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(54) **METHOD FOR PRODUCING HIGH-STRENGTH SEAMLESS CR-NI ALLOY PIPE**

(57) A method for producing a high-strength Cr-Ni alloy seamless pipe, excellent in hot workability and stress corrosion cracking resistance, without causing the lamination during piercing-rolling, comprising:
preparing an alloy billet that has a chemical composition comprising, by mass%, of C: 0.05% or less, Si: 1.0% or less, Mn: less than 3.0%, P: 0.005% or less, S: 0.005% or less, Cu: 0.01 to 4.0%, Ni: 25% or more and less than 35%, Cr: 20 to 30%, Mo: 0.01% or more and less than 4.0%, N: 0.10 to 0.30%, Al: 0.03 to 0.30%, O (oxygen): 0.01% or less, REM (rare earth metal): 0.01 to 0.20%, and the balance being Fe and impurities, and satisfying the following formula (1);
hot working to make a seamless material pipe on the basis of a cross roll piercing process; subjecting a solution treatment; and
cold working.

$$N \times P/REM \leq 0.10 \quad \dots\dots\dots \text{formula (1)}$$

wherein P, N and REM in formula (1) represent the contents (mass%) of P, N and REM, respectively.
The Cr-Ni alloy may further contain one or more of W, Ti, Nb, Zr, V, Ca and Mg.

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Description

[Technical Field]

5 **[0001]** The present invention relates to a method for producing a high-strength Cr-Ni alloy seamless pipe excellent in hot workability and stress corrosion cracking resistance.

[Background Art]

10 **[0002]** Recently, with the increase of the price of crude oil, oil wells and natural gas wells in deep and harsh corrosive environments have been developed. In parallel with the mining of petroleum and natural gas in such harsh environments, the oil well pipes used for such mining have been required to have high strength, excellent corrosion resistance and excellent stress corrosion cracking resistance.

15 **[0003]** Due to the recent enhanced needs for petroleum and natural gas, the oil wells and gas wells for mining petroleum and natural gas tend to be increased in depth. With the increase of the depth of the wells, the materials used for such wells have been required to maintain the corrosion resistance against carbon dioxide gas, hydrogen sulfide and chloride ion, and at the same time to have further higher strength.

20 **[0004]** Examples of the material exhibiting excellent corrosion resistance in corrosive environments include the Cr-Ni alloys disclosed in Patent Document 1, Patent Document 2 and Patent Document 3, disclosing that it is effective to increase the content of N for the purpose of increasing the strength of the Cr-Ni alloy. However, the alloy reinforced by such a method has a problem that the deformation resistance thereof is high and the hot workability thereof is poor.

[0005] Currently, such seamless pipes being high in strength and poor in hot workability as described above are generally produced by the hot extrusion pipe-making process, but are low in productivity.

25 **[0006]** On the contrary, as the method capable of efficiently producing seamless pipes with high productivity, the cross roll piercing process (also referred to as the Mannesmann pipe making process) may be quoted. In this method, by using a piercing mill (cross roll piercing machine), the cross roll piercing (hereinafter, simply referred to as "piercing-rolling") is applied to a stock billet to produce a hollow material pipe (hereinafter, simply referred to as "material pipe"), the resulting material pipe is elongated by performing rolling with a rolling machine such as a plug mill or a mandrel mill, and then finally finished in shape with a sizer or stretch reducer. However, such a seamless pipe that is high in strength and poor in hot workability tends to cause the lamination due to the grain boundary melting, when produced by the cross roll piercing process.

30 **[0007]** The grain boundary melting phenomenon is caused by the melting of the grain boundary due to the processing-incurred heat. The occurrence of the grain boundary melting steeply deteriorates the ductility of the material, and hence tends to cause the lamination due to the grain boundary melting. The cross roll piercing process is higher in working ratio than the hot extrusion pipe-making process, and hence is provided with a larger processing-incurred heat, accordingly exhibiting the problem that the lamination tends to be caused due to the grain boundary melting.

35 **[0008]** Next, Patent Document 4 discloses a technique for preventing the grain boundary melting cracking by heating a material pipe to a temperature equal to or lower than a value determined by a formula involving the circumferential velocity of the roll in the piercing-rolling of a Cr-Ni alloy and the pipe dimension. However, no investigation has been performed for the improvement of the grain boundary melting cracking resistance from the viewpoint of the alloy composition, and moreover, the corrosion resistance improvement that offers a more important issue in high-strength materials has not been considered.

40 **[0009]** Patent Document 5 discloses a technique for preventing the grain boundary melting cracking that exhibits a problem in relation to austenite stainless steel, by reducing the content of P and the content of S according to the dimension of the material pipe to be subjected to piercing-rolling. However, the disclosed technique is different from a technique intended for a higher-strength Cr-Ni alloy capable of being used in an environment requiring a high corrosion resistance.

45 **[0010]** Patent Document 6 discloses an Fe-Ni alloy seamless pipe excellent in mechanical properties and corrosion resistance in a sour gas environment wherein, in the seamless pipe, the lamination and the seam flaw are prevented by performing piercing-rolling by using a material pipe having the content of P and the content of S specified to fall within specific ranges. However, no sufficient investigation has been performed for the purpose of obtaining a higher-strength Cr-Ni alloy seamless pipe having an excellent hot workability and at the same time having an excellent stress corrosion cracking resistance.

