



(11) **EP 4 394 072 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
03.07.2024 Bulletin 2024/27

(21) Application number: **22881305.1**

(22) Date of filing: **11.10.2022**

(51) International Patent Classification (IPC):
C22C 38/02 (2006.01) **C22C 38/04** (2006.01)
C22C 38/06 (2006.01) **C22C 38/60** (2006.01)
C22C 38/14 (2006.01) **C22C 38/00** (2006.01)
B21C 23/08 (2006.01) **C21D 9/52** (2006.01)

(52) Cooperative Patent Classification (CPC):
B21C 23/08; C21D 9/52; C22C 38/00; C22C 38/02;
C22C 38/04; C22C 38/06; C22C 38/14; C22C 38/60

(86) International application number:
PCT/KR2022/015274

(87) International publication number:
WO 2023/063678 (20.04.2023 Gazette 2023/16)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **12.10.2021 KR 20210135091**

(71) Applicant: **POSCO Co., Ltd**
Pohang-si, Gyeongsangbuk-do 37859 (KR)

(72) Inventor: **CHOI, Sangwoo**
Pohang-si Gyeongsangbuk-do 37664 (KR)

(74) Representative: **Nederlandsch Octrooibureau**
P.O. Box 29720
2502 LS The Hague (NL)

(54) **SULFUR-ADDED GRAPHITE STEEL WIRE ROD, STEEL WIRE AND GRAPHITE STEEL, WHICH HAVE EXCELLENT CUTTING PERFORMANCE, AND MANUFACTURING METHODS THEREFOR**

(57) The disclosure relates to a graphite steel wire rod, steel wire, graphite steel and manufacturing methods therefor to which sulfur is added and which have excellent cutting performance to that conventional free-cutting steel. Specifically, the disclosure relates to a graphite steel wire rod and steel wire, and manufacturing methods therefor, the rod and the wire comprising, by wt%, 0.60-0.90% of carbon(C), 2.0-2.5% of silicon(Si), 0.1-0.6% of manganese(Mn), 0.015% or less of phosphorus(P)(excluding O), 0.031-0.3% of sulfur(S),

0.10-0.05% of aluminum(Al), 0.005-0.02% of titanium(Ti), 0.005-0.0020% of boron(B), 0.0030-0.0150% of nitrogen(N), and the balance of Fe and inevitable impurities. In addition, the present invention relates to graphite steel and a manufacturing method therefor, the steel comprising is same as above, having, as a microstructure, graphite grains distributed in a ferrite matrix, having a degree of graphitization of 90% or more, and containing 5% or less of MnS inclusions and pearlite in total.

EP 4 394 072 A1

Description

[Technical Field]

[0001] The disclosure relates to a graphite steel wire rod, steel wire and graphite steel having superior cutting performance and manufacturing methods thereof, and more particularly, to a sulfur-added graphite steel wire rod, steel wire and graphite steel having better cutting performance than common free-cutting steel and manufacturing methods thereof.

[Background Art]

[0002] As a material for e.g., machine parts requiring machinability, free-cutting steel, to which machinability imparting elements such as Pb, Bi, and S are added, is commonly used. To improve machinability of steel materials, low melting point machinability imparting elements such as Pb and Bi are added to the steel to take advantage of the phenomenon of liquid metal embrittlement or a large amount of MnS is formed in the steel, and this free-cutting steel has superior machinability of the steel in terms of surface roughness, chip treatment, life of cutting tool during the cutting process.

[0003] However, Pb-added free-cutting steel that has the best machinability emits harmful substances such as toxic fumes while being cut, which is very harmful to the human body and is very unfavorable for recycling of the steel. Hence, to replace this, addition of S, Bi, Te, Sn, etc., is proposed, which is, however, known to have many problems in that production is difficult because cracking occurs easily while manufacturing the steel material or occurrence of cracks is caused during hot rolling.

[0004] As a free-cutting steel developed to solve the aforementioned problem, there is a graphite steel, and the graphite steel is a steel that contains fine graphite grains in a ferrite matrix or a ferrite-pearlite matrix, and the fine graphite grains act as crack sources to serve as chip breakers, thereby imparting good machinability.

