

(19)



Europäisches
Patentamt
European
Patent Office
Office européen
des brevets



(11)

EP 1 964 939 A1

(12)

EUROPEAN PATENT APPLICATION published in accordance with Art. 158(3) EPC

(43) Date of publication:

03.09.2008 Bulletin 2008/36

(51) Int Cl.:

C22C 38/00 ^(2006.01)**B22D 11/00** ^(2006.01)**B22D 11/115** ^(2006.01)**C22C 38/60** ^(2006.01)(21) Application number: **06811670.6**

(86) International application number:

PCT/JP2006/320373(22) Date of filing: **12.10.2006**

(87) International publication number:

WO 2007/069386 (21.06.2007 Gazette 2007/25)

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR**

(72) Inventors:

- **SAKAMOTO, Koichi**
Hyogo 651-2271 (JP)
- **YOSHIDA, Atsuhiko**
Hyogo 657-0863 (JP)

(30) Priority: **16.12.2005 JP 2005363816**(74) Representative: **Müller-Boré & Partner**

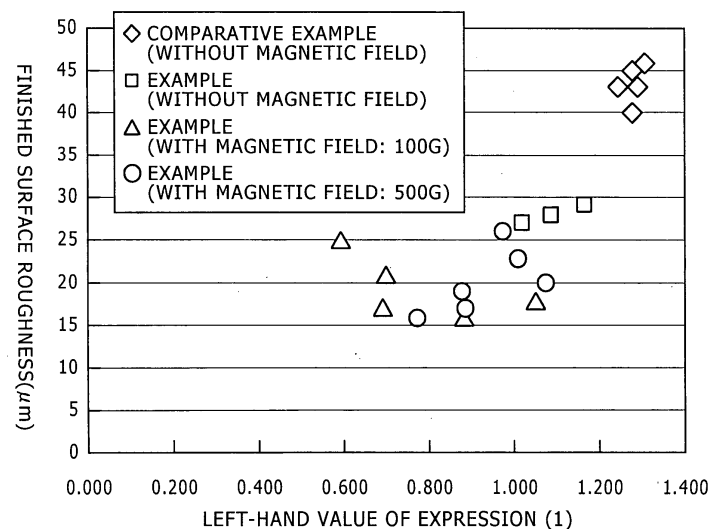
(71) Applicant: **KABUSHIKI KAISHA KOBE SEIKO SHO**
Kobe-shi,
Hyogo 651-8585 (JP)

Patentanwälte
Grafinger Strasse 2
81671 München (DE)

(54) **LOW-CARBON SULFUR-CONTAINING FREE-CUTTING STEEL WITH EXCELLENT CUTTABILITY**

(57) A low-carbon resulfurized free-machining steel is excellent in machinability and contains 0.02% to 0.15% by mass of C; 0.004% by mass or less (exclusive of 0%) of Si; 0.6% to 3% by mass of Mn; 0.02% to 0.2% by mass of P; 0.35% to 1% by mass of S; 0.005% by mass or less (exclusive of 0% by mass) of Al; 0.008% to 0.03% by mass of O; and 0.007% to 0.03% by mass of N, with

the remainder being iron and inevitable impurities, in which the ratio [Mn] / [S] of the manganese content [Mn] to the sulfur content [S] is within the range of 3 to 4, and the carbon content [C], the manganese content [Mn] and the nitrogen content [N] satisfy the following Expression (1): $10[C] \times [Mn]^{-0.94} + 1226[N]^2 \leq 1.2$, wherein [C], [Mn] and [N] represent the contents on the percent by mass basis of carbon, manganese, and nitrogen, respectively.

FIG. 1

EP 1 964 939 A1

Description

Technical Field

5 **[0001]** The present invention relates to low-carbon resulfurized free-machining steels which are free of harmful lead (Pb) and exhibit good finished surface roughness.

Background Art

10 **[0002]** Low-carbon resulfurized free-machining steels are widely used as steels for hydraulic parts of gear box units of automobiles, as well as for small parts, such as screws and printer shafts, which do not require strength so high. When better finished surface roughness and chip disposability are required, lead-sulfur free-machining steels comprising the low-carbon resulfurized free-machining steels combined with lead (Pb) are used.

15 **[0003]** Lead (Pb) contained in free-machining steels is an element very effective for improving machinability, but is harmful to the human body. In addition, lead-containing free-machining steels have some problems typically in fume of lead upon ingot making and chip disposability. Accordingly, free-machining steels exhibiting good machinability without adding lead (Pb) (lead-free) are demanded.

[0004] Various techniques have been proposed to improve the machinability of lead-free low-carbon resulfurized free-machining steels without lead. Patent Document 1, for example, discloses a technique for improving the machinability (finished surface roughness and chip disposability) by controlling the size of sulfide inclusions. Patent Document 2 teaches that the oxygen content in steel must be appropriately controlled in order to control the size of sulfide inclusions. A technique for improving the machinability by specifying oxide inclusions in steel has been proposed, for example, in Patent Document 3. Patent Document 4 proposes a technique for improving the machinability by specifying the ratio of manganese (Mn) to sulfur (S) and by controlling the free oxygen content immediately before casting.

25 **[0005]** Patent Documents 5 to 7, for example, each propose a technique for improving the machinability by appropriately specifying the chemical composition of steel.

[0006] These conventional techniques are useful from the viewpoint of improving the machinability of free-machining steels, but none of them can realize machinability in view of finished surface roughness upon forming as good as with lead-containing steels.

30 **[0007]** It is important that such lead-free steels should have good productivity in addition to satisfactory machinability. From this viewpoint, they must be produced by a continuous casting process, be free typically from surface defects and be capable of easily being rolled. The continuous casting process is believed to be disadvantageous for improving the machinability of steels. It is, therefore, also important to produce free-machining steels excellent in machinability with good productivity by a continuous casting process.

