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TITLE OF THE INVENTION

**Diamond Sintered Body Having High Strength and High
Wear-Resistance and Manufacturing Method Thereof**

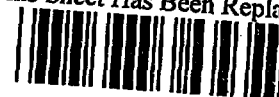
BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to a diamond sintered body used as a material for cutting tools, digging tools, drawing dies, wear-resistant parts and the like and manufacturing method thereof. More particularly, it
10 relates to a diamond sintered body having improved strength and wear-resistance and to the manufacturing method thereof.

Description of the Related Art

A diamond sintered body generally has superior
15 wear-resistance and higher strength as compared with other materials. Therefore, it is used in such a field that requires strength and wear-resistance, e.g. the field of cutting tools, digging tools and drawing dies. Such a diamond sintered body can be obtained by filling diamond
20 powder in a container formed of WC-Co cemented carbide, infiltrating Co-W-C eutectic composition liquid-phase from the cemented carbide base material into the diamond powder under high pressure at high temperature and by sintering the same, as disclosed, for example, in Japanese Patent
25 Publication No. 52-12126. Alternatively, as disclosed in



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Japanese Patent Laying-Open No. 54-114513, a diamond
sintered body can be obtained by premixing diamond powder
with powder containing an iron family solvent metal, and
by holding the mixed powder at such high temperature and
5 high pressure that allows provision of diamond.

The diamond sintered body obtained through the above
described methods suffers from the problem under difficult
conditions of sintering. For example, if the diamond
particles are too fine or if the solvent metal to be mixed
10 is too small in amount, sintering would be impossible as
the solvent metal hardly infiltrates, or the coagurated
portions of diamond particles would not be sintered
locally, as portions in contact with each other of the
diamond particles increase. Accordingly, it is not easy
15 to obtain diamond sintered body having high density, that
is, a diamond sintered body having good wear-resistance
and high content of diamond.

In order to solve such a problem, a method to obtain
a diamond sintered body having high density has been
20 proposed, for example, in Japanese Patent Laying-Open Nos.
63-190756 and 6-32655, and in Research Report No. 58, pp.
38 to 48 of National Institute for Research in Inorganic
Materials, in which method a sintering assistant agent is
applied, as coating, to the surface of each particle of
25 diamond powder and the coated diamond powder is sintered.

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The diamond sintered body obtained through this method has high diamond content, and therefore it has good wear-resistance. However, when the diamond particle size in the sintered body is large, the strength of the diamond sintered body becomes low, and therefore it does not have sufficient reliability for practical use. Further, when the diamond sintered body having high density is to be obtained by such a method, only a small amount of sintering assistant agent can be added. Therefore, depending on the composition of the sintering assistant agent and on the manner of coating, of the temperature range and pressure range allowing production of diamond, relatively high temperature and high pressure are required. In such a case, there would be large strain remaining in the diamond sintered body, which degrades strength of the diamond sintered body, and hence lowers reliability in practical use.

In order to prevent degradation of diamond sintered body at a high temperature, a method has been proposed, for example, in Japanese Patent Laying-Open No. 6-6769 in which the surface of diamond particles is coated by transition metal, B or Si and the coated diamond powder is sintered in solid-phase. However, in this case it is considered that diamond particles are bonded with coating material which is carbonized by solid-phase reaction

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interposed. Therefore, the diamond sintered body obtained by liquid-phase sintering employing as a solvent an iron family metal allowing direct bonding between diamond particles with each other is superior in view of
5 mechanical strength.

SUMMARY OF THE INVENTION

In view of the above described problems of the prior art, an object of the present invention is to provide a diamond sintered body having high strength and high wear-
10 resistance and to manufacturing method thereof.

The diamond sintered body having high strength and high wear-resistance in accordance with one aspect of the present invention includes sintered diamond particles of 80 to 96 percent by volume, and a remaining part of
15 sintering assistant agent and unavoidable impurity, the sintered diamond particles having particle size substantially in the range of 0.1 to 10 μm and directly bonded to each other, the sintering assistant agent including Pd within the range of 0.01 to 40 percent by
20 weight, and as a remaining part, including at least one selected from Fe, Co and Ni.

In the diamond sintered body in accordance with the first aspect of the present invention, since fine diamond particles are sintered with high density in the presence
25 of sintering assistant agent including iron family



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element, high strength and high wear-resistance can be realized.

According to a second aspect, the method of manufacturing a diamond sintered body having high strength and high wear-resistance includes the steps of preparing
5 diamond powder having particle size substantially within a range of 0.1 to 10 μm , precipitating Pd within the range of 10^{-4} to 40 percent by weight on the surface of each particle of the diamond powder, electroless plating a
10 sintering assistant agent including at least one selected from Fe, Co and Ni within the range of 4 to 20 percent by volume to the surface of each particle of the diamond powder and thus preparing coated diamond powder, molding
15 powder compact body of the coated diamond powder and sintering, in liquid-phase, the powder compact body under a high temperature and high pressure condition in which diamond is stable.

In the method of manufacturing a diamond sintered body in accordance with the second aspect of the present
20 invention, a sintering assistant agent including an iron family element is applied as coating, within the range of 4 to 20 percent by volume to the surface of each particle of fine diamond powder, and the coated diamond powder is sintered in liquid-phase under high pressure and high
25 temperature in which diamond is stable, so that a diamond



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sintered body having high strength and high wear distance as well as high diamond content can be obtained.

According to a third aspect of the present invention, the method of manufacturing a diamond sintered body having high strength and high wear-resistance includes the steps of preparing diamond power having particle size substantially within the range of 0.1 to 10 μm , precipitating Pd within the range of 10⁻⁴ to 40 percent by weight on the surface of each particle of the diamond powder and then electroless plating a sintering assistant agent including at least one selected from Fe, Co and Ni within the range of 0.1 to 19.9 percent by volume to the surface of each particle of the diamond powder to prepare coated diamond powder, molding the powder compact body of the coated diamond powder, bringing into contact an additional sintering assistant agent including at least one of Pd, Fe, Co and Ni with the powder compact body, and sintering in liquid-phase the powder compact body at high pressure and high temperature condition in which diamond is stable, while infiltrating the additional sintering assistant agent.

In the method of manufacturing the diamond sintered body in accordance with the third aspect of the present invention, the sintering assistant agent including an iron family element is applied for coating to the surface of

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each particle of fine diamond powder within the range of
0.1 to 19.9 percent by volume, an additional sintering
assistant agent is brought into contact with the coated
diamond powder, and the coated diamond powder is sintered
5 in liquid-phase under high pressure and high temperature
in which diamond is stable while infiltrating the
additional sintering assistant agent. Therefore, a
diamond sintered body having high diamond content and
having high strength and high wear-resistance can be
10 obtained.

Detailed Description of the Invention

First, the inventors studied strength of various
diamond sintered bodies. As a result, it was found that
the strength of the diamond sintered body depends on the
15 size of a defect in the sintered body which serves as an
initiation point of breakage. Here, the term defect means
a diamond larger particle in the diamond sintered body, a
pool of the sintering assistant agent such as the solvent
metal or a void. The smaller the defect, the higher the
20 strength of the diamond sintered body.

It was found that in order to improve strength of the
diamond sintered body, first, the diamond larger particles
must be reduced, and that acceptable particle size of
diamond is at most 10 μm . In order to provide coating of
25 sintering assistant agent on the surface of diamond



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particles, which will be described later, the diamond particle must have the particle size of at least 0.1 μm . In other words, the raw material diamond powder is required to have the particle size within the range of 0.1 to 10 μm .

5 It was found that in order to reduce void and pool portion of sintering assistant agent in the sintered body, it is preferable to sinter coated diamond powder having the sintering assistant agent coating the surface of each
10 particle of diamond powder in liquid-phase. It was found that, preferably, the sintering assistant agent includes Pd and at least one selected from Fe, Co and Ni which are iron family metals. It was found that by preparing coated diamond powder to include such sintering assistant agent
15 within the range of 4 to 20 percent by volume and by sintering the coated diamond powder under high pressure and high temperature condition in which diamond is stable, uniform liquid-phase of sintering assistant agent is generated entirely over the diamond powder, so that
20 diamond sintered body having smaller void and pool of sintering assistant agent is obtained.

Further, it was found that by preparing coated diamond powder to include sintering assistant agent including Pd and at least one of Fe, Co and Ni within the
25 range of 0.1 to 19.9 percent by volume, and bringing into



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contact an additional sintering assistant agent including at least one of Pd, Fe, Co and Ni with the coated diamond powder, uniform infiltration of the additional sintering assistant agent occurs entirely over the coated diamond powder compact body, supplementing the sintering assistant agent coated on the diamond powder under high pressure at high temperature in which diamond is stable, and hence a diamond sintered body having smaller void and pool of sintering assistant agent can be obtained.

5
10 More specifically, by using coated diamond powder on which the above described sintering assistant agent is coated, uniform melting or infiltration of the sintering assistant agent occurs, so that sintering becomes possible under such a condition that is otherwise not suitable for sintering, and hence a diamond sintered body having high diamond content, high strength and high wear assistance can be obtained.

15
20 Here, any of Pd, Fe, Co and Ni may be used as the sintering assistant agent for the diamond powder by itself. However, it was found that when the sintering assistant agent includes Pd in addition to at least one of Fe, Co and Ni, melting point of the sintering assistant agent lowers and sintering property of the diamond powder is remarkably improved. Here, if the content of Pd in the sintering assistant agent is smaller than 0.01 percent by



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weight, sufficient effect of lowering the melting point of the sintering assistant agent cannot be obtained. By contrast, if the content of Pd exceeds 40 percent by weight, the melting point of the sintering assistant agent
5 tends to increase, degrading sintering property of the diamond powder. In other words, the content of Pd in the sintering assistant agent is preferably within the range from 0.01 to 40 percent by weight.

Further, the sintering assistant agent should
10 preferably be included by at least 4 percent by weight when the coated diamond powder coated with the sintering assistant agent is to be sintered, in order to prevent shortage of the sintering assistant agent, which shortage substantially makes sintering of diamond powder
15 impossible. On the other hand, the content of sintering assistant agent should preferably be 20 percent by volume at most, since wear-resistance of the sintered body is remarkably degraded as the diamond content lowers if the sintering assistant agent in the diamond sintered body
20 exceeds 20 percent by volume.

Similarly, when sintering of coated diamond powder is to be performed with additional sintering assistant agent brought into contact with the powder compact body of the coated diamond powder, the amount of sintering assistant
25 agent coating the diamond particle should preferably be at



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least 0.1 percent by volume. The reason for this is that if the amount of coating of the sintering assistant agent is smaller than 0.1 percent by volume, uniform coating by the sintering assisting agent on the surface of the diamond particle becomes difficult, making uniform infiltration of the additional sintering assistant agent impossible. On the other hand, the amount of coating of the sintering assistant agent should preferably be at most 19.9 percent by volume. The reason for this is that after sintering while infiltrating additional sintering assistant agent, if the sintering assistant agent in the sintered body exceeds 20 percent by volume, diamond content is lowered, and hence wear-resistance of the sintered body is significantly degraded.

As a method of providing coating of the sintering assistant agent on each particle of the diamond powder, CVD method, PVD method or solution precipitation method may be possible. However, electroless plating method is most preferably used, from economical view and from the consideration that uniformity of the sintering assistant agent coating the surface of the diamond particle plays a very important part in improving the sintering property of the powder and in the strength of the sintered body.

When the sintering assistant agent is to be precipitated on the surface of diamond particle by



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electroless plating, mixing of impurity in the sintering assistant agent should be prevented as much as possible, in order to obtain high diamond content after sintering. Considering the fact that catalytic nuclei having high
5 catalytic action must exist on the surface of the diamond particle in the initial reaction of electroless plating, it is preferable that Pd exhibiting not only the function of a sintering assistant agent but also the catalytic action be coated first on the surface of the diamond
10 particle. It was found that by providing coating of a sintering assistant agent including at least one of Fe, Co and Ni with Pd serving as catalytic nucleus, coated diamond particle coated with sintering assistant agent with smaller impurity can be obtained.

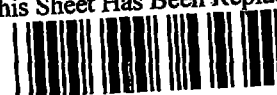
15 Here, it is desired that the amount of precipitation of Pd on the surface of the diamond particle is at least 10^{-4} percent by weight. The reason for this is that if catalytic action is insufficient, electroless plating reaction becomes insufficient, making it difficult to
20 provide coating of the sintering assistant agent. On the other hand, the amount of precipitation of Pd should desirably be 40 percent by weight at most. The reason for this is to prevent degradation of sintering property, which is caused by elevated melting point of the sintering
25 assistant agent caused by excessive Pd.



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Further, it was found that if the sintering assistant agent includes at least one of Sn, P and B in addition to the iron family metal, Sn, P or B serves to lower the melting point of the sintering assistant agent,
5 significantly improving sintering property of the diamond powder coated by the sintering assistant agent.

