(54) **RAW PIPE OF Fe-Ni ALLOY AND METHOD FOR PRODUCTION THEREOF**

ROHROHR AUS FE-NI-LEGIERUNG UND HERSTELLUNGSVERFAHREN DAFÜR

TUYAU BRUT EN ALLIAGE DE Fe-Ni ET SA MÉTHODE DE PRODUCTION

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(56) References cited:
EP-A- 1 498 508   WO-A-03/044239
GB-A- 2 105 368   JP-A- 4 110 419
JP-A- 11 302 801   JP-A- 11 302 801
JP-A- 63 274 743   JP-A- 2003 027 189
JP-A- 2004 003 000   JP-B2- 3 071 506
US-A- 5 858 129

EP 1 777 314 B9

Description

TECHNICAL FIELD

[0001] The present invention relates to Fe-Ni alloy pipe stocks, and Fe-Ni alloy seamless pipes which are manufactured using such pipe stocks. More specifically, the present invention relates to Fe-Ni alloy pipe stocks, being obtained by piercing and rolling by use of a Mannesmann piercing and rolling mill (hereinafter referred also to as "piercer"), which are excellent in corrosion resistance in an environment which is rich in corrosive substance such as carbon dioxide, hydrogen sulfide, S (sulfur) and chloride ion (hereinafter referred to as a "sour gas environment") in addition to excellent mechanical properties, such as strength and ductility, and suitable for pipe stocks for oil country tubular goods and line pipes, and further suitable for pipe stocks for various structural members of nuclear power plants and chemical industrial plants, and also to the manufacturing methods thereof, and Fe-Ni alloy seamless pipes which are manufactured using the above-mentioned pipe stocks.

BACKGROUND ART

[0002] While development of oil wells and gas wells is expanding on a global scale after the first oil shocks, increased demand for energy in developing countries increasingly forces deepening of oil wells and gas wells and the drilling of wells in a sour gas environment with further severe corrosiveness.

[0003] With such increased severity in the oil well and gas well environments, for example, various Ni base alloys, higher in strength than ever before and excellent in corrosion resistance, as shown in the Patent Documents 1 and 2, and further a super austenitic stainless steel as shown in the Patent Document 3, have been developed and practically used.

[0004] However, economic globalization, such as corporate marriage or reorganization which has rapidly progressed on a world scale through the termination of the cold war between the East and the West, the integration of the EU, or the like intensifies the price competition among companies. Consequently, in the development of oil wells and gas wells, higher efficiency and lower cost are in demand in addition to ensuring safety.

[0005] Increased productivity of oil or gas can be attained by using large diameter pipes. Moreover, the further use of strong material enables reduction in the wall thickness of the pipes, resulting in saving of material cost. Therefore, as a steel stock for pipes used in oil wells and gas wells, a material cost saving and having a higher strength than ever before is requested. The enlargement of the diameter of the pipes is also important.

[0006] On the other hand, in the development of oil wells and gas wells, reduced costs can be attained by using inexpensive material which has sufficient strength and corrosion resistance.

[0007] The Patent Document 4 thus discloses a "high Cr-high Ni alloy, excellent in stress corrosion cracking resistance", which is enhanced in economical property by reducing the Mo content in alloys which contain, by weight %, 20 to 35% of Cr and 25 to 50% of Ni.

[0008] If piercing and rolling by a piercer can be adapted, pipe stocks for large diameter pipes or sufficiently long pipes can be efficiently manufactured at a low cost on an industrial scale.

[0009] The Patent Document 5 therefor discloses a "method for piercing a seamless tube of hard-to-work material with piercer", which is intended to provide a manufacturing method of seamless pipes, capable of manufacturing a pipe stock for seamless pipes by a piercer without causing pipe inside surface defects resulting from overheating.

[0010] Further, the Non-Patent Document 1 discloses a technique capable of performing rolling, in the piercing and rolling of high Cr-high Ni alloys, without causing inside surface scabs or two-piece cracks by increasing the roll cross angle and the roll feed angle.

[0011] GB 2 105 368 discloses an alloy for making high strength deep well casting and tubing.

[0012] JP 04-110419 discloses a method for producing high Ni stainless steel plate.

Patent Document 1: US Patent No. 4168188,
Patent Document 2: US Patent No. 4245698,
Patent Document 3: International Patent Publication Pamphlet No. WO 03/044239.
Patent Document 4: Japanese Laid-Open Patent Publication No. 11-302801,
Patent Document 5: Japanese Laid-Open Patent Publication No. 2000-301212,
Non-Patent Document 1: Tomio YAMAKAWA and Chihiro HAYASHI: CAMP-ISIJ, Vol. 6 (1993), 364.

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0013] An alloy with Mo content of not more than 1.5% in the Patent Document 4 among the alloys proposed in the Patent Documents 1 to 4, that is to say, the alloy with Mo content of not more than 1.5% among the "high Cr-high Ni alloys, excellent in stress corrosion cracking resistance" containing 20 to 35% of Cr and 25 to 50% of Ni, which are proposed as materials for oil wells and gas wells, has high hot workability, and causes no flaws and cracks even if pierced and rolled by a piercer. Therefore, if this alloy is used as a steel stock, a pipe stock for an alloy pipe can be manufactured with high productivity. Consequently, this alloy can be used as a material for oil wells and gas wells due to its extremely excellent economical properties.

[0014] However, the corrosion resistance of this alloy is not necessarily satisfactory in an environment in which carbon dioxide partial pressure is raised to, for example, about 1013250 to 2026500 Pa (10 to 20 atm) because of the Mo content as low as not more than 1.5%, although it does have satisfactory corrosion resistance in an environment in which the hydrogen sulfide partial pressure of 101325 to 1013250 Pa (1 to 10 atm), a temperature of 150 to 250°C, and a carbon dioxide partial pressure of about 709275 Pa (7 atm).

[0015] On the other hand, the Ni base alloys and super austenitic stainless alloys simultaneously containing Mo and/or W in large quantities, such a value represented by the equation of Mo (%)+0.5W (%) exceeds 1.5% (hereinafter referred also to as "Mo equivalent value"), in addition to high contents of both Cr and Ni, which are proposed in the Patent Documents 1 to 3, are excellent in corrosion resistance in a severe sour gas environment but too low in hot workability, so that the piercing and rolling by a piercer thereof inevitably involved flaws or cracks in the past.

[0016] Similarly, among the high Cr-high Ni alloys containing 20 to 35% of Cr and 25 to 50% of Ni, which are proposed in the Patent Document 4, an alloy with a Mo content exceeding 1.5% (hereinafter also referred to "Mo equivalent value exceeding 1.5%) is excellent in corrosion resistance in a severe sour gas environment, but too low in hot workability, so that the piercing and rolling by a piercer thereof inevitably involved flaws or cracks in the past.

[0017] That is to say, in the manufacturing of pipe stocks of austenitic materials by piercing and rolling with a piercer, inside surface flaws or two-piece cracks resulting from fusion remarkably occurred even when using austenitic stainless steels such as SUS 316, SUS 321 and SUS 347 regulated by JIS as steel stocks. Accordingly, when an austenitic alloy simultaneously containing Mo and W in large quantities exceeding 1.5% in terms of Mo equivalent value, in addition to high contents of Cr and Ni, which is further harder to work than the above-mentioned austenitic stainless steels, is pierced and rolled with a piercer by the general method, the occurrence of flaws or cracks could not be avoided as described above.

[0018] Consequently, the said pipe stocks for high-strength, high-corrosion resistance seamless pipes for oil wells and gas wells of various high Cr-high Ni alloys, with Mo equivalent value exceeding 1.5%, which have extremely satisfactory corrosion resistance in the sour gas environment, have been ordinarily manufactured by a hot extrusion process such as the Ugine-Sejournet method.

[0019] However, the hot extrusion process is not suitable for a manufacturing of pipe stocks for large diameter pipes or sufficiently long pipes. The pipe stocks manufactured by the hot extrusion process, such as the Ugine-Sejournet method, consequently could not respond to industrial demands for increased productivity of oil or gas and also meet the low cost of manufacturing alloy pipes to be used in oil wells and gas wells.

[0020] The pipe stocks for large diameter pipes or sufficiently long pipes can be manufactured, for example, by hot forging using a transverse press. However, the alloys which have high contents of both Cr and Ni and simultaneously containing Mo and W in large quantities exceeding 1.5% in terms of Mo equivalent value, are hard-to-work materials with extremely low hot workability, and so, the forgeable temperatures thereof are limited to a narrow range. Therefore, the industrial mass production of the pipe stocks for large diameter pipes or sufficiently long pipes by hot forging using these alloys is also problematic because of the necessity of repetition of heating and forging and the resulting extremely poor productivity and yield.

[0021] Accordingly, for various alloys having high contents of both Cr and Ni, simultaneously containing Mo and W in large quantities exceeding 1.5% in terms of Mo equivalent value and having extremely satisfactory corrosion resistance in the sour gas environment, it is highly demanded to efficiently manufacture pipe stocks for the large diameter pipes or sufficiently long pipes by piercing and rolling with a piercer at a low cost on an industrial scale, similarly to the cases of carbon steels and low alloy steels, and further martensitic stainless steels such as so-called "13%-Cr steel".

[0022] However, the "hard-to-work materials", which are intended by the method for piercing with a piercer proposed by the Patent Document 5, are simply those lower in the deformation resistance than the stainless steels as described in paragraph [0004] thereof. Therefore, the above-mentioned high Cr-high Ni austenitic alloys simultaneously containing Mo and W in large quantities, exceeding 1.5% in terms of Mo equivalent value, with respect to Ni, Mo and W each of which is an element increasing the deformation resistance, particularly, the austenitic alloys, including not less than 20% Cr and not less than 30% Ni and further simultaneously containing Mo and W in large quantities, exceeding 1.5% in terms of Mo equivalent value, are not taken into account by the said method in the Patent Document 5. Further, the said

method for piercing with a piercer only comprises adjusting a billet heating temperature in association with a piercing rate by a piercer, thereby performing piercing and rolling while controlling the billet internal temperature to be lower than an overheat temperature.

[0023] The "overheat temperature" intended by the method for piercing with a piercer of the Patent Document 5 is 1260 to 1310°C. The "overheat temperature" means a temperature at which the material causes intergranular fusion. In order to apply the method for piercing with a piercer, as shown in Fig. 5 of the Patent Document 5, even to a material lower in deformation resistance than a stainless steel, it is necessary to control the billet heating temperature to 1180°C maximum, which is lower than that in the conventional rolling of a carbon steel, a low alloy steel and a martensitic stainless steel. Similarly, as shown in Fig. 5 of the same, the piercing rate is also 300 mm/sec maximum, and must be reduced to about a half or less of the conventional one even in the case of the highest 300 mm/sec. For example, manufacturing of a pipe stock of 8 m length requires about 27 seconds which is about twice the conventional one.

