



US 20070009374A1

(19) **United States**(12) **Patent Application Publication****Akaishi et al.**(10) **Pub. No.: US 2007/0009374 A1**(43) **Pub. Date: Jan. 11, 2007**(54) **HEAT-RESISTANT COMPOSITE DIAMOND  
SINTERED PRODUCT AND METHOD FOR  
PRODUCTION THEREOF**(75) Inventors: **Minoru Akaishi**, Tsukuba-shi, Ibaraki  
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§ 371(c)(1),

(2), (4) Date: **Sep. 25, 2006**(30) **Foreign Application Priority Data**

Dec. 18, 2002 (JP) ..... 2002-121802

**Publication Classification**(51) **Int. Cl.****C22C 1/04** (2006.01)(52) **U.S. Cl.** ..... **419/48**

(57)

**ABSTRACT**

Disclosed is a heat-resistant diamond composite sintered body, which is prepared by sintering an ultrafine-grain synthetic diamond powder having an average grain size of 200 nm or less, without using a sintering aid. The composite sintered body comprises a diamond crystal and a minute amount of non-diamond carbon as a product, and has a Vickers hardness of 85 GPa or more. The composite sintered body is produced by a method comprising enclosing in a Ta or Mo capsule a synthetic diamond powder having an average grain size of 200 nm or less, and heating and pressurizing using an ultrahigh-pressure synthesizing apparatus under thermodynamically stable conditions including a temperature of 2100° C. or more and a pressure of 7.7 GPa or more.