As for precipitation of P in addition to the iron family element, a sintering assistant agent having a desired P concentration can be precipitated by using a
10 hypophosphite, for example sodium hypophosphite as a reducing agent in the electroless plating solution, and by adjusting concentration of the reducing agent in the plating solution, pH of the plating solution and temperature during plating. Similarly, for precipitation
15 of B in addition to the iron family element, a sintering assistant agent having a desired B concentration can be precipitated by using a boron hydride compound such as sodium borohydride, as the reducing agent in the electroless plating solution, and by adjusting
20 concentration of the reducing agent in the plating solution, pH of the plating solution and the temperature during plating. Meanwhile, Sn has superior absorption property with respect to the surface of the diamond powder particle. Therefore, it can be directly absorbed to the
25 diamond particle surface from a tin chloride solution, for



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example. Further, precipitation of Pd serving as the catalytic nucleus after absorption of Sn onto the diamond particle surface as pre-processing for electroless plating (sensitizing activating method) or precipitation of Sn and
5 Pd simultaneously (catalyst accelerating method) is preferable, since it promotes absorption of Pd at the surface of the diamond particles.

At this time, if the total content of Sn, P and B in the sintering assistant agent is smaller than 0.01 percent
10 by weight, the effect of lowering the melting point of the sintering assistant agent cannot be obtained. By contrast, if it exceeds 30 percent by weight, melting of diamond to the iron family metal which serves as solvent metal in the sintering assistant agent at the time of
15 sintering is hindered, so that the binding strength between diamond particles with each other becomes lower, degrading strength of the sintered body, and degrading thermal properties of the sintered body. The total content of Sn, P and B should more preferably be within
20 the range of 0.01 to 11.5 percent by weight.

When the diamond particle is to be coated with the sintering assistant agent by electroless plating, the iron family element precipitated by electroless plating is, in most cases, precipitated as an oxide. If sintering is
25 performed using sintering assistant agent including an



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oxide, oxygen derived from the oxide may possibly generate voids in the sintered body, and it may hinder melting and precipitation reaction of diamond in the sintering assistant agent serving as the solvent. Therefore, it may
5 degrade the property of the diamond sintered body. In order to prevent such undesirable effect by oxygen, the coated diamond powder after electroless plating should preferably be reduced by heat treatment in vacuum or in hydrogen atmosphere.

10 It was found that when electroless plating is performed on the diamond powder, the diamond powder can be coated uniformly by the sintering assistant agent if the plating solution including the diamond powder is fluctuated by at least one of stirring and ultrasonic
15 vibration.

Further, in order to obtain diamond sintered body having higher density, it is preferable to perform heat treatment at high temperature on the diamond powder under such condition that makes diamond instable so that the
20 diamond particles are partially turned to graphite from the surface, to coat the partially graphitized diamond particle with the sintering assistant agent and to perform sintering thereafter, or to coat the diamond powder with the sintering assistant agent, to turn the coated diamond
25 particle into graphite partially from the surface and then

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perform sintering. The reason for this is as follows.
Diamond powder is not susceptible to plastic deformation.
Therefore, even under high pressure, spaces tend to remain
between diamond particles. However, if the surface of the
5 diamond particle is turned into graphite, the graphite
portion is more susceptible to plastic deformation, and
hence density of the sintered body can be substantially
improved. Further, considering melting of carbon and re-
precipitation in the sintering assistant agent during
10 sintering, speed of reaction of graphite is faster than
that of diamond, and hence sintering property is improved
if the diamond surface is turned into graphite.

From these reasons, it would be understood that
diamond sintered body having higher density could be
15 obtained if the diamond surface is partially turned to
graphite. At this time, if the ratio of graphitization of
diamond particle is smaller than 0.5 percent by volume,
density of the sintered body is hardly improved.
Meanwhile, if the ratio of graphitization of diamond
20 particle exceeds 80 percent by volume, turning of graphite
to diamond during sintering under such high pressure and
high temperature that keeps diamond stable becomes
imperfect, resulting in graphite left in the diamond
sintered body. Therefore, preferable range of partial
25 graphitization of diamond particle is 0.5 to 80 percent by



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volume.

Now, if the above described diamond sintered body is to be obtained, it is possible that various materials are mixed in small quantity. For example, the coated diamond powder is generally filled in a container formed of a cemented carbide or a refractory metal and sintered. Therefore, W, Ta, Mo, Cr which are the components of the container or carbide thereof may possibly be mixed in the sintered body. However, even if such material is mixed in the sintered body, such material does not cause any problem provided that diamond content in the sintered body is within the range of 80 to 96 percent by volume.

Similarly, even when additional sintering assistant agent is brought into contact with the powder compact body as supplement to the sintering assistant agent in the coated diamond powder and infiltrated to the powder compact body during sintering, it does not cause any problem provided that the diamond content of the sintered body is within the range of 80 to 96 percent by volume. As for the composition of additional sintering assistant agent arranged in contact with such powder compact body, similar compositions as those for the sintering assistant agent used for coating of the diamond particle may be used.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

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(Embodiment 1)

Table 1

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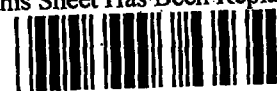
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Powder sample	Diamond particle size (μm)	Method of applying sintering assistant agent	Content of sintering assistant agent (vol.%)	Composition of sintering assistant agent (wt.%)
1A	0.1 - 4	electroless plating	6.0	92.9-Co, 0.05-Pd, 3.95-Fe, 3-P, 0.1-Sn
1B	0.1 - 4	electroless plating	13.0	92.9-Co, 0.05-Pd, 3.95-Fe, 3-P, 0.1-Sn
1C	0.1 - 4	electroless plating	26.0	92.9-Co, 0.05-Pd, 3.95-Fe, 3-P, 0.1-Sn
1D	0.1 - 4	PVD	6.0	92.9-Co, 0.05-Pd, 3.95-Fe, 3-P, 0.1-Sn
1E	0.1 - 4	PVD	13.0	92.9-Co, 0.05-Pd, 3.95-Fe, 3-P, 0.1-Sn
1F	0.1 - 4	PVD	26.0	92.9-Co, 0.05-Pd, 3.95-Fe, 3-P, 0.1-Sn
1G	0.1 - 4	mixing ultra fine powder	6.0	100-Co
1H	0.1 - 4	mixing ultra fine powder	13.0	100-Co
1I	0.1 - 4	mixing ultra fine powder	26.0	100-Co
1J	0.1 - 4	cemented carbide ball mill	6.0	25-Co, 75-WC
1K	0.1 - 4	cemented carbide ball mill	13.0	25-Co, 75-WC
1L	0.1 - 4	cemented carbide ball mill	26.0	25-Co, 75-WC

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Table 1 shows various powder samples prepared for studying influence mainly of the method of applying sintering assistant agent, content and composition on mechanical properties of the diamond sintered body. More



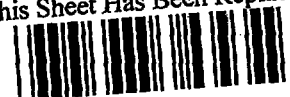
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specifically, powder samples 1A to 1L shown in Table 1 are all raw material diamond powders having the particle size within the range of 0.1 to 4 μm , while the method of applying sintering assistant agent, content and composition are changed variously.

For the samples 1A, 1B and 1C, the following process was performed to coat diamond powder particles by the sintering assistant agent by electroless plating. First, diamond powder was degreased in alcohol. The degreased diamond powder was cleaned in flowing water, cleaned in hydrochloric acid solution of 5 percent by weight, and then again cleaned in flowing water. The diamond powder thus cleaned was immersed for one minute in a solution including stannous chloride and hydrochloric acid in room temperature as pre-processing, so as to cause absorption of Sn at the surface of the diamond particles (sensitizing). The sensitized diamond powder was washed by water and thereafter immersed for one minute in hydrochloric acid solution containing palladium chloride at a room temperature, and thus Pd was precipitated at the surface of the diamond particles (activated).

The activated diamond powder was washed by water, and thereafter immersed for a prescribed time period in a Co-Fe-P electroless plating solution held at 75°C, containing cobalt sulfate, iron sulfate and sodium hypophosphite.

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The longer the time of immersion in the electroless plating solution, the larger the amount of sintering assistant agent coating the surface of the diamond particle, and the larger the content of the sintering assistant agent in the powder samples. In the step of electroless plating, the pre-plating solution and plating solution were stirred and at the same time, subjected to ultrasonic vibration. The coated diamond powder which was subjected to electroless plating in this manner was cleaned, the surface of diamond particles was partially graphitized by heat treatment in vacuum at 1000 °C for 60 minutes, and collected, whereby the coated powder samples 1A to 1C having such content and composition of the sintering assistant agent as shown in Table 1 were obtained.

For the samples 1D to 1F, the sintering assistant agent has the same composition as those for the samples 1A to 1C. However, coating of the sintering assistant agent was performed in accordance with an arc ion plating method. More specifically, the sintering assistant agent is applied to the surface of diamond powder particles by arc ion plating method in which a target corresponding to the composition of the sintering assistant agent and a bias voltage of 350 V were used in an argon atmosphere of 1×10^{-2} torr.

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For samples 1G to 1I, ultra fine Co powder having the particle size of 500 Å was used as the sintering assistant agent. Diamond powder and ultra fine Co powder corresponding to the prescribed content were put in a ball mill container formed of Teflon which contains mixing balls formed of Teflon. The powders were mixed for 4 hours, whereby the mixed powder samples 1G to 1I were obtained.

In preparing the samples 1J to 1L, diamond powder was put in a ball mill having mixing balls and a container formed of cemented carbide WC-Co and the ball mill was driven for a prescribed time period. During the driving of the cemented carbide ball mill, the cemented carbide powder scraped off from the mixing balls and the container were mixed as sintering assistant agent to the diamond powder. The content of the cemented carbide powder mixed in the diamond powder can be adjusted by changing the time of driving the cemented carbide ball mill.

The powder samples 1A to 1L shown in Table 1 were each sealed in a container formed of tantalum, kept at a pressure of 50 kb at a temperature 1400°C for 10 minutes by using a belt type high pressure apparatus, and thus sintered. Table 2 shows diamond content and wear-resistance of the diamond sintered body samples obtained in this manner.

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Table 2

Sintered body sample	Diamond content (vol.%)	Flank wear (μm)
2A	93.8	31
2B	86.9	65
2C	74.2	131
2D	92.3	damaged
2E	86.8	damaged
2F	73.9	damaged
2G	sintering not possible	
2H	86.7	damaged
2I	74.0	damaged
2J	sintering not possible	
2K	sintering not possible	
2L	73.9	142

Sintered body samples 2A to 2L of Table 2 are obtained by sintering powder samples 1A to 1L shown in Table 1. As can be seen from Table 2, in samples 2G, 2J and 2K, the amount of sintering assistant agent is small and distribution thereof is not uniform. Since uniform melting of sintering assistant agent did not occur entirely in the diamond powder, sintering was insufficient, and hence complete sintered body could not be obtained.

Meanwhile, samples providing complete sintered bodies were processed to be cutting tools, and performance was



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evaluated under the following cutting conditions.

Work piece: a round bar of Al-16 wt % Si having six grooves on the surface along the axial direction.

Peripheral surface velocity of the work piece: 500

5 (m/min)

Byte cutting depth: 0.6 (mm)

Byte feeding speed: 0.12 (mm/rev)

Cutting time: 3 (min)

The flank wear of the tools as a result of cutting
10 test were as shown in Table 2. As can be seen from Table
2, sintering is possible in sintered body samples 2A and
2B in accordance with the present invention even when the
amount of sintering assistant agent is small. Therefore,
tools having high diamond content and superior
15 wear-resistance can be obtained. Further, since the
sintered body samples 2A and 2B have uniform sintered body
texture, they have high strength, and it becomes apparent
that they have good damage resistance as cutting tools.

