

(19)



(11)

EP 3 321 000 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

15.02.2023 Bulletin 2023/07

(51) International Patent Classification (IPC):

B22F 1/10 ^(2022.01) **C22C 1/05** ^(1968.09)
C22C 33/02 ^(1968.09) **B22F 1/16** ^(2022.01)

(21) Application number: **16799746.9**

(52) Cooperative Patent Classification (CPC):
(C-Sets available)

C22C 1/05; B22F 1/10; B22F 1/12; C22C 33/0221;
B22F 1/102; B22F 2998/10 (Cont.)

(22) Date of filing: **27.04.2016**

(86) International application number:

PCT/JP2016/063169

(87) International publication number:

WO 2016/190038 (01.12.2016 Gazette 2016/48)

(54) **MIXED POWDER FOR IRON-BASED POWDER METALLURGY, AND METHOD FOR PRODUCING SAME**

PULVERGEMISCH FÜR EISENBASIERTE PULVERMETALLURGIE UND VERFAHREN ZUR
HERSTELLUNG DAVON

MÉLANGE DE POUDRES POUR MÉTALLURGIE DES POUDRES À BASE DE FER, ET PROCÉDÉ
DE FABRICATION DE CE MÉLANGE DE POUDRES

(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**

(74) Representative: **Müller-Boré & Partner**

**Patentanwälte PartG mbB
Friedenheimer Brücke 21
80639 München (DE)**

(30) Priority: **27.05.2015 JP 2015107347**

(56) References cited:

**EP-A2- 1 258 537 WO-A1-2015/008406
JP-A- S5 716 155 JP-A- H09 279 204
JP-A- S49 109 207 JP-A- 2012 144 801
JP-A- 2015 157 973**

(43) Date of publication of application:
16.05.2018 Bulletin 2018/20

(73) Proprietor: **Kabushiki Kaisha Kobe Seiko Sho
(Kobe Steel, Ltd.)
Kobe-shi, Hyogo 651-8585 (JP)**

(72) Inventor: **AKAGI, Nobuaki
Hyogo 676-8670 (JP)**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 3 321 000 B1

(52) Cooperative Patent Classification (CPC): (Cont.)

C-Sets

B22F 2998/10, C22C 1/05, B22F 3/02, B22F 3/10

Description

[0001] The present invention relates to a mixed powder for iron-based powder metallurgy and a method for producing the same.

[0002] Powder metallurgy is widely used as a method for industrial production of various kinds of mechanical parts. A procedure for the iron-based powder metallurgy is such that, first, a mixed powder is prepared by mixing an iron-based powder with a powder for alloy such as a copper (Cu) powder or a nickel (Ni) powder, a graphite powder, and a lubricant. Next, this mixed powder is put into a mold to perform press-molding, and the resultant is sintered to prepare a sintered body. Finally, this sintered body is subjected to cutting such as drilling process or turning on a lathe, so as to be prepared into a mechanical part having a desired shape.

[0003] An ideal for powder metallurgy is such that the sintered body is processed to be made usable as a mechanical part without performing cutting on the sintered body. However, the aforesaid sintering may generate non-uniform contraction of the raw material powder. In recent years, the dimension precision required in the mechanical parts is increasing, and the shapes of the parts are becoming more complex. For this reason, it is becoming essential to perform cutting on the sintered body. From such a technical background, machinability is imparted to the sintered body so that the sintered body can be smoothly processed.

[0004] There is a technique of adding a manganese sulfide (MnS) powder to the mixed powder as means for imparting the machinability. Addition of the manganese sulfide powder is effective for cutting at a comparatively low speed, such as drilling. However, addition of a manganese sulfide powder is not necessarily effective for cutting at a high speed that is performed in recent years, and raises problems such as generation of contamination on the sintered body and decrease in the mechanical strength.

[0005] Patent Literature 1 (Japanese Examined Patent Application Publication No. S52-16684) discloses a method of imparting machinability other than the aforesaid addition of manganese sulfide. Patent Literature 1 discloses a sintered steel in which 0.1 to 1.0% of calcium sulfide (CaS), 0.1 to 2% of carbon (C), and 0.5 to 5.0% of copper (Cu) are incorporated into an iron-based raw material powder obtained by allowing a needed amount of carbon and copper to be contained in an iron powder.

[0006] Incorporation of calcium sulfide into an iron-based raw material powder disclosed in Patent Literature 1 raises problems such as considerable decrease in the strength of the mechanical parts and unstable product quality caused by change with lapse of time of the mixed powder. Further, when the sintered steel disclosed in Patent Literature 1 is processed with use of a cutting tool, the chips are hardly fragmented finely. From this, the sintered steel disclosed in Patent Literature 1 can hardly be said to be excellent to a degree such as to satisfy the current demand for the chip controllability.

[0007] The present invention has been made in view of the aforementioned problems, and an object thereof is to provide a mixed powder for iron-based powder metallurgy capable of preparing a sintered body having a stable product quality and performance.

[0008] Patent Literature 1: Japanese Examined Patent Application Publication No. S52-16684 WO 2015/008406 A1 describes a mixed powder for powder metallurgy, a method for producing the same, and a method for producing a sintered compact of iron-based powder formulation.

[0009] A mixed powder for iron-based powder metallurgy of the present invention comprises an iron-based powder and a CaS raw material powder containing at least calcium sulfide, wherein the CaS raw material powder is coated with at least one selected from a lubricant and a binder; wherein the mixed powder is obtained by mixing the iron-based powder with the CaS raw material powder coated with the lubricant and/or the binder; and wherein the CaS raw material powder is contained such that a weight ratio of CaS after sintering is 0.01 wt% or more to 0.1 wt% or less, wherein the sintering is conducted at a temperature of 1000°C or higher to 1300°C or lower for 5 minutes or more to 60 minutes or less in an atmosphere of a nitrogen atmosphere, a mixed atmosphere of nitrogen and hydrogen, or a hydrocarbon atmosphere.

