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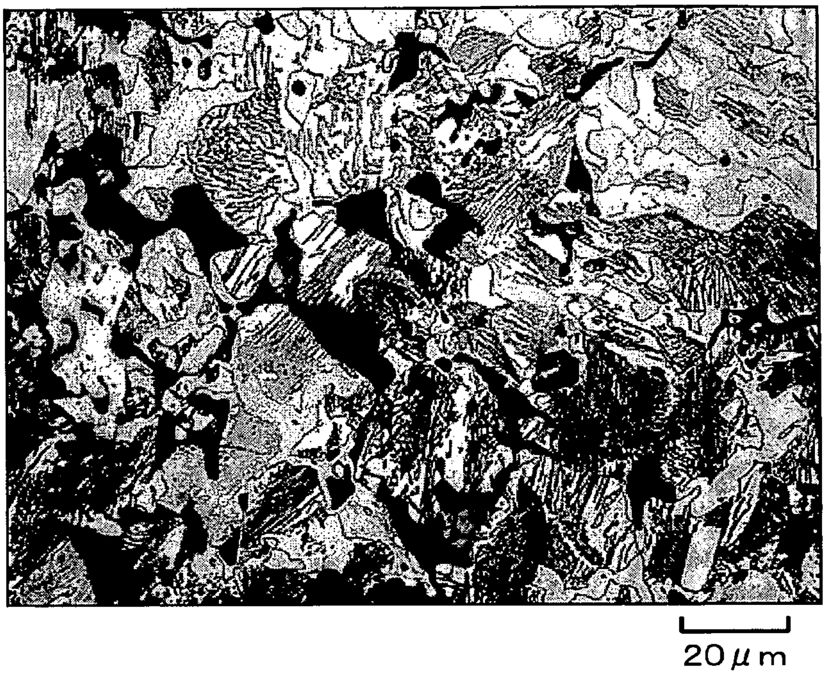
(54) Sintered materials for valve guides and production methods therefor

(57) A sintered material for valve guides consists of, by mass %, 1.3 to 3 % of C, 1 to 4 % of Cu, and the balance of Fe and inevitable impurities. The sintered material exhibits a metallic structure made of pores and a matrix, the matrix is a mixed structure of a pearlite phase, a ferrite phase, an iron carbide phase, and a copper phase, and a part of the pores includes graphite that is dispersed therein. The iron carbide phase is dispersed at 3 to 25 % by area ratio and the copper phase is dispersed at 0.5 to 3.5 % by area ratio with respect to a cross section of the metallic structure, respectively.

Fig. 1A



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Description

BACKGROUND OF THE INVENTION

Technical Field

[0001] The present invention relates to sintered materials for valve guides that may be used in an internal combustion engine, and also relates to production methods for sintered materials for valve guides. Specifically, the present invention relates to a technique for further improving wear resistance of the sintered materials for valve guides while production cost is not greatly increased.

Background Art

[0002] A valve guide used in an internal combustion engine is a tubular component having an inner circumferential surface for guiding valve stems of an intake valve and an exhaust valve. The intake valve may be driven so as to take fuel mixed gas into a combustion chamber of the internal combustion engine, and the exhaust valve may be driven so as to exhaust combustion gas from the combustion chamber. For guiding the valve stems of the intake valve and the exhaust valve, the valve guide is required to have wear resistance and is also required to maintain smooth sliding conditions so as not to cause wear of the valve stems for long periods. Valve guides made of a cast iron are generally used, but valve guides made of a sintered alloy have recently come into wide use. This is because sintered alloys can have a specific metallic structure, which cannot be obtained from ingot materials, and therefore the sintered alloys can have wear resistance. Moreover, once a die assembly has been made, products having the same shape can be mass-produced, and therefore the sintered alloys are suitable for commercial production. Furthermore, a sintered alloy can be formed into a shape similar to that of a product, and thereby material yield can be high in machining. Valve guides made of a sintered alloy are disclosed in, for example, Japanese Examined Patent Publication No. 55-034858, and Japanese Patents Nos. 2680927, 4323069, and 4323467.

[0003] The sintered material for valve guides disclosed in Japanese Examined Patent Publication No. 55-034858 is made of an iron-based sintered alloy consisting of, by weight, 1.5 to 4 % of C, 1 to 5 % of Cu, 0.1 to 2 % of Sn, not less than 0.1 % and less than 0.3 % of P, and the balance of Fe. A photograph and a schematic view of a metallic structure of this sintered material are shown in Figs. 3A and 3B, respectively. As shown in Figs. 3A and 3B, in this sintered material, an iron-phosphorus-carbon compound phase is precipitated in a pearlite matrix which is strengthened by adding copper and tin. The iron-phosphorus-carbon compound absorbs C from the surrounding matrix and grows into a plate shape, whereby a ferrite phase is dispersed at a portion surrounding the iron-phosphorus-carbon compound phase. Moreover, a copper alloy phase is dispersed in the matrix. The copper alloy phase is formed such that Cu is solved in the matrix during sintering at high temperature in an amount greater than the solid solubility limit at room temperature and is precipitated in the matrix by cooling. In the photograph of the metallic structure shown in Fig. 3A, since a graphite phase was exfoliated when the sample was polished so as to observe the metallic structure, the graphite phase cannot be observed. Nevertheless, as shown in the schematic view of Fig. 3B, graphite remains inside a large pore and is dispersed as a graphite phase. This sintered material has superior wear resistance due to the iron-phosphorus-carbon compound phase. Therefore, this sintered material has been commercially used as a common material for internal combustion valve guides for automobiles by domestic and international automobile manufacturers.

[0004] The sintered material for valve guides disclosed in Japanese Patent No. 2680927 is an improved material of the sintered material disclosed in Japanese Examined Patent Publication No. 55-034858. In this material, in order to improve machinability, magnesium metasilicate minerals and magnesium orthosilicate minerals are dispersed as intergranular inclusions in the metallic matrix of the sintered material disclosed in Japanese Examined Patent Publication No. 55-034858. As with the sintered material disclosed in Japanese Examined Patent Publication No. 55-034858, this sintered material has been commercially used by domestic and international automobile manufacturers.

[0005] The sintered materials for valve guides disclosed in Japanese Patent Nos. 4323069 and 4323467 have further improved machinability. The machinabilities thereof are improved by decreasing amount of phosphorus. That is, the dispersion amount of the hard iron-phosphorus-carbon compound phase is decreased to only the amount that is required for maintaining wear resistance of a valve guide. These sintered materials have started to be commercially used by domestic and international automobile manufacturers.

[0006] Recently, requirements for reducing the production costs have been increasing for various industrial machine parts, and also the requirements for reducing the production costs have been increasing for automobile parts. In view of these circumstances, further reduction of the production costs is also required for sintered materials for valve guides for internal combustion engines.

[0007] In the meantime, in accordance with trends toward improving the performance and the fuel efficiency of automobile internal combustion engines in recent years, valve guides have been subjected to higher temperatures and higher pressures while internal combustion engines are running. Moreover, in view of recent environmental issues, amounts of lubricant supplied to an interface between a valve guide and a valve stem have been decreased. Therefore, valve guides must withstand more severe sliding conditions. In view of these circumstances, a sintered material for valve guides is required to have high wear resistance equivalent to those of the sintered materials disclosed in Japanese Examined Patent Publication No. 55-034858 and Japanese Patent No. 2680927.

SUMMARY OF THE INVENTION

[0008] Accordingly, an object of the present invention is to provide valve guide materials and to provide production methods therefor, and the sintered materials for valve guides have high wear resistance but the production cost is reduced. In this case, the sintered materials for valve guides have wear resistance equivalent to those of the conventional sintered materials for valve guides, that is, the sintered materials for valve guides disclosed in Japanese Examined Patent Publication No. 55-034858 and Japanese Patent No. 2680927.

[0009] In order to achieve the above object, according to a first aspect of the present invention, the present invention provides a sintered material for valve guides, consisting of, by mass %, 1.3 to 3 % of C, 1 to 4 % of Cu, and the balance of Fe and inevitable impurities. The sintered material exhibits a metallic structure made of pores and a matrix. The matrix is a mixed structure of a pearlite phase, a ferrite phase, an iron carbide phase, and a copper phase, and a part of the pores includes graphite that is dispersed therein. The iron carbide phase is dispersed at 3 to 25 % by area ratio and the copper phase is dispersed at 0.5 to 3.5 % by area ratio with respect to a cross section of the metallic structure, respectively.

[0010] In order to achieve the above object, according to a second aspect of the present invention, the present invention provides a sintered material for valve guides, consisting of, by mass %, 1.3 to 3 % of C, 1 to 4 % of Cu, 0.05 to 0.5 % of Sn, and the balance of Fe and inevitable impurities. The sintered material exhibits a metallic structure made of pores and a matrix. The matrix is a mixed structure of a pearlite phase, a ferrite phase, an iron carbide phase, and at least one of a copper phase and a copper-tin alloy phase, and a part of the pores includes graphite that is dispersed therein. The iron carbide phase is dispersed at 3 to 25 % by area ratio and the copper phase and the copper-tin alloy phase are dispersed at 0.5 to 3.5 % by area ratio with respect to a cross section of the metallic structure, respectively.

[0011] In the sintered materials for valve guides according to the first and the second aspect of the present invention, the iron carbide phase can be observed as a plate-shaped iron carbide having an area of not less than 0.05 % in a visual field in a cross-sectional structure at 200-power magnification. In this case, when a total area of the plate-shaped iron carbides having an area of not less than 0.15 % in the above visual field is 3 to 50 % with respect to a total area of the plate-shaped iron carbides, wear resistance is improved.

[0012] In addition, at least one kind selected from the group consisting of manganese sulfide particles, magnesium silicate mineral particles, and calcium fluoride particles are preferably dispersed in particle boundaries of the matrix and in the pores at not more than 2 mass %.

[0013] In order to achieve the above object, the present invention provides a production method for the sintered material for valve guides according to the first aspect of the present invention. The production method includes preparing an iron powder, a copper powder, and a graphite powder, and mixing the copper powder and the graphite powder with the iron powder into a raw powder consisting of, by mass %, 1.3 to 3% of C, 1 to 4 % of Cu, and the balance of Fe and inevitable impurities. The production method also includes filling a tube-shaped cavity of a die assembly with the raw powder, and compacting the raw powder into a green compact having a tube shape. The production method further includes sintering the green compact at a heating temperature of 970 to 1070 °C in a nonoxidizing atmosphere so as to obtain a sintered compact.

[0014] In order to achieve the above object, the present invention provides a production method for the sintered material for valve guides according to the second aspect of the present invention. This production method includes preparing an iron powder, a graphite powder, and one selected from the group consisting of a combination of a copper powder and a tin powder, a copper-tin alloy powder, and a combination of a copper powder and a copper-tin alloy powder. This production method also includes mixing the graphite powder and the one selected from the group with the iron powder into a raw powder consisting of, by mass %, 1.3 to 3% of C, 1 to 4 % of Cu, 0.05 to 0.5 % of Sn, and the balance of Fe and inevitable impurities. The production method also includes filling a tube-shaped cavity of a die assembly with the raw powder, and compacting the raw powder into a green compact having a tube shape. The production method further includes sintering the green compact at a heating temperature of 950 to 1050 °C in a nonoxidizing atmosphere so as to obtain a sintered compact.

[0015] In the production methods for the sintered materials for valve guides according to the first and the second aspect of the present invention, the green compact is desirably held at the heating temperature for 10 to 90 minutes in the sintering. Moreover, the sintered compact is cooled from the heating temperature to room temperature after the sintering, and the cooling rate is desirably 5 to 20 °C per minute while the sintered compact is cooled from 850 to 600 °C. In addition, when the sintered compact is cooled from the heating temperature to room temperature, the sintered compact is desirably isothermally held in a temperature range of 850 to 600 °C for 10 to 90 minutes and is then cooled.

In the mixing of the powders, at least one kind selected from the group consisting of a manganese sulfide powder, a magnesium silicate mineral powder, and a calcium fluoride powder is desirably added to the raw powder at not more than 2 mass %.