By contrast, it is apparent that sintered body
20 samples 2C and 2L having low diamond content are inferior
in wear-resistance. Of the sintered body textures of
samples 2D, 2E, 2F, 2H and 2I, uneven distribution of
sintering assistant agent generated in the PVD method or
Co pools derived from aggregation of ultra fine Co powder
25 were observed, which pools lowered strength and hence

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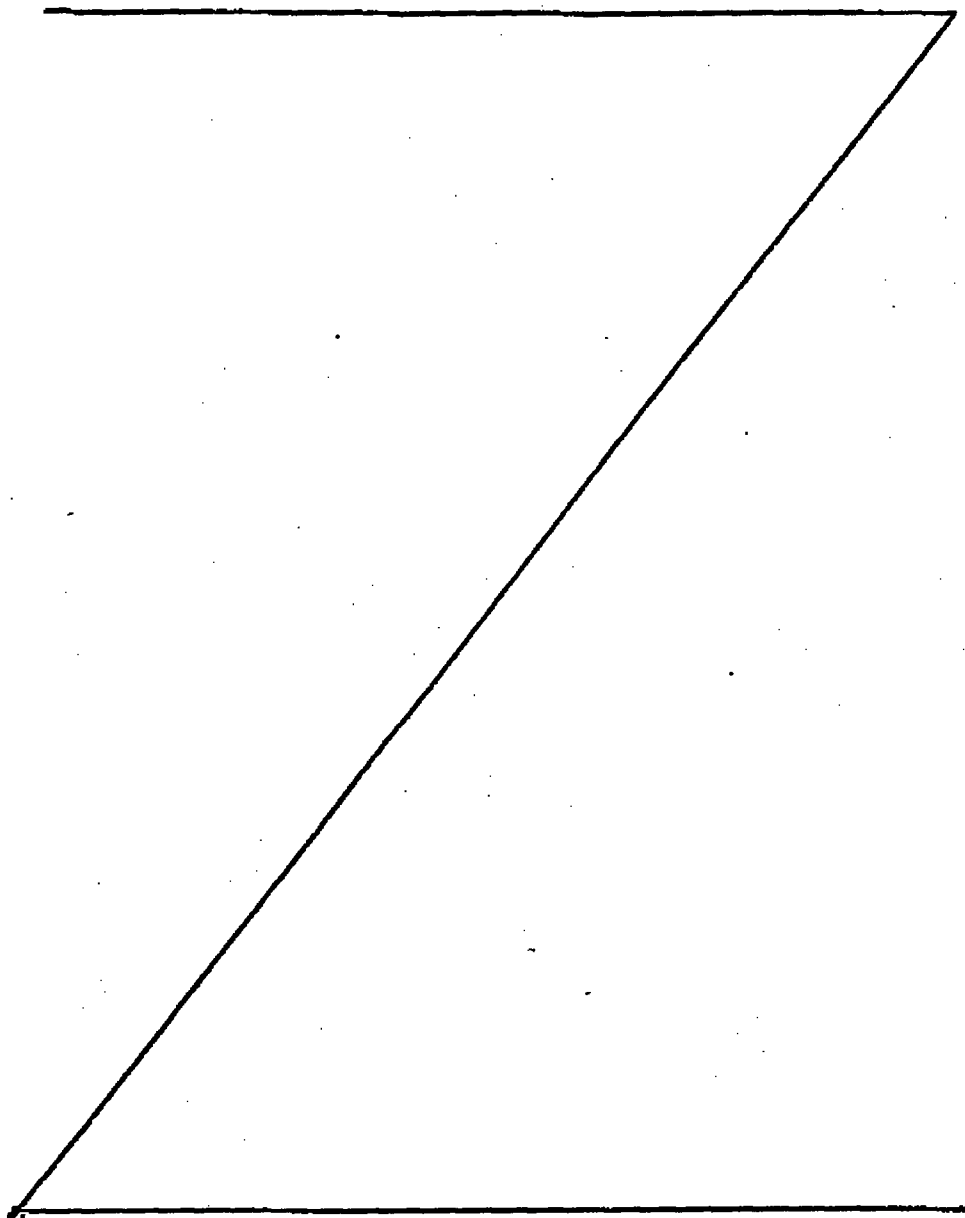


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caused damages to the sintered body during cutting. Thus
the sintered bodies could not be used as the cutting
tools.

(Embodiment 2)

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Table 3

Powder sample	Diamond particle size (μm)	Method of applying sintering assistant agent	Fluctuation of plating solution	Content of sintering assistant agent (vol.%)	Composition of sintering assistant agent (wt.%)
3A	1-2	electroless plating	stirring + ultrasonic vibration	9	97-Ni, 0.5-Pd, 2-P, 0.5-Sn
3B	1-2	electroless plating	stirring + ultrasonic vibration	9	89-Ni, 0.5-Pd, 10-P, 0.5-Sn
3C	1-2	electroless plating	stirring + ultrasonic vibration	9	64-Ni, 0.5-Pd, 35-P, 0.5-Sn
3D	1-2	electroless plating	not fluctuated	9	97-Ni, 0.5-Pd, 2-P, 0.5-Sn
3E	1-2	electroless plating	not fluctuated	9	89-Ni, 0.5-Pd, 10-P, 0.5-Sn
3F	1-2	electroless plating	not fluctuated	9	64-Ni, 0.5-Pd, 35-P, 0.5-Sn
3G	1-2	mixing ultra fine powder	-	9	100-Ni

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Table 3 shows various powder samples prepared for studying influence of the method of applying sintering assistant agent, composition and conditions of electroless plating on mechanical properties of the sintered bodies.

5 For samples 3A to 3C, the surface of diamond particles was partially graphitized by heat treatment in vacuum at 1450 °C for 30 minutes, then diamond powders were degreased and subjected to acid cleaning in the similar manner as Table 1 and thereafter the diamond
10 powders were subjected to surface activation, in order to coat the diamond powder particles by sintering assistant agent by electroless plating. Thereafter, the diamond powders were immersed in an Ni-P electroless plating solution containing nickel sulfate and sodium hypophosphite
15 and held at 60°C. During the step of electroless plating, the pre-plating solution and the plating solution were fluctuated by stirring and ultrasonic vibration. The composition of the sintering assistant agent was adjusted by changing pH of the plating solution.

20 Samples 3D to 3F were prepared by electroless plating similar to samples 3A to 3C. However, fluctuation by stirring and ultrasonic vibration was not applied to the electroless plating solution.

25 As for sample 3G, diamond powder was put in a ball mill container formed of Teflon containing mixing balls

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formed of Teflon, together with ultra fine Ni powder having the powder size of 200 Å, and mixed for 4 hours.

The powder samples of Table 3 were each sealed in a container of Mo and sintered for 15 minutes at a pressure of 45 kb at a temperature of 1350°C by using a belt type high pressure apparatus. Various properties of the sintered body samples obtained in this manner are as shown in Table 4.

Table 4

Sintered body sample	Diamond content (vol.%)	Composition of sintering assistant agent after sintering (wt.%)	Three point bending strength (kg/mm ²)
4A	90.9	97-Ni, 0.5-Pd, 2-P, 0.5-Sn	263
4B	90.8	89-Ni, 0.5-Pd, 10-P, 0.5-Sn	254
4C	90.9	64-Ni, 0.5-Pd, 35-P, 0.5-Sn	193
4D	90.7	97-Ni, 0.5-Pd, 2-P, 0.5-Sn	179
4E	90.8	89-Ni, 0.5-Pd, 10-P, 0.5-Sn	164
4F	90.9	64-Ni, 0.5-Pd, 35-P, 0.5-Sn	142
4G	sintering not possible		

The sintered body samples 4A to 4G shown in Table 4 were obtained from powder samples 3A to 3G of Table 3. However, similar to the sample 2B of Table 2, locally unsintered regions were generated in sample 4G, and complete sintered body could not be obtained.

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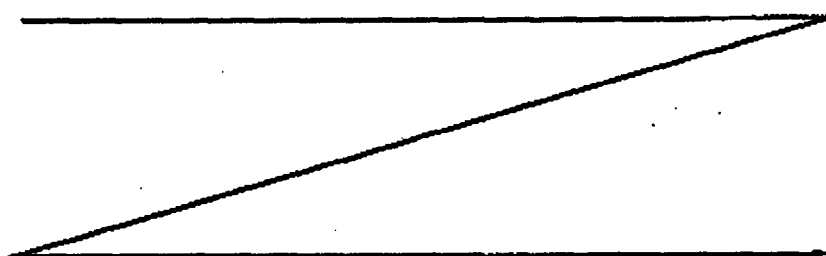


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The samples from which complete sintered bodies were obtained were each processed to a bar-shaped sample piece of 6 x 3 x 0.3 mm, and thereafter strength thereof was evaluated by three point bending test with the span of 4 mm. As a result, as can be seen from Table 4, it is apparent that samples 4A to 4C have improved strengths than samples 4D to 4F. More specifically, as the plating solution was stirred and subjected to ultrasonic vibration during electroless plating of diamond powder, uniform coating of sintering assistant agent was formed on the diamond particles, defects in the diamond sintered body were reduced and hence strength of the sintered body was significantly improved.

Further, in view of the fact that samples 4A and 4B have higher strength than samples 4C and 4F, it was found that when sintering assistant agent includes P and Sn, the total content thereof should desirably be in the range of 0.01 to 30 percent by weight. Further, it was found that when the sintering assisting agent includes B, the desired content thereof is from 0.01 to 30 percent by weight.

(Embodiment 3)



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Table 5

Powder sample	Diamond particle size (μm)	Amount of coating of sintering assistant agent (vol.%)	Composition of coating sintering assistant agent (wt.%)	Composition of additional sintering assistant agent (wt.%)
5A	2-3	0.1	92.0-Ni, 7.0-Pd, 1.0-Sn	100-Ni
5B	2-3	0.1	92.0-Ni, 7.0-Pd, 1.0-Sn	98-Ni, 2-B
5C	2-3	0.1	92.0-Ni, 7.0-Pd, 1.0-Sn	89-Ni, 11-B
5D	2-3	0.1	92.0-Ni, 7.0-Pd, 1.0-Sn	79-Ni, 21-B
5E	2-3	0.1	92.0-Ni, 7.0-Pd, 1.0-Sn	66-Ni, 34-B

Table 5 shows various powder samples prepared for studying influence of composition of additional sintering assistant agent on the strength of the sintered bodies, when the additional sintering assistant agent which is brought into contact with coated diamond powder compact body is infiltrated into the powder compact body during sintering.

For samples 5A to 5E, diamond powder was degreased and subjected to acid cleaning in the similar manner as Table 1, to coat the diamond powder particles by the sintering assistant agent by electroless plating. Thereafter, catalysing was performed as pre-processing of electroless plating, by immersing the diamond powder in a solution containing palladium chloride, stannous chloride and hydrochloric acid for two minutes at a room

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temperature. Thereafter, accelerating of the diamond powder was performed by immersing the powder in a sulfuric acid solution for two minutes at a room temperature.

5 The pre-processed powders were washed by water, and thereafter immersed for two minutes in an Ni-B plating solution including nickel sulfate and sodium borohydride at 90°C, and thus coated diamond powders including the coating sintering assistant agent having such compositions and amounts as shown in Table 5 were obtained. During
10 these steps of alkali degreasing, acid cleaning, pre-processing and plating, while the diamond powders are immersed in the solutions, the solutions were fluctuated by stirring and ultrasonic vibration.

The coated diamond powders were molded into powder
15 compact bodies, and metal plates having such compositions as shown in Table 5 were stacked as additional sintering assistant agent and sealed into a container of Ta. The Ta container was held at a pressure of 60 kb at a temperature of 1550 °C for 10 minutes by using a girdle type high
20 pressure apparatus, and sintered body samples such as shown in Table 6 were obtained.

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Table 6

Sintered body sample	Diamond content (vol.%)	Total content of Sn and B in sintering assistant agent (wt.%)	Strength of sintered body (kgf/mm ²)
6A	85	0.005	197
6B	85	1.99	234
6C	85	11.0	222
6D	85	20.9	208
6E	85	33.8	135

The sintered body samples 6A to 6E shown in Table 6 were obtained from powder samples 5A to 5E of Table 5.

Each of the sintered body samples was processed to a bar-shaped sample piece of 6 x 3 x 0.3 mm, and strength thereof was evaluated by three point bending test with the span of 4 mm.

As can be seen from Table 6, it is apparent that samples 6B, 6C and 6D have improved strength than samples 6A and 6E. More specifically, it can be understood that when the additional sintering assistant agent includes B, the content should preferably be in the range of 0.01 to 30 percent by weight. Further, it was found that if the additional sintering assistant agent includes P and Sn, the preferable content thereof is from 0.01 to 30 percent by weight.

(Embodiment 4)

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**THIS SHEET HAS BEEN
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15

Powder sample	Diamond particle size (μm)	Method of applying sintering assistant agent	Content of sintering assistant agent (vol.%)	Composition of sintering assistant agent (wt.%)
7A	1 - 2	electroless plating	5.0	99.6-Co, 0.1-Pd, 0.3-Sn
7B	2 - 8	electroless plating	5.0	99.6-Co, 0.1-Pd, 0.3-Sn
7C	5 - 15	electroless plating	5.0	99.6-Co, 0.1-Pd, 0.3-Sn
7D	1 - 2	CVD	5.0	99.6-Co, 0.1-Pd, 0.3-Sn
7E	2 - 8	CVD	5.0	99.6-Co, 0.1-Pd, 0.3-Sn
7F	5 - 15	CVD	5.0	99.6-Co, 0.1-Pd, 0.3-Sn
7G	1 - 2	mixing ultra fine powder	5.0	100-Co
7H	2 - 8	mixing ultra fine powder	5.0	100-Co
7I	5 - 15	mixing ultra fine powder	5.0	100-Co
7J	1 - 2	cemented carbide ball mill	5.0	15-Co, 85-WC
7K	2 - 8	cemented carbide ball mill	5.0	15-Co, 85-WC
7L	5 - 15	cemented carbide ball mill	5.0	15-Co, 85-WC

20

Table 7 shows various powder samples prepared for studying influence of the raw material diamond particle size, method of applying sintering assistant agent and composition on mechanical properties of the sintered bodies.