[0010] A method for producing a mixed powder for iron-based powder metallurgy of the present invention comprises coating a CaS raw material powder, which contains at least calcium sulfide, with at least one selected from a lubricant and a binder; and mixing the coated CaS raw material powder with an iron-based powder, wherein the CaS raw material powder is contained such that a weight ratio of CaS after sintering is 0.01 wt% or more to 0.1 wt% or less, wherein the sintering is conducted at a temperature of 1000°C or higher to 1300°C or lower for 5 minutes or more to 60 minutes or less in an atmosphere of a nitrogen atmosphere, a mixed atmosphere of nitrogen and hydrogen, or a hydrocarbon atmosphere.

[0011] In order to achieve the aforementioned object, the present inventor has made investigations on why the sintered body disclosed in Patent Literature 1 undergoes decrease in the product quality and performance with lapse of time. Then, the present inventor has found out that, when the sintered body contains calcium sulfide and hemihydrate calcium sulfate (hereafter, these two components will be referred to as "CaS components"), the product quality and performance of the sintered body decreases. In other words, the present inventor has found out that, when the CaS components

absorb moisture in ambient air, the CaS components are changed into calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), or the CaS components are aggregated by a hardening reaction to form coarse grains of 63 μm or greater. It has been made clear that this lets the CaS components be non-uniformly dispersed in the mixed powder or in the sintered body to decrease the machinability of the sintered body, or lets the moisture adsorbed onto the CaS components be dilated during the sintering to become water vapor, thereby to decrease the strength of the sintered body.

[0012] Based on the above findings, the present inventor has completed the present invention shown below by further making eager studies on the construction of CaS components that hardly absorb moisture.

[0013] According to the present invention, there can be provided a mixed powder for iron-based powder metallurgy capable of preparing a sintered body having a stable product quality and performance.

[0014] Hereafter, a mixed powder for iron-based powder metallurgy according to the present invention and a method for producing the same will be specifically described.

<Mixed powder for iron-based powder metallurgy>

[0015] The mixed powder for iron-based powder metallurgy of the present invention is a mixed powder obtained by mixing an iron-based powder with a CaS raw material powder containing at least calcium sulfide. This CaS raw material powder is characterized by being coated with a lubricant and/or a binder and in that the CaS raw material powder is contained such that a weight ratio of CaS after sintering is 0.01 wt% or more to 0.1 wt% or less. Various kinds of additives such as ternary oxides, binary oxides, powders for alloy, graphite powders, lubricants, and binders may be appropriately added into the mixed powder. In addition to these, the mixed powder may contain a slight amount of inevitable impurities during the process of producing the mixed powder for iron-based powder metallurgy. The mixed powder for iron-based powder metallurgy of the present invention may be put into a mold or the like to be molded and thereafter sintered to give a sintered body. The sintered body thus prepared may be subjected to cutting process, so as to be made usable in various kinds of mechanical parts. The use and the production method of this sintered body will be described later.

< Iron-based powder>

[0016] The iron-based powder is a main constituent component constituting the mixed powder for iron-based powder metallurgy, and is preferably contained at a weight ratio of 60 wt% or more relative to the total amount of the mixed powder for iron-based powder metallurgy. In the present specification, wt% of the iron-based powder as used herein refers to the occupied ratio relative to the total weight of the constituent components of the mixed powder for iron-based powder metallurgy other than the lubricants. Hereafter, it is assumed that, when wt% of each component is defined, the definition refers to the occupied weight ratio relative to the total weight of the constituent components of the mixed powder for iron-based powder metallurgy other than the lubricants.

[0017] The above iron-based powder usable in the present invention may be, for example, a pure iron powder such as an atomized iron powder or a reduced iron powder, a partially diffused alloyed steel powder, a completely alloyed steel powder, a hybrid steel powder obtained by partially diffusing alloy components into a completely alloyed steel powder, or the like. A volume-average particle size of the iron-based powder is preferably 50 μm or more, more preferably 70 μm or more. When the volume-average particle size of the iron-based powder is 50 μm or more, the handling property is excellent. Further, the volume-average particle size of the iron-based powder is preferably 200 μm or less, more preferably 100 μm or less. When the volume-average particle size of the iron-based powder is 200 μm or less, a precision shape can be readily molded, and also a sufficient strength can be obtained.

<CaS raw material powder>

[0018] The mixed powder for iron-based powder metallurgy of the present invention comprises a CaS raw material powder containing at least calcium sulfide, wherein the CaS raw material powder is coated with a lubricant and/or a binder. By using the CaS raw material powder coated with a lubricant and/or a binder in this manner, the moisture absorptivity of the CaS raw material powder can be suppressed, whereby various performances of the sintered body can be stably enhanced.

[0019] Conventionally, calcium sulfide (CaS), dihydrate gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium sulfate anhydrite III (III type CaSO_4), hemihydrate gypsum ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), and the like have been added as a raw material that becomes CaS by being sintered. However, each of the above components may in some cases absorb moisture with lapse of time, thereby decreasing the machinability of the sintered body. Also, the moisture absorbed by the raw material that becomes CaS by being sintered may be dilated during the sintering to become water vapor thereby to decrease the density of the sintered body, or the high-temperature water vapor may oxidize the iron-based powder in the sintered body thereby to decrease the strength of the sintered body. In contrast, in the present invention, a CaS raw material powder coated with a lubricant or a binder is added as described above, so that the CaS raw material powder hardly absorbs moisture even

when the CaS raw material powder is stored for a certain period of time in a state of being contained in the mixed powder for iron-based powder metallurgy. By such an effect, various properties of the sintered body as designed (sintered body density, radial crushing strength, machinability, and the like) are stabilized. Moreover, the above coated CaS raw material powder can enhance the machinability of the sintered body by being changed into CaS after the sintering.

[0020] The CaS raw material powder preferably contains at least one selected from calcium sulfide and hemihydrate calcium sulfate as a major component, and may contain dihydrate calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium sulfate anhydrite II (II type CaSO_4), calcium sulfate anhydrite III (III type CaSO_4), and the like.

[0021] The states that "the CaS raw material powder is coated with at least one selected from a lubricant and a binder" include both of a mode in which the whole surface of the CaS raw material powder is coated with a lubricant and/or a binder and a mode in which the surface of the CaS raw material powder is partially coated with a lubricant and/or a binder. The thickness of the lubricant and/or the binder is not particularly limited as long as the thickness is such that calcium sulfate anhydrite III, calcium sulfate dihydrate, calcium sulfide, and calcium sulfate hemihydrate are not brought into contact with outside ambient air. The thickness is preferably uniform on the surface of the CaS raw material powder; however, there may be partially thick parts or partially thin parts.

