

(19)



(11)

EP 3 358 026 A1

(12)

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

(43) Date of publication:

08.08.2018 Bulletin 2018/32

(51) Int Cl.:

C22C 37/04 (2006.01)

(21) Application number: **16850700.2**

(86) International application number:

PCT/JP2016/055973

(22) Date of filing: **29.02.2016**

(87) International publication number:

WO 2017/056522 (06.04.2017 Gazette 2017/14)

(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 MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

Designated Validation States:

MA MD

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(54) **SPHEROIDAL GRAPHITE CAST IRON WITH EXCELLENT GAS DEFECT RESISTANCE**

(57) There is provided with spheroidal graphite cast iron having excellent gas defect resistance where gas defects such as pinholes attributable to the free N are small in number and having mechanical characteristics and machinability equal to or greater than the conventional ones. The spheroidal graphite cast iron consists

of, in mass ratio, C: 3.3 to 4%; Si: 2 to 3%; P: not more than 0.05%; S: not more than 0.02%; Mn: not more than 0.8%; Cu: not more than 0.8% (0 is not included); Mg: 0.02 to 0.06%; Ti: 0.01 to 0.04%; V: 0.001 to 0.01%; Nb: 0.001 to 0.01%; and N: 0.004 to 0.008%, with the remnant substantially consisting of Fe and an inevitable impurity.

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Description

[Technical Field]

5 **[0001]** The present invention relates to a spheroidal graphite cast iron excellent in gas defect resistance.

[Background Art]

10 **[0002]** Spheroidal graphite cast iron which has excellent mechanical characteristics and good castability is widely used for various automobile parts and machine parts. In the manufacture of the spheroidal graphite cast iron, as main raw materials, pig iron, steel scrap, return scrap (casting return material) and the like are used. Of the above-mentioned raw materials, pig iron for castings was conventionally the main material as the raw material of the spheroidal graphite cast iron; however, in recent years, from the viewpoint of economical use of resources, it has been common to mainly use steel scrap instead of pig iron the price of which has risen. Steel scrap has been more and more heavily used as a raw material of cast iron in general including spheroidal graphite cast iron since it is caused in large amount with the growth of the automobile industry and is supplied inexpensively.

15 **[0003]** Here, the steel scrap caused in the automobile industry is formed of machining scrap for automobile bodies and the like, and in recent years, as the steel material thereof, the ratio of high-tensile steel plates has been increasing. The reason therefor is that for automobile bodies and the like, while weight reduction is required from the viewpoint of environmental preservation by improvement of fuel efficiency, securement of strength and rigidity is also required from the viewpoint of securement of passengers' safety at the time of a collision. For this reason, it is required that automobile bodies and the like attain both weight reduction and strength enhancement/rigidity enhancement, and to respond thereto, high-tensile steel plates containing high levels of Mn, Cr, Mo and the like tend to be used heavily. When steel scrap inevitably containing a large amount of Mn, Cr, Mo and the like is used as the raw material, a problem arises in that ductility (elongation characteristic) is deteriorated since the crystallization of graphite is inhibited or a carbide is generated when it is made into spheroidal graphite cast iron. To solve the problem attributable to Mn, Cr, Mo and the like inevitably contained in the raw material, various proposals have been made to remove these elements from the melt in the melting process of spheroidal graphite cast iron.

20 **[0004]** Some high-tensile steel plates are enhanced in strength by containing N (nitrogen) in addition to Mn, Cr and Mo and undergoing precipitation hardening with a carbonitride or by undergoing nitriding. Some of these high-tensile steel plates contain as much as several hundreds of ppm of N. When spheroidal graphite cast iron is manufactured by using, as the raw material, steel scrap inevitably containing a large amount of N like this, there is a possibility that free N contained in the melt into which this raw material is melted increases. In the following description, "free N" indicates a nitrogen atom in a free state not constituting an atom constituting a solid phase or a solid solution, and "N" indicates nitrogen as an element.

25 **[0005]** Moreover, generally, the melt (raw melt) formed in the melting process of spheroidal graphite cast iron is deoxidized at the stage of the melting process since it contains Si and Mn, and thereafter, is further thoroughly deoxidized by the Mg added in the spheroidizing processing performed after the raw melt is shifted to a ladle and the Si added in the inoculation processing. The thus deoxidized melt for spheroidal graphite cast iron has the property of readily absorbing or occluding the free N in the atmosphere when the melt is exposed to the atmosphere in the process of tapping from a melting furnace into a ladle or in the process of pouring from the ladle into a mold.

30 **[0006]** In the melt for spheroidal graphite cast iron having the property of readily absorbing or occluding the free N derived from the atmosphere as described above, when the content of steel scrap with a high N content inevitably containing a large amount of N as the raw material further increases, the free N in the melt increases because of this free N derived from steel scrap, so that the tendency increases that a gas defect such as a pinhole formed of nitrogen gas (N₂ gas) attributable to the free N is caused in the cast products. Specifically, when a melt excessively containing free N solidifies, there are cases where the free N that cannot be solid-solved is released as nitrogen gas into the solid phase to cause a gas defect such as a pin hole formed of nitrogen gas in the cast products. If a gas defect is caused in the spheroidal graphite cast iron, not only a poor appearance but also a problem can arise in that deterioration of mechanical characteristics such as strength and elongation is caused by the minute hole defect.

35 **[0007]** As a technology of reducing the content of impurities containing N immixed into cast iron such as spheroidal graphite cast iron, Patent Document 1 has a description of a spheroidal graphite cast iron containing, in mass ratio, 2.0 to 4.0% carbon, 0.01 to 0.1% spheroidization promoting element formed of one or more than one of magnesium, calcium and a rare-earth element, 1.0 to 3.0% silicon and not more than 0.02% sulfur with the remnant consisting of iron and inevitable impurities and in which the amount of elements other than cobalt, copper and nickel in the inevitable impurities is made as small as possible so that the absorption energy value in a Charpy impact test at -60 degrees C or -80 degrees C is not less than 14 J/cm² on a V notch test piece by doing the following: An alloy having, in mass ratio, 2.0 to 4.0% carbon, 1.0 to 3.0% silicon and not more than 0.02% sulfur with the remnant consisting of iron and a very small amount

of inevitable impurities is introduced into a cold crucible melting furnace and melted and then, a spheroidizing agent containing a spheroidization promoting element formed of one or more than one of magnesium, calcium and a rare-earth element is added thereto so that the ratio of the spheroidization promoting element is 0.01 to 0.1% in the final composition, cooling is performed without inoculation processing to promote graphitization being performed and a manufacturing method to produce an alloy with iron is applied.