[0024] In the technique disclosed by the Patent Document 5, the billet heating temperature must be adjusted in association with the piercing rate by a piercer to prevent the billet inner part from being heated to the overheat temperature or higher during piercing and rolling. For example, as shown in the said Fig. 5, if the billet heating temperature is raised to about 1180°C, the piercing rate must be set to an extremely low condition of about 50 mm/sec, which cannot be endured through the industrial mass production. If the piercing rate is set to about 300 mm/sec, the manufacturing can be performed with efficiency at about half the conventional one as described above, but the billet heating temperature, as shown in the said Fig. 5, must be set to an extremely low temperature of about 1060°C. Therefore, the manufacturing of pipe stocks of austenitic alloys with high deformation resistance which include not less than 20% Cr and not less than 30% Ni and further simultaneously contains Mo and W in large quantities exceeding 1.5% in terms of Mo equivalent value, needs a piercing performance far more than that of a general piercer, and thus needs an extremely large power source for the piercer.

[0025] The technique disclosed in the Non-Patent Document 1 describes, concretely, that rolling can be performed without inside surface scabs or two-piece cracks by setting the roll cross angle to not less than 10° and the roll feed angle to not less than 14° in the piercing of a 25Cr-35Ni-3Mo alloy and a 30Cr-40Ni-3Mo alloy, and by setting the roll feed angle to not less than 16° with a roll cross angle of 10° or setting the roll feed angle to not less than 14° with a roll cross angle of 15° in the piercing of a 25Cr-5ONi-6Mo alloy.

[0026] However, a general piercer used in a seamless steel pipe manufacturing factory, which has been built for the purpose of piercing and rolling carbon steels and low alloy steels, and further martensitic stainless steels such as so-called "13%-Cr steel", has a roll cross angle of about 0 to 10° and a roll feed angle of about 7 to 14°.

[0027] Accordingly, the replacement of the piercer to having a large roll cross angle and roll feed angle as proposed in the Non-Patent Document 1 for the purpose of piercing and rolling of a high Cr-high Ni alloy necessitates a huge cost, and is not realistic.

[0028] Consequently, the piercing and rolling by a piercer of pipe stocks for large diameter and sufficiently long pipes of austenitic Fe-Ni alloys including not less than 20% Cr and not less than 30% Ni and further simultaneously containing Mo and W in large quantities, exceeding 1.5% in terms of Mo equivalent value, has never been performed on an industrial mass production scale.

[0029] In other words, there are no pipe stocks obtained by the piercing and rolling the austenitic Fe-Ni alloys including not less than 20% Cr and not less than 30% Ni and further simultaneously containing Mo and W in large quantities exceeding 1.5% in terms of Mo equivalent value on an industrial mass production scale.

[0030] In order to solve the above-mentioned problems, the present inventors made detailed examinations for the occurrence state of inside surface flaws in the piercing and rolling by a piercer of hard-to-work Fe-Ni alloys of high Cr-high Ni series, particularly, austenitic Fe-Ni alloys including not less than 20% Cr and not less than 30% Ni and further simultaneously containing Mo and W in large quantities exceeding 1.5% in terms of Mo equivalent value, from the point of microstructure change of the materials. As the result, the following findings (a) to (d) where obtained.

[0031]

(a) Inside surface fracture flaws caused in the Fe-Ni alloys of high Cr-high Ni series can be roughly classified into three groups as follows:

(1) Two-piece cracks resulting from the intergranular fusion involved by work heat generation on the high temperature side;
(2) Inside surface scabs resulting from high deformation resistance; and,
(3) Inside surface cracks and scabs on both the inside and outside surface resulting from the sigma phase formation in a low temperature region caused by a drop in temperature.

(b) The two-piece cracks resulting from the intergranular fusion of the above-mentioned (1) is remarkable when solidification segregation of elements which comprise the material to be pierced and rolled, particularly, the solidi-

fication segregation of C, P and S, is present. The solidification segregation state of C, P and S which greatly depends on the composition balance of Fe, Ni, Cr, Mo and the like, namely, the state of the intergranular fusion can be evaluated by the value of T_{GBm} represented by the following equation (1) in the austenitic Fe-Ni alloys, including not less than 20% Cr and not less than 30% Ni, and further simultaneously containing Mo and W in large quantities exceeding 1.5% in terms of Mo equivalent value. When the value of T_{GBm} is not less than 1300 piercing and rolling property is enhanced, and so, the two-piece cracks can be suppressed in the piercing and rolling by a piercer:

$$T_{GBm} = 1440 - 6000P - 100S - 2000C \qquad ... (1).$$

(c) The deformation resistance in hot working of the material changes mainly depending on the contents of Ni, N, Mo and W, and a material with higher deformation resistance more likely causes the inside surface scabs of above-mentioned (2). The occurrence state of the said inside surface scabs can be evaluated by the value of P_{sr} represented by the following equation (2) in the austenitic Fe-Ni alloys, including not less than 20% Cr and not less than 30% Ni, and further simultaneously containing Mo and W in large quantities exceeding 1.5% in terms of Mo equivalent value. When the value of P_{sr} is not more than 120, the inside surface scabs can be suppressed in the piercing and rolling by a piercer:

$$P_{sr} = Ni + 10(Mo + 0.5W) + 100N \qquad ... (2).$$

(d) When a billet temperature falls, among the elements which comprise the material to be pierced and rolled, the composition balance of Ni, N, Cur, Mo and W mainly has great influence on the formation of the sigma phase. In the said austenitic Fe-Ni alloys including not less than 20% Cr and not less than 30% Ni, and further simultaneously containing Mo and W in large quantities, exceeding 1.5% in terms of Mo equivalent value, the inside surface cracks and the scabs on both the inside and outside surface resulting from the formation of the sigma phase of the above-mentioned (3) are remarkable when the sigma phase is formed at 1000°C. The said inside surface cracks and the said scabs on both the inside and outside surface can be evaluated by the value of P_σ represented by the following equation (3). When the value of P_σ is not less than 0, the said inside surface cracks and the said scabs on both the inside and outside surface can be suppressed in the piercing and rolling by a piercer:

$$P_\sigma = (Ni - 35) + 10(N - 0.1) - 2(Cr - 25) - 5(Mo + 0.5W - 3) + 8 \qquad ... (3).$$

[0032] Each element symbol in the above equations (1) to (3) represents the content by mass% of the element concerned.

[0033] The present inventors further made various examinations for the conditions of the piercing and rolling billets of the austenitic Fe-Ni alloys including not less than 20% Cr and not less than 30% Ni and further simultaneously containing Mo and W in large quantities exceeding 1.5% in terms of Mo equivalent value, by a piercer. As a result, the following findings (e) and (f) were obtained.

[0034]

(e) In the austenitic Fe-Ni alloys in which upper limit values of the contents of C, P and S are controlled to 0.04%, 0.03% and 0.01%, respectively, the value of T_{GBm} represented by the said equation (1) is set to not less than 1300, the two-piece cracks resulting from the intergranular fusion can be easily suppressed by increasing a pipe expansion ratio H represented by the ratio of an outer diameter of a pipe stock to a diameter of a steel stock billet.

(f) In addition to the condition of the above-mentioned (e), the value of fn represented by the following equation (4), that is a relational equation of the pipe expansion ratio H and contents of P and S contained in an Fe-Ni alloy is set to not more than 1, whereby the two-piece cracks resulting from the intergranular fusion in the piercing and rolling by a piercer can be perfectly prevented:

$$fn = \{P / (0.025H - 0.01)\}^2 + \{S / (0.015H - 0.01)\}^2 \qquad ... (4).$$

[0035] In the above equation (4), P and S represent the contents, by mass %, of P and S in a pipe stock, respectively,

and H represents the pipe expansion ratio represented by the ratio of the outer diameter of a pipe stock to the diameter of a steel stock billet.

[0036] The present invention has been accomplished on the basis of the above-mentioned findings. It is an objective of the present invention to provide Fe-Ni alloy pipe stocks of high Cr-high. Ni series simultaneously containing Mo and W in large quantities exceeding 1.5% in terms of Mo equivalent value, and pierced and rolled by a piercer, which have excellent corrosion resistance in a sour gas environment in addition to excellent mechanical properties, such as strength and ductility, and manufacturing methods thereof, particularly, Fe-Ni alloy pipe stocks, including not less than 20% Cr and not less than 30% Ni, and further simultaneously containing Mo and W in large quantities, exceeding 1.5% in terms of Mo equivalent value, and manufacturing methods thereof. It is another objective of the present invention to provide Fe-Ni alloy seamless pipes, excellent in mechanical properties and the corrosion resistance in a sour gas environment, which are manufactured using the above mentioned pipe stocks.

MEANS FOR SOLVING THE PROBLEM

[0037] The present invention provides Fe-Ni alloy pipe stocks shown in the following (1) to (3). Methods for manufacturing Fe-Ni alloy pipe stocks are discussed in (4) and (5), and an Fe-Ni alloy seamless pipe is shown in (6).

1. An Fe-Ni alloy seamless pipe stock, having a chemical composition consisting of, by mass %,

- C: not more than 0.04%,
- Si: not more than 0.50%,
- Mn: 0.01 to 6.0%,
- P: not more than 0.03%,
- S: not more than 0.01%,
- Cr: 20 to 30%,
- Ni 30 to 45 %,
- Mo : 0 to 10%,
- W: 0 to 20%,
- Cu: 0.01 to 1.5%,
- Al: not more than 0.10%,
- N: 0.0005 to 0.20%,

and optionally one or more elements selected from among

- V: 0.001 to 0.3%,
- Nb: 0.001 to 0.3%,
- Ta 0.001 to 1.0%,
- Ti: 0.001 to 1.0%,
- Zr: 0.001 to 1.0%,
- Hf.: 0.001 to 1.0%,
- B: 0.0001 to 0.015%,
- Co: 0.3 to 5.0%
- Mg: 0.0001 to 0.010%,
- Ca: 0.0001 to 0.010%,
- La: 0.0001 to 0.20%,
- Ce: 0.0001 to 0.20%,
- Y: 0.0001 to 0.40%,
- Sm: 0.0001 to 0.40%,
- Pr: 0.0001 to 0.40% and
- Nd: 0.0001 to 0.50%;
  the balance being Fe and impurities,
  with Mo(%) + 0.5W(%): more than 1.5% to not more than 10%, and with values of T_{GBm}, P_{sr} and P_σ represented by the following equations (1) to (3) being not less than 1300, not more than 90 and not less than 0, respectively, and moreover being subjected to piercing and rolling by a Mannesmann piercing and rolling mill:

$$T_{GBm} = 1440 - 6000P - 100S - 2000C \qquad \qquad ...(1),$$

$$P_{sr} = Ni + 10(Mo + 0.5W) + 100N \qquad \qquad ...(2),$$

$$P_\sigma = (Ni - 35) + 10(N - 0.1) - 2(Cr - 25) - 5(Mo + 0.5W - 3) + 8 \quad ...(3),$$

wherein each element symbol in the equations (1) to (3) represents the content by mass% of the element concerned.

(2) The Fe-Ni alloy pipe stock according to the above (1), wherein Mn is 0.01 to 1.0%.

(3) The Fe-Ni alloy seamless pipe stock according to the above (1) or (2), which has the chemical composition according to the said (1) or (2), with the value of fn represented by the following equation (4) being not more than 1:

$$fn = \{P / (0.025H - 0.01)\}^2 + \{S / (0.015H - 0.01)\}^2 \qquad ... (4),$$

wherein P and S represent contents, by mass %, of P and S in the pipe stock, respectively, and H represents the pipe expansion ratio represented by the ratio of the outer diameter of the pipe stock to the diameter of a steel stock billet.