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[Citation List]

[Patent Documents]

5 **[0011]**

[Patent Document 1] JP57-203735A
 [Patent Document 2] JP57-207149A
 [Patent Document 3] JP58-210155A
 10 [Patent Document 4] WO 2008/081866
 [Patent Document 5] WO 2004/112977
 [Patent Document 6] WO 2006/003953

[Summary of Invention]

15

[Technical Problem]

20 **[0012]** An objective of the present invention is to provide a method for producing a Cr-Ni alloy seamless pipe capable of preventing the deterioration of the hot workability and the deterioration of the stress corrosion cracking resistance caused by the presence of the high strength, and further capable of performing the pipe-making without causing the lamination during piercing-rolling.

[Solution to Problem]

25 **[0013]** For the purpose of solving the above-described problems, first the present inventors tried to prepare a higher strength material than conventional materials by increasing the content of N. However, a simple increase of the content of N deteriorates the hot workability and the stress corrosion cracking resistance to impede the production of oil well seamless pipes. Accordingly, as a technique to prevent the deterioration of the hot workability and the deterioration of the stress corrosion cracking resistance caused by the increase of the content of N, the present inventors have focused
 30 attention on the REM (rare earth metal). The REM is known to be able to improve the hot workability by immobilizing the elements such as O, S and P in the alloy. However, no attention has been focused on the effect of the REM on the stress corrosion cracking resistance.

[0014] The present inventors prepared high N alloys having various chemical compositions by melting, and evaluated the performances of the resulting alloys. Consequently, the present inventors have found that the inclusion of the REM improves the stress corrosion cracking resistance. The reason for the improvement of the stress corrosion cracking resistance by the REM is probably ascribable to the immobilization, by the REM, of P adversely affecting the stress corrosion cracking resistance.

35 **[0015]** However, it has been revealed that the inclusion of Ca, Mg or Si, having hitherto been said to be effective for the hot workability, in the REM-containing high N alloy conversely deteriorates the hot workability. Accordingly, the present inventors further made a diligent study and have found that the inclusion of Al enables to obtain a satisfactory hot workability even in the REM-containing high N alloy. Thus, it has been found that for the purpose of obtaining a satisfactory hot workability in the REM-containing high N alloy, it is essential to include Al along with the REM.

[0016] The Cr-Ni alloy having a high content of N for increasing the strength is high in deformation resistance, and hence tends to cause the grain boundary melting due to the processing-incurred heat in the piercing-rolling which is high in working ratio. The occurrence of the grain boundary melting deteriorates the ductility of the material, leading to a problem that the lamination of the material pipe is caused during piercing-rolling.

[0017] Accordingly, the present inventors prepared, by melting, Cr-Ni alloys high in the content of N, having various chemical compositions, and examined the pipe workability during piercing-rolling.

45 **[0018]** Consequently, it has been found that the reduction of the content of P results in a significant effect to increase the grain boundary melting temperature which makes it difficult to cause the grain boundary melting, and hence pipe-making can be performed without causing the lamination during piercing-rolling. It has also been found that the reduction of the content of Si and the content of Mn at the same time with the reduction of the content of P results in an effect to further increase the grain boundary melting temperature, which makes it further difficult to cause the grain boundary melting.

50 **[0019]** The present inventors further made a continuous study on the basis of such new findings as described above, and consequently, obtained the following findings (a) to (g).

[0020]

(a) In the Cr-Ni alloy material, for the purpose of ensuring the strength, the content of N is required to be set at as high as 0.10 to 0.30%, and for the purpose of ensuring the hot workability, the content of A1 is required to be set at 0.03 to 0.30%.

[0021]

(b) However, when the content of N in the Cr-Ni alloy material is set as high as 0.10 to 0.30%, the hot workability and the stress corrosion cracking resistance are deteriorated.

[0022]

(c) In this connection, when the REM is included in the alloy to fix P as P-compounds, not only the hot workability but the stress corrosion cracking resistance can be improved.

[0023]

(d) Accordingly, the content of REM can be determined from the viewpoint that the content of REM is the content necessary for immobilizing P as P-compounds. In other words, the ratio of the content of P to the content of REM [P/REM] is important.

[0024]

(e) The smaller the [P/REM] is, the more effectively the adverse effect due to P on the hot workability is suppressed. Accordingly, even in the case where the content of N is fairly high, when the [P/REM] is set to be small, the deterioration of the hot workability can be suppressed.

[0025]

(f) Consequently, it has been found that Cr-Ni alloy materials satisfactory in stress corrosion cracking resistance are obtained by specifying the relation between the content of N and the content of P and the content of REM so as to fall within the range satisfying the following formula (1):

[0026]

$$N \times P/REM \leq 0.10 \quad \dots\dots\dots \text{formula (1)}$$

wherein P, N and REM in formula (1) represent the contents (mass%) of P, N and REM, respectively.

[0027]

(g) The reduction of the content of P leads to a significant effect to increase the grain boundary melting temperature. By decreasing the content of P to be 0.005% or less, even the piercing-rolling using a Cr-Ni alloy having a high content of N and a high deformation resistance can perform pipe-making without causing the lamination during piercing-rolling. The additional reduction of the content of Si and the content of Mn result in an effect to further increase the grain boundary melting temperature, which makes it further difficult to cause the grain boundary melting. The content of Si is preferably set at 0.3% or less. The content of Mn is set preferably at 0.7% or less and more preferably at 0.6% or less. Although the reduction of the content of either of Si and Mn is effective, the reduction of both of contents of Si and Mn is more preferable.