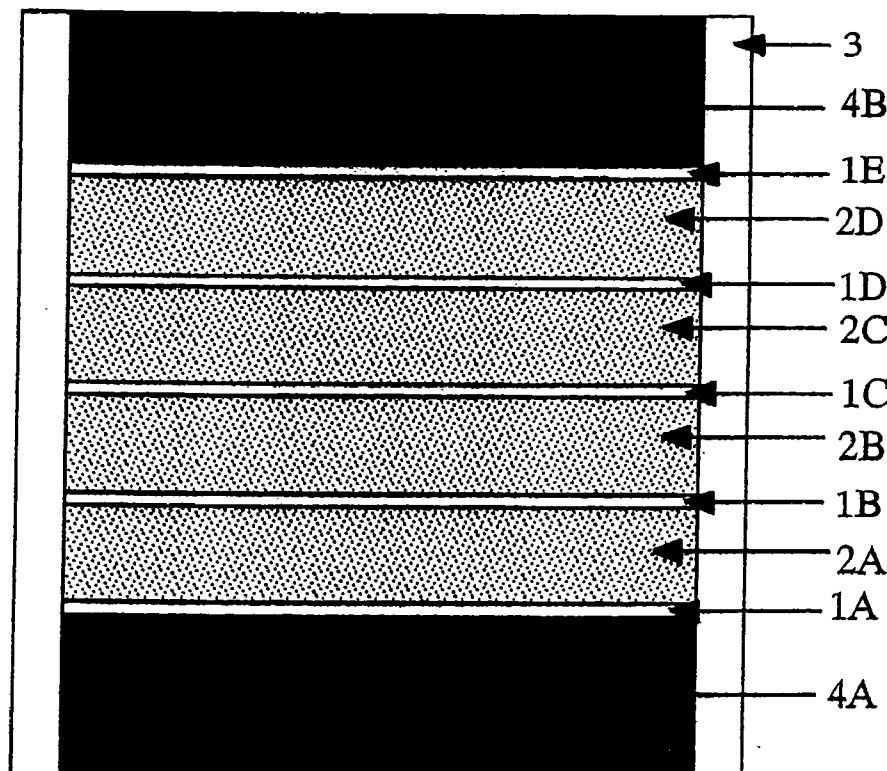


FIG. 1

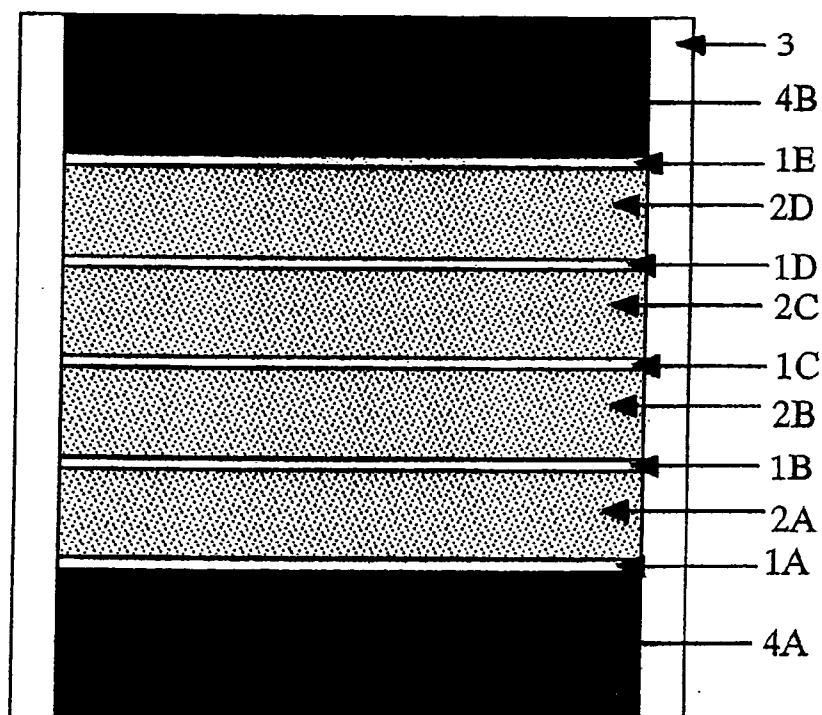


FIG. 2

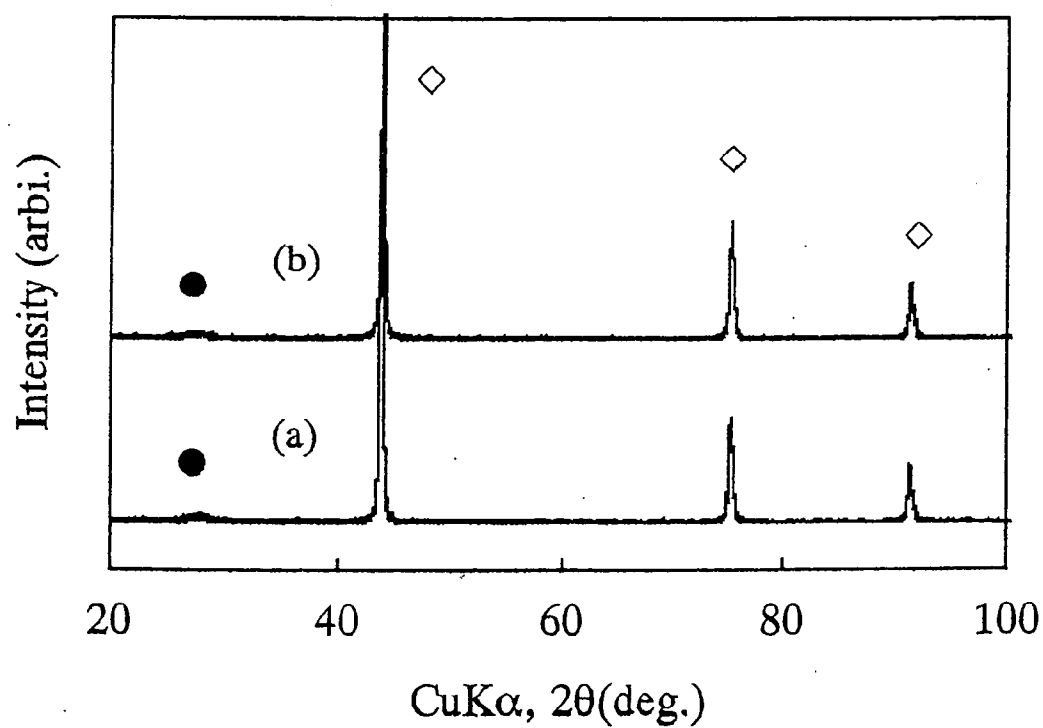
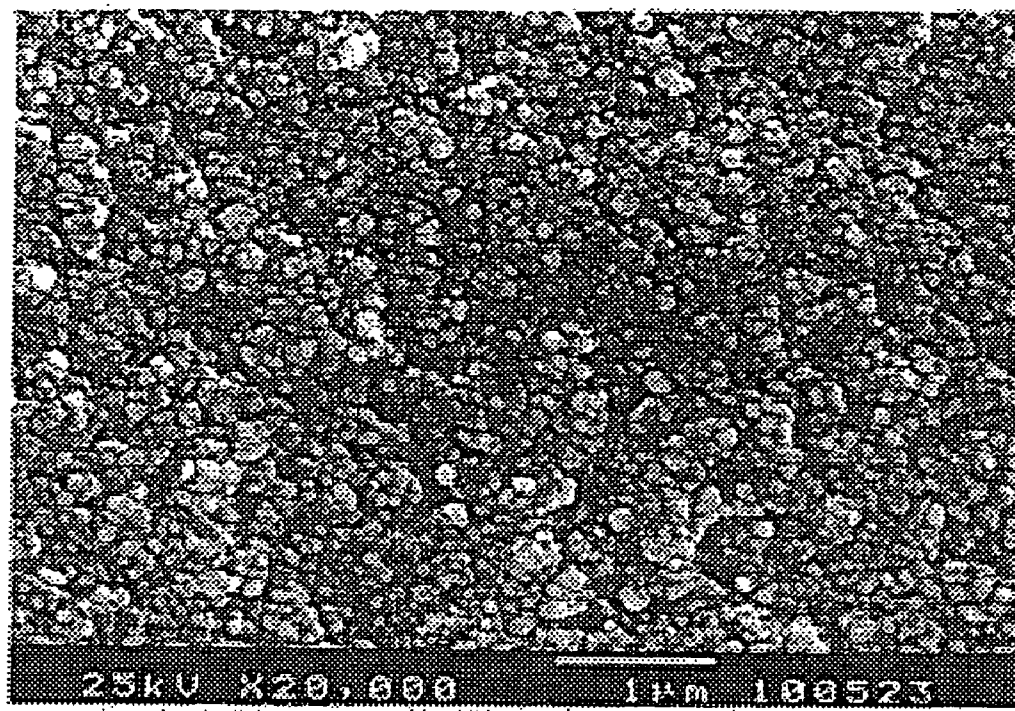


FIG. 3



# HEAT-RESISTANT COMPOSITE DIAMOND SINTERED PRODUCT AND METHOD FOR PRODUCTION THEREOF

## TECHNICAL FIELD

[0001] The present invention relates to a heat-resistant diamond composite sintered body, and a production method thereof.

## BACKGROUND ART

[0002] Heretofore, there has been known a method for producing a diamond sintered body with a sintering aid, for example, carbonate or metal, such as Co, by use of a conventional ultrahigh-pressure synthesizing apparatus (see the following Patent Publications 1 and 2). There has also been known a method for synthesizing a high-hardness diamond sintered body excellent in heat resistance, which comprises performing a sintering treatment under higher pressure/temperature conditions than those in a conventional treatment, using an alkaline-earth metal carbonate as a sintering aid, instead of the metal sintering aid (see the following Non-Patent Publication 1). However, molten carbonate having high viscosity imposes limits on grain size, and thereby these sintered bodies have a relatively large grain size of about 5  $\mu\text{m}$  at minimum.

[0003] The inventors reported a method for producing a fine-grain diamond sintered body, which comprises adding oxalic acid dihydrate serving as a source of a  $\text{CO}_2\text{—H}_2\text{O}$  fluid phase into carbonate to prepare a mixed powder, and applying a natural diamond powder having a grading range (distribution range of particle diameter) of zero to 1  $\mu\text{m}$ , onto the mixed powder to form a layered structure (see the following Patent Publication 3 and Non-Patent Publications 2 and 3). However, this production method essentially requires a high temperature of 2000° C. or more.