[0005] However, despite this advantage of the graphite steel, the graphite steel has not yet commercialized. This is because when carbon is added to the steel, cementite, which is a metastable phase, is precipitated even though the graphite is a stable phase, so precipitation of the graphite without a separate long-term heat treatment for 10 or more hours is difficult, and in the long-term heat treatment process, decarburization occurs, causing adversely effects the final product performance.

[0006] In addition, even when graphite grains are precipitated through the graphitization heat treatment but when they are non-uniformly distributed in an irregular form, property distribution in cutting is irregular, resulting in very poor chip treatment or surface roughness, and further reducing the life of cutting tool, so it is hard to take advantage of the graphite steel. Accordingly, there is a need to provide a method of manufacturing a graphite free-cutting steel with superior machinability by using MnS based inclusions as well as graphite grains.

[Disclosure]

[Technical Problem]

[0007] The disclosure provides a sulfur-added graphite steel wire rod, steel wire, and graphite steel with superior machinability, and a manufacturing method thereof.

[Technical Solution]

[0008] According to an embodiment of the disclosure, a graphite steel wire rod includes, in percent by weight, 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities.

[0009] According to another embodiment of the disclosure, a method of manufacturing a graphite steel wire rod includes manufacturing a billet including, in percent by weight, 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities; heating the billet; hot-rolling the heated billet to be manufactured into a wire rod; and cooling the wire rod.

[0010] According to another embodiment of the disclosure, a graphite steel wire includes, in percent by weight, 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities.

[0011] According to another embodiment of the disclosure, a graphite steel includes, in percent by weight, 0.60 to

0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities, wherein as a microstructure, graphite grains are distributed in a ferrite matrix, a graphitization rate is at least 95%, and a total of 5% or less of MnS inclusions and pearlite are included.

[0012] According to another embodiment of the disclosure, a method of manufacturing a graphite steel includes manufacturing a wire rod including, in percent by weight, 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities; and performing graphitization heat treatment on the manufactured wire rod.

[Advantageous Effects]

[0013] According to the disclosure, a graphite steel having superior machinability may replace the existing free-cutting steel and may be used as an eco-friendly free-cutting steel that replaces a harmful element such as Pb.

Best Mode

[0014] According to an embodiment of the disclosure, a graphite steel wire rod includes, in percent by weight, 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities.

Modes

[0015] A graphite steel wire rod, steel wire and graphite steel with superior machinability and a manufacturing method thereof according to the disclosure will now be described in detail.

[Graphite steel wire rod]

[0016] According to an embodiment of the disclosure, a graphite steel wire rod includes, in percent by weight (wt%), 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities.

[0017] A unit of wt% will now be used unless otherwise mentioned. The term "include (or including)" or "comprise (or comprising)" is inclusive or open-ended and does not exclude additional, unrecited elements or method steps, unless otherwise mentioned.

[Ranges of Ingredients]

Carbon (C): 0.60 to 0.90wt%

[0018] Carbon is an essential element to form graphite grains. In a case that carbon content is less than 0.60wt%, the machinability enhancement effect is not enough and the distribution of the graphite grains is irregular even after completion of graphitization, and in a case that the content is in excess of 0.90wt%, it is likely that the graphite grains are formed coarsely and machinability, surface roughness in particular deteriorates due to an increase in aspect ratio. Accordingly, it is desirable that the carbon content has an upper limit of 0.90wt%.

Silicon (Si): 2.0 to 2.5wt%

[0019] Silicon is actively added because it is a component required as a deoxidizer in manufacturing molten steel and a graphitization promoting element to precipitate the carbon as graphite by unstabilize cementite in steel. In the disclosure, to have this effect, it is desirable that the silicon content is at least 2.0wt%. Otherwise, when the content is excessive, not only the effect may be saturated but also it is likely that the hardness increases due to a solid solution strengthening effect, leading to acceleration of tool wear, brittleness is caused by an increase of nonmetallic inclusions and excessive decarburization is caused during hot rolling. Accordingly, it is desirable that the silicon content has an upper limit of 2.5wt%.