[0028] The present invention has been perfected on the basis of the above-described findings, and the gist of the present invention is as described in the following items (1) to (6) associated with the method for producing a Cr-Ni alloy seamless pipe. The following items (1) to (6) are referred to as the inventions (1) to (6), respectively. The inventions (1) to (6) may be collectively referred to as the present invention.

[0029]

(1) A method for producing a high-strength Cr-Ni alloy seamless pipe, comprising: preparing an alloy billet that has a chemical composition comprising, by mass%, of C: 0.05% or less, Si: 1.0% or less, Mn: less than 3.0%, P: 0.005%

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or less, S: 0.005% or less, Cu: 0.01 to 4.0%, Ni: 25% or more and less than 35%, Cr: 20 to 30%, Mo: 0.01% or more and less than 4.0%, N: 0.10 to 0.30%, Al: 0.03 to 0.30%, O (oxygen): 0.01% or less, REM (rare earth metal): 0.01 to 0.20%, and the balance being Fe and impurities, and satisfying the following formula (1);
hot working to make a seamless material pipe on the basis of a cross roll piercing process; subjecting a solution
treatment; and
cold working.

[0030]

$$N \times P/REM \leq 0.10 \quad \dots\dots\dots \text{formula (1)}$$

wherein P, N and REM in formula (1) represent the contents (mass%) of P, N and REM, respectively.

[0031]

(2) The method for producing a high-strength Cr-Ni alloy seamless pipe according to the item (1) above, wherein the billet has a chemical composition that further contains, by mass%, Si: 0.3% or less and/or Mn: 0.7% or less.

[0032]

(3) The method for producing a high-strength Cr-Ni alloy seamless pipe according to the item (1) or (2) above, wherein the billet has a chemical composition that further contains, by mass%, W: less than 8.0% in place of part of Fe.

[0033]

(4) The method for producing a high-strength Cr-Ni alloy seamless pipe according to any one of the items (1) to (3) above, wherein the billet has a chemical composition that further contains, by mass%, one or more of Ti, Nb, Zr and V in a total content of 0.5% or less in place of part of Fe.

[0034]

(5) The method for producing a high-strength Cr-Ni alloy seamless pipe according to any one of the items (1) to (4) above, wherein the billet has a chemical composition that further contains, by mass%, either of both of Ca and Mg in a total content of 0.01% or less in place of part of Fe.

[0035]

(6) The method for producing a high-strength Cr-Ni alloy seamless pipe according to any one of the items (1) to (5) above, wherein the yield strength after cold working is 900 MPa or more in terms of the 0.2% yield stress.

[Advantageous Effects of Invention]

[0036] According to the present invention, it is possible to produce a high-strength Cr-Ni alloy seamless pipe, excellent in hot workability and stress corrosion cracking resistance, without causing the lamination during piercing-rolling, although the seamless pipe has a high strength due to a high content of N of the Cr-Ni alloy.

[Description of Embodiments]

[0037] Next, description is made on the reasons for limiting the chemical composition of the Cr-Ni alloy according to the present invention. Here, it is to be noted that "%" in each of the contents of the individual elements represents "mass%."

C: 0.05% or less

[0038] C is an impurity contained in the alloy; when the content of C exceeds 0.05%, the stress corrosion cracking accompanied by the grain boundary fracture due to the precipitation of an $M_{23}C_6$ type carbide (M: element such as Cr, Mo or Fe) tends to occur, and accordingly, the content of C is set at 0.05% or less. The content of C is preferably 0.03% or less.

Si: 1.0% or less

[0039] In the present invention, Si is an element to decrease the grain boundary melting temperature and to cause the lamination during piercing-rolling. Even with a reduced content of P, when the content of Si exceeds 1.0%, the lamination occurs during piercing-rolling. Accordingly, the content of Si is set at 1.0% or less. For the purpose of reducing the high deformation resistance during piercing-rolling, it is preferable to perform the piercing at further higher temperatures. In this case, for the purpose of preventing the lamination, it is preferable to further increase the grain boundary melting temperature, and the content of Si is preferably set at 0.3% or less and more preferably at 0.2% or less. The smaller content of Si is the more preferable, and the lower limit of the content of Si is not particularly specified. However, when Si is contained for deoxidation, Si is preferably contained in a content of 0.01% or more.

Mn: less than 3.0%

[0040] In the present invention, Mn is an element to decrease the grain boundary melting temperature and to cause the lamination during piercing-rolling. Even with a reduced content of P, when the content of Mn is 3.0% or more, the lamination occurs during piercing-rolling. Accordingly, the content of Mn is set at less than 3.0%, and is preferably less than 1.0%. For the purpose of reducing the high deformation resistance during piercing-rolling, it is preferable to perform the piercing at further higher temperatures. In this case, for the purpose of preventing the lamination, it is preferable to further increase the grain boundary melting temperature, and the content of Mn is more preferably set at 0.7% or less and furthermore preferably at 0.6% or less. The content of Mn is still furthermore preferably 0.3% or less. The smaller content of Mn is the more preferable, wherein the lower limit of the content of Mn is not particularly specified. However, when Mn is contained for deoxidation, the content of Mn is preferably 0.01% or more.