[0022] The amount of addition of the lubricant can be appropriately set, and is preferably 0.1 wt% or more to 1.5 wt% or less relative to the weight of the mixed powder for iron-based powder metallurgy. Also, the amount of addition of the binder can be appropriately set, and is preferably 0.02 wt% or more to 0.5 wt% or less relative to the weight of the mixed powder for iron-based powder metallurgy. When the lubricant and the binder are added in an excessively large amount, the compressibility at the time of press-molding decreases, leading to decrease in the density. Conversely, when the amount of addition of the lubricant and the binder are excessively small, the CaS raw material powder is liable to be brought into contact with outside ambient air, or is hardly released from the mold at the time of press-molding, thereby raising a possibility of damaging the mold.

[0023] The coating with a lubricant is carried out by mixing the CaS raw material powder with the lubricant in a mixing container and heating the resultant mixture. Alternatively, a CaS raw material powder coated with a lubricant in advance may be prepared, or a surface of the CaS raw material powder may be coated with a lubricant by using the hot-melt method. A procedure of the hot-melt method is such that, first, a lubricant is put into a mixing container together with each of the powders constituting the mixed powder for iron-based powder metallurgy other than the lubricant. After these powders are heated and mixed, the resultant mixture is cooled to room temperature. This allows that each of the powders constituting the mixed powder for iron-based powder metallurgy is coated with the lubricant (not according to the present invention).

[0024] Still another coating method is such that all the powders constituting the mixed powder for iron-based powder metallurgy other than the lubricant are put into a mixing container. Subsequently, a binder solution in which a binder is dissolved in a solvent is added into the mixing container and mixed. Thereafter, the solvent contained in the binder solution is volatilized. Finally, the lubricant may be added to coat the CaS raw material powder with the lubricant and/or the binder. In this case, each of the powders is coated with the lubricant and/or the binder. (Not according to the present invention) Details of this step will be described later.

[0025] The mixed powder for iron-based powder metallurgy contains the CaS raw material powder such that a weight ratio of CaS after sintering is 0.01 wt% or more to 0.1 wt% or less. The CaS raw material powder is contained preferably such that a weight ratio of CaS after sintering is 0.02 wt% or more, still more preferably such that a weight ratio of CaS after sintering is 0.03 wt% or more. A sintered body containing CaS at such a weight ratio is excellent particularly in machinability. On the other hand, the CaS raw material powder is contained preferably such that a weight ratio of CaS after sintering is 0.09 wt% or less, still more preferably such that a weight ratio of CaS after sintering is 0.08 wt% or less. Incorporation of CaS at such a weight ratio can enhance the strength of the sintered body.

[0026] The term "weight ratio of CaS after sintering" refers to the weight ratio occupied by CaS in the sintered body obtained by sintering the mixed powder for iron-based powder metallurgy. The weight ratio of CaS contained in the sintered body after sintering can be adjusted by the weight ratio of the CaS raw material powder contained before the sintering.

[0027] The weight ratio of CaS contained in the sintered body is calculated by collecting a sample piece through processing the sintered body with a drill or the like and converting the weight of Ca, which is obtained by performing quantitative analysis of the weight of Ca contained in the sample piece, into the weight of CaS. Such conversion is carried out by dividing with the atomic weight of Ca (40.078) and multiplying with the molecular weight of CaS (72.143). Little amount of Ca disappears by reacting during the sintering, so that the weight of Ca does not change between before and after the sintering, and Ca and S are bonded at a ratio of 1 : 1.

[0028] The volume-average particle size of the CaS raw material powder is preferably 0.1 μm or more, more preferably 0.5 μm or more, and still more preferably 1 μm or more. Further, the volume-average particle size of the CaS raw material powder is preferably 60 μm or less, more preferably 30 μm or less, and still more preferably 20 μm or less. A CaS raw material powder having such a volume-average particle size can be obtained, for example, by crushing and classifying a commercially available CaS raw material powder with a known crusher. Also, a CaS raw material powder made of

calcium sulfate anhydrite II can be obtained, for example, by heating hemihydrate gypsum to a temperature of 350°C or higher and 900°C or lower, holding the heated hemihydrate gypsum for 1 hour or more to 10 hours or less, and crushing and classifying the resultant. According as the volume-average particle size of the CaS raw material powder is smaller, machinability of the sintered body can be improved even if the amount of addition of the CaS raw material powder is reduced to be smaller. The above volume-average particle size is a value of the particle size D_{50} at an accumulated value of 50% in the particle size distribution obtained by using a laser diffraction particle size distribution measurement device (Microtrac "MODEL9320-X100" manufactured by Nikkiso Co., Ltd.).

<Lubricant>

[0029] The lubricant that coats the CaS raw material powder is added for the purpose of suppressing moisture absorptivity of calcium sulfate anhydrite III, calcium sulfate dihydrate, calcium sulfide, and calcium sulfate hemihydrate. The lubricant also performs a function such that a molded body obtained by compressing the mixed powder for iron-based powder metallurgy in a mold can be readily taken out from the mold. In other words, when a lubricant is added into the mixed powder for iron-based powder metallurgy, the withdrawing pressure at the time of taking the molded body out from the mold can be reduced, and cracking of the molded body and damage of the mold can be prevented. Further, when the hot-melt method is used (not according to the present invention), the lubricant performs a function of allowing the powder for alloy and graphite powder to adhere onto the surface of the iron-based powder, so that segregation of the iron-based mixed powder can be prevented. Besides the lubricant that coats the CaS raw material powder, a lubricant may be added during the process of preparing the mixed powder for iron-based powder metallurgy, or alternatively a lubricant may be applied onto a surface of the mold when the mixed powder for iron-based powder metallurgy is put into the mold.

