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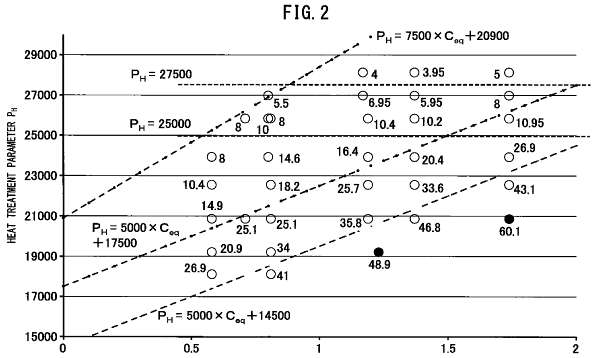
(54) PIERCER PLUG MATERIAL FOR PRODUCING SEAMLESS STEEL TUBE, AND METHOD FOR PRODUCING SAID MATERIAL

(57) The present invention relates to a piercer plug which is used when using the Mannesmann process to manufacture seamless steel pipe, more particularly relates to a material for piercer plug for manufacturing seamless steel pipe which is excellent in season cracking resistance and machinability and a method of manufacturing the same. The material for piercer plug comprises as components, by mass%, C: 0.08 to 0.3%, Si: 0.1 to 1.0%, Mn: 0.2 to 1.5%, Ni: 0.2 to 2.0%, and, furthermore, one or both of W and Mo in a total of 1.5% to 8%, a balance of Fe and impurities, wherein the amount of diffusible hydrogen which is contained as an impurity is in 2 ppm or less. The material for piercer plug has a hardness between HRC 6 and 10.

FIG. 2



EP 2 902 522 A1

Description

[Technical Field]

[0001] The present invention relates to a piercer plug which is used when using the Mannesmann process to manufacture seamless steel pipe (sometimes simply referred to as a "plug"), more particularly relates to a material for piercer plug for manufacturing seamless steel pipe which is excellent in season cracking resistance and machinability and a method of manufacturing the same.

[Background Art]

[0002] In recent years, the environment for oil exploration has become tougher. Along with this, as OCTG (Oil Country Tubular Goods), stainless steel or high alloy steel or other high grade seamless steel pipe has come to be sought. However, when using stainless steel or other high deformation resistance material to manufacture seamless steel pipe, a high contact pressure is applied to the tip of the piercer plug which is used for piercing, the tip is melted, and replacement in a short time is forced.

[0003] For this reason, as disclosed in PLT 1, conventional piercer plugs for manufacturing high grade seamless steel pipe have had W and Mo added to raise the high temperature deformation resistance. Furthermore, to obtain lubricity of the piercer plug surface, the surface has been treated to form a hard-removable low melting point scale layer. The method of manufacturing a piercer plug which is disclosed in PLT 1, as shown in FIG. 3, is characterized by heat treating by high temperature oxidation a base material which is comprised of high strength steel containing W and Mo and which has a predetermined shape so as to cover the surface of a piercer plug with such a predetermined scale layer.

[0004] On the other hand, due to the diversification of sizes and shapes of high grade seamless steel pipe, piercer plugs also have diversified to match them. Large numbers of types are being held as stock and used in accordance with production plans.

[0005] To deal with the diversification of shapes of seamless steel pipe, it has become desirable for piercer plugs to be able to be easily cut into various dimensions.

[0006] Further, plants for manufacturing seamless steel pipe are increasingly dispersed and built at distant locations. Transport times are increasing etc., so from the viewpoint of obtaining inventories, piercer plugs are often stored for longer time.

[0007] From the above situation, it is desirable that the piercer plugs or materials for piercer plug is excellent in machinability and further can be stored for a long period of time. However, if not suitably adjusting the hardness of the piercer plug, during storage, the piercer plug surface suffers from cracks called "season cracking". In particular, it is known that season cracking easily occurs in the winter season. Piercer plugs suffering from "season cracking" cannot be used for manufacturing seamless steel pipe.

[Citations List]

[Patent Literature]

[0008]

PLT 1: Japanese Patent No. 2683861
PLT 2: Japanese Patent No. 2952382
PLT 3: Japanese Patent Publication No. 2003-129184A
PLT 4: PCT International Application WO2008-096708A
PLT 5: Japanese Patent Publication No. 63-69948A
PLT 6: Japanese Patent No. 4279350

[Summary of Invention]

[Technical Problem]

[0009] PLT 1 discloses a piercer plug which is comprised of predetermined components for raising the high temperature deformation resistance plus a large amount of at least one of Mo and W added to suppress surface decarburization and form an internal oxide type scale layer on the surface.

[0010] PLT 2 discloses a method of manufacturing a piercer plug which is comprised of a 3Ni-1Cr steel or other steel base member on the surface of which scale is formed, wherein the steel base member is fabricated by casting using conventional sand mold casting. Further, the method of manufacturing the same is described as improving the strength of the steel base member and having the effect of improving the scale.

[0011] PLT 3, like PLT 2, discloses a base member of a piercer plug which scale is formed on surface thereof and the strength of the base member is improved and there is an effect of improving the scale.

[0012] PLT 4, like PLT 2, discloses a piercer plug which is comprised of a base material on the surface of which a scale is formed wherein a net-like scale layer which is intertwined with the base material is formed as the layer which forms the scale layer. PLT 4 discloses that by the above configuration of the scale layer, peeling or wear of the scale layer is suppressed and the piercer plug can be extended in lifetime.

[0013] PLT 5 discloses that by using a technique similar to PLT 4 so as to form a scale layer as an intergranular oxidation type scale layer, the adhesion with the base material becomes good, peeling or wear of the scale layer is suppressed, and the piercer plug can be extended in lifetime.

[0014] Recently, as disclosed in PLT 6, a coating forming technique utilizing thermal spraying is used to form a protective coating on the surface of the piercer plug to thereby promote longer lifetime of the piercer plug.

[0015] However, in the prior art references, no proposal has been made dealing with the season cracking or machinability of a material for piercer plug.

[0016] Therefore, an object of the present invention is to solve the problem unable to be solved by the prior art of providing a material for a piercer plug which is used when manufacturing seamless steel pipe by the Mannesmann process wherein occurrence of season cracking by long term storage is suppressed, wherein machinability is also excellent, and, furthermore, and the piercer plug has the desired hardness whereby the plug body can be made longer in life.

[Solution to Problem]

[0017] The inventors engaged in intensive research and development for solving the above problem and as a result obtained the following discoveries.

(a) To extend the lifetime of the piercer plug, a certain degree of hardness for obtaining the toughness while strengthening against thermal shock is necessary. For this reason, it was learned that if making the structure one mainly comprised of tempered martensite and/or bainite and the hardness of the plug material is a Rockwell hardness C scale (hereinafter, referred to as "HRC") of 6 or more (preferably 20 or more), a plug which has a suitable toughness and strength is obtained.

(b) It was discovered that season cracking is caused by hydrogen embrittlement of the material for piercer plug. At the time of season cracking, it was learned that the material of the piercer plug contains diffusible hydrogen in about 7 ppm or more and the hardness of the material is an HRC of over 40.