(4) A method for manufacturing an Fe-Ni alloy pipe stock, comprising piercing and rolling a billet, which satisfies the chemical compositions according to any one of the above (1) to (3), by use of a Mannesmann piercing and rolling mill is discussed.

(5) The method for manufacturing an Fe-Ni alloy pipe stock according to the above (4) is discussed wherein the piercing and rolling by the Mannesmann piercing and rolling mill is performed in a condition where the value of fn represented by the following equation (4) is not more than 1:

$$fn = \{P / (0.025H - 0.01)\}^2 + \{S / (0.015H - 0.01)\}^2 \qquad ... (4),$$

wherein P and S represent contents, by mass %, of P and S in the pipe stock, respectively, and H represents the pipe expansion ratio represented by the ratio of the outer diameter of the pipe stock to the diameter of the steel stock billet.

(6) An Fe-Ni alloy seamless pipe, manufactured by use of the Fe-Ni alloy pipe stock according to any one of the above (1) to (3) or by use of the Fe-Ni alloy pipe stock manufactured by the method according to the above (4) or (5).

[0038] The above-mentioned inventions (1) to (3) related to the Fe-Ni alloy pipe stocks, (4) and (5) related to the methods for manufacturing an Fe-Ni alloy pipe stock; and (6) related to the Fe-Ni alloy seamless pipe are referred to as "the present invention (1)" to "the present invention (3)" method (4) and (5), and seamless pipe (6) respectively.

EFFECT OF THE INVENTION

[0039] Oil country tubular goods and line pipes and various structural members of nuclear power plants and chemical industrial plants, which are manufactured using the Fe-Ni alloy pipe stocks of the present invention as steel stocks are excellent in corrosion resistance in a sour gas environment, and also have excellent mechanical properties such as strength and ductility. Therefore, the Fe-Ni alloy pipe stocks of the present invention can be used as pipe stocks for oil country tubular goods and line pipes, and also can be used as pipe stocks for various structural members of nuclear power plants and chemical industrial plants. Further, since the Fe-Ni alloy pipe stocks of the present invention are obtained by piercing and rolling with a piercer, large diameter pipes or sufficiently long pipes can be easily manufactured using them as steel stocks, and the industrial demand for high-efficiency and low cost development of oil wells and gas wells can be sufficiently satisfied.

BEST MODE FOR CARRYING OUT THE INVENTION

[0040] All of the requirements of the present invention will next be described in detail.

(A) Chemical composition of Fe-Ni alloy

[0041] In the following description, the symbol "%" for the content of each element represents "% by mass".

C: not more than 0.04%

[0042] An excessive content of C remarkably increases the amount of $M_{23}C_6$ type carbides, resulting in a deterioration of ductility and toughness of the alloy. Particularly, a content of C exceeding 0.04% causes a remarkable deterioration of ductility and toughness. Therefore, the content of C is set to not more than 0.04%. The content of C is preferably reduced to 0.02% or less. When the content of C is controlled to 0.010% for less, not only the ductility and toughness but also the corrosion resistance can be remarkably improved.
[0043] The "M" in the "$M_{23}C_6$ type carbides" means metal elements such as Mo, Fe, Cr, W and the like in combination.
[0044] A high content of C causes solidification segregation which reduces the intergranular fusion temperature of the Fe-Ni alloy, resulting in a deteriorated piercing and rolling property by a piercer. Therefore, the content of C must be set to an amount in which the value of T_{GBm} represented by the said equation (1) satisfies not less than 1300 from the balance with contents of P and S described later.

Si: not more than 0.50%

[0045] Excessive Si promotes the formation of the sigma phase, causing a deterioration of ductility and toughness. Particularly, a content of Si exceeding 0.50% makes it difficult to suppress the inside surface cracks and the scabs on both the inside and outside surface resulting from the sigma phase formation in the piercing and rolling by a piercer even if the value of P_σ represented by the said equation (3) is not less than 0. Therefore, the content of Si is set to not more than 0.50%. If the content of Si is reduced to 0.10% or less, the grain boundary precipitation of the carbides can be suppressed to largely improve the ductility, toughness and corrosion resistance.

Mn: 0.01 to 6.0%

[0046] Mn has a desulfurizing effect. In order to ensure this effect, the content of Mn must be set to not less than 0.01%. However, a content of Mn exceeding 6.0% promotes the formation of the $M_{23}C_6$ type carbides, and so, the corrosion resistance may be deteriorated. Therefore, the content of Mn is set to 0.01 to 6.0%. A content of Mn exceeding 1.0% promotes the formation of the sigma phase, and may cause the inside surface cracks and the scabs on both the inside and outside surface resulting from the sigma phase formation in piercing and rolling by a piercer even if the value of P_σ represented by the said equation (3) is not less than 0. Accordingly, the content of Mn is set more preferably to 0.01 to 1.0% and further more preferably to 0.01 to 0.50%.

P: not more than 0.03%

[0047] P is an impurity which is generally inevitably included. If it is present in an alloy in large quantities, not only the hot workability but also the corrosion resistance generally deteriorates. Particularly, a content of P exceeding 0.03% makes a remarkable deterioration of hot workability and corrosion resistance. Therefore, the content of P is set to not more than 0.03%. The content of P is set further preferable to not more than 0.01%.
[0048] Since a high content of P causes solidification segregation, the intergranular fusion temperature of the Fe-Ni alloy falls, and this results in a deterioration of the piercing and rolling property by a piercer. Therefore, the content of P must be set to an amount in which the value of T_{GBm} represented by the said equation (1) satisfies not less than 1300 from the balance with the content of C described above and the content of S described below.

S: not more than 0.01%

[0049] S is also an impurity which is generally inevitably included. If it is present in an alloy in large quantities, not only the hot workability but also the corrosion resistance generally deteriorates. Particularly, a content of S exceeding 0.01% makes a remarkable deterioration of hot workability and corrosion resistance. Therefore, the content of S is set to not more than 0.01%. The content of S is set more preferably to not more than 0.005%.
[0050] Since a high content of S causes solidification segregation, the intergranular fusion temperature of the Fe-Ni alloy falls, and this results in a deterioration of the piercing and rolling property by a piercer. Therefore, the content of S must be set to an amount in which the value of T_{GBm} represented by the said equation (1) satisfies not less than 1300 from the balance with the contents of C and P described above.

Cr: 20 to 30%

[0051] Cr, with Mo, W and N, has the effect of improving the corrosion resistance and strength of an alloy. This effect can be remarkably obtained with a content of Cr of not less than 20%. However, if the content of Cr exceeds 30%, the hot workability of the alloy deteriorates. Therefore, the content of Cr is set to 20 to 30%. The content of Cr is set more preferably to 21 to 27%.

[0052] In the present invention, in order to suppress the inside surface cracks and the scabs on both the inside and outside surface resulting from the sigma phase formation, the content of Cr must be set to an amount in which the value of P_σ represented by the said equation (3) satisfies not less than 0 from the balance with the contents of Ni, Mo, W and N described later.

Ni: 30 to 45%

[0053] Ni, with N, has the effect of stabilizing the austenite matrix, and it is an essential element for including elements having a strengthening effect and a corrosion resisting effect such as Cr, Mo and W in the Fe-Ni alloy. Ni also has an effect of suppressing the formation of the sigma phase. Each of the effects described above can be surely obtained when the content of Ni is not less than 30%. On the other hand, a large amount of additional Ni causes an excessive increase of alloy cost, and if the content of Ni exceeds 45%, the cost increases. Therefore, the content of Ni is set to 30 to 45%. The content of Ni is set more preferably to 32 to 42%.

[0054] In the present invention, in order to suppress the excessive rise of deformation resistance and to suppress the inside surface scabs, the content of Ni must be set to an amount in which the value of P_{sr} represented by the said equation (2) satisfies not more than 120 from the balance with the contents of Mo, W and N described later. In order to suppress the inside surface cracks and the scabs on both the inside and outside surface resulting from the sigma phase formation, the content of Ni must be set to an amount in which the value of P_σ represented by the said equation (3) satisfies not less than 0 from the balance with the content of Cr described above and the contents of Mo, W and N described later.

Mo: 0 to 10%, W: 0 to 20%, Mo (%) +0.5W (%): more than 1.5% to not more than 10%

[0055] Both Mo and W have the effect of enhancing the strength of an alloy in coexistence with Cr, and further the effect of remarkably improving corrosion resistance, particularly, pitting resistance. In order to ensure these effects, Mo and/or W must be included in an amount exceeding 1.5% in terms of value represented by the expression Mo(%) + 0.5W(%), namely, in terms of Mo equivalent value. However, a Mo equivalent value exceeding 10% causes a deterioration of mechanical properties such as ductility and toughness. Mo and W do not need a composite addition, and can be added simply so that the Mo equivalent value is within the above range. Therefore, the content of Mo is set to 0 to 10%, and the content of W is set to 0 to 20%, and the value of Mo(%) + 0.5W(%) is set to more than 1.5% to not more than 10%.

[0056] In the present invention, in order to suppress the excessive rise of deformation resistance to suppress the inside surface scabs, the contents of Mo and W and the Mo equivalent value must be set to amounts so that the value of P_{sr} represented by the said equation (2) satisfies not more than 120 from the balance with the content of Ni described above and the content of N described later. In order to suppress the inside surface cracks and the scabs on both the inside and outside surface resulting from the sigma phase formation, the contents of Mo and W and the Mo equivalent value must be set to amounts so that the value of P_σ represented by the said equation (3) satisfies not less than 0 from the balance with the contents of Cr and Ni described above and the content of N described later.

Cu: 0.01 to 1.5%

[0057] Cu is an element effective for improving the corrosion resistance in a sour gas environment and, particularly, it has the effect of highly enhancing the corrosion resistance, in coexistence with Cr, Mo and W, in a sour gas environment where S (sulfur) is observed as a separated element. This effect is obtained with a content of Cu of not less than 0.01%. However, a content of Cu exceeding 1.5% may cause a deterioration of ductility, and toughness. Therefore, the content of Cu is set to 0.01 to 1.5%. The content of Cu is set more preferably to 0.5 to 1.0%.

Al: not more than 0.10%

[0058] Al is the most harmful element which promotes the formation of the sigma phase. Particularly, a content of Al exceeding 0.10% makes it difficult to suppress the inside surface cracks and the scabs on both the inside and outside surface resulting from the sigma phase formation in the piercing and rolling by a piercer even if the value P_σ represented by the said equation (3) is not less than 0. Therefore, the content of Al is set to not more than 0.10%. The content of Al

is set more preferably to not more than 0.06%.

N: 0.0005 to 0.20%

5 **[0059]** N is one of important elements in the present invention, and with Ni, it has the effect of stabilizing the austenite matrix and the effect of suppressing the formation of the sigma phase. The above-mentioned effects can be obtained with a content of N of not less than 0.0005%. However; excessive addition of N may cause a deterioration of toughness, and particularly a content exceeding 0.20% may cause a remarkable deterioration of toughness. Therefore, the content of N is set to 0.0005 to 0.20%. The content of N is set more preferably to 0.0005 to 0.12%.