[0030] The lubricant is contained preferably at a ratio of 0.01 wt% or more, more preferably at a ratio of 0.1 wt% or more, and still more preferably at a ratio of 0.2 wt% or more, relative to the weight of the mixed powder for iron-based powder metallurgy. When the content of the lubricant is 0.01 wt% or more, contact of the CaS raw material powder with outside ambient air can be suppressed, so that an effect of stabilizing the performance of the sintered body can be readily obtained. Also, the lubricant is contained preferably at a ratio of 1.5 wt% or less, more preferably at a ratio of 1.2 wt% or less, and still more preferably at a ratio of 1.0 wt% or less, relative to the weight of the mixed powder for iron-based powder metallurgy. When the content of the lubricant is 1.5 wt% or less, a sintered body having a high density can be readily obtained, and a sintered body having a high strength can be obtained.

[0031] As the lubricant, it is preferable to use a wax-based lubricant, and it is more preferable to use an amide-based lubricant from the viewpoint of having a good performance of allowing the powder for alloy, graphite powder, or the like to adhere onto the iron-based powder surface and being capable of readily reducing the segregation of the iron-based mixed powder. The amide-based lubricant may be, for example, monoamide stearate, fatty acid amide, amide wax, or the like. As the lubricant other than the amide-based lubricant, it is possible to use one or more selected from the group consisting of hydrocarbon-based wax, zinc stearate, and cross-linked alkyl (meth)acrylate resin.

<Binder>

[0032] The binder that coats the CaS raw material powder is added for the purpose of suppressing moisture absorptivity of calcium sulfate anhydrite III, calcium sulfate dihydrate, calcium sulfide, and calcium sulfate hemihydrate and preventing segregation of the iron-based mixed powder. The binder also performs a function of allowing the powder for alloy to adhere onto the iron-based powder surface. Besides the binder that coats the CaS raw material powder, a binder may be added during the process of preparing the mixed powder for iron-based powder metallurgy.

[0033] A procedure of coating the CaS raw material powder with the binder is such that, first, an organic solvent containing the binder is prepared by dissolving the binder into an organic solvent such as toluene. Subsequently, the organic solution is mixed with the CaS raw material powder. Finally, the organic solvent is volatilized to coat the CaS raw material powder with the binder.

[0034] As the binder, it is more preferable to use one or more selected from the group consisting of a styrene-butadiene rubber, an isoprene rubber, a butene-based polymer, and a methacrylate-based polymer. As the butene-based polymer, it is preferable to use a 1-butene homopolymer made of butene alone or a copolymer of butene and alkene. The alkene is preferably a lower alkene, and is preferably ethylene or propylene. As the methacrylate-based polymer, it is possible to use one or more selected from the group consisting of methyl methacrylate, ethyl methacrylate, butyl methacrylate, cyclohexyl methacrylate, ethylhexyl methacrylate, lauryl methacrylate, methyl acrylate, and ethyl acrylate.

[0035] The binder is contained preferably at a ratio of 0.01 wt% or more, more preferably at a ratio of 0.05 wt% or more, relative to the weight of the mixed powder for iron-based powder metallurgy. When the binder is contained at a ratio of 0.01 wt% or more, moisture absorptivity of calcium sulfate anhydrite III, calcium sulfate dihydrate, calcium sulfide, and calcium sulfate hemihydrate can be suppressed. Also, the binder is contained preferably at a ratio of 0.5 wt% or

less, more preferably at a ratio of 0.4 wt% or less, and still more preferably at a ratio of 0.3 wt% or less, relative to the weight of the mixed powder for iron-based powder metallurgy. When the content of the binder is set to be 0.5 wt% or less, a molded body having a high density can be readily obtained at the time of press-molding.

<Ternary oxides>

[0036] Ternary oxides may be added in order to improve the machinability when the sintered body is used for a long period of time in a cutting process. Addition of the ternary oxides in combination with addition of the CaS raw material powder can considerably enhance the machinability of the sintered body. The ternary oxide means a composite oxide of three types of elements. Specifically, the ternary oxide is preferably a composite oxide of three types of elements selected from the group consisting of Ca, Mg, Al, Si, Co, Ni, Ti, Mn, Fe, and Zn, and is more preferably a Ca-Al-Si oxide, a Ca-Mg-Si oxide, or the like. The Ca-Al-Si oxide may be, for example, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ or the like. The Ca-Mg-Si oxide may be, for example, $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ or the like. Among these, it is preferable to add $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. The aforementioned $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ reacts with TiO_2 contained in the cutting tool or in the coating formed on the cutting tool to form a protection coating film on the surface of the cutting tool, whereby the wear resistance of the cutting tool can be considerably increased.

[0037] A shape of the ternary oxide is not particularly limited; however, the ternary oxide preferably has a spherical shape or a crushed spherical shape, that is, a shape that is round as a whole.

[0038] A lower limit of the volume-average particle size of the ternary oxide is preferably 0.1 μm or more, more preferably 0.5 μm or more, and still more preferably 1 μm or more. There is a tendency such that, according as the volume-average particle size is smaller, the machinability of the sintered body can be improved by a smaller amount of addition. Further, an upper limit of the volume-average particle size of the ternary oxide is preferably 15 μm or less, more preferably 10 μm or less, and still more preferably 9 μm or less. When the volume-average particle size is too large, it is difficult to improve the machinability of the sintered body. The volume-average particle size of the ternary oxide is a value obtained by a measurement method similar to the above-described method for measuring the volume-average particle size of the CaS raw material powder.

[0039] A lower limit of the content of the ternary oxides is preferably 0.01 wt% or more, more preferably 0.03 wt% or more, and still more preferably 0.05 wt% or more. Further, an upper limit of the content of the ternary oxides is preferably 0.25 wt% or less, more preferably 0.2 wt% or less, and still more preferably 0.15 wt% or less. When the ternary oxides are contained at such a weight ratio, a sintered body can be obtained that has an excellent machinability even in a cutting process of a long period of time while suppressing the costs. Use of the ternary oxides in combination with the CaS raw material powder can improve the machinability in a cutting process of a long period of time even when the amount of addition of the ternary oxides is small.

[0040] The weight ratio of the ternary oxides and CaS after the sintering is preferably 1 : 9 to 9 : 1, more preferably 3 : 7 to 9 : 1, and still more preferably 4 : 6 to 7 : 3. When the two components are contained at such a weight ratio, the machinability of the sintered body can be considerably improved.