(c) Further, it was discovered that to suppress season cracking of the material, the concentration of the diffusible hydrogen should be made 2 ppm or less and the hardness of the material should be made an HRC of 40 or less. Further, it was confirmed that the hardness also falls, so the machinability was improved. Furthermore, it was confirmed that if an HRC of 40 or less, there is sufficient toughness as a plug material.

(d) The inventors engaged in intensive studies on the heat treatment conditions which satisfy the conditions of the above concentration of diffusible hydrogen and the HRC hardness. As a result, they discovered that the heat treatment should be performed by holding the material for piercer plug at 550 to 900°C after casting, more preferably 700 to 900°C in temperature range for 0.5 hour to not over 10 hours in time, preferably for 0.5 hour to not over 4 hours in time, then cooling by a cooling rate of 5°C/min or less. Furthermore, the inventors investigated the relationship between the heat treatment conditions (in particular the heat treatment temperature and the retention time) and hardness and discovered that it is possible to use the relationship of the heat treatment parameter (P_H) and the carbon equivalent (C equivalent) to adjust the hardness of the plug material (HRC hardness).

(e) The inventors confirmed that by establishing suitable conditions for the above heat treatment, it is possible to adjust the hardness of the material for piercer plug and possible to remove the diffusible hydrogen in the material.

(f) In the past, oxidation heat treatment had been performed after forming the plug, so the plug material before shaping was too hard and the machinability was poor. However, the plug material according to the present invention could be given suitable hardness by performing heat treatment under predetermined conditions before shaping and could be remarkably improved in machinability.

[0018] By casting the material for piercer plug, then suitably heat treating the material, it is possible to adjust the plug material to an HRC hardness of 6 to 40 and possible to reduce the diffusible hydrogen, which is the cause of season cracking, to a prescribed value or less.

[0019] The present invention was made based on these discoveries and has as its gist the following:

(1) A material for piercer plug for manufacturing seamless steel pipe according to one aspect of the present invention is a material for piercer plug for manufacturing seamless steel pipe, comprising as components, by mass%,
C: 0.08 to 0.3%,
Si: 0.1 to 1.0%,
Mn: 0.2 to 1.5%,
Ni: 0.2 to 2.0%,
furthermore, one or both of W and Mo in a total of 1.5% to 8%,
a balance of Fe and impurities, and,
diffusible hydrogen which is contained as an impurity in 2 ppm or less, and,
having a HRC6 to 40 hardness.
(2) The material for piercer plug for manufacturing seamless steel pipe according to the above (1) further comprising, by mass%, one or more of
Cu: 0.5% or less,
Cr: 1.0% or less,
Nb: 1.0% or less,
V: 1.0% or less,
Ti: 1.0% or less, and
B: 0.1% or less.
(3) The material for piercer plug for manufacturing seamless steel pipe according to the above (1) or (2) may further comprises, by mass%, one or more of
Ca: 0.5% or less,
Mg: 0.5% or less, and
REM: 0.5% or less
in a total of 0.5% or less.
(4) The material for piercer plug for manufacturing seamless steel pipe according to any one of the above (1) to (3) wherein the hardness may be HRC 20 to 40.
(5) The material for piercer plug for manufacturing seamless steel pipe according to any of the above (1) to (4) may be a cast steel material.
(6) A method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to one aspect of the present invention comprises casting a material for piercer plug which contains as components, by mass%,
C: 0.08 to 0.3%,
Si: 0.1 to 1.0%,
Mn: 0.2 to 1.5%,
Ni: 0.2 to 2.0%, and
furthermore one or both of W and Mo in a total of 1.5% to 8% and
has a balance of Fe and impurities,
performing heat treatment on the cast material for piercer plug under conditions where a heat treatment parameter P_H defined by the following formula 1 satisfies the formula 2 and formula 3, and shaping the heat treated material for piercer plug; wherein

$$P_H = T \times (22 + \log_{10} Hr) \cdots \text{formula 1}$$

$$P_H \leq 7500 \times C_{eq} + 20900 \text{ and } P_H \leq 27500 \cdots \text{formula 2}$$

$$P_H \geq 5000 \times C_{eq} + 14500 \cdots \text{formula 3},$$

and
wherein

T indicates the heat treatment temperature in units of °K, and
Hr indicates the retention time at the heat treatment temperature in units of hours, and
C_{eq} indicates the carbon equivalent defined by the following formula 4;

wherein

$$C_{eq}=C+Si/4+Mn/6+(Cu+Ni)/15+Cr/5+Mo/5 \quad \cdots \text{ formula 4,}$$

and
wherein notations of the elements express the contents of the elements by mass%.
(7) The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to (6) wherein the material for piercer plug may further contain by mass% one or more of:

Cu: 0.5% or less,
Cr: 1.0% or less,
Nb: 1.0% or less,
V: : 1.0% or less,
Ti: 1.0% or less, and
B: 0.1% or less.

(8) The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to (6) or (7) wherein the material for piercer plug may further contain, by mass%, one or more of
Ca: 0.5% or less,
Mg: 0.5% or less, and
REM: 0.5% or less
in a total of 0.5% or less.
(9) The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to any one of (6) to (8) wherein the heat treatment parameter P_H may satisfy the following formula 5:

$$P_H \leq 5000 \times C_{eq} + 17500 \text{ and } P_H \leq 25000 \quad \cdots \text{ formula 5}$$

(10) The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to any one of (6) to (9) wherein the heat treatment temperature may be 550°C to 900°C and the retention time at the heat treatment temperature may be 0.5 hour to 10 hours.
(11) The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to (10) wherein the heat treatment temperature may be 700°C to 900°C and the retention time may be 0.5 hour to 4 hours.
(12) The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to (11) may further comprise of cooling the material for piercer plug by a cooling rate of 5°C/min or less down to a 480°C or lower temperature after heat treatment.
(13) The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to any one of (6) to (12) wherein the material for piercer plug is cast steel.

[Advantageous Effects of Invention]

[0020] According to the present invention, it is possible to provide a material for piercer plug for manufacturing seamless steel pipe which is used at the time of manufacturing seamless steel pipe by the Mannesmann process and which is in particular excellent in season cracking resistance and machinability.

[Brief Description of Drawings]

[0021]

FIG. 1 is a flow chart of a method of manufacturing a material for piercer plug for manufacturing seamless steel pipe of the present invention.
FIG. 2 is a graph which shows the ranges of the heat treatment parameter P_H and carbon equivalent C_{eq} for manufacturing a material for piercer plug for manufacturing seamless steel pipe of the present invention.
FIG. 3 is a flow chart of a method of manufacturing a piercer plug which is disclosed in PLT 1.

[Description of Embodiments]

[0022] Below, the present invention will be explained in detail. Note that, the embodiments of the present invention are not limited to the embodiments which are shown below:

Components

[0023] The values of the components (%) are indicated by mass% unless otherwise indicated.

C: 0.08 to 0.3%

[0024] C is an effective component for improving the high temperature strength, but has no effect if the content is smaller than 0.08%. Further, if over 0.3%, the hardness becomes too high and season cracking more easily occurs. Further, control of the state of precipitation of carbides also becomes difficult. Therefore, C is made 0.08 to 0.3%. If considering the variation for obtaining this effect, the lower limit is preferably 0.10%, more preferably 0.12%. Further, similarly, the upper limit is preferably 0.25%, more preferably 0.20%.