35 **[0008]** The continuous casting process realizes good surface quality, internal quality, and good yield. Patent Document 8 discloses a technique for providing a free-machining steel excellent in machinability (finished surface roughness) by the continuous casting process. This technique indicates that a free-machining steel excellent in machinability can be obtained in good yield according to a continuous casting process, by incorporating a relatively large amount of oxygen of 100 to 300 ppm to a steel and incorporating nitrogen (N) thereto in a larger amount than those of conventional equivalents. By satisfying this, built-up edges can be suppressed, which built-up edges occur in a tool surface upon machining.

40 **[0009]** However, if a steel is high both in oxygen content and nitrogen content, blow holes caused by carbon monoxide gas (CO gas) and nitrogen gas (N₂ gas) are often formed, which may deteriorate the finished surface roughness of the steel.

45 Patent Document 1: Japanese Patent Laid-Open No. 2003-253390
 Patent Document 2: Japanese Patent Laid-Open No. H09-31522
 Patent Document 3: Japanese Patent Laid-Open No. H10-158781
 Patent Document 4: Japanese Patent Laid-Open No. 2005-23342
 50 Patent Document 5: Japanese Patent Laid-Open No. 2001-152281
 Patent Document 6: Japanese Patent Laid-Open No. 2001-152282
 Patent Document 7: Japanese Patent Laid-Open No. 2001-152283
 Patent Document 8: Japanese Patent Laid-Open No. H05-345951

55

Disclosure of Invention

Problems to be Solved by the Invention

[0010] The present invention has been achieved under these circumstances, and an object of the present invention is to provide a low-carbon resulfurized free-machining steel which exhibits good machinability typified by finished surface roughness, even being free from lead, and can be produced with good productivity by a continuous casting process while suppressing blow holes.

Means for Solving the Problems

[0011] The present invention has been accomplished to achieve the above object and provides a low-carbon resulfurized free-machining steel excellent in machinability, containing:

0.02% to 0.15% (on the percent by mass basis; hereinafter the same) of carbon (C);
 0.004% or less (exclusive of 0 percent) of silicon (Si);
 0.6% to 3% of manganese (Mn);
 0.02% to 0.2% of phosphorus (P);
 0.35% to 1% of sulfur (S);
 0.005% or less (exclusive of 0%) of aluminum (Al);
 0.008% to 0.03% of oxygen (O); and
 0.007% to 0.03% of nitrogen (N), with the remainder being iron and inevitable impurities, wherein the ratio [Mn]/[S] of the manganese content [Mn] to the sulfur content [S] is within the range of 3 to 4, and wherein the carbon content [C], the manganese content [Mn] and the nitrogen content [N] satisfy the following Expression (1):

$$10[C] \times [Mn]^{-0.94} + 1226[N]^2 \leq 1.2 \quad (1)$$

wherein [C], [Mn] and [N] represent the contents on the percent by mass basis of carbon, manganese, and nitrogen, respectively.

[0012] The low-carbon resulfurized free-machining steels according to the present invention each preferably have a chemical composition in which (1) the content of soluble nitrogen is 0.002% to 0.02% and/or (2) the total content of at least one selected from the group consisting of Ti, Cr, Nb, V, Zr, and B is 0.02% or less (exclusive of 0%). By satisfying these requirements, the low-carbon resulfurized free-machining steels according to the present invention have further improved properties. The steels are preferably produced by subjecting to electromagnetic stirring in which a magnetic field of 100 to 500 gauss is applied during casting. The resulting steels have better surface quality.

Advantages

[0013] The present invention controls the contents of carbon, manganese, and nitrogen in steel so as to satisfy a specific relational expression. By satisfying this, low-carbon resulfurized free-machining steels good in finished surface roughness can be produced with good productivity while suppressing blow holes even according to a continuous casting process.

Brief Description of the Drawings

[0014]

FIG. 1 is a graph showing how the finished surface roughness (maximum height of irregularities Rz) varies depending on the left-hand value of Expression (1) and on the presence or absence of a magnetic field.

Best Mode for Carrying Out the Invention

[0015] The finished surface roughness of a free-machining steel varies significantly depending on generation, size, shape and uniformity of built-up edges. Generation of built-up edges is a phenomenon that part of a work attaches to a surface of a tool and actually behaves as part (cutting edge) of the tool. It may adversely affect the finished surface

roughness of a work material. The built-up edges generate only under specific conditions, but free-machining steels are generally cut in the art under such conditions as to induce the built-up edges.

[0016] The built-up edges are believed to provide fatal defects due to variation in their size. On the other hand, the built-up edges play a role to protect the edge of a tool to thereby prolong the lifetime of the tool. All factors considered, therefore, it is not advantageous to remove such a built-up edge fully, and the built-up edges must be stably formed with uniformized sizes and shapes.

[0017] To stably form built-up edges with uniformized sizes and shapes, a large number of fine cracks must be formed in primary and secondary shear zones in a region to be cut. A large number of crack-forming sites must be introduced to form a large number of fine cracks. MnS inclusions are known to be useful as sites for forming fine cracks. Not all MnS inclusions but large-sized (wide) spherical MnS inclusions act as fine-crack-forming sites. Such MnS inclusions elongate in the primary and secondary shear zones, but if they become too thin as thin as matrix, they do not work as fine-crack-forming sites. Accordingly, a work (steel to be cut) must comprise large-sized spherical MnS inclusions before cutting.

[0018] Oxygen (total oxygen) in steel affects the size and sphericity of MnS inclusions (for example, Patent Document 2), and it is believed that the size (diameter) of sulfides increases with an increasing oxygen content of steel. Consequently, the oxygen content of steel must be increased to some extent in order to make MnS inclusions larger and more spherical. In addition, the manganese content and sulfur content must be higher than those in conventional free-machining steels, such as Japanese Industrial Standards (JIS) SUM 23 steel and SUM 24L steel, so as to increase MnS inclusions working as fine-crack-forming sites.

[0019] The present inventors have found that soluble nitrogen in steel also significantly affects the formation of fine cracks and that free-machining steels good in machinability can be realized by appropriately adjusting the content of soluble nitrogen. The temperatures in the primary and secondary shear zones significantly vary from a position to another. The deformation resistance varies depending on temperatures at individual positions when the soluble nitrogen is present in a certain amount. The difference (variation) in deformation resistance causes fine-crack-forming sites. Accordingly, a certain level or more of the soluble nitrogen can be effectively ensured by controlling the total amount of Ti, Cr, Nb, V, Zr, B to a specific level or less. This is because these components work to fix the soluble nitrogen, namely, they work to form nitrides.