<Binary oxides>

[0041] Binary oxides may be added in order to improve the machinability at an initial stage of cutting when the sintered body is used in a cutting process. The binary oxide means a composite oxide of two types of elements. Specifically, the binary oxide is preferably a composite oxide of two types of elements selected from the group consisting of Ca, Mg, Al, Si, Co, Ni, Ti, Mn, Fe, and Zn, and is more preferably a Ca-Al oxide, a Ca-Si oxide, or the like. The Ca-Al oxide may be, for example, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, or the like. The Ca-Si oxide may be, for example, $2\text{CaO} \cdot \text{SiO}_2$ or the like.

[0042] The shape and the volume-average particle size of the binary oxide as well as the method of measurement and the weight ratio thereof are preferably similar to those of the ternary oxide described above.

<Binary oxides and ternary oxides>

[0043] The mixed powder for iron-based powder metallurgy of the present invention preferably contains both of binary oxides and ternary oxides in a sum weight of 0.02 wt% or more to 0.3 wt% or less. The sum weight of the binary oxides and ternary oxides is preferably 0.05 wt% or more, more preferably 0.1 wt% or more. In view of costs, the weight ratio of the binary oxides and ternary oxides is preferably as small as possible. Further, the sum weight of the binary oxides and ternary oxides is preferably 0.25 wt% or less, more preferably 0.2 wt% or less. When the sum weight of the oxides is 0.25 wt% or less, the radial crushing strength of the sintered body can be sufficiently ensured.

[0044] The weight ratio of the binary oxides and CaS after the sintering is preferably 1 : 9 to 9 : 1, more preferably 3 : 6 to 9 : 1, and still more preferably 4 : 6 to 7 : 3. When the two components are contained at such a weight ratio, a sintered body having an excellent machinability at an initial stage of cutting can be prepared.

<Powder for alloy>

[0045] A powder for alloy is added for the purpose of promoting bonding between the iron-based powders and enhancing the strength of the sintered body after the sintering. Such a powder for alloy is contained preferably at a ratio of 0.1 wt% or more to 10 wt% or less relative to the whole of the mixed powder for iron-based powder metallurgy. When the ratio is 0.1 wt% or more, the strength of the sintered body can be enhanced. Further, when the ratio is 10 wt% or less, the dimension precision of the sintered body at the time of sintering can be ensured.

[0046] The powder for alloy may be, for example, a non-ferrous metal powder such as copper (Cu) powder, nickel (Ni) powder, Mo powder, Cr powder, V powder, Si powder, or Mn powder, a copper suboxide powder, or the like. These may be used either alone as one kind or in combination of two or more kinds.

<Method for producing mixed powder for iron-based powder metallurgy>

[0047] The mixed powder for iron-based powder metallurgy can be prepared, for example, by a production method of the following (1) to (3).

(1) A surface of the CaS raw material powder is coated with a lubricant. Subsequently, the coated CaS raw material powder is mixed with an iron-based powder and powders of other components in a mechanical agitation mixer, so as to prepare a mixed powder for iron-based powder metallurgy.

(2) A surface of the CaS raw material powder is not coated with a lubricant in advance, and the powders of all the components are heated and mixed in a tightly closed container. Subsequently, with use of the hot-melt method, a surface of the powders of all the components is coated with a lubricant, so as to prepare a mixed powder for iron-based powder metallurgy. (Not according to the present invention)

(3) All the powders constituting the mixed powder for iron-based powder metallurgy excluding the lubricant are added into a tightly closed container. Further, an organic solution obtained by dissolving a binder is added into the tightly closed container and mixed, and thereafter the organic solvent is volatilized. Finally, a lubricant is added into the tightly closed container, and the powders constituting the mixed powder for iron-based powder metallurgy are mixed. Thus, the mixed powder for iron-based powder metallurgy is prepared by coating the surface of all the powders excluding the lubricant with the lubricant and/or the binder. (Not according to the present invention) The volume-average particle size of the CaS raw material powder is preferably 0.1 μm or more to 60 μm or less.

[0048] Regarding the heating temperature in the hot-melt method, the optimum temperature may differ depending on the melting point of the lubricant; however, the heating temperature is preferably, for example, 50°C or higher to 150°C or lower. When the heating temperature is 50°C or higher, the fluidity of the lubricant can be readily enhanced. When the heating temperature is 150°C or lower, oxidation of the iron-based powder can be suppressed in the process of preparing the mixed powder, and moreover the costs needed for heating can be reduced.

[0049] The heating time in the hot-melt method is preferably 10 minutes or more to 5 hours or less. The higher the heating temperature is, the shorter the heating time can be made. When the heating time is short, there is a possibility that it may be difficult to coat the whole surface of the CaS raw material powder with the lubricant and/or the binder.

[0050] The mixed powder for iron-based powder metallurgy of the present invention can be prepared by mixing the iron-based powder with the CaS raw material powder prepared in the above with use of, for example, a mechanical agitation mixer. In addition to these powders, various kinds of additives such as a ternary oxide, a powder for alloy, a graphite powder, a binary oxide, a binder, and a lubricant may be suitably added. The mechanical agitation mixer may be, for example, a high-speed mixer, a Nauta Mixer, a V-type mixer, a double-cone blender, or the like. The mixing temperature is not particularly limited; however, the mixing temperature is preferably 150°C or lower in view of suppressing oxidation of the iron-based powder in the mixing step.

<Method for producing sintered body>

[0051] After the mixed powder for iron-based powder metallurgy prepared in the above is put into a mold, a pressure of 300 MPa or higher to 1200 MPa or lower is applied to produce a pressed-powder molded body. The molding temperature during this time is preferably 25°C or higher to 150°C or lower.

[0052] The pressed-powder molded body prepared in the above is sintered by an ordinary sintering method to obtain a sintered body. The sintering conditions may be a non-oxidizing atmosphere or a reducing atmosphere. The above pressed-powder molded body is sintered at a temperature of 1000°C or higher to 1300°C or lower for 5 minutes or more to 60 minutes or less in a nitrogen atmosphere, a mixed atmosphere of nitrogen and hydrogen, or a hydrocarbon atmosphere.