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For samples 7A to 7C, catalytic layer for electroless
plating was applied to the surface of diamond powder
particles in the similar manner as in Embodiment 3 so as
to coat the diamond powders with sintering assistant agent
5 by electroless plating.

The pre-processed diamond powder was washed by water,
and thereafter immersed in a Co electroless plating
solution containing cobalt chloride and hydrazinium
chloride and held at 80°C, and thus Co coating was
10 provided on the surface of diamond particles. During pre-
processing related to electroless plating and during
plating, the solutions together with diamond powder were
fluctuated by stirring and ultrasonic vibration. The
electroless plated diamond powder was washed and
15 collected, thereafter heated in vacuum at 1250°C for 60
minutes, so that the sintering assistant agent was reduced
and diamond particles were partially graphitized from the
surface. As a result, powder samples 7A to 7C having such
content and composition of sintering assistant agent as
20 shown in Table 7 were obtained. The amount of oxygen
contained in the powders of samples 7A to 7C was 0.05
percent by weight.

*b3mOW

For samples 7D to 7F, coated diamond powders having
the same composition of sintering assistant agent as
25 samples 7A to 7C were fabricated by using microwave plasma

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CVD method.

For samples 7G to 7I, diamond powders were put together with ultra fine Co powder into a ball mill container formed of Teflon including mixing balls of Teflon, and mixed for three hours. For samples 7J to 7L, diamond powders were put in cemented carbide ball mill container including mixing balls formed of cemented carbide, and the cemented carbide ball mill was driven for a prescribed time period, so that diamond powders mixed with cemented carbide powder were obtained. As already described, the cemented carbide powder was scraped off from the cemented carbide balls and the container and mixed with the diamond powders.

Each of the powder samples 7A to 7L shown in Table 7 was molded to a powder compact body, and a Co plate was stacked on the powder compact body and the powder compact body with the plate stacked was sealed in a container of cemented carbide. The cemented carbide container was held at a pressure of 50 kb at a temperature of 1500°C for 15 minutes by a belt type high pressure apparatus, so that the stacked Co plate was melt and infiltrated in the powder compact body during sintering, and as a result, sintered body samples such as shown in Table 8 were obtained.

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Table 8

Sintered body sample	Diamond content (vol.%)	Composition of sintering assistant agent after sintering (wt.%)	Flank wear (μm)
8A	86.9	99.88-Co, 0.03-Pd, 0.09-Sn	88
8B	88.3	99.85-Co, 0.04-Pd, 0.11-Sn	67
8C	90.2	99.93-Co, 0.02-Pd, 0.05-Sn	blade chipping
8D	86.7	99.88-Co, 0.03-Pd, 0.09-Sn	damaged
8E	87.9	99.85-Co, 0.04-Pd, 0.11-Sn	damaged
8F	90.3	99.93-Co, 0.02-Pd, 0.05-Sn	damaged
8G	sintering not possible		
8H	87.1	100Co	damaged
8I	90.0	100Co	damaged
8J	79.6	57.7-Co, 42.3-WC	211
8K	79.8	48.3-Co, 51.7-WC	153
8L	88.3	35.5-Co, 64.5-WC	blade chipping

The sintered body samples 8A to 8L shown in Table 8 were obtained from powder samples 7A to 7L of Table 7.

In sample 8G, since the raw material diamond powder has fine particles as shown in Table 7, space between particles is narrow and mixed Co powder is not uniformly distributed. Therefore, when Co plate was stacked on the powder compact body of the mixed powder for infiltration, infiltration proceeded unevenly in the powder compact body. As a result, unsintered portions were generated partially in sample 8G and complete sintered body could



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not be obtained.

Samples providing complete sintered bodies were processed to cutting tools, and performance thereof was evaluated under the following cutting conditions.

5 Work piece: round bar of Al-10 wt % Si having four grooves along the axial direction

Peripheral surface velocity of the work piece: 500 (m/min)

Byte cutting depth: 1.5 (mm)

10 Byte feeding speed: 0.2 (mm/rev)

Cutting time: 160 (min)

Table 8 shows flank wear of sintered body samples as a result of cutting test. As can be seen from Table 8, sintered body samples 8D, 8E, 8F, 8H and 8I including
15 pools of sintering assistant agent were damaged at initial stage of cutting and continuous cutting was impossible. In sintered body samples 8C and 8L having large diamond particle size, chipping was observed at the blade of the tool during cutting test. As for sintered body samples 8J
20 and 8K having low diamond content, though there was not a damage, the flank wear was too large to be practical.

Meanwhile, sintered body samples 8A and 8B in accordance with the present invention had small diamond particle size, and uniform sintered body texture without
25 void or Co pool could be obtained, and hence the sintered



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bodies had high strength and free of chipping or damage.
In addition, it becomes apparent that samples 8A and 8B
have sufficient wear-resistance as shown in Table 8, since
they have sufficiently high diamond content.

5 (Embodiment 5)

Table 9

10

Powder sample	Conditions for heat treatment of diamond powder	Amount of coating of sintering assistant agent (vol.%)	Conditions for heat treatment of coated diamond powder	Degree of graphitization (vol.%)
9A	1400°C, 60 min.	4	heat treatment not performed	5.3
9B	1450°C, 60 min.	4	heat treatment not performed	52.6
9C	1500°C, 60 min.	4	heat treatment not performed	93.8
9D	heat treatment not performed	4	heat treatment not performed	0
9E	heat treatment not performed	4	1200°C, 60 min.	5.2
9F	heat treatment not performed	4	1350°C, 60 min.	32.1

15

20 Table 9 shows various powder samples prepared for
studying influence of the degree of graphitization of
diamond powder on diamond content in the sintered body.

In samples 9A to 9C, raw material diamond powders
having the particle size of 5 to 10 μ m was heat treated in
vacuum under the conditions shown in Table 9 so as to
25 partially graphitize the powders from the surface of the

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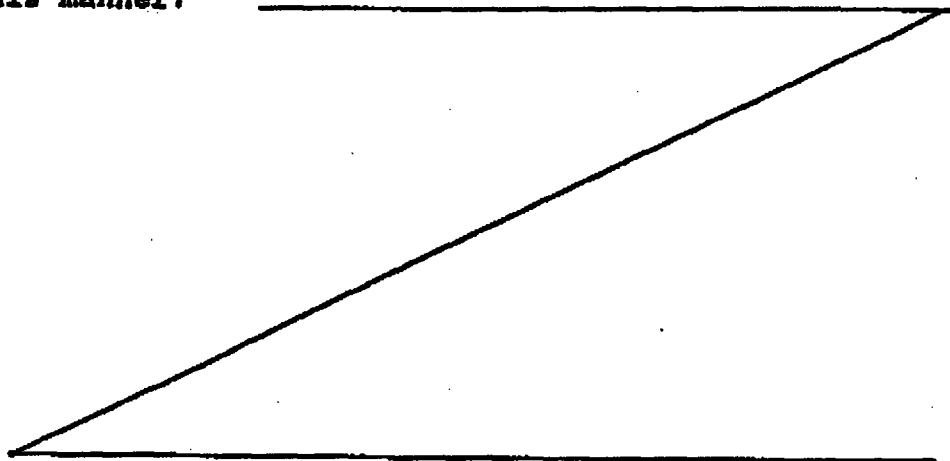


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particles. The partially graphitized diamond particles were coated by the sintering assistant agent in the similar manner as Embodiment 1.

5 In samples 9D to 9F, raw material diamond powder particles having the particle size of 5 to 10 μm were coated by the sintering assistant agent in the similar manner as in Embodiment 1, and thereafter the coated diamond particles were partially graphitized from the surface under the heat treatment conditions shown in Table
10 9 in vacuum.

The partially graphitized coated diamond powders were molded to powder compact bodies, a metal plate of 100 % Co was stacked as additional sintering assistant agent, and then the powder compact bodies were sealed in a container
15 of Mo and sintered under a pressure of 50 kb at a temperature of 1550°C for 10 minutes. Table 10 shows diamond contents of the sintered body samples obtained in this manner.



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Table 10

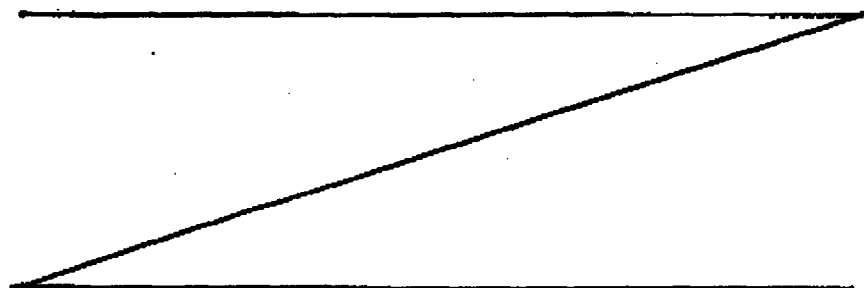
Sintered body sample	Diamond content (wt.%)
10A	94.4
10B	95.1
10C	partial sintering (Gr left)
10D	92.2
10E	94.5
10F	94.8

10

5
15 The sintered body samples 10A to 10F of Table 10 were obtained from powder samples 9A to 9F of Table 9. As can be seen from Table 10, it is apparent that sintered body samples 10A, 10B, 10E and 10F have higher diamond contents than sample 10D. Meanwhile, sample 10C partially included remaining graphite (Gr), and hence complete sintered body
20 could not be obtained.

More specifically, the degree of graphitization of the coated diamond powder should preferably be in the range of 0.5 to 50 percent by volume.

(Embodiment 6)



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Table 11

Powder sample	Diamond particle size (μm)	Amount of absorption of Pd (wt.%)	Amount of coating of sintering assistant agent (vol.%)	Composition of sintering assistant agent (wt.%)
11A	5 - 10	5×10^{-5}	not precipitated	
11B	5 - 10	8×10^{-3}	5	Pd-0.08, Co-99.82, Sn-0.1
11C	5 - 10	8×10^{-3}	5	Pd-2.7, Co-97.2, Sn-0.1
11D	5 - 10	8×10^{-3}	5	Pd-38.7, Co-61.2, Sn-0.1
11E	5 - 10	8×10^{-3}	5	Pd-52.1, Co-47.8, Sn-0.1

Table 11 shows various powder samples prepared for studying influence of the amount of application of Pd on catalytic property in electroless plating and sintering property of diamond powder at the time of sintering.

For samples 11A to 11E, Pd was applied to the surfaces of diamond particles, in the similar manner as in Embodiment 4, so as to coat diamond powder particles by sintering assistant agent by electroless plating. Thereafter, diamond powder particles were electroless-plated by Pd, using electroless plating solution including palladium tetra chloride. Further, diamond powder particles were coated by Co using an electroless plating solution containing hydrazine.

As a result, as shown in Table 11, the amount of absorption of Pd at the particles of diamond powder was too small in sample 11A, so that catalytic action by Pd



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was insufficient and Co was not successfully precipitated at the surface of the diamond particles.

Each of the powder samples 11B to 11E coated with Co was molded into powder compact body and sealed in a container formed of cemented carbide. The cemented carbide container was held under a pressure of 50 kb at a temperature of 1500°C for 15 minutes to perform sintering, by using a belt type high pressure apparatus. Sample 11E containing much Pd did not result in complete sintered body, as melting of the sintering assistant agent did not occur. Meanwhile, complete sintered bodies could be obtained from samples 11B to 11D.

In other words, the preferable content of Pd in the sintering assistant agent is within the range of 0.01 to 40 percent by weight.

As described above, according to the present invention, a diamond sintered body having both high strength and high wear-resistance can be provided, which can be preferably used for cutting tools, digging tools, drawing dices and wear-resistant parts.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.



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WHAT IS CLAIMED IS:

1. A diamond sintered body having high strength and high wear-resistance, comprising

sintered diamond particles of 80 to 96 percent by volume and a remaining part of sintering assistant agent and unavoidable impurity,

said sintered diamond particles having particle size substantially in a range of 0.1 to 10 μ m and directly bonded to each other,

said sintering assistant agent including Pd within a range of 0.01 to 40 percent by weight and as a remaining part, at least one selected from Fe, Co and Ni.

2. The diamond sintered body having high strength and high wear-resistance according to claim 1, wherein

said sintering assistant agent further includes at least one of Sn, P and B.

3. The diamond sintered body having high strength and high wear-resistance according to claim 2, wherein

said sintering assistant agent includes at least one of Sn, P and B within a range of 0.01 to 30 percent by weight.



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4. A method of manufacturing a diamond sintered body having high strength and high wear-resistance, comprising the steps of:

5 preparing diamond powder having particle size substantially within a range of 0.1 to 10 μ m;

precipitating Pd within a range of 10^{-4} to 40 percent by weight on a surface of each particle of said diamond powder, and thereafter electroless plating a sintering assistant agent including at least one of Fe, Co and Ni to
10 the surface of each particle of said diamond powder within a range of 4 to 20 percent by volume to prepare coated diamond powder; and

under a condition of high pressure and high temperature in which diamond is stable, sintering said
15 coated diamond powder in liquid-phase.

5. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 4, wherein

said sintering assistant agent further includes at
5 least one of Sn, P and B.

6. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 5, wherein



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said sintering assistant agent includes at least one
5 of Sn, P and B within a range of 0.01 to 30 percent by
weight.

7. The method of manufacturing a diamond sintered
body having high strength and high wear-resistance
according to claim 4, wherein 0.5 to 80 percent by volume
of each particle of said diamond powder is graphitized
5 from its surface by heat treatment at a high temperature
condition in which diamond is instable, and thereafter
said sintering assistant agent is applied as coating.

8. The method of manufacturing a diamond sintered
body having high strength and high wear-resistance
according to claim 4, wherein 0.5 to 80 percent by volume
of each particle of said coated diamond powder is
5 graphitized from its surface by heat treatment at a high
temperature condition in which diamond is instable, and
thereafter said sintering in liquid-phase is performed.

9. The method of manufacturing a diamond sintered
body having high strength and high wear-resistance
according to claim 4, wherein

during said electroless plating, plating solution to
5 which said diamond powder is immersed is fluctuated by at



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least one of stirring and ultrasonic vibration.

10. A method of manufacturing a diamond sintered body having high strength and high wear-resistance, comprising the steps of:

5 preparing diamond powder having particle size substantially in a range of 0.1 to 10 μm ;

precipitating Pd in a range of 10^{-4} to 40 percent by weight on a surface of each particle of said diamond powder and thereafter electroless plating a sintering assistant agent including at least one of Fe, Co and Ni to
10 the surface of each particle of said diamond powder within a range of 0.1 to 19.9 percent by volume to prepare coated diamond powder;

molding a powder compact body of said coated diamond powder;

15 bringing into contact an additional sintering assistant agent including at least one of Pd, Fe, Co and Ni to said powder compact body; and

sintering said powder compact body in liquid-phase while infiltrating said additional sintering assistant
20 agent under a condition of high pressure and high temperature in which diamond is stable.

11. The method of manufacturing a diamond sintered

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body having high strength and high wear-resistance
according to claim 10, wherein

5 said sintering assistant agent coating said diamond
particle further includes at least one of Sn, P and B.

12. The method of manufacturing a diamond sintered
body having high strength and high wear-resistance
according to claim 11, wherein

5 said sintering assistant agent coating said diamond
particle includes at least one of Sn, P and B within a
range of 0.01 to 30 percent by volume.

13. The method of manufacturing a diamond sintered
body having high strength and high wear-resistance
according to claim 10, wherein

5 0.5 to 80 percent by volume of each particle of said
diamond powder is graphitized from its surface by heat
treatment under a high temperature condition in which
diamond is instable, and thereafter said sintering
assistant agent is applied as coating.

14. The method of manufacturing a diamond sintered
body having high strength and high wear-resistance
according to claim 10, wherein 0.5 to 80 percent by volume
of each particle of said coated diamond powder is



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5 graphitized from its surface by heat treatment at a high temperature condition in which diamond is instable and thereafter said sintering in liquid-phase is performed.

15. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 10, wherein

said additional sintering assistant agent further
5 includes at least one of Sn, P and B.

16. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 15, wherein

said additional sintering assistant agent further
5 includes at least one of Sn, P and B within a range of 0.01 to 30 percent by weight.

17. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 10, wherein

in said electroless plating, plating solution to
5 which said diamond powder is immersed is fluctuated by at least one of stirring and ultrasonic vibration.

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ABSTRACT OF THE DISCLOSURE

A method of manufacturing a diamond sintered body includes the steps of preparing diamond powder having particle size within a range of 0.1 to 10 μm , coating the
5 surface of each particle of the diamond powder by a sintering assistant agent including Pd within a range of 0.01 to 40 percent by weight and at least one of an iron family metal as remaining part, and sintering the coated
10 diamond powder in liquid-phase under high pressure and high temperature condition, so that a diamond sintering body having high strength and high wear-resistance containing diamond particles of 80 to 96 percent by volume can be obtained.



TITLE OF THE INVENTION

Diamond Sintered Body Having High Strength and High
Wear-Resistance and Manufacturing Method Thereof

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to a diamond sintered
body used as a material for cutting tools, digging tools,
drawing dies, wear-resistant parts and the like and
manufacturing method thereof. More particularly, it
10 relates to a diamond sintered body having improved
strength and wear-resistance and to the manufacturing
method thereof.

Description of the Related Art

A diamond sintered body generally has superior
15 wear-resistance and higher strength as compared with other
materials. Therefore, it is used in such a field that
requires strength and wear-resistance, e.g. the field of
cutting tools, digging tools and drawing dies. Such a
diamond sintered body can be obtained by filling diamond
20 powder in a container formed of WC-Co cemented carbide,
infiltrating Co-W-C eutectic composition liquid-phase from
the cemented carbide base material into the diamond powder
under high pressure at high temperature and by sintering
the same, as disclosed, for example, in Japanese Patent
25 Publication No. 52-12126. Alternatively, as disclosed in

Japanese Patent Laying-Open No. 54-114513, a diamond sintered body can be obtained by premixing diamond powder with powder containing an iron family solvent metal, and by holding the mixed powder at such high temperature and high pressure that allows provision of diamond.

The diamond sintered body obtained through the above described methods suffers from the problem under difficult conditions of sintering. For example, if the diamond particles are too fine or if the solvent metal to be mixed is too small in amount, sintering would be impossible as the solvent metal hardly infiltrates, or the coagurated portions of diamond particles would not be sintered locally, as portions in contact with each other of the diamond particles increase. Accordingly, it is not easy to obtain diamond sintered body having high density, that is, a diamond sintered body having good wear-resistance and high content of diamond.

In order to solve such a problem, a method to obtain a diamond sintered body having high density has been proposed, for example, in Japanese Patent Laying-Open Nos. 63-190756 and 6-32655, and in Research Report No. 58, pp. 38 to 48 of National Institute for Research in Inorganic Materials, in which method a sintering assistant agent is applied, as coating, to the surface of each particle of diamond powder and the coated diamond powder is sintered.

The diamond sintered body obtained through this method has high diamond content, and therefore it has good wear-resistance. However, when the diamond particle size in the sintered body is large, the strength of the diamond sintered body becomes low, and therefore it does not have sufficient reliability for practical use. Further, when the diamond sintered body having high density is to be obtained by such a method, only a small amount of sintering assistant agent can be added. Therefore, depending on the composition of the sintering assistant agent and on the manner of coating, of the temperature range and pressure range allowing production of diamond, relatively high temperature and high pressure are required. In such a case, there would be large strain remaining in the diamond sintered body, which degrades strength of the diamond sintered body, and hence lowers reliability in practical use.

In order to prevent degradation of diamond sintered body at a high temperature, a method has been proposed, for example, in Japanese Patent Laying-Open No. 6-6769 in which the surface of diamond particles is coated by transition metal, B or Si and the coated diamond powder is sintered in solid-phase. However, in this case it is considered that diamond particles are bonded with coating material which is carbonized by solid-phase reaction

interposed. Therefore, the diamond sintered body obtained by liquid-phase sintering employing as a solvent an iron family metal allowing direct bonding between diamond particles with each other is superior in view of mechanical strength.

SUMMARY OF THE INVENTION

In view of the above described problems of the prior art, an object of the present invention is to provide a diamond sintered body having high strength and high wear-resistance and to manufacturing method thereof.

The diamond sintered body having high strength and high wear-resistance in accordance with one aspect of the present invention includes sintered diamond particles of 80 to 96 percent by volume, and a remaining part of sintering assistant agent and unavoidable impurity, the sintered diamond particles having particle size substantially in the range of 0.1 to 10 μm and directly bonded to each other, the sintering assistant agent including Pd within the range of 0.01 to 40 percent by weight, and as a remaining part, including at least one selected from Fe, Co and Ni.

In the diamond sintered body in accordance with the first aspect of the present invention, since fine diamond particles are sintered with high density in the presence of sintering assistant agent including iron family

element, high strength and high wear-resistance can be realized.

According to a second aspect, the method of manufacturing a diamond sintered body having high strength and high wear-resistance includes the steps of preparing diamond powder having particle size substantially within a range of 0.1 to 10 μm , precipitating Pd within the range of 10^{-4} to 40 percent by weight on the surface of each particle of the diamond powder, electroless plating a sintering assistant agent including at least one selected from Fe, Co and Ni within the range of 4 to 20 percent by volume to the surface of each particle of the diamond powder and thus preparing coated diamond powder, molding powder compact body of the coated diamond powder and sintering, in liquid-phase, the powder compact body under a high temperature and high pressure condition in which diamond is stable.

In the method of manufacturing a diamond sintered body in accordance with the second aspect of the present invention, a sintering assistant agent including an iron family element is applied as coating, within the range of 4 to 20 percent by volume to the surface of each particle of fine diamond powder, and the coated diamond powder is sintered in liquid-phase under high pressure and high temperature in which diamond is stable, so that a diamond

sintered body having high strength and high wear distance as well as high diamond content can be obtained.

According to a third aspect of the present invention, the method of manufacturing a diamond sintered body having high strength and high wear-resistance includes the steps of preparing diamond power having particle size substantially within the range of 0.1 to 10 μm , precipitating Pd within the range of 10^{-4} to 40 percent by weight on the surface of each particle of the diamond powder and then electroless plating a sintering assistant agent including at least one selected from Fe, Co and Ni within the range of 0.1 to 19.9 percent by volume to the surface of each particle of the diamond powder to prepare coated diamond powder, molding the powder compact body of the coated diamond powder, bringing into contact an additional sintering assistant agent including at least one of Pd, Fe, Co and Ni with the powder compact body, and sintering in liquid-phase the powder compact body at high pressure and high temperature condition in which diamond is stable, while infiltrating the additional sintering assistant agent.

In the method of manufacturing the diamond sintered body in accordance with the third aspect of the present invention, the sintering assistant agent including an iron family element is applied for coating to the surface of

each particle of fine diamond powder within the range of 0.1 to 19.9 percent by volume, an additional sintering assistant agent is brought into contact with the coated diamond powder, and the coated diamond powder is sintered in liquid-phase under high pressure and high temperature in which diamond is stable while infiltrating the additional sintering assistant agent. Therefore, a diamond sintered body having high diamond content and having high strength and high wear-resistance can be obtained.

Detailed Description of the Invention

First, the inventors studied strength of various diamond sintered bodies. As a result, it was found that the strength of the diamond sintered body depends on the size of a defect in the sintered body which serves as an initiation point of breakage. Here, the term defect means a diamond larger particle in the diamond sintered body, a pool of the sintering assistant agent such as the solvent metal or a void. The smaller the defect, the higher the strength of the diamond sintered body.

It was found that in order to improve strength of the diamond sintered body, first, the diamond larger particles must be reduced, and that acceptable particle size of diamond is at most 10 μm . In order to provide coating of sintering assistant agent on the surface of diamond

particles, which will be described later, the diamond particle must have the particle size of at least 0.1 μm . In other words, the raw material diamond powder is required to have the particle size within the range of 0.1 to 10 μm .

It was found that in order to reduce void and pool portion of sintering assistant agent in the sintered body, it is preferable to sinter coated diamond powder having the sintering assistant agent coating the surface of each particle of diamond powder in liquid-phase. It was found that, preferably, the sintering assistant agent includes Pd and at least one selected from Fe, Co and Ni which are iron family metals. It was found that by preparing coated diamond powder to include such sintering assistant agent within the range of 4 to 20 percent by volume and by sintering the coated diamond powder under high pressure and high temperature condition in which diamond is stable, uniform liquid-phase of sintering assistant agent is generated entirely over the diamond powder, so that diamond sintered body having smaller void and pool of sintering assistant agent is obtained.

Further, it was found that by preparing coated diamond powder to include sintering assistant agent including Pd and at least one of Fe, Co and Ni within the range of 0.1 to 19.9 percent by volume, and bringing into

contact an additional sintering assistant agent including at least one of Pd, Fe, Co and Ni with the coated diamond powder, uniform infiltration of the additional sintering assistant agent occurs entirely over the coated diamond powder compact body, supplementing the sintering assistant agent coated on the diamond powder under high pressure at high temperature in which diamond is stable, and hence a diamond sintered body having smaller void and pool of sintering assistant agent can be obtained.

More specifically, by using coated diamond powder on which the above described sintering assistant agent is coated, uniform melting or infiltration of the sintering assistant agent occurs, so that sintering becomes possible under such a condition that is otherwise not suitable for sintering, and hence a diamond sintered body having high diamond content, high strength and high wear assistance can be obtained.

Here, any of Pd, Fe, Co and Ni may be used as the sintering assistant agent for the diamond powder by itself. However, it was found that when the sintering assistant agent includes Pd in addition to at least one of Fe, Co and Ni, melting point of the sintering assistant agent lowers and sintering property of the diamond powder is remarkably improved. Here, if the content of Pd in the sintering assistant agent is smaller than 0.01 percent by

weight, sufficient effect of lowering the melting point of the sintering assistant agent cannot be obtained. By contrast, if the content of Pd exceeds 40 percent by weight, the melting point of the sintering assistant agent tends to increase, degrading sintering property of the diamond powder. In other words, the content of Pd in the sintering assistant agent is preferably within the range from 0.01 to 40 percent by weight.