[0016] According to the sintered materials for valve guides of the present invention, since phosphorus is not used in the entire composition, the production cost can be low. Moreover, the iron carbide phase is dispersed in a similar shape and in similar amount as in the case of a conventional sintered material for valve guides, whereby degree of wear resistance is maintained. Therefore, the sintered materials for valve guides of the present invention can be obtained at low production cost but have superior wear resistance. According to the production methods for the sintered materials for valve guides of the present invention, the sintered materials for valve guides of the present invention can be produced as easily as in a conventional manner.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

Figs. 1A and 1B show a metallic structure of a sintered material for valve guides of the present invention, which was etched with a nital. Fig. 1A is a photograph of the metallic structure, and Fig. 1B is a schematic view of the photograph of the metallic structure of Fig. 1A.

Figs. 2A and 2B show a metallic structure of a sintered material for valve guides of the present invention, which was etched with Murakami's reagent. Fig. 2A is a photograph of the metallic structure, and Fig. 2B is a schematic view of the photograph of the metallic structure of Fig. 2A, which was processed so as to extract an iron carbide phase.

Figs. 3A and 3B show a metallic structure of a conventional sintered material for valve guides. Fig. 3A is a photograph of the metallic structure, and Fig. 3B is a schematic view of the photograph of the metallic structure of Fig. 3A.

PREFERRED EMBODIMENTS OF THE INVENTION

[0018] In a common iron-copper-carbon sintered material, iron carbides, which improve wear resistance, are not dispersed in the shape of plates in a matrix. On the other hand, in a conventional sintered material for valve guides, which includes P (for example, Japanese Examined Patent Publication No. 55-034858), iron-phosphorus-carbon eutectic compounds are dispersed in a matrix, and the compounds absorb C from the surrounding matrix and grow into a plate shape. From this point of view, in order to obtain plate-shaped iron carbides, P is expected to be essential to generate the iron-phosphorus-carbon eutectic compounds. In view of these circumstances, the inventors of the present invention have researched the reason that the plate-shaped iron carbides are not generated in the iron-copper-carbon sintered material.

[0019] A copper powder and a graphite powder may be added to an iron powder so as to obtain a raw powder, and the raw powder may be compacted and sintered, whereby an iron-copper-carbon sintered material is obtained. Some of the iron-copper-carbon sintered materials may be used as a material for general structure, and some may be used as a material for sliding such as a bearing.

[0020] In general, in the iron-copper-carbon sintered material used as the material for general structure, sintering is performed at a heating temperature (sintering temperature) of not less than the melting point of Cu (1084.5 °C). Therefore, the copper powder that was added to raw powder is melted under such temperature and generates a liquid phase. The liquid phase fills spaces among the raw powder particles due to capillary force and wets and covers the surface of the iron powder particles, and Cu is diffused from this liquid phase into the iron powder. Therefore, Cu is uniformly diffused and is solid solved in the iron matrix. In addition, C added in the form of the graphite powder starts to be diffused to the iron matrix at approximately 800 °C in the sintering. Since C is rapidly diffused into the iron matrix, the entire amount of C is diffused to the iron matrix, and the graphite powder disappears under the above heating temperature. Thus, in the iron-copper-carbon sintered material, Cu and C are relatively uniformly diffused in the iron matrix.

[0021] Cu is an element for decreasing the critical cooling rate of a steel and improves hardenability of the steel. That is, Cu shifts the pearlite nose to the later time side (right side) in the continuous cooling transformation diagram. Therefore, when the sintered material is cooled from the heating temperature in a condition that Cu having such effects is uniformly diffused in the iron matrix, the pearlite nose is shifted to the later time side. As a result, the sintered material is cooled at a cooling rate in an ordinary sintering furnace before the iron carbides (Fe_3C) grow sufficiently. Accordingly, a fine pearlite structure is formed, and the plate-shaped iron carbides are not easily obtained.

[0022] The iron-copper-carbon sintered materials that may be used for sliding materials are disclosed in, for example, Japanese Patent No. 4380274 and Japanese Patent Application of Laid-Open No. 2008-202123. In these iron-copper-carbon sintered materials, in order to make graphite powder remain and act as a solid lubricant, sintering is performed at a heating temperature of approximately 750 to 800 °C, in which the graphite powder is not easily dispersed. In this case, diffusion amount of C into the iron matrix is decreased, and the matrix has a hypoeutectoid composition. Therefore, the metallic structure after the sintering is a mixed phase of pearlite and ferrite, and the plate shaped iron carbides (Fe_3C) are not obtained.

[0023] For these reasons, the inventors of the present invention came to have an idea that the plate-shaped iron carbides (Fe_3C) may be precipitated in the cooling after the sintering by controlling the diffusion condition of Cu. Then, the inventors of the present invention have researched the idea and found that iron carbides (Fe_3C) in a predetermined plate shape can be obtained even without adding P. The present invention was achieved based on this finding.

Sintered Material for Valve Guides of First Embodiment

[0024] In a sintered material for valve guides according to a first embodiment of the present invention based on the above finding, diffusion of Cu in an iron matrix is controlled. The matrix includes portions having high and low concentrations of Cu and not uniformly includes Cu. In the matrix, plate-shaped iron carbides (Fe_3C) are precipitated at the portion having low concentration of Cu.

[0025] A metallic structure of a cross section of a sintered material for valve guides of the present invention is shown in Figs. 1A and 1B. The cross-sectional structure was mirror polished and was etched with a nital (solution of 1 mass % of nitric acid and alcohol). Fig. 1A is a photograph of the metallic structure, and Fig. 1B is a schematic view of the photograph of the metallic structure. As shown in Figs. 1A and 1B, the metallic structure of the sintered material of the present invention is made of pores and a matrix, and the pores are dispersed in the matrix. The pores were generated by spaces that remained among raw powder particles when the raw powder was compacted. The matrix (iron matrix) was mainly made of an iron powder in the raw powder. The matrix is a mixed structure of a pearlite phase, a ferrite phase, an iron carbide phase, and a copper phase. In the photograph of the metallic structure shown in Fig. 1A, since a graphite phase was exfoliated when the sample was polished so as to observe the metallic structure, the graphite phase is not observed. However, as shown in the schematic view of Fig. 1B, graphite remained inside the large pores and is dispersed as a graphite phase.

[0026] An iron carbide (Fe_3C) phase is precipitated in the shape of plates, and the shape and the amount of the iron carbide phase are approximately the same as those of the conventional sintered material shown in Figs. 3A and 3B. The copper phase exists in a condition in which a part of the amount of the copper powder is not dispersed and remains in the matrix, and the powder particles of Cu are not completely diffused.

[0027] Moreover, according to analysis of a metallic structure of a sintered material for valve guides of the present invention by an EMPA (Electron Probe Micro Analyzer), plate-shaped iron carbide (Fe_3C) phase was precipitated at a portion having low concentration of Cu. That is, by controlling diffusion of Cu in an iron matrix and by forming a matrix including portions having high and low concentrations of Cu, plate-shaped iron carbides (Fe_3C) are obtained at the portion having low concentration of Cu even without adding P.

[0028] Fig. 2A shows a photograph of the metallic structure of the sintered material used for the EPMA analysis. The sintered material was etched with Murakami's reagent (a solution of 10 mass % of potassium ferricyanide and 10 mass % of potassium hydroxide). Fig. 2B is a schematic view obtained by analyzing the photograph of Fig. 2A. As shown in Figs. 2A and 2B, plate-shaped iron carbides (Fe_3C) were deeply etched (the gray colored portions), and pearlite portions were lightly etched (the white colored portions). The black portions shown in Figs. 2A and 2B are pores. Accordingly, the plate-shaped iron carbide (Fe_3C) phase can be distinguished from the iron carbides (Fe_3C) that form the pearlite as described above.

[0029] In the sintered material for valve guides of the present invention, Cu is essential for strengthening the sintered material. In addition, Cu is essential for forming the copper phase and thereby improving adaptability to a mating material (valve stem). When the amount of Cu is less than 1 mass %, these effects are not sufficiently obtained. Therefore, the amount of Cu is set to be not less than 1 mass %. On the other hand, when the amount of Cu is more than 4 mass %, the amount of Cu diffused in the iron matrix becomes too great, whereby plate-shaped iron carbides are difficult to obtain in the cooling after the sintering. Accordingly, the amount of Cu in the sintered material is set to be 1 to 4 mass %.

[0030] In the sintered material for valve guides of the present invention, C is essential for forming the iron carbide phase and the graphite phase that can be used as a solid lubricant. Therefore, the amount of C is set to be not less than 1.3 mass %. In this case, C is added in the form of a graphite powder. If the amount of the graphite powder is more than 3.0 mass % in the raw powder, flowability, fillability, and compressibility of the raw powder are greatly decreased, and the sintered material is difficult to produce. Accordingly, the amount of C in the sintered material is set to be 1.3 to 3.0 mass %.

[0031] When the amount of the plate-shaped iron carbide phase is small, the wear resistance is decreased. Therefore, the amount of the plate-shaped iron carbide phase is required to be not less than 3 % by area ratio with respect to a metallic structure including pores in cross-sectional observation. In contrast, when the amount of the plate-shaped iron carbide phase is too great, the degree of wear characteristics with respect to a mating material (valve stem) is increased, whereby the mating material may be worn. In addition, strength of a valve guide is decreased, and machinability of a valve guide is decreased. Therefore, the upper limit of the amount of the plate-shaped iron carbide phase is set to be

25 %. It should be noted that the pearlite has a lamellar structure of fine iron carbides and ferrite, and the plate-shaped iron carbide phase of the present invention does not include the iron carbides of the pearlite. The plate-shaped iron carbide phase of the present invention is identified in a cross-sectional metallic structure as the dark colored portion as shown in Fig. 2B by using image analyzing software, such as "WinROOF" produced by Mitani Corporation. The dark colored portion, that is, the iron carbide phase is separately extracted by controlling a threshold. Therefore, the area ratio of the plate-shaped iron carbide phase can be measured by analyzing the area of the dark colored portions.

[0032] When the above image analysis is performed, each of the plate-shaped iron carbides is recognized as a portion having an area of not less than 0.05 % in a visual field of a cross-sectional structure at 200-power magnification as described above. Accordingly, the area ratio of the plate-shaped iron carbide phase also can be measured by adding up the areas of the portions having an area of not less than 0.05 %. The area ratio of the plate-shaped iron carbide phase is set to be the above area ratio in cross section. Moreover, as already described above, in view of the wear resistance, the amount of large plate-shaped iron carbides is preferably 3 to 50 % with respect to the entire amount of the plate-shaped iron carbides. In this case, the large plate-shaped iron carbides have an area of not less than 0.15 %, which is measured in a visual field of a cross-sectional structure at 200-power magnification.

[0033] When the amount of the copper phase is small, the degree of the wear characteristics to a mating material (valve stem) is increased, whereby the mating material (valve stem) may be worn. Therefore, the amount of the copper phase is set to be not less than 0.5 % by area ratio with respect to a metallic structure including pores in cross-sectional observation. In this case, the copper phase is made of the copper powder added to the raw powder. If the amount of the copper phase is too great, that is, if the amount of the copper powder added to the raw powder is too great, the diffusion amount of Cu into the iron matrix is increased, whereby the plate-shaped iron carbide phase is difficult to obtain. Therefore, the amount of the copper phase is set to be not more than 3.5 % by area ratio with respect to a metallic structure including pores in cross-sectional observation.

Sintered Material for Valve Guides of Second Embodiment

[0034] A sintered material for valve guides according to a second embodiment of the present invention is a modification of the sintered material for valve guides of the First Embodiment, in which the strength is improved by adding Sn. In order to improve the strength, the amount of Sn is set to be not less than 0.05 mass %. On the other hand, when the amount of Sn is too great, too much of the Cu-Sn eutectic liquid phase is generated, as described below. In this case, the amount of the diffusion of Cu into the iron matrix is increased, and the plate-shaped iron carbides are difficult to obtain in the cooling after the sintering. Therefore, the upper limit of the amount of Sn is set to be 0.5 mass %.

