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**ARTICLES WITH DIAMOND COATING FORMED THEREON BY VAPORPHASE
SYNTHESIS**

ABSTRACT

The objective of the present invention is to produce a material with a tenaciously adherent diamond coating made by forming a diamond coating on a base material by vapor-phase synthesis without causing any warp of the coating. The diamond coating layer is formed on the surface of a base material having a number of cavities formed by electric discharge or laser beams, and the cavity is a pore having a depth of 0.0001-0.2 mm and a diameter of 0.001-0.2 mm. The pores may be connected to one another to form a groove. Suitable examples of the base material include molybdenum, tungsten, silicon, tungsten carbide, silicon carbide, silicon nitride, and cemented carbide mainly comprising tungsten carbide and cobalt and/ or nickel.

BACKGROUND AND OBJECTIVES

The present invention relates to a base material covered with diamond coating and the manufacturing process thereof which is used for cutting tool such as cutting chip, drill, and end mill, whetstone tool, and wear resistant abrasion tool. Particularly, it relates to a diamond coated material and the manufacturing process thereof which has no warp and flat shape and tenacious adherence with a base material by dispersedly reducing internal

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stress originated in the diamond coating during forming.

According to the development of vapor-phase synthesis of diamond, development of diamond coating tools formed by vapor-phase synthesis has been actively proceeded, wherein the diamond has been coated on a base material for tool such as cutting chip, drill, and end mill. In the case of directly coating the diamond on a base material for tool by vapor-phase synthesis, the diamond coating may peel off from the base material depending on the method due to the stress resulting from thermal expansion coefficient difference between the material of the base material and diamond, that is, the residual stress caused by temperature difference of during coating of the diamond on the base material from during cooling after coating, and therefore, it is difficult for practical use. On the other hand, the diamond has been coated in advance on a specific base material by vapor-phase synthesis, and then the base material covered with diamond coating obtained has been soldered with tool in such a manner as directly attaching with the base material and tool, or the base material has been removed by polishing after soldering with tool in such a manner as directly attaching with the diamond surface and tool, or the diamond coating alone has been soldered with tool after peeling the diamond coating from the diamond coated base material. In these methods, the thicker the thickness of the diamond coating is, the more residual stress increases, and in case of a thin base material, the base material covered with the diamond coating warps. Once warp occurs, troublesome increases which is that the longer polishing time is required to polish the coating surface or the

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diamond coating is easily cracked during soldering with tool. For example, laid-open Japanese patent Hei 1-167211, Hei 3-197677, and Hei 4-99278 disclose that the coating is formed at plural step for the purpose of improving tenacious adherence during forming the diamond coating on the base material, and the thus precipitated coating has multilayered structure. Moreover, laid-open Japanese patent Hei 5-306195 discloses the prevention of warp of the coating during forming the diamond coating.

Laid-open Japanese patent Hei 1-167211 disclose a diamond-like carbon coating and the synthesis thereof having small coating stress and smooth surface flatness comprising diamond like carbon layer including high content of amorphous carbon and that including low content of amorphous carbon. The objective of that invention is to obtain a diamond like carbon layer having flat surface and high light transmissivity for coating of lens or window and protecting film of magnetic disk, and it produces a coating of diamond like carbon formed by alternate precipitation of diamond like carbon layer including high content of amorphous carbon and that including low content of amorphous carbon periodically changing temperature of the base material, electromagnetic wave energy such as microwave and high frequency, concentration of carbon source, and reaction pressure. However, the objective of that invention is to obtain a diamond like carbon layer having flat surface and high light transmissivity, and in order to obtain the coating having smooth surface flatness without

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surface polishing such as lapping after forming coating, the uppermost surface layer should have smooth surface flatness and have low hardness of diamond like carbon layer including high content of amorphous carbon, and therefore, it is not suitably used as hard coating layer for tool due to insufficient wear resistance, which is the objective of the present invention.

Laid-open Japanese patent Hei-3-197677 discloses a diamond coated tool and the manufacturing process thereof which has multilayers of diamond coating coated on the base material such as cemented carbide, cermet, silicon nitride sintering, or aluminum oxide sintering, in which impurity composition of the first layer is higher than that of the second layer and grain size of diamond of the first layer is smaller than that of the second layer. In that invention the coating should be formed in the separated process, respectively, in which the coating of the first layer is formed by filament CVD, and then the coating of the second layer is formed by plasma CVD. Therefore, it is lacking in the productivity and it has possibility of the deposition of impurity such as particles of dust on the coating surface after forming the first layer which produces defects in the second layer.

Laid-open Japanese patent Hei 4-99278 discloses a diamond coated tool part having multilayered diamond coating layer having a thickness of 0.5-200 μ m formed on a hard material, which has not less than one layer of the diamond coating including carbon component except for diamond and not less than one layer without it, respectively. That invention intends to relax the impact given on the whole coating layer and to have

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peeling resistance and wear resistance at the same time by forming a high toughness diamond layer including carbon component as amorphous carbon which is the same component as diamond between diamond layer excluding carbon component except for diamond and the base material. However, it has a problem that the coating is easy to peel off, since stress originated in the coating increases as the thickness of the coating increases.

Laid-open Japanese patent Hei 5-306195 discloses a manufacturing process of CVD diamond thin coating having internal tensile stress released and flatness by forming the surface of the base material on which diamond coating precipitates into a convex shape having curvature radius, which compensates internal tensile stress supposed to be originated in the diamond thin coating obtained removing from the base material, and warping the thin coating removed from the base material in the opposite direction of the curvature of the base material. That invention is characterized to previously foresee the degree of warp of the coating caused by internal stress in the coating during precipitation of the diamond coating on the base material and to previously form the base material into a convex shape for compensating warp of the coating so that a flat coating could be obtained after releasing internal stress by removing the coating from the base material. However, it is lacking in practical use, since the forming condition of the diamond coating should precisely be controlled due to the shape of the convex base material for the reason that the internal stress originated in the coating is varied depending on forming equipment of it and the forming condition, for example, the greater the forming velocity of the coating, the greater the internal stress originated in the coating.

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SUMMARY OF THE INVENTION

The objective of the present invention is to produce a tenaciously adherent diamond coated material in which diamond coating is formed by vapor-phase synthesis on a base material without causing any warp of the coating.

The diamond coated material of the present invention has a diamond coating layer formed by vapor-phase synthesis on a surface of a base material having a number of cavities.

The cavities are preferably formed by electric discharge or laser beam irradiation and preferably is a pore having a depth of 0.0001-0.2 mm, especially 0.01-0.15 mm and a diameter of 0.001-0.2 mm, especially, not more than 0.01-0.1 mm.

Moreover, the pores are preferably connected to one another to form a groove.

The base material is preferably any one of molybdenum, tungsten, silicon, tungsten carbide, silicon carbide, silicon nitride, and cemented carbide mainly comprising tungsten carbide and cobalt and/or nickel.