[0020] Specifically, the present inventors have found that built-up edges can be stably formed with uniformized sizes and shapes, for example, by the two phenomena, namely, (1) making MnS inclusions become larger and spherical, and (2) increasing soluble nitrogen. The resulting steels have dramatically improved finished surface roughness in forming process and thereby exhibit properties as good as lead-free-machining steels.

[0021] The free-machining steels according to the present invention must have appropriately specified chemical compositions. The reasons for specifying the contents of basic components C, Si, Mn, P, S, Al, O, and N are as follows.

Carbon (C): 0.02% to 0.15%

[0022] Carbon (C) is an essential element to ensure the strength of steel, and, if added to a specific amount or more, acts to improve the finished surface roughness. The carbon content must be 0.02% or more to exhibit these activities. An excessively high content thereof, however, may shorten the lifetime of a tool upon cutting to thereby deteriorate the machinability, and may induce defects due to carbon monoxide (CO) gas upon casting. From these viewpoints, the carbon content is preferably 0.15% or less. Preferred lower and upper limits of the carbon content are 0.05% and 0.12%, respectively.

Silicon (Si): 0.004% or less (exclusive of 0%)

[0023] Silicon (Si) is an element effective for ensuring the strength of steel as a result of solid-solution strengthening, but it basically acts as a deoxidizing agent to form silicon dioxide (SiO₂). The silicon dioxide SiO₂ serves to form MnO-SiO₂-Mn inclusions. If the silicon content exceeds 0.004%, the SiO₂ content in the inclusions becomes too high to ensure a necessary oxygen content in MnS inclusions. Thus, the finished surface roughness deteriorates. From these viewpoints, the silicon content must be 0.004% or less and is preferably 0.003% or less.

Manganese (Mn) : 0.6% to 3%

[0024] Manganese (Mn) acts to improve hardenability, to enhance the formation of the bainite, and to improve the machinability. It is an element effective for ensuring the strength of steel. Further, it combines with sulfur to form MnS and combines with oxygen to form MnO to thereby form MnO-MnS composite inclusions. Thus, it acts to improve the machinability. To exhibit these actions, the manganese content must be 0.6% or more, but if it exceeds 3%, the strength increases excessively to deteriorate the machinability. Preferred lower and upper limits of the manganese content are

1% and 2%, respectively.

Phosphorus (P) : 0.02% to 0.2%

[0025] Phosphorus (P) acts to improve the finished surface roughness. It also acts to significantly improve the chip disposability by facilitating crack propagation in chip. To exhibit these advantages, the phosphorus content must be 0.02% or more. An excessively high phosphorus content, however, deteriorates the hot workability, and the phosphorus content must be 0.2% or less. Preferred lower and upper limits of the phosphorus content are 0.05% and 0.15%, respectively.

Sulfur (S): 0.35% to 1%

[0026] Sulfur (S) is an element which combines with manganese in steel to form manganese sulfide (MnS), thereby acts as a stress concentrator upon cutting. Thus, chips are partitioned to thereby improve the machinability. To exhibit these actions, the sulfur content must be 0.35% or more. If the sulfur content is excessively high exceeding 1%, the hot workability may deteriorate. Accordingly, a preferred upper limit of the sulfur content is 0.8%.

Total aluminum: 0.005% or less (exclusive of 0%)

[0027] Aluminum (Al) is an element useful for ensuring the strength of steel as a result of solid-solution strengthening and for deoxidization. It also acts as a strong deoxidizing agent to form an oxide (Al_2O_3). The oxide Al_2O_3 constitutes MnO- Al_2O_3 -MnS inclusions. If the aluminum content exceeds 0.005%, the Al_2O_3 content of the inclusions becomes too high to ensure a necessary oxygen content in MnS inclusions to thereby adversely affect the finished surface roughness. The aluminum content is preferably 0.003% or less and more preferably 0.001% or less.

Oxygen (O): 0.008% to 0.03%

[0028] Oxygen (O) combines with manganese (Mn) to form manganese oxide (MnO). The MnO contains a large amount of sulfur to thereby constitute MnO-MnS composite inclusions. The MnO-MnS composite inclusions are resistant to elongation upon rolling, are present as relatively spherical inclusions and thereby act as stress concentrator zones upon cutting. Accordingly, oxygen is positively added to the steel. If the oxygen content is less than 0.008%, these actions are insufficient, but if it exceeds 0.03%, internal defects caused by carbon monoxide gas may occur in steel ingots. Accordingly, the oxygen content (total oxygen content) must be within the range of 0.008% to 0.03%.

[0029] Oxygen (total oxygen) forms manganese oxide (MnO) in molten steel, and the MnO contains a large amount of sulfur to thereby form MnO-MnS composite inclusions. These MnO-MnS composite inclusions act as nuclei so as to precipitate MnS inclusions during solidification. Thus, the resulting billet (ingot prepared as a result of continuous casting) contains MnO-MnS composite inclusions mainly comprising MnS. The billet then undergoes heating, blooming, and wire rod rolling or bar mill rolling. With an increasing oxygen content, the MnO-MnS composite inclusions mainly comprising MnS are more resistant to elongation in the blooming, wire rod rolling or bar mill rolling, and they constitute large-sized spherical MnS inclusions in final products such as wire steels and bar steels.

[0030] The lower limit of oxygen (total oxygen) is set in view of these mechanisms in which the oxygen content is preferably high. However, the upper limit of oxygen content is also set in actuality. The reasons of this will be explained below. Oxygen (total oxygen) comprises oxygen in the form of oxides, and soluble oxygen (free oxygen) dissolved in molten steel. The oxygen in the form of oxides, namely, oxygen in MnO is very useful. In contrast, the free oxygen (O) reacts with carbon (C) in molten steel to form CO gas [$C+O = CO$ (gas)], and the CO gas, if not released sufficiently, causes blow holes. In addition, the nitrogen content of steel is increased according to the present invention, and soluble nitrogen in molten steel forms N_2 (gas) [$N+N = N_2$ (gas)] during a solidification process, because the nitrogen solubility in molten steel decreases with a descending temperature. The N_2 gas also causes blow holes. Specifically, blow holes mainly comprise CO (gas) and N_2 (gas).