[0008] According to Patent Document 1, in melting the raw material, after the melting furnace chamber is evacuated, argon gas is introduced to make the inside of the melting furnace chamber an argon atmosphere and by using a water-cooled highly pure copper crucible and using a cold crucible melting furnace which is an apparatus that simulatively brings the copper crucible and the molten metal into a non-contact state and melts them (levitation melting), the immixture of impurities from the crucible or the gas phase (environment) into the molten metal as in the conventional melting process is prevented and a highly pure material can be produced. Moreover, in the spheroidal graphite cast iron of Patent Document 1, by making not more than 0.003% in mass ratio the ratio of each of the elements other than cobalt, copper and nickel in the inevitable impurities, the inclusion can be further reduced and a spheroidal graphite cast iron where the internal brittle part is reduced can be provided.

[Prior Art Document]

[Patent Document]

[0009] [Patent Document 1] Japanese Patent Application Laid-Open No. 2004-169167

[Summary of the Invention]

[Problem to be Solved by the Invention]

[0010] In the method of manufacturing spheroidal graphite cast iron disclosed in Patent Document 1, since the raw material is melted in the argon atmosphere and solidified as it is to form spheroidal graphite cast iron, the free N contained in the melt is reduced and consequently, there is a possibility that the gas defect attributable to the free N caused in spheroidal graphite cast iron is suppressed. However, highly pure electrolytic iron of, for example, approximately 4N (99.99%, mass ratio) level, silicon for semiconductors, highly purified graphite and the like are used as the raw materials, and the starting materials themselves are highly pure raw materials. Furthermore, the manufacturing method thereof is provided by making the inside of the melting furnace chamber the argon atmosphere and using a cold crucible melting furnace which is a special apparatus formed of a water-cooled highly pure copper crucible. The cold crucible melting furnace is generally used for the manufacture of a highly pure material such as the manufacture of a highly pure alloy ingot. When a highly pure raw material and a special apparatus are used as described above, although the content of inevitable impurities can be significantly reduced, for the manufacture of spheroidal graphite cast iron applied to automobile parts and machine parts, the obtained cast products are extremely expensive, which is a problem from the viewpoint of economic rationality.

[0011] Moreover, according to the manufacturing method of Patent Document 1, after the raw material is melted in the copper crucible and the spheroidizing agent is added, cooling and solidification of the melt are performed in the copper crucible. According to this manufacturing method, the obtained spheroidal graphite cast iron is a massive cast product of a shape copying the shape of the space in the crucible. With this, advantages of casting which is a work method having a high shape freedom degree in nature cannot be enjoyed.

[0012] That is, to obtain cast products having free shapes such as automobile parts and machine parts, it is necessary to perform cooling and solidification after pouring into a mold having a cavity defining the product shape directly from the melting furnace or through a ladle. To manufacture cast products at an industrially realistic and rational cost, it is important that the process of tapping from the melting furnace into the ladle and the process of pouring from the ladle into the mold can be performed in the atmosphere.

[0013] Although it is considered to dispose a ladle and a mold inside the chamber and perform tapping and pouring after making the inside of the chamber an argon gas atmosphere or vacuum in order to suppress penetration (absorption, occlusion) of free N into the melt, the equipment and apparatus are special and large-scale ones and the obtained cast products are further expensive, which is neither economical nor realistic. In addition, there is no effective and practical method to remove the free N from the melt of spheroidal graphite cast iron, and even if dilution with a material with a low N content is attempted, the low N raw material such as highly pure pig iron and a base metal is expensive and uneconomical.

[0014] In recent years, the situation has been such that a large amount of N is unavoidably contained as an inevitable content in the raw material of spheroidal graphite cast iron as described above. Moreover, in addition to steel scrap and the atmosphere which are typical examples of origins of the free N as described above, there exists plenty of origins of

the free N that can be dissolved in the melt such as other materials constituting the raw material and a furnace material of the melting furnace that melts the raw material. For this reason, it is industrially very effective if a spheroidal graphite cast iron can be obtained in which, for example, without the free N derived from steel scrap being removed or dilution with expensive pig iron or the like being performed, no gas defect such as a pin hole attributable to this free N is caused while the free N is contained in the melt.

[0015] The present invention is made in view of the above-described conventional problems, and an object thereof is to provide spheroidal graphite cast iron having excellent gas defect resistance where gas defects such as pinholes attributable to the free N are small in number and having mechanical characteristics and machinability equal to or greater than the conventional ones.

[Means for Solving the Problem]

[0016] That is, a spheroidal graphite cast iron excellent in gas defect resistance of the present invention consists of, in mass ratio:

C: 3.3 to 4%;
Si: 2 to 3%;
P: not more than 0.05%;
S: not more than 0.02%;
Mn: not more than 0.8%;
Cu: not more than 0.8% (0 is not included);
Mg: 0.02 to 0.06%;
Ti: 0.01 to 0.04%;
V: 0.001 to 0.01%;
Nb: 0.001 to 0.01%; and
N: 0.004 to 0.008%,

with the remnant substantially consisting of Fe and an inevitable impurity.

[0017] Preferably, the spheroidal graphite cast iron of the present invention contains, in mass ratio, 0.015 to 0.045 % Ti, V and Nb in total and further, contains Ti, V, Nb and N so as to satisfy the following expression (1):

$$0.8 \leq (0.29\text{Ti} + 0.27\text{V} + 0.15\text{Nb}) / \text{N} \leq 2.0 \dots (1).$$

[0018] Here, the element symbols in the expression (1) represent the contents [mass ratio (%)] of the elements in the spheroidal graphite cast iron.

[0019] Preferably, the spheroidal graphite cast iron of the present invention contains, in mass ratio, not less than 0.005% P and not less than 0.005% S or/further contains, in mass ratio, not less than 0.2% Mn and not less than 0.1% Cu.

[0020] Preferably, the spheroidal graphite cast iron is not less than 600 MPa in tensile strength and not less than 12% in elongation.

[Effects of the Invention]

[0021] The spheroidal graphite cast iron of the present invention has excellent gas defect resistance with few gas defects such as pinholes attributable by the free N.

[Brief Description of the Drawings]

[0022]

FIG. 1A is a schematic plan view of a flat test piece for measuring a gas defect.
FIG. 1B is a schematic side view of the flat test piece for measuring a gas defect.

[Mode for Carrying out the Invention]

[0023] The composition of the spheroidal graphite cast iron of the present invention will be described below in detail. The contents of the elements constituting the alloy are expressed by mass ratios (%) unless otherwise specified. More-

over, while in the embodiment described below, reduction in the gas defect attributable to the free N derived from steel scrap is described as an embodiment of the present invention, the present invention is not limited to the embodiment described below.