Further, the sintering assistant agent should preferably be included by at least 4 percent by weight when the coated diamond powder coated with the sintering assistant agent is to be sintered, in order to prevent shortage of the sintering assistant agent, which shortage substantially makes sintering of diamond powder impossible. On the other hand, the content of sintering assistant agent should preferably be 20 percent by volume at most, since wear-resistance of the sintered body is remarkably degraded as the diamond content lowers if the sintering assistant agent in the diamond sintered body exceeds 20 percent by volume.

Similarly, when sintering of coated diamond powder is to be performed with additional sintering assistant agent brought into contact with the powder compact body of the coated diamond powder, the amount of sintering assistant agent coating the diamond particle should preferably be at

least 0.1 percent by volume. The reason for this is that if the amount of coating of the sintering assistant agent is smaller than 0.1 percent by volume, uniform coating by the sintering assisting agent on the surface of the diamond particle becomes difficult, making uniform infiltration of the additional sintering assistant agent impossible. On the other hand, the amount of coating of the sintering assistant agent should preferably be at most 19.9 percent by volume. The reason for this is that after sintering while infiltrating additional sintering assistant agent, if the sintering assistant agent in the sintered body exceeds 20 percent by volume, diamond content is lowered, and hence wear-resistance of the sintered body is significantly degraded.

As a method of providing coating of the sintering assistant agent on each particle of the diamond powder, CVD method, PVD method or solution precipitation method may be possible. However, electroless plating method is most preferably used, from economical view and from the consideration that uniformity of the sintering assistant agent coating the surface of the diamond particle plays a very important part in improving the sintering property of the powder and in the strength of the sintered body.

When the sintering assistant agent is to be precipitated on the surface of diamond particle by

electroless plating, mixing of impurity in the sintering assistant agent should be prevented as much as possible, in order to obtain high diamond content after sintering. Considering the fact that catalytic nuclei having high catalytic action must exist on the surface of the diamond particle in the initial reaction of electroless plating, it is preferable that Pd exhibiting not only the function of a sintering assistant agent but also the catalytic action be coated first on the surface of the diamond particle. It was found that by providing coating of a sintering assistant agent including at least one of Fe, Co and Ni with Pd serving as catalytic nucleus, coated diamond particle coated with sintering assistant agent with smaller impurity can be obtained.

Here, it is desired that the amount of precipitation of Pd on the surface of the diamond particle is at least 10^{-4} percent by weight. The reason for this is that if catalytic action is insufficient, electroless plating reaction becomes insufficient, making it difficult to provide coating of the sintering assistant agent. On the other hand, the amount of precipitation of Pd should desirably be 40 percent by weight at most. The reason for this is to prevent degradation of sintering property, which is caused by elevated melting point of the sintering assistant agent caused by excessive Pd.

Further, it was found that if the sintering assistant agent includes at least one of Sn, P and B in addition to the iron family metal, Sn, P or B serves to lower the melting point of the sintering assistant agent, significantly improving sintering property of the diamond powder coated by the sintering assistant agent.

As for precipitation of P in addition to the iron family element, a sintering assistant agent having a desired P concentration can be precipitated by using a hypophosphite, for example sodium hypophosphite as a reducing agent in the electroless plating solution, and by adjusting concentration of the reducing agent in the plating solution, pH of the plating solution and temperature during plating. Similarly, for precipitation of B in addition to the iron family element, a sintering assistant agent having a desired B concentration can be precipitated by using a boron hydride compound such as sodium borohydride, as the reducing agent in the electroless plating solution, and by adjusting concentration of the reducing agent in the plating solution, pH of the plating solution and the temperature during plating. Meanwhile, Sn has superior absorption property with respect to the surface of the diamond powder particle. Therefore, it can be directly absorbed to the diamond particle surface from a tin chloride solution, for

example. Further, precipitation of Pd serving as the catalytic nucleus after absorption of Sn onto the diamond particle surface as pre-processing for electroless plating (sensitizing activating method) or precipitation of Sn and Pd simultaneously (catalyst accelerating method) is preferable, since it promotes absorption of Pd at the surface of the diamond particles.

At this time, if the total content of Sn, P and B in the sintering assistant agent is smaller than 0.01 percent by weight, the effect of lowering the melting point of the sintering assistant agent cannot be obtained. By contrast, if it exceeds 30 percent by weight, melting of diamond to the iron family metal which serves as solvent metal in the sintering assistant agent at the time of sintering is hindered, so that the binding strength between diamond particles with each other becomes lower, degrading strength of the sintered body, and degrading thermal properties of the sintered body. The total content of Sn, P and B should more preferably be within the range of 0.01 to 11.5 percent by weight.

When the diamond particle is to be coated with the sintering assistant agent by electroless plating, the iron family element precipitated by electroless plating is, in most cases, precipitated as an oxide. If sintering is performed using sintering assistant agent including an

oxide, oxygen derived from the oxide may possibly generate voids in the sintered body, and it may hinder melting and precipitation reaction of diamond in the sintering assistant agent serving as the solvent. Therefore, it may
5 degrade the property of the diamond sintered body. In order to prevent such undesirable effect by oxygen, the coated diamond powder after electroless plating should preferably be reduced by heat treatment in vacuum or in hydrogen atmosphere.

10 It was found that when electroless plating is performed on the diamond powder, the diamond powder can be coated uniformly by the sintering assistant agent if the plating solution including the diamond powder is fluctuated by at least one of stirring and ultrasonic
15 vibration.

Further, in order to obtain diamond sintered body having higher density, it is preferable to perform heat treatment at high temperature on the diamond powder under such condition that makes diamond instable so that the
20 diamond particles are partially turned to graphite from the surface, to coat the partially graphitized diamond particle with the sintering assistant agent and to perform sintering thereafter, or to coat the diamond powder with the sintering assistant agent, to turn the coated diamond
25 particle into graphite partially from the surface and then

perform sintering. The reason for this is as follows. Diamond powder is not susceptible to plastic deformation. Therefore, even under high pressure, spaces tend to remain between diamond particles. However, if the surface of the diamond particle is turned into graphite, the graphite portion is more susceptible to plastic deformation, and hence density of the sintered body can be substantially improved. Further, considering melting of carbon and re-precipitation in the sintering assistant agent during sintering, speed of reaction of graphite is faster than that of diamond, and hence sintering property is improved if the diamond surface is turned into graphite.

From these reasons, it would be understood that diamond sintered body having higher density could be obtained if the diamond surface is partially turned to graphite. At this time, if the ratio of graphitization of diamond particle is smaller than 0.5 percent by volume, density of the sintered body is hardly improved.

Meanwhile, if the ratio of graphitization of diamond particle exceeds 80 percent by volume, turning of graphite to diamond during sintering under such high pressure and high temperature that keeps diamond stable becomes imperfect, resulting in graphite left in the diamond sintered body. Therefore, preferable range of partial graphitization of diamond particle is 0.5 to 80 percent by

volume.

Now, if the above described diamond sintered body is to be obtained, it is possible that various materials are mixed in small quantity. For example, the coated diamond powder is generally filled in a container formed of a cemented carbide or a refractory metal and sintered. Therefore, W, Ta, Mo, Cr which are the components of the container or carbide thereof may possibly be mixed in the sintered body. However, even if such material is mixed in the sintered body, such material does not cause any problem provided that diamond content in the sintered body is within the range of 80 to 96 percent by volume.

Similarly, even when additional sintering assistant agent is brought into contact with the powder compact body as supplement to the sintering assistant agent in the coated diamond powder and infiltrated to the powder compact body during sintering, it does not cause any problem provided that the diamond content of the sintered body is within the range of 80 to 96 percent by volume. As for the composition of additional sintering assistant agent arranged in contact with such powder compact body, similar compositions as those for the sintering assistant agent used for coating of the diamond particle may be used.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

(Embodiment 1)

Table 1

Powder sample	Diamond particle size (μm)	Method of applying sintering assistant agent	Content of sintering assistant agent (vol.%)	Composition of sintering assistant agent (wt.%)
1A	0.1 - 4	electroless plating	6.0	92.9-Co, 0.05-Pd, 3.95-Fe, 3-P, 0.1-Sn
1B	0.1 - 4	electroless plating	13.0	92.9-Co, 0.05-Pd, 3.95-Fe, 3-P, 0.1-Sn
1C	0.1 - 4	electroless plating	26.0	92.9-Co, 0.05-Pd, 3.95-Fe, 3-P, 0.1-Sn
1D	0.1 - 4	PVD	6.0	92.9-Co, 0.05-Pd, 3.95-Fe, 3-P, 0.1-Sn
1E	0.1 - 4	PVD	13.0	92.9-Co, 0.05-Pd, 3.95-Fe, 3-P, 0.1-Sn
1F	0.1 - 4	PVD	26.0	92.9-Co, 0.05-Pd, 3.95-Fe, 3-P, 0.1-Sn
1G	0.1 - 4	mixing ultra fine powder	6.0	100-Co
1H	0.1 - 4	mixing ultra fine powder	13.0	100-Co
1I	0.1 - 4	mixing ultra fine powder	26.0	100-Co
1J	0.1 - 4	cemented carbide ball mill	6.0	25-Co, 75-WC
1K	0.1 - 4	cemented carbide ball mill	13.0	25-Co, 75-WC
1L	0.1 - 4	cemented carbide ball mill	26.0	25-Co, 75-WC

Table 1 shows various powder samples prepared for studying influence mainly of the method of applying sintering assistant agent, content and composition on mechanical properties of the diamond sintered body. More

specifically, powder samples 1A to 1L shown in Table 1 are all raw material diamond powders having the particle size within the range of 0.1 to 4 μm , while the method of applying sintering assistant agent, content and composition are changed variously.

For the samples 1A, 1B and 1C, the following process was performed to coat diamond powder particles by the sintering assistant agent by electroless plating. First, diamond powder was degreased in alcohol. The degreased diamond powder was cleaned in flowing water, cleaned in hydrochloric acid solution of 5 percent by weight, and then again cleaned in flowing water. The diamond powder thus cleaned was immersed for one minute in a solution including stannous chloride and hydrochloric acid in room temperature as pre-processing, so as to cause absorption of Sn at the surface of the diamond particles (sensitizing). The sensitized diamond powder was washed by water and thereafter immersed for one minute in hydrochloric acid solution containing palladium chloride at a room temperature, and thus Pd was precipitated at the surface of the diamond particles (activated).

The activated diamond powder was washed by water, and thereafter immersed for a prescribed time period in a Co-Fe-P electroless plating solution held at 75°C, containing cobalt sulfate, iron sulfate and sodium hypophosphite.

The longer the time of immersion in the electroless plating solution, the larger the amount of sintering assistant agent coating the surface of the diamond particle, and the larger the content of the sintering assistant agent in the powder samples. In the step of electroless plating, the pre-plating solution and plating solution were stirred and at the same time, subjected to ultrasonic vibration. The coated diamond powder which was subjected to electroless plating in this manner was cleaned, the surface of diamond particles was partially graphitized by heat treatment in vacuum at 1000 °C for 60 minutes, and collected, whereby the coated powder samples 1A to 1C having such content and composition of the sintering assistant agent as shown in Table 1 were obtained.

For the samples 1D to 1F, the sintering assistant agent has the same composition as those for the samples 1A to 1C. However, coating of the sintering assistant agent was performed in accordance with an arc ion plating method. More specifically, the sintering assistant agent is applied to the surface of diamond powder particles by arc ion plating method in which a target corresponding to the composition of the sintering assistant agent and a bias voltage of 350 V were used in an argon atmosphere of 1×10^{-2} torr.

For samples 1G to 1I, ultra fine Co powder having the particle size of 500 Å was used as the sintering assistant agent. Diamond powder and ultra fine Co powder corresponding to the prescribed content were put in a ball mill container formed of Teflon which contains mixing balls formed of Teflon. The powders were mixed for 4 hours, whereby the mixed powder samples 1G to 1I were obtained.

In preparing the samples 1J to 1L, diamond powder was put in a ball mill having mixing balls and a container formed of cemented carbide WC-Co and the ball mill was driven for a prescribed time period. During the driving of the cemented carbide ball mill, the cemented carbide powder scraped off from the mixing balls and the container were mixed as sintering assistant agent to the diamond powder. The content of the cemented carbide powder mixed in the diamond powder can be adjusted by changing the time of driving the cemented carbide ball mill.

The powder samples 1A to 1L shown in Table 1 were each sealed in a container formed of tantalum, kept at a pressure of 50 kb at a temperature 1400°C for 10 minutes by using a belt type high pressure apparatus, and thus sintered. Table 2 shows diamond content and wear-resistance of the diamond sintered body samples obtained in this manner.