10 **[0060]** In the present invention, in order to suppress the excessive rise of deformation resistance and to suppress the inside surface scabs, the content of N must be set to an amount in which the value of P_{sr} represented by the said equation (2) satisfies not more than 120 from the balance with the contents of Ni, Mo and W described above. Moreover, in order to suppress the inside surface cracks and the scabs on both the inside and outside surface resulting from the sigma phase formation, the content of N must be set to an amount in which the value of P_{σ} represented by the said equation

15 (3) satisfies not less than 0 from the balance with the contents of Cr, Ni, Mo and W described above.

Fe: substantial balance

[0061] Fe has the effect of ensuring the strength of an alloy and also reducing the content of Ni in order to decrease
20 the cost of the alloy. Therefore, in the alloys of steel stocks for the Fe-Ni alloy pipe stocks of the present invention, a substantial balance of the element Fe is included.

Value of T_{GBm}: not less than 1300

25 **[0062]** As described above, among the inside surface flaws which are present in the Fe-Ni alloys of the high Cr-high Ni series, the two-piece cracks resulting from the intergranular fusion involved by work heat generation on the high temperature side is remarkable, when the solidification segregation of elements which comprise the material to be pierced and rolled, particularly the solidification segregation of C, P and S is present. In the austenitic Fe-Ni alloys, including not less than 20% Cr and not less than 30% Ni, and further simultaneously containing Mo and W in large quantities, exceeding
30 1.5% in terms of Mo equivalent value, the state of the intergranular fusion can be evaluated by the value of T_{GBm}, represented by the said equation (1). When the value of T_{GBm} is not less than 1300, the two-piece cracks can be suppressed in the piercing and rolling by a piercer, therefore, the value of T_{GBm} is set to not less than 1300. The value of T_{GBm} is set more preferably to not less than 1320.

35 Value of P_{sr}: not more than 120

[0063] As described above, among the inside surface flaws which are present in the hard-to-work Fe-Ni alloys of the high Cr-high Ni series, particularly in the austenitic Fe-Ni alloys, including not less than 20% Cr and not less than 30% Ni, and further simultaneously containing Mo and W in large quantities, exceeding 1.5% in terms of Mo equivalent value,
40 the inside surface scabs resulting from high deformation resistance can be evaluated by the value of P_{sr}, represented by the said equation (2). When the value of P_{sr} is not more than 120, the inside surface scabs can be suppressed in the piercing and rolling by a piercer, therefore, the value of P_{sr} is set to not more than 120. The value of P_{sr} is set more preferably to not more than 90.

45 Value of P_{σ}: not less than 0

[0064] Among the inside surface flaws which are present in the Fe-Ni alloys of the high Cr-high Ni series, particularly, in the austenitic Fe-Ni alloys, including not less than 20% Cr and not less than 30% Ni, and further simultaneously containing Mo and W in large quantities, exceeding 1.5% in terms of Mo equivalent value, the inside surface cracks and
50 the scabs on both the inside and outside surface resulting from the sigma phase formation in a low temperature region involved by a temperature drop can be evaluated by the value of P_{σ}, represented by the said equation (3). When the value of P_{σ} is not less than 0, the inside surface cracks and the scabs on both inside and outside surface can be suppressed in the piercing and rolling by a piercer, therefore, the value of P_{σ} is set to not less than 0. The value of P_{σ} is set more preferably to not less than 3.0.

55 **[0065]** Accordingly, the chemical compositions of the alloy as the steel stock for the Fe-Ni alloy pipe stock of the present invention (1) was regulated to include elements of from C to N in the above-mentioned ranges, and the balance substantially being Fe, with the value of T_{GBm} being not less than 1300, the value of P_{sr} being not more than 120, and the value of P_{σ} being not less than 0.

[0066] In the Fe-Ni alloy pipe stock of the present invention (1), the content of Mn is preferably regulated from 0.01 to 1.0%.

[0067] The alloys as steel stocks for the Fe-Ni alloy pipe stocks of the prevent invention can selectively contain, in addition to the above-mentioned components, one or more of elements of each group described below as occasion demands:

(i) One or more elements selected from among V: 0.001 to 0.3%, Nb: 0.001 to 0.3%, Ta: 0.001 to 1.0%, Ti: 0.001 to 1.0%, Zr: 0.001 to 1.0% and Hf: 0.001 to 1.0%;
(ii) B: 0.0001 to 0.015%;
(iii) Co: 0.3 to 5.0%; and
(iv) One or more elements selected from among Mg: 0.0001 to 0.010%, Ca: 0.0001 to 0.010%, La: 0.0001 to 0.20%, Ce: 0.0001 to 0.20%, Y: 0.0001 to 0.40%, Sm: 0.0001 to 0.40%, Pr: 0.0001 to 0.40% and Nd: 0.0001 to 0.50%. That is to say, one or more elements of the four groups (i) to (iv) can be added thereto as optional additive elements.

[0068] The optional additive elements are described as follows:

(i) V: 0.001 to 0.3%, Nb: 0.001 to 0.3%, Ta: 0.001 to 1.0%, Ti: 0.001 to 1.0%, Zr: 0.001 to 1.0% and Hf: 0.001 to 1.0%

[0069] Each of V, Nb, Ta, Ti, Zr and Hf, if added, has the effect of remarkably enhancing the corrosion resistance in a sour gas environment where S (sulfur) is observed as a separated element. Further, it forms MC type carbides (M means any one element of V, Nb, Ta, Ti, Zr and Hf or a combination thereof) to effectively stabilize C, and also has the effect of enhancing the strength.

[0070] In order to ensure the above-mentioned effects, the content of each element of V, Nb, Ta, Ti, Zr and Hf is preferably set to not less than 0.001%. However, if the contents of V and Nb exceed 0.3%, and the contents of Ta, Ti, Zr and Hf exceed 1.0%, their independent carbides are precipitated in large quantities, causing a deterioration of ductility and toughness.

[0071] Therefore, if V, Nb, Ta, Ti, Zr and Hf are added, the respective contents are preferably set to 0.001 to 0.3% for V, 0.001 to 0.3% for Nb, 0.001 to 1.0% for Ta, 0.001 to 1.0% for Ti, 0.001 to 1.0% for Zr, and 0.001 to 1.0% for Hf.

[0072] From the above reason, the chemical compositions of the alloy as the steel stock for the Fe-Ni alloy pipe stock of the present invention (1) is optionally regulated to contain, in lieu of part of Fe of the Fe-Ni alloy, one or more elements selected from among V: 0.001 to 0.3%, Nb: 0.001 to 0.3%, Ta: 0.001 to 1.0%, Ti: 0.001 to 1.0%, Zr: 0.001 to 1.0%, and Hf: 0.001 to 1.0%.

[0073] In the alloy as the steel stock for the Fe-Ni alloy pipe stock of the present invention (1), further preferable content ranges of the elements, if added, are 0.10 to 0.27% for V, 0.03 to 0.27% for Nb, 0.03 to 0.70% for Ta, 0.03 to 0.70% for Ti, 0.03 to 0.70 for Zr, and 0.03 to 0.70% for Hf.

[0074] The above-mentioned V, Nb, Ta, Ti, Zr and Hf can be added alone or in combination of two or more thereof.

[0075] -

(ii) B: 0.0001 to 0.015%

[0076] B, if added, has the effect of refining precipitates and austenite grain size. In order to definitely obtain the said effect, the content of B is preferably set to not less than 0.0001%. However, excessive addition of B may cause a deterioration of hot workability by the formation of low melting point compounds, and a content thereof exceeding 0.016%, particularly, can make a remarkable deterioration of hot workability. Therefore, the content of B, if added, is preferably set to 0.0001 to 0.015%.

[0077] From the above reason, the chemical compositions of the alloy as the steel stock for the Fe-Ni alloy pipe stock of the present invention (1) is optionally regulated to contain B: 0.0001 to 0.015% in lieu of part of Fe of the Fe-Ni alloy.

[0078] In the alloy of the steel stock for the Fe-Ni alloy pipe stock of the present invention (1), a further preferable content range of B, if added, is 0.0010 to 0.0050%.

(iii) Co: 0.3 to 5.0%

[0079] Co, if added, has the effect of stabilizing austenite. In order to ensure the said effect, the content of Co is preferably set to not less than 0.3%. However, excessive addition of Co causes excessive rise of alloy cost, and a content of Co exceeding 5.0%, particularly, makes the cost increase excessive, therefore, the content of Co, if added, is preferably set to 0.3 to 5.0%.

[0080] From the above reason, the chemical compositions of the alloy as the steel stock for the Fe-Ni alloy pipe stock of the present invention (1) is optionally regulated to contain Co: 0.3 to 5.0%, in lieu of part of Fe of the Fe-Ni alloy.

[0081] In the alloy of the steel stock for the Fe-Ni alloy pipe stock of the present invention (1), a further preferable content range of Co, if added, is 0.35 to 4.0%.

(iv) Mg: 0.0001 to 0.010%, Ca: 0.0001 to 0.010%, La: 0.0001 to 0.20%, Ce: 0.0001 to 0.20%, Y: 0.0001 to 0.40%, Sm: 0.0001 to 0.40%, Pr: 0.0001 to 0.40% and Nd: 0.0001 to 0.50%

[0082] Each of Mg, Ca, La, Ce, Y, Sm, Pr and Nd, if added, has the effect of preventing solidification cracks in ingot casting. They also have the effect of suppressing a deterioration of ductility after a long-term use.

[0083] In order to ensure the above effects, the content of each element of Mg, Ca, La, Ce, Y, Sm, Pr and Nd is set preferably to not less than 0.0001%. However, when the contents of Mg and Ca exceed 0.010%, the contents of La and Ce exceed 0.20%, the contents of Y, Sm and Pr exceed 0.40%, or the content of Nd exceeds 0.50%, coarse inclusions are produced, causing a deterioration of toughness.

[0084] Therefore, the contents of Mg, Ca, La, Ce, Y, Sm, Pr and Nd, if added, are preferably set to 0.0001 to 0.010% for Mg, 0.0001 to 0.010% for Ca, 0.0001 to 0.20% for La, 0.0001 to 0.20% for Ce, 0.0001 to 0.40% for Y, 0.0001 to 0.40% for Sm, 0.0001 to 0.40% for Pr, and 0.0001 to 0.50% for Nd.

[0085] From the above reason, the chemical compositions of the alloy as the steel stock for the Fe-Ni alloy pipe stock of the present invention (1) is optionally regulated to contain, in lieu of part of Fe of the Fe-Ni alloy, one or more elements selected from among Mg: 0.0001 to 0.010%, Ca: 0.0001 to 0.010%, La: 0.0001 to 0.20%, Ce: 0.0001 to 0.20%, Y: 0.0001 to 0.40%, Sm: 0.0001 to 0.40%, Pr: 0.0001 to 0.40%, and Nd: 0.0001 to 0.60%.

