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(54) Low pressure bonding of PCD bodies and method.

(57) A temperature stable diamond product (30) having a temperature stability up to about 1,200°C comprising a metal matrix carrier, at least one diamond piece (31a-31f) of a predetermined geometrical shape and which is temperature stable up to about 1,200°C having at least one surface (41) contacting at least a portion of said carrier (32), each diamond piece (31a-31f) being coated with a metal which is a carbide former on at least the portion thereof contacting said metal matrix carrier, said carbide forming coating being of a thickness of at least about 1 micron and including a relatively thin portion of a carbide material adjacent to said portion thereof contacting said diamond piece, and said temperature stable diamond product (30) being characterized by a chemical bond between said temperature stable diamond and said coating and said coating and the portion of said matrix carrier (32) which is in contact with said coating.

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LOW PRESSURE BONDING OF PCD BODIES AND METHOD

Field of Invention

The present invention relates to an improved synthetic diamond product and method of making the same and more particularly to an improved and novel temperature stable diamond assembly which may be of a variety of sizes, shapes, and thickness, the diamond assembly being formed by an improved and novel bonding method which does not require the comparatively high temperatures and pressures normally used in the synthesis of synthetic diamond products thus to provide a diamond assembly which may be relatively large and in which the diamond, preferably in the form of a temperature stable synthetic polycrystalline diamond, is firmly and chemically bonded on or to a support structure.

Background of the Invention

Various types of synthetic diamond products are known and commercially available. Typically such products are used industrially for material removal purposes, for example drilling products such as core bits, mining bits, drilling bits for oil and gas, saw products, cutting tools, grinding wheels, and products such as wire-drawing and extruding dies, bearing surfaces, dressers, lead bonding tools and abrasives.

These synthetic diamond materials may vary somewhat in their character, one being an unleached polycrystalline product having a temperature stability of up to about 700-750 degrees C., see United States Patents 3,745,623 and 3,608,818. This synthetic diamond product itself is usually formed by diamond-to-diamond bonds and is carried on a substrate which may be cemented tungsten carbide, for example. The substrate is usually preformed and contains cobalt, the diamond product being formed and affixed to the substrate at very high temperatures and pressures, usually referred to as the diamond stable region of temperature and pressure, as set forth in prior patents and other literature, and typically above 50 kbar and at a temperature above 1,200 degrees C.

In this processing the cobalt in the substrate is used as a binder for the tungsten carbide and as a solvent/catalyst for the formation of diamond-to-diamond bonds. The presence of cobalt results in somewhat limited temperature stability of the diamond as noted. It is not uncommon to refer to these products as polycrystalline diamond products (PCD) as contrasted to single crystal diamonds.

PCD elements offer the advantage that upon fracture, only a relatively small fragment of the PCD element is lost as compared to a single crystal diamond in which fracture takes place along a plane with the possibility of losing a relatively large piece of the diamond.

Unleached PCD elements may be formed with the high temperature and high pressure apparatus as disclosed, for example, in United States Patent 2,941,248. PCD products thus far described are available in various sizes and shapes, for example circular, half-circles, quarter round, square, rectangular, half-rounds with a pointed section, and the like. The PCD face or disc, joined to a backing member of tungsten carbide or the like is sometimes mounted, by brazing, on a steel tool body or tungsten carbide slug support. The PCD materials may be as small as several millimeters to as large as 80 millimeters in diameter, see for example United States Patent Application Serial Number 909,168, filed September 11, 1986, and assigned to the same assignee (CHP 6149).

Inclusions such as cobalt, iron or nickel present in unleached PCD elements as residual material initially used as solvents/catalysts in the synthesis of the PCD tend to reduce the temperature stability of the PCD to well below 1,200 degrees C., for example, to about 750 degrees C.

The fabrication of the larger diameter materials requires rather large and expensive processing equipment capable of generating high pressures and temperatures. The temperatures and pressures are those in the diamond forming region of the phase diagram for carbon, see for example United States Patents 4,108,614 and 4,411,672. The length of the substrate or backing is a limitation since the processing equipment must be capable of fabricating a diamond facing on a rather long piece which takes up room in the press. The result is that in at least one instance, the length of the backing, axially to the rear of the PCD face, is rather short and after formation, a longer tungsten carbide member or member of other material is attached to the formed product by any one of several well known procedures, and as described in United States Patent 4,200,159, for example.

In one typical use of these products, for example in oil and gas drilling bits and core bits, the usual practice is to form the bit body and thereafter to mount the PCD cutting element in the bit body. The bit body may be steel and the PCD cutter is a slug type cutter which is press fitted into apertures in the bit body. These procedures are well known. The difficulty with the use of steel bodies is that the body and/or the cutter assembly may be sub-

ject to erosion by the relatively abrasive flow of the drilling fluid used to clean and cool the bit. Thus, the practice has been to hard face the steel body or to use a carbide slug. In the case of matrix body bits which offer erosion resistance, the practice has been to mount the PCD cutter, normally having an added backing or of a sufficiently long length integrally formed as one piece, by brazing the cutter to the matrix body. One of the problems associated with this procedure, in addition to the increased cost, is the desire to use a relatively high temperature braze material and the need to keep the PCD face cool to prevent thermal damage (above about 750 degrees C.) to the cutter face during the brazing operation. Even so, a large number of bits have been made as described by a variety of bit manufacturers.

Another commercially available form of PCD, sold under the mark GEOSET, is an unbacked leached product, see United States Patents 4,224,380 and 4,288,248, which has a temperature stability of up to 1,200 degrees C., but which may have a porosity of up to about 15% and may not be as impact resistant as desired in a particular application. The temperature stability of these PCD products offers the advantage that they can be processed during the infiltration of the matrix material used to form the bit body and may be exposed to the relatively high tempeatures used during the infiltration procedure without degradation of the PCD, thus eliminating the need for brazing. In general, temperature stability is also an advantage in the cutting action of the PCD during use. For the purposes of this invention, temperature stability means that the PCD element, regardless of type, is stable to about 1,200 degrees C. without significant deterioration in its properties and will be referred to herein as TSPCD. Typical temperature stable leached PCD material is available under the trademark GEOSET, which obtains porosity.

Temperature stable PCD elements are known which are not porous and are not leached. A typical such material, available under the trademark SYNDAX-3 is a PCD in which silicon is present in the form of silicon carbide.

Significantly, the TSPCD materials are not commercially available as backed products, as contrasted to the previously described low temperature products. The TSPCD materials are available as unbacked materials in a wide variety of shapes and sizes, for example, triangular, square, cylindrical with flat ends or pointed at one end, round discs, rectangular, ovoid, and the like. These products may also be cut to form other shapes by using a laser or other means.

While temperature stability is not required in all uses, there are many applications in which it is required. Further, there are processing steps such as brazing in which the PCD part may be exposed to temperatures above 750 degrees C. In these instances it is necessary to cool the PCD part or to otherwise prevent it from being exposed to the higher temperature. As a result, there are limitations in the processing of such unstable PCD products which tend to limit the use thereof.

TSPCD elements, are available in a limited range of sizes that are generally too small for individual use in many applications. To overcome this problem, TSPCD elements have been formed into a mosaic type of structure in which the individual TSPCD elements are mounted and mechanically affixed in a support structure, e.g., a hot-pressed segment or the like, see United States Patent Applications Serial Number 797,098; 794,569 and 797,568, filed respectively on November 14,1985, November 4, 1985 and November 13,1984, and all assigned to the same assignee as this application.

While these mosaic structures have been operated satisfactorily and provide a large PCD cutter having temperature stability, the mosaic elements lack the advantages of the large one piece PCD cutters (up to 50 mm diameter or more) which are not temperature stable but which have been used in oil and gas drill bits and core bits. Even though the bits using the mosaic cutters avoid the necessity of having to braze the mosaic into the matrix of the bit, the mosaic cutters do not function as a large one piece PCD with the result that the individual mechanically mounted TSPCD elements can be broken free of the supporting structure. A mechanical type of mounting also limits the shape and size and contour of the cutter, even though the assembly is temperature stable.

Another problem with mosaic cutters is that bending stresses tend to cause release of the mechanically mounted TSPCD elements. Moreover, unlike a large integral brazed PCD cutter of the same size in which only small portions of the PCD are fractured off during use, the tendency in the mosaic cutters is to release the TSPCD elements as the supporting structure around the TSPCD is abraded away and support for the TSPCD is reduced, i.e., the individual TSPCD element is lost rather than losing on a small fragment.

In general there is a need for a TSPCD containing product in which one or more TSPCD elements are firmly anchored or locked into or mounted on a suitable support, which optionally may be mounted to another structure. It is desirable to

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mount one or more of such TSPCD elements by more than merely a mechanical mounting, and preferably it is desired that the mounting be by a firm chemical bond.

United States Patent 3,650,714 of March 21, 1972, issued to Farkas, describes a method for coating natural single crystal diamond particles in the range of 200 to 250 mesh with either titanium or zirconium. The coating is applied from dry powder, the resultant material is then heated in a graphite mold, under vacuum conditions for between 10 and 15 minutes at a temperature in the range of 850 to 900 degrees C. The relatively low temperature of heating to form a carbide at the interface indicates that the titanium or zirconium coating is quite thin. The result is said to be a coated diamond particle in which the coating is about 5% by weight of the resultant product and in which a carbide is formed at the interface, with the outer surface of the coating being non-carbided. The calculated thickness of the coating is about 0.445 of a micron for 200 mesh material and 0.344 of a micron for 250 mesh material. Since subsequent processing in an oxidizing atmosphere would result in the formation of an oxide which is not easily wetted by other materials, the coated natural diamond particles are overcoated with either nickel or copper with a film thickness of between 0.002 and 0.005 of an inch (between 50.8 and 127 microns thick). This outer coating is said to serve as a protective coating to prevent oxidation of the titanium or zirconium or their carbides during subsequent processing under oxidizing conditions. The subsequent processing described is hot or cold pressing and subsequent sintering or infiltration with brazing alloys.

An important difficulty with the above procedure and the resulting product is that the carbide containing coating is quite thin, substantially less than one micron, with the result that under certain types of subsequent processing such as with the use of liquid binders in infiltration, as for example in the formation of an infiltrated matrix for earth boring bits, the liquid binder penetrates the protective coating and the relatively thin carbide containing coating. The problem would be particularly acute with PCD elements since their surface is rather "rocky" and irregular and includes a certain amount of surface porosity. Thin coatings such as described in Farkas would contain substantial imperfections and voids that would permit the liquid infiltrating binds to attack the carbide interface between the PCD and the coating and to separate the coating from the PCD. In addition, the processing of such coated diamonds, whether PCD elements or natural, in an oxidizing atmosphere is not practical since any imperfection or dissolution of the outer nickel or copper coating, for instance by the action of the liquid binder, would result in the oxidation and destruction of the underlining titanium and titanium carbide layer.

Also known in the prior art are products which might generically referred to as diamond impregnated products. Typically these products are composed of natural or synthetic diamond particles which may be of a variety of mesh sizes. Whereas a large integral PCD element may be between 70% and 97% by volume of diamond material, depending upon the processing, the amount of residual inclusions or porosity, the impregnated products generally have a much lower volume percent of diamond, typically less than 40%. The result is that the impregnated product performs better as an abrasive or cutting element than does the same material without the diamond grit, but the problem is that the small diamond particles are easily lost as the surrounding supporting structure is abraded away. To improve the retention of the diamond grit in the supporting structure it has been proposed to coat the particles of the grit with various metals such as tungsten, tantalum, columbium, niobium or molybdenum, and the like by chemical vapor deposition techniques using a fluidized bed procedure, see for example United States Patents 3,871,840 and 3,841,852. The products there described are about 25% by volume of diamond grit of particle size from 40 to 100 mesh and represent an improved impregnated product in contrast to an improved large diamond product. The coated diamond grit is formed into various shapes by a hot pressing procedure or by infiltration at an elevated temperature.

Coatings have also been used to form diamond products as contrasted to impregnated products. For example, United States Patent 3,879,901 describes the vacuum deposition of a metal such as molybdenum or titanium on diamond materials with subsequent processing at 60 Kbar and between 1,200 and 1,400 degrees C. to form a diamond product in contrast to a diamond impregnated product. In another instance, see United States Patent 4,378,975, an abrasive body with diamond is formed by forming a green body by cold pressing with a nickel based alloy. The green body is then sintered at 650 degrees C. with a diamond volume of between 10% and 40 % by volume.