In the present invention, it has been possible to obtain a diamond coated material having tenacious adhesion with a base material caused by anchoring effect produced by forming a diamond coating by vapor-phase synthesis on a base material having a number of cavities formed by electric discharge or laser beam irradiation.

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BRIEF EXPLANATION OF THE FIGURES

Figure 1 is a pattern of points arranged as zigzag which are illustrated on a base material;

Figure 2 is a pattern of circles arranged as zigzag which are illustrated on a base material;

Figure 3 is a pattern of rectangular lattices which are illustrated on a base material;

and Figure 4 is a pattern of honeycomb which are illustrated on a base material.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described in further detail by examples mentioned below.

An usable base material on which a diamond coating is formed by vapor-phase synthesis in the present invention includes metal such as silicon, molybdenum, tungsten, niobium, iron, copper, silver, gold, platinum, manganese, nickel, cobalt, tantalum, titanium, chromium, and zirconium, nonmetallic simple substance such as boron and graphite, carbide such as silicon carbide, tungsten carbide, titanium carbide, and tantalum carbide, oxide such as alumina, silica, zirconia, nitride such as boron nitride, silicon nitride, titanium nitride, and cemented carbide mainly comprising tungsten carbide and cobalt and/or nickel or that additionally comprising titanium carbide and/or tantalum carbide.

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However, the one having small thermal expansion coefficient difference from the precipitated diamond on the base material is preferable and also from the viewpoints of economy and practical use, any one of molybdenum, tungsten, silicon, tungsten carbide, silicon carbide, silicon nitride, and cemented carbide mainly comprising tungsten carbide and cobalt is suitable as the base material on which the diamond coating is formed in the present invention.

For the purpose of improving tenacious adhesion between the base material and the diamond coating formed on the surface of it by anchoring effect, a number of cavities (single pore, the pores which are intermittently connected, or a groove formed by the pores continuously connected to one another) having a depth of 0.0001-0.2 mm, preferably, 0.01-0.15 mm and a diameter of 0.001-0.2 mm, preferably, 0.01-0.1 mm are formed on the surface of the base material mentioned above.

These cavities are numerous formed in the points, lines (straight lines or curved lines), circles, ellipses, polygons, geometric patterns combined thereof or at random. The geometric patterns formed by the cavities, for example, may be arranged as zigzag at a constant pitch by points, circles, polygons or arranged as groove of square stitch lattice shaping grooves formed by a series of cavities continuously connected to one another so as to form two kinds of parallel lines at the same distance and crossing them at 90 degree angle with each other.

Moreover, a number of grooves may be arranged at random by polishing the surface of the base material with a diamond whetstone.

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The depth of the cavity less than 0.0001 mm cannot obtain sufficient anchoring effect and in case of thick diamond coating formed in particular, peeling of the coating is easy to occur.

On the other hand, if the depth of the cavity is over 0.2mm, improvement effect of tenacious adhesion of the coating is saturated, therefore, it is not necessary to deep the pore more further.

Also, in the case of forming pores by irradiation of YAG laser, it is difficult to produce a pore having a diameter less than 0.001 mm, which forms cavity, even if the beam is focalized. However, if the diameter of the cavity is over 0.2 mm, sufficient anchoring effect cannot be obtained, therefore, peeling of the coating is easy to occur.

Moreover, sufficient tenacious adhesion of the coating can be obtained when a pitch of single pore or geometric pattern, a distance of pores formed by cavities, lattice, or a geometric pattern, or a long diameter of geometric pattern is not more than 5 mm length.

As mentioned above, by forming a number of cavities on the surface of the base material whose depth is 0.0001-0.2 mm, tenacious adhesion between the surface of the base material and the diamond coating can be obtained due to anchoring effect.

As a method to form cavities on the surface of the base material, for example, YAG laser is preferable to use and another laser such as excimer laser and carbonic acid gas laser may be used, and another method such as diamond whestone, ion beam, and photo-resist may be possible to use.



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The adhesion between the base material and the diamond coating becomes more tenacious using the base material whose surface for coating the diamond is previously ground by electric discharge such as wire electric discharge machining, and forming cavities on that surface as mentioned above.

Next, the diamond coating is formed on the surface of the base material mentioned above using vapor-phase synthesis in the source gas comprising hydrogen and hydrocarbon. Microwave plasma CVD, filament CVD, DC plasma CVD, and RF plasma CVD can be applied as vapor-phase synthesis, and microwave plasma CVD is preferable to use for the present invention due to easy control of forming condition. Saturated hydrocarbon such as methane, ethane, propane, and butane, unsaturated hydrocarbon such as ethylene, propylene, and acetylene, alcohol such as methanol, butanol, and isopropanol, ketone such as acetone and methyl ethyl ketone, and aromatic compound such as benzene and toluene can be used as the hydrocarbon for source of carbon in the source gas, and from the viewpoints of economy and practical use, methane is preferably used. The hydrocarbon is mixed with hydrogen at a constant volume ratio. In some cases, it is possible to dilute the mixed gas by further mixing of inert gas such as argon. The mixed gas is supplied into the reaction chamber at a constant pressure. Microwave output power is applied in the source gas and the diamond coating is formed on the base material.

The diamond coated material obtained as mentioned above is used as it is covered with

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diamond coating in case of use for whetsone tool.

On the other hand, in case of use for cutting tool and wear resistant abrasion tool, it is used after the surface of the diamond coating is lapped.

EMBODIMENT

Example 1:

A cemented carbide of a diameter of 20 mm comprising tungsten carbide of 94% and cobalt of 6% was selected as a base material for diamond coating and it was cut off at a thickness of 0.7mm by wire electric discharge machining.

A base material having random arranged pattern (Cavity No.1), zigzaggingly arranged pattern of points (Cavity No.2, 3) as shown in Figures 1-4, zigzaggingly arranged pattern of circles (Cavity No.4, 5), rectangular lattice pattern (Cavity No. 6, 7), or honeycomb pattern (Cavity No. 8) described on the surface of the base material by YAG laser on the condition of Table 1 and a base material without forming cavities were produced as the base material for diamond coating respectively.

These base materials were cleaned by ultrasonic cleaning in acetone, then the diamond coating of a thickness of 0.25-0.3 mm was formed by microwave plasma CVD.

The warp of the diamond coated material obtained was measured as a maximum deviation (warp) by a two dimensional surface roughness meter and was evaluated by curvature radius R calculated from the Pythagorean theorem.



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Also, adhesion between the diamond coating and the base material was evaluated by visual inspection of the degree of peeling of the diamond coating formed. The results are shown in Table 2.

[Measurement of curvature radius]

Measuring equipment : two dimensional roughness meter Surfcom 1500 A manufactured by TOKYO SEIMITSU Co., Ltd.