[0031] A feature (concept) of the present invention is that the free oxygen (O) and nitrogen (N) contents are set highest within such ranges that the CO (gas) and N_2 (gas) do not form blow holes. The formation of blow holes in steel can also be improved by carrying out electromagnetic stirring, in addition to setting the chemical composition of steel. This is because blow holes, if formed, can be eliminated from the steel by electromagnetic stirring carried out in a mold in continuous casting.

[0032] Under these ideas, the present inventors made investigations to determine which affects the free oxygen (O) content and have found that the manganese content [Mn] and the sulfur content [S] mainly affect the free oxygen (O) content. Accordingly, the amount of CO (gas) can be controlled by [C], [Mn], and [S], and the amount of CO (gas)+ N_2 (gas) can be determined according to Expression (1), wherein the nitrogen content [N] is added to these parameters.

Thus, blow holes can be controlled. The detail of this will be described later.

[0033] The free oxygen (O) content in molten steel is preferably controlled to about 0.0050% or less from the viewpoint of preventing internal defects caused by CO gas, while it varies depending on the carbon and nitrogen contents [C] and [N] or electromagnetic stirring conditions. Preferred lower and upper limits of the oxygen content (total oxygen content) of steel are 0.01% and 0.03%, respectively.

Nitrogen (N): 0.007% to 0.03%

[0034] Nitrogen (N) is an element affecting the amount of built-up edges, and the content thereof affects the finished surface roughness. If the nitrogen content is less than 0.007%, excessively large amounts of built-up edges occur to thereby adversely affect the finished surface roughness. Nitrogen is liable to segregate in dislocations in the matrix. It segregates in dislocations during cutting to thereby make the matrix brittle and facilitate crack propagation. Thus, nitrogen serves to improve chip breakability (chip disposability). However, an excessively high nitrogen content exceeding 0.03% causes bubbles (blow holes) upon casting, which may often become internal and surface defects of the resulting ingot. The nitrogen content must therefore be controlled to 0.03% or less. Preferred lower and upper limits of the nitrogen content are 0.005% and 0.025%, respectively.

[0035] Specifying the chemical composition of the low-carbon resulfurized free-machining steels according to the present invention as above alone is not enough to achieve the objects of the present invention. In addition to this, the ratio [Mn]/[S] of the manganese content [Mn] to the sulfur content must be controlled within a specific appropriate range and these parameters must satisfy the condition represented by Expression (1). The reasons why these requirements are set are as follows.

Ratio [Mn]/[S]: 3 to 4

[0036] The ratio [Mn]/[S] is an important factor affecting, for example, cracking during hot working. If the manganese content is insufficient relative to the sulfur content, namely, [Mn] / [S] is less than 3, FeS often forms, and this causes hot crack. When the ratio [Mn]/[S] is within the range of 3 to 4, the manganese content is sufficient relative to the sulfur content, which prevents the formation of FeS to thereby prevent hot crack. If the ratio [Mn]/[S] exceeds 4, this effect is saturated and the free oxygen (O) content decreases to thereby adversely affect the finished surface roughness. The free oxygen content varies depending on [Mn] and [S].

$10[C] \times [Mn]^{-0.94} + 1226[N]^2 \leq 1.2$

[0037] The above condition must be satisfied for preventing blow holes and ensuring satisfactory machinability. If the left-hand value ($10[C] \times [Mn]^{-0.94} + 1226[N]^2$) exceeds 1.2, blow holes may form. The left-hand value is preferably 1.1 or less and more preferably 0.9 or less.

[0038] The condition represented by Expression (1) has been determined after various experiments, and the reason for which will be described below. Carbon (C), oxygen, and nitrogen (N) dissolved in molten steel undergo microsegregation due to solid-liquid separation and are enriched in a liquid. The soluble oxygen nearly equals the free oxygen (O), whereas the free oxygen means the oxygen activity. The solubilities of carbon, oxygen, and nitrogen in the liquid decreases with a descending temperature. Specifically, the enriched carbon, oxygen, and nitrogen due to microsegregation react as $C+O = CO$ (gas) and $N = 1/2N_2$ (gas) with decreasing solubilities with a descending temperature. The resulting gases, if overcome the local pressure, form bubbles (blow holes) in the liquid part of the molten steel. The local pressure mainly comprises the total of the atmospheric pressure, molten steel static pressure, and (interfacial energy between liquid and gas) / (diameter of bubble). The bubbles often form in the vicinity of menisci in which the molten steel static pressure is low. The gas (bubbles) comprises CO (gas) and N_2 (gas). If the gas (bubbles) floats due to difference in density and escapes from the molten steel to the atmosphere, it does not remain as blow holes in the billet. However, if it is engulfed, for example, by solidified crystals, it remains as blow holes and as defects in the billet.

[0039] Assuming the above mechanism, the formation of blow holes probably varies depending on the carbon content [C], free oxygen content [O], and nitrogen content [N]. Accordingly, the phenomenon can be thermodynamically expressed by following Expressions (2) to (7):

$$CO \text{ (gas)} = [C] + [O] \quad (2)$$

$$K_{CO} = (a_{CO})/P_{CO} = f_C[C]f_O[O])/P_{CO} \quad (3)$$

$$\log(K_{CO}) = -1160/T - 2.003 \quad (4)$$

$$C_L^C = C_0^C / \{1 - (1 - k_C) f\} \quad (5)$$

$$C_L^O = C_0^O / \{1 - (1 - k_O) f\} \quad (6)$$

$$P_{CO} = (f_C f_O C_0^C C_0^O) / [\{1 - (1 - k_C) f\} \{1 - (1 - k_O) f\} K_{CO}] \quad (7)$$