Si: 0.1 to 1.0%

[0025] Si is an effective component for deoxidation, but the effect is small if smaller than 0.1%. If over 1.0%, the base material starts to deteriorate in toughness. Therefore, Si is made 0.1 to 1.0%. If considering the variation for obtaining this effect, the lower limit is preferably 0.20%, more preferably 0.30%. Further, similarly, the upper limit is preferably 0.90%, more preferably 0.80%.

Mn: 0.2 to 1.5%

[0026] Mn stabilizes the austenite at a high temperature. That is, it suppresses the formation of δ-ferrite to suppress the drop in toughness. That effect is obtained at 0.2% or more. However, if adding more than 1.5%, the hardness becomes too high and season cracking easily occurs after piercing. Therefore, Mn is made 0.2 to 1.5%. If considering the variation for obtaining this effect, the lower limit is preferably 0.30%, more preferably 0.40%. Further, similarly, the upper limit is preferably 1.30%, more preferably 1.00%.

Ni: 0.2 to 2.0%

[0027] Ni has the action of improving the toughness of the quenched phase which is formed on the surface part of the plug. To obtain this effect, 0.2% or more is necessary, but the effect becomes substantially saturated at 2.0%. The above addition becomes a factor increasing the cost. Therefore, Ni is made 0.2 to 2.0%. If considering the variation for obtaining this effect, the lower limit is preferably 0.30%, more preferably 0.40%. Further, similarly, the upper limit is preferably 1.90%, more preferably 1.80%.

One or both of Mo and W: 1.5 to 8.0%

[0028] Mo and W are both effective for improving the high temperature strength and have the effect of raising the Ac1 point to reduce the quenched part at the surface after piercing. These effects are equivalent with Mo and W. The effect becomes small if one or the total of both of Mo and W is less than 1.5%, so these are added to become greater than this. Further, if one or the total of both of Mo and W exceeds 8.0%, ferrite remains even at a high temperature, the strength starts to fall, and the toughness is also caused to fall. Accordingly, the total of Mo+W is made 1.5 to 8.0%. If considering the variation for obtaining this effect, the lower limit is preferably 1.7%, more preferably 2.0%. Further, similarly, the upper limit is preferably 7.5%, more preferably 7.0%.

Diffusible hydrogen: 2 ppm or less

[0029] The H (hydrogen) which is contained as diffusible hydrogen in the material for piercer plug is an element which aggravates the season cracking of the piercer plug, so the content has important meaning in the present invention. Diffusible hydrogen is hydrogen which diffuses in the material. Hydrogen which is trapped in voids in the material etc. is not included. Further, the method of measurement of the diffusible hydrogen will be explained in the later explained examples. The content of diffusible hydrogen should be as small as possible. The inventors discovered that if the diffusible hydrogen is 2 ppm or less, season cracking does not occur (see Table 5). For this reason, the content of the material for piercer plug according to the present invention is given an upper limit of 2 ppm. To reliably obtain the effect of suppression of season cracking, the upper limit is preferably 1.5 ppm, more preferably 1.0 ppm or less. Normally, the steel material obtained by casting contains 7 ppm or more of diffusible hydrogen. The diffusible hydrogen in the material can be reduced at the time of heat treatment holding the material at a 700 to 900°C temperature range for 0.5 hour to 4 hours. Details of the dehydrogenation will be explained in the later explained method of manufacturing the same.

One or more of Nb, V, Cr, and Ti: each 1.0% or less

[0030] Nb, V, and Ti have the effect of refining the crystal grains. However, if added over 1.0%, brittle phases precipitate and deterioration of the toughness is invited. Therefore, one or more of Nb, V, and Ti may be added in respectively 1.0% or less. If considering the variation for obtaining this effect, the upper limit is preferably 0.5%, more preferably 0.1%. Cr has the action of improving the toughness of the steel material and deformation resistance at a high temperature. However, from the economic viewpoint, the upper limit of the content is made 1.0%.

Cu: 0.5% or less

[0031] Cu is an element which stabilizes austenite and has the action of improving the toughness of the surface part of the plug which becomes austenite when held at a high temperature at the time of piercing. To obtain that effect, 0.01% or more is necessary, but the effect becomes substantially saturated at 0.5%. Therefore, Cu is made 0.5% or less. If considering the variation for obtaining this effect, the lower limit is preferably 0.01%, more preferably 0.1%. Further, similarly, the upper limit is preferably 0.5%, more preferably 0.3%.

B: 0.1% or less

[0032] B has the action of strengthening the grain boundaries of the surface layer of a steel material held at a high temperature at the time of piercing and becoming austenite and improving the high temperature deformation resistance and deformability, but if included in more than 0.1%, the toughness falls due to precipitation of brittle phases etc. If considering the variation for obtaining this effect, the upper limit is preferably 0.05%, more preferably 0.01%.

Ca, Mg, and REM: total 0.5% or less

[0033] Ca, Mg, and REM can all be added for the purpose of desulfurization etc. In particular, this is effective for grain refinement and improves the toughness of the steel material. However, if the contents in total exceed 0.5%, brittle phases precipitate and invite a drop in toughness. Therefore, the contents of these components were made a total of 0.5% or less. If considering the variation for obtaining this effect, the upper limit is preferably 0.2%, more preferably 0.1%.

Hardness

Hardness: HRC6 to 40

[0034] The hardness of the material for piercer plug of the present invention is preferably HRC6 to 40. If becoming an over HRC40 high hardness, season cracking easily occurs. On the other hand, it falling under HRC6, the piercing lifetime of the piercer plug falls. That is, due to insufficient strength, the piercer plug is liable to greatly deform at the time of piercing-rolling. The more preferable lower limit is HRC20.

Structure

[0035] The structure of the material for piercer plug is preferably tempered martensite and/or bainite. However, if just leaving the material for piercer plug in as-cast state, the structure will mainly become tempered martensite. By heat treatment after casting, the structure mainly becomes tempered martensite and/or bainite and the toughness can be obtained.

Method of Manufacturing Same

[0036] Next, the method of manufacturing the material for piercer plug according to the present invention will be explained. The material of the piercer plug according to the present invention has a hardness of HRC6 to 40 and is characterized by having a content of diffusible hydrogen limited to 2 ppm or less and by having a structure which comprises mainly tempered martensite and/or bainite. These characteristics are built by the heat treatment conditions after casting the component materials forming the piercer plug. The method of manufacturing the material for piercer plug according to the present invention, as shown in FIG. 1, first smelts steel having the above predetermined composition, then casts the steel at a casting step S1 to obtain material for piercer plug. After that, at the heat treatment step S2, it performs heat treatment for adjusting the hardness and dehydrogenating the material for piercer plug.

Heat Treatment

[0037] The heat treatment step S2 comprises heating the material for piercer plug to be heat treated up to a predetermined heat treatment temperature, holding the material for piercer plug at the heat treatment temperature for a predetermined time, and cooling the material for piercer plug after the elapse of the predetermined time. The heat treatment conditions will be explained from the viewpoint of the hardness of the material for piercer plug and the viewpoint of the concentration of diffusible hydrogen. Note that, in the present invention, the heat treatment temperature indicates the surface temperature of the material for piercer plug.