[0086] In the alloy of the steel stock for the Fe-Ni alloy pipe stock of the present invention (1), preferable content ranges of the elements, if added, are 0.0010 to 0.0050% for Mg, 0.0010 to 0.0050% for Ca, 0.01 to 0.15% for La, 0.01 to 0.15% for Ce, 0.01 to 0.15% for Y, 0.02 to 0.30% for Sm, 0.02 to 0.30% for Pr and 0.01 to 0.30% for Nd.

[0087] The above-mentioned Mg, Ca, La, Ce, Y, Sm, Pr and Nd can be added alone or in combination of two or more thereof.

[0088] Oil country tubular goods and line pipes and various structural members of nuclear power plants and chemical industrial plants, which are manufactured using the Fe-Ni alloy pipe stocks having the chemical compositions described above as steel stocks are excellent in corrosion resistance in a sour gas environment, and also have excellent mechanical properties such as strength and ductility. Therefore, when the Fe-Ni alloy pipe stocks, having the above-mentioned chemical compositions are applied to pipe stocks for oil country tubular goods and line pipes, and also to pipe stocks for various structural members of nuclear power plants and chemical industrial plants, significant durability and safety can be improved. That is to say, that Fe-Ni alloy pipe stocks are extremely favorable for the use of members which are exposed in the above-mentioned environment.

(B) Manufacturing method of the Fe-Ni alloy pipe stock

[0089] Not only to obtain pipe stocks for various members which are excellent in mechanical properties such as strength and ductility, and also have excellent corrosion resistance in a sour gas environment, but also to satisfy the industrial demand for high-efficiency and low cost development of oil wells and gas wells, industrial mass production of pipe stocks for large diameter pipes or sufficiently long pipes is needed. The piercing and rolling by a piercer is suitable for such industrial mass production of pipe stocks for large diameter pipes or sufficiently long pipes.

[0090] However, as already described, it has been difficult in the past to mass produce Fe-Ni alloy pipe stocks, particularly Fe-Ni alloy pipe stocks, including not less than 20% Cr and not less than 30% Ni and simultaneously containing Mo .and W in large quantities exceeding 1.5% in terms of Mo equivalent value, which are excellent in mechanical properties, such as strength and ductility, and in corrosion resistance in a sour gas environment and also suitable as steel stocks for oil country tubular goods and line pipes and various structural members of nuclear power plants and chemical industrial plants, by piercing and rolling with a piercer by the same method as in the case of carbon steels and low alloy steels and further martensitic stainless steels, such as so-called "13%-Cr steel" (hereinafter referred to as "general method"). This is attributable to the piercing and rolling by a piercer of such a high Cr-high Ni alloy with large Mo equivalent value by the general method inevitably causes the occurrence of flaws or cracks.

[0091] On the other hand, in the Fe-Ni alloys having the chemical compositions described in the above (A), the contents of elements of from C to N are optimized, the value of T_{GBm} represented by the said equation (1), the value of P_{sr} represented by the said equation (2), and the value of P_σ represented by the said equation (3), which all have correlations with the two-piece cracks resulting from the intergranular fusion on the high temperature side in the piercing and rolling by a piercer, the inside surface scabs resulting from high deformation resistance, and the inside surface cracks and the scabs on both the inside and outside surface resulting from the sigma phase formation, are set to not less than 1300, to not more than 120, and to not less than 0, respectively. Therefore, billets of the Fe-Ni alloys, having the chemical compositions described in the above (A), can be pierced and rolled with a piercer by the general method while preventing all of the two-piece cracks, the inside surface scabs, and the inside surface cracks and the scabs on both the inside and

outside surface resulting from the sigma phase formation. Therefore, the pipe stocks which have satisfactory surface properties can be obtained.

[0092]   Accordingly, method (4) can respond to the industrial demand for industrial mass-production of large diameter pipes or sufficiently long pipes by piercing and rolling the billets of Fe-Ni alloys, having the compositions described in the above (A), with a piercer. And the Fe-Ni alloy pipe stocks according to the present inventions (1) to (3) are regulated to have the chemical compositions described in the above (A) and to be pierced and rolled by a piercer.

[0093]   The pipe stocks manufactured by the method (4), namely, the pipe stocks obtained by piercing and rolling the billets having the chemical compositions of the above (A) by a piercer have satisfactory surface properties in which all of the two-piece cracks, the inside surface scabs, and inside surface cracks and the scabs on both the inside and outside surface resulting from the sigma phase formation are suppressed. Therefore, the Fe-Ni alloy pipe stocks of the present inventions (1) to (3) can sufficiently respond to the above-mentioned industrial demand.

[0094]   The piercing and rolling by a piercer of the billets having the chemical compositions described in the above (A) can be performed by the general method.

[0095]   That is to say, the piercing and rolling by a piercer can be performed in the same condition as in the case of carbon steels and low alloy steels, and further martensitic stainless steels such as so-called "13%-Cr steel". Concretely, for example, the piercing and rolling can be performed with a billet heating temperature of 1200 to 1300°C, a roll cross angle of 0 to 10°, a roll feed angle of 7 to 14°, a draft rate of 8 to 14%, and a plug tip draft rate of 4 to 7%.

[0096]   The draft rate and the plug tip draft rate are represented by the following equations (6) and (6), respectively.

$$\text{Draft rate (\%)} = \{(\text{Diameter of the steel stock} - \text{Gauge space of the roll}) / \text{Diameter of the steel stock}\} \times 100 \quad \dots (5),$$

$$\text{Plug tip draft rate (\%)} = \{(\text{Diameter of the steel stock} - \text{Roll gap at the foremost end of the plug}) / \text{Diameter of the steel stock}\} \times 100 \quad \dots (6).$$

[0097]   As described above, the piercing and rolling by a piercer of the billets, having the chemical compositions described in the above (A), can be performed by the general method without providing any special conditions. However, as already described, the pipe expansion ratio H, represented by the ratio of an outer diameter of the pipe stock to a diameter of the steel stock billet, is increased whereby the two-piece cracks resulting from the intergranular fusion can be easily suppressed. Further, if the value of fn, presented by the said equation (4), is set to not more than 1, the two-piece cracks resulting from the intergranular fusion in the piercing and rolling by a piercer can be absolutely prevented.

[0098]   Therefore, in method (5), the piercing and rolling by a piercer of billets of the Fe-Ni alloys, having the chemical compositions described in the above (A), is performed with the value of fn represented by the said equation (4) being set to not more than 1. Also the Fe-Ni alloy pipe stock of the present invention (3) is regulated to have the chemical composition described in the above (A) with the value of fn represented by the said equation (4) satisfying not more than 1, and also to be pierced and rolled by a piercer.

[0099]   As described above, by increasing the value of the pipe expansion ratio H in the piercing and rolling by a piercer, the two-piece cracks resulting from the intergranular fusion can be easily suppressed. However, if the value of the pipe expansion ratio H exceeds 2, the phenomenon of the pipe stock becoming excessively swollen, and the steel stock protruding to a clearance between a roll and a disk or guide shoe, each of them is an outside surface regulating tool, and a fracture can be easily caused, resulting in rolling troubles. Therefore, the upper limit value of the pipe expansion ratio H is preferably set to 2. When the lower limit value of the pipe expansion ratio H is less than 1, a plug or a mandrel, each of them is a tool for inside surface working, must be reduced in the outer diameter, since the outer diameter of the resulting pipe stock becomes smaller than the diameter of the steel stock billet, which impractically causes erosion of the plug or curving of the mandrel, due to insufficient heat capacity.

(C) Fe-Ni alloy seamless pipe

[0100]   The Fe-Ni alloy seamless pipe manufactured by use of the Fe-Ni alloy pipe stock according to any one of the present inventions (1) to (3), or by use of the Fe-Ni alloy pipe stock manufactured by method (4) or (5) has satisfactory surface properties, and also is excellent in mechanical properties and in the corrosion resistance in a sour gas environment. Therefore, such seamless pipes are suitable to be used as oil country tubular goods or line pipes, and as various structural members of nuclear power plants and chemical industrial plants.

[0101]   Therefore, in seamless pipe (6), the Fe-Ni alloy seamless pipe is regulated to be manufactured using the Fe-Ni alloy pipe stock, according to any one of the present inventions (1) to (3), or using the Fe-Ni alloy pipe stock manu-

factured by method (4) or Invention (5).

[0102] The Fe-Ni alloy pipe stock according to any one of the present inventions (1) to (3) or the Fe-Ni alloy pipe stock manufactured by method (4) or (5) can be easily manufactured into a desired Fe-Ni alloy seamless pipe by working it by the general method, for example, by expanding the diameter by use of an elongator, such as a mandrel mill, a plug mill, an Assel mill or a push bench to reduce the wall thickness, and then by narrowing the outer diameter by use of a reducing mill, such as a stretch reducing mill or a sizing mill.

[0103] The present invention will be described in more detail in reference to preferred embodiments.

PREFERRED EMBODIMENT

[Example 1]

[0104] Various Fe-Ni alloys, having chemical compositions shown in Tables 1 and 2, were melted by use of a 160 kg vacuum induction melting furnace in the ordinary manner, and casted to form ingots. In Tables 1 and 2, the alloys 1 to 23 are the alloys of the inventive examples in which the chemical compositions are within the range regulated by the present invention, and the alloys a to q are the alloys of comparative examples in which the content of any one of the components is out of the range regulated by the present invention. Among the alloys of comparative examples, the alloys a and b roughly correspond to conventional alloys ASM UNS No. 08028 and No. 08535 respectively.

[Table 1]

[0105]

Table 1

Alloy	Chemical composition (% by mass) Balance : Fe and impurities										
	C	Si	Mn	P	S	Cr	Ni	Mo	W	Mo+0.5W	Cu
1	0.007	0.38	0.77	0.014	0.0060	22.65	35.88	4.10	-	4.10	0.83
2	0.013	0.36	0.92	0.008	0.0054	25.13	34.46	3.57	-	3.57	0.97
3	0.016	0.41	0.85	0.010	0.0050	26.38	38.31	3.03	-	3.03	0.86
4	0.005	0.26	0.47	0.014	0.0016	25.16	40.42	4.33	-	4.33	1.03
5	0.026	0.35	0.89	0.003	0.0009	24.17	35.41	3.78	-	3.78	1.44
6	0.009	0.28	0.58	0.013	0.0006	28.85	35.98	3.03	-	3.03	0.85
7	0.021	0.27	0.43	0.008	0.0007	25.32	38.57	4.26	-	4.26	0.82
8	0.004	0.33	0.32	0.015	0.0058	25.14	35.15	3.16	-	3.16	0.93
9	0.006	0.25	0.08	0.014	0.0062	27.87	34.76	1.59	2.04	2.61	0.75
10	0.012	0.27	0.83	0.009	0.0015	24.98	40.65	0.46	6.33	3.63	0.46
11	0.036	0.31	0.26	0.004	0.0028	26.11	37.33	0.00	3.84	1.92	0.48
12	0.005	0.15	0.16	0.013	0.0030	24.97	31.52	0.21	5.68	3.05	0.86
13	0.015	0.28	0.50	0.007	0.0022	28.19	35.85	2.43	-	2.43	0.90
14	0.007	0.06	0.21	0.014	0.0060	22.06	38.78	-	11.92	5.96	0.29
15	0.011	0.08	0.05	0.012	0.0015	24.36	32.16	3.33	0.56	3.61	0.63
16	0.002	0.41	0.44	0.015	0.0067	25.11	39.23	4.60	-	4.60	0.65
17	0.016	0.32	0.60	0.007	0.0010	25.10	32.68	3.18	-	3.18	0.87
18	0.007	0.26	0.52	0.010	0.0006	25.53	34.77	3.65	-	3.65	0.85
19	0.005	0.22	0.59	0.008	0.0040	25.33	34.56	3.61	-	3.61	0.80
20	0.006	0.35	0.48	0.012	0.0023	23.08	43.72	6.56	-	6.56	1.33
21	0.013	0.05	5.20	0.016	0.0012	24.58	32.47	3.84	-	3.84	0.56
22	0.016	0.12	2.68	0.009	0.0044	25.31	36.66	4.12	-	4.12	1.13
23	0.009	0.18	4.89	0.005	0.0036	28.82	42.30	3.33	1.23	3.95	0.85
a	0.012	0.38	1.51	0.024	0.0021	27.12	30.33	3.45	-	3.45	* -
b	0.014	0.28	1.45	0.021	0.0028	24.85	32.55	3.30	-	3.30	1.05
c	*0.051	0.44	0.85	0.029	0.0050	27.04	32.89	2.43	-	2.43	1.27
d	0.012	*0.73	0.77	0.026	0.0085	24.46	35.85	3.65	-	3.65	*1.85