[0004] The inventors also reported a method similar to the above method, which comprises sintering a finer-grain diamond powder, for example, having a grading range of zero to 0.1  $\mu\text{m}$  (see the following Non-Patent Publication 4). In this case, any high-hardness diamond sintered body could not be obtained due to occurrence of abnormal grain growth in diamond.

[0005] Recently, an article has been published that discloses a method for synthesizing a diamond sintered body under a pressure of 12 to 25 GPa at a temperature of 2000 to 2500° C. without a sintering aid through a direct conversion reaction from graphite to diamond. This article reports that the obtained diamond sintered body has light transparency (see the following Non-Patent Publication 5).

[0006] Parent Publication 1: Japanese Patent Publication No. 52-012126

[0007] Parent Publication 2: Japanese Patent Publication No. 04-050270

[0008] Parent Publication 3: Japanese Patent Laid-Open Publication No. 2002-187775

[0009] Non-Patent Publication 1: Diamond and Related Mater., Vol. 5, pp 34-37, Elsevier Science S. A., 1996

[0010] Non-Patent Publication 2: Journal of the 41st High Pressure Symposium, p 108, the Japan Society of High Pressure Science and Technology, 2000

[0011] Non-Patent Publication 3: Proceedings of the 8th NIRIM International Symposium on Advanced Materials, pp 33-34, the National Institute for Research in Inorganic Materials, 2001

[0012] Non-Patent Publication 4: Journal of the 42nd High Pressure Symposium, p 89, the Japan Society of High Pressure Science and Technology, 2001

[0013] Non-Patent Publication 5: T. Irifune et al., "Characterization of polycrystalline diamonds synthesized by direct conversion of graphite using multi anvil apparatus, 6th High Pressure Mineral Physics Seminar, 28 Aug., 2002, Verbania, Italy

## DISCLOSURE OF INVENTION

[0014] There is the need for providing a diamond sintered body usable as a high-performance tool in the field of cutting tools and an ultraprecision machining tool as an alternative to single crystals previously limited largely, and valuable as jewelry. Particularly, in connection of higher cutting speed in oil-drilling bits and particular automobile components, it is desired to achieve enhanced heat resistance in diamond sintered-body tool.

[0015] Heretofore, with a sintering aid without distinction of metal or nonmetal, a high-hardness diamond sintered body has been produced through a high-pressure/high-temperature sintering treatment under an ultrahigh pressure condition of 5.5 to 7.7 GPa. In such a diamond sintered body production method using a sintering aid, a material used as the sintered body inevitably remains as a solid in a sintered body after the high-pressure/high-temperature sintering treatment to cause decrease in bonding area between diamond grains. As compared to an ideal diamond sintered body containing no sintering aid, diamond sintered body with the sintering aid is liable to have a lower hardness, and poor properties due to a chemical reaction between diamond and the sintering aid remaining in the sintered body. Further, the conventional sintered body synthetic method using no sintering aid requires an extremely high pressure and temperature.

[0016] A natural diamond powder having a grading range of zero to 0.1  $\mu\text{m}$  can be sintered using a sintering aid consisting of a carbonate-C—O—H fluid phase to readily synthesize a high-hardness fine-grain diamond sintered body with carbonate homogeneously distributed between diamond grains, under the conditions of 7.7 GPa and 1700° C. or more (Japanese Patent Application No. 2002-030863=Laid-Open Publication No. 2003-226578).

[0017] In order to reduce synthesis costs of a high-hardness fine-grain diamond sintered body using carbonate as a sintering aid, the inventors attempted to synthesize a diamond sintered body by applying a synthetic hydrogen-terminated diamond powder with an average grain size of 100 nm, onto a sintering aid consisting of a carbonate-C—H fluid phase to form a layered structure, and subjecting the layered structure to a sintering treatment under high-pressure/high-temperature conditions. In the result, while a recovered sample had layer-like cracks and carbonate part-way infiltrated, homogenous infiltration of the carbonate-C—H fluid phase as a sintering aid could not be achieved.