[0038] The Steel Nos. 1 to 18 of the compositions which are described in Table 1 were subject to high frequency melting and cast into molds for piercer plug (size: 160ϕ×400L). The cast steels were heat treated under the Heat Treatment Conditions 1-1 to 8-3 which are described in Table 2 to obtain the Test Piece Nos. 1 to 37 which are shown in Table 3. The results of measurement of the surface hardness (HRC) and the carbon equivalents and heat treatment parameters of the test piece are shown in Table 3. Further, the compositions of the test pieces correspond to the composition numbers of Table 1. The inventors plotted the relationship between the carbon equivalents and heat treatment parameters described in Table 3 as shown in FIG. 2 and studied the relationship between hardness (HRC) and the carbon equivalent (C equivalent).

Table 1

(mass%)											
Composition No.	C	Si	Mn	Cu	Ni	Cr	Mo	W	Ce, La	Nb	C equivalent
1	0.15	0.50	0.50	-	1.00	-	1.40	12.95	-	-	0.71
2	0.15	0.50	0.50	-	1.00	0.50	1.40	2.95	-	0.03	0.81
3	0.15	0.50	0.50	0.02	1.00	0.50	1.40	3.00	-	-	0.81
4	0.08	0.45	0.21	0.02	0.64	0.53	1.01	2.95	-	-	0.58
5	0.25	0.50	1.48	0.02	0.57	0.52	2.34	3.00	-	-	1.23
6	0.17	0.70	0.60	0.02	1.10	0.00	1.41	2.90	-	-	0.80
7	0.14	0.50	0.50	0.02	0.90	0.52	1.42	3.00	0.05	-	0.80
8	0.15	0.50	0.52	-	1.00	0.50	1.40	3.20	-	-	0.81
9	0.15	0.50	0.49	-	1.00	0.47	1.40	3.00	0.05	-	0.80
10	0.10	0.50	0.22		0.50	0.50	2.05	3.00	-	-	0.81
11	0.10	0.45	0.21	0.02	0.48	0.47	1.05	3.10	-	-	0.58
12	0.25	0.60	1.45	0.02	0.50	0.52	2.05	3.10	-	-	1.19
13	0.29	0.50	0.90	0.02	1.00	0.97	1.80	3.50	-	-	1.19
14	0.29	0.60	0.40	-	2.00	0.95	1.70	3.40	-	-	1.17
15	0.28	0.70	1.32	-	1.50	0.99	2.00	3.90	-	-	1.37
16	0.15	0.45	0.30	-	1.00	0.49	0.51	4.00	-	-	0.58
17	0.29	0.80	1.49	-	1.50	0.99	3.50	4.10	-	-	1.74
18	0.16	0.55	0.70	-	1.20	0.55	2.95	4.00	-	-	1.19

Table 2

Heat treatment condition	Retention temperature (°C)	Retention time (Hr)	Cooling condition
Condition 1-2	950	10	2
Condition 2-1	900	10	1
Condition 3-1	870	4	1
Condition 3-2	870	4	2
Condition 4-2	800	2	2
Condition 5-2	730	3	2
Condition 6-1	650	4	1
Condition 6-3	650	4	3
Condition 7-2	600	1	2
Condition 8-3	550	1	3

Cooling Condition 1: Retaining material for piercer plug in furnace at retention temperature (°C) for retention time (Hr), then furnace cooling by 2°C/min average cooling rate down to room temperature (25°C).
Cooling Condition 2: Retaining material for piercer plug in furnace at retention temperature (°C) for retention time (Hr), then furnace cooling by 2°C/min average cooling rate down to 480°C, then taking out material for piercer plug from furnace and allowing the material to naturally cool in air.
Cooling Condition 3: Retaining material for piercer plug in furnace at retention temperature (°C) for retention time (Hr), then taking out material for piercer plug from furnace and allowing the material to naturally cool in air.

Table 3

Test Piece No.	Composition (Composition No. of Table 1)	Carbon equivalent (C equivalent)	Heat treatment condition (see Table 2)	Heat treatment parameter (P_H)	Surface hardness (HRC)
1	4	0.58	4-2	23929	8.0
2	4	0.58	5-2	22545	10.4
3	11	0.58	6-1	20862	14.9
4	11	0.58	7-2	19206	20.9
5	16	0.58	8-3	18106	26.9
6	1	0.71	3-1	25834	8.0
7	1	0.71	3-2	25834	8.0
8	1	0.71	6-3	20861	25.1
9	2	0.81	3-1	25834	8.0
10	2	0.81	3-2	25834	8.0
11	2	0.81	6-3	20861	25.1
12	6	0.80	2-1	26979	5.5
13	7	0.80	3-2	25834	10.0
14	9	0.80	4-2	23929	14.6
15	3	0.81	5-2	22545	18.2
16	8	0.81	6-1	20862	25.1
17	10	0.81	7-2	19206	34.0

(continued)

Test Piece No.	Composition (Composition No. of Table 1)	Carbon equivalent (C equivalent)	Heat treatment condition (see Table 2)	Heat treatment parameter (P_H)	Surface hardness (HRC)
18	10	0.81	8-3	18106	41.0
19	14	1.17	1-2	28129	4.0
20	14	1.17	2-1	26979	6.95
21	12	1.19	3-2	25834	10.4
22	13	1.19	4-2	23929	16.4
23	18	1.19	5-2	22545	25.7
24	18	1.19	6-1	20862	35.8
25	5	1.23	7-2	19206	48.9
26	15	1.37	1-2	28129	3.95
27	15	1.37	2-1	26979	5.95
28	15	1.37	3-1	25834	10.2
29	15	1.37	4-2	23929	20.4
30	15	1.37	5-2	22545	33.6
31	15	1.37	6-3	20862	46.8
32	17	1.74	1-2	28129	5.0
33	17	1.74	2-1	26979	8.0
34	17	1.74	3-2	25834	10.95
35	17	1.74	4-2	23929	26.9
36	17	1.74	5-2	22545	43.1
37	17	1.74	6-3	20862	60.1

[0039] Here, the heat treatment parameter (P_H) is defined as in the following formula 1. Further, the carbon equivalent (C equivalent) has a large effect on the hardness of the steel composition, so was used as an indicator. The carbon equivalent is defined by the following formula 4.

[0040] FIG. 2 shows the relationship between the carbon equivalent (C equivalent) and the heat treatment parameter P_H. The numerical values which are attached near the white circles in FIG. 2 show the HRC values of the test pieces. From FIG. 2, the inventors discovered that to adjust the hardness of the material for piercer plug to a suitable range of HRC6 to 40 in range, the heat treatment conditions should be set so that the heat treatment parameter P_H satisfies the following formula 2 and formula 3.

$$P_H = T \times (22 + \log_{10} Hr) \quad \cdots \text{ formula 1}$$

$$P_H \leq 7500 \times C_{eq} + 20900 \text{ and } P_H \leq 27500 \cdots \text{formula 2}$$

$$P_H \geq 5000 \times C_{eq} + 14500 \cdots \text{formula 3}$$

wherein,

T indicates the heat treatment temperature in units of °K. Note that, the heat treatment temperature T is the surface temperature of the material for piercer plug. Hr indicates the retention time, that is, the time for retaining the material for piercer plug at the heat treatment temperature T in units of hours. C_{eq} indicates the carbon equivalent of the material for piercer plug and is defined by the following formula 4.

$$C_{eq}=C+Si/4+Mn/6+(Cu+Ni)/15+Cr/5+Mo/5 \quad \cdots \text{formula 4}$$

Note that, in formula 4, C, Si, P, Al, and Mn are the contents of the elements (mass%).