Table 2

Sintered body sample	Diamond content (vol.%)	Flank wear (μm)
2A	93.8	31
2B	86.9	65
2C	74.2	131
2D	92.3	damaged
2E	86.8	damaged
2F	73.9	damaged
2G	sintering not possible	
2H	86.7	damaged
2I	74.0	damaged
2J	sintering not possible	
2K	sintering not possible	
2L	73.9	142

Sintered body samples 2A to 2L of Table 2 are obtained by sintering powder samples 1A to 1L shown in Table 1. As can be seen from Table 2, in samples 2G, 2J and 2K, the amount of sintering assistant agent is small and distribution thereof is not uniform. Since uniform melting of sintering assistant agent did not occur entirely in the diamond powder, sintering was insufficient, and hence complete sintered body could not be obtained.

Meanwhile, samples providing complete sintered bodies were processed to be cutting tools, and performance was

evaluated under the following cutting conditions.

Work piece: a round bar of Al-16 wt % Si having six grooves on the surface along the axial direction.

Peripheral surface velocity of the work piece: 500

5 (m/min)

Byte cutting depth: 0.6 (mm)

Byte feeding speed: 0.12 (mm/rev)

Cutting time: 3 (min)

10 The flank wear of the tools as a result of cutting test were as shown in Table 2. As can be seen from Table 2, sintering is possible in sintered body samples 2A and 2B in accordance with the present invention even when the amount of sintering assistant agent is small. Therefore, tools having high diamond content and superior

15 wear-resistance can be obtained. Further, since the sintered body samples 2A and 2B have uniform sintered body texture, they have high strength, and it becomes apparent that they have good damage resistance as cutting tools.

By contrast, it is apparent that sintered body

20 samples 2C and 2L having low diamond content are inferior in wear-resistance. Of the sintered body textures of samples 2D, 2E, 2F, 2H and 2I, uneven distribution of sintering assistant agent generated in the PVD method or Co pools derived from aggregation of ultra fine Co powder

25 were observed, which pools lowered strength and hence

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caused damages to the sintered body during cutting. Thus the sintered bodies could not be used as the cutting tools.

(Embodiment 2)

Table 3

Powder sample	Diamond particle size (μm)	Method of applying sintering assistant agent	Fluctuatn of plating solution	Content of sintering assistant agent (vol.%)	Composition of sintering assistant agent (wt.%)
3A	1 - 2	electroless plating	stirring + ultrasonic vibration	9	97-Ni, 0.5-Pd, 2-P, 0.5-Sn
3B	1 - 2	electroless plating	stirring + ultrasonic vibration	9	89-Ni, 0.5-Pd, 10-P, 0.5-Sn
3C	1 - 2	electroless plating	stirring + ultrasonic vibration	9	64-Ni, 0.5-Pd, 35-P, 0.5-Sn
3D	1 - 2	electroless plating	not fluctuated	9	97-Ni, 0.5-Pd, 2-P, 0.5-Sn
3E	1 - 2	electroless plating	not fluctuated	9	89-Ni, 0.5-Pd, 10-P, 0.5-Sn
3F	1 - 2	electroless plating	not fluctuated	9	64-Ni, 0.5-Pd, 35-P, 0.5-Sn
3G	1 - 2	mixing ultra fine powder	-	9	100-Ni

Table 3 shows various powder samples prepared for studying influence of the method of applying sintering assistant agent, composition and conditions of electroless plating on mechanical properties of the sintered bodies.

5 For samples 3A to 3C, the surface of diamond particles was partially graphitized by heat treatment in vacuum at 1450 °C for 30 minutes, then diamond powders were degreased and subjected to acid cleaning in the similar manner as Table 1 and thereafter the diamond
10 powders were subjected to surface activation, in order to coat the diamond powder particles by sintering assistant agent by electroless plating. Thereafter, the diamond powders were immersed in an Ni-P electroless plating solution containing nickel sulfate and sodium hypophosphite
15 and held at 60°C. During the step of electroless plating, the pre-plating solution and the plating solution were fluctuated by stirring and ultrasonic vibration. The composition of the sintering assistant agent was adjusted by changing pH of the plating solution.

20 Samples 3D to 3F were prepared by electroless plating similar to samples 3A to 3C. However, fluctuation by stirring and ultrasonic vibration was not applied to the electroless plating solution.

 As for sample 3G, diamond powder was put in a ball
25 mill container formed of Teflon containing mixing balls

formed of Teflon, together with ultra fine Ni powder having the powder size of 200 Å, and mixed for 4 hours.

The powder samples of Table 3 were each sealed in a container of Mo and sintered for 15 minutes at a pressure of 45 kb at a temperature of 1350°C by using a belt type high pressure apparatus. Various properties of the sintered body samples obtained in this manner are as shown in Table 4.

Table 4

Sintered body sample	Diamond content (vol.%)	Composition of sintering assistant agent after sintering (wt.%)	Three point bending strength (kgf/mm ²)
4A	90.9	97-Ni, 0.5-Pd, 2-P, 0.5-Sn	263
4B	90.8	89-Ni, 0.5-Pd, 10-P, 0.5-Sn	254
4C	90.9	64-Ni, 0.5-Pd, 35-P, 0.5-Sn	193
4D	90.7	97-Ni, 0.5-Pd, 2-P, 0.5-Sn	179
4E	90.8	89-Ni, 0.5-Pd, 10-P, 0.5-Sn	164
4F	90.9	64-Ni, 0.5-Pd, 35-P, 0.5-Sn	142
4G	sintering not possible		

The sintered body samples 4A to 4G shown in Table 4 were obtained from powder samples 3A to 3G of Table 3. However, similar to the sample 2B of Table 2, locally unsintered regions were generated in sample 4G, and complete sintered body could not be obtained.

The samples from which complete sintered bodies were obtained were each processed to a bar-shaped sample piece of 6 x 3 x 0.3 mm, and thereafter strength thereof was evaluated by three point bending test with the span of 4 mm. As a result, as can be seen from Table 4, it is apparent that samples 4A to 4C have improved strengths than samples 4D to 4F. More specifically, as the plating solution was stirred and subjected to ultrasonic vibration during electroless plating of diamond powder, uniform coating of sintering assistant agent was formed on the diamond particles, defects in the diamond sintered body were reduced and hence strength of the sintered body was significantly improved.

Further, in view of the fact that samples 4A and 4B have higher strength than samples 4C and 4F, it was found that when sintering assistant agent includes P and Sn, the total content thereof should desirably be in the range of 0.01 to 30 percent by weight. Further, it was found that when the sintering assisting agent includes B, the desired content thereof is from 0.01 to 30 percent by weight.

(Embodiment 3)

Table 5

Powder sample	Diamond particle size (μm)	Amount of coating of sintering assistant agent (vol.%)	Composition of coating sintering assistant agent (wt.%)	Composition of additional sintering assistant agent (wt.%)
5A	2 - 3	0.1	92.0-Ni, 7.0-Pd, 1.0-Sn	100-Ni
5B	2 - 3	0.1	92.0-Ni, 7.0-Pd, 1.0-Sn	98-Ni, 2-B
5C	2 - 3	0.1	92.0-Ni, 7.0-Pd, 1.0-Sn	89-Ni, 11-B
5D	2 - 3	0.1	92.0-Ni, 7.0-Pd, 1.0-Sn	79-Ni, 21-B
5E	2 - 3	0.1	92.0-Ni, 7.0-Pd, 1.0-Sn	66-Ni, 34-B

Table 5 shows various powder samples prepared for studying influence of composition of additional sintering assistant agent on the strength of the sintered bodies, when the additional sintering assistant agent which is brought into contact with coated diamond powder compact body is infiltrated into the powder compact body during sintering.

For samples 5A to 5E, diamond powder was degreased and subjected to acid cleaning in the similar manner as Table 1, to coat the diamond powder particles by the sintering assistant agent by electroless plating.

Thereafter, catalysing was performed as pre-processing of electroless plating, by immersing the diamond powder in a solution containing palladium chloride, stannous chloride and hydrochloric acid for two minutes at a room

temperature. Thereafter, accelerating of the diamond powder was performed by immersing the powder in a sulfuric acid solution for two minutes at a room temperature.

5 The pre-processed powders were washed by water, and thereafter immersed for two minutes in an Ni-B plating solution including nickel sulfate and sodium borohydride at 90°C, and thus coated diamond powders including the coating sintering assistant agent having such compositions and amounts as shown in Table 5 were obtained. During
10 these steps of alkali degreasing, acid cleaning, pre-processing and plating, while the diamond powders are immersed in the solutions, the solutions were fluctuated by stirring and ultrasonic vibration.

The coated diamond powders were molded into powder
15 compact bodies, and metal plates having such compositions as shown in Table 5 were stacked as additional sintering assistant agent and sealed into a container of Ta. The Ta container was held at a pressure of 60 kb at a temperature of 1550 °C for 10 minutes by using a girdle type high
20 pressure apparatus, and sintered body samples such as shown in Table 6 were obtained.

Table 6

Sintered body sample	Diamond content (vol.%)	Total content of Sn and B in sintering assistant agent (wt.%)	Strength of sintered body (kgf/mm ²)
6A	85	0.005	197
6B	85	1.99	234
6C	85	11.0	222
6D	85	20.9	208
6E	85	33.8	135

The sintered body samples 6A to 6E shown in Table 6 were obtained from powder samples 5A to 5E of Table 5.

Each of the sintered body samples was processed to a bar-shaped sample piece of 6 x 3 x 0.3 mm, and strength thereof was evaluated by three point bending test with the span of 4 mm.

As can be seen from Table 6, it is apparent that samples 6B, 6C and 6D have improved strength than samples 6A and 6E. More specifically, it can be understood that when the additional sintering assistant agent includes B, the content should preferably be in the range of 0.01 to 30 percent by weight. Further, it was found that if the additional sintering assistant agent includes P and Sn, the preferable content thereof is from 0.01 to 30 percent by weight.

(Embodiment 4)

Table 7

Powder sample	Diamond particle size (μm)	Method of applying sintering assistant agent	Content of sintering assistant agent (vol.%)	Composition of sintering assistant agent (wt.%)
7A	1 - 2	electroless plating	5.0	99.6-Co, 0.1-Pd, 0.3-Sn
7B	2 - 8	electroless plating	5.0	99.6-Co, 0.1-Pd, 0.3-Sn
7C	5 - 15	electroless plating	5.0	99.6-Co, 0.1-Pd, 0.3-Sn
7D	1 - 2	CVD	5.0	99.6-Co, 0.1-Pd, 0.3-Sn
7E	2 - 8	CVD	5.0	99.6-Co, 0.1-Pd, 0.3-Sn
7F	5 - 15	CVD	5.0	99.6-Co, 0.1-Pd, 0.3-Sn
7G	1 - 2	mixing ultra fine powder	5.0	100-Co
7H	2 - 8	mixing ultra fine powder	5.0	100-Co
7I	5 - 15	mixing ultra fine powder	5.0	100-Co
7J	1 - 2	cemented carbide ball mill	5.0	15-Co, 85-WC
7K	2 - 8	cemented carbide ball mill	5.0	15-Co, 85-WC
7L	5 - 15	cemented carbide ball mill	5.0	15-Co, 85-WC

Table 7 shows various powder samples prepared for studying influence of the raw material diamond particle size, method of applying sintering assistant agent and composition on mechanical properties of the sintered bodies.

For samples 7A to 7C, catalytic layer for electroless plating was applied to the surface of diamond powder particles in the similar manner as in Embodiment 3 so as to coat the diamond powders with sintering assistant agent by electroless plating.

The pre-processed diamond powder was washed by water, and thereafter immersed in a Co electroless plating solution containing cobalt chloride and hydrazinium chloride and held at 80°C, and thus Co coating was provided on the surface of diamond particles. During pre-processing related to electroless plating and during plating, the solutions together with diamond powder were fluctuated by stirring and ultrasonic vibration. The electroless plated diamond powder was washed and collected, thereafter heated in vacuum at 1250°C for 60 minutes, so that the sintering assistant agent was reduced and diamond particles were partially graphitized from the surface. As a result, powder samples 7A to 7C having such content and composition of sintering assistant agent as shown in Table 7 were obtained. The amount of oxygen contained in the powders of samples 7A to 7C was 0.05 percent by weight.

For samples 7D to 7F, coated diamond powders having the same composition of sintering assistant agent as samples 7A to 7C were fabricated by using microwave plasma

CVD method.

For samples 7G to 7I, diamond powders were put together with ultra fine Co powder into a ball mill container formed of Teflon including mixing balls of Teflon, and mixed for three hours. For samples 7J to 7L, diamond powders were put in cemented carbide ball mill container including mixing balls formed of cemented carbide, and the cemented carbide ball mill was driven for a prescribed time period, so that diamond powders mixed with cemented carbide powder were obtained. As already described, the cemented carbide powder was scraped off from the cemented carbide balls and the container and mixed with the diamond powders.