[0018] As the result of studies on this reason, the inventors arrived at a conclusion that a synthetic diamond powder is

liable to be plastically deformed, and a space between diamond grains is partly decreased due to the plastic deformation to preclude the infiltration of the molten sintering aid.

[0019] Further, in a system using no sintering aid, the inventions attempted to sinter a natural diamond powder having a grading range of zero to 0.1  $\mu\text{m}$  under the conditions of 7.7 GPa and 2300° C. for 15 minutes. In the result, it was proven that a high-hardness diamond sintered body is hardly synthesized from the natural diamond powder having a grading range of zero to 0.1  $\mu\text{m}$ .

[0020] The inventors found that the above problem does not unexpectedly occur when a synthetic diamond powder having an average grain size of 200 nm or less is used as a starting material, and sintered under high-pressure/high-temperature conditions equivalent to those in the conventional method for producing a diamond sintered body using a sintering aid, such as carbonate. Based on this knowledge, the inventors finally achieved to synthesize a heat-resistant and time-grained diamond sintered body without use of sintering aid.

[0021] In addition, a sintered body obtained through this production method contains a minute amount of non-diamond carbon as a product. That is, this sintered body is formed as a composite sintered body of a diamond crystal and a non-diamond carbon, and electric conductivity is created therein. This non-diamond carbon would be derived from graphitization in a part of diamond powder as a starting material. Thus, the obtained composite sintered body having electric conductivity can be subjected to an electric discharge machining process. Furthermore, the composite sintered body has luster and glaze which cannot be seen in conventional diamond sintered bodies.

[0022] Specifically, the present invention provides a heat-resistant diamond composite sintered body prepared by sintering an ultrafine-grain synthetic diamond powder having an average grain size of 200 nm or less, without using a sintering aid. The composite sintered body comprises a diamond crystal and a minute amount of non-diamond carbon as a product, and has a Vickers hardness of 85 GPa or more.

[0023] The present invention also provides a method of producing the above heat-resistant diamond composite sintered body, which comprises enclosing a synthetic diamond powder having an average grain size of 200 nm or less, in a capsule made of Ta or Mo, and heating and pressurizing using an ultrahigh-pressure synthesizing apparatus under thermodynamically stable conditions including a temperature of 2100° C. or more and a pressure of 7.7 GPa or more.

[0024] In the comparison with a natural diamond powder under the condition that each diamond powder has approximately the same grain size, a synthetic diamond powder is subject to plastic deformation. As compared with a powder having a large grain size distribution, a powder having a less grain size distribution would have a smaller size distribution in the inter-grain space. Thus, if a synthetic diamond powder having an approximately even grain size and the smallest possible average grain size is used as a starting material, a heat-resistant diamond composite sintered body would be synthesized without any sintering aid by utilizing plastic deformation easily occurring in diamond grains, and large surface energy inherent in small diamond grain, as a driving force.

[0025] If a synthetic diamond powder having an average grain size of greater than 200 nm is used, the surface energy of diamond grains will be reduced along with increase in grain size, to cause difficulties in synthesizing a diamond sintered body.

[0026] The heat-resistant diamond composite sintered body synthesized by the production method of the present invention can be used not only for industrial purposes, such as a high-performance tool in cutting tool fields, and oil bits requiring high heat resistance, but also for jewelry items by taking advantage of high refractive index inherent in diamond, luster peculiar to a sintering agent-free diamond sintered body and producibility of a large sintered body.

[0027] The production method of the present invention can be implemented under pressure/temperature conditions equivalent to those in the conventional method for producing a diamond sintered body using carbonate as a sintering aid.

#### BRIEF DESCRIPTION OF DRAWINGS

[0028] FIG. 1 is a sectional view conceptually showing one example of a sintered-body synthesis capsule which is filled a diamond powder to be sintered through a production method of the present invention.

[0029] FIG. 2 is a graph showing an X-ray diffraction pattern of a sintered body obtained in Inventive Example 1 ((a): before a heat treatment, (b): after the treatment).

[0030] FIG. 3 is an electron micrograph of a fracture surface of the sintered body obtained in Inventive Example 1.