Manganese (Mn): 0.1 to 0.6wt%

[0020] Manganese improves strength and impact properties of steel materials and contributes to machinability enhancement by combining with sulfur in steel and forming MnS inclusions. In the disclosure, to have this effect, it is desirable that manganese is contained in at least 0.1wt%. On the other hand, when the content is excessive, it may interfere with graphitization, delaying graphitization completion time and may increase the strength and hardness, thereby deteriorating machinability. Accordingly, it is desirable that the manganese content has an upper limit of 0.6wt%.

Phosphorus (P): 0.015wt% or less (except 0)

[0021] Phosphorus is an impurity unavoidably contained. Although phosphorus helps machinability by weakening grain boundaries of steel, it increases hardness of ferrite through a significant solid solution strengthening effect, reduces toughness and delayed fracture resistance of the steel and promotes occurrence of surface defects, so it is desirable to maintain the content as low as possible. It is advantageous to control the phosphorus content to be 0wt% in theory, but the phosphorus is inevitably contained in a manufacturing process. Hence, it is important to manage the upper limit, and in the disclosure, the upper limit is kept to 0.015wt%.

sulfur (S): 0.031 to 0.3wt%

[0022] Sulfur has a machinability enhancement effect with creation of MnS, but when contained in excess, mechanical anisotropy appears due to MnS elongated by rolling. In the disclosure, production of MnS was induced by adding sulfur within a range that may contribute to improving machinability without causing the mechanical anisotropy. Specifically, when sulfur is included in the range of 0.031 to 0.3wt%, MnS is generated and machinability is improved, and 100% of cutting performance appears as compared to lead free-cutting steel. However, when the content of sulfur is controlled to less than 0.031 wt%, it leads to a failure of making a fraction of MnS inclusions enough to improve the cutting performance. Furthermore, when it exceeds 0.3wt%, anisotropy of the material increases, causing breakage during the cutting process, which incurs a risk during the processing.

Aluminum (Al): 0.01 to 0.05wt%

[0023] Aluminum is a second element that promotes graphitization after silicon. This is because aluminum makes cementite unstable when it exists as solid solution Al, so it needs to exist as the solid solution Al. In the disclosure, to have this effect, it is desirable to contain at least 0.01wt%. On the other hand, when the content is excessive, not only is the effect saturated, but it may also cause nozzle clogging during continuous casting and AlN is formed at the austenite grain boundaries, so graphite with the AlN as the nucleus is distributed non-uniformly at the grain boundaries. Accordingly, it is desirable that the aluminum content has an upper limit of 0.05wt%.

Titanium (Ti): 0.0051 to 0.02wt%

[0024] Titanium is combined with nitrogen together with boron, aluminum, etc., to produce nitrides such as TiN, BN, AlN, etc., and the nitrides act as nuclei for graphite formation during isothermal heat treatment. However, BN, AlN, etc., have a low formation temperature and are precipitated irregularly at the grain boundaries after austenite is formed, whereas TiN has a higher formation temperature than AlN or BN and is crystallized before austenite formation is completed, so it is uniformly distributed at the austenite grain boundaries and within the grains. Therefore, the graphite grains produced using TiN as the nucleation site are also distributed finely and uniformly. To have this effect, it is desirable to contain at least 0.0051wt%, but when the content is added in excess of 0.02%, they become coarse carbonitrides that consume carbon required to form graphite, thereby inhibiting graphitization. Accordingly, it is desirable that the titanium content has an upper limit of 0.02wt%.

Nitrogen (N): 0.0030 to 0.0150wt%

[0025] Nitrogen combines with titanium, boron and aluminum to produce TiN, BN, AlN, etc., and the nitrides such as BN, AlN, etc., in particular are mostly formed at austenite grain boundaries. During graphitization heat treatment, graphite is formed with these nitrides as nuclei, which may cause non-uniform distribution of graphite, so an appropriate amount of addition is necessary. When an amount of nitrogen added is excessive, it may not combine with nitride forming elements, and when it exists in steel as solid solution nitrogen, it adversely acts to delay graphitization by increasing strength and stabilizing cementite. Accordingly, in the disclosure, the nitrogen content was limited to 0.0030wt% as a lower limit and 0.0150wt% as an upper limit in order to consume them to form nitrides that act as graphite nucleation

sites and not to leave them as solid solution nitrogen.