[0041] As shown in FIG. 2, it was learned that test pieces which have C equivalents of 0.5 to 1.8 are given HR6 to 40 hardnesses by heat treatment conditions in the ranges of formula 2 which shows the upper limit of the heat treatment parameter P_H and formula 3 which shows the lower limit. Further, if comparing a plurality of test pieces which have similar C equivalents, it will be understood that the HRC value becomes higher the lower the heat treatment parameter P_H.

[0042] Further, as shown in FIG. 2, when test pieces which have C equivalent=0.5 to 1.8 in carbon equivalent were heat treated by heat treatment conditions exceeding the upper limits defined by the formula 2, the hardnesses of the test pieces after heat treatment remained less than HRC6. Further, when heat treating test pieces which have C equivalents inside the above range by heat treatment conditions under the lower limit which is defined in formula 3, the hardnesses of the test pieces after heat treatment became over HRC40. Note that, in FIG. 2, the black dots show the occurrence of season cracking.

[0043] Further, as explained above, the hardness of the material for piercer plug after heat treatment is preferably HRC20 to 40. A material for piercer plug which has such a preferable range of hardness can be manufactured by heat treating a material for piercer plug which has a composition in the range of the above C equivalent under heat treatment conditions which include a heat treatment parameter P_H satisfying the following formula 5:

$$P_H \leq 5000 \times C_{eq}+17500 \text{ and } P_H \leq 25000 \quad \cdots \text{formula 5}$$

[0044] The heat treatment step is preferably completed within 24 hours including the temperature elevation and cooling from the viewpoint of productivity. The upper limit of the retention time Hr at the heat treatment step is preferably 10 hours or less, more preferably is 4 hours or less in time. From the above results of the test pieces, it was confirmed that by performing heat treatment at a 550°C to 900°C heat treatment temperature for 0.5 hour to 10 hours, more preferably 0.5 hour to 4 hours in retention time so that the heat treatment parameter P_H satisfies the above formula 2 and formula 3, a material for piercer plug with a C equivalent=0.5 to 1.8 in carbon equivalent has a HRC6 to 40 hardness.

[0045] In the temperature range of the heat treatment according to the present invention, the thickness of the oxide scale which was formed on the surface of the material for piercer plug was usually 100 μm or so. It was confirmed that this extent of oxide scale can be easily removed by cutting, grinding, etc.

[0046] Next, consider this from the viewpoint of the dehydrogenation of the material for piercer plug. Heat treatment comprising retaining the material at 550°C to 900°C in temperature range for 0.5 hour to 10 hours can be used to reduce the content of diffusible hydrogen in the material for piercer plug. Normally, the content of diffusible hydrogen of the material for piercer plug after casting is 7 ppm or more, but it was confirmed that if retaining the material at this temperature range for at least 0.5 hour, the content of diffusible hydrogen of the material for piercer plug becomes 2 ppm or less. The heat treatment atmosphere may be the air.

[0047] The cooling after this heat treatment is the step which determines the structure of the material for piercer plug. The structure of the material for piercer plug is suitably tempered martensite and/or bainite. However, if material for piercer plug with a carbon equivalent of 0.5 to 1.8 in range is cast, then left in as-cast state, as explained above, the structure becomes mainly tempered martensite. Therefore, to obtain toughness, a 550°C to 900°C heat treatment temperature is used for heat treatment. Further, the cooling after heat treatment also has the effect of causing the precipitated carbides to grow to a certain extent and become spheroidal. Furthermore, the state of precipitation of Mo and W appears in the hardness. That is, by suitable precipitation, the hardness can be suppressed. From the findings of the inventors, when suitably forming precipitates of Mo and W, the hardness of the material for piercer plug falls. By performing heat treatment at a 700°C to 900°C range of temperature for 0.5 hour or more, the Mo and W which form a solid solution in the material for piercer plug precipitate and the hardness falls. In this case, to obtain the desired hardness of the material for piercer plug, the material for piercer plug is preferably cooled by a 5°C/min or less cooling rate down to a 480°C or less temperature. The cooling rate is preferably a 1°C/min or less cooling rate.

[0048] The cooling rate is slow and gradual cooling. The higher the heat treatment temperature and, further, the longer the retention time, the more the hardness falls. In this way, by heat treating the material for piercer plug, it is possible to control the state of precipitation of precipitates of Mo and W and as a result control the hardness. However, if over 900°C, transformation to austenite gradually proceeds, so even with a 5°C/min or less cooling rate, the hardness sometimes rises. On the other hand, the lower limit of the cooling rate is not particularly limited, but if the cooling rate is too slow, the time of exposure to the high temperature range becomes long and a drop in hardness or coarsening of the carbides occurs. Further, in operation, the operating time in heat treatment becomes longer and a problem arises from the viewpoint of economy. For this reason, the cooling rate is preferably 0.1°C/min or more.

[0049] Note that, to realize this cooling condition, it is sufficient to cool the material for piercer plug inside the heat treatment furnace. Furnace cooling can be used for gradual cooling. For example, it is possible to cool down the furnace to 480°C or less, then take out the material for piercer plug from the furnace and allow it to cool in air. Alternatively, it is possible to cool down the furnace to room temperature, then take out the material for piercer plug from the furnace.

[0050] The natural cooling of the cooling condition 3 of Table 2 is performed from when the material for piercer plug becomes a temperature lower than 480°C, so does not affect the structure, precipitates, and hydrogen content of the material for piercer plug.

[0051] The material for piercer plug which is adjusted by the heat treatment step S2 to a HRC6 to 40 hardness is shaped by the shaping step S3 to a material for piercer plug for manufacturing seamless steel pipe which has a predetermined shape. The shaping step S3 can be cut etc. Further, the shaping step S3 may be performed right after the heat treatment step S2 or may be performed after long term storage of the material for piercer plug since no season cracking occurs.

[0052] Further, the material for piercer plug for manufacturing seamless steel pipe of the present invention can be shaped by the shaping step S3 to a predetermined tool shape, then a protective coating can be formed on its surface by various methods in a protective coating forming step S4. As the protective coating forming step S4, for example, it is possible to perform at least one type of heat treatment which forms a scale layer, treatment for coating a ceramic or other protective coating by thermal spraying, or other treatment. The method in a protective coating forming step S4 is not particularly limited.

Examples

[0053] Next, examples of the material for piercer plug according to the present invention will be explained. Steels of the compositions which are described in Table 1 were used and heat treated under predetermined heat treatment conditions to prepare examples of the present invention. The examples of the present invention were measured for amounts of hydrogen, tested for season cracking, tested for machinability, tested to evaluate toughness, and tested for plug deformation.

Measurement of Content of Diffusible Hydrogen

(1) Preparation of Measurement Samples

[0054] Test Piece No. 6 to No. 11 which are described in Table 3 were prepared as Examples 1 to 6 of the present invention which are shown in Table 4. Further, for comparison with the present invention, except for using Steel No. 1 and Steel No. 2 which were described in Table 1 and heat treating the Steel No. 1 and Steel No. 2 under the following Heat Treatment Condition A, the same manufacturing conditions as for the examples of Table 1 were used for manufacturing the materials for piercer plug of Comparative Examples 1 and 2.