<Sintered body>

[0053] The sintered body thus prepared contains CaS at a ratio of 0.01 wt% or more to 0.1 wt% or less. An upper limit of CaS in the sintered body is preferably 0.09 wt% or less, more preferably 0.08 wt% or less. Further, a lower limit of CaS in the sintered body is preferably 0.02 wt% or more, more preferably 0.03 wt% or more. The sintered body can be used as a mechanical part of an automobile, an agricultural instrument, a power tool, a home electrical appliance, or the like by being processed with various kinds of tools such as a cutting tool in accordance with the needs. The cutting tool for processing the sintered body may be, for example, a drill, an end mill, a cutting tool for milling, a cutting tool for turning on a lathe, a reamer, a tap, or the like.

[0054] According to the mixed powder for iron-based powder metallurgy of the above-described embodiment, the surface of calcium sulfide and calcium sulfate hemihydrate is coated with a lubricant or a binder, so that the moisture absorptivity of these components can be suppressed, and various performances of the sintered body can be stably enhanced.

[0055] The mixed powder for iron-based powder metallurgy further contains one or more ternary oxides selected from the group consisting of Ca-Al-Si oxides and Ca-Mg-Si oxides, so that the machinability in a cutting process for a long period of time can be improved.

[0056] The mixed powder for iron-based powder metallurgy contains the CaS raw material powder such that a weight ratio of CaS after sintering is 0.01 wt% or more to 0.1 wt% or less, and accordingly the machinability of the sintered body after the sintering is excellent.

[0057] The mixed powder for iron-based powder metallurgy contains ternary oxides and the CaS raw material powder such that the weight ratio of the ternary oxides and CaS after the sintering is 3 : 7 to 9 : 1, so that the machinability in a cutting process for a long period of time can be improved.

[0058] Since the CaS raw material powder has a volume-average particle size of 0.1 μm or more to 60 μm or less, the machinability of the sintered body can be enhanced.

[0059] The sintered body prepared by using the above mixed powder for iron-based powder metallurgy is stably excellent in various properties such as machinability. Also, the mixed powder for iron-based powder metallurgy prepared by the above production method exhibits a stable performance because the CaS raw material powder hardly absorbs moisture.

Examples

(Example 1 (Reference Example))

[0060] First, a commercially available calcium sulfide powder was classified with a sieve into -63/+45 μm (volume-average particle size of 54 μm). The classified calcium sulfide powder was put into a tightly closed container in an amount such that the weight of CaS after sintering would be 0.5 wt%. Into this tightly closed container, 0.75 wt% of an amide-based lubricant (trade name: ACRAWAX C (manufactured by Lonza Ltd.)) was added. Then, the resultant was mixed for 10 minutes while being heated to 100°C, so as to coat the surface of the calcium sulfide powder with the amide-based lubricant.

[0061] Next, a pure iron powder (trade name: 300M (manufactured by Kobe Steel, Ltd.)) was mixed with 2 wt% of copper powder (trade name: CuATW-250 (manufactured by Fukuda Metal Foil & Powder Co., Ltd.)), 0.8 wt% of graphite powder (trade name: CPB (manufactured by Nippon Graphite Industries Co., Ltd.)), and the calcium sulfide powder coated with the lubricant prepared in the above, so as to prepare a mixed powder for iron-based powder metallurgy. The graphite powder was added at an amount such that the amount of carbon after the sintering would be 0.75 wt%. The calcium sulfide powder coated in the above was added at an amount such that the weight of CaS after the sintering would be 0.5 wt%.

(Example 2 (Reference Example))

[0062] In Example 1, a calcium sulfide powder and an amide-based lubricant (trade name: ACRAWAX C (manufactured by Lonza Ltd.)) were put into a tightly closed container and heated to 100°C. In Example 2, the powders of all the components used in Example 1 were put into a tightly closed container and heated to 100°C and mixed for 30 minutes by using the hot-melt method, so as to coat the surface of the powders of all the components with the amide-based lubricant. Thereafter, the resultant was cooled to room temperature, thereby to prepare a mixed powder for iron-based powder metallurgy.

(Example 3 (Reference Example))

[0063] In Example 3, the same powders as those of Example 2 were mixed except that the amide-based lubricant used in Example 2 was changed to a toluene solution containing styrene-butadiene rubber. The toluene solution was added so that the weight of styrene-butadiene rubber after volatilization of toluene would be 0.1 wt%. Thereafter, toluene was volatilized at 100°C to coat the surface of the CaS raw material grains with the styrene-butadiene rubber. Thereafter, the amide-based lubricant used in Example 1 was added and mixed in the same amount as the amount used in Example 1, thereby to prepare the mixed powder for iron-based powder metallurgy of Example 3.

(Comparative Examples 1 to 3)

[0064] In Comparative Example 1, a mixed powder for iron-based powder metallurgy was prepared in the same manner as in Example 1 except that the CaS raw material powder was not added. In Comparative Examples 2 and 3, a mixed powder for iron-based powder metallurgy was prepared in the same manner as in Example 1 except that the CaS raw material powder was not coated with a lubricant and a binder though the CaS raw material powder shown in the section of "CaS component" in Table 1 was used.

[0065] With use of the above mixed powder for iron-based powder metallurgy of each Example and each Comparative Examples, two types of sintered bodies were prepared. One was a sintered body using the mixed powder for iron-based powder metallurgy which was in a state immediately after the preparation (which will be hereafter referred to as "sintered body immediately after"), and the other one was a sintered body using the mixed powder for iron-based powder metallurgy which was in a state after ten days had passed from the preparation (which will be hereafter referred to as "sintered body after 10 days").

[0066] A procedure of producing the sintered body immediately after is as follows. First, the mixed powder for iron-based powder metallurgy which was in a state of immediately after the preparation was put into a mold, and a test piece was molded so as to have a ring shape with an outer diameter of 64 mm, an inner diameter of 24 mm, and a thickness of 20 mm and to have a molding density of 7.00 g/cm³. Next, this test piece having a ring shape was sintered at 1130°C for 30 minutes in a 10 vol% H₂-N₂ atmosphere, so as to prepare a sintered body. On the other hand, the sintered body after 10 days was prepared in the same manner as the sintered body immediately after except that the mixed powder for iron-based powder metallurgy was left to stand in ambient air for ten days after the preparation, and thereafter put into a mold.