Measuring method:

1) Measuring surface : a base material surface or a diamond coating surface precipitated

2) Measuring method and calculation:

Warp (maximum deviation : h) between two points having a distance : L (21) on a base material surface or a surface of the deposited diamond coating was measured and a curvature radius : R was calculated from the equation mentioned below using the Pythagorean theorem, that is,

$$(R - h)^2 + l^2 = R^2 ; R = (l^2 + h^2) / 2h$$

If the value of R is smaller than 500, warp of the diamond coated material formed becomes larger, therefore, in the present invention, not less than 500 was the passing grade.

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Table 1

Table 2

Example 2:

A cemented carbide of a diameter of 20 mm comprising tungsten carbide of 99% and cobalt of 1% was selected as a base material for diamond coating and it was cut off at a thickness of 0.7 mm by diamond cutter, then the surface was polished as a mirror surface using a table grinding machine.

Next, a base material on which Cavity No. 6 as shown in Table 1 was formed by YAG laser and a base material without forming cavities were produced as the base material for diamond coating, respectively. The base materials were cleaned by ultrasonic cleaning in acetone, then the diamond coating of a thickness of 0.25-0.3 mm was formed by microwave plasma CVD on the same condition described in Example 1. Warp (curvature radius R) of the diamond coated material obtained and the degree of peeling of the diamond coating formed are shown in Table 3.

Table 3

Example 3:

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Molybdenum, tungsten, tungsten carbide, and silicon carbide of a diameter of 20 mm were selected as base materials for diamond coating and were cut off at a thickness of 0.6-0.7 mm by wire electric discharge machining. Base materials on which Cavity No.3 and Cavity No.4 were formed by YAG laser on the condition of Table 1 in the same manner as Example 1 and base materials without forming cavities were produced as the base materials for diamond coating, respectively.

The base materials were cleaned by ultrasonic cleaning in acetone, then the diamond coating of a thickness of 0.25-0.3 mm was formed by microwave plasma CVD on the same condition described in Example 1. Warp (curvature radius R) of the diamond coated material obtained and the degree of peeling of the diamond coating formed are shown in Table 4 and 5.

Table 4

Table 5

Example 4:

Commercial silicon wafer and silicon nitride wafer having a thickness of 1 mm were selected as base materials for diamond coating and were cut off into squares of 30 mm. Base material on which Cavity No.8 was formed by YAG laser on the



condition of Table 1 in the same manner as Example 1 and base materials without forming cavities were produced as the base materials for diamond coating, respectively.

The base materials were cleaned by ultrasonic cleaning in acetone, then the diamond coating of a thickness of 0.25-0.3 mm was formed by microwave plasma CVD on the same condition described in Example 1. Warp (curvature radius R) of the diamond coated wafer obtained and the degree of peeling of the diamond coating formed are shown in Table 6.

Table 6

As shown in examples, the diamond coated materials of little warp and flat shape were obtained on the surface of the base material by diamond whetstone or YAG laser. The diamond coated materials having tenacious adhesion were also obtained.

As mentioned above, it is possible to produce a diamond coated material having tenacious adhesion in which a diamond coating is formed on a base material by vapor-phase synthesis without causing any warp in the present invention.

We claim:

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1. A diamond coated material having a diamond coating layer formed by vapor-phase synthesis on a surface of a base material having a number of cavities.
2. A diamond coated material as claimed in claim 1, wherein said cavity is formed by electric discharge or laser beam.
3. A diamond coated material as claimed in claim 1 or claim 2, wherein said cavity is a pore having a depth of 0.0001-0.2 mm and a diameter of 0.001-0.2 mm.
4. A diamond coated material as claimed in claim 1 or claim 2, wherein said cavity is a pore having a depth of 0.01-0.15 mm and a diameter of 0.01-0.1 mm.
5. A diamond coated material as claimed in claim 3 or claim 4, wherein said pores are connected to one another to form a groove.
6. A diamond coated material as claimed in any of claims 1-5, characterized in that said base material is any one of molybdenum, tungsten, silicon, tungsten carbide, silicon carbide, silicon nitride, and cemented carbide mainly comprising tungsten carbide and cobalt and/or nickel.

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Cavity No.	Depth (mm)	Diameter of pore (mm)	Pattern shape		Reference figure
1	0.01	0.05	Random (Polished by diamond whetstone)		
2	0.00005	0.001	Points (zigzaggingly arranged)	Distance of points is 0.5 mm.	Figure 1
3	0.0001	0.005		Distance of points is 0.5 mm.	
4	0.001	0.01	Circles (zigzaggingly arranged)	diameter of circle = 2 mm distance between center of circles = 5 mm	Figure 2
5	0.01	0.3		diameter of circle = 2 mm distance between center of circles = 5 mm.	
6	0.10	0.05	Rectangular lattice	Distance of lattice = 3 mm	Figure 3
7	0.18	0.13		Distance of lattice = 7 mm	
8	0.10	0.10	Honeycomb (length of one side = 3mm)		Figure 4

Table 2

Sample No.	Base material		Characteristics of diamond coated material		Classification
	Composition	Cavity No.	Radius of curvature	Peeling of coating	
11	Cemented carbide (94% WC + 6% Co)	7	690	No	Present invention
12		4	760	No	Present invention
13		5	830	No	Present invention
14		8	860	No	Present invention
15		3	1220	No	Present invention
16		6	1280	No	Present invention
17		1	1310	No	Present invention
18		2	1340	No	Present invention
19		-	Impossible to be measured	Overall	Comparative example

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Table 3

Sample No.	Base material		Characteristics of diamond coated material		Classification
	Composition	Cavity No.	Radius of curvature	Peeling of coating	
20	Cemented carbide (99% WC + 1% Co)	6	770	No	Present invention
21		-	Impossible to be measured	Overall	Comparative example

Table 4

Sample No.	Base material		Characteristics of diamond coated material		Classification
	Composition	Cavity No.	Radius of curvature	Peeling of coating	
22	Molybdenum (Mo)	3	630	No	Present invention
23		-	Impossible to be measured	Overall	Comparative example
24	Tungsten (W)	3	600	No	Present invention
25		-	Impossible to be measured	Overall	Comparative example

Table 5

Sample No.	Base material		Characteristics of diamond coated material		Classification
	Composition	Cavity No.	Radius of curvature	Peeling of coating	
26	Tungsten carbide (WC)	4	810	No	Present invention
27		-	Impossible to be measured	Overall	Comparative example
28	Silicon carbide (SiC)	4	660	No	Present invention
29		-	Impossible to be measured	Overall	Comparative example



Table 6

Sample No.	Base material		Characteristics of diamond coated material		Classification
	Composition	Cavity No.	Radius of curvature	Peeling of coating	
30	Silicon (Si)	8	770	No	Present invention
31		-	Impossible to be measured	Overall	Comparative example
32	Silicon nitride (Si ₃ N ₄)	8	920	No	Present invention
33		-	Impossible to be measured	Overall	Comparative example