5 (1) C (carbon): 3.3 to 4%

[0024] C is an element that contributes to the flowability of the melt and the crystallization of graphite. When the C content is less than 3.3%, the flowability at the time of casting decreases and the number of graphite grains decreases so that chill (Fe_3C : cementite) is apt to be formed, which decreases the elongation of the spheroidal graphite cast iron. On the other hand, when the C content exceeds 4%, shrinkage cavity is apt to appear and abnormal graphite is apt to be formed, so that strength decreases. For this reason, the C content is made 3.3 to 4%. The lower limit of the C content is preferably 3.4%, and is more preferably 3.6%. Moreover, the upper limit of the C content is preferably 3.9%, and is more preferably 3.8%.

15 (2) Si (silicon): 2 to 3%

[0025] Si is necessary for promoting the crystallization of graphite and enhancing the flowability of the melt. When the Si content is less than 2%, chill is apt to be formed, so that the machinability and elongation of the spheroidal graphite cast iron decrease. However, when the Si content exceeds 3%, the matrix of the spheroidal graphite cast iron becomes brittle, so that ductility (impact value) and elongation extremely decrease and strength and machinability deteriorate. For this reason, the Si content is made 2 to 3%. The lower limit of the Si content is preferably 2.1%, and is more preferably 2.2%. Moreover, the upper limit of the Si content is preferably 2.9%, and is more preferably 2.8%.

25 (3) P (phosphorus): not more than 0.05%

[0026] P is an element inevitably immixed from the raw material. P inhibits the spheroidization of graphite, and is solid-solved in the matrix to embrittle the structure. For this reason, the P content is made not more than 0.05%. On the other hand, although no lower limit is set, since it is not economical to reduce it, for example, to not more than the detection limit, it is desirable that the lower limit thereof be approximately 0.005%. The upper limit of the P content is preferably 0.03%.

(4) S (sulfur): not more than 0.02%

[0027] S is an element inevitably immixed from the raw material. S is a graphite spheroidization inhibiting element, and the content thereof is made not more than 0.02%. On the other hand, although no lower limit is set, since it is not economical to reduce it, for example, to not more than the detection limit, it is desirable that the lower limit thereof be approximately 0.005%. The upper limit of the S content is preferably 0.01%.

40 (5) Mn (manganese): not more than 0.8%

[0028] Mn, which is an element inevitably immixed from the raw material, precipitates a pearlite phase as a pearlite phase stabilizing element. When a spheroidal graphite cast iron the strength of which is improved by stably precipitating a pearlite phase in the matrix structure is obtained, it is preferable that the Mn content be not less than 0.2%. On the other hand, when the content thereof exceeds 0.8%, the formation of chill is conspicuous, so that the ductility, elongation and machinability of the spheroidal graphite cast iron are deteriorated. For this reason, the Mn content is made not more than 0.8%. The upper limit of the Mn content is preferably 0.5%.

(6) Cu (copper): not more than 0.8% (0 is not included)

[0029] Cu, which is a pearlite phase stabilizing element, is an element that is effective when a spheroidal graphite cast iron containing a pearlite phase in the matrix structure and having its strength improved is obtained. For this reason, it may be contained in an appropriate amount without 0% included according to a desired strength. To stably generate a pearlite phase, it is preferable that the Cu content be not less than 0.1%. However, when the Cu content exceeds 0.8%, the spheroidal graphite cast iron becomes too hard, and graphite spheroidization is inhibited, so that the elongation and ductility of the spheroidal graphite cast iron decrease. For this reason, the Cu content is set to not more than 0.8%. The upper limit of the Cu content is preferably 0.6%.

(7) Mg (magnesium): 0.02 to 0.06%

[0030] Mg is an element necessary for graphite spheroidization that is important in improving mechanical characteristics such as the strength and elongation of the spheroidal graphite cast iron, and when the content thereof is less than 0.02%, the effect of graphite spheroidization is insufficient. On the other hand, when the Mg content exceeds 0.06%, chill and shrinkage cavity are apt to be formed, so that the machinability and ductility of the spheroidal graphite cast iron decrease. For this reason, the Mg content is made 0.02 to 0.06%. The lower limit of the Mg content is preferably 0.025%, and is more preferably 0.03%. Moreover, the upper limit of the Mg content is preferably 0.05%, and is more preferably 0.04%.

(8) Ti (titanium): 0.01 to 0.04%, V (vanadium): 0.001 to 0.01%, Nb (niobium): 0.001 to 0.01%

[0031] Ti, V and Nb are essential elements that are most important as constituents constituting the spheroidal graphite cast iron of the present invention. From the viewpoint of being the structural elements of the spheroidal graphite cast iron obtained by the melt, the free N contained in the melt of the spheroidal graphite cast iron is considered to be finally released as nitrogen gas without being fixed (1) in the matrix phase, (2) in a nitride or a carbonitride or (3) to the structural elements of the above (1) and (2) and exist as N mainly in these three structural elements in the gas defect formed of the nitrogen gas. The upper limit of the amount of N that can be contained in the matrix phase of (1) is the solid solubility limit of the austenite phase generated in the neighborhood of 1000 degrees C which is the austenitizing temperature.

[0032] Ti, V and Nb are powerful carbonitride forming elements (hereinafter, the three elements of Ti, V and Nb will sometimes be referred to as carbonitride forming elements), and by these elements being contained in not less than a predetermined amount, a nitride or a carbonitride (hereinafter, these will sometimes be collectively called carbonitride) is formed by a chemical combination with the free N in the melt. The crystallization temperature of the carbonitride formed by the above-mentioned carbonitride forming elements is higher than the crystallization start temperature of the austenite phase (matrix phase), and in the process of the melt being cooled to solidify, the carbonitride is formed earlier than the matrix phase. As a result, the free N excessively dissolved in the melt beyond the solid solubility limit of N of the austenite phase is fixed as a carbonitride. Thereby, even in a spheroidal graphite cast iron formed by using a raw material containing N more than desired, the free N exceeding the solid solubility limit of the austenite phase is inhibited from being released as nitrogen gas from inside the melt at the time of solidification, so that the occurrence of the gas defect is prevented.