It is also known in the sintering of synthetic diamond to use a thin coating of between 300 and 8,000 Angstroms of a strong carbide former, with a second coating of copper with subsequent processing at 5 Kbar at a temperature of 600 to 700 degrees C. in an inert atmosphere, see United States Patent 3,356,473. In United States Patent

3,464,894 it is proposed to form a chemically bonded coating of titanium such that a titanium-carbon bond is formed followed by processing at 62,000 atmospheres of pressure.

In general, the coating procedures of the prior art are related to pretreatment of diamond forming materials which are thereafter processed at relatively high temperatures and pressures to form a diamond element or to form a coating on diamond grit used to form an impregnated product in which the volume of diamond is well below about 50% by volume.

The provision of improved methods for the fabrication of large TSPCD products, which are temperature stable in the range of about 1,200 degrees C. and which may be fabricated at lower pressures and temperatures than have been used in the synthesis of diamond products, would have unique advantages. For example, the cost for fabrication equipment is vastly reduced as well as the cost for each of the products. The ability to fabricate various shapes and sizes and thickness, i.e., to be free of the shape and size limitations of high-temperature and high pressure equipment, would also offer advantages from a processing and application point of view.

One of the significant advantages of the present invention is the ability to fabricate a TSPCD product of a particular configuration and in which the TSPCD starting element or elements are firmly anchored in place. For example, the use of a TSPCD structure in accordance with this invention in various types of cutting tools and lead bond tools as may be used in semiconductor chip processing to form electrical connections to the chip elements through accurate control and positioning of a heated TSPCD faced lead bond tool, or in diamond tracing tools, for example, offers unique advantages as compared to current practices.

Thus, it is an object of this invention to provide a temperature stable diamond product of various sizes and shapes and capable of being used in various products, but which is substantially less expensive than the diamond products currently available and which may be firmly bonded to a supporting structure.

Another object of this invention is to provide an improved and novel process using relatively low temperatures and pressures for the fabrication of a diamond product from smaller temperature stable diamond elements in which the diamond product is temperature stable.

Still another object of this invention is the provision of an improved relatively low temperature and relatively low pressure process for the formation of a temperature stable diamond product.

Yet another object of this invention is the provision of an improved temperature stable diamond cutting element for us in earth boring and core bits which is less expensive than comparable sized elements and which may be fabricated at relatively low temperatures and pressures into shapes and sizes not presently economically feasible.

It is also an object of this invention to provide a mor effective method and means of attaching a temperature stable PCD to a tool or supporting body.

Another object of this invention is to bond TSPCD elements by a chemical bond so that they can be firmly attached to a tool body.

Yet another object of this invention is to bond TSPCD elements to form a specific pattern of cutting elements so that the wear mechanism, such as regenerating sharp cutting edges as the cutter wears, can be controlled.

It is also an object of this invention to form an improved diamond product in which the bonded PCD pieces form an integral part rather than a collection of individual elements.

It is also an object of this invention to provide a strong substrate backing to TSPCD, in which the properties of the backing can be adjusted to suit specific applications.

Brief Description of the Invention

In accordance with the present invention, a temperature stable synthetic polycrystalline diamond (PCD) product is provided which is fabricated from smaller TSPCD elements by improved relatively low pressure and low temperature procedures.

In general the products of the present invention may be formed by either liquid state infiltration or solid state sintering to affix a relatively thin PCD element on a hard ceramic substrate. The method includes the common steps of coating a temperature stable polycrystalline diamond element with a selected carbide former, preferably one which is stable against oxidation, arranging the coated elements in a mold in a predetermined relation with each other. Thereafter, a hard ceramic powder such as tungsten carbide powder containing an organic binder is placed over and around the assembled coated TSPCD elements. The powder is preferably monosized, although bimodial sizes and mixtures may be used.

The resulting assembly is cold pressed to compact the powder to about 50 volume percent, i.e., about 50% of the volume is porosity which will later be filled up by sintering or infiltration. The thus pressed assembly may then optionally be cold

isostatic pressed to increase the volume percent of the powder to about 60-65%. The cold isostatic pressed part has sufficient integrity to be handled and machined, if that is needed.

Thereafter if liquid state infiltration is used, the formed part is first heated to vaporize off the organic binder and then infiltrated preferably in a vacuum or under inert or reducing atmosphere with a metal binder which melts and fills the voids in the hard ceramic powder and binds it together. The infiltration also causes the metal binder and powder to bond metallurgically to the coating of the TSPCD since the binder wets the outer portion of the coating which partially dissolves in or reacts with the binder for the matrix or matrix carrier powder to form a solid solution of binder and coating metal at the interface. The binder is fluid or near fluid at this point in the processing. It is believed that the bond from the coating is through the binder for the matrix carrier powder.

The metal binder is preferably one which has a melting point within the temperature stable range of the TSPCD and which possesses strength and toughness. In this operation, the coated TSPCD elements are bonded together into a unitary assembly of a TSPCD. The infiltration is carried out at a temperature below the thermal degradation temperature of the TSPCD elements, above the melting point of the binder, and below the melting point of the metal of the coating. In accordance with the invention, a thin carbide layer is formed at the interface between the TSPCD and the carbide former coating. This carbide layer may be formed either before the powder is placed around the elements by heating the elements under carbide forming conditions or simultaneously with the infiltration or sintering. In either case the heating is controlled to promote formation of a relatively thin carbide layer on that portion of the surface of the TSPCD which has been coated by the carbide former. During the controlled heating, under carbide forming conditions, carbon diffuses from the PCD into the coating to form a carbide.

During the heating, it is believed that the temperature used to form the carbide is more important than the rate of heating. The evidence suggests, in the case of a tungsten coating for example, that the coating on the diamond can form a carbide above about 850 degrees C. and preferably at about 1,100 degrees C. no matter how fast the heating is conducted. Thus, heating at 1,100 degrees C. for about 15 minutes is normally sufficient. A longer time of heating at 1,100 degrees C. can increase the thickness of the carbide, but in general longer heating periods at high temperatures may damage the diamond because of too much carbide formation and results in an ineffective chemical bond being formed. If the heating is excessive, the result is that more and more of the carbon from the TSPCD diffuses into the coating with possible damage to the PCD. Thus, while the dimension of the thickness of the coating of the carbide forming metal may vary within wide limits, the dimension of the carbide coating, for a single coating which is stable against oxidation, such as tungsten, should be in the range of at least about 1 micron and up to about 15 to 30 microns, for reasons which will be discussed.

The thickness of the carbide forming metal coating may be as low as one micron, although coating thicknesses above about 3 microns provide stronger bonding strength. Films of above about 30 microns in thickness may be used, but increasing the thickness above about 30 microns does not seem to increase bond strength appreciably over the strengths achieved in the range of 10 to about 30 microns. Film thicknesses of 1 to about 3 microns are acceptable in some applications, but substantially increased bond strength is achieved above about 3 microns for the binder system tested. Coatings of less the about 1 micron tend to result in unacceptable separating of the coating from the TSPCD element during infiltration or sintering.

The resulting product of the invention has a chemical bond from the TSPCD to the coating to the matrix carrier. The term "matrix carrier" as used herein describes the powder and binder material which is placed around or in contact with the TSPCD element or elements and which is processed in accordance with this disclosure. The matrix carrier is to be distinguished from the more generic term "matrix" which generally refers to the supporting structure in which the matrix carrier is mounted, for exaple a drill bit body. the term "chemical bond" is used herein to refer to the strong bonds that are formed between the diamond and the metal coating through the medium of the carbide layer at the interface, and between the exterior surface of the metal coating and the matrix carrier. While not fully understood, it is believed that the former is an atom to atom level bond between the carbon of the diamond and the carbide layer. The latter is believed to be a metallurgical bond in which the binder alloy used in the liquid state infiltration or with the sintered material of the matrix carrier if solid state sintering is used. This contrasts sharply with the mechanical bonds that were formed in the prior art systems.

The term "diamond product" used herein and in the claims includes cubic boron nitride.

A solid state sintering operation (also referred to as tungsten powder activated sintering) may also be used to bind the TSPCD element to the matrix carrier. This operation involves vacuum sintering or sintering in a controlled atmosphere or hot pressing

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or hot isostatic pressing of the cold pressed part. If processed by solid state sintering, the materials used for casting and for the backing and the like have to be adjusted to reflect the different but related processing. Here again, if the formation of the carbide layer is simultaneous with the sintering operation, control of the heating and the duration of the heating is such that a relatively thin carbide layer is formed. Since this form of processing does not use a binder for matrix carrier formation, a portion of the coating wets the powder and bonds to the powder during sintering, again forming the chemical bond described. In the case of solid state sintering of tungsten, it is preferred to use a sintering activator such as nickel or nickel-iron. The activator is placed around the tungsten particles and promotes the sintering of the matrix carrier and the bonding to the coating of the TSPCD.

Various shapes and sizes may be formed in accordance with the present invention, and the testing thereof indicates that the bond between adjacent TSPCD elements is stronger than that which may be achieved through merely mechanical mounting of the TSPCD part or parts in a support matrix carrier.

The methods described above permit the formation of a wide variety of shaped cutting elements for use in various cutting and abrading devices. Large and shaped diamond bearings may be fabricated. The larger or shaped TSPCD product of this invention may be processed with a backing or supporting element of a variety of shapes and configurations and compositions. Relative thick and shaped TSPCD products may be fabricated at relatively low pressures and temperatures. In general, however, the principal advantage of this invention is the ability to provide a TSPCD structure in which one or more TSPCD elements are firmly anchored in a support structure by a bond which is significantly stronger than a mere mechanical mounting. The result is that the assembly of several TSPCD pieces in the form of a predetermined pattern will result in action of the part as one large diamond rather than as a plurality of diamonds held together as an aggregate.

Brief Description of the Drawings

Figure 1 is a flow chart depicting the steps in formation of a TSPCD product in accordance with the present invention;

Figure 2 is a plan view of one form of a TSPCD product in accordance with the present invention;

Figure 3 is a side view as seen along the line 3-3 of Figure 2;

Figure 4 is an enlarged fragmentary view illustrating the bonding path between adjacent TSPCD elements in accordance with this invention;

Figure 5 is a view in perspective of a TSPCD product having a single TSPCD element in accordance with this invention;

Figure 6 is a plan view of one form of bearing in accordance with this invention;

Figure 6a is a sectional view taken along the line 6a-6a of Figure 6;

Figure 7 is a view in perspective of a dressing tool in accordance with the present invention;

Figure 8 is a plan view of a saw blade segment in accordance with this invention;

Figure 8a is a sectional view as seen along the line 8a-8a of Figure 8;

Figure 9 is a sectional view of a lead bonding tool in accordance with this invention;

Figure 10 is a plan view of a TSPCD product in accordance with this invention in which a multiplicity of individual elements is bonded together into a larger TSPCD structure;

Figure 11 is a perspective view of another form of TSPCD product in accordance with this invention;

Figure 11a is a view, partly in section and partly in elevation, illustrating the mounting and use of the product illustrated in Figure 11;

Figures 12a to 12d are diagrammatic views of various structures and the test protocol for three point testing;

Figure 13 is a view in perspective of another form of TSPCD product in accordance with this invention;

Figure 13a is a view similar to that of Figure 13 but illustrating a modified form of product in accordance with this invention;

Figure 14 is a view in section illustrating still another form of product in accordance with this invention;

Figure 15 is a view, in perspective, of a twist drill in accordance with the present invention;

Figure 16 is a view in perspective of still another product in accordance with this invention;

Figure 17 is a perspective view of one form of earth boring bit in accordance with this invention, and

Figure 18 is an enlarged fragmentary view of the cutters illustrated in Figure 17 and produced in accordance with this invention.

Detailed Description of the Invention

In accordance with this invention the starting diamond material is preferably a temperature stable polycrystalline diamond material composed of aggregate diamond particles having a size in the

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range of submicron to over 100 microns, for example, although the particle sizes need not be uniform; i.e., mixtures of particles of the sizes indicated may be used as is known in the art. The TSPCD should contain at least 80% by volume of diamond aggregates, as described, and the product may be leached or unleached with some diamond to diamond bonding or diamond to metal bonding in the assembly. For products to be used in cutting or abrasive operations where the surface finish of the cut or abraded part is important, it is preferred that the smaller particles of diamond be used, for example, below about 15 microns. By way of example, wire drawing dies may require smaller particle sizes in order to provide a certain surface finish on the drawn wire product.