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Figure 1

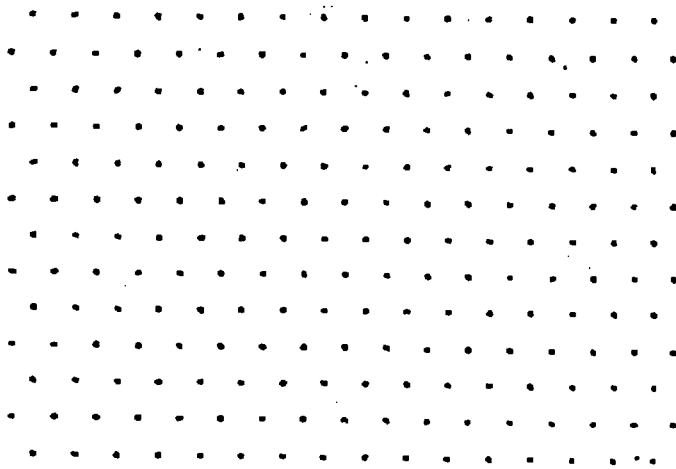
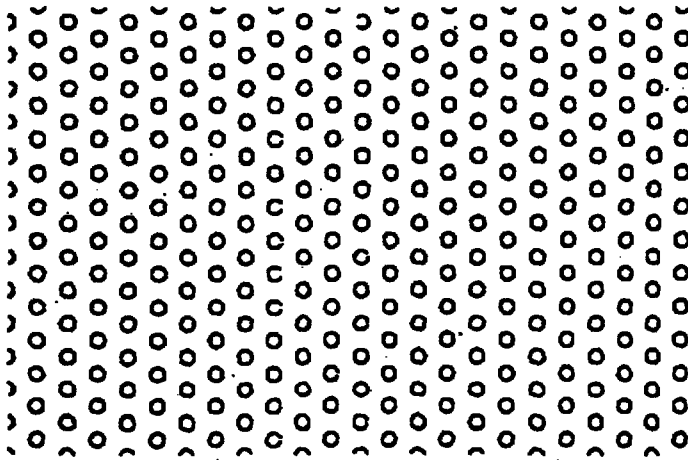


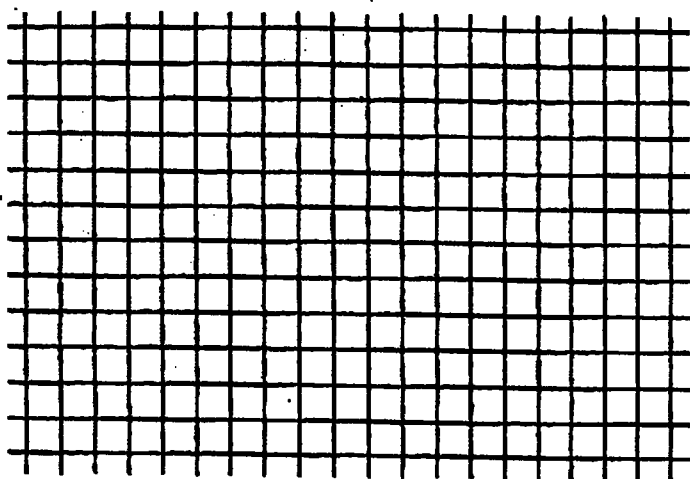
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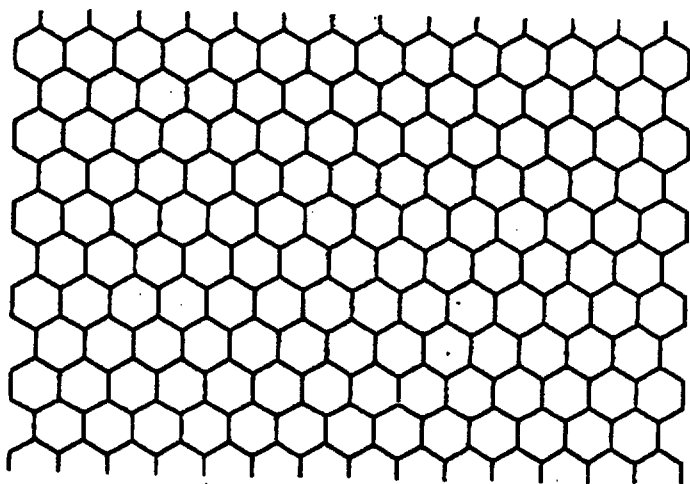


Figure 3



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Figure 4



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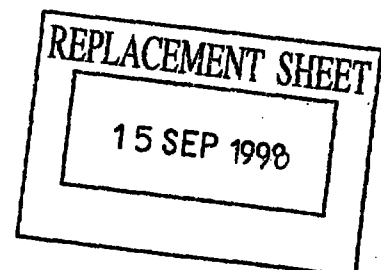
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SYNTHESIS**

ABSTRACT

The objective of the present invention is to produce a material with a tenaciously adherent diamond coating made by forming a diamond coating on a base material by vapor-phase synthesis without causing any warp of the coating. The diamond coating layer is formed on the surface of a base material having a number of cavities formed by electric discharge or laser beams, and the cavity is a pore having a depth of 0.0001-0.2 mm and a diameter of 0.001-0.2 mm. The pores may be connected to one another to form a groove. Suitable examples of the base material include molybdenum, tungsten, silicon, tungsten carbide, silicon carbide, silicon nitride, and cemented carbide mainly comprising tungsten carbide and cobalt and/ or nickel.

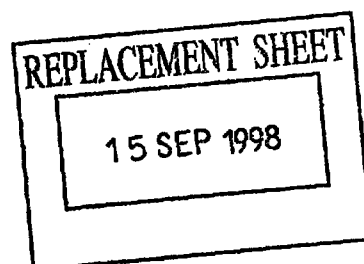
BACKGROUND AND OBJECTIVES

The present invention relates to a base material covered with diamond coating and the manufacturing process thereof which may be used for cutting tool such as cutting chip, drill, and end mill, whetstone tool, and wear resistant abrasion tool. Particularly, it relates to a diamond coated material and the manufacturing process thereof which has no warp and flat shape and tenacious adherence with a base material by dispersedly reducing internal



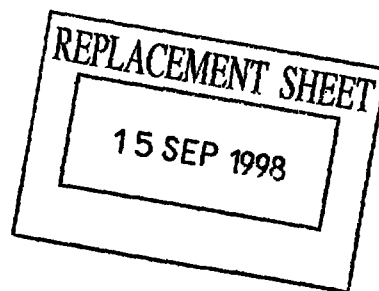
stress originated in the diamond coating during forming.