[0033] In addition to the above-described effects of preventing the occurrence of the gas defect, an effect can also be produced in that variation in the mechanical characteristics of the obtained spheroidal graphite cast iron can be reduced by suppressing variation in the amount of N solid-solved in the austenite phase by the fixing of the free N in the melt by the carbonitride forming elements. That is, N is a powerful pearlite phase stabilizing element together with Mn and Cu, and promotes the precipitation of the pearlite phase from the austenite phase. When a steel scrap with little N is used as has conventionally been done, the amount of N contained in the raw material among the melting lots (charges) is comparatively uniform, and variation in the free N in the melt dissolved in the raw material is small. For this reason, to obtain a desired pearlite phase, the precipitation amount of the pearlite phase can be controlled by adjusting the additive amounts of elements such as Mn and Cu the contents of which can be comparatively easily controlled.

[0034] However, when a steel scrap with a large amount of N is used as the raw material in addition to the steel scrap with little N, the amount of N contained in the raw material among the melting lots varies according to the composition of the steel scrap contained in the raw material, and the variation in the amount of free N in the melt is also large. For this reason, the amount of N solid-solved in the austenite phase also varies and the precipitation amount of the pearlite phase is unstable, which causes variation in the mechanical characteristics (strength and elongation) of the spheroidal graphite cast iron among the melting lots. On the other hand, in the present invention, pearlitization by N is suppressed by reducing the amount of N solid-solved in the austenite phase by the fixing of the free N by the carbonitride forming elements as described above. Thereby, the precipitation amount of the pearlite phase can be stably adjusted by controlling the contents of Mn and Cu, so that variation in the mechanical characteristics of the spheroidal graphite cast iron can be reduced.

[0035] To obtain the effect of fixing the free N by the carbonitride formed by the above-mentioned carbonitride forming elements, it is necessary that the contents of Ti, V and Nb be not less than 0.01%, not less than 0.001% and not less than 0.001%, respectively. On the other hand, when the contents of Ti, V and Nb exceed 0.04%, 0.01% and 0.01%, respectively, an extremely hard carbide or nitride is formed, so that the machinability and mechanical characteristics (strength and elongation) of the spheroidal graphite cast iron decrease. For this reason, the Ti content is made 0.01 to 0.04%, the V content is made 0.001 to 0.01%, and the Nb content is made 0.001 to 0.01%.

[0036] The lower limit of the Ti content is preferably 0.012%, and is more preferably 0.013%. Moreover, the upper limit of the Ti content is preferably 0.035%, and is more preferably 0.025%.

[0037] The lower limit of the V content is preferably 0.002%. Moreover, the upper limit of the V content is preferably 0.004%, and is more preferably 0.003%.

[0038] The lower limit of the Nb content is preferably 0.002%, and is more preferably 0.004%. Moreover, the upper

limit of the Nb content is preferably 0.006%, and is more preferably 0.005%.

[0039] By the carbonitride forming elements being contained in a predetermined amount as described above and fixing the free N as a carbonitride, a spheroidal graphite cast iron can be obtained that has an excellent gas defect resistance with few gas defects such as pinholes attributable by the free N and further, has mechanical characteristics (strength and elongation) and machinability equal to or greater than the conventional ones by the variation in its mechanical characteristics being reduced and the excessive carbonitride formation being suppressed.

[0040] Further, one significant feature of the present invention is that Ti, V and Nb are not contained singly but these three elements are contained in combination and the contents thereof are controlled to appropriate amounts. By Ti, V and Nb being all contained in the above-mentioned numerical ranges as described above, the total amount of these carbonitride forming elements can be reduced more than when these are contained singly or only two kinds are contained. Specifically, in forming the same amount of carbonitride, by the above-mentioned three kinds of carbonitride forming elements being contained in combination, the total amount of contained carbonitride forming elements can be suppressed compared with when they are contained singly or only two kinds are contained. Thereby, the amount of carbonitride that affects the mechanical characteristics and machinability is made in an appropriate range while the above-described effect of fixing the free N by the carbonitride formed by the carbonitride forming elements is sufficiently produced, and consequently, a spheroidal graphite cast iron can be obtained where both gas defect resistance, and mechanical characteristics and machinability are obtained.

(9) Ti, V and Nb: preferably 0.015 to 0.045% in total

[0041] The total amount of contents of Ti, V and Nb in combination can be in a range of 0.012 to 0.06% from the total amount of upper limits and lower limits of the respective elements. To suppress the occurrence of the gas defect by fixing the free N as a carbonitride and make more conspicuous the effects of reducing the mechanical characteristic variation in a range of the N content described later, it is preferable that the total content of Ti, V and Nb be not less than 0.015%. On the other hand, when the total amount of Ti, V and Nb exceeds 0.045%, a tendency to form a hard carbide or nitride increases, so that the deterioration of the machinability and mechanical characteristics (strength and elongation) of the spheroidal graphite cast iron is conspicuous. Therefore, the total content of Ti, V and Nb is made 0.015 to 0.045%. The lower limit of the total content of Ti, V and Nb is preferably 0.02%. Moreover, the upper limit of the total content of Ti, V and Nb is preferably 0.03%.

(10) N (nitrogen): 0.004 to 0.008%

[0042] N is an element immixed mainly from steel scrap such as a high-tensile steel plate. The melt of the spheroidal graphite cast iron obtained through a melting process with such steel scrap as the raw material contains approximately 0.008 to 0.015% free N. Even in the spheroidal graphite cast iron obtained by using a melt with plenty of free N like this, by the carbonitride forming elements being contained in a predetermined amount as described above, the free N in the melt is fixed to the carbonitride formed by the carbonitride forming elements. As a result, the content of N contained in the spheroidal graphite cast iron, together with the N fixed (solid-solved) to the matrix phase, is not less than 0.004%. On the other hand, when the N content is less than 0.004% in spite of a spheroidal graphite cast iron obtained by using a melt with plenty of free N, there is a possibility that at the time of casting, excessive N that cannot be solid-solved is released as nitrogen gas into the solid phase when the melt solidifies and this causes a gas defect such as a pin hole in the spheroidal graphite cast iron. For this reason, the N content is made not less than 0.004%. On the other hand, when the N content exceeds 0.008%, the carbonitride fixing N also increases, so that there is a possibility that the machinability and mechanical characteristics (strength and elongation) of the obtained spheroidal graphite cast iron decrease. For this reason, the N content is made not more than 0.008%. Therefore, the N content is made 0.004 to 0.008%. The upper limit of the N content is preferably 0.007%, and is more preferably 0.006%.