P: 0.005% or less

[0041] In the present invention, P is an important element. P is an impurity contained in the alloy; when piercing-rolling is performed, a high content of P tends to cause the lamination. Accordingly, the content of P is set at 0.005% or less and is preferably 0.003% or less. Additionally, as described below, the content of P is required to satisfy formula (1), in relation to the content of N and the content of REM.

S: 0.005% or less

[0042] Although S does not affect the lamination, S is an impurity contained in the alloy, and remarkably deteriorates the hot workability at low temperatures. Accordingly, from the viewpoint of preventing the deterioration of the hot workability, the allowable content of S is required to be 0.005% or less, and the smaller content of S is the more preferable. The content of S is preferably 0.002% or less and more preferably 0.001% or less.

Cu: 0.01 to 4.0%

[0043] Cu is effective in stabilizing the passive film formed on the surface of the alloy, and is necessary for improving the pitting resistance and the general corrosion resistance. When the content of Cu is less than 0.01%, Cu is not effective, and when the content of Cu exceeds 4.0%, the hot workability is deteriorated. Accordingly, the content of Cu is set at 0.01 to 4.0%. The content of Cu is preferably 0.1 to 2.0% and more preferably 0.6 to 1.4%.

Ni: 25% or more and less than 35%

[0044] Ni is made to be contained as an austenite stabilizing element. From the viewpoint of the corrosion resistance, the content of Ni is required to be 25% or more. The content of Ni of 35% or more leads to the increase of the cost. Accordingly, the content of Ni is set at 25% or more and less than 35%. The content of Ni is preferably 28% or more and less than 33%

Cr: 20 to 30%

[0045] Cr is a component to remarkably improve the stress corrosion cracking resistance. When the content of Cr is less than 20%, the effect of Cr is not sufficient, and when the content of Cr exceeds 30%, nitrides such as CrN and Cr₂N and the M₂₃C₆ type carbides adversely affecting the stress corrosion cracking accompanied by the grain boundary fracture tend to occur. Accordingly, the content of Cr is set at 20 to 30%. The content of Cr is preferably 23 to 28%.

Mo: 0.01% or more and less than 4.0%

[0046] Mo is effective, like Cu, in stabilizing the passive film formed on the surface of the alloy, and is effective in improving the stress corrosion cracking resistance. When the content of Mo is less than 0.01%, Mo is not effective, and when the content of Mo is 4.0% or more, the hot workability and the economic efficiency are deteriorated. Accordingly, the content of Mo is set at 0.01% or more and less than 4.0%. The content of Mo is preferably 0.1% to 3.5%.

N: 0.10 to 0.30%

[0047] N is effective to increase the strength of the alloy. When the content of N is less than 0.10%, the intended high strength cannot be ensured, and when the content of N exceeds 0.30%, the hot workability and the stress corrosion cracking resistance are deteriorated. Accordingly, the content of N is set at 0.10 to 0.30%. A preferable range of the content of N is 0.16 to 0.25%. Additionally, as described below, the content of N is required to satisfy formula (1), in relation to the content of P and the content of REM.

Al: 0.03 to 0.30%

[0048] Al binds O (oxygen) in the alloy to improve the hot workability, and is also effective in preventing the oxidation of REM. When REM is contained but Al is not contained, inclusions are produced in large amounts which significantly deteriorate the hot workability of the alloy. Accordingly, when REM is contained, it is essential for Al to be contained together. When the content of Al is less than 0.03%, the effect of Al is not sufficient. When the content of Al exceeds 0.30%, the hot workability is deteriorated. Accordingly, the content of Al is set at 0.03 to 0.30%. The content of Al is preferably 0.05 to 0.30% and more preferably more than 0.10% and 0.20% or less.

O (oxygen): 0.01% or less

[0049] O (oxygen) is an impurity contained in the alloy, and remarkably deteriorates the hot workability. Accordingly, the content of O (oxygen) is set at 0.01% or less. The content of O (oxygen) is preferably 0.005% or less.

REM: 0.01 to 0.20%

[0050] REM (rare earth metal) is effective in improving the hot workability and the stress corrosion cracking resistance, and hence is required to be contained. REM tends to be oxidized, and hence it is essential to contain REM along with Al. When the total content of REM is less than 0.01%, the effect of REM is not sufficient. When the total content of REM exceeds 0.20%, no more improvement effect is found in the hot workability and the stress corrosion cracking resistance, and even the deterioration phenomena of these properties are found. Accordingly, the content of REM is set at 0.01 to 0.20%. The content of REM is preferably 0.02 to 0.10%.

[0051] Here, it is to be noted that REM is a generic name for the 17 elements which include 15 lanthanoid elements and Y and Sc, and one or more of these elements can be contained. The content of REM means the sum of the contents of these elements. The method for containing REM may be such that one or more of these elements are added or industrially added in the form of a mish metal.

[0052] Additionally, the content of REM is required to satisfy the following formula (1) in relation to the content of N and the content of P:

[0053]

$$N \times P/REM \leq 0.10 \quad \dots \quad \text{formula (1)}$$

wherein P, N and REM in formula (1) represent the contents (mass%) of P, N and REM, respectively.

[0054] When the content of N is 0.10 to 0.30%, and the relation among the content of N, the content of P and the content of REM satisfies the above-presented formula (1), the strength is high and additionally the stress corrosion cracking resistance is satisfactory. When a better stress corrosion cracking resistance is demanded, it is more preferable to satisfy the relation $N \times P/REM \leq 0.05$.