Boron (B): 0.0005 to 0.0020%

[0026] It is actively added because it combines with N to form BN, which acts as a nucleus for crystallization of graphite and promotes graphitization, but the effect is small at less than 0.0005wt% and when it is added in excess of 0.0020wt%, excessive BN is formed at austenite grain boundaries, not only causing non-uniform distribution of graphite grains after graphitization heat treatment but also weakening the grain boundaries and then significantly reducing hot rolling properties, so it is desirable to contain boron in a range of 0.0005 to 0.0020wt%.

[0027] In the disclosure, the remaining ingredients are iron (Fe) and unavoidable impurities. This may not be excluded because unintended impurities may be inevitably mixed from raw materials or surroundings in the normal steel manufacturing process. These impurities may be known to anyone skilled in the ordinary steel manufacturing process, so not all of them are specifically mentioned in this specification.

[0028] Furthermore, in an embodiment of the disclosure, a wire rod for graphitization heat treatment may have an area fraction of pearlite of at least 95%. In the disclosure, graphite grains are produced by decomposition of pearlite, so when the area fraction of pearlite is low, the fraction of graphite grains is also bound to be low, showing non-uniform distribution, which is undesirable. As it is advantageous to have a high area fraction of pearlite to secure uniform and fine graphite grains, the upper limit is not particularly limited.

[Method of manufacturing wire rod]

[0029] In an embodiment of the disclosure, a method of manufacturing a graphite steel wire rod includes manufacturing a billet including, in percent by weight (wt%), 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except O) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities;

heating the billet;

hot-rolling the heated billet to be manufactured into a wire rod; and

cooling the wire rod.

Wire rod heating process

[0030] In an embodiment of the disclosure, the heating may include performing heat treatment by maintaining at a range of 1050 ± 100 °C for at least 60 minutes.

[0031] Before wire rod rolling, the billet is maintained at a range of 1050 ± 100 °C for at least 60 minutes. It is disadvantageous at a low heating temperature because the rolling load may increase at less than 950 °C of heating temperature of the billet, which reduces rolling productivity. When the heating temperature exceeds 1150 °C, it not only increases the expense but also accelerates decarburization, making the decarburized layer thickened, which undesirably remains even in the final product. The reason for setting the heating holding time to at least 60 minutes is that it is difficult to secure uniform temperature distribution in and outside the billet for wire rod rolling during less than 60 minutes.

Wire rod rolling process

[0032] In an embodiment of the disclosure, the hot-rolling the billet to be manufactured into a wire rod may include hot-rolling at a temperature range of 900 to 1150 °C.

[0033] The reason for setting the wire rod rolling temperature into a range of 900~1150°C is that surface blemishes may easily occur during hot rolling or rolling may be hard because the rolling load increases at less than 900 °C, and that austenite grain size (AGS) becomes coarse at higher than 1150°C, increasing graphitization heat treatment hours after wire rod rolling.

Cooling process

[0034] In an embodiment of the disclosure, the cooling may include cooling down to 500 °C at 0.1~10.0°C/s.

[0035] Furthermore, an embodiment of the disclosure may further include air cooling after the cooling.

[0036] At a cooling rate that exceeds 10.0 °C, it is undesirable because a hard phase such as martensite is generated

and wire breakage may occur during cold drawing, which is a process following wire rod rolling, and at a cooling rate of less than 0.1°C, it is undesirable because a proeutectoid phase is excessively generated, reducing the pearlite fraction or coarsening the grain size so that the graphite grains produced after the graphitization heat treatment may have a non-uniform distribution.

[Graphite steel wire]

[0037] In an embodiment of the disclosure, a graphite steel wire includes, in percent by weight (wt%), 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities.