[0035] In the sintered material for valve guides according to the Second Embodiment, since Sn is added, Sn is solid solved into a part or the entire area of the copper phase in the sintered material for valve guides of the first embodiment. Therefore, a combination of a copper phase and a copper-tin alloy phase, or a copper-tin alloy phase is dispersed. The amount of these copper system phases (the copper phase and the copper-tin alloy phase, or the copper-tin alloy phase) is set to be not less than 0.5 % by area ratio with respect to a metallic structure in cross-sectional observation in view of the adaptability to a mating material. On the other hand, when this area ratio is more than 3.5 %, the diffusion amount of Cu into the iron matrix is increased, whereby the plate-shaped iron carbide phase is difficult to obtain. Therefore, in the sintered material for valve guides according to the Second Embodiment, the amount of the copper system phases (the copper phase and the copper-tin alloy phase, or the copper-tin alloy phase) is set to be 0.5 to 3.5 % by area ratio with respect to a metallic structure in cross-sectional observation.

Production Method for Sintered Material for Valve Guides of First Embodiment

[0036] In the sintered material for valve guides, diffusion of Cu in the iron matrix is controlled, whereby the matrix includes portions having high and low concentration of Cu and not uniformly includes Cu. The plate-shaped iron carbides (Fe_3C) are precipitated at the portion having low concentration of Cu in the matrix. In a production method for the sintered material for valve guides according to the First Embodiment of the present invention, a copper powder and a graphite powder are mixed with an iron powder so as to obtain a mixed powder as a raw powder. In this case, sintering is performed at a heating temperature (sintering temperature) of less than the melting point of Cu (1085 °C) so as to prevent generation of a Cu liquid phase. Therefore, Cu is diffused into the iron matrix only by solid-phase diffusion.

[0037] In this case, the graphite powder is added to the raw powder at not less than the amount at which C diffused at the heating temperature forms hypereutectoid composition. As a result, a part of the amount of C added in the form of the graphite powder is uniformly diffused and is solved in the iron matrix (austenite). The residual amount of C remains as a graphite phase which functions as a solid lubricant.

[0038] When the sintered compact in such conditions is cooled, in the portion having low concentration of Cu in the iron matrix, the effect for improving the hardenability of the iron matrix is decreased, and the pearlite nose is not greatly shifted to the later time side in the continuous cooling transformation diagram. Therefore, the time required for growing iron carbides (Fe_3C) is secured, and the iron carbides are precipitated from the austenite in the cooling after the sintering and grow sufficiently. Accordingly, carbides (Fe_3C) in a predetermined plate shape are obtained even without adding phosphorus (P).

[0039] The sintering is performed in a nonoxidizing atmosphere as is conventionally done. In this case, the upper limit of the heating temperature is set to be less than the melting point of Cu in the sintering. In view of decreasing diffusion of Cu, the upper limit of the heating temperature is set to be 1070 °C. On the other hand, Cu is essential for improving the strength of the sintered material, and if the amount of Cu diffused into the iron matrix is too small, the strength of the sintered material is decreased. From this point of view, the lower limit of the heating temperature in the sintering is set to be 970 °C.

[0040] In the sintering at the above heating temperature, the copper powder is added at 1 to 4 mass %. When the amount of the copper powder is less than 1 mass %, the strength of the sintered material is decreased. On the other hand, when the amount of the copper powder is more than 4 mass %, the amount of Cu diffused in the iron matrix becomes too great, whereby the plate-shaped iron carbides are difficult to obtain in the cooling after the sintering. Therefore, the copper powder is added to the raw powder at 1 to 4 mass %.

[0041] In addition, in the sintering at the above heating temperature, the amount of the graphite powder is selected so that C diffused in the iron matrix forms an eutectoid composition or a hypereutectoid composition and so that a part of the amount of the graphite powder remains as a solid lubricant. Therefore, the graphite powder is added to the raw powder at not less than 1.3 mass %. On the other hand, when the graphite powder is added to the raw powder at more than 3.0 mass %, the flowability, the fillability, and the compressibility of the raw powder are greatly decreased, and the sintered material is difficult to produce. Therefore, the graphite powder is added to the raw powder at 1.3 to 3.0 mass %.

[0042] The diffusions of the elements of Cu and C are greatly affected by the heating temperature and are relatively less affected by the holding time at the heating temperature. Nevertheless, because Cu and C may not be sufficiently diffused if the holding time is too short in the sintering, the holding time is preferably set to be not less than 10 minutes. On the other hand, because Cu may be too diffused if the holding time is too long in the sintering, the holding time is preferably set to be not more than 90 minutes.

[0043] After the sintering, while the sintered compact is cooled from the heating temperature to room temperature, the sintered compact is preferably cooled from 850 to 600 °C at a cooling rate of not more than 20 °C/minute. In this case, the precipitated iron carbides tend to grow in the shape of plates. On the other hand, if the cooling rate is too low, a long time is required for the cooling and thereby the production cost is increased. Therefore, the cooling rate is preferably not less than 5 °C/minute in the temperature range of 850 to 600 °C.

[0044] In addition, after the sintering, while the sintered compact is cooled from the heating temperature to room temperature, the sintered compact may be isothermally held at a temperature during cooling from 850 to 600 °C so as to grow the precipitated iron carbides in the shape of plates. In this case, the isothermal holding time is preferably not less than 10 minutes. On the other hand, if the isothermal holding time is too long, a long time is required for the cooling, and thereby the production cost is increased. Therefore, the isothermal holding time is preferably not more than 90 minutes at the temperature in the range of 850 to 600 °C.

[0045] As described above, in the production method for the sintered material for valve guides according to the First Embodiment, an iron powder, a copper powder, and a graphite powder are prepared. The copper powder and the graphite powder are mixed with the iron powder into a raw powder consisting of, by mass %, 1.3 to 3% of C, 1 to 4 % of Cu, and the balance of Fe and inevitable impurities. Then, the obtained raw powder is filled in a tube-shaped cavity of a die assembly, and the raw powder is compacted into a green compact having a tube shape. The compacting is conventionally performed as a process for producing a sintered material for valve guides. Moreover, the green compact obtained by the compacting is sintered at a heating temperature of 970 to 1070 °C in a nonoxidizing atmosphere.

Production Method for Sintered Material for Valve guides of Second Embodiment

[0046] In the production method for the sintered material for valve guides according to the First Embodiment, in order to control the diffusion amount of Cu, copper powder is used, and the sintering is performed by solid-phase diffusion. In this case, since the diffusion bonding between the iron powder particles is also performed by solid-phase diffusion, the strength is lower than that of an iron-copper-carbon sintered material used as a structural material. Therefore, in the production method for the sintered material for valve guides according to the Second Embodiment, the strength of the sintered material is improved. That is, Sn having low melting point is used for generating liquid-phase sintering in the same manner as Japanese Examined Patent Publication No. 55-034858.

[0047] The melting point of Sn is 232 °C, and the liquid-phase generating temperature of a copper-tin alloy varies with the amount of Sn. When the amount of Sn is increased in the copper-tin alloy, the liquid-phase generating temperature is decreased. Even when the amount of Sn is approximately 15 mass % in the copper-tin alloy, a liquid phase is generated at 798 °C. Sn is added in the form of at least one of a tin powder and a copper-tin alloy powder. When the tin powder is used, Sn liquid phase is generated while the temperature is rising in the sintering. The Sn liquid phase is filled in the spaces among the raw powder particles by capillary force and covers the copper powder particles, and the Sn liquid phase forms a Cu-Sn eutectic liquid phase on the surface of the copper powder particles. When the copper-tin alloy powder is used, a Cu-Sn eutectic liquid phase is generated in accordance with the temperature while the temperature is increasing in the sintering. The Cu-Sn liquid phase is filled in spaces among the raw powder particles by capillary force and wets and covers the iron powder particles. As a result, growth of necks between the iron powder particles is accelerated, and the diffusion bonding of the iron powder particles is facilitated.

[0048] In order to obtain the effect of Sn for facilitating the sintering, not less than 0.05 mass % of Sn is required. On the other hand, if the amount of Sn is too great, too much of the Cu-Sn eutectic liquid phase is generated. In this case, the diffusion of Cu into the iron matrix is increased, whereby the plate-shaped iron carbides are difficult to obtain in the cooling after the sintering. Therefore, the upper limit of the amount of Sn is set to be 0.5 mass %.

[0049] In a case of using Sn, since the effect for facilitating the sintering is obtained by the Cu-Sn liquid phase, the lower limit of the heating temperature in the sintering can be low. In this case, predetermined diffusion conditions of Cu are obtained at 950 °C, which is lower than that in the production method for the sintered material for valve guides according to the First Embodiment. On the other hand, since the amount of the diffusion of Cu into the iron matrix is increased, the upper limit of the heating temperature in the sintering is required to be 1050 °C in order to control the diffusion of Cu into the iron matrix.

[0050] When the copper-tin alloy powder is used, in order to generate the Cu-Sn eutectic liquid phase in the heating temperature range (950 to 1050 °C), a copper-tin alloy powder including not less than 8 mass % of Sn (eutectic liquid phase generating temperature: 900 °C) may be used. The preferable production conditions such as the heating time in the sintering, the cooling rate in the cooling, and the isothermal holding time in the cooling, are the same as those in the sintered material for valve guides according to the First Embodiment.

[0051] As described above, in the production method for the sintered material for valve guides according to the Second Embodiment, an iron powder, a graphite powder, and one selected from the group consisting of a combination of a copper powder and a tin powder, a copper-tin alloy powder, and a combination of a copper powder and a copper-tin alloy powder, are prepared. The graphite powder and the one selected from the group are mixed with the iron powder into a raw powder consisting of, by mass %, 1.3 to 3% of C, 1 to 4 % of Cu, 0.05 to 0.5 % of Sn, and the balance of Fe and inevitable impurities. Then, the obtained raw powder is filled in a tube-shaped cavity of a die assembly, and the raw powder is compacted into a green compact having a tube shape. The compacting is conventionally performed as a process for producing a sintered material for valve guides. Moreover, the green compact obtained by the compacting is sintered at a heating temperature of 950 to 1050 °C in a nonoxidizing atmosphere.

[0052] In the sintered materials for valve guides according to the First Embodiment and the Second Embodiment, the machinability may be improved by conventional methods such as the method disclosed in Japanese Patent No. 2680927. That is, at least one kind selected from the group consisting of a manganese sulfide powder, a magnesium silicate mineral powder, and a calcium fluoride powder may be added to the raw powder at not more than 2 mass %. Then, by compacting and sintering this raw powder, a sintered material for valve guides is obtained. This sintered material has particle boundaries in the matrix and pores, in which at least one of manganese sulfide particles, magnesium silicate mineral particles, and calcium fluoride particles are dispersed at not more than 2 mass %. Accordingly, the machinability of the sintered material is improved.

EXAMPLES

First Example

[0053] First, an iron powder, a copper powder, and a graphite powder were prepared. The copper powder, in the amounts shown in Table 1, and 2 mass % of the graphite powder, were added to the iron powder, and they were mixed to form a raw powder. The raw powder was compacted at a compacting pressure of 650 MPa into a green compact with a tube shape. Some of the green compacts had an outer diameter of 11 mm, an inner diameter of 6 mm, and a length of 40 mm (for a wear test). The other green compacts had an outer diameter of 18 mm, an inner diameter of 10 mm, and a length of 10 mm (for a compressive strength test). These green compacts with the tube shapes were sintered at a heating temperature of 1000 °C for 30 minutes in an ammonia decomposed gas atmosphere and were cooled, whereby sintered compact samples of samples Nos. 01 to 10 were obtained. When the sintered compacts were cooled from the heating temperature to room temperature, the cooling rate in a temperature range from 850 to 600 °C was 10 °C/minute.

[0054] Another sintered compact sample of sample No. 11 was formed as a conventional example as follows. A copper-tin alloy powder consisting of 10 mass % of Sn and the balance of Cu and inevitable impurities, and an iron-phosphorus alloy powder including 20 mass % of P, were also prepared. Then, 5 mass % of the copper-tin alloy powder, 1.4 mass % of the iron-phosphorus alloy powder, and 2 mass % of the graphite powder were added to the iron powder, and they were mixed to form a raw powder. This raw powder was also compacted into two kinds of green compacts having the above shapes and was sintered under the above sintering conditions. This conventional example corresponds to the sintered material disclosed in Japanese Examined Patent Publication No. 55-034858. The entire compositions of these sintered compact samples are shown in Table 1.