[0055] The Cr-Ni alloy according to the present invention may further contain, in addition to the above-described alloying elements, one or more elements selected from at least one group of the following first group to third group.

[0056]

First group: W: less than 8.0%

Second group: Ti, Nb, V, Zr: 0.5% or less

Third group: Ca, Mg: 0.01% or less

5 Hereinafter, these optional elements are described in detail.

First group: W: less than 8.0%.

10 **[0057]** W is an optionally contained element. W has an effect to improve the stress corrosion cracking resistance. Accordingly, when it is intended to improve the stress corrosion cracking resistance, W can be contained if necessary. However, when the content of W is 8.0% or more, the hot workability and the economic efficiency are deteriorated, and hence, when W is contained, the upper limit of the content of W is set at 8.0%. For the purpose of certainly developing the improvement effect of the stress corrosion cracking resistance, it is preferable to contain W in a content of 0.01% or more. The content of W is more preferably 0.1 to 7.0%.

15 **[0058]** Second group: one or more selected from Ti: 0.5% or less, Nb: 0.5% or less, V: 0.5% or less and Zr: 0.5% or less, with the total content of one or more elements of 0.5% or less.

20 Ti, Nb, V and Zr are optionally contained elements. These elements have an effect to make grains fine and to improve the ductility. Accordingly, when an even better ductility is demanded, one or more of these elements can be contained, if necessary. However, when the total content of one or more of these elements exceed 0.5%, inclusions are produced in large amounts to cause the ductility deterioration phenomenon, and hence, when one or more of these elements are contained, the upper limit of the content of such elements is set at a total content of such elements of 0.5%. For the purpose of certainly developing the improvement effect of the ductility, it is preferable to contain such elements in a total content of 0.005% or more. The content of such elements is more preferably 0.01 to 0.5% and furthermore preferably 0.05 to 0.3%.

25 Third group: either or both of Ca: 0.01% or less and Mg: 0.01% or less.

[0059] Ca and Mg are optionally contained elements. These elements have an effect to improve the hot workability, and accordingly either or both of these elements can be contained if necessary.

30 **[0060]** However, when either or both of these elements are contained in a content exceeding 0.01%, coarse inclusions are produced to cause the deterioration phenomenon of the hot workability. Accordingly, when either or both of these elements are contained, the upper limit of the total content is set at 0.01%. For the purpose of certainly developing the improvement effect of the hot workability, it is preferable to contain such elements in a total content of 0.0003% or more. The total content of such elements is more preferably 0.0003 to 0.01% and furthermore preferably 0.0005 to 0.005%.

35 **[0061]** The Cr-Ni alloy seamless pipe according to the present invention contains the above-described essential elements or further the above-described optional elements, and the balance is Fe and impurities.

[0062] The "impurities" as referred to herein mean the substances that contaminate the materials when the Cr-Ni alloys are industrially produced, due to the raw materials such as ores and scraps, and due to various other factors in the production process, and are allowed to contaminate within the ranges not adversely affecting the present invention.

40 **[0063]** For the melting of the Cr-Ni alloy of the present invention, there can be used an electric furnace, an AOD furnace, a VOD furnace or the like. When the molten alloy obtained by melting is cast into ingots, the ingots can be converted by subsequent forging into slabs, blooms and billets. Alternatively, the molten alloy can be converted by a continuous casting method into slabs, blooms and billets.

45 **[0064]** In the present invention, a seamless material pipe is made by hot working on the basis of a cross roll piercing pipe-making process. The cross roll piercing pipe-making process is also referred to as the Mannesmann pipe making process. This is a process in which the billet as the stock is subjected to cross roll piercing by using a piercing mill (cross roll piercing machine) to produce a hollow material pipe, the material pipe is rolled to be elongated with a rolling machine such as a mandrel mill or a plug mill, and finally the resulting pipe is finished in shape by using a sizer or a stretch reducer. The cross roll piercing includes the cross roll piercing with a toe angle.

50 **[0065]** The yield strength of a Cr-Ni alloy seamless pipe suitable for use in deep oil wells and deep gas wells is 900 MPa or more in terms of the 0.2% yield stress. The concerned yield strength is more preferably 964 MPa or more. A Cr-Ni alloy seamless pipe having a yield strength of 900 MPa or more is produced by the production process in which the seamless material pipe for cold working, made into a pipe by the above-described cross roll piercing process, is subjected to a solution treatment and further subjected to a cold working.

55 **[0066]** For the purpose of obtaining a high strength Cr-Ni alloy seamless pipe having the above-described yield strength, the seamless material pipe for cold working subjected to hot working with the cross roll piercing process is subjected, after the solution heat treatment to a cold working based on the cold rolling such as cold drawing or pilger rolling. The cold working may be performed once or a plurality of times, or alternatively, if necessary, after heat treatment,

the cold working may be performed once or a plurality of times.

[0067] The high-strength Cr-Ni alloy pipe obtained by the cold working after the solution treatment, having a yield strength of 900 MPa or more, is suitable for the oil well seamless pipe for use in deep oil wells or deep gas wells. In the case where the final cold working after the solution heat treatment is performed by cold drawing, the cold working ratio is preferably set at 10 to 40% in terms of the reduction of area. When the cold working ratio is less than 10%, no intended high strength may be obtained. On the other hand, when the cold working ratio exceeds 40%, the strength is made high, but the ductility or the toughness may be deteriorated. The cold working ratio is more preferably set at 20 to 35%. In the case where the cold working is performed by a cold rolling such as a pilger mill rolling, the cold working is preferably performed with the cold working ratio of 30 to 80% in terms of the reduction of area. When the cold working ratio is less than 30%, no intended high strength may be obtained. On the other hand, when the cold working ratio exceeds 80%, the strength is made high but the ductility or the toughness may be deteriorated.

