Water Cooling	25	630	60	Example
10	B	30	Water Cooling	25	630	60	Example
11	C	30	Water Cooling	25	600	60	Example
12	C	30	Water Cooling	25	600	60	Example
13	D	30	Water Cooling	25	600	60	Example
14	E	30	Water Cooling	25	590	60	Example
15	E	30	Water Cooling	25	600	60	Example
16	E	30	Water Cooling	25	610	60	Example
17	E	30	Water Cooling	25	610	60	Example
18	F	30	Water Cooling	25	600	60	Comparative Example
19	G	30	Water Cooling	25	600	60	Comparative Example

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

TABLE 3

Corrosion Resistance													
Steel		Microstructure					Tensile Property			Toughness	Corrosion	Existence	Note
Tube No.	Steel No.	Kind*	M (vol %)	F (vol %)	$\gamma$ (vol %)	GSI (line/mm)	YS (MPa)	TS (MPa)	El (%)	vE <sub>-10</sub> (J)	Rate (mm/year)	of Pitting Corrosion	
1	A	M + F + $\gamma$	58	35	7	88	812	987	25.4	25	0.105	No	Comparative Example
2	A	M + F + $\gamma$	58	34	8	113	833	974	23	38	0.098	No	Comparative Example
3	A	M + F + $\gamma$	59	33	8	131	786	913	24.1	62	0.102	No	Example
4	A	M + F + $\gamma$	55	37	8	145	823	952	22.8	105	0.978	No	Example
5	A	M + F + $\gamma$	57	38	5	182	811	965	23.4	145	0.965	No	Example
6	A	M + F + $\gamma$	59	33	8	194	798	987	24.4	152	0.104	No	Example
7	B	M + F + $\gamma$	63	29	8	79	799	944	24.1	23	0.108	No	Comparative Example
8	B	M + F + $\gamma$	55	39	6	105	783	916	23.6	32	0.093	No	Comparative Example
9	B	M + F + $\gamma$	57	41	2	132	800	933	21.5	82	0.078	No	Example
10	B	M + F + $\gamma$	60	32	8	140	812	945	25.4	125	0.069	No	Example
11	C	M + F + $\gamma$	65	28	7	135	868	1025	22.9	45	0.099	No	Example

TABLE 3-continued

Steel		Microstructure					Tensile Property			Toughness	Corrosion Resistance		Note
											Corrosion	Existence	
Tube No.	Steel No.	Kind*	M (vol %)	F (vol %)	$\gamma$ (vol %)	GSI (line/mm)	YS (MPa)	TS (MPa)	El (%)	vE <sub>-10</sub> (J)	Rate (mm/year)	of Pitting Corrosion	
12	C	M + F + $\gamma$	62	31	7	142	876	1033	22	79	0.087	No	Example
13	D	M + F + $\gamma$	59	36	5	136	796	987	23.2	84	0.082	No	Example
14	E	M + F + $\gamma$	59	33	8	140	823	976	24.4	105	0.093	No	Example
15	E	M + F + $\gamma$	61	33	6	133	856	1001	23	55	0.103	No	Example
16	E	M + F + $\gamma$	59	33	8	137	889	1052	23.5	69	0.11	No	Example
17	E	M + F + $\gamma$	61	31	8	141	901	1085	23.2	89	0.09	No	Example
18	F	M + F + $\gamma$	47	49	4	132	812	974	24.9	29	0.101	No	Comparative Example
19	G	M + F + $\gamma$	62	31	7	135	796	966	23.9	65	<u>0.179</u>	Yes	Comparative Example

\*) M; martensite, F: ferrite,  $\gamma$ : austenite

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

**[0088]** All of Examples had a high strength of 758 MPa (110 ksi) or more and a high toughness of vE<sub>-10</sub> (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<sub>2</sub> and Cl<sup>-</sup>, 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.

**[0089]** On the other hand, in the Comparative Examples, corresponded to one or more of when the desired high strength was not achieved, when a GSI value was less than 120 and vE<sub>-10</sub> (J) was less than 40 J, which means high toughness was not stably achieved, and when a decrease in weight due to corrosion was more than 0.127 mm/year, which means there was a deteriorate in corrosion resistance.

#### 1.-6. (canceled)

7. A method of manufacturing a high-strength seamless stainless steel tube for oil country tubular goods having a wall thickness of more than 25.4 mm, comprising:

heating a steel material;

hot rolling including piercing rolling the steel material into a seamless steel tube; and

cooling the seamless steel tube 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,

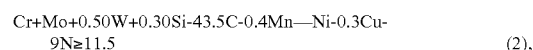
S: 0.005% or less, Cr: 15.5% or more and 18.0% or less,

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 expressions (1) and (2) 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:



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

8. The method according to claim 7, 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.

9. The method according to claim 7, wherein the chemical composition further contains, by mass %, Ca: 0.01% or less.

10. 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,

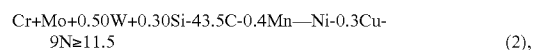
S: 0.005% or less, Cr: 15.5% or more and 18.0% or less,

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 expressions (1) and (2) 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 a number of ferrite-martensite grain boundaries per unit length of a line segment drawn in a wall thickness direction, is 120

or more in a central portion in the wall thickness direction, and having excellent low-temperature toughness and excellent corrosion resistance:



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

**11.** The high-strength seamless stainless steel tube according to claim **10**, 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.

**12.** The high-strength seamless stainless steel tube according to claim **10**, wherein the chemical composition further contains, by mass %, Ca: 0.01% or less.

**13.** The method according to claim **8**, wherein the chemical composition further contains, by mass %, Ca: 0.01% or less.

**14.** The high-strength seamless stainless steel tube according to claim **11**, wherein the chemical composition further contains, by mass %, Ca: 0.01% or less.

\* \* \* \* \*