The TSPCD element may be as small as 250 microns, (i.e., 10 mils) on an edge and as large as one carat or more. It is preferred that the edge length of the starting TSPCD be above 1,000 microns (i.e., one millimeter) since pieces of this size are easier to manipulate or handle. Typically, TSPCD elements of a size of three pieces per carat (0.165 of an inch per side triangles) are easily handled.

In some instances the smaller particle sizes of TSPCD material below 250 microns may be used as a grit in the material used to bind the larger TSPCD elements described in order to provide an impregnated support or to increase the amount of diamond material between adjacent larger TSPCD elements.

It is preferred that the TSPCD starting material be of a regular geometrical shape which may be any of the shapes already mentioned. The principal reason for a fixed and known geometrical shape is that it vastly simplifies the arrangement of the TSPCD elements in the desired relationship for processing and thus offers maximum control of placement, spacing and overall configuration and content of the final part. Since one of the advantages of the present invention is the ability to form large TSPCD structures, it is also preferred that the geometrical shape be such that the TSPCD starting elements have side surfaces or faces which can be positioned in a close and controlled spacing to an adjacent TSPCD element, e.g., triangular, square, rectangular and the like, it being understood, as will be discussed in detail, that a TSPCD structure may include TSPCD elements of different geometrical configurations.

In the processing in accordance with this invention, as diagrammatically illustrated in the flow chart of Figure 1, the starting TSPCD material 10 is preferably cleaned by heating in hydrogen at about 800 to 1,000 degrees C. for about 10 to 60 minutes as indicated at 12. Other cleaning procedures may be used provided they are effective to remove oxidants and other surface contaminants. Thereafter the cleaned TSPCD material is surface coated with a metal by any one of several known procedures to form an essentially continuous coating which is essentially free of discontinuities. For reasons which will become apparent, the presence of discontinuities in the coating tends to promote lifting of the carbide containing coating off the surface of the TSPCD or provide a defect through which other materials may migrate to adversely affect the underlying TSPCD.

One such coating procedure is chemical vapor deposition by which a metal compound such as a chloride or a fluoride is heated to decompose the compound to form a mist of the metal which then deposits on the TSPCD material. Another procedure is fused salt both coating methods.

Tungsten is preferred as the coating metal because it is a strong carbide former, not subject to excessive oxidation damage, has similar thermal expansion characteristics as the TSPCD elements, and is not easily dissolved by the liquid binder metals during later processing. Other metals may be used are any one of the Group IVA, VA, VIA, VIIA metals and alloys and mixtures thereof and silicon, such as tantalum, molybdenum, titanium, niobium, vanadium, zirconium, manganese, molybdenum/manganese, or tungsten/manganese. As a class, these materials have a melting point higher than the temperatures used in subsequent processing and are strong carbide formers and form a strong bond to the diamond. Metals of Group VIIIA, such as cobalt, iron and nickel are less preferable because of the tendency to weaken the TSPCD by back conversion of the diamond or possibly by other means. Zirconium and titanium have been observed to have a volume expansion in response to elevated temperatures which is more than that of diamond but less than that of cobalt and iron, but these materials are subject to oxidation damage in subsequent processing in normal atmospheres unless protected by an overcoating of nickel or copper or some other material. Even so, care must taken to assure that the carbide containing coating is sufficiently thick to prevent penetration by the surrounding metal should the copper or nickel or other coating dissolve into the matrix carrier.

For chemical vapor deposition one may use the hexahalides, tetrahalides, pentahalides, e.g., the hexa-, tetra-and penta-forms of the bromides, chlorides fluorides of the metals mentioned. The thickness of the coating on the TSPCD may vary so long as it is greater than about one micron, but it is preferred that the coating be between about 1

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micron and up to 80 microns. Thicker coatings may be used but do not seem to increase the bond stregth over that acieved in the range of 20 to 30 microns.

The application of the coating does not necessarily result in a chemical bond to the TSPCD at this point in the processing. As near as has been determined, the processing temperature used in chemical vapor deposition is not sufficiently high to form a chemical bond as indicated by the essential absence of any diffused carbon into the metal of the coating and the absence of any metal of the coating being diffused into the TSPCD. While it is believed that the coating is essentially uniform in dimension and essentially covers the entire outer exposed surface of the TSPCD, it is not essential to form an absolutely continuous coating. In the case of porous leached TSPCD elements, the coating should be thick enough to bridge over the pores in the TSPCD surface so that it is effectively coated with the metal.

Of the carbide forming materials described, tungsten is the most preferred for several reasons. When a tungsten coating, previously converted to a carbide at the interface of the TSPCD as described herein, is furnaced in a graphite mold or oxidative environment, the tungsten is relatively stable against oxidation as compared to titanium, for example, unless the titanium is protected by an overcoating. Another reason for the preferance is that the thermal expansion of tungsten or tungsten carbide is close to the thermal expansion of diamond. Further, tungsten dissolves in the binder at a relatively slow rate. The overcoating requires a second coating operation and thus increases cost. Further, if the overcoating is not continuous, for example if there are defects which expose portions of the underlying oxidation sensitive coating, subsequnet processing in an oxidizing environment may destroy the metal and the carbide interface or a local portion of the underlying diamond material or both. So too, there are some types of matricies, which tend to dissolve the oxidation protective layer deposited over the oxidation sensitive carbide formers with the result that the oxidation protective material dissolves or is otherwise absorbed in the matrix and a gap tends to form between the partially oxidized coating and the surrounding structure, thereby resulting in a marked reduction in the strength of the bond between the coating and the surrounding structure. Ideally, the bond between the outer surface of the coating and the matrix carrier is a metallurgical bond which is not easily formed if the coating is not of compatible material or if it is oxidized.

More particularly, if the matrix or infiltrant includes copper or nickel or alloys thereof, as is normally the case in abrasive resistance matrix carrier, the matrix or infiltrant rapidly dissolves the oxidation protective layer so that the presence of a thin carbide forming layer, even if overcoated with an oxidation resistant material tends not to produce as strong a metallurgical bond as is the case with tungsten.

The use of materials such as zirconium or titanium or chromium may be acceptable provided those coatings are sufficiently thick to essentially prevent adverse reactions which cause damage to the carbide layer or to the underlying diamond since copper and nickel in the binder in contact with the coating will protect the coating from oxidation during infiltration. This is especially true where the matrix composition or the infiltrant is a material as above or hereinafter described. Thus, even if there is penetration of the infiltrant or a component of the matrix through or into the oxidation protective layer, oxidation sensitive material may be used as the coating, provided they are sufficiently thick. Thicknesses of less than one micron tend to be subject to subsequent processing problems, even if coated with an oxidation protective layer. Thicker layers, especially above about 3 microns tend to provide improved bonding but not as great as that provided by tungsten.

An important advantage of this invention is the ability to form a backing or supporting structure for the TSPCD elements of widely varying configuration and composition. The backing is formed in situ as the TSPCD elements are bonded chemically together and to the support structure.

To assist in handling, it is preferred to compress the powder and the TSPCD elements in an axial compression operation. Ultimately the backing or support structure will achieve a volume percentage of metal and/or metal carbide and/or abrasive particel (e.g., oxides or non-metal carbides) which is in the range of 40% to 80%. Optionally, the compacted structure may be further compressed by isostatic pressing in which the volume percentage is increased to about 60% to 90%. If the structure is to be sintered, isostatic pressing is preferred.

The hard ceramic powders used to form the matrix carrier may be metal carbids such as tungsten carbide, titanium carbide, tantalum carbide, molybdenum carbide, and cemented tungsten carbide (tungsten carbide cemented with cobalt). Alternatively, it could be made of other hard ceramic powders such as alumina or titanium or silicon nitride. The abrasive particles may be alumina,

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silicon carbide or silicon nitride. For applications such as earth boring bits, where strength and toughness are important, tungsten carbide is the preferred hard ceramic powder.

The particular powder used and the particle size or sizes is related to the desired volume percent of the matrix powder, the final product which in turn is related to the hardness (rigidity) and impact resistance (toughness) of the backing or support structure. Also a consideration is the type of processing, e.g., liquid state infiltration or solid state sintering.

In the case of liquid state infiltration, the hard ceramic powder, for example tungsten carbide, has a particle size which is typically below 325 mesh (Tyler), i.e., below 44 microns (Standard), for example 30 microns. The size distribution and the percentage distribution may vary depending upon the supplier. However, the size may also be varied. For example the same packing efficiency may be obtained by appropriate selection of particle sizes, e.g., 30 microns and 6 microns in a ratio of 70% to 30%.

A preferred infiltrating material is a copper-lithium-manganese alloy. If the alloy does not include manganese or nickel, thinner coatings of about 1 micron may be used, as will be discussed.

In the case of solid state sintering, for example using a tungsten powder, the powder particles are preferably coated with a metal such as nickel, for example 0.35 weight percent. This may be doen by mixing tungsten powder of a particle size of 0.5 microns with a solution of nickel nitrate in alcohol, followed by heating at about 80 degrees C. to evaporate the alcohol with the result that the nickel nitrate is deposited on the tungsten powder. the nickel nitrate coated tungsten powder was then heated at 600 degrees C. for 3 hours in a reducing atmosphere (hydrogen) to eliminate the nitrate. The processed tungsten powder was then ball milled for 24 hours using tungsten rods as the milling media and then sieved and screened to 200 mesh (74 microns). The purpose of the nickel, as will be described, is to act as a diffusion activator for the tungsten. Other binder materials which may be used are tantalum, molybdenum, and nickel based alloys, copper-nickel alloys and cobalt based alloys.

In either liquid state infiltration or solid state sintering, the appropriate powder of the appropriate particle size or sizes is mixed with a temporary binder material which is preferably an organic material as indicated at 15. The temporary binder is used to coat the powder material to form a temporary adhesive bond between the powder particles during the initial compaction step. Since this temporary binder remains in the processed product through the cold isostatic pressing operation, it should preferably be a material which is present in a relatively low volume percentage. If the volume percentage of the temporary binder needed to achieve a temporary bond is too high, this may affect the volume percentage of the powder in the final product, i.e. too great an amount of the temporary binder may prevent the achievement of higher powder volume percentages. Various organic polymeric or resinous binders which are easily volatilized at elevated temperature may be used. A preferred material is paraffin which is easily dissolved in an organic solvent. The amount of paraffin relative to the tungsten carbide is about 2 weight percent. The paraffin is easily and completely removed in the processing. It is also desirable to use a lubricant which may be volatilized completely at elevated temperatures in order to facilitate powder movement during the various pressing operations, especially the optional cold isostatic pressing operation. One such material is mineral oil which may also be dissolved with the temporary binder to coat the powder. A typical useable amount is 20 grams of paraffin per 1,000 grams of cast carbide in 0.2 grams of glycerine per 1,000 grams of cast carbide, by way of example.

The powder is dispersed into the solution of the temporary binder and lubricant in hexane (for the paraffin) and the binder and lubricant coat the powder which is then dried and reground into a powder. Other coating procedures may be used as is known in the art.

The next step in the sequence, as indicated at 20, is to arrange the coated TSPCD elements in the desired relationship as needed to form a product. If the product is to contain multiple TSPCD elements it is preferred to use a template or die configured to position the TSPCD elements with respect to each other. The spacing between adjacent TSPCD elements may vary widely, depending upon the configuration and nature of the final product. Where the part includes multiple TSPCD pieces, the side faces of the TSPCD elements may be spaced from each other to provide a gap of from about less than 1 mil to 500 mils and preferably in the range of 6 to about 30 mils (150 to 750 microns), by way of example. Thereafter, the processed powder is placed in the gaps between the adjacent TSPCD pieces and tilled in in contact with the surfaces of the TSPCD elements to be bonded to the matrix carrier.