[Example 1]

[0068] Table 1 shows the chemical compositions (mass%) of Invention Examples (Test Nos. 1 to 23) and the Comparatives (Test Nos. A to J). The alloys according to Invention Examples were melted and cast into 30 kg ingots by using a vacuum induction melting furnace. The resulting ingots were subjected to hot forging to be molded into billets of 100 mm in outer diameter. The billets heated at 1240°C and 1260°C were subjected to piercing-rolling with a small sized cross roll piercing apparatus to be produced into pipes of 116 mm in outer diameter and 20 mm in wall thickness.

[0069] [Table 1]

Test No.	Chemical composition											(mass%, the balance being Fe and impurities)					
	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	W	N	Al	Ca	O	REM	others	
1	0.011	0.27	0.48	0.002	0.0004	0.80	32.2	25.1	2.94	-	0.190	0.12	0.0019	0.003	0.026 Nd		
2	0.011	0.21	0.50	0.003	0.0008	0.78	31.9	25.0	3.01	-	0.192	0.12	0.0020	0.003	0.019 Nd		
3	0.012	0.23	0.41	0.002	0.0004	0.82	31.8	25.0	2.90	-	0.200	0.12	0.0021	0.003	0.020 Nd	0.02Nb	
4	0.010	0.28	0.50	0.004	0.0008	2.10	31.9	25.1	3.05	-	0.205	0.10	0.0019	0.002	0.028 Nd	0.01Zr	
5	0.011	0.27	0.45	0.004	0.0008	3.21	31.8	25.0	2.93	-	0.197	0.12	0.0018	0.003	0.013 Nd		
6	0.011	0.20	0.43	0.004	0.0008	0.18	32.1	24.9	3.07	-	0.195	0.11	0.0018	0.003	0.034 Nd	0.03V	
7	0.010	0.28	0.44	0.003	0.0003	0.78	27.3	25.0	3.09	-	0.198	0.13	0.0019	0.001	0.031 Nd		
8	0.010	0.24	0.44	0.002	0.0008	0.80	34.1	21.9	2.93	-	0.198	0.10	-	0.003	0.021 Nd		
9	0.010	0.28	0.41	0.003	0.0007	0.80	32.0	21.4	3.04	-	0.203	0.10	0.0021	0.003	0.023 Nd	0.02Ti	
10	0.011	0.25	0.42	0.003	0.0008	0.80	31.9	28.3	2.95	-	0.203	0.12	0.0021	0.002	0.028 Nd		
11	0.011	0.25	0.42	0.002	0.0007	0.78	32.1	25.1	0.53	-	0.200	0.13	0.0019	0.001	0.035 Nd		
12	0.010	0.29	0.43	0.002	0.0005	0.81	32.2	24.9	3.01	-	0.124	0.11	0.0022	0.004	0.011 Nd		
13	0.011	0.22	0.44	0.003	0.0003	0.80	32.0	24.8	2.90	-	0.261	0.13	0.0017	0.003	0.033 Nd		
14	0.011	0.21	0.48	0.003	0.0007	0.79	32.1	24.9	2.93	-	0.201	0.12	0.0019	0.003	0.037 Nd + 0.016 Ce		
15	0.012	0.22	0.46	0.003	0.0008	0.82	32.1	28.6	3.02	-	0.193	0.11	0.0019	0.003	0.121 Nd		
16	0.012	0.30	0.50	0.003	0.0005	0.81	32.0	24.9	3.01	-	0.196	0.12	0.0022	0.003	0.011 Nd + 0.014 Ce	0.0025Mg	
17	0.012	0.22	0.46	0.003	0.0005	0.78	32.0	25.0	3.03	-	0.200	0.10	0.0020	0.003	0.037 La		
18	0.041	0.26	0.48	0.002	0.0004	0.79	31.9	24.8	2.93	-	0.205	0.12	0.0022	0.003	0.021 Nd		
19	0.010	0.29	0.40	0.003	0.0004	0.81	32.3	25.2	0.50	6.01	0.203	0.11	0.0022	0.002	0.032 Nd		
20	0.011	0.21	0.20	0.003	0.0006	0.81	31.9	25.0	3.09	-	0.203	0.11	0.0017	0.001	0.025 Nd		
21	0.010	0.50	0.82	0.003	0.0008	0.80	32.1	24.9	2.91	-	0.193	0.05	0.0019	0.003	0.029 Nd		
22	0.011	0.74	0.42	0.004	0.0004	0.81	32.2	24.8	2.99	-	0.203	0.11	0.0022	0.002	0.025 Nd		
23	0.012	0.80	0.14	0.004	0.0008	0.80	31.9	24.9	3.00	-	0.194	0.08	0.0021	0.001	0.026 Nd		
A	0.011	0.25	0.48	0.003	0.0004	0.79	32.2	25.0	2.91	-	0.081	0.10	0.0020	0.002	0.036 Nd		
B	0.011	0.71	1.60	0.008	0.0010	0.80	32.0	25.1	3.05	-	0.194	0.11	0.0022	0.002	0.032 Nd		
C	0.011	0.35	0.60	0.018	0.0012	0.80	32.0	24.8	3.05	-	0.196	0.11	0.0018	0.003	0.042 Nd		
D	0.010	0.25	4.31	0.004	0.0005	0.79	31.9	25.1	3.03	-	0.192	0.13	0.0017	0.002	0.026 Nd		
E	0.011	0.28	6.02	0.002	0.0003	0.81	31.8	25.1	2.98	-	0.193	0.11	0.0022	0.002	0.038 Nd		
F	0.011	1.64	0.58	0.003	0.0007	0.81	32.2	24.9	2.96	-	0.198	0.11	0.0022	0.003	0.010 Nd		
G	0.011	0.31	0.60	0.003	0.0006	0.81	32.1	25.2	3.02	-	0.203	0.12	0.0019	0.003	-		
H	0.011	0.26	0.61	0.005	0.0008	0.79	31.9	25.0	2.96	-	0.282	0.12	0.0023	0.003	0.013 Nd		
I	0.011	0.30	0.59	0.005	0.0008	0.80	31.8	25.2	2.90	-	0.287	0.11	0.0018	0.003	0.012 Nd		
J	0.011	0.28	0.62	0.004	0.0004	0.79	31.9	25.0	2.98	-	0.291	0.11	0.0021	0.003	0.010 Nd		