Each of the powder samples 7A to 7L shown in Table 7 was molded to a powder compact body, and a Co plate was stacked on the powder compact body and the powder compact body with the plate stacked was sealed in a container of cemented carbide. The cemented carbide container was held at a pressure of 50 kb at a temperature of 1500°C for 15 minutes by a belt type high pressure apparatus, so that the stacked Co plate was melt and infiltrated in the powder compact body during sintering, and as a result, sintered body samples such as shown in Table 8 were obtained.

Table 8

Sintered body sample	Diamond content (vol.%)	Composition of sintering assistant agent after sintering (wt.%)	Flank wear (μm)
8A	86.9	99.88-Co, 0.03-Pd, 0.09-Sn	88
8B	88.3	99.85-Co, 0.04-Pd, 0.11-Sn	67
8C	90.2	99.93-Co, 0.02-Pd, 0.05-Sn	blade chipping
8D	86.7	99.88-Co, 0.03-Pd, 0.09-Sn	damaged
8E	87.9	99.85-Co, 0.04-Pd, 0.11-Sn	damaged
8F	90.3	99.93-Co, 0.02-Pd, 0.05-Sn	damaged
8G	sintering not possible		
8H	87.1	100Co	damaged
8I	90.0	100Co	damaged
8J	79.6	57.7-Co, 42.3-WC	211
8K	79.8	48.3-Co, 51.7-WC	153
8L	88.3	35.5-Co, 64.5-WC	blade chipping

The sintered body samples 8A to 8L shown in Table 8 were obtained from powder samples 7A to 7L of Table 7.

In sample 8G, since the raw material diamond powder has fine particles as shown in Table 7, space between particles is narrow and mixed Co powder is not uniformly distributed. Therefore, when Co plate was stacked on the powder compact body of the mixed powder for infiltration, infiltration proceeded unevenly in the powder compact body. As a result, unsintered portions were generated partially in sample 8G and complete sintered body could

not be obtained.

Samples providing complete sintered bodies were processed to cutting tools, and performance thereof was evaluated under the following cutting conditions.

5 Work piece: round bar of Al-10 wt % Si having four grooves along the axial direction

Peripheral surface velocity of the work piece: 500 (m/min)

Byte cutting depth: 1.5 (mm)

10 Byte feeding speed: 0.2 (mm/rev)

Cutting time: 160 (min)

Table 8 shows flank wear of sintered body samples as a result of cutting test. As can be seen from Table 8, sintered body samples 8D, 8E, 8F, 8H and 8I including
15 pools of sintering assistant agent were damaged at initial stage of cutting and continuous cutting was impossible. In sintered body samples 8C and 8L having large diamond particle size, chipping was observed at the blade of the tool during cutting test. As for sintered body samples 8J
20 and 8K having low diamond content, though there was not a damage, the flank wear was too large to be practical.

Meanwhile, sintered body samples 8A and 8B in accordance with the present invention had small diamond particle size, and uniform sintered body texture without
25 void or Co pool could be obtained, and hence the sintered

bodies had high strength and free of chipping or damage. In addition, it becomes apparent that samples 8A and 8B have sufficient wear-resistance as shown in Table 8, since they have sufficiently high diamond content.

5 (Embodiment 5)

Table 9

Powder sample	Conditions for heat treatment of diamond powder	Amount of coating of sintering assistant agent (vol.%)	Conditions for heat treatment of coated diamond powder	Degree of graphitization (vol.%)
9A	1400°C, 60 min.	4	heat treatment not performed	5.3
9B	1450°C, 60 min.	4	heat treatment not performed	52.6
9C	1500°C, 60 min.	4	heat treatment not performed	93.8
9D	heat treatment not performed	4	heat treatment not performed	0
9E	heat treatment not performed	4	1200°C, 60 min.	5.2
9F	heat treatment not performed	4	1350°C, 60 min.	32.1

Table 9 shows various powder samples prepared for studying influence of the degree of graphitization of diamond powder on diamond content in the sintered body.

In samples 9A to 9C, raw material diamond powders having the particle size of 5 to 10 μm was heat treated in vacuum under the conditions shown in Table 9 so as to partially graphitize the powders from the surface of the

particles. The partially graphitized diamond particles were coated by the sintering assistant agent in the similar manner as Embodiment 1.

5 In samples 9D to 9F, raw material diamond powder particles having the particle size of 5 to 10 μm were coated by the sintering assistant agent in the similar manner as in Embodiment 1, and thereafter the coated diamond particles were partially graphitized from the surface under the heat treatment conditions shown in Table 10 9 in vacuum.

The partially graphitized coated diamond powders were molded to powder compact bodies, a metal plate of 100 % Co was stacked as additional sintering assistant agent, and then the powder compact bodies were sealed in a container 15 of Mo and sintered under a pressure of 50 kb at a temperature of 1550°C for 10 minutes. Table 10 shows diamond contents of the sintered body samples obtained in this manner.

Table 10

Sintered body sample	Diamond content (wt.%)
10A	94.4
10B	95.1
10C	partial sintering (Gr left)
10D	92.2
10E	94.5
10F	94.8

The sintered body samples 10A to 10F of Table 10 were obtained from powder samples 9A to 9F of Table 9. As can be seen from Table 10, it is apparent that sintered body samples 10A, 10B, 10E and 10F have higher diamond contents than sample 10D. Meanwhile, sample 10C partially included remaining graphite (Gr), and hence complete sintered body could not be obtained.

More specifically, the degree of graphitization of the coated diamond powder should preferably be in the range of 0.5 to 50 percent by volume.

(Embodiment 6)

Table 11

Powder sample	Diamond particle size (μm)	Amount of absorption of Pd (wt.%)	Amount of coating of sintering assistant agent (vol.%)	Composition of sintering assistant agent (wt.%)
11A	5 - 10	5×10^{-5}	not precipitated	
11B	5 - 10	8×10^{-3}	5	Pd-0.08, Co-99.82, Sn-0.1
11C	5 - 10	8×10^{-3}	5	Pd-2.7, Co-97.2, Sn-0.1
11D	5 - 10	8×10^{-3}	5	Pd-38.7, Co-61.2, Sn-0.1
11E	5 - 10	8×10^{-3}	5	Pd-52.1, Co-47.8, Sn-0.1

Table 11 shows various powder samples prepared for studying influence of the amount of application of Pd on catalytic property in electroless plating and sintering property of diamond powder at the time of sintering.

For samples 11A to 11E, Pd was applied to the surfaces of diamond particles, in the similar manner as in Embodiment 4, so as to coat diamond powder particles by sintering assistant agent by electroless plating. Thereafter, diamond powder particles were electroless-plated by Pd, using electroless plating solution including palladium tetra chloride. Further, diamond powder particles were coated by Co using an electroless plating solution containing hydrazine.

As a result, as shown in Table 11, the amount of absorption of Pd at the particles of diamond powder was too small in sample 11A, so that catalytic action by Pd

was insufficient and Co was not successfully precipitated at the surface of the diamond particles.

Each of the powder samples 11B to 11E coated with Co was molded into powder compact body and sealed in a container formed of cemented carbide. The cemented carbide container was held under a pressure of 50 kb at a temperature of 1500°C for 15 minutes to perform sintering, by using a belt type high pressure apparatus. Sample 11E containing much Pd did not result in complete sintered body, as melting of the sintering assistant agent did not occur. Meanwhile, complete sintered bodies could be obtained from samples 11B to 11D.

In other words, the preferable content of Pd in the sintering assistant agent is within the range of 0.01 to 40 percent by weight.

As described above, according to the present invention, a diamond sintered body having both high strength and high wear-resistance can be provided, which can be preferably used for cutting tools, digging tools, drawing dices and wear-resistant parts.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.



WHAT IS CLAIMED IS:

1. A diamond sintered body having high strength and high wear-resistance, comprising

sintered diamond particles of 80 to 96 percent by volume and a remaining part of sintering assistant agent and unavoidable impurity,

said sintered diamond particles having particle size substantially in a range of 0.1 to 10 μm and directly bonded to each other,

said sintering assistant agent including Pd within a range of 0.01 to 40 percent by weight and as a remaining part, at least one selected from Fe, Co and Ni.

2. The diamond sintered body having high strength and high wear-resistance according to claim 1, wherein

said sintering assistant agent further includes at least one of Sn, P and B.

3. The diamond sintered body having high strength and high wear-resistance according to claim 2, wherein

said sintering assistant agent includes at least one of Sn, P and B within a range of 0.01 to 30 percent by weight.

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4. A method of manufacturing a diamond sintered body having high strength and high wear-resistance, comprising the steps of:

5 preparing diamond powder having particle size substantially within a range of 0.1 to 10 μm ;

precipitating Pd within a range of 10^{-4} to 40 percent by weight on a surface of each particle of said diamond powder, and thereafter electroless plating a sintering assistant agent including at least one of Fe, Co and Ni to
10 the surface of each particle of said diamond powder within a range of 4 to 20 percent by volume to prepare coated diamond powder; and

under a condition of high pressure and high temperature in which diamond is stable, sintering said
15 coated diamond powder in liquid-phase.

5. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 4, wherein

said sintering assistant agent further includes at
5 least one of Sn, P and B.

6. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 5, wherein



said sintering assistant agent includes at least one
5 of Sn, P and B within a range of 0.01 to 30 percent by
weight.

7. The method of manufacturing a diamond sintered
body having high strength and high wear-resistance
according to claim 4, wherein 0.5 to 80 percent by volume
of each particle of said diamond powder is graphitized
5 from its surface by heat treatment at a high temperature
condition in which diamond is instable, and thereafter
said sintering assistant agent is applied as coating.

8. The method of manufacturing a diamond sintered
body having high strength and high wear-resistance
according to claim 4, wherein 0.5 to 80 percent by volume
of each particle of said coated diamond powder is
5 graphitized from its surface by heat treatment at a high
temperature condition in which diamond is instable, and
thereafter said sintering in liquid-phase is performed.

9. The method of manufacturing a diamond sintered
body having high strength and high wear-resistance
according to claim 4, wherein

during said electroless plating, plating solution to
5 which said diamond powder is immersed is fluctuated by at

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least one of stirring and ultrasonic vibration.

10. A method of manufacturing a diamond sintered body having high strength and high wear-resistance, comprising the steps of:

- 5 preparing diamond powder having particle size substantially in a range of 0.1 to 10 μm ;
- precipitating Pd in a range of 10^{-4} to 40 percent by weight on a surface of each particle of said diamond powder and thereafter electroless plating a sintering assistant agent including at least one of Fe, Co and Ni to
- 10 the surface of each particle of said diamond powder within a range of 0.1 to 19.9 percent by volume to prepare coated diamond powder;
- molding a powder compact body of said coated diamond powder;
- 15 bringing into contact an additional sintering assistant agent including at least one of Pd, Fe, Co and Ni to said powder compact body; and
- sintering said powder compact body in liquid-phase while infiltrating said additional sintering assistant
- 20 agent under a condition of high pressure and high temperature in which diamond is stable.

11. The method of manufacturing a diamond sintered



body having high strength and high wear-resistance according to claim 10, wherein

5 said sintering assistant agent coating said diamond particle further includes at least one of Sn, P and B.

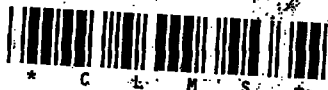
12. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 11, wherein

5 said sintering assistant agent coating said diamond particle includes at least one of Sn, P and B within a range of 0.01 to 30 percent by volume.

13. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 10, wherein

5 0.5 to 80 percent by volume of each particle of said diamond powder is graphitized from its surface by heat treatment under a high temperature condition in which diamond is instable, and thereafter said sintering assistant agent is applied as coating.

14. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 10, wherein 0.5 to 80 percent by volume of each particle of said coated diamond powder is



5 graphitized from its surface by heat treatment at a high temperature condition in which diamond is instable and thereafter said sintering in liquid-phase is performed.

15. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 10, wherein

said additional sintering assistant agent further
5 includes at least one of Sn, P and B.

16. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 15, wherein

said additional sintering assistant agent further
5 includes at least one of Sn, P and B within a range of 0.01 to 30 percent by weight.

17. The method of manufacturing a diamond sintered body having high strength and high wear-resistance according to claim 10, wherein

in said electroless plating, plating solution to
5 which said diamond powder is immersed is fluctuated by at least one of stirring and ultrasonic vibration.

DIAMOND SINTERED BODY HAVING HIGH STRENGTH AND HIGH
WEAR-RESISTANCE AND MANUFACTURING METHOD THEREOF

ABSTRACT OF THE DISCLOSURE

A method of manufacturing a diamond sintered body includes the steps of preparing diamond powder having particle size within a range of 0.1 to 10 μm , coating the surface of each particle of the diamond powder by a sintering assistant agent including Pd within a range of 0.01 to 40 percent by weight and at least one of an iron family metal as remaining part, and sintering the coated diamond powder in liquid-phase under high pressure and high temperature condition, so that a diamond sintering body having high strength and high wear-resistance containing diamond particles of 80 to 96 percent by volume can be obtained.