In some instances it is not necessary to form a gap as described since the TSPCD may be assembled with adjacent surface portions in contact with each other. In this instance where liquid state infiltration is used, the binder penetrates between the TSPCD elements and chemically bonds the adjacen coated TSPCD elements together. Such a butting arrangement o of the TSPCD's may be

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used where erosion is not a potential problem, e.g., in bearings, saw blades and wire dies and the like, for example. Where erosion is likely to be a problem, such as exposure to relatively high velocity flow or the use of abrasive materials, the use of a gap in which powder is present is preferred for erosion resistance.

The thus assembled TSPCD-powder temporary assembly is then assembled into a pressure die of suitable configuration which preferably defines the outside contour of the finished part. One manner of carrying this out is to use an open ended die, invert the die and move the temporary assembly of TSPCD elements up into the bottom of the die, re-invert the die right side up so that the assembly is in the bottom of the die and then add the processed powder material to the required volume. The amount of powder added is related to the thickness of the support or backing and the volume percentage of the metal in the final product.

The assembled material is then axially cold compressed in the die, as indicated at 22, at a pressure of between 10,000 psi and 30,000 psi to increase the tungsten carbide packing density to about 60 to 65 volume percent. As a result of this processing, a compacted intermediate is formed which is fragile but still capable of being handled with care. As another example, if the subsequent processing is solid state sintering, pressures around 10,000 psi may be used and the resultant product has a packing density of about 60 volume percent.

An additional step in the processing is the cold isostatic pressing operation, as shown at 24, in which the compacted intermediate is isostatically cold pressed at a pressure of up to about 30,000 psi for five minutes or longer, for example. The isostatic pressing typically achieves a tungsten carbide packing density of about 62 volume percent. In the case of tungsten powder in solid state sintering, the density is about 69 volume percent. During this operation, the tungsten or the carbide powders are moved and compacted uniformly to a more dense product. The step of cold isostatic pressing is optional although in many cases it is preferred particularly for sintered products.

At this point in the processing, two alternate processing routes are available, as indicated in the dotted lines of Figure 1, liquid state infiltration, as seen at 26 or solid state sintering as seen at 28.

In the case of solid state sintering, the product of the isostatic pressing is sintered in a vacuum furnace at 10 to the minus 5 torr, at 1,200 degrees C. for about 1 hour. The result is a sintered product having a density of about 90 volume percent. The finished product indicates a bond between the tungsten material with the tungsten coating on the TSPCD, i.e., a tungsten-tungsten metal bond. The nickel or other activator is used to promote diffusion and metallurgical bonding. The mechanical properties of this bond are quite strong, and the finished product, although somewhat brittle is quite useable.

There are, however, some limitations of solid state sintering. For example, the limitation of sintering at a temperature below 1,200 degrees C. renders it difficult to find a material with high strength and high modulus. Even if the high modulus materials can be sintered below about 1,200 degrees C., as by activation sintering, the sintered product may contain 5% or more porosity which may act as pre-existing cracks. While this may not be a problem in some cases, it is a consideration where the finished part is in a part which is subject to relatively high impact loads, e.g. a drill bit for example.

In those instances in which the bonded TSPCD product is to be mounted to a high modulus backing, the processing may involve two thermal cycles to bond the TSPCD product to a tungsten carbide back-up element. While effective, the processing steps increase the costs.

Even though these problems exist, the advantage of this form of processing is the ability to provide a high strength, low thermal expansion material to bond the TSPCD together. There are known ductile materials which may be added to the powder or the binder in accordance with this invention to decrease the brittleness of the sintered matrix carrier.

It is preferred to use liquid phase infiltration as the last process step. In this processing, the product from the isostatic pressing operation is heated to cause a metal binder to flow through the compacted powder and bind it together and to the TSPCD elements.

Regardless of the type of processing as herein described, the hard ceramic powder in the matrix carrier can be of relatively high volume percentage, e.g., above 50% and up to 90% by volume. The provision of a relatively high density final product, which is formed in situ at relatively low pressures and temperatures and which is temperature stable to about 1,200 degrees C. offers advantages not heretofore obtained.

The metal binder material should be one which in a liquid state can wet the coating on the TSPCD and the hard ceramic powder particles. It is also preferred that the binder metal have good mechanical properties such as ductility and strength. Typical such binders are copper or nickel based brazing alloys, copper-tin-manganese-nickel alloys, the latter being the preferred binder material.

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The processing above described, as already noted may be used to form a wide variety of products which are characterized as having a strong chemical bond between the coating and the TSPCD and between the coating and the supporting structure. It is this chemical bonding which provides the significant strength over that which can be achieved by merely a mechanical gripping of the TSPCD. The advantage of this invention is that the TSPCD elements or element are effectively locked in or on a support structure to provide a TSPCD cutting element as contrasted to the prior temperature sensitive supported TSPCD elements commercially available.

Referring to the drawings which illustrate preferred forms of the present invention, Figure 2 illustrates a TSPCD product 30 which includes six (6) of initially separate TSPCD elements 31a to 31f of generally triangular shape. The TSPCD elements may be bonded together in or on a support structure 32, see also Figure 3 which may be an infiltrated or sintered powdered material. The support structure may be of various dimensions and of various axial lengths, as indicated by the break line 33.

As seen in Figures 2 and 3, the TSPCD elements include at least one side face 34a which may be positioned adjacent to but spaced a small distance from the side face 34b of the adjacent TSPCD element. The distance between adjacent TSPCD elements, referred to as the gap and illustrated as 35 in Figure 3, may be of the dimensions previously indicated.

Referring to Figure 4, for example, the gap 35 is illustrated with reference to its condition after cold isostatic pressing and before further processing. Each of the TSPCD elements 37 and 38 includes the coating 37a and 38a, respectively, the TSPCD elements being spaced from each other by the gap width. Between the coated surfaces is the powder material 40 such that the gap is TSPCD face-coating-powder-coating-TSPCD face. In subsequent processing, a strong chemical bond is formed from the TSPCD face through the coating, through the powder, through the coating of the adjacent TSPCD face and to the adjacent TSPCD.

Again referring to Figures 2 and 3, in the resulting TSPCD product 30, essentially all surfaces of the TSPCD elements, save one, are in contact with bonded support material, i.e., there is material on the bottom face 41 and peripherally around the outer faces, as indicated at 42 and in the gap 35, while one face 44 is exposed. This form provides the optimum bonding of the TSPCD elements together. This product may be assembled to a bit body during infiltration of the bit to form the matrix bit body. It is also possible to braze the product into the bit body, in which event, higher temperature braze alloys may be used than have heretofor been used.

The form of TSPCD product in accordance with this invention shown diagrammatically in Figure 5 illustrates that not all of the faces need be fully in contact and bonded to the support element. Here a triangular TSPCD element 50 includes side faces 50a, 50b and 50c which are only partially beneath the top surface 52 of the support structure 53 shown as triangular for purposes of illustration. Due to the strong chemical bonding between the TSPCD and the support structure, it is possible to expose a substantial portion of the large flat face 50d of the TSPCD while the body of the TSPCD is substantially above the support body. Thus, for example it is possible in accordance with this invention to form large bearings from smaller TSPCD elements.

Referring to Figures 6 and 6a, for example, a TSPCD product 60 is illustrated which may be used as a bearing or the like. This form of product also illustrates that TSPCD elements of different geometrical shapes may be used to form a useful TSPCD products. In this form, TSPCD elements 61 and 63 are half circular disks while TSPCD element 64 is square, although it may also be rectangular. The TSPCD elements are bonded to a support 65 of metal powder processed as already described with gaps 66a and 66b between adjacent elements. As illustrated the gaps, however, are not filled with matrix carrier material thus effectively providing channels between the spaced and facing exposed side faces 61f-64f and 64g-63f, the elements 61, 63 and 64 being positioned such that a substantial portion is exposed as noted with reference to Figure 5. When used as a bearing, the channels may provide for flow of cooling or lubricating fluid, if desired. If channels are not needed, the gaps may be substantially filled as illustrated in Figure 3, i.e., the surface of the support is even with the top surface of the TSPCD elements.

Not all of the side faces need be in contact with and bonded to the support material. Thus, for example as illustrated in Figure 7, a single point dressing tool 70 is shown which includes a TSPCD element 72 mounted on and bonded to a support 74 such that one face 72a is fully contacted by the support material which effectively forms a shoulder 76 to the rear of the element 72. Faces 72b and 72c are fully exposed while the bottom surface is bonded to the support. While element 72 is indicated as triangular, it may be other shapes such as square, rectangular, semi-circular or circular, for example.

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The ability to bond a TSPCD element firmly in a support structure permits the fabrication of unique cutting and abrading products. For example, Figures 8 and 8a illustrate an improved saw blade segment 80 composed of a plurality of TSPCD elements 81a through 81k, bonded to a support structure 83. In the form illustrated, the TSPCD elements are circular in shape although other geometrical shapes may be used. Circular shapes, however, have the advantage of providing a relatively large surface area for firmly bonding the elements to the support structure. The diameter of the elements may be in the range of one millimeter or larger depending upon the use of the segment. In prior segments, they were either impregnated with diamond dust or used spherical natural diamonds. In the either case as the supporting matrix carrier was worn due to use, the diamond material was lost due to loss of supporting structure. This problem is largely overcome by the present invention since the TSPCD elements are firmly chemically bonded over a comparatively large surface area.

The TSPCD elements are preferably arranged in a redundant pattern such that elements 81e through 81g are to the rear and in the space between the adjacent lead elements 81a-81d, with elements 81b-81k oriented in the spaces between 81e-81g. Thus, for example if the thickness of the elements is equal to or greater than the gap dimension between adjacent side-by-side elements 81a-81d, the entire face of the cut in the workpiece is traversed by at least one cutter. The redundancy may be two or more, that is, additional elements may be arranged to provide added redundancy as may be needed.

As illustrated in Figure 8a, each element 81a-81k includes an exposed arcuate cutting face, for example 81aa, 81ea and 81hh extending above the surface 84 of the support 83, with a substantial portion of each element firmly and chemically bonded to the support. As the segment wears in use, the elements are retained to a much greater degree than the prior diamond cutting segments. While circular elements have been described, one may use a half-circle or quarter-round TSPCD elements, preferably mounted such that the curved peripheral surface is exposed to form the leading cutting edge. Such materials are commercially available or may be cut off a cylindrical TSPCD part to the desired thickness.

The ability to anchor and firmly bond a TSPCD element to a support structure permits the fabrication of a wide variety of cutting and abrading tools. It also permits the fabrication of products that are other than abrading or cutting tools, such as bearings, as described and, for example, a lead bonding tool. Heretofore, lead bonding tools have been made of a single crystal diamond cut to a precise shape and dimension with a flat working face. Typically these tools are used to bond lead elements to solid state chips and the like by being brought into contact with the chip and bonding the leads in a precise and exact location to the chip through heat and pressure. Normally the temperature is about 600 degrees C. and natural diamonds are able to withstand this temperature. However, it is difficult to support these natural diamonds in a support structure and if they move even slightly relative to the support structure, problems may be encountered in their use since the bonding operation is a precision operation. In accordance with this invention, an improved lead bonding tool is provided which is firmly anchored in a support structure and which is temperature stable.

Referring to Figure 9 and improved lead bonding tool 90 is illustrated and includes a TSPCD element 92 bonded to a support structure 94, the latter being metallic and including an aperture 95 therein for a heater and including a shank 96 for mounting in the lead bonding machine. The support usually includes a cylindrical section 97 having a frusto-conical end 98 with the element 92 mounted at the tip of the end 98. The element 92 includes a working face 99 which projects beyond the end 98 and which is of a precise flatness and face dimension, i.e., length and width. The face contour may be square or rectangular, or any other shape, as may be desired. Heat may be applied to heat the element in a conventional manner normally used to heat the lead bonding tool. In use the tool is subject to vibration and heat which requires that the element be firmly and accurately mounted and maintained in that accurate mounting during use. By the present invention, the TSPCD element 92 may be chemically bonded to the support structure which may be the support 94 or a separate insert to be received in the support. The advantage of this invention is that a TSPCD element may be used which may be relatively easily affixed to a support structure.

Thus, for example, the element 92 may be shaped to the precise required length and width dimensions and in situ bonded to a support structure. If the support structure is the support 94, the face of the TSPCD may be precision ground to the desired flatness such that the plane of the face 99 is referenced to the support structure, an operation which is difficult to achieve with single crystal diamonds. It is also possible to form a lead bonding tool by formation of a TSPCD support structure which is then assembled to the body 94, rather than forming the entire assembly as herein described.