[0070] The seamless material pipes after piercing-rolling were cut perpendicularly to the longitudinal direction, at a position of 50 mm in the longitudinal direction from the rear end of the pipe, and it was observed whether the lamination of the material pipe was caused or not. As a result, the mark O shows that no lamination was caused, and the mark × shows that the lamination was caused.

[0071] Further, the seamless material pipes heated at 1240°C and subjected to piercing-rolling were then subjected to a solution treatment in which the material pipes were heated and maintained at 1050°C for 1 hour, and then water cooled. The material pipes were subjected to a cold drawing with a reduction of area of 30%, which are the seamless pipes according to Invention Examples and Comparatives. It is found that, in Invention Examples, omitting the subsequent hot elongation rolling process and hot shaping rolling process after piercing-rolling causes no adversely affection to the mechanical properties and the corrosion resistance. Accordingly, in a more simplified manner, the seamless material pipes that were subjected to piercing-rolling with a small size cross roll piercing apparatus and directly solution-treated and cold worked were to be used for evaluation.

[0072] Room-temperature tensile test specimens, 6 mm in diameter and 40 mm in length in the parallel portion, were cut out to the longitudinal direction from the seamless pipes after the cold working, and subjected to a tensile test at room temperature in the air to measure the 0.2% yield stress. Further, for the purpose of evaluating the stress corrosion

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cracking resistance, test specimens, 3.81 mm in diameter and 25.4 mm in length in the parallel portion, were cut out to the longitudinal direction from the same pipes after the cold working, and the low strain rate tensile test was performed. In the low strain rate tensile test, in a corrosive environment of 25% NaCl + 0.5% CH₃COOH + 7 atm H₂S and 232°C, tensile rupture was made to occur at a strain rate of $4 \times 10^{-6} \text{ sec}^{-1}$, and the reduction of area of each of the ruptured test specimens was measured. At the same time, the same low strain rate tensile test was performed in an inert environment, the reduction of area of each of the ruptured test specimens was measured. The ratio of the reduction of area in the corrosive environment to the reduction of area in the inert environment was used as the index for the stress corrosion cracking resistance; when the ratio was 0.8 or more, the stress corrosion cracking resistance was determined to be satisfactory (O), and when the ratio was less than 0.8, the stress corrosion cracking resistance was determined to be poor (×). In Test Nos. B to F, the lamination was caused, and hence the measurements of the 0.2% yield stress and the stress corrosion cracking resistance were not conducted.

[0073] Table 2 shows the test results and the N × P/REM values.

[0074] [Table 2]

Table 2

	Test No.	Lamination (1240° C)	Lamination (1260° C)	0.2% yield stress (MPa)	Stress corrosion cracking resistance	N x P/REM
Invention Examples	1	○	○	1034	○	0.01
	2	○	○	1025	○	0.03
	3	○	○	1013	○	0.02
	4	○	○	1046	○	0.03
	5	○	○	1035	○	0.06
	6	○	○	1012	○	0.02
	7	○	○	1055	○	0.02
	8	○	○	1031	○	0.02
	9	○	○	1030	○	0.03
	10	○	○	1051	○	0.02
	11	○	○	1046	○	0.01
	12	○	○	904	○	0.02
	13	○	○	1121	○	0.02
	14	○	○	1032	○	0.01
	15	○	○	1022	○	0.00
	16	○	○	1038	○	0.02
	17	○	○	1021	○	0.01
	18	○	○	1030	○	0.02
	19	○	○	1023	○	0.02
	20	○	×	1030	○	0.02
	21	○	×	1029	○	0.02
	22	○	×	1038	○	0.03
	23	○	×	1008	○	0.03
Comparatives	A	○	○	872	○	0.01
	B	×	×	-	-	0.05
	C	×	×	-	-	0.08
	D	×	×	-	-	0.03
	E	×	×	-	-	0.01
	F	×	×	-	-	0.05
	G	○	○	1032	×	(no REM contained)
	H	○	○	1137	×	0.11
	I	○	○	1187	×	0.12
	J	○	○	1166	×	0.12

[0075] As shown in Table 2, in the cases of the seamless material pipes of Test Nos. 1 to 19 according to Invention Examples of the present invention, even when the billets heated to 1240°C and 1260°C were subjected to cross roll piercing, no lamination was caused in any one of the billets. The 0.2% yield stress was 900 MPa or more in any one of the pipes. Any one of the pipes satisfied the above-presented formula (1) was satisfactory in the stress corrosion cracking resistance.