According to the development of vapor-phase synthesis of diamond, development of diamond coating tools formed by vapor-phase synthesis has been actively proceeded, wherein the diamond has been coated on a base material for tool such as cutting chip, drill, and end mill. In the case of directly coating the diamond on a base material for tool by vapor-phase synthesis, the diamond coating may peel off from the base material depending on the method due to the stress resulting from thermal expansion coefficient difference between the material of the base material and diamond, that is, the residual stress caused by temperature difference of during coating of the diamond on the base material from during cooling after coating, and therefore, it is difficult for practical use. On the other hand, the diamond has been coated in advance on a specific base material by vapor-phase synthesis, and then the base material covered with diamond coating obtained has been soldered with tool in such a manner as directly attaching with the base material and tool, or the base material has been removed by polishing after soldering with tool in such a manner as directly attaching with the diamond surface and tool, or the diamond coating alone has been soldered with tool after peeling the diamond coating from the diamond coated base material. In these methods, the thicker the thickness of the diamond coating is, the more residual stress increases, and in case of a thin base material, the base material covered with the diamond coating warps. Once warp occurs, troublesome increases which is that the longer polishing time is required to polish the coating surface or the



diamond coating is easily cracked during soldering with tool. For example, laid-open Japanese patent Hei 1-167211, Hei 3-197677, and Hei 4-99278 disclose that the coating is formed at plural step for the purpose of improving tenacious adherence during forming the diamond coating on the base material, and the thus precipitated coating has multilayered structure. Moreover, laid-open Japanese patent Hei 5-306195 discloses the prevention of warp of the coating during forming the diamond coating.

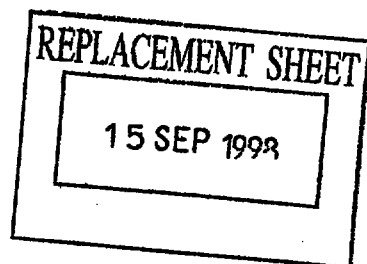
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surface polishing such as lapping after forming coating, the uppermost surface layer should have smooth surface flatness and have low hardness of diamond like carbon layer including high content of amorphous carbon, and therefore, it is not suitably used as hard coating layer for tool due to insufficient wear resistance, which is the objective of the present invention.

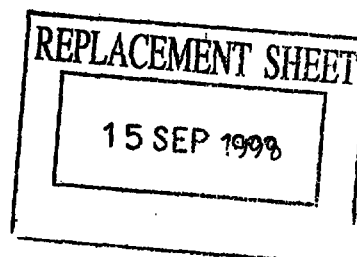
Laid-open Japanese patent Hei-3-197677 discloses a diamond coated tool and the manufacturing process thereof which has multilayers of diamond coating coated on the base material such as cemented carbide, cermet, silicon nitride sintering, or aluminum oxide sintering, in which impurity composition of the first layer is higher than that of the second layer and grain size of diamond of the first layer is smaller than that of the second layer. In that invention the coating should be formed in the separated process, respectively, in which the coating of the first layer is formed by filament CVD, and then the coating of the second layer is formed by plasma CVD. Therefore, it is lacking in the productivity and it has possibility of the deposition of impurity such as particles of dust on the coating surface after forming the first layer which produces defects in the second layer.

Laid-open Japanese patent Hei 4-99278 discloses a diamond coated tool part having multilayered diamond coating layer having a thickness of 0.5-200 μ m formed on a hard material, which has not less than one layer of the diamond coating including carbon component except for diamond and not less than one layer without it, respectively. That invention intends to relax the impact given on the whole coating layer and to have



peeling resistance and wear resistance at the same time by forming a high toughness diamond layer including carbon component as amorphous carbon which is the same component as diamond between diamond layer excluding carbon component except for diamond and the base material. However, it has a problem that the coating is easy to peel off, since stress originated in the coating increases as the thickness of the coating increases.

Laid-open Japanese patent Hei 5-306195 discloses a manufacturing process of CVD diamond thin coating having internal tensile stress released and flatness by forming the surface of the base material on which diamond coating precipitates into a convex shape having curvature radius, which compensates internal tensile stress supposed to be originated in the diamond thin coating obtained removing from the base material, and warping the thin coating removed from the base material in the opposite direction of the curvature of the base material. That invention is characterized to previously foresee the degree of warp of the coating caused by internal stress in the coating during precipitation of the diamond coating on the base material and to previously form the base material into a convex shape for compensating warp of the coating so that a flat coating could be obtained after releasing internal stress by removing the coating from the base material. However, it is lacking in practical use, since the forming condition of the diamond coating should precisely be controlled due to the shape of the convex base material for the reason that the internal stress originated in the coating is varied depending on forming equipment of it and the forming condition, for example, the greater the forming velocity of the coating, the greater the internal stress originated in the coating.



SUMMARY OF THE INVENTION

The objective of the present invention is to produce a tenaciously adherent diamond coated material in which diamond coating is formed by vapor-phase synthesis on a base material without causing any warp of the coating.

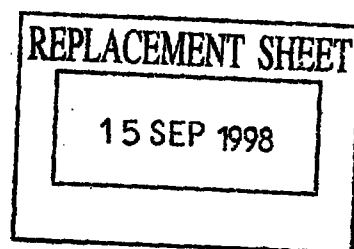
The diamond coated material of the present invention has a diamond coating layer formed by vapor-phase synthesis on a surface of a base material having a number of cavities.

The cavities are preferably formed by electric discharge or laser beam irradiation and preferably is a pore having a depth of 0.0001-0.2 mm, especially 0.01-0.15 mm and a diameter of 0.001-0.2 mm, especially, not more than 0.01-0.1 mm.

Moreover, the pores are preferably connected to one another to form a groove.

The base material is preferably any one of molybdenum, tungsten, silicon, tungsten carbide, silicon carbide, silicon nitride, and cemented carbide mainly comprising tungsten carbide and cobalt and/or nickel.

In the present invention, it has been possible to obtain a diamond coated material having tenacious adhesion with a base material caused by anchoring effect produced by forming a diamond coating by vapor-phase synthesis on a base material having a number of cavities formed by electric discharge or laser beam irradiation.



BRIEF EXPLANATION OF THE FIGURES

Figure 1 is a pattern of points arranged as zigzag which are illustrated on a base material in accordance with an embodiment of the invention.

Figure 2 is a pattern of circles arranged as zigzag which are illustrated on a base material;

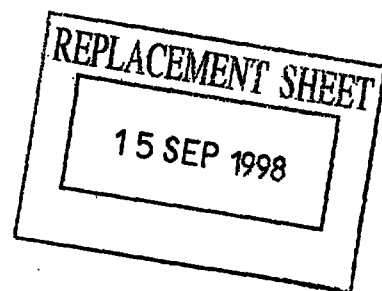
Figure 3 is a pattern of rectangular lattices which are illustrated on a base material;

and Figure 4 is a pattern of honeycomb which are illustrated on a base material.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

Embodiments of the present invention will be described in further detail by way of examples only with reference to the drawings.

An usable base material on which a diamond coating is formed by vapor-phase synthesis in the present invention includes metal such as silicon, molybdenum, tungsten, niobium, iron, copper, silver, gold, platinum, manganese, nickel, cobalt, tantalum, titanium, chromium, and zirconium, nonmetallic simple substance such as boron and graphite, carbide such as silicon carbide, tungsten carbide, titanium carbide, and tantalum carbide, oxide such as alumina, silica, zirconia, nitride such as boron nitride, silicon nitride, titanium nitride, and cemented carbide mainly comprising tungsten carbide and cobalt and/or nickel or that additionally comprising titanium carbide and/or tantalum carbide.