#### BEST MODE FOR CARRYING OUT THE INVENTION

[0031] In a diamond sintered-body production method of the present invention, a synthetic ultrafine diamond powder is used as a starting material. FIG. 1 is a sectional view showing one example of a sintered-body synthesis capsule which is filled a diamond powder to be sintered through a production method of the present invention.

[0032] As shown in FIG. 1, a cylindrical-shaped capsule 3 made of Ta has a graphite disc 4A attached to the bottom thereof to prevent the deformation of the capsule. A diamond powder layer 2A is formed on the graphite disc 4A through a Ta or Mo foil 1A under a given compacting pressure. The Ta or Mo foil is used for separating diamond powder layers from each other to synthesize a sintered body having a desired thickness, separating the graphite discs from the diamond powder layer, preventing a pressure medium from getting in the capsule, and sealing a fluid phase. Then, a Ta or Mo foil 1B is placed on the diamond powder layer 2A. In the same manner, second, three diamond powder layers 2B, 2C, 2D are formed while interposing Ta or Mo foils 1C, 1D therebetween. Then, a Ta or Mo foil 1E is placed on the diamond powder layer 2D, and a graphite disc 4B is placed on the Ta or Mo foil 1E to prevent the deformation of the capsule.

[0033] This capsule is placed in a pressure medium, and pressurized up to 7.7 GPa or more at room temperature by use of an ultrahigh-pressure apparatus based on a static compression process, such as a belt-type ultrahigh-pressure

synthesizing apparatus. Then, under this pressure, the capsule is heated up to a given temperature of 2100° C. or more to perform a sintering treatment. If the pressure is less than 7.7 GPa, a desired heat-resistant sintered body cannot be obtained even if the temperature is equal to or greater than 2100° C. Further, if the temperature is less than 2100° C., a desired heat-resistant sintered body cannot be obtained even if the pressure is equal to or greater than 7.7 GPa. It is desirable to limit the temperature and pressure to a bare minimum in consideration of the capacity of the apparatus, because excessive temperature or pressure simply leads to deterioration in energy efficiency.

[0034] A synthetic diamond powder having an average grain size of 200 nm or less is obtained by grinding a synthetic diamond powder having a large grain size and classifying the ground powder. The grain size herein is a measured value using a Microtrac UPA particle size analyzer. This measurement method is publicly known (see, for example, Japanese Patent Laid-Open Publication No. 2002-35636). Such a synthetic diamond powder is commercially available (for example, Trade Name: MD200 (average grain size: 200 nm); MD 100 (average grain size: 100 nm) manufactured by Tomei Diamond Co., Ltd.)

#### EXAMPLE

##### Inventive Example

[0035] A commercially-available synthetic diamond powder having an average grain size of 100 nm was used as a starting material.

[0036] A cylindrical-shaped Ta capsule having a wall thickness of 0.8 mm and an outer diameter of 11.6 mm was prepared, and a graphite disc having a thickness of 2.6 mm was attached to the bottom of the capsule to prevent the deformation of the capsule. 250 mg of the diamond powder was placed on the graphite disc through a Ta foil, and pressed at a compacting pressure of 100 MPa to form a diamond powder layer. Then, a Ta foil was placed on the diamond powder layer, and then a graphite disc having a thickness of 2.6 mm was placed on this Ta foil to prevent the deformation of the capsule. The capsule was subjected to pressure forming, and then an excess part of the upper graphite disc was chipped off.

[0037] Then, the capsule was placed in a pressure medium of NaCl-10% ZrO<sub>2</sub>, and subjected to a sintering treatment under a pressure of 7.7 GPa at a temperature of 2200° C. for 30 minutes, using a belt-type ultrahigh pressure synthesizing apparatus. After completion of the sintering treatment, the capsule was taken out of the capsule.

[0038] Then, a product, such as TaC, formed on the surface of the sintered body was removed using a hydrofluoric acid-nitric acid solution, and each of top and bottom surfaces of the sintered body was ground using a diamond wheel to flatten the surfaces. The sintered body has a high grinding resistance, and the sintered body after the grinding had an average value of Vickers hardness of 90 GPa or more.