[0040] Initially, Expression (2) will be examined provided that a reaction proceeds from the right to the left. The equilibrium constant K_{CO} in Expression (2) is given by the activity coefficient of carbon (f_C), the carbon content $[C]$, the activity factor of oxygen (f_O), the oxygen content $[O]$, and the CO partial pressure (P_{CO}). The equilibrium constant is determined according to Expression (4), in which T represents the absolute temperature. The carbon content $[C]$ and the oxygen content $[O]$ refer to contents after microsegregation and are determined according to the Sheil Equation as in Expressions (5) and (6). In Expressions (5) and (6), C_0^C and C_0^O represent the initial carbon content $[C]$ and oxygen content $[O]$ of molten steel before casting, respectively; and C_L^C and C_L^O represent the carbon content $[C]$ and oxygen content $[O]$ of the liquid phase during solidification where a solid phase and a liquid phase are coexistent. The C_L^C and C_L^O represent the contents after enrichment due to microsegregation. By substituting these parameters into Expression (3), the CO partial pressure (P_{CO}) can be represented by Expression (7). In these expressions, " f " represents the fraction of solid phase; and K_C and k_O represent the equilibrium distribution coefficients of carbon and oxygen, respectively.

[0041] The phenomenon relating to nitrogen can be represented by following Expressions (8) to (12).

$$1/2N_2 \text{ (gas)} = [N] \quad (8)$$

$$K_{N_2} = (a_N) / \sqrt{P_{N_2}} = f_N[N] / \sqrt{P_{N_2}} \quad (9)$$

$$\log(K_{N_2}) = -518/T - 1.063 \quad (10)$$

$$C_L^N = C_0^N / \{1 - (1 - k_N) f\} \quad (11)$$

$$\sqrt{P_{N_2}} = (f_N C_0^N) / \{1 - (1 - k_N) f\} K_{N_2} \quad (12)$$

Specifically, the equilibrium constant K_{N_2} in Expression (8) can be represented by Expression (9), and the equilibrium constant can be represented by Expression (10). The nitrogen content $[N]$ of the molten steel after microsegregation can be represented by Expression (11), and by substituting this into Expression (9), the N_2 partial pressure (P_{N_2}) can be represented by Expression (12).

[0042] Blow holes are formed when the total sum ($P_{CO} + P_{N_2}$) of the partial pressures represented by Expressions (7) and (12) thus estimated exceeds the total of the external pressure (atmospheric pressure), molten steel static pressure, and (interfacial energy between liquid and gas) / (diameter of bubble), as represented by following Expression (13):

$$P_g \geq P_a + \rho Lgh + 2\sigma/r \quad (13)$$

wherein P_g represents the total sum of partial pressures of gases in molten steel;

P_a represents the external pressure;
 ρLgh represents the liquid static pressure;
 σ represents the interfacial energy between liquid and gas; and
 $"r"$ represents the diameter of bubble.

[0043] The present inventors examined how the occurrence frequency of blow holes varies depending on the total of partial pressures ($P_{CO} + P_{N_2}$) calculated according to the above-mentioned method of calculation having these physical meanings. As a result, they have found that blow holes occur when the total of partial pressures ($P_{CO} + P_{N_2}$) exceeds 1.2 atm.

[0044] The present inventors made an attempt to convert the total of partial pressures ($P_{CO} + P_{N_2}$) into an index. The carbon and nitrogen contents [C] and [N] can be easily determined by on-line analyses, but the free oxygen content must be determined using a free-oxygen analyzer. It may be accompanied by a large error in some determination procedures. The present inventors examined what affects the free oxygen content [O] and have found that the manganese content [Mn] and the sulfur content [S] affect the free oxygen content [O]. This is also apparent from the fact that oxygen forms MnO-MnS oxide-sulfide inclusions in molten steel. This shows that the formation of blow holes can be indicated by a relational expression among [C], [Mn], [S], and [N]. In addition, the manganese and sulfur contents [Mn] and [S] have a relation in which the ratio [Mn]/[S] is 3 to 4. In view of this relation, the formation of blow holes can be schematically expressed by the relational expression among [C], [Mn], and [N].

[0045] Under these ideas, the right-hand value of Expression (7) and data of the contents such as [Mn] experimentally show that P_{CO} equals $10[C] \times [Mn]^{-0.94}$, because Expression (7) shows that P_{CO} is proportional to [C] and [O], and [O] varies depending on [Mn]. The square of the right-hand value of Expression (12) and data of the contents such as [N] show that the nitrogen partial pressure P_{N_2} equals $1226[N]^2$, because Expression (12) shows that P_{N_2} is proportional to $[N]^2$.

[0046] Blow holes occur to thereby cause surface defects with an increased total of the partial pressures of carbon monoxide and nitrogen $P_{CO} + P_{N_2}$ ($= 10[C] \times [Mn]^{-0.94} + 1226[N]^2$). The formation of blow holes naturally affects the finished surface roughness. The total of the partial pressures of carbon monoxide and nitrogen $P_{CO} + P_{N_2}$ has such a relation with the finished surface roughness as shown in after-mentioned FIG. 1. FIG. 1 shows that the threshold of the total of partial pressures is about 1.2 in view of the formation of surface defects and the finished surface roughness.

[0047] The low-carbon resulfurized free-machining steels according to the present invention comprise the above-mentioned components with the remainder basically being iron. However, they can further comprise trace components in addition to these components, and those further comprising such trace components are also included within the scope of the present invention. The low-carbon resulfurized free-machining steels according to the present invention comprise inevitable impurities such as Cu, Sn, and Ni, and these inevitable impurities are accepted within ranges not adversely affecting the advantages of the present invention.

[0048] The low-carbon resulfurized free-machining steels according to the present invention preferably have (1) a content of soluble nitrogen of 0.002% to 0.02% and/or (2) a total content of at least one selected from the group consisting of Ti, Cr, Nb, V, Zr, and B of 0.02% or less (exclusive of 0 percent), according to necessity. The reasons for setting these specific ranges are as follows.