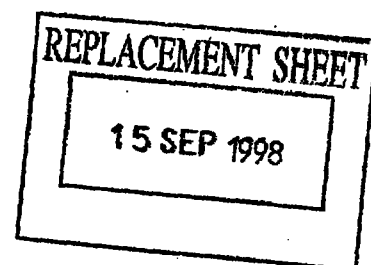


However, the one having small thermal expansion coefficient difference from the precipitated diamond on the base material is preferable and also from the viewpoints of economy and practical use, any one of molybdenum, tungsten, silicon, tungsten carbide, silicon carbide, silicon nitride, and cemented carbide mainly comprising tungsten carbide and cobalt is suitable as the base material on which the diamond coating is formed in the present invention.

For the purpose of improving tenacious adhesion between the base material and the diamond coating formed on the surface of it by anchoring effect, a number of cavities (single pore, the pores which are intermittently connected, or a groove formed by the pores continuously connected to one another) having a depth of 0.0001-0.2 mm, preferably, 0.01-0.15 mm and a diameter of 0.001-0.2 mm, preferably, 0.01-0.1 mm are formed on the surface of the base material mentioned above.

These cavities are numerous formed in the points, lines (straight lines or curved lines), circles, ellipses, polygons, geometric patterns combined thereof or at random. The geometric patterns formed by the cavities, for example, may be arranged as zigzag at a constant pitch by points, circles, polygons or arranged as groove of square stitch lattice shaping grooves formed by a series of cavities continuously connected to one another so as to form two kinds of parallel lines at the same distance and crossing them at 90 degree angle with each other.

Moreover, a number of grooves may be arranged at random by polishing the surface of the base material with a diamond whetstone.



The depth of the cavity less than 0.0001 mm cannot obtain sufficient anchoring effect and in case of thick diamond coating formed in particular, peeling of the coating is easy to occur.

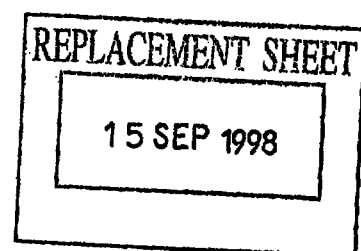
On the other hand, if the depth of the cavity is over 0.2mm, improvement effect of tenacious adhesion of the coating is saturated, therefore, it is not necessary to deep the pore more further.

Also, in the case of forming pores by irradiation of YAG laser, it is difficult to produce a pore having a diameter less than 0.001 mm, which forms cavity, even if the beam is focalized. However, if the diameter of the cavity is over 0.2 mm, sufficient anchoring effect cannot be obtained, therefore, peeling of the coating is easy to occur.

Moreover, sufficient tenacious adhesion of the coating can be obtained when a pitch of single pore or geometric pattern, a distance of cavity formed by cavities, lattice, or a geometric pattern, or a long diameter of geometric pattern is not more than 5 mm length.

As mentioned above, by forming a number of cavities on the surface of the base material whose depth is 0.0001-0.2 mm, tenacious adhesion between the surface of the base material and the diamond coating can be obtained due to anchoring effect.

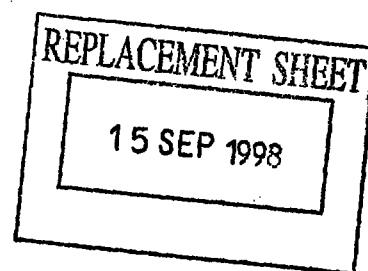
As a method to form cavities on the surface of the base material, for example, YAG laser is preferable to use and another laser such as excimer laser and carbonic acid gas laser may be used, and another method such as diamond whestone, ion beam, and photo-resist may be possible to use.



The adhesion between the base material and the diamond coating becomes more tenacious using the base material whose surface for coating the diamond is previously ground by electric discharge such as wire electric discharge machining, and forming cavities on that surface as mentioned above.

Next, the diamond coating is formed on the surface of the base material mentioned above using vapor-phase synthesis in the source gas comprising hydrogen and hydrocarbon. Microwave plasma CVD, filament CVD, DC plasma CVD, and RF plasma CVD can be applied as vapor-phase synthesis, and microwave plasma CVD is preferable to use for the present invention due to easy control of forming condition. Saturated hydrocarbon such as methane, ethane, propane, and butane, unsaturated hydrocarbon such as ethylene, propylene, and acetylene, alcohol such as methanol, butanol, and isopropanol, ketone such as acetone and methyl ethyl ketone, and aromatic compound such as benzene and toluene can be used as the hydrocarbon for source of carbon in the source gas, and from the viewpoints of economy and practical use, methane is preferably used. The hydrocarbon is mixed with hydrogen at a constant volume ratio. In some cases, it is possible to dilute the mixed gas by further mixing of inert gas such as argon. The mixed gas is supplied into the reaction chamber at a constant pressure. Microwave output power is applied in the source gas and the diamond coating is formed on the base material.

The diamond coated material obtained as mentioned above is used as it is covered with



diamond coating in case of use for whetsone tool.

On the other hand, in case of use for cutting tool and wear resistant abrasion tool, it is used after the surface of the diamond coating is lapped.

EMBODIMENT

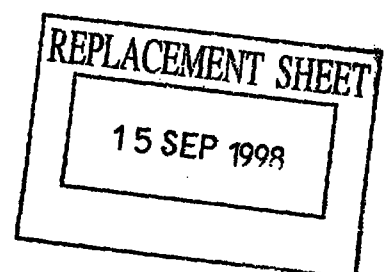
Example 1:

A cemented carbide of a diameter of 20 mm comprising tungsten carbide of 94% and cobalt of 6% was selected as a base material for diamond coating and it was cut off at a thickness of 0.7mm by wire electric discharge machining.

A base material having random arranged pattern (Cavity No.1), zigzaggingly arranged pattern of points (Cavity No.2, 3) as shown in Figures 1-4, zigzaggingly arranged pattern of circles (Cavity No.4, 5), rectangular lattice pattern (Cavity No. 6, 7), or honeycomb pattern (Cavity No. 8) described on the surface of the base material by YAG laser on the condition of Table 1 and a base material without forming cavities were produced as the base material for diamond coating respectively.

These base materials were cleaned by ultrasonic cleaning in acetone, then the diamond coating of a thickness of 0.25-0.3 mm was formed by microwave plasma CVD.

The warp of the diamond coated material obtained was measured as a maximum deviation (warp) by a two dimensional surface roughness meter and was evaluated by curvature radius R calculated from the Pythagorean theorem.



Also, adhesion between the diamond coating and the base material was evaluated by visual inspection of the degree of peeling of the diamond coating formed. The results are shown in Table 2.

[Measurement of curvature radius]

Measuring equipment : two dimensional roughness meter Surfcom 1500 A manufactured by TOKYO SEIMITSU Co., Ltd.