Heat Treatment Condition A (Comparative Example): Natural Cooling in Air as-Cast state

[0055] From the materials for piercer plug of Examples 1 to 6 and Comparative Examples 1 and 2, $\phi 20 \times 10$ mm test pieces were cut out to prepare analysis samples for measurement of the contents of diffusible hydrogen corresponding to Examples 1 to 6 and Comparative Examples 1 and 2 (hereinafter, referred to as "H_2 analysis samples"). The H_2 analysis samples were stored immersed in liquid nitrogen right after being cut out from the materials for piercer plug.

(2) Measurement Conditions of Diffusible Hydrogen

[0056] Right before measurement of the diffusible hydrogen, the above H_2 analysis sample was taken out from liquid nitrogen and washed by ultrasonic washing. After that, the H_2 analysis sample was dried by cold air, weighed, and used for various measurements. The diffusible hydrogen which is contained in the H_2 analysis sample was measured by inserting the H_2 analysis sample in a mass spectrometry apparatus, exhausting the air for 10 minutes, then heating in a vacuum with an initial pressure at the start of measurement of about 1.4×10^{-5} Pa by a 100°C/hour (1.67°C/min) constant rate of temperature rise from room temperature to 600°C and analyzing the mass spectral intensity of hydrogen which arises at the time of heating. Further, the mass spectral intensity of hydrogen was analyzed by using a mass spectrometer (made by Canon-Anelva, quadrapole mass spectrometer M201QA-TDM).

(3) Measurement Results of Content of Diffusible Hydrogen

[0057] The measurement results of the contents of diffusible hydrogen which were measured for the H_2 analysis samples corresponding to Examples 1 to 6 and Comparative Examples 1 and 2 are shown in Table 4. If comparing Examples 1 to 6 and the comparative examples shown in Table 4 for hydrogen content, it can be confirmed that the cast steels in the scope of composition defined by the present invention were dehydrogenated by the heat treatment defined by the present invention.

Table 4

	Heat treatment condition	Composition	Hydrogen content (ppm)
Example 1	3-1	Steel No. 1	2
Example 2	3-2	Steel No. 1	1
Example 3	6-3	Steel No. 1	1
Example 4	3-1	Steel No. 2	2
Example 5	3-2	Steel No. 2	1
Example 6	6-3	Steel No. 2	1
Comp. Ex. 1	A	Steel No. 1	7
Comp. Ex. 2	A	Steel No. 2	7

Results of Season cracking Test

[0058] Twenty samples of the material for piercer plug were prepared for each of the Steel 1 and the Steel 2 under the same heat treatment conditions as the heat treatment conditions of Examples 1 to 6 and Comparative Examples 1 and 2. The number of days required until occurrence of season cracking when left in air for 30 days was investigated and the frequency of occurrence was noted. Table 5 shows the results.

[0059] Examples 1 to 6, that is, materials for piercer plug of the Heat Treatment Conditions 3-1, 3-2, and 6-3 according to the present invention, did not suffer from any season cracking at all regardless of the differences in compositions of the Steel 1 and the Steel 2 even if held for 30 days in air. On the other hand, Comparative Examples 1 and 2, that is, materials of the Heat Treatment Condition A, suffered from season cracking from 14 days. After the elapse of 30 days, 16 samples (80%) were confirmed to suffer from season cracking. No season cracking was confirmed in the materials of Heat Treatment Conditions 3-1, 3-2, and 6-3. From the above, it was confirmed that season cracking was suppressed by the dehydrogenation effect according to the present invention.

Table 5

	Heat treatment condition	Days standing		
		Within 10 days	11 to 20 days	21 to 30 days
Examples 1 and 4	Condition 3-1	0	0	0
Examples 2 and 5	Condition 3-2	0	0	0
Examples 3 and 6	Condition 6-3	0	0	0
Comp. Ex. 1 and 2	Condition A	0	7 (35%)	16 (80%)

Machinability

[0060] One each material for piercer plug of the Steel 2 heat treated under the Heat Treatment Conditions 3-1, 3-2, 6-3, and A was prepared and evaluated for machinability by the presence of any breakage of the cutting tool when drilling the core metal part of the piercer plug. The results are shown in Table 6. As shown in Table 6, under the Heat Treatment Conditions 3-1, 3-2, and 6-3, there was no breakage. However, under the Heat Treatment Condition A, breakage of the drill tip was confirmed. Actual drilling was not possible.

Table 6

	Heat treatment condition	Machinability	Remarks
Example 4	Condition 3-1	Good	No particular problem
Example 5	Condition 3-2	Good	No particular problem
Example 6	Condition 6-3	Good	No particular problem
Comp. Ex. 2	Condition A	Poor	Machining not possible due to breakage of drill tip

Evaluation of Toughness

[0061] The toughness was evaluated by a Charpy impact test at 20°C. Two each test pieces were prepared by being cut from the materials for piercer plug of Examples 1 to 6 and Comparative Examples 1 to 4 and were tested at room temperature (20°C) by a Charpy impact test. Further, for the test for evaluation of the toughness, the Test Piece No. 24 of Table 3 was used as the material for piercer plug of Example 7. The same technique as for Examples 1 to 6 and Comparative Examples 1 and 2 was used for the Charpy impact test of Example 7. The results of evaluation of toughness by the Charpy impact test are shown in Table 7. Under the Heat Treatment Conditions 3-1, 3-2, 6-1, and 6-3, the results were 17 to 70J/cm^2 in level. On the other hand, under the Condition A, the result was 5 to 7J/cm^2 in level. There was a remarkable difference from the results of Conditions 3-1, 3-2, 6-1, and 6-3 according to examples of the present invention.

Table 7

	Heat treatment condition	Composition	Charpy impact value (J/cm^2)
Example 1	3-1	Steel No. 1	50
Example 2	3-2	Steel No. 1	58
Example 3	6-3	Steel No. 1	70
Example 4	3-1	Steel No. 2	58
Example 5	3-2	Steel No. 2	70
Example 6	6-3	Steel No. 2	70
Example 7	6-1	Steel No. 18	17
Comp. Ex. 1	A	Steel No. 1	7
Comp. Ex. 2	A	Steel No. 2	5

Plug Deformation Test

(1) Formation of Thermal Sprayed Coating

[0062] Steel of each composition which is described in Table 8 was melted by high frequency induction heating and was cast using a piercer plug mold (size: 160ϕ×400L). Each cast steel, as shown in Table 8, was heat treated by the heat treatment condition which is described in Table 2. Examples A1 to A4 and Comparative Examples B1 and B2 were obtained. One each material for piercer plug of Examples A1 to A4 and Comparative Examples B1 and B2 was prepared. The entire surface of the base material was formed with a protective coating by thermal spraying an iron-based material.

(2) Piercing-rolling

[0063] Using as a model piercer (test-use piercer) each piercer plug, the following round billet heated to 1200°C was shaped by rotary piecing. Each plug was used for piercing-rolling five times, then the size of deformation of the tip of the plug from the initial shape was measured as the amount of deformation. The results are shown in Table 8.