Content of soluble nitrogen: 0.002% to 0.02%

[0049] As is described above, soluble nitrogen in steel affects the formation of fine cracks, and free-machining steels with good machinability can be realized by appropriately controlling the content of the soluble nitrogen. To exhibit these advantages, the content of soluble nitrogen in steel is preferably controlled to 0.002% or more. If it exceeds 0.02%, however, surface defects may increase.

Total content of at least one element selected from the group consisting of Ti, Cr, Nb, V, Zr, and B: 0.02% or less (exclusive of 0%)

[0050] These elements combine with nitrogen to form nitrides, and if the contents thereof are excessively high, the content of soluble nitrogen becomes too small below the necessary content of soluble nitrogen. From this viewpoint, the total content of these elements is preferably controlled to 0.02% or less.

[0051] The low-carbon resulfurized free-machining steels according to the present invention are basically produced by a continuous casting process. They can be specifically produced, for example, according to the following procedure. Initially, carbon is blown down to a carbon content of 0.04% or less in a converter so as to make molten steel have a high free oxygen content (soluble oxygen content). The free oxygen content herein is preferably 500 ppm or more. Next, alloys such as Fe-Mn alloy and Fe-S alloy are added upon tapping. These alloys contain silicon and aluminum as impurities. By adding these alloys to high-oxygen molten steel upon tapping from the converter, silicon and aluminum are oxidized to form SiO_2 and Al_2O_3 . These float and separate into slag upon subsequent ladle refining process of the molten steel. Thus, silicon and aluminum remained in steel decrease to be target contents. It is important in this processing that 70% or more of additional components such as Fe-Mn alloy and Fe-S alloy added for adjusting the chemical composition is added upon tapping from the converter so as to reduce aluminum and silicon, and the remainder (30% or less) of them is added in the ladle refining process of the molten steel. By carrying out these procedures, the steel can have a silicon content of 0.004% or less.

[0052] In the production of steels, electromagnetic stirring is preferably carried out, in which a predetermined magnetic field is applied to the steels upon casting. The electromagnetic stirring is carried out from the viewpoint of reducing blow holes to thereby prevent defects and to provide good surface quality. The production of steels in combination with the electromagnetic stirring is very useful for making MnS inclusions large-sized and spherical and for preventing the formation of blow holes. The magnetic field to be applied in the electromagnetic stirring preferably has an intensity of about 100 to about 500 gaussses. If the intensity of the magnetic field is less than 100 gaussses, the effect of electromagnetic stirring may not be exhibited. In contrast, if it exceeds 500 gaussses, the molten steel in a continuous casting mold may flow at an excessively high rate, and the steel may involve a mold powder and make casting difficult.

[0053] The present invention will be illustrated in further detail with reference to several examples below. It should be noted, however, that the following examples are never intended to limit the scope of the present invention, various modifications and variations are possible unless departing from the spirit and scope of the present invention, and those modifications and variations are included within the technical scope of the present invention.

[Examples]

[0054] A series of molten steels having varying contents of, for example, Si, Mn, S, Al, and N were made using a 3-ton induction furnace, a 100-ton converter, and molten steel refining facilities including a pouring ladle. In this procedure, the silicon and aluminum contents were adjusted by varying the silicon and aluminum contents in Fe-Mn alloys and Fe-S alloys to be added, respectively. The free oxygen contents in the resulting molten steels were determined immediately before casting into a predetermined mold using a free oxygen probe (the product of Heraeus Electro-Nite under the trade name of "HYOP 10A-C150"), and they were defined as the free oxygen contents.

[0055] The molten steels were subjected to continuous casting using a (bloom-type) mold having a sectional size of 300 mm wide and 430 mm long. Alternatively, they were cast in the 3-ton induction furnace using a cast-iron mold having a sectional size of 300 mm wide and 430 mm long which had been designed to achieve a cooling rate as in bloomed billets. Where necessary, a magnetic field was applied to the mold during casting so as to carry out electromagnetic stirring.

[0056] Samples were taken from quenched portion in the surface layer of the resulting billets or ingots and were chemically analyzed to determine their chemical compositions. The results are shown in Table 1 below.

[0057]

Table 1

Sample No.	Chemical composition (percent by mass)											[Mn]/[S]
	C	Si	Mn	P	S	Al	Total oxygen	Free oxygen	N	Pb	Other components	
1	0.10	0.002	0.9	0.080	0.30	0.003	0.0284	0.0066	0.0124	-	Ti: 0.06, Cr: 0.005, Zr: 0.005, V: 0.005	3.0
2	0.11	0.002	1.1	0.087	0.32	0.001	0.0223	0.0054	0.0160	-	-	3.4
3	0.11	0.001	1.3	0.081	0.36	0.002	0.0185	0.0046	0.0189	-	-	3.6
4	0.11	0.003	1.5	0.086	0.42	0.002	0.0160	0.0040	0.0210	-	-	3.6
5	0.11	0.007	2.1	0.079	0.59	0.003	0.0114	0.0029	0.0241	-	Ti: 0.02, Cr: 0.003	3.6
6	0.08	0.003	1.2	0.082	0.31	0.001	0.0208	0.0049	0.0070	0.300	-	3.8
7	0.11	0.003	1.7	0.080	0.49	0.001	0.0168	0.0036	0.0186	-	Ti: 0.003, Cr: 0.004	3.5
8	0.12	0.004	1.9	0.081	0.53	0.003	0.0155	0.0032	0.0173	-	Ti: 0.002, Cr: 0.006	3.6
9	0.11	0.007	2.3	0.082	0.65	0.009	0.0111	0.0027	0.0234	-	Ti: 0.003, Cr: 0.003, Zr: 0.002	3.5
10	0.10	0.003	1.3	0.079	0.37	0.001	0.0198	0.0046	0.0150	-	-	3.5
11	0.10	0.003	1.5	0.081	0.45	0.002	0.0181	0.0040	0.0125	-	Ti: 0.002, Cr: 0.003	3.3
12	0.08	0.004	1.7	0.084	0.50	0.004	0.0146	0.0036	0.0180	-	-	3.4
13	0.08	0.003	1.9	0.077	0.55	0.002	0.0125	0.0032	0.0143	-	-	3.5
14	0.08	0.003	2.1	0.079	0.59	0.005	0.0117	0.0029	0.0156	-	Ti: 0.003, Cr: 0.004	3.6
15	0.08	0.004	2.3	0.075	0.65	0.003	0.0104	0.0027	0.0135	-	Ti: 0.003, Cr: 0.005, Nb: 0.001	3.5
16	0.10	0.002	1.3	0.083	0.35	0.001	0.0222	0.0046	0.0155	-	-	3.7
17	0.08	0.001	1.5	0.077	0.43	0.001	0.0192	0.0040	0.0135	-	Ti: 0.001, Cr: 0.003	3.5
18	0.09	0.003	1.7	0.083	0.48	0.002	0.0160	0.0036	0.0167	-	Ti: 0.003, Cr: 0.005, Nb: 0.001	3.5
19	0.10	0.001	1.9	0.079	0.55	0.003	0.0145	0.0032	0.0165	-	Ti: 0.003, Cr: 0.004	3.5
20	0.10	0.004	2.1	0.078	0.61	0.002	0.0135	0.0029	0.0205	-	-	3.4
21	0.15	0.003	2.3	0.077	0.70	0.001	0.0111	0.0027	0.0155	-	Ti: 0.002, Cr: 0.004	3.3