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(continued)

Alloy	Chemical composition (% by mass) Balance : Fe and impurities										
	C	Si	Mn	P	S	Cr	Ni	Mo	W	Mo+0.5W	Cu
e	0.016	0.44	1.86	0.024	0.0066	27.65	30.88	3.57	-	3.57	1.43
f	0.025	0.22	0.81	*0.038	0.0068	27.44	33.31	4.45	-	4.45	1.27
g	0.019	0.47	0.88	0.015	*0.0143	27.06	37.68	8.18	-	8.18	1.45
h	0.003	0.48	0.35	0.011	0.0065	*18.65	31.50	6.45	-	6.45	1.24
i	0.021	0.41	0.92	0.017	0.0074	*32.47	40.74	4.48	0.25	4.61	1.39
j	0.016	0.49	0.83	0.008	0.0057	28.91	*28.59	4.20	-	4.20	0.84
k	0.008	0.34	0.68	0.011	0.0083	21.73	33.14	*12.06	-	*12.05	1.22
l	0.008	0.34	0.68	0.011	0.0083	21.73	33.14	0.25	*25.34	*12.92	0.51
m	0.018	0.48	0.84	0.017	0.0070	24.14	34.62	3.41	1.55	4.19	*1.96
n	0.023	0.38	0.97	0.009	0.0059	24.36	32.00	3.08	0.56	3.36	1.48
o	0.019	0.43	0.76	0.018	0.0083	25.17	31.55	4.18	2.47	5.42	1.21
p	0.015	0.35	0.51	0.011	0.0015	26.31	31.84	*0.31	-	*0.31	*1.85
q	0.013	0.28	*7.51	0.018	0.0052	27.85	32.55	3.12	-	3.12	1.41

A mark * indicate falling outside the conditions specified by the present invention.

[Table 2]

[0106]

Table 2 (continued from Table 1)

Alloy	Chemical composition (% by mass) Balance: Fe and impurities			Value of T$_{GBm}$	Value of P$_{sr}$	Value of P$_\sigma$
	Al	N	others			
1	0.036	0.008	-	1341.4	77.68	7.2
2	0.068	0.092	-	1365.5	79.4	4.3
3	0.045	0.044	-	1347.5	73.0	7.8
4	0.083	0.008	V:0.23	1345.8	84.5	5.5
5	0.008	0.120	Nb:0.11	1369.9	85.2	6.4
6	0.047	0.078	B:0.0041	1343.9	74.1	0.9
7	0.055	0.104	Co:3.1	1349.9	91.6	4.7
8	0.059	0.083	Ca:0.0032	1341.4	75.1	6.9
9	0.023	0.083	-	1343.4	69.2	3.8
10	0.038	0.086	Nd:0.20	1361.9	85.5	10.4
11	0.044	0.049	Zr0.05,B:0.0020	1343.7	61.4	13.0
12	0.041	0.086	Ta:0.31,Co:2.36	1351.7	70.6	4.2
13	0.042	0.094	V:0.25,Nd:0.14	1367.8	69.6	5.3
14	0.061	0.023	Hf:0.15,B:0.0016,Co:1.05	1341.4	100.7	2.1
15	0.046	0.083	B0.0043,Nb:0.13,Nd:0.05	1345.9	76.6	3.2
16	0.065	0.081	Co:0.37,Y:0.22,B:0.0014	1345.3	93.3	3.8
17	0.078	0.087	-	1365.9	73.2	4.5
18	0.050	0.156	V:0.17,B:0.0044,Co:0.43,Mg:0.0025	1365.9	86.9	4.0
19	0.063	0.075	-	1381.6	78.2	3.6
20	0.028	0.056	-	1355.8	114.9	2.3
21	0.013	0.088	V:0.12,Nd:0.05	1317.9	79.7	2.0
22	0.089	0.142	Nd:0.03	1353.6	92.1	3.9
23	0.011	0.166	-	1391.6	98.4	3.6
a	*0.130	0.085	-	* 1271.8	73.3	* -3.3
b	*0.150	0.083	-	* 1285.7	73.9	4.2

(continued)

Alloy	Chemical composition (% by mass) Balance: Fe and impurities			Value of T_{GBm}	Value of P_{sr}	Value of P_σ
	Al	N	others			
c	*0.230	0.054	-	* 1163.5	62.6	4.2
d	0.080	0.016	-	* 1269.2	74.0	5.8
e	0.089	0.189	-	* 1263.3	85.5	* -3.4
f	0.076	0.086	-	* 1161.3	86.4	* -6.0
g	0.065	0.007	-	1310.6	* 120.2	*-20.3
h	0.097	0.005	-	1367.4	96.5	* -1.0
i	0.038	*0.235	-	* 1295.3	110.3	* -7.9
j	0.078	0.133	-	1359.4	83.9	* -11.9
k	0.033	0.047	-	1357.2	* 158.3	* -33.1
l	0.046	0.015	-	1357.2	* 163.8	* -37.8
m	0.057	0.012	-	1301.3	77.7	2.5
n	*0.130	0.108	-	1839.4	76.4	4.6
o	0.038	*0.220	-	* 1293.2	107.7	* -6.7
p	0.073	0.083	-	1343.9	43.2	15.5
q	0.140	0.085	-	1305.5	72.3	* -0.9
A mark * indicate falling outside the conditions specified by the present invention.						

[0107]   Each of the ingots was soaked at 1200°C for 2 hours, and then hot forged in the ordinary manner to produce, for each Fe-Ni alloy, one billet with a 85 mm in diameter, two billets 70 mm in diameter, and one billet 55 mm in diameter for changing the pipe expansion ratio in the piercing and rolling. The finishing temperature of forging in each case was set to not lower than 1000°C.

[0108]   Each of the thus-obtained billets was heated at 1250°C for 1 hour, and pierced and rolled into a pipe stock of a size shown in Table 3 by use of a model mill with a pipe expansion ratio H of 1.09 to 1.74. In Table 3, the relationship among the pipe expansion ratio, the billet size and the pipe stock size is shown. The roll cross angle, roll feed angle, draft rate and plug tip draft rate that are piercing conditions of the model mill, that is a piercing and rolling device, are shown in Table 4.

[0109]   In Table 5, the value of fn represented by the said equation (4) of each alloy is shown separately, for each pipe expansion ratio H of 1.09, 1.36, 1.64 or 1.74 in the piercing and rolling.

[Table 3]

[0110]

Table 3

Billet diameter (mm)	Pipe stock outer diameter (mm)	Pipe stock wall thickness (mm)	Pipe expansion ratio H
85.0	93.0	6.5	1.09
85.0	115.5	5.5	1.36
70.0	115.0	6.5	1.64
55.0	95.5	5.5	1.74

[Table 4]

[0111]

Table 4

Piercing and rolling condition by model mill	
Roll cross angle	7 deg.

(continued)

Piercing and rolling condition by model mill	
Roll feed angle	9 deg.
Draft rate	10.7%
Plug tip draft rate	6%

[Table 5]

[0112]

Table 5

Alloy	fn value for following expansion ratio H			
	1.09	1.36	1.64	1.74
1	** 1.551487	0.673118	0.372841	0.313533
2	0.938250	0.380712	0.203396	0.169524
3	0.956065	0.404750	0.221341	0.185554
4	0.722173	0.363946	0.215964	0.184525
5	0.050334	0.023114	0.013165	0.011144
6	0.576876	0.296731	0.177547	0.151979
7	0.227233	0.115641	0.068896	0.058919
8	** 1.590417	0.701646	0.391947	0.330269
9	** 1.611999	0.695677	0.384288	0.322946
10	0.328012	0.161428	0.094843	0.080857
11	0.248203	0.100263	0.053429	0.044503
12	0.791148	0.376613	0.218080	0.185311
13	0.284704	0.129818	0.073695	0.062334
14	** 1.551487	0.673118	0.372841	0.313533
15	0.539732	0.270803	0.160399	0.136994
16	** 1.869418	0.805658	0.444724	0.373670
17	0.189471	0.094315	0.055680	0.047520
18	0.344992	0.176940	0.105747	0.090496
19	0.611882	0.259040	0.141658	0.118754
20	0.615124	0.298909	0.174661	0.148722
21	0.896036	0.457758	0.273145	0.233669
22	0.752341	0.319619	0.175111	0.146865
23	0.405425	0.163225	0.086814	0.072275
* a	** 2.045096	** 1.040773	0.620064	0.530268
* b	** 1.676474	0.838110	0.495677	0.423206
* c	** 3.446298	** 1.691208	0.992413	0.845834
* d	** 4.063595	** 1.841603	** 1.042381	0.881093
* e	** 3.016018	** 1.402737	0.803729	0.681304
* f	** 5.999516	** 2.934459	** 1.719528	** 1.465089
* g	** 5.827506	** 2.281250	** 1.193457	0.989387
* h	** 1.454439	0.600694	0.324118	0.270814
* i	** 2.329275	** 1.008023	0.557625	0.468776
* j	** 1.020834	0.411499	0.219018	0.182371
* k	** 2.115113	0.846996	0.449095	0.373588
* l	** 2.115113	0.846996	0.449095	0.373588
* m	** 2.186427	0.954769	0.530603	0.446554
* n	** 1.135501	0.462463	0.247592	0.206469
* o	** 2.797322	** 1.199427	0.660333	0.554475

(continued)

Alloy	fn value for following expansion ratio H			
	1.09	1.36	1.64	1.74
* p	0.462437	0.230872	0.136466	0.116499
* q	** 1.759440	0.812500	0.464002	0.393023
A mark * indicate the alloy whose chemical compositions are falling outside the conditions specified by the present invention. A mark ** indicate falling outside the conditions specified by the present inventions (7) and (9).				

[0113] Each of the thus-obtained pipe stocks was examined for cracks and flaws, namely, for the two-piece cracks resulting from the intergranular fusion, the inside surface scabs, and the inside surface cracks and the scabs on both the inside and outside surface resulting from the sigma phase formation.