· Dimensions of billet: outside diameter 75 mm, length 700 mm
· Material of billet: SUS304
· Dimensions of plug: outside diameter 60 mm

Table 8

	Heat treatment condition (see Table 2)	Composition of steel (Composition of Table 1)	HRC	Deformation (mm)
Example A1	5-2	No. 15	33.6	0.80
Example A2	6-1	No. 18	35.8	0.80
Example A3	7-2	No. 11	20.9	1.10
Example A4	3-1	No. 1	8.0	1.40
Comp. Ex. B1	1-2	No. 14	4.0	2.25
Comp. Ex. B2	1-2	No. 15	3.95	2.35

[0064] Examples A1 to A4 have hardnesses in the range of the present invention, so the amount of deformation of the plug after five repeated piercing-rolling operations is small. As opposed to this, Comparative Examples B1 and B2 have hardnesses of less than HRC6, so the amount of deformation of the plug after five repeated piercing-rolling operations is a large one of about two times. Note that, if the amount of deformation is 1.5 mm or less, the plug can be recycled.

[0065] From the above, it could be confirmed that according to the material for piercer plug according to the present invention, the occurrence of season cracking can be suppressed. Further, it was confirmed that the machinability was also good. Due to this, it became possible to deal with the diversification of seamless steel pipe, store the material on site, and work it into a suitable shape of a piercer plug.

[Industrial Applicability]

[0066] The present invention can be utilized as a material for a piercer plug for manufacturing seamless steel pipe. Further, the material for piercer plug according to the present invention can be stored for a long time and is easy to work into a suitable shape.

Claims

1. A material for piercer plug for manufacturing seamless steel pipe, comprising as components, by mass%,
   C: 0.08 to 0.3%,
   Si: 0.1 to 1.0%,
   Mn: 0.2 to 1.5%,
   Ni: 0.2 to 2.0%, and,
   furthermore, one or both of W and Mo in a total of 1.5% to 8%,
   a balance of Fe and impurities, and
   diffusible hydrogen which is contained as an impurity in 2 ppm or less, and,
   having a HRC 6 to 40 hardness.

2. The material for piercer plug for manufacturing seamless steel pipe according to claim 1 further comprising, by mass%, one or more of
   Cu: 0.5% or less,
   Cr: 1.0% or less,
   Nb: 1.0% or less,
   V: 1.0% or less,
   Ti: 1.0% or less, and
   B: 0.1% or less.

3. The material for piercer plug for manufacturing seamless steel pipe according to claim 1 or 2, further comprising, by mass%, one or more of
   Ca: 0.5% or less,
   Mg: 0.5% or less, and
   REM: 0.5% or less
   in a total of 0.5% or less.

4. The material for piercer plug for manufacturing seamless steel pipe according to any one of claims 1 to 3 wherein the hardness is HRC 20 to 40.

5. The material for piercer plug for manufacturing seamless steel pipe according to any of claims 1 to 4 wherein said material for piercer plug is cast steel.

6. A method of manufacturing a material for piercer plug for manufacturing seamless steel pipe comprising casting a material for piercer plug which contains as components, by mass%,
C: 0.08 to 0.3%,
Si: 0.1 to 1.0%,
Mn: 0.2 to 1.5%,
Ni: 0.2 to 2.0%, and
furthermore one or both of W and Mo in a total of 1.5% to 8% and
has a balance of Fe and impurities,
performing heat treatment on the cast material for piercer plug under conditions where a heat treatment parameter P_H defined by the following formula 1 satisfies the formula 2 and formula 3, and
shaping the heat treated material for piercer plug;
wherein

$$P_H = T \times (22 + \log_{10} Hr) \quad \cdots \text{ formula 1}$$

$$P_H \leq 7500 \times C_{eq} + 20900 \text{ and } P_H \leq 27500 \cdots \text{formula 2}$$

$$P_H \geq 5000 \times C_{eq} + 14500 \cdots \text{formula 3,}$$

and
wherein

T indicates the heat treatment temperature in units of °K, and
Hr indicates the retention time at the heat treatment temperature in units of hours, and
C_{eq} indicates the carbon equivalent defined by the following formula 4;

wherein

$$C_{eq} = C + Si/4 + Mn/6 + (Cu+Ni)/15 + Cr/5 + Mo/5 \quad \cdots \text{ formula 4,}$$

and
wherein notations of the elements express the contents of the elements by mass%.

7. The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to claim 6 wherein the material for piercer plug further contains by mass% one or more of:
Cu: 0.5% or less,
Cr: 1.0% or less,
Nb: 1.0% or less,
V: : 1.0% or less,
Ti: 1.0% or less, and
B: 0.1% or less.

8. The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to claim 6 or 7 wherein the material for piercer plug further contains, by mass%, one or more of
Ca: 0.5% or less,
Mg: 0.5% or less, and
REM: 0.5% or less

in a total of 0.5% or less.

9. The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to any one of claims 6 to 8 wherein the heat treatment parameter P_H satisfies the following formula 5:

$$P_H \leq 5000 \times C_{eq} + 17500 \text{ and } P_H \leq 25000 \cdots \text{formula 5}$$

10. The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to any one of claims 6 to 9 wherein the heat treatment temperature is 550°C to 900°C and the retention time at the heat treatment temperature is 0.5 hour to 10 hours.

11. The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to claim 10 wherein the heat treatment temperature is 700°C to 900°C and the retention time is 0.5 hour to 4 hours.

12. The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to claim 11 which further comprises cooling the material for piercer plug by a cooling rate of 5°C/min or less down to a 480°C or lower temperature after heat treatment.

13. The method of manufacturing a material for piercer plug for manufacturing seamless steel pipe according to any one of claims 6 to 12 wherein the material for piercer plug is cast steel.