[Graphite steel]

[0038] In an embodiment of the disclosure, a graphite steel includes, in percent by weight (wt%), 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities, wherein as a micro-structure, graphite grains are distributed in a ferrite matrix, a graphitization rate is at least 95%, and a total of 5% or less of MnS inclusions and pearlite are included.

[0039] In the meantime, the graphitization rate refers to a ratio of the carbon content that exists in the form of graphite to the carbon content added to the steel and is defined by the following [relational equation 1], and at least 95% of graphitization means that most of the added carbon was used to form graphite (the amount of the solid solution carbon in ferrite and solid solution carbon in fine carbides is very tiny, so it is ignored), meaning that there is no undissolved pearlite, that is, it has a microstructure in which graphite grains are distributed in the ferrite matrix.

$$\text{Graphitization rate (\%)} = (1 - \text{carbon content in undissolved pearlite} / \text{carbon content in steel}) \times 100 \quad [\text{relational equation 1}]$$

(Graphitization rate is 100% when there is no undissolved pearlite)

[Method of manufacturing graphite steel]

[0040] In an embodiment of the disclosure, a method of manufacturing a graphite steel includes manufacturing a wire rod including, in percent by weight (wt%), 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities; and performing graphitization heat treatment on the manufactured wire rod.

[0041] In an embodiment of the disclosure, the performing of the graphitization heat treatment may include performing heat treatment at a range of 700 to 800 °C for at least 5 hours.

[0042] When the heat treatment is maintained at the range of 700 to 800 °C for at least 5 hours, the graphitization rate may reach at least 95%. On the other hand, at less than 700 °C, the graphitization heat treatment time increases and exceeds at least 10 hours, and at higher than 800 °C, not only does the graphitization time increases, but also austenite is generated due to reverse transformation of pearlite and pearlite may form again during cooling, both cases of which are not desirable.

Embodiments of the disclosure will now be described in more detail.

[0043] The following embodiments are provided to deliver the idea of the disclosure to those of ordinary skill in the art, but the disclosure is not limited to the embodiments and may be implemented in other forms.

(Embodiments)

[0044] A billet containing ingredients in table 1 below was maintained for 90 minutes under a heating temperature condition and subjected to high-speed wire rod rolling to be manufactured into a wire rod having a diameter of 19 mm. Wire rod cooling rate, area fraction of wire rod pearlite and graphitization heat treatment time and graphitization fraction

EP 4 394 072 A1

for this case are shown in table 1 below.

[0045] In tables 1 and 2, embodiments 1 to 11 correspond to graphite steel wire rods that satisfy an alloy composition range and manufacturing conditions of the disclosure, and comparative examples 1 to 7 correspond to wire rods that do not satisfy the alloy composition range and/or manufacturing conditions of the disclosure.

[Table 1]

	C	Si	Mn	S	Ti	B	P	Al	N	Cutting performance (%)
Embodiment 1	0.65	2.1	0.25	0.14	0.015	0.0006	0.005	0.015	0.005	100
Embodiment 2	0.87	2.15	0.36	0.24	0.017	0.0015	0.008	0.023	0.008	100
Embodiment 3	0.72	2.35	0.47	0.035	0.007	0.0008	0.006	0.043	0.010	100
Embodiment 4	0.68	2.18	0.16	0.26	0.009	0.0009	0.009	0.035	0.009	100
Embodiment 5	0.82	2.25	0.55	0.05	0.012	0.0012	0.012	0.040	0.014	100
Embodiment 6	0.62	2.48	0.50	0.09	0.006	0.0018	0.014	0.042	0.012	100
Embodiment 7	0.73	2.42	0.2	0.16	0.011	0.0007	0.009	0.034	0.006	100
Embodiment 8	0.78	2.32	0.32	0.19	0.016	0.0017	0.008	0.019	0.008	100
Embodiment 9	0.85	2.15	0.48	0.27	0.009	0.0011	0.004	0.027	0.013	100
Embodiment 10	0.75	2.26	0.14	0.21	0.018	0.001	0.010	0.030	0.007	100
Embodiment 11	0.73	2.46	0.41	0.15	0.008	0.0015	0.012	0.020	0.008	100
Comparative example 1	0.63	2.0	0.23	0.005	0.016	0.000	0.017	0.005	0.001	88
Comparative example 2	0.68	2.2	0.35	0.003	0.02	0.0002	0.020	0.006	0.002	95
Comparative example 3	0.73	2.25	0.45	0.006	0.009	0.0004	0.025	0.075	0.018	89
Comparative example 4	0.95	2.15	0.3	0.007	0.018	0.0025	0.023	0.060	0.020	92
Comparative example 5	0.55	2.6	0.56	0.4	0.025	0.0025	0.019	0.003	0.025	91
Comparative example 6	0.8	2.75	0.9	0.45	0.03	0.0024	0.018	0.065	0.021	93
Comparative example 7	0.75	2.8	0.8	0.35	0.002	0.003	0.020	0.06	0.022	90