[0055] In these sintered compact samples, wear amounts of valve guides and wear amounts of valve stems were measured by the wear test, and compressive strength was measured by the compressive strength test. In addition, an area ratio of an iron carbide phase and an area ratio of a copper phase were measured by observing a cross section of a metallic structure.

[0056] The wear test was performed as follows by using a wear testing machine. The sintered compact sample having the tube shape was secured to the wear testing machine, and a valve stem of a valve was inserted into the sintered compact sample. The valve was mounted at a lower end portion of a piston that would be vertically reciprocated. Then, the valve was reciprocated at a stroke speed of 3000 times/minute and at a stroke length of 8 mm at 500 °C in an exhaust gas atmosphere, and at the same time, a lateral load of 5 MPa was applied to the piston. After the valve was reciprocated for 30 hours, wear amount (in μm) of the inner circumferential surface of the sintered compact and wear amount (in μm) of the outer circumferential surface of the valve stem were measured.

[0057] The compressive strength test was performed as follows according to the method described in Z2507 specified by the Japanese Industrial Standard. A sintered compact sample with a tube shape had an outer diameter of D (mm), a wall thickness of e (mm), and a length of L (mm). The sintered compact sample was radially pressed by increasing the pressing load, and a maximum load F (N) was measured when the sintered compact sample broke. Then, a compressive strength K (N/mm^2) was calculated from the following first formula.

First formula

$$K = F \times (D - e) / (L \times e^2)$$

[0058] The area ratio of the copper phase was measured as follows. The cross section of the sample was mirror polished and was etched with a nital. This metallic structure was observed by a microscope at 200-power magnification and was analyzed by using image analyzing software "WinROOF" that is produced by Mitani Corporation., whereby the area of the copper phases was measured so as to obtain an area ratio. The area ratio of the iron carbide phase was measured in the same manner as in the case of the area ratio of the copper phase except that Murakami's reagent was used as the etching solution. The area of each phase identified by the image analysis is not less than 0.05 % with respect to the visual field.

[0059] These results are also shown in Table 1. It should be noted that the wear amount of the valve guide is represented by the symbol "VG", and the wear amount of the valve stem is represented by the symbol "VS" in the Tables. In addition, the total of the wear amounts of the valve guide and the valve stem is represented by the symbol "Total" in the Tables. The samples were evaluated based on acceptable levels to use as a valve guide. That is, the target level of the compressive strength is approximately not less than 500 MPa, and the target level of the wear amount is not more than 75 μm in the total wear amount.

Table 1

Sample No.	Mixing ratio mass %			Composition mass %			Area ratio %		Compressive strength MPa	Wear amount µm			Notes
	Iron powder	Copper powder	Graphite powder	Fe	Cu	C	Iron carbide phase	Copper phase		VG	VS	Total	
01	Bal.	0.00	2.00	Bal.	0.00	2.00	19.1	0.0	439	89	7	96	Exceeds lower limit of amount of Cu
02	Bal.	0.50	2.00	Bal.	0.50	2.00	18.9	0.1	487	82	5	87	Exceeds lower limit of amount of Cu
03	Bal.	1.00	2.00	Bal.	1.00	2.00	18.6	0.5	546	66	2	68	Lower limit of amount of Cu
04	Bal.	1.50	2.00	Bal.	1.50	2.00	18.7	0.8	563	64	2	66	
05	Bal.	2.00	2.00	Bal.	2.00	2.00	18.3	1.4	620	63	2	65	
06	Bal.	2.50	2.00	Bal.	2.50	2.00	17.7	2.0	642	65	2	67	
07	Bal.	3.00	2.00	Bal.	3.00	2.00	13.1	2.4	652	67	2	69	
08	Bal.	3.50	2.00	Bal.	3.50	2.00	8.4	2.8	686	69	1	70	
09	Bal.	4.00	2.00	Bal.	4.00	2.00	3.1	3.5	740	73	1	74	Upper limit of amount of Cu
10	Bal.	4.50	2.00	Bal.	4.50	2.00	1.0	4.2	769	86	3	89	Exceeds upper limit of amount of Cu
11	Iron powder + 1.4 % of iron-phosphorus alloy powder + 5 % of copper-tin alloy powder + 2 % of graphite powder			Fe-0.28%P-4.5%Cu-0.5%Sn-2%C			17.7	3.2	680	61	2	63	Conventional example

[0060] According to the samples of the samples Nos. 01 to 10 in Table 1, the effects of the amount of Cu in the entire composition of the sintered material and the effects of the amount of the copper powder in the raw powder are shown. In the samples of the samples Nos. 01 to 06 including not more than 2.5 mass % of Cu (the copper powder), the area ratio of the plate-shaped iron carbide phase was approximately constant in the cross-sectional metallic structure and was approximately the same as that of the conventional example (sample No. 11). On the other hand, when the amount of Cu (the copper powder) was more than 2.5 mass %, the area ratio of the plate-shaped iron carbide phase was decreased. That is, in the sample of the sample No. 09 including 4.0 mass % of Cu, the area ratio of the plate-shaped iron carbide phase was decreased to approximately 3 %. Moreover, in the sample of the sample No. 10 including more than 4.0 mass % of Cu, the area ratio of the plate-shaped iron carbide phase was decreased to 1 %.

[0061] The copper phase was increased in proportion to the amount of Cu (the copper powder). In the sample of the sample No. 03 including 1.0 mass % of Cu (the copper powder), the area ratio of the copper phase was 0.5 % in the cross-sectional metallic structure. In the sample of the sample No. 09 including 4.0 mass % of Cu (the copper powder), the area ratio of the copper phase was increased to 3.5 %. Moreover, in the sample of the sample No. 10 including more than 4.0 mass % of Cu (the copper powder), the area ratio of the copper phase was increased to approximately 4 %.

[0062] In the sample of the sample No. 01 including 0 mass % of Cu (the copper powder), since Cu was not included, the strength of the matrix was low, and the compressive strength was low. According to the increase in the amount of Cu (the copper powder), the effect of Cu for strengthening the matrix was increased. Therefore, the compressive strength was increased in proportion to the amount of Cu (the copper powder). In the samples of the samples Nos. 01 and 02 including less than 1.0 mass % of Cu (the copper powder), the compressive strength was low, whereby these samples cannot be used as a valve guide. On the other hand, in the samples of the samples Nos. 03 to 10 including not less than 1.0 mass % of Cu (the copper powder), the compressive strength was not less than 500 MPa, and the strength was at an acceptable level sufficient to use as a valve guide.

[0063] In the sample of the sample No. 01 including 0 mass % of Cu (the copper powder), since the copper phase for improving the adaptability was not included, the valve stem was slightly worn. On the other hand, in the sample of the sample No. 02 including 0.5 mass % of Cu (the copper powder), the copper phase was dispersed and thereby the adaptability was improved. Therefore, the wear amount of the valve stem was decreased. Moreover, in the samples of the samples Nos. 03 to 10 including not less than 1.0 mass % of Cu (the copper powder), sufficient amount of the copper phase was dispersed, whereby the wear amount of the valve stem was low and was constant.

[0064] In the sample of the sample No. 01 including 0 mass % of Cu (the copper powder), since Cu was not included, the strength of the matrix was low. Therefore, the wear amount of the valve guide was great, and the total wear amount was large. In contrast, in the sample of the sample No. 02 including 0.5 mass % of Cu (the copper powder), the strength of the matrix was improved by the effect of Cu. Therefore, the wear amount of the valve guide was decreased, and the total wear amount was also decreased. In the samples of the samples Nos. 03 to 06 including 1.0 to 2.5 mass % of Cu (the copper powder), the effect of Cu for strengthening the matrix was sufficiently obtained, and the precipitation amount of the plate-shaped iron carbides were great. Accordingly, the wear amounts of the valve guides were approximately the same as that of the conventional example (sample No. 11) and were approximately constant and low. As a result, the total wear amounts were also approximately the same as that of the conventional example (sample No. 11) and were approximately constant and low. On the other hand, in the samples of the samples Nos. 07 to 09 including 3.0 to 4.0 mass % of Cu (the copper powder), the influence of the decrease in the amount of the plate-shaped iron carbides was greater than the effect of Cu for strengthening the matrix. Therefore, the wear resistances were decreased, and the wear amounts of the valve guides were slightly increased. In the sample of the sample No. 10 including more than 4.0 mass % of Cu (the copper powder), the wear resistance was greatly decreased due to the decrease in the amount of the plate-shaped iron carbides. As a result, the wear amount of the valve guide was increased, and the total wear amount was greatly increased.

[0065] According to the above results, when the amount of Cu (the copper powder) was 1.0 to 4.0 mass %, the wear resistances of the sintered compacts were approximately equal to that of the sintered material disclosed in Japanese Examined Patent Publication No. 55-034858. In addition, when the amount of Cu was in this range, the sintered compacts had strength at an acceptable level to use as a valve guide. The area ratio of the copper phase was 0.5 to 3.5 % in the cross-sectional metallic structure when the amount of Cu was in this range. In this case, the area ratio of the plate-shaped iron carbide phase was required to be approximately not less than 3 % in the cross-sectional metallic structure.

Second Example

[0066] The iron powder, the copper powder, and the graphite powder, which were used in the First Example, were prepared. Then, 2 mass % of the copper powder and the graphite powder at the amount shown in Table 2 were added to the iron powder, and they were mixed to form a raw powder. The raw powder was compacted and was sintered in the same conditions as in the First Example, whereby samples of samples Nos. 12 to 17 were formed. The entire compositions of these samples are shown in Table 2. In these samples, the wear test and the compressive strength test were performed under the same conditions as those in the First Example. Moreover, the area ratio of the iron carbide phase and the area ratio of the copper phase were measured. These results are also shown in Table 2. It should be noted that the values of the sample of the sample No. 05 in the First Example are also shown in Table 2 as an example including 2 mass % of the graphite powder.

Table 2

Sample No.	Mixing ratio mass %			Composition mass %			Area ratio %		Compressive strength MPa	Wear amount μm			Notes
	Iron powder	Copper powder	Graphite powder	Fe	Cu	C	Iron carbide phase	Copper phase		VG	VS	Total	
12	Bal.	2.00	1.00	Bal.	2.00	1.00	0.0	1.3	889	87	4	91	Exceeds lower limit of amount of C
13	Bal.	2.00	1.30	Bal.	2.00	1.30	3.0	1.2	837	73	2	75	Lower limit of amount of C
14	Bal.	2.00	1.50	Bal.	2.00	1.50	9.8	1.2	664	68	2	70	
05	Bal.	2.00	2.00	Bal.	2.00	2.00	18.3	1.3	620	63	2	65	
15	Bal.	2.00	2.50	Bal.	2.00	2.50	22.4	1.3	544	60	3	63	
16	Bal.	2.00	3.00	Bal.	2.00	3.00	25.1	1.2	502	67	5	72	Upper limit of amount of C
17	Bal.	2.00	3.50	Bal.	2.00	3.50	27.7	1.3	423	79	9	88	Exceeds upper limit of amount of C
11	Iron powder + 1.4 % of iron-phosphorus alloy powder + 5 % of copper-tin alloy powder + 2 % of graphite powder			Fe-0.28%P-4.5%Cu-0.5%Sn-2%C			17.7	3.2	680	61	2	63	Conventional example

[0067] According to the samples of the samples Nos. 05 and 12 to 17 in Table 2, the effects of the amount of C in the entire composition of the sintered material and the effects of the amount of the graphite powder in the raw powder are shown. In the sample of the sample No. 12 including 1 mass % of C (the graphite powder), the amount of C diffused in the matrix was small, whereby the plate-shaped iron carbide phase was not precipitated. In contrast, in the sample of the sample No. 13 including 1.3 mass % of C (the graphite powder), the amount of C diffused in the matrix was sufficient, and the area ratio of the plate-shaped iron carbide phase was approximately 3 % in the cross-sectional metallic structure. According to the increase of the amount of C (the graphite powder), the area ratio of the plate-shaped iron carbide phase was increased in the cross-sectional metallic structure. That is, in the sample of the sample No. 16 including 3 mass % of C (the graphite powder), the area ratio of the plate-shaped iron carbide phase was approximately 25 %. Moreover, in the sample of the sample No. 17 including more than 3 mass % of C (the graphite powder), the area ratio of the plate-shaped iron carbide phase was increased to approximately 28 %. On the other hand, the area ratio of the copper phase was constant in the cross-sectional metallic structure regardless of the amount of C (the graphite powder). This was because the amount of Cu (the copper powder) was constant and the sintering conditions were the same.