EP 1 964 939 A1

[0058] The resulting billets and ingots were heated at 1250°C for one hour, subjected to blooming to a sectional size of 155 mm wide and 155 mm long, rolled to a diameter of 25 mm, subjected to acidpickling to yield cold finished steel bars having a diameter of 22 mm, and subjected to cutting tests. The rolling herein was conducted at 1000°C and the rolled steels were cooled forcedly at an average cooling rate from 800°C to 500°C of about 1.5°C per second. The temperatures of steels were determined using a radiation pyrometer.

[0059] The steels were measured on content of soluble nitrogen and subjected to cutting tests under the following conditions. The finished surface and surface defects of the steels after cutting tests were evaluated according to the following criteria.

[Determination of content of soluble nitrogen]

[0060] The content of soluble nitrogen was determined as the difference between the total nitrogen and the nitrogen in compound. The total nitrogen was determined according to a method using a conductivity of an inert gas heat of fusion, and the nitrogen in compound was determined by dissolving and extracting a sample with a methanol solution containing 10% of acetylacetone and 1% of tetramethylammonium chloride, collecting nitrogen through a 1-μm filter and determining nitrogen using an indophenol-absorptiometer.

[Cutting test conditions]

[0061]

Tool: high-speed tool steel SKH4A

Cutting rate: 100 m/min.

Feed rate: 0.01 mm per revolution

Depth of cut: 0.5 mm

Cutting oil: chlorine-containing water-insoluble cutting oil Length of cut: 500 m

[Criteria]

[0062] Finished surface evaluation: The surface roughness was evaluated in terms of the maximum height of irregularities Rz according to JIS B 0601 (2001).

Surface defect evaluation: Surface defects on bloomed sample billets having a sectional size of 155 mm wide and 155 mm long were detected using an automatic defect detector. A sample in which no defect was detected by the automatic defect detector was evaluated as "Good"; a sample having some defects that can be removed by a processing was evaluated as "Fair"; and a sample having defects that are not removable was evaluated as "Failure".

[0063] The results in the cutting tests with other data, such as the left-hand value of Expression (1) and the intensity of magnetic field, are shown in Table 2 below.

Table 2

Sample No.	Left-hand value of Expression (1)	Magnetic field (gauss)	Dissolved nitrogen (percent by mass)	Finished surface roughness Rz (μm)	Surface defects	Remarks
1	1.293	-	0.0052	45	Failure	Comparative Example
2	1.320	-	0.0138	46	Failure	Comparative Example
3	1.298	-	0.0162	43	Failure	Comparative Example
4	1.292	-	0.0183	40	Failure	Comparative Example
5	1.260	-	0.0198	43	Failure	Comparative Example

(continued)

Sample No.	Left-hand value of Expression (1)	Magnetic field (gauss)	Dissolved nitrogen (percent by mass)	Finished surface roughness Rz (μm)	Surface defects	Remarks
6	0.734	100	0.0036	17	Good	Referential Example
7	1.092	-	0.0140	28	Fair	Example
8	1.023	-	0.0130	27	Fair	Example
9	1.174	-	0.0190	29	Fair	Example
10	1.057	100	0.0120	18	Good	Example
11	0.875	100	0.0090	17	Good	Example
12	0.833	100	0.0155	16	Good	Example
13	0.688	100	0.0113	17	Good	Example
14	0.697	100	0.0120	21	Good	Example
15	0.589	100	0.0080	25	Good	Example
16	1.076	500	0.0128	20	Good	Example
17	0.770	500	0.0101	16	Good	Example
18	0.888	500	0.0120	17	Good	Example
19	0.881	500	0.0125	19	Good	Example
20	1.013	500	0.0181	23	Good	Example
21	0.980	500	0.0113	26	Good	Example

[0064] These results show that samples satisfying the requirements specified in the present invention (Sample Nos. 7 to 21) have small finished surface roughness (maximum height of irregularities Rz) and exhibit good machinability; and that, among them, the samples subjected to electromagnetic stirring (Sample Nos. 10 to 21) are reduced in surface defect caused by blow holes.

[0065] In contrast, samples not satisfying at least one of the requirements specified in the present invention are poor in at least one of the properties.

[0066] FIG. 1 shows how the finished surface roughness (maximum height of irregularities Rz) varies depending on the left-hand value of Expression (1) and on the presence or absence of a magnetic field.