[0046] The cutting performance has a numerical value based on cutting performance of lead free-cutting steel (100% refers to an equivalent level).

[Table 2]

section	wire rod			graphitization	
	Cooling start temperature (°C)	cooling rate (°C/s)	Area fraction of pearlite (%)	Holding time (hr)	Graphitization fraction (%)
Embodiment 1	880	0.5	95.1	6.5	99
Embodiment 2	865	7.5	96.5	8.1	99
Embodiment 3	815	1.5	95.1	7.5	100

(continued)

section	wire rod			graphitization	
	Cooling start temperature (°C)	coolingrate (°C/s)	Area fraction of pearlite (%)	Holding time (hr)	Graphitization fraction (%)
Embodiment 4	795	3.2	96.0	5.5	100
Embodiment 5	865	5.0	97.5	9.4	100
Embodiment 6	850	2.0	95.5	5.6	99.5
Embodiment 7	795	9.0	96.5	6.4	100
Embodiment 8	755	4.5	96.0	7.2	98.5
Embodiment 9	890	6.0	96.5	8.5	100
Comparative example 1	915	0.05	93.0	1.5	75
Comparative example 2	865	12.0	93.5	2.5	85
Comparative example 3	815	11.5	94.2	3.0	86
Comparative example 4	740	0.07	93.2	2.5	85
Comparative example 5	880	15.5	93.5	3.4	86
Comparative example 6	830	14.0	94.1	4.2	84

[0047] The structure of (100% - graphitized fraction) consists of MnS inclusions and pearlite, and the graphitized structure consists of ferrite + graphite grains. It can be seen that the area fraction of pearlite and the graphitization fraction are attained under wire rod and graphitization manufacturing conditions as shown in table 2 above.

[0048] The embodiments and the comparative examples will now be evaluated with reference to tables 1 and 2.

[0049] Embodiments 1 to 11 satisfy the alloy composition range and manufacturing conditions of the disclosure, so that the area fraction of pearlite in the graphite steel wire rod is at least 95%, the graphitization rate is at least 98.5%, and the cutting performance is 100% as compared to lead free-cutting steel.

[0050] On the other hand, the cutting performance of the graphite steel of comparative example 1, in which the sulfur content was only 0.005wt% and no boron is substantially contained, was only 88% as compared to the lead free-cutting steel, and according to the method of manufacturing a wire rod of comparative example 1, a wire rod cooled at a cooling rate of 0.05 °C/s and including 93% of area fraction of pearlite was obtained and subjected to heat treatment for 1.5 hours, so that the graphitization fraction was only 75%.

[0051] The cutting performance of the graphite steel of comparative example 2, in which the sulfur content was only 0.003wt% and the boron content was only 0.0002wt%, was only 95% as compared to the lead free-cutting steel, and according to the method of manufacturing a wire rod of comparative example 2, a wire rod cooled at a cooling rate of 12.0 °C/s and including 93.5% of area fraction of pearlite was obtained and subjected to heat treatment for 2.5 hours, so that the graphitization fraction was only 85%.

[0052] The cutting performance of the graphite steel of comparative example 3, in which the sulfur content was only 0.006wt% and the boron content was only 0.0004wt%, was only 89% as compared to the lead free-cutting steel, and according to the method of manufacturing a wire rod of comparative example 3, a wire rod cooled at a cooling rate of 11.5 °C/s and including 94.2% of area fraction of pearlite was obtained and subjected to heat treatment for 3.0 hours, so that the graphitization fraction was only 86%.