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One aspect of this invention is the ability to form a TSPCD product of virtually any shape or size from smaller TSPCD elements. The TSPCD product illustrated in Figure 10 is an example. There a large TSPCD product 100 is composed of a multiplicity of triangular TSPCD elements 101 in a TSPCD part which is essentially circular in overall shape, although it may be of any shape. In the form illustrated, there is a surrounding portion 105 of tungsten carbide, for example. The tungsten carbide may be of 70 volume percent tungsten carbide By way of example, the part may be 50 mm in diameter and is useful as a cutter for oil and gas drill and core bits.

Figure 11 illustrates another TSPCD product 110 in accordance with this invention composed of a plurality of TSPCD elements 112 illustrated as being triangular pieces which may be for instance 3 per carat or 1 per carat. The elements 112 are bonded together and to a support 115 such as tungsten carbide by any of the methods already described, so as to form a unitary structure in which the previously separate elements are chemically bonded together and to the tungsten carbide and to the tungsten carbide backing 115. It is understood that the backing may be any of the carbide materials already described.

The form of the invention illustrated in Figure 11 illustrates the variety of TSPCD products that may be fabricated in accordance with this invention. This particular structure provides for a plurality of cutting elements 112a and b, 112c and d, and 112e and f, which form pairs which together provides a series of cutting points 116, 117 and 118. In use in a bit, as shown in Figure 11a, the cutting product 110 may be mounted directly into the body matrix during body matrix infiltration or formation. In this form, there is a back support 121 provided which contacts the backing 115, the cutting direction being indicated by the arrow 123. The tungsten carbide backing 115 provides for increased impact strength.

The cutting product 110 is exposed such that at least one top row of elements 112a-112f are essentially fully exposed. In use as the top row of cutters wear, new cutting surfaces are regenerated from the cutter elements below the top row. This product also illustrates the fact that adjacent elements include at least one side surface which is located adjacent to the adjoining piece, the spacing being as already described.

To improve the cutter performance in terms of regenerating cutter edges and points, the amount of matrix carrier between adjacent TSPCD elements may be reduced in cross-sectional thickness in order to provide controlled weakness planes in the cutter structure thereby providing for fracture of the cutter along predetermined planes of fracture. In this way as the loading on a cutter region increases, the cutter is broken out of the support to provide a new cutter element. Since earth boring, in part, relies upon a kerfing type of cutting, the formation of an uneven overall cutting surface generally tends to improve the cutting action in certain types of formations.

As already noted, the products of the present invention are much stronger than products previously described as mechanical mosaic structures. Referring to Figures 12a to 12d, Figure 12a illustrates diagrammatically a three point bending test in which loads are applied to a part 130 in one direction as indicated by the arrows 131 and 132 and a load is applied in another direction as indicated by the arrow 133. The force necessary to bring about fracture through the joint 135 or through the joined parts 136 is measured and expressed in terms of pounds per square inch to failure.

Figure 12b illustrates a TSPCD part 140 in accordance with this invention made up of triangular TSPCD elements 141 joined together as indicated at the joints 142 by the methods already described. The part 140 was processed by sintering tungsten coated 3 per carat TSPCD elements with tungsten powder which had been compressed to a volume percentage of 90%. In the three point test, the failure mode was in the joint between adjacent elements, as indicated at 145. The load to failure was 21,000 psi.

Figure 12c is similar in structure to that of Figure 12b, but the part 150 was formed from tungsten coated 3 per carat TSPCD elements which were liquid state infiltrated with tungsten carbide using a copper binder, as described, and processed as described. In the three point test, the failure mode was through the TSPCD as indicated at 155 and the load to failure was 28,000 psi.

Figure 12d illustrates a mechanical mosaic structure 160 which is essentially the same as 150, but in which the TSPCD elements were not coated and in which the part was processed using conventional infiltration techniques with the same tungsten carbide and binder used to form the part 150. In the three point test, the failure was through the joint, as indicated at 165, and the load to failure was zero psi.

Other test data indicates that the thickness of the carbide forming coating is significant. These data were derived from the use of a matrix material in which the binder included nickel and manganese. In the case of tungsten coated material, it has been observed that nickel and/or manganese tend to adversely affect the coating if the coating is too thin, for example below about 3 microns. However, if the binder for the matrix is copper or tin or combinations thereof, thinner coatings of one mi-

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cron may be used. Thus if the binder for the matrix is compatible with the coating, thinner coatings of 1 micron may be used. If the binder for the matrix is from the iron group, e.g., nickel or manganese, somewhat thicker coatings are preferred to prevent the binder from penetrating the coating on the diamonds, for example a tungsten coating. It is thus preferred to use binders which are compatible with tungsten, in the preferred form of this invention, in which instance the coating thickness may be 1 micron in thickness.

For example, in a shear test where coated TSPCD is bonded to a matrix carrier, as described, and subject to a lateral pushing force, the results indicate that in the range of 1 to 5 microns, there is improvement in the bond strength to about 6,000 psi over an uncoated product. The failure mode at this range of coating thickness is by failure at the interface of the coating and the matrix carrier. In the range of about 7 to 10 microns thickness, the fracture is mixed in nature, in that the fracture sometimes is at the stated interface and sometimes through the TSPCD. The stated fractures occur at bond strengths in the range of about 5,000 psi and up to about 22,000 psi. In this range of bond strengths, the TSPCD product in accordance with this invention has a wide variety of uses. Above about 10 microns, the fracture mode is through the TSPCD and not through the bond, i.e., this means that the interfaces between the PCD and the coating, the coating and the bond, the coating itself and the bond itself are all stronger than the PCD. These fractures of the TSPCD, rather than at the interface between the support structure and the TSPCD occur typically at strengths in the range of above 22,000 psi. Above about 18 microns of coating thickness, the bond strengths seem to level off at about 27,000 psi, with fracture through the TSPCD rather than the bond interfaces, even though the coating thickness increases to 20 microns or more. For coating thicknesses above about 30 microns, there does not appear to be any increase in bond strength over that achieved in the range of 18 to 30 microns.

By way of further comparison, a titanium carbide coated TSPCD having a thickness of about 5 to 10 microns, typically at 7 microns, and a total coating thickness (including a nickel oxidation protective coating) of about 30 to 50 microns exhibited mixed failures through the bond and through the TSPCD at about 15,000 psi. These data also tend to establish that a tungsten coating, absent any oxidation protective coating, having the thickness dimensions described, is far superior than products with a titanium carbide coating and a nickel protective coating, wherein the titanium coating was about 7 microns and the nickel coating was about 40 microns, since the failure mode of the letter is a mixed mode, either at the bond rather than only through the TSPCD. The achievement of sufficiently high bond strengths to result in the failure of the TSPCD rather than the bond of the latter to the supporting structure offers considerable advantages, especially in the cases of those products which require a strong bond of a cutter-type product in some form of support structure.

The relatively high strength of the bonded joint between the TSPCD and the supporting structure permits wide variation in the types of products in accordance with this invention. One of the advantages is the ability to provide a TSPCD element which is securely bonded to a support structure. Referring to Figure 13, there is illustrated a product 170 which includes a TSPCD element 172 firmly secured to a tungsten carbide support element 174. While the product 170 superficially resembles the appearance of a STRATAPAX brand cutter, it is vastly different.

More specifically, the TSPCD element may be a product available commercially as SYNDAX, TSPCD material in the form of a thin one-piece disc. The dimensions of the disc 172 may vary widely from a diameter of 2 to 3 mm to as much as 50mm or more. The disc 172 is firmly chemically bonded to the support element 174 through the chemical bond formed through the coating applied to the disc 172 which in turn is bonded to the infiltrated or sintered material 176.

The support 174 may be separately formed and the disc 172 and the material 175 may be assembled and processed as described. The result is the chemical bonding of a TSPCD to a preformed support. The advantage is that the length, diameter and shape of the support is not limited by the size of the high pressure high temperature presses normally used to form STRATAPAX types of products. The cost for making a product as shown and described in Figure 13 is less than that for the temperature sensitive product, but the more important advantage is the ability to form the support of essentially any length, as indicated by the break line 178, without requiring larger presses. This form of product has the advantage of being temperature stable up to about 1,200 degrees C. and may thus be infiltrated simultaneously with the formation of a supporting matrix, for example a matrix body for a drill bit. Alternatively, the product may be brazed into the bit body by the use of higher temperature brazing materials than have been heretofore used. It is also understood that the coated diamond may be brazed to a suitable support such as cemented tungsten carbide, and the like, since the braze joint is between the coating on the diamond and the support element. Since the

diamond is temperature stable, higher melting point brazing alloys may be used as compared to those alloys which are used with diamond product which are not temperature stable, as herein defined.

As illustrated in Figure 13, the side surface 179 of the disc is free or sintered or infiltrated material. In the form illustrated in Figure 13a, the sintered or infiltrated material may cover the sides of the disc 178a, as indicated at 179 for added strength.

Figure 14 illustrates a structure in which one or more TSPCD elements 180 are affixed to a supporting body such that the back side 183 of the elements are in contact with the support body while the side faces are adjacent to each other or include a fully exposed side face, as indicated at 187. In this particular case, the support body may be a saw blade segment or a preformed and preshaped cutter for an earth boring bit. While the configuration of the product illustrated in this figure may appear similar to some of the illustrations of United States Patent 3,938,599 issued to Horn, there are significant differences. Unlike the Horn structure, that of the present invention is chemically bonded to the supporting matrix carrier and is far stronger than a mere mechanical bond as described in the referenced patent, see also the data previously described. This strong bonding allows for the provision of a variety of products.

Thus, for example, Figure 15 illustrates a twist drill 190 having segments 192 and 194 mounted thereon. Segments 192 and 194 may be a TSPCD product in accordance with this invention containding one or more TSPCD elements in a support structure. The drill bit may be a 1/4 inch or larger size.

Figure 16 illustrates a form of the invention similiar to that of Figure 13 wherein the TSPCD elements 200 are square in shape, although rectangular shapes and mixtures of geometrical shapes may be used. The TSPCD elements are bonded to each other through the material 201 and to the base 202, as described. The base may be of a shape other than square and may be of any length as indicated by the break line 208.

Figures 17 and 18 illustrate a drill bit 220 in accordance with the present invention. The bit includes a body 222, preferably of matrix material such as carbide, having a plurality of waterways 225 associated with a plurality of blades 230. It is to be understood that in referring to the bit body as a matrix body, the matrix material of the bit body may be relatively thin coating on a suitable support structure. The bit also includes nozzles 235 for flow of fluid form the interior of the body to the waterways to cool and clean the bit.

As shown in Figure 18, each blade includes a plurality of cutters 240 having a configuration as illustrated in Figure 2, for example. The cutters 240 are mounted in the matrix body during infiltation of the body thus eliminating the need to braze the individual cutters into the bit body. As mentioned, each of the cutters, by virtue of the production thereof is temperature stable to 1,200 degrees C. It is understood that other cutter configuration in accordance with this invention may be used, for example that illustrated in Figure 10 or in Figure 13, for example. It is also possible to provide cutters of selected geometry, e.g., quarter circles, half circles and the like. It is also possible to have temperature stable cutters which are larger in diameter than about 14mm, the usual maximum size for the STRATAPAX brand products.

Drill bit or core bit bodies may be of any of a number of types, as is known in the art. Thus, for example, stepped bit designs may be used with a significant cutter exposure, to mention only one variant. The ability to fabricate cutter to different desired geometries as may be needed for effective cutting action in various formations is now possible in accordance with this invention.

One of the features of the present invention is the fact that a wide variety of shapes and sizes is possible in the provision of a temperature stable PCD assembly through the use of processing steps that do not involve the high temperature and high pressure regime used in the synthesis of PCD materials.

Typical processing of TSPCD elements in accordance with this invention is set forth in the following specific example, by way of illustration.

Triangular temperature stable TSPCD elements of a size of 3 per carat were coated with tungsten metal to a thickness of about 6 microns. The powder used to form the matrix carrier was tungsten carbide powder of 3 to 5 micron particle size. About 1,000 grams of this powder were completely and thoroughly mixed with a solution of 200 ml. of hexane in which 20 grams of paraffin and mineral oil had been dissolved. The resultant mixture was heated to between 80 to 100 degrees C. for 45 minutes to evaporate the hexane completely. The processed powder was then ball milled, as described, for thirty minutes to break up the flocculated powder and then screened through a 200 mesh screen.