FIG. 1

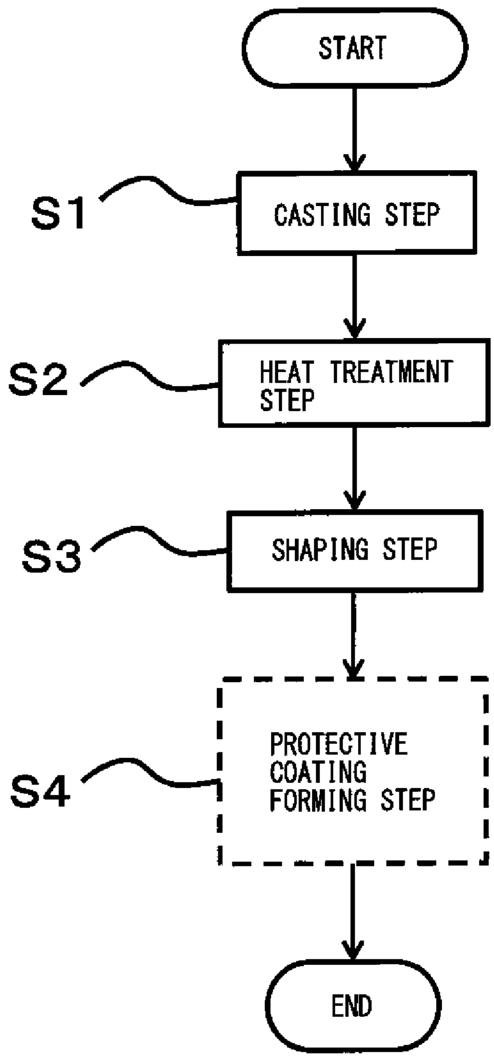
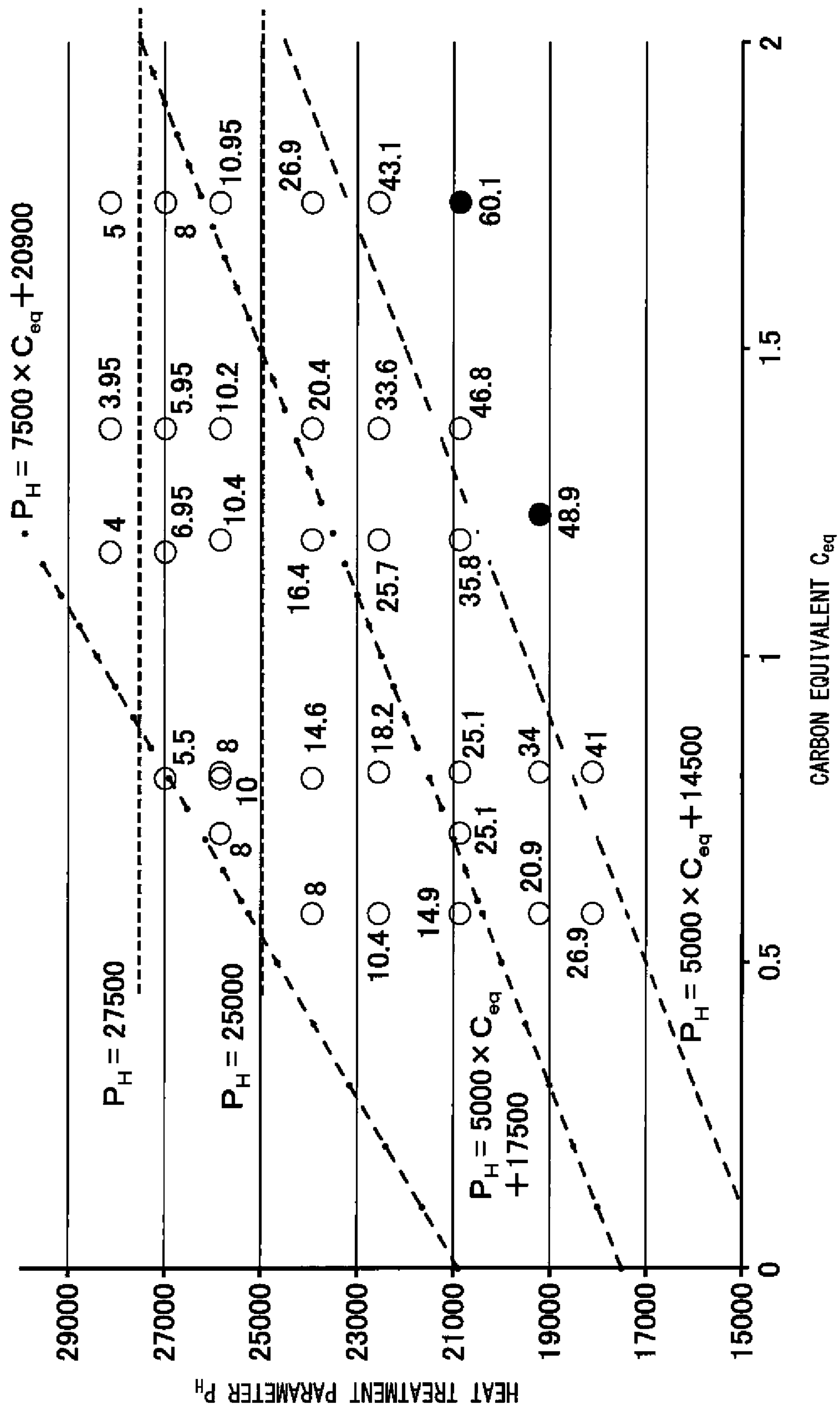
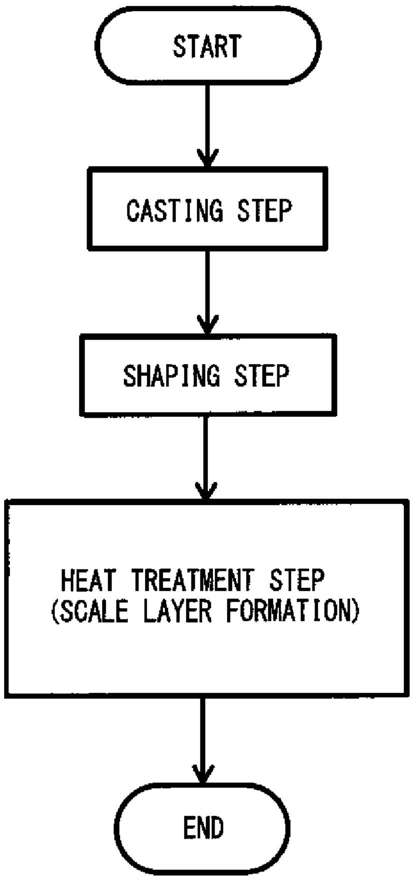

START
S1
CASTING STEP
S2
HEAT TREATMENT STEP
S3
SHAPING STEP
S4
PROTECTIVE COATING FORMING STEP
END

FIG. 2



$P_H = 7500 \times C_{eq} + 20900$
$P_H = 27500$
$P_H = 25000$
$P_H = 5000 \times C_{eq} + 17500$
$P_H = 5000 \times C_{eq} + 14500$
HEAT TREATMENT PARAMETER P_H
CARBON EQUIVALENT C_{eq}
29000
27000
25000
23000
21000
19000
17000
15000
0
0.5
1
1.5
2

FIG. 3


START
CASTING STEP
SHAPING STEP
HEAT TREATMENT STEP
(SCALE LAYER FORMATION)
END

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/076081

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *B22C9/22*(2006.01)i, *C21D1/32*(2006.01)i, *C21D3/06*(2006.01)i, *C21D9/00*(2006.01)i, *C22C38/12*(2006.01)i, *C22C38/54*(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)
C22C38/00, B22C9/22, C21D1/32, C21D3/06, C21D9/00, C22C38/12, C22C38/54

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 11-179407 A (NKK Corp.), 06 July 1999 (06.07.1999), entire text (Family: none)	1-13
A	JP 10-137818 A (Kawasaki Steel Corp.), 26 May 1998 (26.05.1998), entire text (Family: none)	1-13
A	JP 2002-47534 A (Japan Casting Co., Ltd., NKK Corp.), 15 February 2002 (15.02.2002), entire text (Family: none)	1-13

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

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 December, 2013 (17.12.13)	07 January, 2014 (07.01.14)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2013/076081

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-103301 A (Kawasaki Steel Corp.), 08 April 2003 (08.04.2003), entire text (Family: none)	1-13

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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- JP 2683861 B **[0008]**
- JP 2952382 B **[0008]**
- JP 2003129184 A **[0008]**
- WO 2008096708A A **[0008]**
- JP 63069948 A **[0008]**
- JP 4279350 B **[0008]**