[0068] In the sample of the sample No. 12, the plate-shaped iron carbide phase was not precipitated in the matrix, and the compressive strength was the highest. When the amount of C (the graphite powder) was increased, the iron carbide phase precipitated in the matrix was increased, whereby the compressive strength was decreased. In the sample of the sample No. 16 including 3 mass % of C (the graphite powder), the compressive strength was approximately 500 MPa. Therefore, when the amount of C (the graphite powder) was not more than 3 mass %, the strength of the sintered compact was at an acceptable level sufficient to use as a valve guide.

[0069] In the sample of the sample No. 12 including 1 mass % of C (the graphite powder), since the iron carbide phase for improving the wear resistance was not precipitated, the wear amount of the valve guide was great. In contrast, in the sample of the sample No. 13 including 1.3 mass % of C (the graphite powder), the plate-shaped iron carbide phase was precipitated in the matrix, and the wear amount of the valve guide was decreased. According to the increase of C (the graphite powder), the amount of the plate-shaped iron carbide phase precipitated in the matrix was increased. Therefore, the wear resistance was improved by the plate-shaped iron carbide phase, whereby the wear amount of the valve guide was decreased. This tendency was observed until the sample of the sample No. 15 including 2.5 mass % of C (the graphite powder). On the other hand, in the sample of the sample No. 16 including 3 mass % of C (the graphite powder), since the plate-shaped iron carbide phase was greatly increased, the strength of the sintered compact sample was decreased. Therefore, the wear amount of the valve guide was slightly increased. Moreover, in the sample of the sample No. 17 including more than 3 mass % of C (the graphite powder), the wear amount of the valve guide was greatly increased. Since the amount of the hard plate-shaped iron carbide phase precipitated in the matrix was increased with the increase of C (the graphite powder), the wear amount of the valve stem was increased with the increase of C (the graphite powder). According to these wear conditions, the total wear amount was decreased when the amount of C (the graphite powder) was in the range of 1.3 to 3 mass %.

[0070] As described above, when the amount of C (the graphite powder) was 1.3 to 3 mass %, the wear resistances of the sintered compacts were approximately equal to that of the sintered material disclosed in Japanese Examined Patent Publication No. 55-034858. In addition, when the amount of C was in this range, the sintered compacts had strength at an acceptable level to use as a valve guide. In this case, the area ratio of the plate-shaped iron carbide phase was 3 to 25 % in the cross-sectional metallic structure when the amount of C was in this range.

Third Example

[0071] The iron powder, the copper powder, and the graphite powder, which were used in the First Example, were prepared. Then, 2 mass % of the copper powder and 2 mass % of the graphite powder were added to the iron powder, and they were mixed to form a raw powder. The raw powder was compacted in the same conditions as in the First Example so as to obtain a green compact. The green compact was sintered in the same conditions as in the First Example except that the heating temperature was changed to the temperature shown in Table 3, whereby samples of samples Nos. 18 to 24 were formed. In these samples, the wear test and the compressive strength test were performed under the same conditions as those in the First Example. Moreover, the area ratio of the iron carbide phase and the area ratio of the copper phase were measured. These results are also shown in Table 3. It should be noted that the values of the sample of the sample No. 05 in the First Example are also shown in Table 3 as an example in which the heating temperature was 1000 °C.

Table 3

Sample No.	Heating temperature °C	Area ratio %		Compressive strength MPa	Wear amount µm			Notes
		Iron carbide phase	Copper phase		VG	VS	Total	
18	900	0.0	2.0	411	103	2	105	Exceeds lower limit of heating temerature
19	950	1.9	1.7	474	83	2	85	Exceeds lower limit of heating temerature
20	970	17.6	1.6	556	68	3	71	Lower limit of heating temerature
05	1000	18.3	1.4	620	63	2	65	
21	1020	16.9	1.2	644	61	2	63	
22	1050	10.6	0.9	702	65	2	67	
23	1070	6.4	0.6	727	72	3	75	Upper limit of heating temerature
24	1100	2.7	0.2	754	83	3	86	Exceeds upper limit of heating temerature
11	1000	17.7	3.2	680	61	2	63	Conventional example

[0072] According to the samples of the samples No. 05 and 18 to 24 in Table 3, the effects of the heating temperature in the sintering are shown. According to the increase of the heating temperature in the sintering, the diffusion amount of Cu into the matrix was increased, whereby the amount of Cu that remained as a copper phase was decreased. Therefore, the area ratio of the copper phase in the cross-sectional metallic structure was decreased with the increase of the heating temperature. In the sample of the sample No. 24 in which the heating temperature was 1100 °C and was more than the melting point of Cu (1085 °C), the entire amount of Cu in the form of the copper powder was diffused in the matrix, and the copper phase almost disappeared.

[0073] In the sample of the sample No. 18 in which the heating temperature was 900 °C and the sample of the sample No. 19 in which the heating temperature was 950 °C, the heating temperatures were low. Therefore, C was not sufficiently diffused, and the plate-shaped iron carbide phases were hardly precipitated. On the other hand, in the samples of the samples Nos. 20, 05, and 21 in which the heating temperature was 970 to 1020 °C, C was sufficiently diffused. Therefore, the area ratios of the plate-shaped iron carbide phases in the cross-sectional metallic structures were approximately equal to that of the conventional example (sample No. 11). However, when the heating temperature was increased, the amount of Cu diffused in the matrix was increased and thereby the plate-shaped iron carbide phase was difficult to be formed. Accordingly, the precipitation amount of the plate-shaped iron carbide phase was decreased, and the area ratio of the plate-shaped iron carbide phase was decreased in the cross-sectional metallic structure. That is, in the sample of the sample No. 24 in which the heating temperature was 1100 °C and was more than the melting point of Cu (1085 °C), Cu was uniformly diffused into the matrix. As a result, C was not precipitated as a large plate-shaped iron carbide phase and was precipitated in the shape of a pearlite. Therefore, the area ratio of the plate-shaped iron carbide phase was extremely small in the cross-sectional metallic structure.

[0074] According to the increase of the heating temperature in the sintering, since a greater amount of Cu for strengthening the matrix was diffused in the matrix, the compressive strength was increased. In the sample of the sample No. 19 in which the heating temperature was 950 °C, Cu was not sufficiently diffused. Therefore, the compressive strength was less than 500 MPa and was not at a level that is required in a case of using the sintered compact as a valve guide.

On the other hand, in the samples of the samples Nos. 20, 05, and 21 to 24 in which the heating temperature was not less than 970 °C, the diffusion amount of Cu into the matrix was increased. As a result, the compressive strengths were not less than 500 MPa and were at acceptable levels to use as valve guides.

[0075] In the sample of the sample No. 18 in which the heating temperature was 900 °C, C was not sufficiently diffused, and the plate-shaped iron carbide phase for improving the wear resistance was not precipitated. Therefore, the wear amount of the valve guide was great. In the sample of the sample No. 19 in which the heating temperature was 950 °C, C was still not sufficiently diffused, and the plate-shaped iron carbide phase was precipitated but the amount thereof was insufficient. Therefore, the wear amount of the valve guide was large. On the other hand, in the sample of the sample No. 20 in which the heating temperature was 970 °C, C was sufficiently diffused. Therefore, the precipitation amount of the plate-shaped iron carbide phase was approximately equal to that of the conventional example (sample No. 11), and the wear amount of the valve guide was decreased. Moreover, in the samples of the samples Nos. 05 and 21 in which the heating temperature was 1000 to 1020 °C, the wear amount of the valve guide was more decreased by the above effects. According to the increase of the heating temperature, the diffusion amount of Cu into the matrix was increased. Therefore, in the samples of the samples Nos. 22 and 23 in which the heating temperature was 1050 to 1070 °C, the precipitation amount of the plate-shaped iron carbide phase was decreased with the increase of the heating temperature. Accordingly, the wear amounts of the valve guides were slightly increased. In the sample of the sample No. 24 in which the heating temperature was more than 1070 °C, the precipitation amount of the plate-shaped iron carbide phase was greatly decreased. Therefore, the wear resistance was decreased, and the wear amount of the valve guide was greatly increased. The wear amount of the valve stem was approximately constant regardless of the heating temperature. Therefore, the total wear amount was decreased when the heating temperature was in the range of 970 to 1070 °C.

[0076] According to the above results, in the case of forming the sintered material by using the iron-copper-carbon sintered alloy, when the heating temperature was 970 to 1070 °C in the sintering, the wear resistance was superior. In addition, when the heating temperature was in this range, the sintered compacts had strength at an acceptable level to use as a valve guide.

Fourth Example

[0077] The iron powder, the copper powder, and the graphite powder, which were used in the First Example, were prepared. In addition, the copper-tin alloy powder used for forming the conventional example (sample No. 11), and a tin powder were prepared. The copper-tin alloy powder consisted of 10 mass % of Sn and the balance of Cu and inevitable impurities. Then, 3 mass % of the copper powder, 2 mass % of the graphite powder, and the tin powder at the amount shown in Table 4 were added to the iron powder, and they were mixed to form a raw powder. The raw powder was compacted and was sintered in the same conditions as in the First Example, whereby samples of samples Nos. 25 to 34 were formed. The entire compositions of these samples are shown in Table 4. In these samples, the wear test and the compressive strength test were performed under the same conditions as those in the First Example. Moreover, the area ratio of the iron carbide phase and the area ratio of the copper alloy phase were measured. These results are also shown in Table 4. It should be noted that the values of the sample of the sample No. 07 in the First Example are also shown in Table 4 as an example in which the tin powder was not added.

Table 4

Sample No.	Mixing ratio mass %				Composition mass %				Area ratio %		Compressive strength MPa	Wear amount μm			Notes
	Iron powder	Copper powder	Tin powder	Graphite powder	Fe	Cu	Sn	C	Iron carbide phase	Copper alloy phase		VG	VS	Total	
07	Bal.	3.00	-	2.00	Bal.	3.00	0.00	2.00	13.1	2.4	652	67	2	69	Sn was not added
25	Bal.	3.00	0.01	2.00	Bal.	3.00	0.01	2.00	12.9	2.1	654	67	2	69	Exceeds lower limit of amount of Sn
26	Bal.	3.00	0.05	2.00	Bal.	3.00	0.05	2.00	11.7	1.8	673	66	1	97	Lower limit of amount of Sn
27	Bal.	3.00	0.10	2.00	Bal.	3.00	0.10	2.00	10.9	1.1	684	67	2	69	
28	Bal.	3.00	0.20	2.00	Bal.	3.00	0.20	2.00	8.6	0.8	697	68	2	70	
29	Bal.	3.00	0.30	2.00	Bal.	3.00	0.30	2.00	6.9	0.7	708	70	2	72	
30	Bal.	3.00	0.33	2.00	Bal.	3.00	0.33	2.00	6.4	0.7	711	71	2	73	
31	Bal.	3.00	0.40	2.00	Bal.	3.00	0.40	2.00	5.8	0.6	717	72	2	74	
32	Bal.	3.00	0.50	2.00	Bal.	3.00	0.50	2.00	5.0	0.5	729	73	2	75	Upper limit of amount of Sn
33	Bal.	3.00	0.60	2.00	Bal.	3.00	0.60	2.00	3.5	0.4	741	87	7	94	Exceeds upper limit of amount of Sn
34	Bal.	Copper-tin alloy powder 3.33		2.00	Bal.	3.00	0.33	2.00	6.0	0.7	713	70	2	72	Alloy powder was added
11	Iron powder + 1.4 % of iron-phosphorous alloy powder + 5 % of copper-tin alloy powder + 2 % of graphite powder				Fe-0.28%P-4.5%Cu-0.5%Sn-2%C				17.7	3.2	680	61	2	63	Conventional example

[0078] According to the samples of the samples Nos. 07 and 25 to 33 in Table 4, the effects of the amount of Sn in a case of adding Sn are shown. In addition, according to the samples of the samples Nos. 30 and 34, the forms of Sn added to the raw powders can be compared.