Measuring method:

1) Measuring surface : a base material surface or a diamond coating surface precipitated

2) Measuring method and calculation:

Warp (maximum deviation : h) between two points having a distance : L (21) on a base material surface or a surface of the deposited diamond coating was measured and a curvature radius : R was calculated from the equation mentioned below using the Pythagorean theorem, that is,

$$(R - h)^2 + l^2 = R^2 ; R = (l^2 + h^2) / 2h$$

If the value of R is smaller than 500, warp of the diamond coated material formed becomes larger, therefore, in the present invention, not less than 500 was the passing grade.

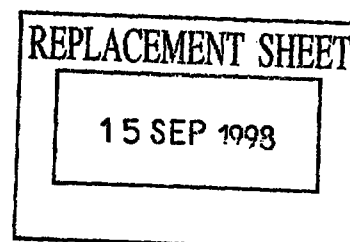


Table 1

Cavity No.	Depth (mm)	Diameter of pore (mm)	Pattern shape		Reference figure
1	0.01	0.05	Random (Polished by diamond whetstone)		
2	0.00005	0.001	Points (zigzaggingly arranged)	Distance of points is 0.5 mm.	Figure 1
3	0.0001	0.005		Distance of points is 0.5 mm.	
4	0.001	0.01	Circles (zigzaggingly arranged)	diameter of circle = 2 mm distance between center of circles = 5 mm	Figure 2
5	0.01	0.3		diameter of circle = 2 mm distance between center of circles = 10 mm	
6	0.10	0.05	Rectangular lattice	Distance of lattice = 3 mm	Figure 3
7	0.18	0.13		Distance of lattice = 7 mm	
8	0.10	0.10	Honeycomb (length of one side = 3mm)		Figure 4

Table 2

Sample No.	Base material		Characteristics of diamond coated material		Classification
	Composition	Cavity No.	Radius of curvature	Peeling of coating	
11	Cemented carbide (94% WC + 6% Co)	7	690	No	Present invention
12		4	760	No	Present invention
13		5	830	No	Present invention
14		8	860	No	Present invention
15		3	1220	No	Present invention
16		6	1280	No	Present invention
17		1	1310	No	Present invention
18		2	1340	No	Present invention
19		-	Impossible to be measured	Overall	Comparative example

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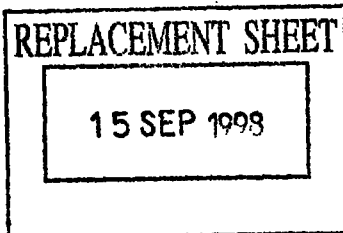
Example 2:

A cemented carbide of a diameter of 20 mm comprising tungsten carbide of 99% and cobalt of 1% was selected as a base material for diamond coating and it was cut off at a thickness of 0.7 mm by diamond cutter, then the surface was polished as a mirror surface using a table grinding machine.

Next, a base material on which Cavity No. 6 as shown in Table 1 was formed by YAG laser and a base material without forming cavities were produced as the base material for diamond coating, respectively. The base materials were cleaned by ultrasonic cleaning in acetone, then the diamond coating of a thickness of 0.25-0.3 mm was formed by microwave plasma CVD on the same condition described in Example 1. Warp (curvature radius R) of the diamond coated material obtained and the degree of peeling of the diamond coating formed are shown in Table 3.

Table 3

Sample No.	Base material		Characteristics of diamond coated material		Classification
	Composition	Cavity No.	Radius of curvature	Peeling of coating	
20	Cemented carbide (99% WC + 1% Co)	6	770	No	Present invention
21		-	Impossible to be measured	Overall	Comparative example



Example 3:

Molybdenum, tungsten, tungsten carbide, and silicon carbide of a diameter of 20 mm were selected as base materials for diamond coating and were cut off at a thickness of 0.6-0.7 mm by wire electric discharge machining. Base materials on which Cavity No.3 and Cavity No.4 were formed by YAG laser on the condition of Table 1 in the same manner as Example 1 and base materials without forming cavities were produced as the base materials for diamond coating, respectively.

The base materials were cleaned by ultrasonic cleaning in acetone, then the diamond coating of a thickness of 0.25-0.3 mm was formed by microwave plasma CVD on the same condition described in Example 1. Warp (curvature radius R) of the diamond coated material obtained and the degree of peeling of the diamond coating formed are shown in Table 4 and 5.

Table 4

Sample No.	Base material		Characteristics of diamond coated material		Classification
	Composition	Cavity No.	Radius of curvature	Peeling of coating	
22	Molybdenum (Mo)	3	630	No	Present invention
23		-	Impossible to be measured	Overall	Comparative example
24	Tungsten (W)	3	600	No	Present invention
25		-	Impossible to be measured	Overall	Comparative example

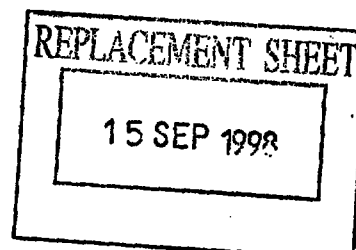


Table 5

Sample No.	Base material		Characteristics of diamond coated material		Classification
	Composition	Cavity No.	Radius of curvature	Peeling of coating	
26	Tungsten carbide (WC)	4	810	No	Present invention
27		-	Impossible to be measured	Overall	Comparative example
28	Silicon carbide (SiC)	4	660	No	Present invention
29		-	Impossible to be measured	Overall	Comparative example

Example 4:

Commercial silicon wafer and silicon nitride wafer having a thickness of 1 mm were selected as base materials for diamond coating and were cut off into squares of 30 mm. Base material on which Cavity No.8 was formed by YAG laser on the condition of Table 1 in the same manner as Example 1 and base materials without forming cavities were produced as the base materials for diamond coating, respectively

The base materials were cleaned by ultrasonic cleaning in acetone, then the diamond coating of a thickness of 0.25-0.3 mm was formed by microwave plasma CVD on the same condition described in Example 1. Warp (curvature radius R) of the diamond coated wafer obtained and the degree of peeling of the diamond coating formed are shown in Table 6.

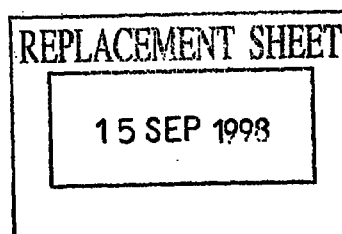


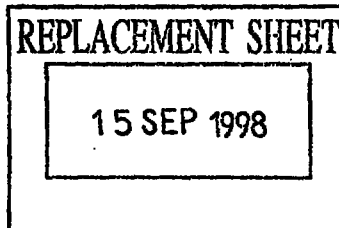
Table 6

Sample No.	Base material		Characteristics of diamond coated wafer		Classification
	Composition	Cavity No.	Radius of curvature	Peeling of coating	
30	Silicon (Si)	8	770	No	Present invention
31		-	Impossible to be measured	Overall	Comparative example
32	Silicon nitride (Si ₃ N ₄)	8	920	No	Present invention
33		-	Impossible to be measured	Overall	Comparative example

As shown in examples, the diamond coated materials of little warp and flat shape were obtained on the surface of the base material by diamond whetstone or YAG laser. The diamond coated materials having tenacious adhesion were also obtained.