The tungsten coated TSPCD elements were arranged in a suitable hexagonal die and 4.5 grams of the processed tungsten carbide powder was placed in the mold to fill the space between the TSPCD elements and to cover them. The resulting assembly was then cold pressed at 20,000 psi to form a hexagonal preform.

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The hexagonal preform was then loaded into a rubber mold which was then evacuated and sealed and then isostatically pressed at 29,000 psi. The resulting product was then ground to specific size.

The isostatically processed hexagonal product was the placed on a crucible with 2.6 grams of a copper based alloy (Cu-Sn-Mn-Ni) on the powder side. The preform was then heated in a vacuum furnace (10 to the minus 5 torr) at the rate of 5 degrees C. per minute up to 400 degrees C. for one hour and then at 10 degrees C. per minute to a temperature of 1160 degrees C. for one hour for infiltration, later followed by cooling.

Heating at a temperature over 1100 degrees C. for one hour is important because it is at this stage that tungsten carbide formation takes place. Typically the tungsten carbide layer thus formed is about 3 microns thick.

If the preform is heated quickly to 1,000 degrees C. and held for 1.5 hours, the formed tungsten carbide layer is about 0.3 microns thick. Heating to the carbide forming temperature at the rate of 10 degree C. per minute may also be used.

After the thermal cycle, the finished product is surface ground to a thickness of about 0.315 of an inch and may be used.

As a variant, cemented tungsten carbide grit (94% by weight of tungsten carbide bonded with 6% by weight of cobalt, a commercially available material) of 400 mesh size was mixed with a solution of 2% by weight paraffin in hexane.

It is within the scope of this invention to form the isostatically pressed part and then process that part so that it is simultaneously bonded to a supporting structure such as a matrix bit body or other support structure while effecting conversion to the carbide layer described. For example, carburized tungsten powder in the nominal size range of 3 to 5 microns was ball milled with 1% by weight of nickel powder (-325 mesh) for one hour. The milled powder mixture was then mixed with a solution of 2% by weight of paraffin wax in hexane.

The mixture was dried by heating and then the processed powders were used with triangular TSPCD elements, coated as already described, to form a much larger assembly, as described. The larger assembly was cold axially pressed and then isostatically pressed as described. The resulting product was a "green" hexagonal cutter as shown in Figure 3. The green assembly was then heated to burn off the organic material and held at a temperature of 1,000 degrees C. for one hour.

Thereafter, the processed green assembly, sufficiently strong to be handled was assembled to a matrix powder material in a mold, e.g. the matrix bit forming operation, and the matrix infiltrated at 1,200 degrees C. During the matrix infiltration, the green assembly was bonded to the matrix and the coating was formed into the carbide layer. In this processing there was a strong bond between the metal binder of the matrix and that in the green assembly and between the coating, powder and matrix supporting structure. Essentially the same processing may be used to form other products already described in or on a matrix carrier support element.

Another form of one step infiltration involves the use of powders processed as follows: As received carburized tungsten carbide powder in a particle size range of from 3 to 5 microns was screened through a mesh screen to break up the agglomerates which tend to form in the fine powder. The screened powders were mixed with 7 weight percent of nickel powder having a particle size in the range of 3 to 7 microns and mixed in a suitable mixer for one hour. A second tungsten carbide powder of a particle size in the range of 3 to 5 microns was screened through a 200 mesh screen to break of the larger agglomerates. The screened material was then ball milled with 3 weight percent of nickel powder of a particle size range of from 3 to 7 microns with 2 weight percent of paraffin in a hexane solution for about eight hours. The ball milled powders were then dried and coated with paraffin.

Six pieces of tungsten coated triangular TSPCD elements, coated as already described, of a size of 3 per carat were arranged in a hexagonal punch and about 0.8 grams of the second powder was placed between the TSPCD elements, spaced as already described. About 4 grams of the first powder was then placed in the die and a hexagon product was formed under pressure of 15, 000 psig. The cold pressed hexagonal product was then isostatically pressed at 29,000 psig. After isostatic pressing the hexagonal product was infiltrated directly into a matrix, such as a drill bit matrix using a copper-manganese-tin-nickel alloy.

In another example, tungsten carbide powder in the size range of 20 to 30 microns and in the range of 60 to 70 microns was ball milled with 3 weight percent of nickel powder, of the type and size described, with 2 weight percent of paraffin in a hexane solution. The powders were dried, screend through a 200 mesh screen, assembled to TSPCD elements as already described and cold pressed in the fixture.

The cold pressed material with the TSPCD elements was then transferred to a high vacuum furnace, optionally a hydrogen furnace, to burn off the organic components by heating relatively slowly. This was accomplished by heating at a rate of about 5 degrees C. per minute to a temperature of

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800 degrees C. The burned off hexagonal shapes were then assembled in a mold, and infiltrated into a matrix to provide a finished part, in this case a drill bit.

It is to be understood that the one-step infiltration process described may be used to form any of a variety of products in accordance with this invention.

In those cases where it is contemplated that the product of the present invention is to be assembled to a matrix material supporting structure, such as a matrix body drill or core bit, it is desirable to coat the product of this invention with a carbide forming material, as already described. Such processing has the advantage of of providing a coating, of the thickness described, which may in turn form a carbide layer for effective bonding to the matrix carrier in which the part is to be mounted. The carbide layer may be formed by a separate preheating operation or by controlled heating during body matrix formation.

The abrasive character of the products in accordance with the present invention may be enhanced somewhat by adding to the powder materials relatively small particles of diamond or TSPCD material in the form of particles having the approximate size of the powders used. The volume percent of such diamond powders may be as high as 40% and the resulting material is processed as already described with the bonding as already described. The starting diamond material is preferably synthetic polycrystalline diamond which is temperature stable though natrual diamond material may also be used in some instances.

It will be apparent to those skilled in the art that there may be variations and alterations, based on the above detailed disclosures, of the various procedures and product here described. It is to be considered that the same may come within the scope of the present invention as set forth in the appended claims.

Claims

Claim 1. A temperature stable diamond product having a temperature stability up to about 1,200 degrees C. comprising:
a metal matrix carrier;
at least one diamond piece of a predetermined geometrical shape and which is temperature stable up to about 1,200 degrees C. having at least one surface contacting at least a portion of said carrier,
each diamond piece being coated with a metal which is a carbide former on at least the portion thereof contacting said metal matrix carrier,
said carbide forming coating being of a thickness of at least about 1 micron and including a relatively thin portion of a carbide material adjacent to said portion thereof contacting said diamond piece, and
said temperature stable diamond product being characterized by a chemical bond between said temperature stable diamond and said coating and said coating and the portion of said matrix carrier which is in contact with said coating.

Claim 2. A temperature stable diamond product as set forth in Claim 1 wherein said diamond piece is a synthetic diamond piece which includes a face, at least a portion of said face being in contact with said matrix carrier, and
said metal matrix carrier being tungsten carbide and extending to the rear of the face a predetermined distance and forming a backing integral with said diamond piece.

Claim 3. A temperature stable diamond product as set forth in Claim 1 wherein said temperature stable diamond includes at least one side face, and
said side face being coated with said metal which is a carbide former and being at least partially in contact with said matrix carrier.

Claim 4. A temperature stable diamond product as set forth in claim 1 wherein said product includes a plurality of initially separate temperature stable diamond pieces arranged in a predetermined pattern and including opposed surface portions forming a small gap therebetween, and
matrix carrier being located in said gap and contacting at least a portion of the surface portions of said temperature stable diamond elements.

Claim 5. A temperature stable diamond product as set forth in claim 4 wherein at least some of said temperature stable diamond elements are generally triangular in shape.

Claim 6. A temperature stable diamond product as set forth in claim 1 wherein said product is generally circular in shape and said temperature stable diamond is generally circular in shape.

Claim 7. A temperature stable diamond product as set forth in claim 1 wherein said product is a cutter for an earth boring bit.

Claim 8. A temperature stable diamond product as set forth in claim 7 in which said product includes more than one initially separate temperature stable diamond elements.

Claim 9. A temperature stable diamond product as set forth in claim 4 in which said gap is between 6 and 30 mils.

Claim 10. A temperature stable diamond product as set forth in claim 1 in which said coating has a thickness of up to about 30 microns.

Claim 11. A temperature stable diamond product as set forth in claim 1 in which said matrix carrier includes a carbide and a binder.

Claim 12. A temperature stable diamond product as set forth in claim 1 in which said matrix carrier is a sintered metal.

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Claim 13. A temperature stable diamond product as set forth in claim 1 in which said coating includes at least one metal selected from the metals of Group IVA, VA, VIA, VIIA and alloys and mixtures thereof.

Claim 14. A temperature stable diamond product as set forth in claim 11 in which said carbide is selected from the group consisting of the carbides of tungsten, chromium, niobium, titanium, tantalum, zirconium and molybdenum.

Claim 15. A temperature stable diamond product as set forth in claim 12 in which said sintered metal is selected from the group consisting of tungsten, nickel, tantalum, molybdenum, cobalt and sintered tungsten body infiltrated by a copper based alloy.

Claim 16. A temperature stable diamond product as set forth in claim 1 wherein said diamond piece is composed of at least 80% by volume of diamond aggregates.

Claim 17. A temperature stable diamond product having a temperature stability up to about 1,200 degrees C. comprising:
a metal matrix carrier selected from the group consisting of tungsten metal powder and the carbides of tungsten, titanium, tantalum and molybdenum,
at least one diamond piece of a predetermined geometrical shape and which is temperature stable up to about 1,200 degrees C. at least some of which have at least one surface contacting at least a portion of said carrier,
said diamond being a polycrystalline diamond composed of at least 80% by volume of diamond aggregates,
each diamond piece being coated with a metal which is a carbide former on at least the portion thereof contacting said metal matrix carrier,
said coating on said temperature stable diamond having a thickness of at least about one micron and including a carbide layer which is of a thickness of less than about 20 microns, said carbide former being a metal selected from the group consisting of Groups IVA, VA, VIA and VIIA metals and alloys and mixtures thereof, and
said temperature stable diamond product being characterized by a chemical bond between said temperature stable diamond and said coating and said coating and the portion of said matrix carrier which is in contact with said coating.

Claim 18. A temperature stable diamond product as set forth in claim 17 which includes a plurality of initially separate temperature stable diamond elements arranged in a predetermined relationship and including opposed surface portions forming a gap therebetween,
said gap being in the range of between less than 1 mil and 500 mils, and
said matrix carrier being located in said gap and contacting at least a portion of the surface portions of said temperature stable diamond elements.

Claim 19. A temperature stable diamond product as set forth in claim 17 in which said product is a saw blade segment.

Claim 20. A temperature stable diamond product as set forth in claim 17 in which said product is a bearing element.

Claim 21. A temperature stable diamond product as set forth in claim 17 in which said product is a dressing tool.

Claim 22. A temperature stable diamond product as set forth in claim 17 in which said product is a cutter adapted to be mounted on an earth boring bit.

Claim 23. A temperature stable diamond product as set forth in claim 17 in which said product is a component of a twist drill.

Claim 24. A temperature stable diamond product as set forth in claim 17 in which said product is a lead bonding tool.

Claim 25. A temperature stable diamond product as set forth in claim 17 in which said product is a single point dressing tool.

Claim 26. In an earth boring bit including a body, the improvement comprising:
at least one cutter element supported by said body,
said cutter element including at least one polycrystalline diamond element which is temperature stable to at least about 1,200 degrees C. supported by a carrier matrix, said temperature stable diamond element having a coating thereon at least on that surface thereof which is in contact with said carrier matrix,
said coating including being of a thickness of at least about 1 micron and including a relatively thin carbide layer adjacent to said surface, and
said temperature stable diamond element being bonded to the contacting portion of said matrix carrier by a chemical bond between said temperature stable diamond element and said coating and said coating and the portion of said matrix carrier which is in contact with said coating.

Claim 27. An earth boring bit as set forth in claim 26 wherein said cutter element includes a plurality of polycrystalline diamond elements.