[Table 1]

Experiment number	Example 1*	Example 2*	Example 3*	Comparative Example 1	Comparative Example 2	Comparative Example 3
CaS component	CaS	CaS	CaS	None	CaS	Hemihydrate gypsum
Coating material	Amide-based lubricant		Organic binder	None	None	None
Molded body density (g/cm ³)	7.00/7.00	7.00/7.00	7.00/7.00	7.00/7.00	7.00/7.00	7.00/7.00
Sintered body density (g/cm ³)	6.82/6.81	6.80/6.80	6.81/6.81	6.94/6.94	6.83/6.78	6.80/6.76
Radial crushing strength (MPa)	780/783	779/769	785/786	915/920	781/714	775/708
Tool wear amount (μm)	50/54	52/54	49/47	253/248	57/144	44/160
* Reference Example						

<Evaluation>

[0067] In Table 1, the evaluation results of molded body density, sintered body density, radial crushing strength, and tool wear amount were given in a form of "sintered body immediately after / sintered body after 10 days". Such notation means that the value on the left side of the slash mark is the evaluation result of the sintered body immediately after, whereas the value on the right side of the slash mark is the evaluation result of the sintered body after 10 days.

[0068] The molded body density and the sintered body density of the sintered body immediately after and the sintered body after 10 days of each Example and each Comparative Example were values as determined by making measurements in accordance with Japan Powder Metallurgy Association Standard (JPMA M 01). Further, the radial crushing strength was a value as determined by making measurements in accordance with JIS Z 2507-2000. The higher the radial crushing strength is, the less likely the sintered body is broken, so that the sintered body has a higher strength.

[0069] The sintered body prepared in each Example and each Comparative Example was turned on a lathe for 1150 m by using a cermet tip (ISO type number: SNGN120408 non-breaker) under conditions with a circumferential speed of 160 m/min, a cutting rate of 0.5 mm/pass, and a feed rate of 0.1 mm/rev, and with a dry type. The tool wear amount (μm) of the cutting tool after the sintered body was turned on the lathe was measured with a tool microscope. The results thereof are shown in the section of "tool wear amount" in Table 1. The smaller the value of the tool wear amount is, the more excellent the machinability of the sintered body is.

[0070] From the results of each Example and each Comparative Example shown in Table 1, it has been found out that various properties (sintered body density, radial crushing strength, and tool wear amount) of the sintered body immediately after and the sintered body after 10 days are almost equivalent when the CaS raw material powder is coated with a lubricant or a binder as in each Example. On the other hand, in Comparative Examples 2 and 3, though CaS single or hemihydrate gypsum was contained as the CaS component, no coating treatment was performed on the surface, so that various properties of the sintered body after 10 days were considerably deteriorated as compared with those of the sintered body immediately after.

[0071] The reason why the product quality and performance of the sintered body after 10 days were considerably deteriorated in Comparative Examples 2 and 3 seems to be that the CaS or hemihydrate gypsum in the mixed powder for iron-based powder metallurgy absorbed moisture during the period of time in which the mixed powder for iron-based powder metallurgy was left to stand for ten days. In other words, this seems to be due to the fact that, in Comparative Examples 2 and 3, the CaS single or hemihydrate gypsum in the mixed powder for iron-based powder metallurgy absorbed moisture during the storage in ambient air for 10 days, so that the density of the sintered body decreased, or the radial crushing strength decreased. In Comparative Example 1, the CaS component was not contained, so that the tool wear amount was considerably high both in the sintered body immediately after and in the sintered body after 10 days, and the machinability of the sintered body was considerably low.

[0072] From the results shown in Table 1, it has been made clear that, when the CaS raw material powder is coated with a lubricant or a binder, various properties (sintered body density, radial crushing strength, and tool wear amount) of the sintered body immediately after and the sintered body after 10 days are almost equivalent, and the product quality and performance of the sintered body is stable, thereby showing the effect of the present invention.

Claims

1. A mixed powder for iron-based powder metallurgy, which comprises an iron-based powder and a CaS raw material powder containing at least calcium sulfide, wherein the CaS raw material powder is coated with at least one selected from a lubricant and a binder;

wherein the mixed powder is obtained by mixing the iron-based powder with the CaS raw material powder coated with the lubricant and/or the binder; and

wherein the CaS raw material powder is contained such that a weight ratio of CaS after sintering is 0.01 wt% or more to 0.1 wt% or less, wherein the sintering is conducted at a temperature of 1000°C or higher to 1300°C or lower for 5 minutes or more to 60 minutes or less in a nitrogen atmosphere, a mixed atmosphere of nitrogen and hydrogen, or a hydrocarbon atmosphere.

2. The mixed powder for iron-based powder metallurgy according to claim 1, further comprising one or more ternary oxides selected from the group consisting of Ca-Al-Si oxides and Ca-Mg-Si oxides.

3. The mixed powder for iron-based powder metallurgy according to claim 2, wherein the ternary oxides and the CaS raw material powder are contained such that a weight ratio of the ternary oxides and CaS after sintering is 3 : 7 to 9 : 1.

4. The mixed powder for iron-based powder metallurgy according to claim 1, wherein the CaS raw material powder has a volume-average particle size of 0.1 μm or more to 60 μm or less, wherein the volume-average particle size is a value of the particle size D_{50} at an accumulated value of 50% in the particle size distribution obtained by using a laser diffraction particle size distribution measurement device.

5. A method for producing a mixed powder for iron-based powder metallurgy, comprising:

coating a CaS raw material powder, which contains at least calcium sulfide, with at least one selected from a lubricant and a binder; and
 mixing the coated CaS raw material powder with an iron-based powder,
 wherein the CaS raw material powder is contained such that a weight ratio of CaS after sintering is 0.01 wt% or more to 0.1 wt% or less, wherein the sintering is conducted at a temperature of 1000°C or higher to 1300°C or lower for 5 minutes or more to 60 minutes or less in an atmosphere of a nitrogen atmosphere, a mixed atmosphere of nitrogen and hydrogen, or a hydrocarbon atmosphere.