As mentioned above, it is possible to produce a diamond coated material having tenacious adhesion in which a diamond coating is formed on a base material by vapor-phase synthesis without causing any warp in the present-invention.

The embodiments have been described by way of example only and modifications are possible within the spirit and scope of the invention as defined by the claims.

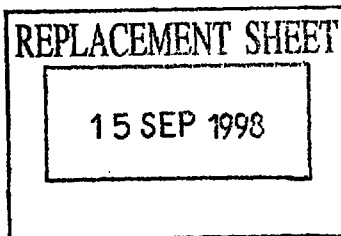




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CLAIMS

1. A diamond coated material having a diamond coating layer formed by vapor-phase synthesis on a surface of a base material having a number of cavities.
2. A diamond coated material as claimed in claim 1, wherein said cavity is formed by electric discharge or laser beam.
3. A diamond coated material as claimed in claim 1 or claim 2, wherein said cavity is a pore having a depth of 0.0001-0.2 mm and a diameter of 0.001-0.2 mm.
4. A diamond coated material as claimed in claim 1 or claim 2, wherein said cavity is a pore having a depth of 0.01-0.15 mm and a diameter of 0.01-0.1 mm.
5. A diamond coated material as claimed in claim 3 or claim 4, wherein said pores are connected to one another to form a groove.
6. A diamond coated material as claimed in any of claims 1-5, characterized in that said base material is any one of molybdenum, tungsten, silicon, tungsten carbide, silicon carbide, silicon nitride, and cemented carbide mainly comprising tungsten carbide and cobalt and/or nickel.



ABSTRACT

The objective of the present invention is to produce a material with a tenaciously adherent diamond coating made by forming a diamond coating on a base material by vapor-phase synthesis without causing any warp of the coating. The diamond coating layer is formed on the surface of a base material having a number of cavities formed by electric discharge or laser beams, and the cavity is a pore having a depth of 0.0001-0.2 mm and a diameter of 0.001-0.2 mm. The pores may be connected to one another to form a groove. Suitable examples of the base material include molybdenum, tungsten, silicon, tungsten carbide, silicon carbide, silicon nitride, and cemented carbide mainly comprising tungsten carbide and cobalt and/ or nickel.

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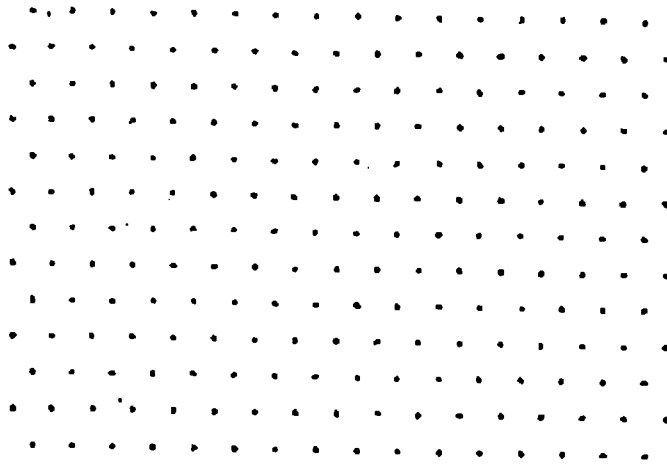


Figure 1

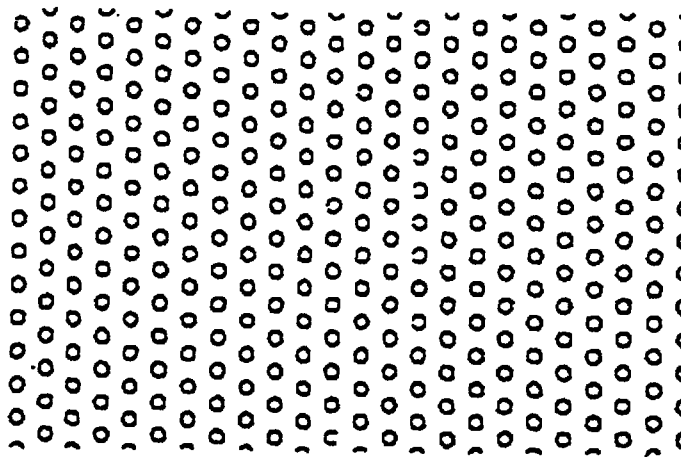
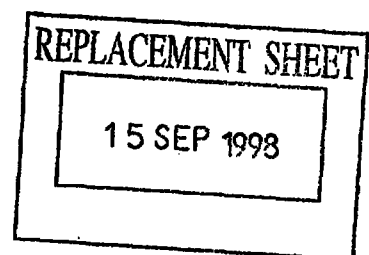


Figure 2



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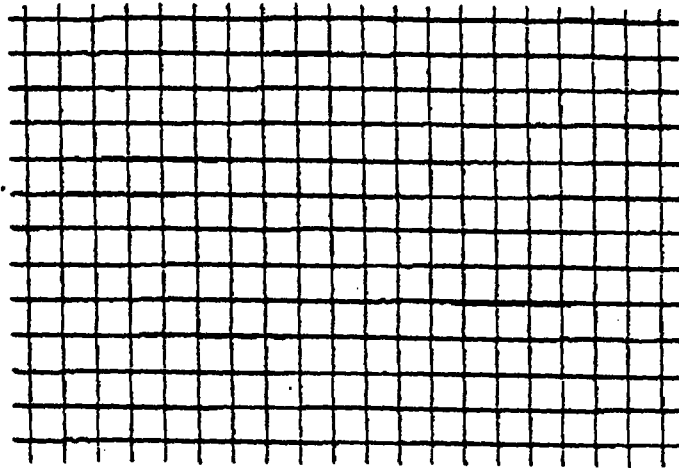


Figure 3

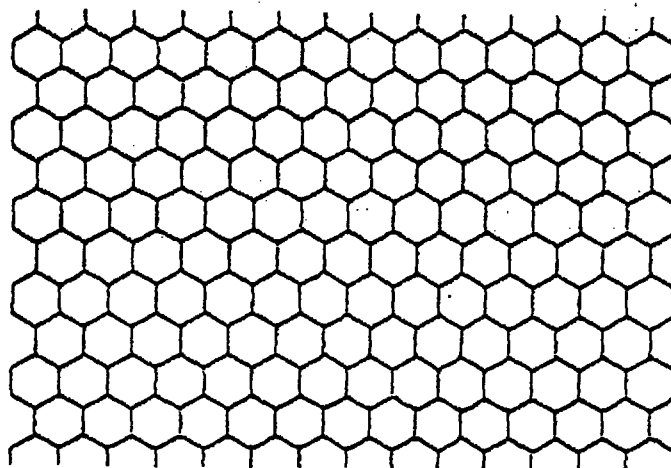


Figure 4