(11) Expression (1): $0.8 \leq (0.29\text{Ti} + 0.27\text{V} + 0.15\text{Nb})/\text{N} \leq 2.0$

[0043] In the spheroidal graphite cast iron of the present invention, to further improve the gas defect resistance and further improve the mechanical characteristics (strength and elongation) and machinability, it is preferable to satisfy the expression (1) with the above-described composition range requirements being satisfied. The element symbols in the expression (1) represent the contents [mass ratio (%)] of the elements in the spheroidal graphite cast iron. Since Ti, V and Nb which are carbonitride forming elements are united with N in one-to-one correspondence in the number of atoms, if the ratio between the total amount of substance (T) of carbonitride forming elements shown in the following expressions (2) and (3) and the amount of substance (N) of N, that is, the amount of substance ratio (molar ratio) T/N is within a predetermined range, the balance between the carbonitride forming elements and N is appropriate, so that the total content of Ti, V and Nb is one that is necessary and sufficient for the N content. By the amount of substance ratio (molar

ratio) T/N being within a predetermined range, in the spheroidal graphite cast iron obtained by using a melt with plenty of free N, the formation of excessive carbonitride is also suppressed while N exceeding the solid solubility limit of the austenite phase is fixed as a carbonitride by Ti, V and Nb, so that the gas defect resistance, the mechanical characteristics (strength and elongation) and the machinability are further improved.

$$T=(Ti/48)+(V/51)+(Nb/93) \dots (2)$$

$$N=N/14 \dots (3)$$

The amount of substance ratio T/N between the total amount of substance (T) of the carbonitride forming elements and the amount of substance (N) of N, which is straightened up in consideration of the atomic weight, is $(0.29Ti+0.27V+0.15Nb)/N$ in the expression (1). The coefficients by which the carbonitride forming elements are multiplied are coefficients obtained from the ratio between the atomic weight of N and the elements; 0.29 represents the ratio between the atomic weights of N and Ti (14/48), 0.27 represents the ratio between the atomic weights of N and V (14/51), and 0.15 represents the ratio between the atomic weights of N and Nb (14/93).

[0044] When the value of the expression (1) is not less than 0.8, since an appropriate amount of carbonitride forming elements for N is contained, even in a spheroidal graphite cast iron obtained by using a melt with plenty of free N, N exceeding the solid solubility limit of the austenite phase is fixed neither too much nor too little by the carbonitride forming elements, so that sufficient gas defect resistance is obtained. On the other hand, when the value of the expression (1) is not more than 2.0, the formation of a carbonitride is suppressed to the minimum, so that the mechanical characteristics (strength and elongation) and machinability improve. Therefore, in the spheroidal graphite cast iron of the present invention, it is preferable that the value of $(0.29Ti+0.27V+0.15Nb)/N$ be in a range of 0.8 to 2.0. Theoretically, it is assumed that when the amount of substance ratio between Ti, V and Nb, and N in the spheroidal graphite cast iron is 1, that is, the value of the expression (1) is 1, N is formed as a carbonitride neither too much nor too little and there is no solid-solution of N into the austenite phase; however, when in consideration of the yield of formation of the carbonitride, the promotion of precipitation of the pearlite phase by appropriate solid-solution of N into the austenite phase, and the point that two free Ns (atoms) are necessary for molecularization as nitrogen gas, in actuality, a range of 0.8 to 2.0 is suitable. The value of the left side of the expression (1) is more preferably 1.0, and is most preferably 1.2. Moreover, the value of the right side of the expression (1) is more preferably 1.7, and is most preferably 1.5.

(12) Mechanical characteristics

[0045] Regarding the mechanical characteristics of the spheroidal graphite cast iron of the present invention, it is preferable that the tensile strength be not less than 600 MPa and the elongation be not less than 12%. The spheroidal graphite cast iron having mechanical characteristics where the tensile strength is not less than 600 MPa and the elongation is not less than 12% is suitable for use for constructional members and the like similarly to the conventional spheroidal graphite cast iron since it has mechanical characteristics equal to or greater than the conventional ones. The tensile strength is more preferably not less than 610 MPa, and is most preferably not less than 620 Pa. Moreover, the elongation is more preferably not less than 13%, and is most preferably not less than 14%. To make the tensile strength not less than 600 MPa and make the elongation not less than 12%, it is preferable to adjust the additive amounts of elements such as Mn and Cu the contents of which are comparatively easily controlled, and specifically, it is preferable that the Mn content be 0.2 to 0.5% and the Cu content be 0.2 to 0.6%.

[Examples]

[0046] While the present invention will be described in more detail by the following examples, the present invention is not limited to these examples. In the following, the contents of the elements constituting the spheroidal graphite cast iron are also expressed in mass ratio (%) unless otherwise specified. Moreover, the Examples described below are examples within the range of the present invention, the Comparative examples are examples outside the range of the present invention, and the Reference example is an example representative of the reference of the conventional technology.

[0047] A melt was formed by melting pig iron, steel scrap and return scrap of spheroidal graphite cast iron as the raw material in a high frequency melting furnace with a capacity of 100 kg and adding a recarburizing agent and Fe-Ti, Fe-V, Fe-Nb and Fe-Si alloys for ingredient adjustment. The steel scrap was a high-tensile steel plate with an N content of 0.05%, and of the compounded amount ratio 100% of the raw material which was the total of the pig iron, the steel scrap

and the return scrap, the compounded amount ratio of the steel scrap was 40% in first to sixteenth Examples 1 to 16 and Comparative examples 1 to 11 described later, and was 0% in the Reference example where they were not compounded. This melt was tapped at approximately 1500 degrees C into a ladle where an Fe-Si-Mg alloy and a cover member made of steel scrap covering this were placed as a graphite spheroidizing agent, and spheroidizing processing by a sandwiching method was performed. The amount of N (free N) contained in the melt having undergone the spheroidizing processing was in a range of 0.005 to 0.009% in all the Examples and Comparative examples described below, and was 0.003% in the Reference example. The melt having undergone the spheroidizing processing was poured into a sand mold at approximately 1400 degrees C, and was cast into a plurality of one-inch Y blocks, a mold for a flat test piece for a gas defect area ratio evaluation described later and a mold for a cylindrical test piece for a machinability evaluation. At the time of pouring, Fe-Si alloy powder was added to the flow of the melt to perform inoculation.

[0048] In the above-described manner, spheroidal graphite cast irons having the compositions shown in Table 1 were obtained. The Examples 1 to 16 (Ex.1 to Ex.16) are spheroidal graphite cast irons within the composition range defined by the present invention, and the Comparative examples 1 to 11 (Com.1 to Com. 11) and the Reference example (Ref.) are spheroidal graphite cast irons outside the composition range defined by the present invention. The Comparative example 1 and the Comparative examples 7 to 11 are spheroidal graphite cast irons where the content of one or more than one element of Ti, V, Nb and N is too large, and the Comparative examples 2 to 6 and the Reference example are spheroidal graphite cast irons where the content of one or more than one element of Ti, V, Nb and N is too small. The compositions of the obtained spheroidal graphite cast irons were checked by a glow-discharge mass spectrometer (manufactured by VG, the trade name: VG9000, hereinafter, referred to merely as GDMS). The GDMS cannot measure, of the N existing in the above-described structural elements, the N contained in the gas defect of (3). Therefore, the amount (mass ratio) of N shown in Table 1 is the amount of N solid-solved in the matrix phase of (1) and N fixed to the carbonitride of (2).