[0114] The examination results for cracks and flaws are collectively shown in Table 6. The marks "○○", "○" "Δ" and "×" in Table 6 mean that "no cracks or flaws were observed", "small flaws were observed in spite of absence of cracks", "large flaws were observed in spite of absence of cracks", and "cracks were observed", respectively.

[0115] With respect to the alloys 1 to 23 and the alloys p and q whose examination results for cracks and flaws in the said pipe stocks include the evaluation "○○", those with a pipe expansion ratio H of 1.36 were representatively subjected to a solution heat treatment holding at 1050°C for 30 minutes followed by water cooling. Thereafter, an oblong steel stock 5 mm in thickness, 12 mm in width and 150 mm in length was cut off and cold rolled by the general method into a plate 3.5 mm in thickness, and this was used as a steel stock and examined for tensile properties and corrosion resistance.

[0116] That is to say, a tensile test piece with a diameter of 3 mm and a gauge length of 15 mm was cut off from the above mentioned 3.5 mm thick plate and subjected to a tensile test at room temperature in the atmosphere to measure the yield strength (YS) and the elongation (El).

[0117] A four-point bending corrosion test piece 10 mm in width, 2 mm in thickness and 75 mm in length, having a notch part with radius of 0.25 mm, was produced from the 3.5 mm thick plate, and the corrosion resistance, namely, the stress corrosion cracking resistance in a sour gas environment in the following condition was evaluated.

Test solution: 20% NaCl - 0.5% CH_3COOH,
Test gas: Hydrogen sulfide partial pressure 1013250. Pa - carbon dioxide partial pressure 2026500 Pa (10 atm H_2S 20 atm CO_2),
Test temperature: 177°C,
Dipping time: 1000 hours
Applied stress: $1 \times YS$.

[0118] The tensile test results and the corrosion test results are collectively shown in Table 6. In Table 6, the marks "○" and "×" of the column of corrosion resistance (stress corrosion cracking resistance in sour gas environment) mean that no cracks were observed and that cracks were observed, respectively. The mark "-", in the columns of tensile properties and corrosion resistance for the alloys a to ○, means that no test was carried out because of the absence of pierced and rolled pipe stocks having the evaluation of "○○" for cracks and flaws.

[Table 6]

[0119]

Table 6

Alloy	Cracks and flaws on the pipe stock for following pipe expansion ratio H				Tensile properties		Corrosion resistance (stress corrosion resistance in sour gas environment)
	1.09	1.36	1.64	1.74	Yield strength [YS] (MPa)	Elongation [El] (%)	
1	○	○○	○○	○○	820	28.3	○
2	○○	○○	○○	○○	861	26.7	○
3	○○	○○	○○	○○	859	30.3	○
4	○○	○○	○○	○○	1023	25.3	○

(continued)

Alloy	Cracks and flaws on the pipe stock for following pipe expansion ratio H				Tensile properties		Corrosion resistance (stress corrosion resistance in sour gas environment)
	1.09	1.36	1.64	1.74	Yield strength [YS] (MPa)	Elongation [El] (%)	
5	○○	○○	○○	○○	977	24.7	○
6	○○	○○	○○	○○	883	27.7	○
7	○○	○○	○○	○○	921	24.7	○
8	○	○○	○○	○○	1006	22.3	○
9	○○	○○	○○	○○	833	30	○
10	○○	○○	○○	○○	856	27.7	○
11	○○	○○	○○	○○	902	25.3	○
12	○○	○○	○○	○○	844	24.3	○
13	○○	○○	○○	○○	878	28	○
14	○○	○○	○○	○○	865	26.3	○
15	○○	○○	○○	○○	910	24.7	○
16	○○	○○	○○	○○	847	25.3	○
17	○	○○	○○	○○	926	27.3	○
18	○○	○○	○○	○○	870	26	○
19	○	○○	○○	○○	941	23.3	○
20	○○	○○	○○	○○	1056	24.7	○
21	○○	○○	○○	○○	932	27.3	○
22	○○	○○	○○	○○	867	26.6	○
23	○○	○○	○○	○○	1024	22.7	○
* a	×	○	○	○	-	-	-
* b	×	×	○	○	-	-	-
* c	×	×	×	○	-	-	-
* d	×	×	×	○	-	-	-
* e	×	×	×	○	-	-	-
* f	×	×	×	○	-	-	-
* g	×	×	×	○	-	-	-
* h	Δ	○	○	○	-	-	-
* i	×	×	○	○	-	-	-
* j	Δ	Δ	Δ	Δ	-	-	-
* k	Δ	Δ	Δ	Δ	-	-	-
* l	Δ	Δ	Δ	Δ	-	-	-
* m	×	×	×	○	-	-	-
* n	×	Δ	○	○	-	-	-
* o	×	×	×	○	-	-	-
* p	○	○○	○○	○○	806	29.3	×
* q	Δ	○○	○○	○○	921	21.3	×

A mark "-" in the columns of tensile properties and corrosion resistance means that no tests were carried out because of absence of pierced and rolled pipe stock having the evaluation of "○○" for cracks and flaws.

A mark * indicate the alloy whose chemical compositions are falling outside the conditions specified by the present invention.

[0120]   As is apparent from Table 6, when the alloys 1 to 23, which are the Fe-Ni alloys according to the present invention, are used, the examination results for cracks and flaws after piercing and rolling was "○○" in most cases, with a slight number of cases with "○". That is to say, these alloys are excellent in surface property with no cracks and only small flaws.

[0121]   Further, the examination results for tensile properties and corrosion resistance in the use of the alloys 1 to 23 were satisfactory. That is to say, these alloys are excellent in strength and toughness with a large YS exceeding 800

MPa and a large elongation exceeding 20%, and also excellent in the corrosion resistance in the said severe sour gas environment.

[0122] Consequently, it is apparent that seamless pipes excellent in the corrosion resistance in a sour gas environment in addition to excellent mechanical properties can be mass-produced on an industrial scale by using the pipe stocks obtained by piercing and rolling billets of the Fe-Ni alloys according to the present invention by the general method.

[0123] In contrast to this, the examination results for cracks and flaws after piercing and rolling in the use of the alloy p, that is an alloy of comparative example, were "○○" or "○". That is to say, it is excellent in surface properties with no cracks and only small flaws. However, the corrosion test results thereof was "×", which apparently shows that the corrosion resistance in the said severe sour gas environment was poor.

[0124] The examination results for cracks and flaws after piercing and rolling in the use of the alloy q, that is an alloy of comparative examples, where "○○" or "Δ". That is to say, it shows that large flaws were present in spite of absence of cracks. And the corrosion resistance test result thereof was "×", which apparently shows that the corrosion resistance in the said severe sour gas environment was also poor.

[0125] In the use of the alloys a to ○, which are the alloys of comparative examples, the examination results for cracks and flaws after piercing and rolling were "○" at most. That is to say, the piercing and rolling thereof caused large flaws although no cracks was caused. Therefore, it is apparent that, even if the pipe stocks obtained by piercing and rolling billets of such alloys by the general method are used, seamless pipes excellent in the corrosion resistance in a sour gas environment in addition to excellent mechanical properties cannot be mass-produced on an industrial scale.

[Example 2]

[0126] An Fe-Ni alloy having a chemical composition, equivalent to that of the alloy 3 in Table 1, was melted by use of real equipment, and then bloomed and rolled to produce five billets 147 mm in diameter. The chemical composition of this Fe-Ni alloy is shown in Table 7.

[Table 7]

[0127]

Table 7

Chemical composition (% by mass) Balance: Fe and impurities												
C	Si	Mn	P	S	Cr	Ni	Mo	W	Mo+0.5W	Cu	Al	N
0.015	0.35	0.61	0.011	0.0023	25.83	38.01	3.03	-	3.03	0.81	0.038	0.041

Value of T_{GBm}		Value of P_{sr}		Value of P_{σ}	
1303.8		72.4		8.6	

[0128] Each billet was heated to 1230°C and made into a pipe by use of real equipment in a condition shown in Table 8 to produce a pipe stock with outer diameter of 235 mm and thickness of 15 mm. Since the pipe expansion ratio H in piercing and rolling of this case is 1.5, the value of in represented by the said equation (4) is 0.193856. As a piercer plug suitable for piercing and rolling of Fe-Ni alloys, one made of a material consisting of 0.5% Cr 1.0%. Ni-3.0% W series with a tensile strength at 900°C of 90 MPa and a total scale thickness before use of 600 μm was used.

[Table 8]

[0129]

Table 8

Piercing and rolling condition by real equipment	
Roll cross angle	7 deg.
Roll feed angle	9 deg.
Draft rate	10.7%
Plug tip draft rate	6%

[0130] The five pipe stocks were examined for the cracks and flaws, namely, for the two-piece cracks resulting from the intergranular fusion, the inside surface scabs, and the inside surface cracks and the scabs on both the inside and outside surface resulting from the sigma phase formation. Consequently, each pipe stock could be conformed to have satisfactory surface properties free from cracks and flaws.

[0131] Each of the said five pipe stocks was cold drawn at 30% in terms of the reduction in the cross-sectional area and then carried out a solution heat treatment of heating to 1090°C followed by water cooling, and further subjected to a cold drawing of 30% in terms of the reduction in the cross-sectional area.

[0132] The same tensile test pieces and corrosion test pieces as in Example 1 were cut off from the longitudinal direction of the thus-obtained pipes, and examined for tensile properties and corrosion resistance.

[0133] That is to say, a tensile test piece with a diameter of 3 mm and a gauge length of 15 mm was cut off from the longitudinal direction of each pipe, and subjected to a tensile test at room temperature in the atmosphere to measure the yield strength (YS) and the elongation (El).

[0134] A four-point bending corrosion test piece 10 mm in width, 2 mm in thickness and 75 mm in length, having a notch part with radius of 0.25 mm, was produced from the said pipe, and the corrosion resistance, namely, the stress corrosion cracking resistance in a sour gas environment in the following condition was evaluated.

Test solution: 20% NaCl - 0.5% CH_3COOH,
Test gas: Hydrogen sulfide partial pressure 1013250 Pa - carbon dioxide partial pressure 2026500 Pa (10 atm H_2S - 20 atm CO_2),
Test temperature: 177°C,
Dipping time: 1000 hours
Applied stress: 1 × YS.

[0135] The tensile test results and corrosion resistance test results are collectively shown in Table 9. In Table 9, the mark "○" of the column of corrosion resistance (stress corrosion cracking resistance in sour gas environment) means that no cracks were observed.

[Table 9]

[0136]

Table 9

Pipe	Tensile properties		Corrosion resistance (stress corrosion resistance in sour gas environment)
	Yield strength [YS] (MPa)	Elongation [El] (%)	
1	881	28.1	○
2	869	27.5	○
3	875	24,6	○
4	892	28.3	○
5	880	27.7	○

[0137] As is apparent from Table 9, each pipe has satisfactory strength and ductility, and further extremely satisfactory corrosion resistance.