[0079] By adding Sn to the sintered material, the area ratio of the plate-shaped iron carbide phase and the area ratio of the copper alloy phase were decreased in the cross-sectional metallic structure. The decrease amounts of the area ratio of the iron carbide phase and the area ratio of the copper alloy phase were increased with the increase of the amount of Sn. This was because a greater amount of the Cu-Sn liquid phase was generated in the sintering according to the increase of the amount of Sn, whereby the diffusion amount of Cu into the matrix was increased. In the sample of the sample No. 32 including 0.5 mass % of Sn, the area ratio of the plate-shaped iron carbide phase was approximately 5 % and the area ratio of the copper alloy phase was approximately 0.5 % in the cross-sectional metallic structure. On the other hand, in the sample of the sample No. 33 including more than 0.5 mass % of Sn, the area ratio of the plate-shaped iron carbide phase was decreased to less than 5 % and the area ratio of the copper alloy phase was decreased to less than 0.5 % in the cross-sectional metallic structure.

[0080] In the samples of the samples Nos. 25 to 33 including Sn, the compressive strength was increased compared with the sample of the sample No. 07 which did not include Sn. The compressive strength was increased with the increase of the amount of Sn. This was because a greater amount of the Cu-Sn liquid phase was generated in the sintering according to the increase of the amount of Sn. In this case, the diffusion amount of Cu into the matrix was increased, and the Cu-Sn liquid phase wetted and covered the surface of the iron powder particles and thereby accelerating neck growth between the iron powder particles. In the sample of the sample No. 25 including less than 0.05 mass % of Sn, the effect for improving the compressive strength was small. In the samples of the samples Nos. 26 to 33 including not less than 0.05 % of Sn, the effect for improving the compressive strength was great.

[0081] In the samples of the samples Nos. 25 to 28 including 0.01 to 0.2 mass% of Sn, the wear amount of the valve guide was approximately equal to that of the sample of the sample No. 07 which did not include Sn. When the amount of Sn was 0.3 to 0.5 mass % (samples Nos. 29 to 32), the wear amount of the valve guide was slightly increased. Although the plate-shaped iron carbide phase was decreased with the increase of the amount of Sn as described above, the wear amount of the valve guide was not greatly increased. This was because the neck between the iron powder particles grew and thereby the strength was improved. In the sample of the sample No. 33 including more than 0.5 mass %, the wear resistance was greatly decreased due to the decrease of the plate-shaped iron carbide phase. Therefore, the wear amount of the valve guide was suddenly increased. The wear amount of the valve stem was approximately constant regardless of the amount of Sn. Accordingly, when the amount of Sn was in the range of not more than 0.5 mass %, the total wear amount was small, and superior wear resistance was obtained.

[0082] As described above, by adding not less than 0.05 mass % of Sn to the sintered material, the strength of the sintered material was improved. In this case, when the amount of Sn was more than 0.5 mass %, the wear resistance was decreased. Therefore, when Sn is added, it is required that the amount of Sn be 0.05 to 0.5 mass %.

[0083] In the sample of the sample No. 30, Sn was added in the form of the tin powder. On the other hand, in the sample of the sample No. 34, Sn was added in the form of the copper-tin alloy powder. In these samples of the samples Nos. 30 and 34, the area ratios of the plate-shaped iron carbide phase and the area ratios of the copper alloy phase in the cross-sectional metallic structure were approximately equal, respectively. Moreover, the compressive strengths and the wear amounts were approximately equal, respectively. Therefore, Sn can be added in either form of the tin powder or the copper-tin alloy powder. It should be noted that the copper-tin alloy powder in the sample of the sample No. 34 included 3.0 mass % of Cu and 0.33 mass % of Sn with respect to the entire composition.

Fifth Example

[0084] The iron powder and the graphite powder used in the First Example, and the copper-tin alloy powder used in the Fourth Example were prepared. Then, 2 mass % of the copper-tin alloy powder and 2 mass % of the graphite powder were added to the iron powder, and they were mixed to form a raw powder. The raw powder was compacted in the same conditions as in the First Example so as to obtain a green compact. The green compact was sintered in the same conditions as in the First Example except that the heating temperature was changed to the temperature shown in Table 5 in the sintering, whereby samples of samples Nos. 35 to 42 were formed. These samples consisted of, by mass %, 1.8 % of Cu, 0.2 % of Sn, 2.0 % of C, and the balance of Fe and inevitable impurities. In these samples, the wear test and the compressive strength test were performed under the same conditions as those in the First Example. Moreover, the area ratio of the plate-shaped iron carbide phase and the area ratio of the copper alloy phase were measured. These results are also shown in Table 5.

Table 5

Sample No.	Heating temperature °C	Area ratio % Iron Copper		Compressive strength MPa	Wear amount µm			Notes
		carbide phase	alloy phase		VG	VS	Total	
35	900	0.4	1.4	463	84	4	88	Exceeds lower limit of heating temerature
36	950	11.0	1.0	505	66	2	68	Lower limit of heating temerature
37	970	14.7	0.8	588	63	2	65	
38	1000	16.0	0.7	667	61	1	62	
39	1020	16.7	0.6	696	59	1	60	
40	1050	11.3	0.6	719	64	2	66	Upper limit of heating temerature
41	1070	2.7	0.4	751	86	2	88	Exceeds upper limit of heating temerature
42	1100	1.6	0.3	787	90	4	94	Exceeds upper limit of heating temerature
11	1000	17.7	3.2	680	61	2	63	Conventional example

[0085] According to the samples of the samples Nos. 35 to 42 in Table 5, the effects of the heating temperature in the sintering are shown. According to the increase of the heating temperature in the sintering, the diffusion amount of Cu into the matrix was increased, whereby the amount of Cu remained as a copper phase was decreased. Therefore, the area ratio of the copper phase in the cross-sectional metallic structure was decreased with the increase of the heating temperature in the sintering.

[0086] In the sample of the sample No. 35 in which the heating temperature was 900 °C, since the heating temperature was low in the sintering, C was not sufficiently diffused, and the iron carbide phase hardly precipitated. In contrast, in the sample of the sample No. 36 in which the heating temperature was 950 °C, C was sufficiently diffused, whereby the area ratio of the plate-shaped iron carbide phase was increased in the cross-sectional metallic structure. Moreover, in the samples of the samples Nos. 37 to 40 in which the heating temperature was 970 to 1050 °C, the area ratio of the plate-shaped iron carbide phase in the cross-sectional metallic structure was approximately equal to that of the conventional example (sample No. 11). On the other hand, in the samples of the samples Nos. 41 and 42 in which the heating temperature was more than 1050 °C, the amount of Cu diffused in the matrix was increased, whereby the plate-shaped iron carbide phase was difficult to be formed. Therefore, the precipitation amounts of the iron carbide phases were decreased, and the area ratios of the plate-shaped iron carbide phases were decreased in the cross-sectional the metallic structures.

[0087] According to the increase of the heating temperature in the sintering, since a greater amount of Cu for strengthening the matrix was diffused in the matrix, the compressive strength was increased. In the sample of the sample No. 35 in which the heating temperature was 900 °C, Cu was not sufficiently diffused. Therefore, the compressive strength was less than 500 MPa and was not at a level that is required in a case of using the sintered compact as a valve guide. On the other hand, in the samples of the samples Nos. 36 to 42 in which the heating temperature was not less than 950 °C, the diffusion amount of Cu into the matrix was increased. As a result, the compressive strengths were not less than 500 MPa and were at acceptable levels to use for valve guides.

[0088] In the sample of the sample No. 35 in which the heating temperature was 900 °C, C was not sufficiently diffused, and the iron carbide phase for improving the wear resistance was not precipitated. Therefore, the wear amount of the valve guide was great. On the other hand, in the sample of the sample No. 36 in which the heating temperature was 950 °C, C was sufficiently diffused, and the area ratio of the plate-shaped iron carbide phase was increased to 11 %. Therefore, the wear amount of the valve guide was decreased. Moreover, in the samples of the samples Nos. 37 to 39 in which the heating temperature was 970 to 1020 °C, the area ratio of the plate-shaped iron carbide phase was increased to a degree equivalent to that of the conventional example (sample No. 11). As a result, the wear amounts of the valve guides were even less. According to the increase of the heating temperature, the diffusion amount of Cu into the matrix was increased. Therefore, in the sample of the sample No. 40 in which the heating temperature was 1050 °C, the area ratio of the precipitated plate-shaped iron carbide phase was decreased to approximately 11 %. Accordingly, the wear amount of the valve guide was slightly increased. Moreover, in the samples of the samples Nos. 41 and 42 in which the heating temperature was more than 1050 °C, the precipitation amount of the plate-shaped iron carbide phase was greatly decreased, and the wear resistance was decreased. As a result, the wear amounts of the valve guides were greatly increased. The wear amount of the valve stem was approximately constant regardless of the heating temperature. Accordingly, the total wear amount was decreased when the heating temperature was in the range of 950 to 1050 °C.

[0089] According to the above results, in a case of using Sn, when the heating temperature was 950 to 1050 °C, the wear resistance was superior. In addition, when the heating temperature was in this range, the sintered compacts had strength at an acceptable level to use as a valve guide.

Sixth Example

[0090] The iron powder, the copper powder, and the graphite powder, which were used in the First Example, were prepared. Then, 2 mass % of the copper powder and 2 mass % of the graphite powder were added to the iron powder, and they were mixed to form a raw powder. The raw powder was compacted and was sintered in the same conditions as in the First Example except for the cooling rate, whereby samples of samples Nos. 43 to 47 were formed. When the sintered compact was cooled from the heating temperature to room temperature, the cooling rate was changed to the cooling rate shown in Table 6 while the sintered compact was cooled from 850 to 600 °C. In these samples, the wear test and the compressive strength test were performed under the same conditions as those in the First Example. Moreover, the area ratio of the plate-shaped iron carbide phase and the area ratio of the copper phase were measured. These results are also shown in Table 6. It should be noted that the values of the sample of the sample No. 05 in the First Example are also shown in Table 6 as an example in which the cooling rate in the above temperature range was 10 °C/minute.

Table 6

Sample No.	Cooling rate °C/minute	Area ratio %		Compressive strength MPa	Wear amount μm			Notes
		Iron carbide phase	Copper phase		VG	VS	Total	
43	5	21.7	1.4	542	59	2	61	
05	10	18.3	1.4	620	63	2	65	
44	15	16.4	1.3	640	65	2	67	
45	20	11.5	1.4	663	67	2	69	
46	25	5.3	1.4	722	71	4	75	Upper limit of cooling rate
47	30	2.0	1.4	754	85	5	90	Exceeds upper limit of cooling rate
11	10	17.7	3.2	680	61	2	63	Conventional example

[0091] When the cooling rate in the temperature range of from 850 to 600 °C was lower, the area ratio of the iron carbides was increased in the cross-sectional metallic structure. In other words, when the cooling rate was greater, the area ratio of the iron carbides was decreased. That is, C at amount in which C was supersaturated at room temperature, was solved in the austenite in the heating temperature range in the sintering, and supersaturated C in this heating temperature range was precipitated as iron carbides (Fe_3C). If the sintered compact in this temperature range is cooled at a low cooling rate, the precipitated iron carbides grow, whereby the amount of the iron carbide phase is increased. On the other hand, if the sintered compact in this temperature range is cooled at a high cooling rate, the precipitated iron carbides do not grow. Therefore, the ratio of the pearlite, in which fine iron carbides are dispersed, is increased, and the amount of the iron carbide phase is decreased. When the cooling rate was increased to 25 °C/minute during the cooling from 850 to 600 °C, the area ratio of the iron carbide phase came to approximately 5 % in the cross-sectional metallic structure. Moreover, when the cooling rate was more than 25 °C/minute, the area ratio of the iron carbide phase was less than 5 %.