[0039] This sintered body was subjected to a heat treatment in vacuum at 1200° C. for 30 minutes to evaluate heat resistance. After the treatment, the sintered body maintained the same Vickers hardness as that before the treatment. An X-ray diffraction pattern of the obtained sintered body is

shown in FIG. 2. FIG. 2(a) and FIG. 2(b) shows an X-ray diffraction pattern before the heat treatment in vacuum at 1200° C. for 30 minutes, and an X-ray diffraction pattern after the heat treatment, respectively. As seen from the result in FIG. 2(a), a diffraction line of non-diamond carbon is observed as a wide diffraction line at  $d=3.26$  to  $3.19$  on the higher angle side relative to a diffraction line of (002) of graphite, and diamond and an extremely small amount of non-diamond carbon (indicated by • in FIG. 2) are found. As seen from the result in FIG. 2(b), this diffraction line has no change in position and intensity. This shows that the amount of non-diamond carbon after the heat treatment is not changed at all. As shown in FIG. 3, through microscopic observation of the structure of a fracture surface of the sintered body, it was proven that the sintered body comprises fine grains having an average grain size of 80 nm.

##### Comparative Example 1

[0040] Except that a sintering temperature was set at 2000° C., a sintering treatment was performed in the same manner as that in Inventive Example 1. An obtained sintered body has poor grinding resistance, and an average value of Vickers hardness was 50 GPa.

##### Inventive Example 2

[0041] Except that a synthetic diamond powder having an average grain size of 200 nm was used as a starting material, and a sintering temperature was set at 2300° C., a sintering treatment was performed in the same manner as that in Inventive Example 1. An obtained sintered body exhibited significantly high grinding resistance and remarkably high hardness. Specifically, an average value of Vickers hardness was had an 85 GPa.

##### Comparative Example 2

[0042] Except that a synthetic diamond powder having an average grain size of 300 nm was used as a starting material, a sintering treatment was performed in the same manner as that in Inventive Example 2. In an obtained sintered body, layer-like cracks were observed, and grinding resistance was extremely lower than that in Inventive Example 2. Thus, an excessively increased average grain size makes it difficult to synthesize a high-hardness diamond sintered body.

#### INDUSTRIAL APPLICABILITY

[0043] The diamond sintered body of the present invention has excellent heat resistance, and high wear resistance, and high hardness. For example, when this diamond sintered body is used in a finishing cutting work for a difficult-to-machine material, such as high-Si—Al alloy, or an ultraprecision machining process for metal or alloy, it can exhibit excellent cutting and wire drawing performances. In addition, this diamond sintered body has sufficient heat resistance suitable for a high cutting speed in oil-drilling bits and particular automobile components. Further, non-diamond carbon is created to form a composite sintered body exhibiting electric conduction properties. The properties make it possible to use an electric discharge machining process as a cutoff process of the sintered body so as to facilitate reduction in machining cost. Furthermore, the composite sintered body has luster and glaze which cannot be seen in conventional diamond sintered bodies. The sintered body can be formed in various shapes by lasering, grinding and polishing

as well as the electric discharge machining process. Therefore, it can be expected to use as black diamond for jewelry having luster and glaze which cannot be seen in conventional diamond sintered bodies.

1. A heat-resistant diamond composite sintered body prepared by sintering an ultrafine-grain synthetic diamond powder having an average grain size of 200 nm or less, by use of an ultrahigh-pressure synthesizing apparatus through static compression process without using a sintering aid, said composite sintered body comprising a diamond crystal and a minute amount of non-diamond carbon as a product, and having a Vickers hardness of 85 GPa or more.

2. A method of producing the heat-resistant diamond composite sintered body as defined in claim 1, comprising:

enclosing a synthetic diamond powder having an average grain size of 200 nm or less, in a capsule made of Ta or Mo;

placing the capsule in a pressure medium; and

heating and pressurizing the capsule under thermodynamically stable conditions including a temperature of 2100° C. or more and a pressure of 7.7 GPa or more, by use of an ultrahigh-pressure synthesizing apparatus through static compression process.

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