Patentansprüche

1. Pulvergemisch für Pulvermetallurgie auf Eisenbasis, das ein Pulver auf Eisenbasis und ein CaS-Rohmaterialpulver, enthaltend mindestens Calciumsulfid, umfasst, wobei das CaS-Rohmaterialpulver mit mindestens einem, ausgewählt aus einem Schmiermittel und einem Bindemittel, beschichtet ist;

wobei das Pulvergemisch durch Mischen des Pulvers auf Eisenbasis mit dem CaS-Rohmaterialpulver, beschichtet mit dem Schmiermittel und/oder dem Bindemittel, erhalten ist; und
 wobei das CaS-Rohmaterialpulver so enthalten ist, dass ein Gewichtsanteil von CaS nach Sintern 0,01 Gew.-% oder mehr bis 0,1 Gew.-% oder weniger beträgt, wobei das Sintern bei einer Temperatur von 1000°C oder höher bis 1300°C oder niedriger für 5 Minuten oder mehr bis 60 Minuten oder weniger in einer Stickstoffatmosphäre, einem Atmosphäremischung von Stickstoff und Wasserstoff oder einer Kohlenwasserstoffatmosphäre durchgeführt wird.

2. Pulvergemisch für Pulvermetallurgie auf Eisenbasis nach Anspruch 1, weiter umfassend ein oder mehrere ternäre Oxide, ausgewählt aus der Gruppe, bestehend aus Ca-Al-Si-Oxiden und Ca-Mg-Si-Oxiden.

3. Pulvergemisch für Pulvermetallurgie auf Eisenbasis nach Anspruch 2, wobei die ternären Oxide und das CaS-Rohmaterialpulver so enthalten sind, dass ein Gewichtsverhältnis von den ternären Oxiden und CaS nach Sintern 3 : 7 bis 9 : 1 beträgt.

4. Pulvergemisch für Pulvermetallurgie auf Eisenbasis nach Anspruch 1, wobei das CaS-Rohmaterialpulver eine volumengemittelte Teilchengröße von 0,1 µm oder mehr bis 60 µm oder weniger aufweist, wobei die volumengemittelte Teilchengröße ein Wert der Teilchengröße D_{50} bei einem akkumulierten Wert von 50% in der Teilchengrößenverteilung ist, erhalten unter Verwendung einer Laserbeugungs-Teilchengrößenverteilungs-Messvorrichtung.

5. Verfahren zur Herstellung eines Pulvergemischs für Pulvermetallurgie auf Eisenbasis, umfassend:

Beschichten eines CaS-Rohmaterialpulvers, das mindestens Calciumsulfid enthält, mit mindestens einem, ausgewählt aus einem Schmiermittel und einem Bindemittel; und
 Mischen des beschichteten CaS-Rohmaterialpulvers mit einem Pulver auf Eisenbasis,
 wobei das CaS-Rohmaterialpulver so enthalten ist, dass ein Gewichtsanteil von CaS nach Sintern 0,01 Gew.-% oder mehr bis 0,1 Gew.-% oder weniger beträgt, wobei das Sintern bei einer Temperatur von 1000°C oder höher bis 1300°C oder niedriger für 5 Minuten oder mehr bis 60 Minuten oder weniger in einer Atmosphäre aus einer Stickstoffatmosphäre, einem Atmosphäremischung von Stickstoff und Wasserstoff oder einer Kohlenwasserstoffatmosphäre durchgeführt wird.

Revendications

1. Poudre mélangée pour métallurgie des poudres à base de fer, qui comprend une poudre à base de fer et une poudre de matière première de CaS contenant au moins du sulfure de calcium, dans laquelle la poudre de matière première de CaS est enrobée d'au moins un élément sélectionné parmi un lubrifiant et un liant ;

dans laquelle la poudre mélangée est obtenue en mélangeant la poudre à base de fer à la poudre de matière première de CaS enrobée du lubrifiant et/ou du liant ; et
 dans laquelle la poudre de matière première de CaS est contenue de sorte qu'un rapport pondéral du CaS après frittage est de 0,01 % en poids ou plus à 0,1 % en poids ou moins, dans laquelle le frittage est réalisé à une température de 1000 °C ou supérieure à 1300 °C ou inférieure pendant 5 minutes ou plus à 60 minutes

ou moins dans une atmosphère d'azote, une atmosphère mélangée d'azote et d'hydrogène ou une atmosphère d'hydrocarbure.

2. Poudre mélangée pour métallurgie des poudres à base de fer selon la revendication 1, comprenant en outre un ou plusieurs oxydes ternaires sélectionnés parmi le groupe constitué d'oxydes de Ca-Al-Si et d'oxydes de Ca-Mg-Si.

3. Poudre mélangée pour métallurgie des poudres à base de fer selon la revendication 2, dans laquelle les oxydes ternaires et la poudre de matière première de CaS sont contenus de sorte qu'un rapport pondéral des oxydes ternaires et du CaS après frittage est de 3/7 à 9/1.

4. Poudre mélangée pour métallurgie des poudres à base de fer selon la revendication 1, dans laquelle la poudre de matière première de CaS a une taille particulaire moyenne en volume de 0,1 μm ou plus à 60 μm ou moins, dans laquelle la taille particulaire moyenne en volume est une valeur de la taille particulaire D_{50} à une valeur accumulée de 50 % dans la distribution de taille particulaire obtenue en utilisant un dispositif de mesure de distribution de taille particulaire à diffraction laser.

5. Procédé de production d'une poudre mélangée pour métallurgie des poudres à base de fer, comprenant :

enrober une poudre de matière première de CaS, qui contient au moins du sulfure de calcium, d'au moins un élément sélectionné parmi un lubrifiant et un liant ; et
 mélanger la poudre de matière première de CaS enrobée à une poudre à base de fer,
 dans lequel la poudre de matière première de CaS est contenue de sorte qu'un rapport pondéral du CaS après frittage est de 0,01 % en poids ou plus à 0,1 % en poids ou moins, dans lequel le frittage est réalisé à une température de 1000 °C ou supérieure à 1300 °C ou inférieure pendant 5 minutes ou plus à 60 minutes ou moins dans une atmosphère parmi une atmosphère d'azote, une atmosphère mélangée d'azote et d'hydrogène ou une atmosphère d'hydrocarbure.

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- JP S5216684 B [0005] [0008]
- WO 2015008406 A1 [0008]