[0053] The cutting performance of the graphite steel of comparative example 4, in which the carbon content was 0.95wt%, the sulfur content was 0.007wt% and the boron content was 0.0025wt%, was only 92% as compared to the lead free-cutting steel, and according to the method of manufacturing a wire rod of comparative example 4, a wire rod cooled at a cooling rate of 0.07 °C/s and including 93.2% of area fraction of pearlite was obtained and subjected to heat treatment for 2.5 hours, so that the graphitization fraction was only 85%.

[0054] The cutting performance of the graphite steel of comparative example 5, in which the carbon content was 0.55wt%, the silicon content was 2.6wt%, the sulfur content was 0.4wt%, the titanium content was 0.025wt% and the boron content was 0.0025wt%, was only 91% as compared to the lead free-cutting steel, and according to the method of manufacturing a wire rod of comparative example 5, a wire rod cooled at a cooling rate of 15.5 °C/s and including 93.5% of area fraction of pearlite was obtained and subjected to heat treatment for 3.4 hours, so that the graphite fraction was only 86%.

[0055] The cutting performance of the graphite steel of comparative example 6, in which the silicon content was

2.75wt%, the manganese content was 0.9wt%, the sulfur content was 0.45wt%, the titanium content was 0.03wt% and the boron content was 0.0024wt%, was only 93% as compared to the lead free-cutting steel, and according to the method of manufacturing a wire rod of comparative example 6, a wire rod cooled at a cooling rate of 14.0 °C/s and including 94.1% of area fraction of pearlite was obtained and subjected to heat treatment for 4.2 hours, so that the graphite fraction was only 84%.

[0056] Furthermore, the graphite steel of comparative example 7, which contained 2.8wt% of silicon, 0.8wt% of manganese, 0.35wt% of sulfur, 0.002wt% of titanium, and 0.003wt% of boron, was only 90% as compared to the lead free-cutting steel.

[0057] From the evaluation of the aforementioned embodiments and comparative examples, it can be seen that all the properties of the graphite steel wire rod and graphite steel in the disclosure may be satisfied only when the alloy composition range and manufacturing conditions in the disclosure are satisfied.

[Industrial Applicability]

[0058] According to the disclosure, a graphite steel having superior machinability may replace the existing free-cutting steel and may be used as an eco-friendly free-cutting steel that replaces a harmful element such as Pb, so the industrial applicability is acknowledged.

Claims

1. A graphite steel wire rod having superior cutting performance, the graphite steel wire rod comprising:
in percent by weight, 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities.
2. The graphite steel wire rod of claim 1, wherein an area fraction of pearlite is at least 95%.
3. A method of manufacturing a graphite steel wire rod with superior cutting performance, the method comprising:
manufacturing a billet including, in percent by weight, 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities; and
heating the billet;
hot-rolling the heated billet to be manufactured into a wire rod; and
cooling the wire rod.
4. The method of claim 3, wherein the heating comprises performing heat treatment by maintaining at a range of 1050 ± 100 °C for at least 60 minutes.
5. The method of claim 3, wherein the hot-rolling for manufacturing the wire rod comprises hot-rolling at a temperature range of 900 to 1150 °C.
6. The method of claim 3, wherein the cooling comprises cooling down to 500 °C at a cooling rate of 0.1 to 10.0 °C/s.
7. The method of claim 3, further comprising: air-cooling after the cooling.
8. A graphite steel wire having superior cutting performance, the graphite steel wire comprising:
in percent by weight, 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities.
9. A graphite steel with superior cutting performance, the graphite steel comprising:
in percent by weight, 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn),

0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities,

wherein as a microstructure, graphite grains are distributed in a ferrite matrix, a graphitization rate is at least 95%, and a total of 5% or less of MnS inclusions and pearlite are included.