Claim 28. An earth boring bit as set forth in claim 26 wherein said body includes a surface of matrix carrier material.

Claim 29. An earth boring bit as set forth in claim 27 wherein at least some of said polycrystalline diamond elements are triangular in shape.

Claim 30. An earth boring bit as set forth in claim 26 wherein said polycrystalline diamond element is in the form of a facing on said carrier matrix and chemically bonded thereto.

Claim 31. An earth boring bit as set forth in claim 28 wherein said cutter element is of a diameter greater than 14mm.

Claim 32. An earth boring bit as set forth in claim 28 in which said bit includes a plurality of said cutter elements.

Claim 33. A temperature stable diamond product having a temperature stability up to about 1,200 degrees C, comprising:
a metal matrix carrier including a powdered material and a binder therefor,
a plurality of diamond pieces of a predetermined geometrical shape each of which is temperature stable up to about 1,200 degrees C. and at least some of which have at least one surface contacting at least a portion of said carrier,
at least some of said diamond pieces being in butting relation with an adjacent diamond piece,
each diamond piece being coated with a metal which is a carbide former on at least the portion thereof contacting said metal matrix carrier and on the surface portion which is adjacent to another diamond piece,
the coating on said diamond piece being at least about 3 microns in thickness, and
said temperature stable diamond product being characterized by a chemical bond between said temperature stable diamond and said coating and said coating and the binder for said matrix carrier which is in contact with said coating.

Claim 34. A method of forming a temperature stable diamond product having a temperature stability of up to about 1,200 degrees C. from at least one initially separate temperature stable diamond element of a predetermined geometric shape, comprising the steps of:
coating at least a portion of the surface of said temperature stable diamond element with a metallic carbide former,
said coating being of a thickness of at least about 3 microns,
assembling with said coating temperature stable diamond element a matrix carrier powder such that the powder contacts at least the coated surface of said temperature stable diamond,
cold pressing said assembled powder and said temperature stable diamond to compact said powder to a volume density of more than 40% to form a cold pressed intermediate,
cold isostatic pressing said cold pressed intermediate to compact said powder to a volume density of greater than 80% to provide an isostatic pressed intermediate, and
heating said isostatic pressed intermediate at an elevated temperature and in a controlled atmosphere for a period of time sufficient form of a chemical bond between the coating on the surface of said temperature stable diamond element and said diamond element and between said coating and the matrix carrier material in contact with said coating.

Claim 35. A method as set forth in Claim 34 wherein heating of said isostatic pressed intermediate includes heating at a rate not greater than about 10 degrees C. per minute in the range of between about 800 degrees C. and 1,100 degrees C. to effect conversion of a portion of said carbide forming coating to a carbide.

Claim 36. A method as set forth in Claim 34 wherein said matrix carrier powder is a mixture of a carbide and a binder therefor.

Claim 37. A method as set forth in Claim 34 wherein said assembly step includes the assembly of a plurality of coated temperature stable diamond elements in a predetermined configuration.

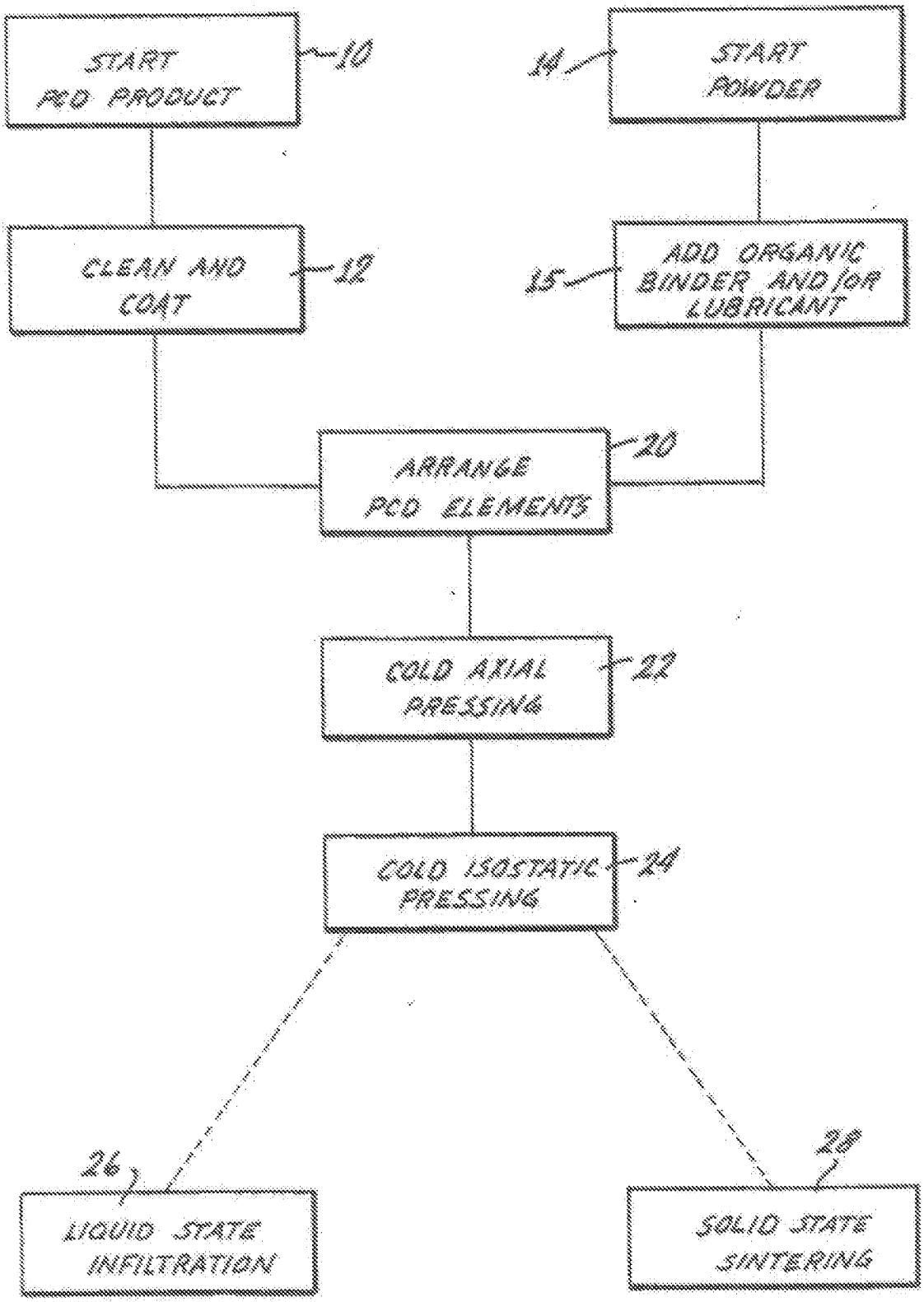
Claim 38. A method as set forth in Claim 37 wherein said elements are assembled such that there is a gap between adjacent elements.

Claim 39. A method as set forth in Claim 37 wherein said elements are assembled such that at least some of them are in butting relation.

Claim 40. A method as set forth in Claim 34 wherein said metallic carbide former is a metal selected from the group consisting of the metals of Group IVA, VA, VIA,VII and alloys and mixtures thereof.

Claim 41. A method as set forth in Claim 34 further including the step of assembling said isostatic pressed intermediate to a powdered support material, and
said heating operation including heating the isostatic pressed intermediate and said powdered material to effect the chemical bonding and to effect formation of said powdered material into a support for said temperature stable synthetic diamond element.

Fig. 1


START PCD PRODUCT
10
14
START POWDER
CLEAN AND COAT
12
15
ADD ORGANIC BINDER AND/OR LUBRICANT
ARRANGE PCD ELEMENTS
20
COLD AXIAL PRESSING
22
COLD ISOSTATIC PRESSING
24
26
LIQUID STATE INFILTRATION
28
SOLID STATE SINTERING