Claims

1. A low-carbon resulfurized free-machining steel excellent in machinability, comprising:

0.02 to 0.15 percent by mass of carbon (C);
 0.004 percent by mass or less (exclusive of 0 percent) of silicon (Si);
 0.6 to 3 percent by mass of manganese (Mn);
 0.02 to 0.2 percent by mass of phosphorus (P);
 0.35 to 1 percent by mass of sulfur (S);
 0.005 percent by mass or less (exclusive of 0 percent by mass) of aluminum (Al);
 0.008 to 0.03 percent by mass of oxygen (O); and
 0.007 to 0.03 percent by mass of nitrogen (N), with the remainder being iron and inevitable impurities,

wherein the ratio $[\text{Mn}] / [\text{S}]$ of the manganese content [Mn] to the sulfur content [S] is within the range of 3 to 4, and wherein the carbon content [C], the manganese content [Mn] and the nitrogen content [N] satisfy the following Expression (1) :

$$10 [C] \times [Mn]^{-0.94} + 1226 [N]^2 \leq 1.2 \quad (1)$$

5 wherein [C], [Mn] and [N] represent the contents on the percent by mass basis of carbon, manganese, and nitrogen, respectively.

2. The low-carbon resulfurized free-machining steel according to Claim 1, wherein the content of soluble nitrogen is 0.002 to 0.02 percent by mass.

10 3. The low-carbon resulfurized free-machining steel according to Claim 2, wherein the total content of at least one element selected from the group consisting of Ti, Cr, Nb, V, Zr, and B is 0.02 percent by mass or less.

15 4. The low-carbon resulfurized free-machining steel according to any one of Claims 1 to 3, as a product underwent electromagnetic stirring in which a magnetic field of 100 to 500 gaussses is applied during casting.

20

25

30

35

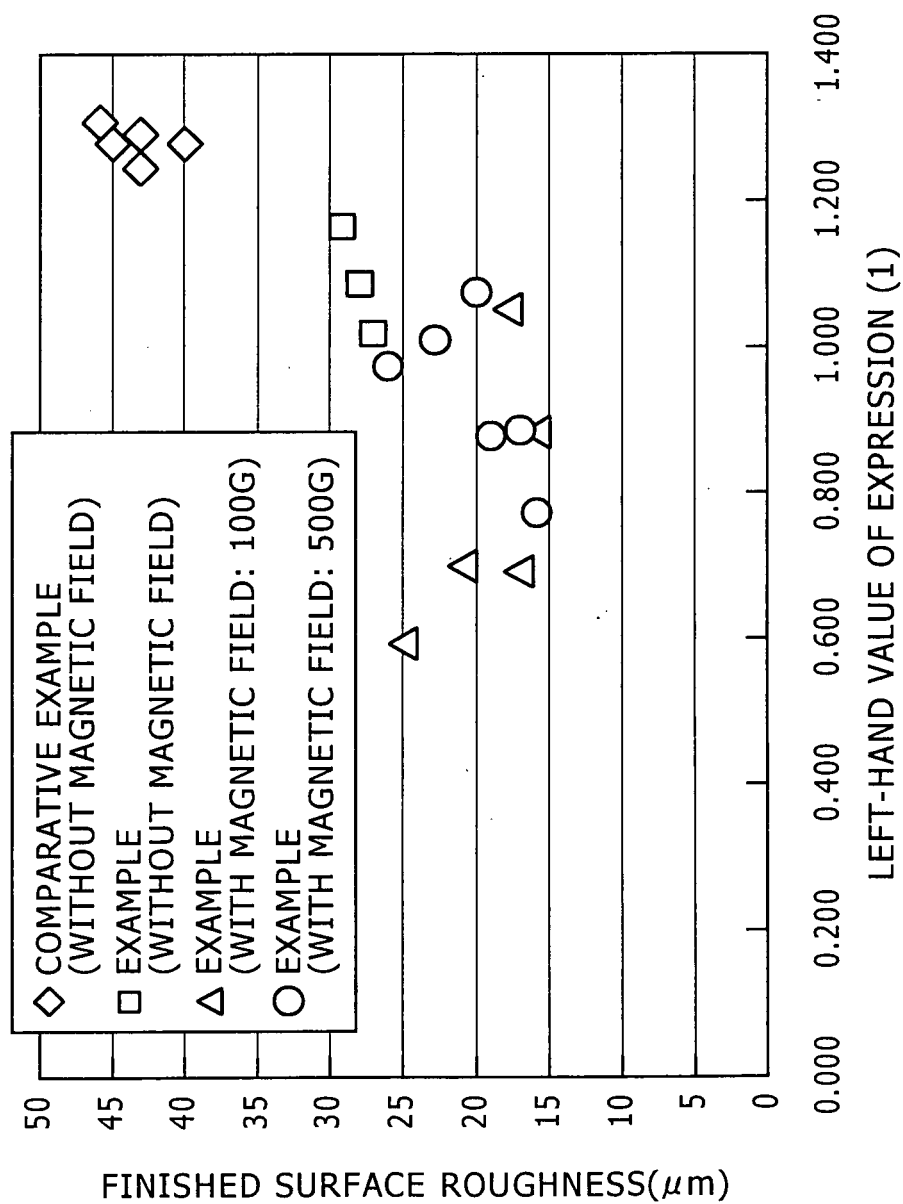
40

45

50

55

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2006/320373

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, B22D11/00(2006.01)i, B22D11/115(2006.01)i, C22C38/60(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)

C22C38/00-38/60, B22D11/00, B22D11/115

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	1996-2006
Kokai Jitsuyo Shinan Koho	1971-2006	Toroku Jitsuyo Shinan Koho	1994-2006

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.
X	WO 2004/050932 A1 (Nippon Steel Corp.), 17 June, 2004 (17.06.04), Claims; tables 1, 2 & EP 1580287 A1 & US 2006-013720 A1	1-4
A	JP 2005-187935 A (Kobe Steel, Ltd.), 14 July, 2005 (14.07.05), Par. Nos. [0052] to [0055] & WO 2005-054532 A1 & CA 2544931 A	1-4
A	JP 10-158781 A (Kobe Steel, Ltd.), 16 June, 1998 (16.06.98), Par. No. [0030] (Family: none)	1-4

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
06 December, 2006 (06.12.06)Date of mailing of the international search report
19 December, 2006 (19.12.06)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2003253390 A [0009]
- JP H0931522 B [0009]
- JP H10158781 B [0009]
- JP 2005023342 A [0009]
- JP 2001152281 A [0009]
- JP 2001152282 A [0009]
- JP 2001152283 A [0009]
- JP H05345951 B [0009]