10. A method of manufacturing a graphite steel having superior cutting performance, the method comprising:

manufacturing a wire rod including, in percent by weight, 0.60 to 0.90% of carbon (C), 2.0 to 2.5% of silicon (Si), 0.1 to 0.6% of manganese (Mn), 0.015% or less (except 0) of phosphorus (P), 0.031 to 0.3% of sulfur (S), 0.01 to 0.05% of aluminum (Al), 0.005 to 0.02% of titanium (Ti), 0.0005 to 0.0020% of boron (B), 0.0030 to 0.0150% of nitrogen (N) and the remainder having Fe and unavoidable impurities; and performing graphitization heat treatment on the manufactured wire rod.

11. The method of claim 10, wherein the performing graphitization heat treatment comprises performing heat treatment at a temperature range of 700 to 800 °C for at least 5 hours.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2022/015274

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/02(2006.01)i; C22C 38/04(2006.01)i; C22C 38/06(2006.01)i; C22C 38/60(2006.01)i; C22C 38/14(2006.01)i;
C22C 38/00(2006.01)i; B21C 23/08(2006.01)i; C21D 9/52(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)

C22C 38/02(2006.01); B21B 1/16(2006.01); B21J 5/00(2006.01); C21D 8/06(2006.01); C21D 9/46(2006.01);
C22C 38/00(2006.01)

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

Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: 흑연강(graphite steel), 펄라이트(pearlite), 절삭(cutability), 흑연화(graphitization),
유황(sulfur)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 11-131187 A (KOBEL STEEL LTD.) 18 May 1999 (1999-05-18) See paragraphs [0031]-[0033], [0036] and [0038] and claims 1 and 4-5.	1-11
A	KR 10-2224044 B1 (POSCO) 09 March 2021 (2021-03-09) See claims 1, 3 and 5.	1-11
A	KR 10-0349008 B1 (NIPPON STEEL CORPORATION) 17 August 2002 (2002-08-17) See claims 1-2 and 13.	1-11
A	JP 11-350066 A (NKK JOKO K.K.) 21 December 1999 (1999-12-21) See paragraph [0119] and claims 1-4.	1-11
A	EP 2530177 A1 (NIPPON STEEL CORPORATION) 05 December 2012 (2012-12-05) See paragraph [0030] and claim 1.	1-11

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“D” document cited by the applicant in the international application

“E” earlier application or patent but published on or after the international filing date

“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)

“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

“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

“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

“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

“&” document member of the same patent family

Date of the actual completion of the international search

08 February 2023

Date of mailing of the international search report

09 February 2023

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208

Facsimile No. +82-42-481-8578

Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2022/015274

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 11-131187 A	18 May 1999	None	
KR 10-2224044 B1	09 March 2021	KR 10-2020-0075643 A	26 June 2020
KR 10-0349008 B1	17 August 2002	DE 69931601 T2	26 April 2007
		EP 1045044 A1	18 October 2000
		EP 1045044 B1	31 May 2006
		JP 11-246936 A	14 September 1999
		JP 11-246939 A	14 September 1999
		JP 4119516 B2	16 July 2008
		JP 4119517 B2	16 July 2008
		KR 10-2001-0012168 A	15 February 2001
		US 6419761 B1	16 July 2002
		WO 99-45162 A1	10 September 1999
JP 11-350066 A	21 December 1999	JP 3764273 B2	05 April 2006
EP 2530177 A1	05 December 2012	BR 112012019585 A2	06 October 2020
		CA 2787564 A1	28 July 2011
		CA 2787564 C	06 October 2015
		CN 102725431 A	10 October 2012
		CN 102725431 B	12 March 2014
		EP 2530177 B1	04 May 2016
		ES 2578352 T3	26 July 2016
		JP 4837806 B2	14 December 2011
		JP WO2011-090205 A1	23 May 2013
		KR 10-1463666 B1	19 November 2014
		KR 10-2012-0099500 A	10 September 2012
		MX 2012008539 A	07 September 2012
		MX 341381 B	18 August 2016
		PL 2530177 T3	31 October 2016
		US 2012-0295123 A1	22 November 2012
		US 8945719 B2	03 February 2015
		WO 2011-090205 A1	28 July 2011