Table 1

Composition (mass ratio (%)) ⁽¹⁾											
No.	C	Si	P	S	Mn	Cu	Mg	Ti	V	Nb	N
Ex.1	3.55	2.45	0.018	0.010	0.35	0.41	0.035	0.015	0.002	0.005	0.004
Ex.2	3.65	2.35	0.021	0.009	0.42	0.37	0.034	0.035	0.006	0.002	0.007
Ex.3	3.66	2.38	0.025	0.008	0.44	0.38	0.036	0.040	0.009	0.010	0.008
Ex.4	3.56	2.41	0.028	0.009	0.41	0.39	0.038	0.037	0.004	0.002	0.006
Ex.5	3.68	2.40	0.022	0.007	0.38	0.41	0.036	0.037	0.005	0.007	0.007
Ex.6	3.57	2.39	0.019	0.008	0.45	0.40	0.039	0.025	0.004	0.006	0.006
Ex.7	3.60	2.37	0.017	0.009	0.46	0.39	0.034	0.020	0.003	0.005	0.006
Ex.8	3.62	2.40	0.018	0.007	0.39	0.42	0.035	0.018	0.002	0.005	0.005
Ex.9	3.59	2.44	0.023	0.008	0.42	0.38	0.037	0.015	0.002	0.004	0.005
Ex.10	3.61	2.39	0.016	0.010	0.40	0.37	0.033	0.013	0.002	0.003	0.005
Ex.11	3.58	2.37	0.020	0.008	0.41	0.43	0.032	0.012	0.001	0.002	0.004
Ex.12	3.63	2.42	0.021	0.007	0.39	0.40	0.036	0.011	0.001	0.001	0.004
Ex.13	3.66	2.95	0.019	0.011	0.75	0.42	0.058	0.038	0.008	0.009	0.007
Ex.14	3.86	2.98	0.045	0.019	0.40	0.43	0.021	0.037	0.007	0.008	0.007
Ex.15	3.31	2.09	0.048	0.018	0.39	0.37	0.022	0.035	0.008	0.007	0.007
Ex.16	3.32	2.89	0.020	0.008	0.76	0.50	0.053	0.036	0.007	0.007	0.008
Com.1	3.62	2.41	0.017	0.011	0.39	0.39	0.038	0.053	0.003	0.005	0.009
Com.2	3.57	2.42	0.022	0.008	0.38	0.37	0.041	0.008	0.005	0.004	0.003
Com.3	3.61	2.39	0.021	0.009	0.42	0.38	0.035	0.004	0.002	0.003	0.005
Com.4	3.58	2.40	0.018	0.010	0.40	0.41	0.038	0.034	0.0004	0.004	0.004
Com.5	3.60	2.43	0.020	0.007	0.37	0.36	0.039	0.036	0.003	0.0003	0.004

(continued)

Composition (mass ratio (%)) ⁽¹⁾											
No.	C	Si	P	S	Mn	Cu	Mg	Ti	V	Nb	N
Com.6	3.59	2.38	0.019	0.008	0.38	0.38	0.042	0.014	0.001	0.002	0.003
Com.7	3.62	2.35	0.019	0.008	0.36	0.39	0.037	0.065	0.002	0.002	0.007
Com.8	3.61	2.41	0.021	0.009	0.44	0.39	0.036	0.027	0.024	0.001	0.006
Com.9	3.60	2.40	0.022	0.012	0.37	0.42	0.040	0.030	0.001	0.023	0.007
Com.10	3.58	2.39	0.018	0.010	0.35	0.41	0.039	0.037	0.002	0.005	0.012
Com. 11	3.57	2.38	0.020	0.008	0.38	0.40	0.043	0.051	0.001	0.020	0.008
Ref.	3.61	2.41	0.021	0.009	0.41	0.39	0.045	0.004	0.003	0.0008	0.003
Note:(1) Remnant consisting of Fe and inevitable impurity											

[0049] Test pieces were cut from samples of the spheroidal graphite cast irons obtained by the above-described casting, and the following evaluations were performed.

(1) Gas defect area ratio

[0050] To find out the occurrence tendency of the gas defect of the spheroidal graphite cast irons of the Examples and the Comparative examples, flat test pieces were made that had a shape where the gas defect was caused more readily than in the actual products. For this reason, the measurement values of the gas defect area ratio were extremely higher than those of the actual products. FIGS. 1A and 1B are schematic views of the flat test pieces for measuring the gas defect, FIG. 1A is a plan view, and FIG. 1B is a side view. These flat test pieces 10 were 60 mm in width, 150 mm in length and 10 to 15 mm in thickness. The flat test pieces 10 were each obtained by doing as follows: After the melts same as the one-inch Y blocks were each poured from the sprue at not less than 1400 degrees C into a sand mold defining a cavity formed of the flat test piece 10, a riser 11 with a diameter of 45 mm and a height of 60 mm, the sprue (not shown), a runner 12a with a width of 35 mm and a thickness of 3 mm and an ingate 12b with a width of 40 mm and a thickness of 9 mm, cooling and shake-out were performed, the riser 11 was cut to be separated, and shot blast processing was performed.

[0051] To observe the gas defects on the surface and inside, by using transmission X-ray equipment (manufactured by Toshiba Corporation, the trade name: EX-260GH-3), X-rays were applied from above the flat test pieces (the direction perpendicular to the paper of FIG. 1A) on condition that the tube voltage was 192 kV and the application time was three minutes, and transmission X-ray pictures were taken.

[0052] After only the gas defects on the surface and inside were visually extracted from each transmission X-ray picture and traced, image processing was performed by using an image analysis device (manufactured by Asahi Kasei Corporation, the trade name: IP-1000), and the total area (mm²) of the gas defects was measured. The total area of the gas defects was divided by the whole projected area of the flat test piece to obtain the gas defect area ratio (%). It is needless to say that the lower the gas defect area ratio, the more excellent as the spheroidal graphite cast iron. The results of the gas defect area ratio measurement are shown in Table 2. Table 2 also shows the total amounts of Ti, V and Nb and the values of the expression (1) in the Examples 1 to 16, the Comparative examples 1 to 11 and the Reference example.