[0092] On the other hand, the copper phase was not formed of supersaturated Cu that was precipitated and was diffused, but was formed of copper powder that was not dispersed and remained as a copper phase. Therefore, the area ratio of the copper phase in the cross-sectional metallic structure was constant regardless of the cooling rate.

[0093] When the cooling rate was greater during the cooling from 850 to 600 °C, the amount of the fine iron carbides were increased, and the amount of the plate-shaped iron carbide phase was decreased. Therefore, the compressive strength was increased with the increase of the cooling rate. When the cooling rate was greater during the cooling from 850 to 600 °C, since the amount of the iron carbide phase for improving the wear resistance was decreased, the wear amount of the valve guide was slightly increased. Moreover, when the cooling rate was increased to more than 25 °C/minute during the cooling from 850 to 600 °C, the area ratio of the iron carbide phase was less than 5 %, and the wear amount of the valve guide was suddenly increased.

[0094] According to the above results, by controlling the cooling rate during the cooling from 850 to 600 °C, the amount of the plate-shaped iron carbide phase was controlled. In this case, by setting the cooling rate to be not more than 25 °C/minute during the cooling from 850 to 600 °C, the area ratio of the plate-shaped iron carbide phase was made to be not less than 5 % in the cross-sectional metallic structure, and superior wear resistance was obtained. It should be noted that if the cooling rate is too low during the cooling from 850 to 600 °C, the time required for cooling from the heating temperature to room temperature becomes long, and the production cost is increased. Accordingly, the cooling rate is preferably set to be not less than 5 °C/minute during the cooling from 850 to 600 °C.

Seventh Example

[0095] The iron powder, the copper powder, and the graphite powder, which were used in the First Example, were prepared. Then, 2 mass % of the copper powder and 2 mass % of the graphite powder were added to the iron powder, and they were mixed to form a raw powder. The raw powder was compacted and was sintered in the same conditions as in the First Example except for the cooling process, whereby samples of samples Nos. 48 to 51 were formed. When the sintered compact was cooled from the heating temperature to room temperature, the cooling rate was set to be 30 °C/minute during the cooling from 850 to 780 °C. Then, the sintered compact was isothermally held at 780 °C for a holding time shown in Table 7 and was cooled from 780 to 600 °C at a cooling rate of 30 °C/minute. In these samples, the wear test and the compressive strength test were performed under the same conditions as those in the First Example. Moreover, the area ratio of the plate-shaped iron carbide phase and the area ratio of the copper phase were measured. These results are also shown in Table 7. It should be noted that the values of the sample of the sample No. 47 in the Sixth Example are also shown in Table 7 as an example. The sample of the sample No. 47 was cooled from 850 to 600 °C at a cooling rate of 30 °C/minute and was not isothermally held.

Table 7

Sample No.	Holding time minutes	Area ratio %		Compressive strength MPa	Wear amount μm			Notes
		Iron carbide phase	Copper phase		VG	VS	Total	
47	0	2.0	1.4	754	85	6	91	Exceeds lower limit of holding time
48	10	6.7	1.3	695	71	2	73	Lower limit of holding time
49	30	18.6	1.3	648	62	1	63	
50	60	22.4	1.3	550	61	2	63	
51	90	23.0	1.4	531	63	5	68	

[0096] The samples of the samples Nos. 48 to 51 were cooled at the cooling rate at which the area ratio of the plate-shaped iron carbide phase was less than 5 % in the cross-sectional metallic structure in the Sixth Example. In this case, these samples were isothermally held at the temperature in the range of 850 to 600 °C during the cooling from the heating temperature to room temperature. Therefore, the area ratio of the plate-shaped iron carbide phase was increased to not less than 5 %. According to the increase of the isothermal holding time, the area ratio of the plate-shaped iron carbide phase was increased. That is, by isothermal holding at the temperature range in which supersaturated C in the austenite was precipitated as iron carbides, the iron carbides sufficiently grew, and the area ratio of the plate-shaped iron carbide phase was increased. Therefore, according to the increase of the isothermal holding time in this temperature range, the area ratio of the plate-shaped iron carbide phase can be increased. Accordingly, when the sintered compact is isothermally held in this temperature range, since the plate-shaped iron carbide phase grows during the isothermal holding, the cooling rate before and after the isothermal holding can be increased.

[0097] On the other hand, the copper phase was not formed of supersaturated Cu that was precipitated and was diffused, but was formed of copper powder that was not dispersed and remained as a copper phase. Therefore, the area ratio of the copper phase in the cross-sectional metallic structure was constant regardless of the isothermal holding time.

[0098] When the isothermal holding time at the temperature in the range of 850 to 600 °C was shorter, the time required for growing the plate-shaped iron carbides was shorter, and the area ratio of the plate-shaped iron carbide phase was decreased. In other words, when the isothermal holding time was longer, the time required for growing the iron carbides were longer, and the area ratio of the plate-shaped iron carbide phase was increased. Therefore, the compressive strength was decreased with the increase of the isothermal holding time. When the isothermal holding time at the temperature in the range of 850 to 600 °C was longer, the amount of the plate-shaped iron carbide phase for improving the wear resistance was increased. Therefore, the wear amount of the valve guide was decreased with the increase of the isothermal holding time.

[0099] According to the above results, by isothermal holding at the temperature in the range of 850 to 600 °C, the amount of the plate-shaped iron carbide phase was controlled. When the isothermal holding was performed, by setting the holding time to be not less than 10 minutes, the area ratio of the plate-shaped iron carbide phase was made to be not less than 5 % in the cross-sectional metallic structure, and superior wear resistance was obtained. In this case, if the isothermal holding time is too long, the time required for cooling from the heating temperature to room temperature becomes long, and the production cost is increased. Therefore, the isothermal holding time is preferably set to be not more than 90 minutes.

Claims

1. A sintered material for valve guides, consisting of, by mass %, 1.3 to 3 % of C, 1 to 4 % of Cu, and the balance of Fe and inevitable impurities,
   the sintered material exhibiting a metallic structure made of pores and a matrix, the matrix being a mixed structure of a pearlite phase, a ferrite phase, an iron carbide phase, and a copper phase, and a part of the pores including graphite that is dispersed therein,
   wherein the iron carbide phase is dispersed at 3 to 25 % by area ratio and the copper phase is dispersed at 0.5 to 3.5 % by area ratio with respect to a cross section of the metallic structure, respectively.

2. A sintered material for valve guides, consisting of, by mass %, 1.3 to 3 % of C, 1 to 4 % of Cu, 0.05 to 0.5 % of Sn, and the balance of Fe and inevitable impurities,
   the sintered material exhibiting a metallic structure made of pores and a matrix, the matrix being a mixed structure of a pearlite phase, a ferrite phase, an iron carbide phase, and at least one of a copper phase and a copper-tin alloy phase, and a part of the pores including graphite that is dispersed therein,
   wherein the iron carbide phase is dispersed at 3 to 25 % by area ratio and the copper phase and the copper-tin alloy phase are dispersed at 0.5 to 3.5 % by area ratio with respect to a cross section of the metallic structure, respectively.

3. The sintered material for valve guides according to claim 1 or 2, wherein the iron carbide phase is a plate-shaped iron carbide having an area of not less than 0.05 % in a visual field in a cross-sectional structure at 200-power magnification, and a total area of the plate-shaped iron carbides having an area of not less than 0.15 % in the visual field is 3 to 50 % with respect to a total area of the plate-shaped iron carbides.

4. The sintered material for valve guides according to one of claims 1 to 3, wherein at least one kind selected from the group consisting of manganese sulfide particles, magnesium silicate mineral particles, and calcium fluoride particles are dispersed in particle boundaries of the matrix and in the pores at not more than 2 mass %.

5. A production method for a sintered material for valve guides, comprising:

preparing an iron powder, a copper powder, and a graphite powder;
mixing the copper powder and the graphite powder with the iron powder to produce a raw powder consisting of, by mass %, 1.3 to 3% of C, 1 to 4 % of Cu, and the balance of Fe and inevitable impurities;
filling a tube-shaped cavity of a die assembly with the raw powder;
compacting the raw powder into a green compact having a tube shape; and
sintering the green compact at a heating temperature of 970 to 1070 °C in a nonoxidizing atmosphere so as to obtain a sintered compact.

6. A production method for a sintered material for valve guides, comprising:

preparing an iron powder, a graphite powder, and one selected from the group consisting of a combination of a copper powder and a tin powder, a copper-tin alloy powder, and a combination of a copper powder and a copper-tin alloy powder;
mixing the graphite powder and the one selected from the group with the iron powder to produce a raw powder consisting of, by mass %, 1.3 to 3% of C, 1 to 4 % of Cu, 0.05 to 0.5 % of Sn, and the balance of Fe and inevitable impurities;
filling a tube-shaped cavity of a die assembly with the raw powder;
compacting the raw powder into a green compact having a tube shape; and
sintering the green compact at a heating temperature of 950 to 1050 °C in a nonoxidizing atmosphere so as to obtain a sintered compact.

7. The production method for the sintered material for valve guides according to claim 5 or 6, wherein the green compact is held at the heating temperature for 10 to 90 minutes in the sintering.

8. The production method for the sintered material for valve guides according to one of claims 5 to 7, wherein the sintered compact is cooled from the heating temperature to room temperature after the sintering, and the sintered compact is cooled from 850 to 600 °C at a cooling rate of 5 to 20 °C per minute.

9. The production method for the sintered material for valve guides according to one of claims 5 to 7, wherein the sintered compact is cooled from the heating temperature to room temperature, and the sintered compact is isothermally held in a temperature range of 850 to 600 °C for 10 to 90 minutes and is then cooled.

10. The production method for the sintered material for valve guides according to one of claims 5 to 9, wherein at least one kind selected from the group consisting of a manganese sulfide powder, a magnesium silicate mineral powder, and a calcium fluoride powder is added to the raw powder at not more than 2 mass % in the mixing.