INDUSTRIAL APPLICABILITY

[0138] The Fe-Ni alloy pipe stocks of the present invention have excellent inside surface properties. Therefore, the pipe stocks can be manufactured into seamless pipes of desired dimensions by working them by the general method, for example, by expanding the diameter by use of an elongator, such as a mandrel mill, a plug mill, an Assel mill or a push bench to reduce the wall thickness, and then by narrowing the outer diameter by use of a reducing mill, such as a stretch reducing mill or a sizing mill. The resulting seamless pipes have excellent mechanical properties and moreover have excellent corrosion resistance in a sour gas environment, and thus, the Fe-Ni alloy pipe stocks of the present invention can be used as pipe stocks for oil country tubular goods and line pipes and further as pipe stocks for various structural members of nuclear power plants and chemical industrial plants. The Fe-Ni alloy pipe stocks can be easily mass-produced at a low cost by the method discussed in the present invention.

Claims

1. An Fe-Ni alloy seamless pipe stock, having a chemical composition consisting of, by mass %,

    • C: not more than 0.04%,
    • Si: not more than 0.50%,
    • Mn: 0.01 to 6.0%,
    • P: not more than 0.03%,
    • S: not more than 0.01 %,
    • Cr: 20 to 30%,
    • Ni 30 to 45 %,
    • Mo: 0 to 10 %,
    • W: 0 to 20%,
    • Cu: 0.01 to 1.5%,
    • Al: not more than 0.10%,
    • N: 0.0005 to 0.20%,

    and optionally one or more elements selected from among

    • V: 0.001 to 0.3%,
    • Nb: 0.001 to 0.3%,
    • Ta 0.001 to 1.0%,
    • Ti: 0.001 to 1.0%,
    • Zr: 0.001 to 1.0%,
    • Hf: 0.001 to 1.0%,
    • B: 0.0001 to 0.015%,
    • Co: 0.3 to 5.0%,
    • Mg: 0.0001 to 0.010%,
    • Ca: 0.0001 to 0.010%,
    • La: 0.0001 to 0.20%,
    • Ce: 0.0001 to 0.20%,
    • Y: 0.0001 to 0.40%,
    • Sm: 0.0001 to 0.40%,
    • Pr: 0.0001 to 0.40% and
    • Nd: 0.0001 to 0.50%;

    the balance being Fe and impurities,
    with Mo(%) + 0.5W(%): more than 1.5% to not more than 10%, and with values of T_{GBm}, P_{sr} and P_{σ} represented by the following equations (1) to (3) being not less than 1300, not more than 90 and not less than 0, respectively, and moreover being subjected to piercing and rolling by a Mannesmann piercing and rolling mill:

$$T_{GBm} = 1440 - 6000P - 100S - 2000C \qquad \ldots(1),$$

$$P_{sr} = Ni + 10(Mo + 0.5W) + 100N \qquad \ldots(2),$$

$$P_{\sigma} = (Ni - 35) + 10(N - 0.1) - 2(Cr - 25) - 5(Mo + 0.5W - 3) + 8 \quad \ldots(3),$$

    wherein each element symbol in the equations (1) to (3) represents the content by mass% of the element concerned.

2. An Fe-Ni alloy seamless pipe stock according to claim 1, wherein the Mn content is 0.01 to 1.0%.

3. The Fe-Ni alloy seamless pipe stock according to claim 1 or 2 which has the chemical composition according to claim 1 or 2, with the value of fn represented by the following equation (4) being not more than 1:

$$fn = \{P / (0.025H - 0.01)\}^2 + \{S / (0.015H - 0.01)\}^2 \qquad ...(4),$$

wherein P and S represent contents, by mass %, of P and S in the pipe stock, respectively, and H represents the pipe expansion ratio represented by the ratio of the outer diameter of the pipe stock to the diameter of a steel stock billet.

4. An Fe-Ni alloy seamless pipe, manufactured by use of the Fe-Ni alloy seamless pipe stock according to any one of claims 1 to 3.

Patentansprüche

1. Nahtloses Fe-Ni-Legierung-Rohrohr mit einer chemischen Zusammensetzung bestehend, bezogen auf Masse-%, aus

  • C: nicht mehr als 0,04 %,
  • Si: nicht mehr als 0,50 %,
  • Mn: 0,01-6,0 %,
  • P: nicht mehr als 0,03 %,
  • S: nicht mehr als 0,01 %,
  • Cr: 20-30 %,
  • Ni: 30-45%,
  • Mo: 0-10 %,
  • W: 0-20 %,
  • Cu: 0,01-1,5 %,
  • Al: nicht mehr als 0,10 %,
  • N: 0,0005-0,20,

und gegebenenfalls einem oder mehreren Elementen, die ausgewählt sind aus

  • V: 0,001-0,3%,
  • Nb: 0,001-0,3%,
  • Ta: 0,001-1,0 %,
  • Ti: 0,001-1,0 %,
  • Zr: 0,001-1,0 %,
  • Hf 0,001-1,0 %,
  • B: 0,0001-0,15 %,
  • Co: 0,3-5,0 %,
  • Mg:0,0001-0,010%,
  • Ca: 0,0001-0,010 %,
  • La: 0,0001 bis 0,20 %,
  • Ce: 0,0001-0,20 %,
  • Y: 0,0001-0,40 %,
  • Sm: 0,0001 bis 0,40 %
  • Pr: 0,0001-0,40 % und
  • Nd: 0,0001-0,50 %,

wobei der Rest Fe und Verunreinigungen ist,
mit Mo(%) +0,5W(%): mehr als 1,5 % bis nicht mehr als 10 %, und wobei die Werte von T_{GBm}, P_{sr} und P_σ, die durch die folgenden Gleichungen (1) bis (3) dargestellt sind, nicht weniger als 1300, nicht mehr als 90 bzw. nicht weniger als 0 betragen, und das ferner durch ein Mannesmann-Hohlwalzwerk folgendem unterzogen wird:

$$T_{GBm,} = 1440\text{-}6000P\text{-}100S\text{-}2000C \qquad (1)$$

$$P_{Sr} = Ni+10(Mo+0,5W)+100N \qquad (2)$$

$$P_\sigma = (Ni-35) + 10(N-0,1)-2(Cr-25)-5(Mo+0,5W-3)+8 \quad (3)$$

wobei jedes Elementsymbol in den Gleichungen (1) bis (3) den Gehalt in Masse-% des betroffenen Elements darstellt.

2. Nahtloses Fe-Ni-Legierung-Rohrohr nach Anspruch 1, wobei der Mn-Gehalt 0,01 bis 1,0 % beträgt.

3. Nahtloses Fe-Ni-Legierung-Rohrohr nach Anspruch 1 oder 2, das die chemische Zusammensetzung nach Anspruch 1 oder 2 aufweist, wobei der Wert, der durch die folgende Gleichung (4) dargestellt ist, nicht mehr als 1 beträgt:

$$fn = \{P/(0,025H-0,01)\}^2 + \{S/(0,015H-0,01)\}^2 \qquad (4)$$

wobei P bzw. S die Gehalte, in Masse-%, von P bzw. S in dem Rohrohr darstellen und H das Ausdehnungsverhältnis darstellt, das durch das Verhältnis des Außendurchmessers des Rohrohrs zum Durchmesser eines Stahlrohknüppels dargestellt ist.

4. Nahtloses Rohrohr aus Fe-Ni-Legierung, hergestellt durch die Verwendung des nahtlosen Fe-Ni-Legierung-Rohrohrs nach einem der Ansprüche 1 bis 3.

Revendications

1. Matière première de tuyau sans soudure en alliage de Fe-Ni, ayant une composition chimique constituée, en % en masse, de :

• C : pas plus de 0,04 %,
• Si : pas plus de 0,50 %,
• Mn: 0,01 à 6,0 %,
• P : pas plus de 0,03 %,
• S : pas plus de 0,01 %,
• Cr : 20 à 30 %,
• Ni : 30 à 45 %,
• Mo : 0 à 10 %,
• W : 0 à 20 %,
• Cu : 0,01 à 1,5 %,
• Al : pas plus de 0,10 %,
• N : 0,0005 à 0,20 %,

et éventuellement un ou plusieurs éléments choisis parmi

• V : 0,001 à 0,3 %,
• Nb : 0,001 à 0,3 %,
• Ta : 0,001 à 1,0 %,
• Ti : 0,001 à 1,0 %,
• Zr : 0,001 à 1,0 %,
• Hf : 0,001 à 1,0 %,
• B : 0,0001 à 0,015 %,
• Co : 0,3 à 5,0 %,
• Mg : 0,0001 à 0,010 %,
• Ca : 0,0001 à 0,010 %,
• La : 0,0001 à 0,20 %,

• Ce : 0,0001 à 0,20 %,
• Y : 0,0001 à 0,40 %,
• Sm : 0,0001 à 0,40 %,
• Pr : 0,0001 à 0,40 %, et
• Nd : 0,0001 à 0,50 % ;

le reste étant du Fe et des impuretés,
avec Mo (%) + 0,5W (%) : de plus de 1,5 % à au plus 10 %, et avec les valeurs de T_{GBm}, P_{sr} et P_σ, représentées par les équations (1) à (3), qui sont respectivement d'au moins 1300, d'au plus 90 et d'au moins 0, et en outre qui est soumise à une perforation et un laminage par un laminoir perceur Mannesmann :

$$T_{GBm} = 1440 - 6000P - 100S - 2000C \qquad ... (1)$$

$$P_{sr} = Ni + 10(Mo + 0,5W) + 100N \qquad ... (2)$$

$$P_\sigma = (Ni - 35) + 10(N - 0,1) - 2(Cr - 25) - 5(Mo + 0,5W - 3) + 8 \qquad ...(3)$$

où chaque symbole d'élément dans les équations (1) à (3) représente la teneur, en % en masse, en l'élément concerné.

2. Matière première de tuyau sans soudure en alliage de Fe-Ni selon la revendication 1, dans laquelle la teneur en Mn est de 0,01 à 1,0 %.

3. Matière première de tuyau sans soudure en alliage de Fe-Ni selon la revendication 1 ou 2 qui a une composition chimique selon la revendication 1 ou 2, avec la valeur de fn, représentée par l'équation (4) suivante, qui est d'au plus 1 :

$$fn = \{P / (0,025H - 0,01)\}^2 + \{S / (0,015\,H - 0,01)\}^2 \qquad ... (4)$$

où P et S représentent les teneurs, en % en masse, en P et S de la matière première de tuyau, respectivement, et H représente le rapport d'expansion de tuyau représenté par le rapport du diamètre extérieur de la matière première de tuyau au diamètre d'une billette en matière première d'acier.

4. Tuyau sans soudure en alliage de Fe-Ni fabriqué par utilisation de la matière première de tuyau sans soudure en alliage de Fe-Ni de l'une quelconque des revendications 1 à 3.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- GB 2105368 A **[0011]**
- JP 4110419 A **[0012]**
- US 4168188 A **[0012]**
- US 4245698 A **[0012]**
- WO 03044239 A **[0012]**
- JP 11302801 A **[0012]**
- JP 2000301212 A **[0012]**

Non-patent literature cited in the description

- **TOMIO YAMAKAWA ; CHIHIRO HAYASHI.** *CAMP-ISIJ,* 1993, vol. 6, 364 **[0012]**