[0053] As is apparent from Table 2, the test pieces of the Examples 1 to 16 where the contents of Ti, V, Nb and N were within the composition range of the present invention were lower in gas defect area ratio than the test pieces of the Comparative examples 2 to 6 where the content of one or more than one element of Ti, V, Nb and N was too small. It was confirmed that even in the spheroidal graphite cast iron obtained by using a melt containing excessive free N, the gas defect occurrence tendency could be reduced by defining the lower limits of the contents of Ti, V and Nb as described above. In the spheroidal graphite cast iron of the present invention, the gas defect area ratio is preferably not more than 11%, is more preferably not more than 10.5%, and is most preferably not more than 10%.

(2) Tool life

[0054] Turning was performed on end surfaces of cylindrical test pieces with an outside diameter of 100 mm, an inside diameter of 62 mm and a length of 100mm by using a cemented insert P10 (JIS B 4053) CDV-coated with TiCN under

the following conditions:

Cutting speed: 180 m/min.
 Feed: 0.25 mm/rev.
 Depth of cut: 2.0 mm
 Cutting fluid: water-soluble cutting fluid

[0055] In the milling of each cylindrical test piece, it was determined that the end of the life was reached when the depth of the flank wear of the cemented insert became 0.3 mm, and the cutting time (minute) until that was reached was the tool life. Needless to say, the longer the tool life is, the more excellent machinability is.

[0056] Since the absolute value of the tool life is affected by the cutting condition, the test piece shape and the like, the "tool life improvement rate" was used as the index of the machinability improvement effect not affected thereby. The tool life improvement rate is a value (A/B) obtained by dividing the tool life A of each of the spheroidal graphite cast irons of the Examples and the Comparative examples by the tool life B of the spheroidal graphite cast iron of the Reference example representative of the conventional technical level. The tool life improvement rates (times) of the Examples 1 to 16, the Comparative examples 1 to 11 and the Reference example are shown in Table 2.

[0057] As is apparent from Table 2, the tool life improvement rates of the Examples 1 to 16 within the composition range of the present invention were all in a range of 1.0 to 1.3 times. From the results of the Examples 1 to 16, it is apparent that the spheroidal graphite cast iron of the present invention has machinability equal to or greater than the conventional one. On the other hand, the tool life improvement rates of the Comparative example 1 and the Comparative examples 7 to 11 where the content of one or more than one element of Ti, V, Nb and N was too large were all less than 1.0 time, and machinability was poor. In the spheroidal graphite cast iron of the present invention, the tool life improvement rate is preferably not less than 1.1 times, is more preferably not less than 1.2 times, and is most preferably 1.3 times.

(3) Tensile test

[0058] A test piece of 14A of JIS Z 2201 was made from a one-inch Y block, a tensile test was performed at room temperature by an Amsler tensile testing machine (AG-IS250kN manufactured by Shimadzu Corporation) according to JIS Z 2241, and the tensile strength, the 0.2% yield strength and the elongation were measured. The results are shown in Table 2.

[0059] As shown in Table 2, in all of the Examples 1 to 16 within the composition range of the present invention, the tensile strength was not less than 600 MPa, the 0.2% yield strength was not less than 350 MPa and the elongation was not less than 12%, and it was confirmed that all had mechanical characteristics equal to or greater than the conventional ones shown in the Reference example. On the contrary, in all of the Comparative examples 2, 5, 7 and 11 outside the composition range of the present invention, the tensile strength was as low as less than 600 MPa, and in all of the Comparative example 1 and the Comparative examples 7 to 11 where the content of one or more than one element of Ti, V, Nb and N was too large, the elongation was as low as less than 12%. Moreover, in the case of the Comparative examples 3, 4 and 6 having a tensile strength of not less than 600 MPa and an elongation of not less than 12%, although they had mechanical characteristics, the gas defect area rate was as high as not less than 12.7% in all of them.

[0060] As described above, it was confirmed that the spheroidal graphite cast iron of the present invention was a spheroidal graphite cast iron having mechanical characteristics and machinability equal to or greater than the conventional ones and further, having excellent gas effect resistance at the same time.

Table 2

Evaluation result							
No.	Ti+V+Nb total amount (mass ratio (%))	Value of expression (1)(2)	Gas defect area ratio (%)	Tool life Improvement rate (times)	Tensile strength (MPa)	0.2% yield strength (MPa)	Elongation (%)
Ex.1	0.022	1.4	9.5	1.3	608	367	13.7
Ex.2	0.043	1.7	9.2	1.2	605	358	12.2
Ex.3	0.059	1.9	8.0	1.1	603	361	13.7
Ex.4	0.043	2.0	9.3	1.2	607	365	13.5
Ex.5	0.049	1.9	9.1	1.1	609	366	13.5

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(continued)

Evaluation result							
No.	Ti+V+Nb total amount (mass ratio (%))	Value of expression (1) ⁽²⁾	Gas defect area ratio (%)	Tool life Improvement rate (times)	Tensile strength (MPa)	0.2% yield strength (MPa)	Elongation (%)
Ex.6	0.035	1.5	9.5	1.2	621	368	13.2
Ex.7	0.028	1.2	9.9	1.3	615	367	13.1
Ex.8	0.025	1.3	9.8	1.4	621	369	13.2
Ex.9	0.021	1.1	10.1	1.3	604	364	13.8
Ex.10	0.018	1.0	10.7	1.3	602	360	13.7
Ex.11	0.015	1.0	10.8	1.4	641	375	12.5
Ex.12	0.013	0.9	10.9	1.4	613	367	13.5
Ex.13	0.055	2.1	8.3	1.0	644	419	13.3
Ex.14	0.052	2.0	8.6	1.1	601	404	14.7
Ex.15	0.050	1.9	8.8	1.1	626	360	12.0
Ex.16	0.050	1.7	9.4	1.1	690	435	12.0
Com. 1	0.061	1.9	8.5	0.1	607	363	11.8
Com. 2	0.017	1.4	15.6	1.0	591	357	13.5
Com. 3	0.009	0.4	12.7	1.3	609	362	13.6
Com. 4	0.038	2.6	13.5	1.1	623	369	13.1
Com. 5	0.039	2.8	12.9	1.0	592	357	14.0
Com. 6	0.017	1.5	14.4	1.2	602	359	13.8
Com. 7	0.069	2.8	8.9	0.1	590	356	10.9
Com. 8	0.052	2.4	9.3	0.3	612	369	11.7
Com. 9	0.054	1.8	9.4	0.4	613	370	11.5
Com. 10	0.044	1.0	11.5	0.6	614	365	11.8
Com. 11	0.072	2.3	8.7	0.1	572	362	9.5
Ref	0.008	0.7	10.7	1.0	611	365	13.6
Note: (2) Value of expression (1) is value calculated by $(0.29\text{Ti}+0.27\text{V}+0.15\text{Nb})/\text{N}$							