Fig. 1A

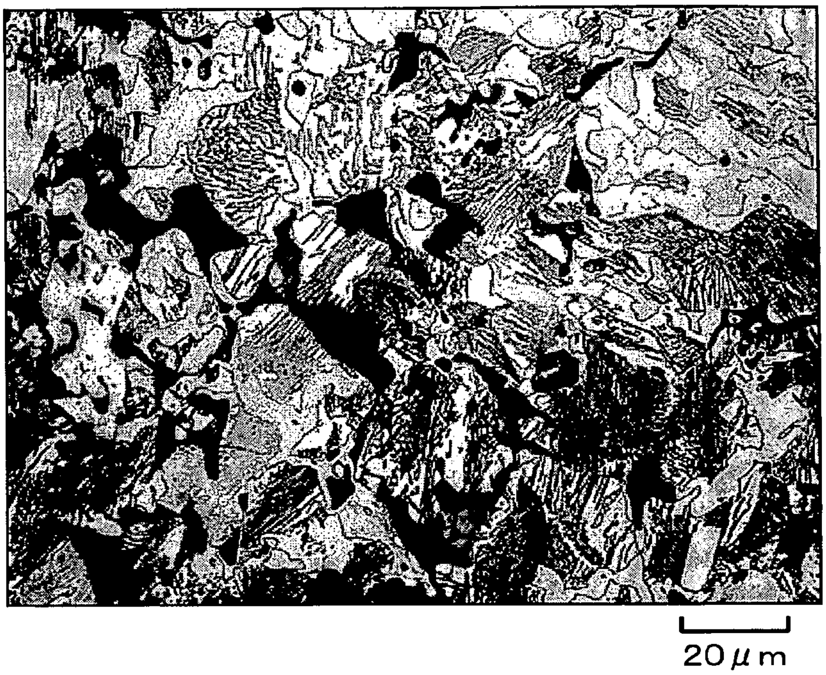

20 μm

Fig. 1B

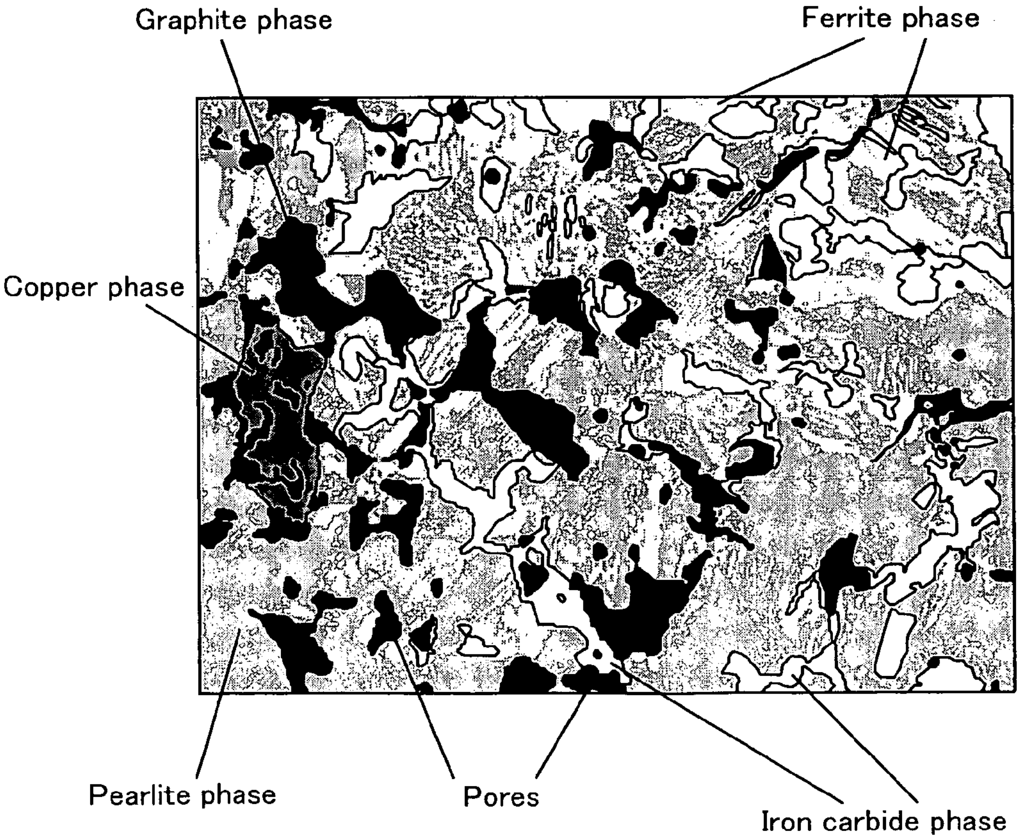

Graphite phase
Ferrite phase
Copper phase
Pearlite phase
Pores
Iron carbide phase

Fig. 2A

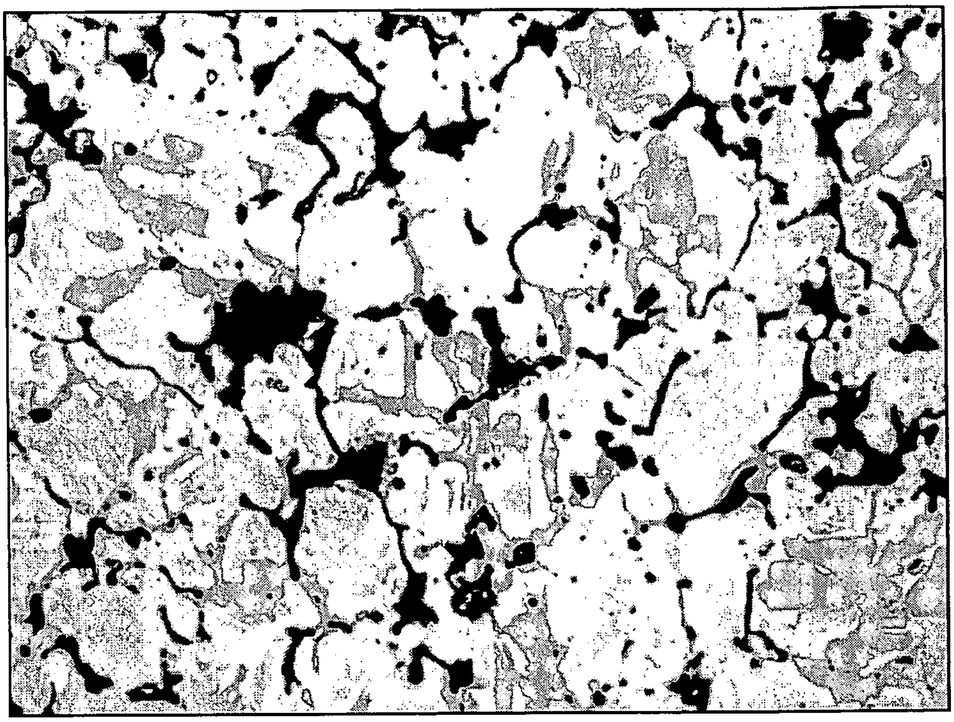


Fig. 2B

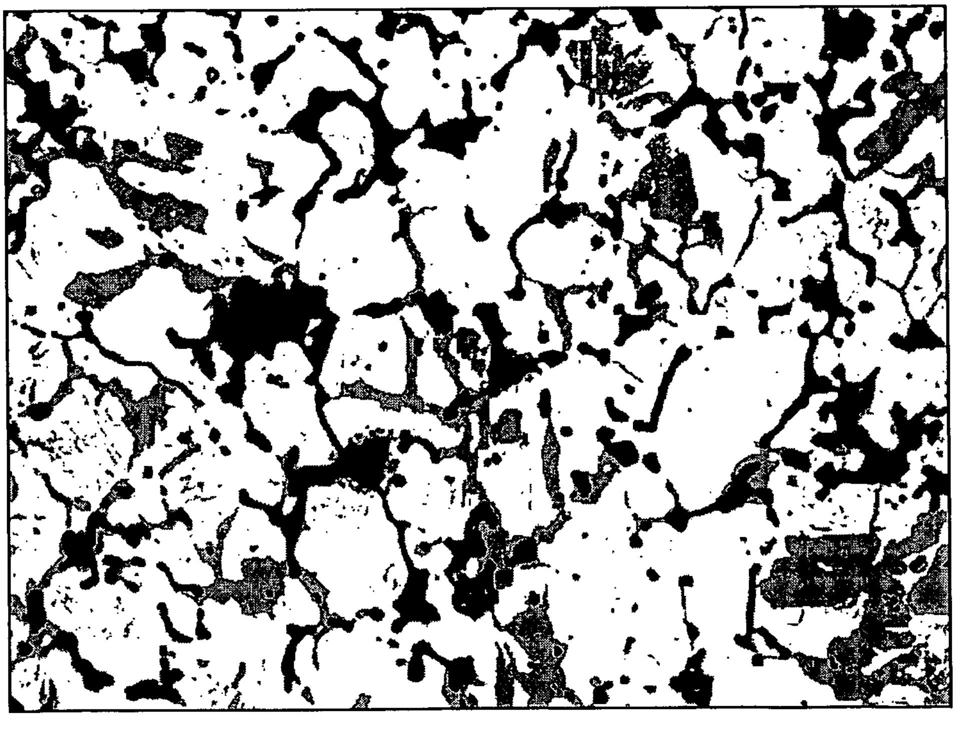


Fig. 3A

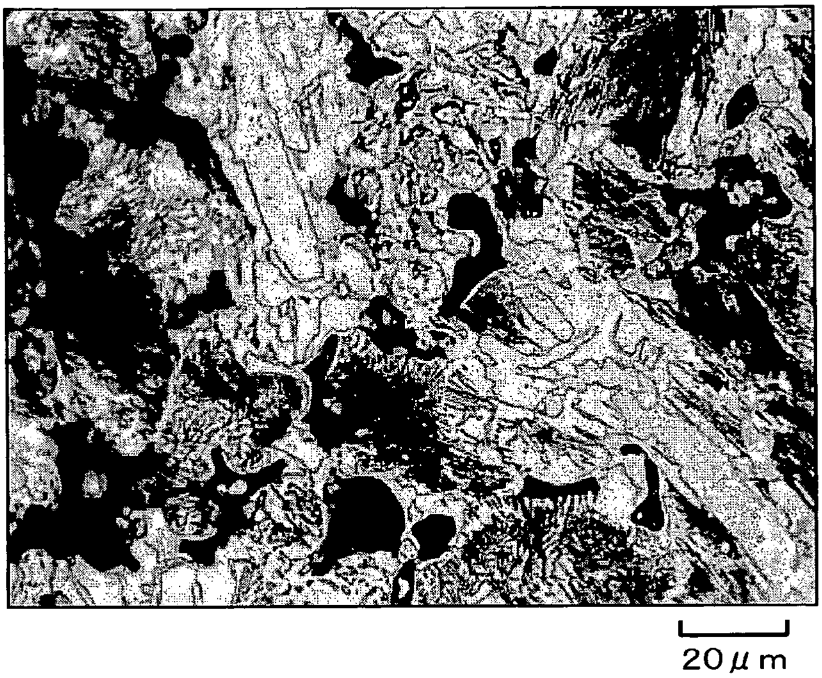
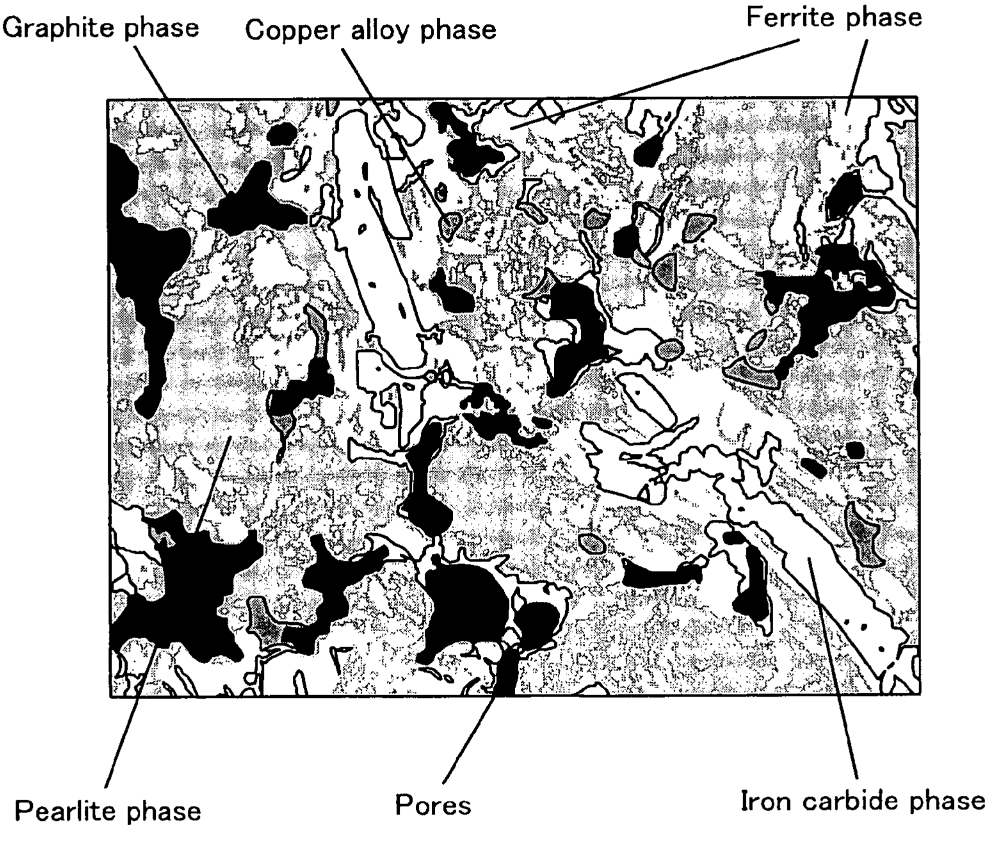

20 μm

Fig. 3B


Graphite phase
Copper alloy phase
Ferrite phase
Pearlite phase
Pores
Iron carbide phase

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