[0076] In the cases of the seamless material pipes of Test Nos. 20 to 23 according to Invention Examples of the present invention, even when the billets heated to 1240°C were subjected to cross roll piercing, no lamination was caused in any one of the billets. However, in these cases, because the content of Si and the content of Mn were comparatively large, when the billets heated to 1260°C were subjected to cross roll piercing, the lamination was caused.

[0077] In Comparative A, neither the heating to 1240°C nor the heating to 1260°C resulted in causing the lamination, and the stress corrosion cracking resistance was satisfactory. In Comparative A, however, the content of N was outside

the range restricted by the present invention, and hence the 0.2% yield stress was low. In each of Comparatives B and C, P was contained excessively, and hence both of the heating to 1240°C and the heating to 1260°C resulted in causing the lamination. In each of Comparatives D and E, Mn was contained excessively, and hence both of the heating to 1240°C and the heating to 1260°C resulted in causing the lamination. In Comparative F, Si was contained excessively, and hence both of the heating to 1240°C and the heating to 1260°C resulted in causing the lamination. In Comparative G, REM was not contained, and hence the stress corrosion cracking resistance was poor. In each of Comparatives H to J, the chemical composition of the alloy was within the range specified by the present invention, but did not satisfy formula (1), and hence the stress corrosion cracking resistance was poor.

[Industrial Applicability]

[0078] According to the present invention, it is possible to produce a high-strength Cr-Ni alloy seamless pipe, excellent in hot workability and stress corrosion cracking resistance, without causing the lamination during piercing-rolling, although the seamless pipe has a high strength provided by a high content of N. The high-strength Cr-Ni alloy seamless pipe obtained by the present invention can be used for mining of petroleum and natural gas in deep and harsh corrosive environments, having hitherto been unmineable, and hence significantly contributes to stable supply of energy.

Claims

1. A method for producing a high-strength Cr-Ni alloy seamless pipe, comprising: preparing an alloy billet that has a chemical composition comprising, by mass%, of C: 0.05% or less, Si: 1.0% or less, Mn: less than 3.0%, P: 0.005% or less, S: 0.005% or less, Cu: 0.01 to 4.0%, Ni: 25% or more and less than 35%, Cr: 20 to 30%, Mo: 0.01% or more and less than 4.0%, N: 0.10 to 0.30%, Al: 0.03 to 0.30%, O (oxygen): 0.01% or less, REM (rare earth metal): 0.01 to 0.20%, and the balance being Fe and impurities, and satisfying the following formula (1); hot working to make a seamless material pipe on the basis of a cross roll piercing process; subjecting a solution treatment; and cold working.

$$N \times P/REM \leq 0.10 \quad \dots\dots\dots \text{formula (1)}$$

wherein P, N and REM in formula (1) represent the contents (mass%) of P, N and REM, respectively.

2. The method for producing a high-strength Cr-Ni alloy seamless pipe according to claim 1, wherein the billet has a chemical composition that further contains, by mass%, Si: 0.3% or less and/or Mn: 0.7% or less.
3. The method for producing a high-strength Cr-Ni alloy seamless pipe according to claim 1 or 2, wherein the billet has a chemical composition that further contains, by mass%, W: less than 8.0% in place of part of Fe.
4. The method for producing a high-strength Cr-Ni alloy seamless pipe according to any one of claims 1 to 3, wherein the billet has a chemical composition that further contains, by mass%, one or more of Ti, Nb, Zr and V in a total content of 0.5% or less in place of part of Fe.
5. The method for producing a high-strength Cr-Ni alloy seamless pipe according to any one of claims 1 to 4, wherein the billet has a chemical composition that further contains, by mass%, either of both of Ca and Mg in a total content of 0.01% or less in place of part of Fe.
6. The method for producing a high-strength Cr-Ni alloy seamless pipe according to any one of claims 1 to 5, wherein the yield strength after cold working is 900 MPa or more in terms of the 0.2% yield stress.

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER C21D8/10 (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) C21D8/00-8/10, C22C38/00-38/60		
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 1996-2010 Kokai Jitsuyo Shinan Koho 1971-2010 Toroku Jitsuyo Shinan Koho 1994-2010		
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 2006/003953 A1 (Sumitomo Metal Industries, Ltd.), 12 January 2006 (12.01.2006), & AU 2005258506 A1 & CN 1977060 A & EP 1777314 A1 & US 2007/0175547 A1	1-6
A	JP 2009-30153 A (Sumitomo Metal Industries, Ltd.), 12 February 2009 (12.02.2009), & WO 2009/004970 A1	1-6
P, A	JP 2009-84668 A (Sumitomo Metal Industries, Ltd.), 23 April 2009 (23.04.2009), & US 2009/0291017 A1 & WO 2009/044758 A1	1-6
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
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Date of the actual completion of the international search 16 June, 2010 (16.06.10)		Date of mailing of the international search report 29 June, 2010 (29.06.10)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
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REFERENCES CITED IN THE DESCRIPTION

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