[Explanation of Reference Numerals]

[0061]

- 10 Flat test piece
- 11 Riser
- 12a Runner
- 12b Ingate

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Claims

1. A spheroidal graphite cast iron excellent in gas defect resistance consisting of, in mass ratio:

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C: 3.3 to 4%;
 Si: 2 to 3%;
 P: not more than 0.05%;
 S: not more than 0.02%;
 15 Mn: not more than 0.8%;
 Cu: not more than 0.8% (0 is not included);
 Mg: 0.02 to 0.06%;
 Ti: 0.01 to 0.04%;
 V: 0.001 to 0.01%;
 20 Nb: 0.001 to 0.01%; and
 N: 0.004 to 0.008%,

with the remnant substantially consisting of Fe and an inevitable impurity.

- 25 2. The spheroidal graphite cast iron according to claim 1, wherein the spheroidal graphite cast iron contains, in mass ratio, 0.015 to 0.045 % Ti, V and Nb in total and further, contains Ti, V, Nb and N so as to satisfy the following expression (1):

30

$$0.8 \leq (0.29\text{Ti} + 0.27\text{V} + 0.15\text{Nb}) / \text{N} \leq 2.0 \dots (1)$$

here, the element symbols in the expression (1) represent the contents [mass ratio (%)] of the elements in the spheroidal graphite cast iron.

- 35 3. The spheroidal graphite cast iron according to claim 1 or 2,
 wherein the spheroidal graphite cast iron contains, in mass ratio, not less than 0.005% P and not less than 0.005% S.
4. The spheroidal graphite cast iron according to any one of claims 1 to 3,
 wherein the spheroidal graphite cast iron contains, in mass ratio, not less than 0.2% Mn and not less than 0.1% Cu.
- 40 5. The spheroidal graphite cast iron according to any one of claims 1 to 4,
 wherein the spheroidal graphite cast iron is not less than 600 MPa in tensile strength and not less than 12% in elongation.

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FIG. 1A

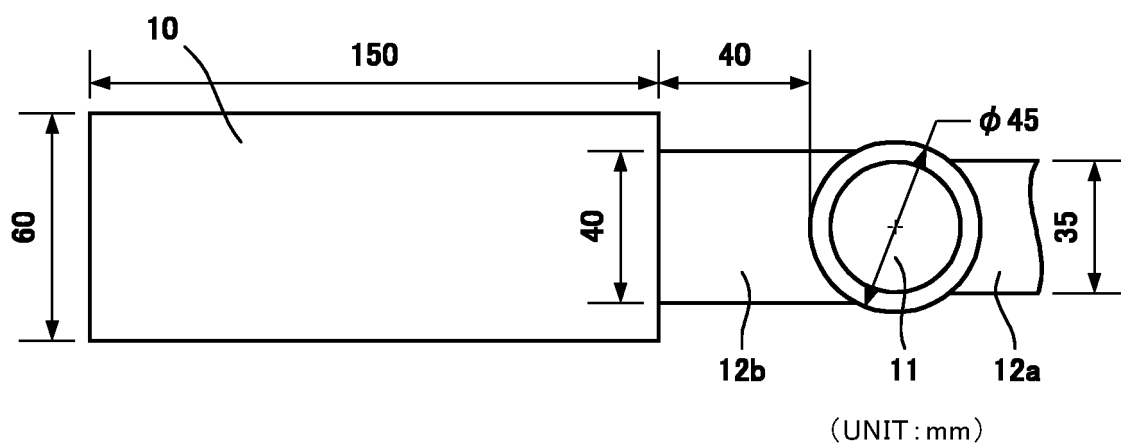
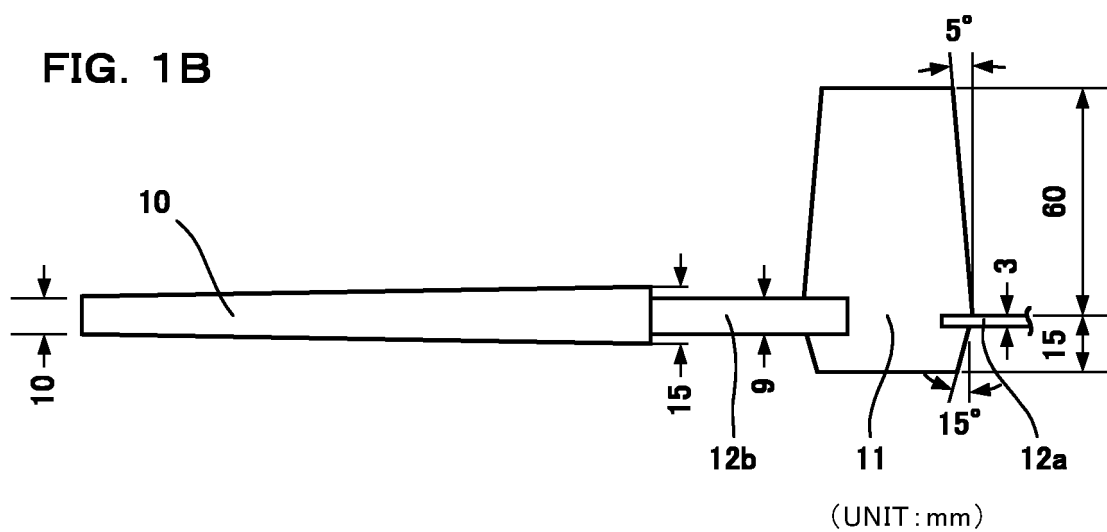


FIG. 1B



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/055973

A. CLASSIFICATION OF SUBJECT MATTER

C22C37/04(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)

C22C37/00-37/10

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 1996-2016

Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

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

DWPI(Thomson Innovation)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 10-68042 A (AE Goetze GmbH), 10 March 1998 (10.03.1998), & EP 821073 A1 & CN 1176315 A & DE 19654893 A1	1-5
A	JP 2012-122085 A (Suzuki Motor Corp.), 28 June 2012 (28.06.2012), (Family: none)	1-5

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

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Date of the actual completion of the international search

13 May 2016 (13.05.16)

Date of mailing of the international search report

24 May 2016 (24.05.16)

Name and mailing address of the ISA/
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3-4-3, Kasumigaseki, Chiyoda-ku,
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REFERENCES CITED IN THE DESCRIPTION

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