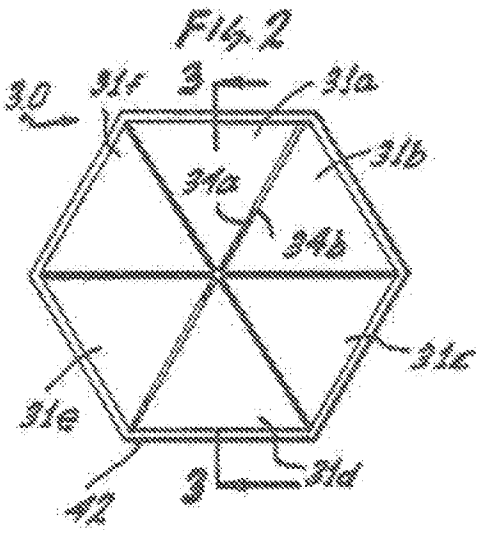


Fig. 2

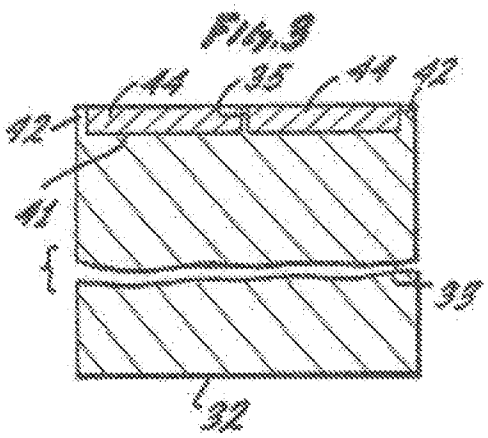


Fig. 3

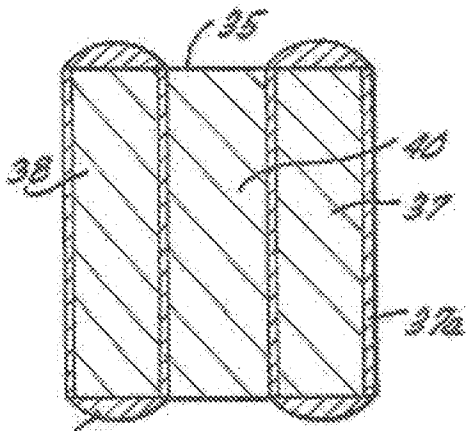


Fig. 4

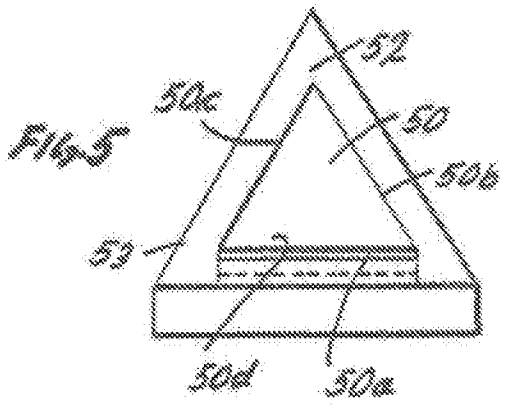


Fig. 5

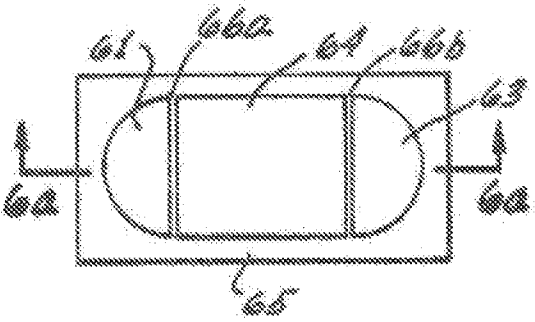


Fig. 6

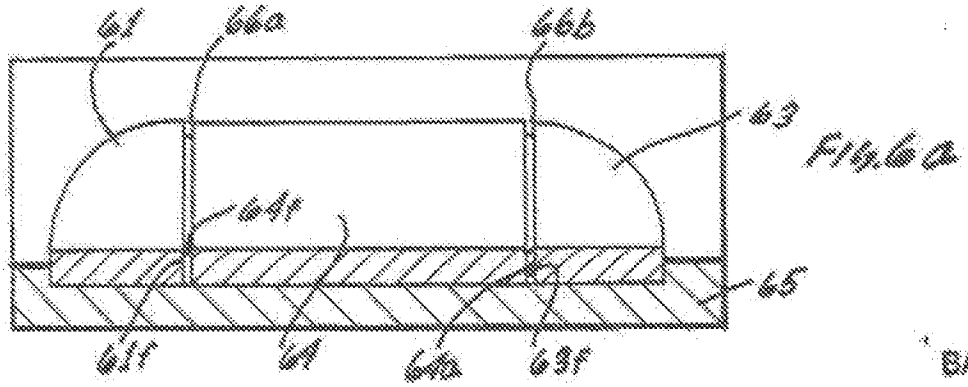


Fig. 6a

BAD ORIGINAL

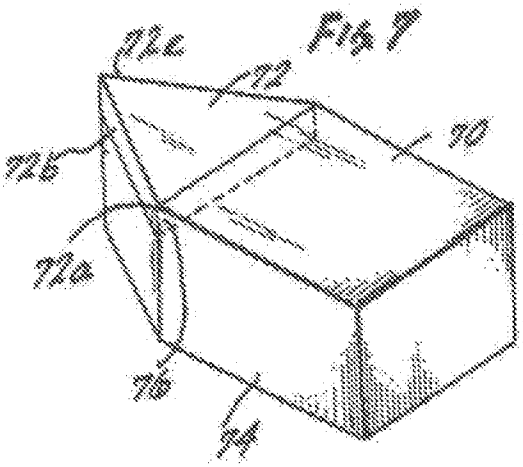


Fig. 8

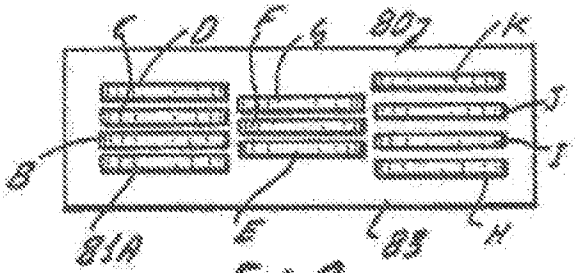


Fig. 8a

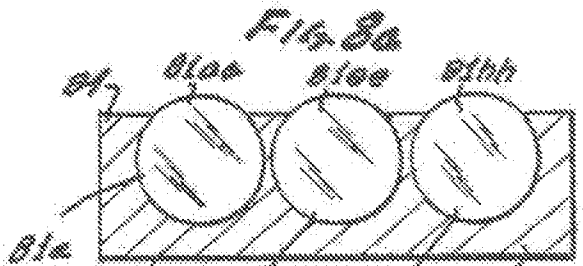


Fig. 9

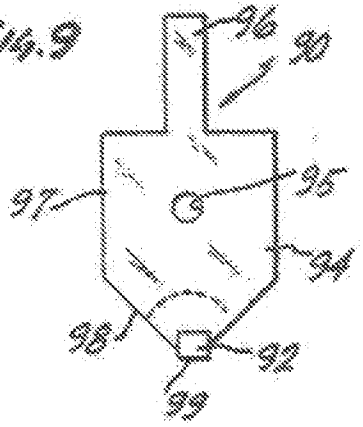
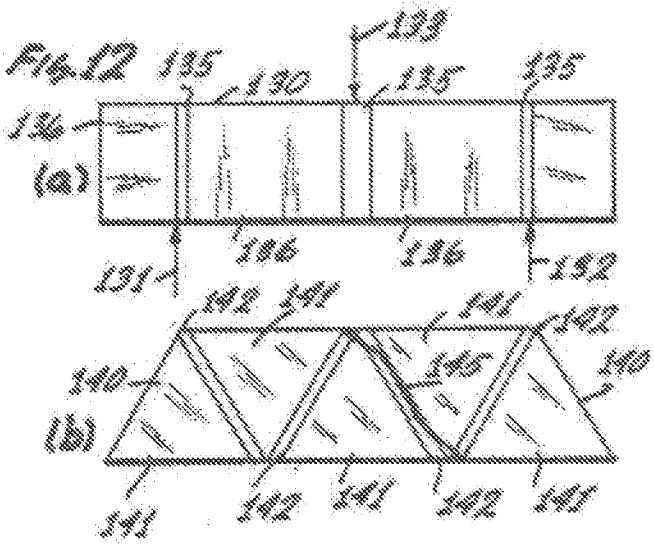


Fig. 12



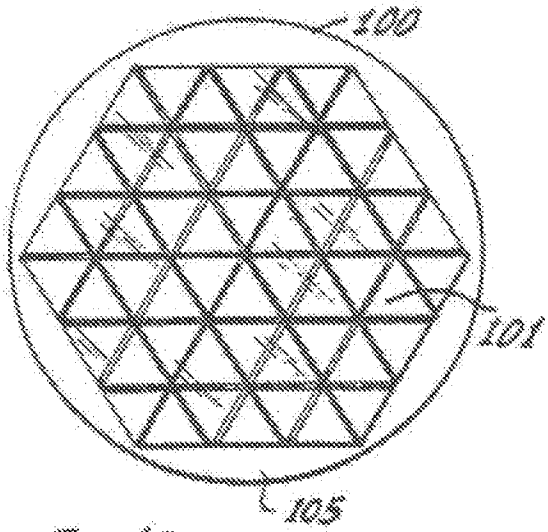
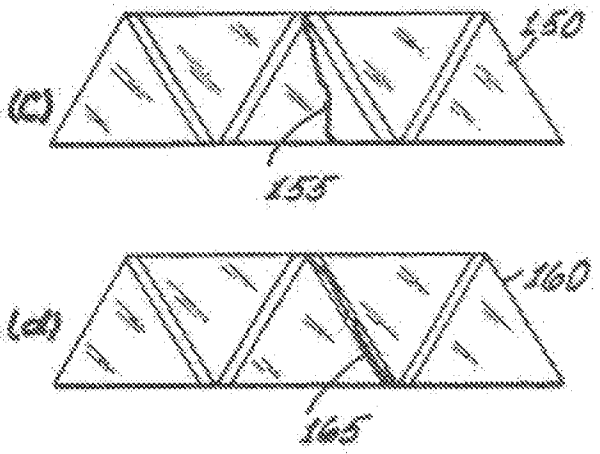


Fig. 10



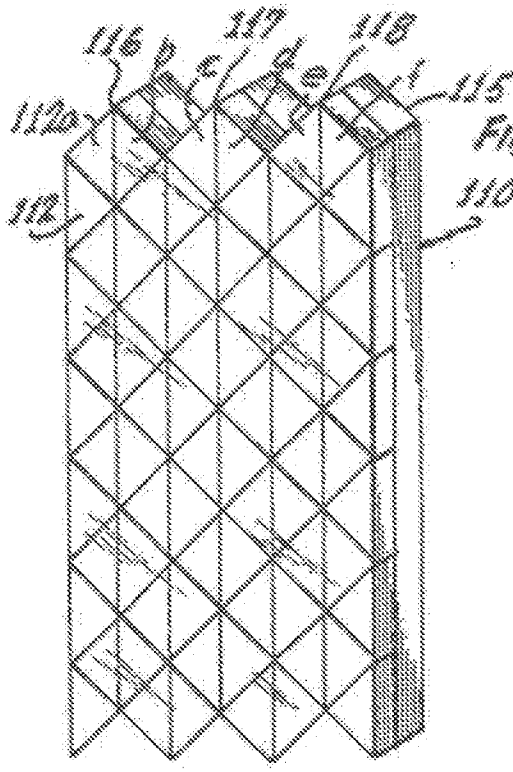


Fig.11

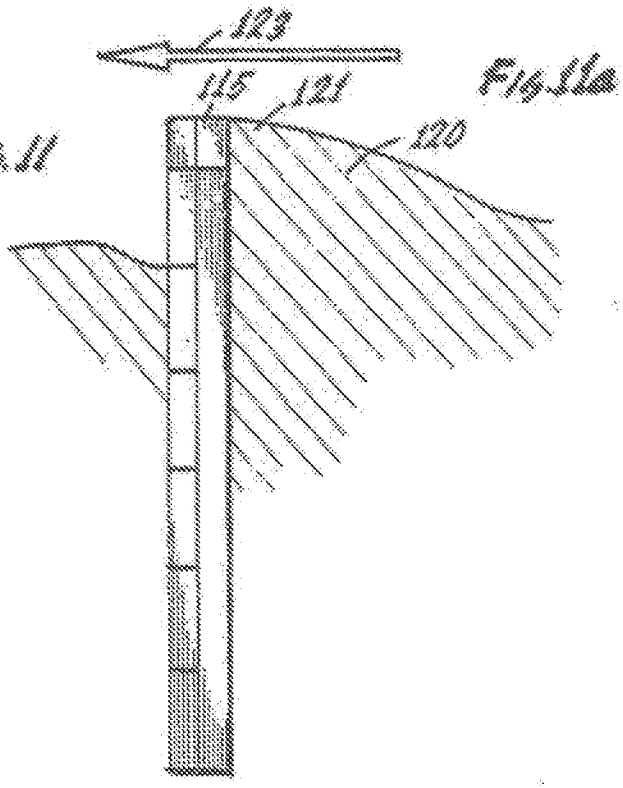


Fig.16a

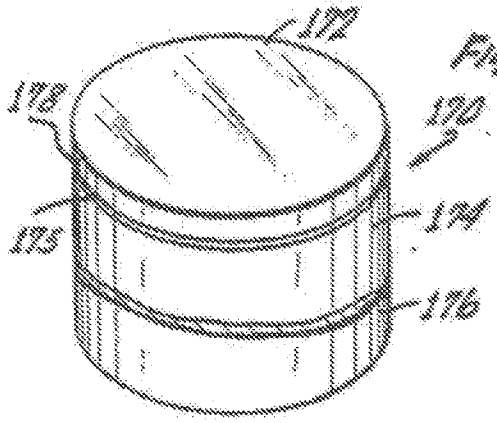


Fig.13

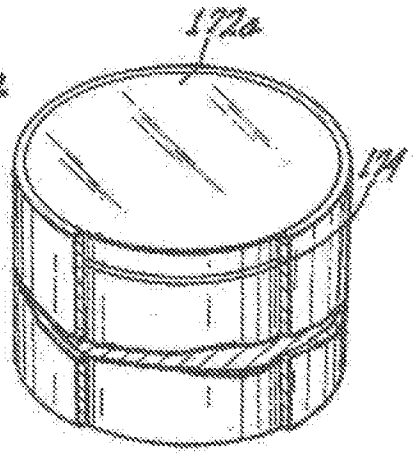


Fig.19a

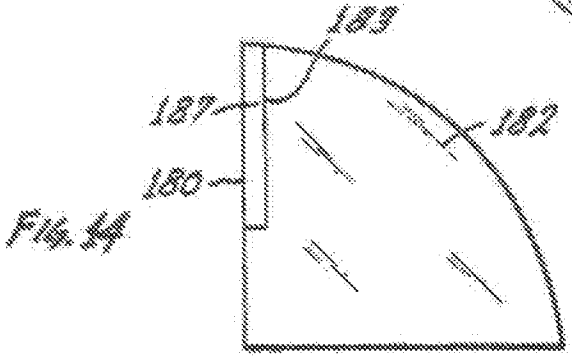


Fig.14

U.S. PATENT DOCUMENTS

Fig. 15

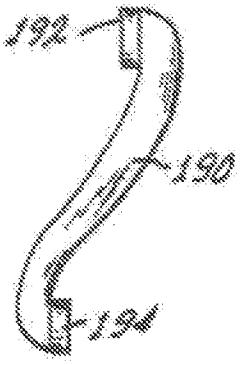
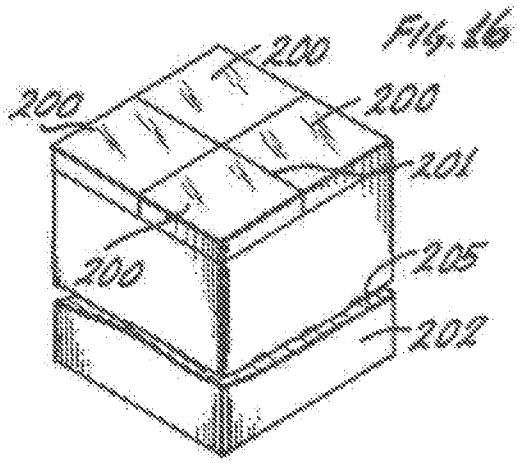


Fig. 16



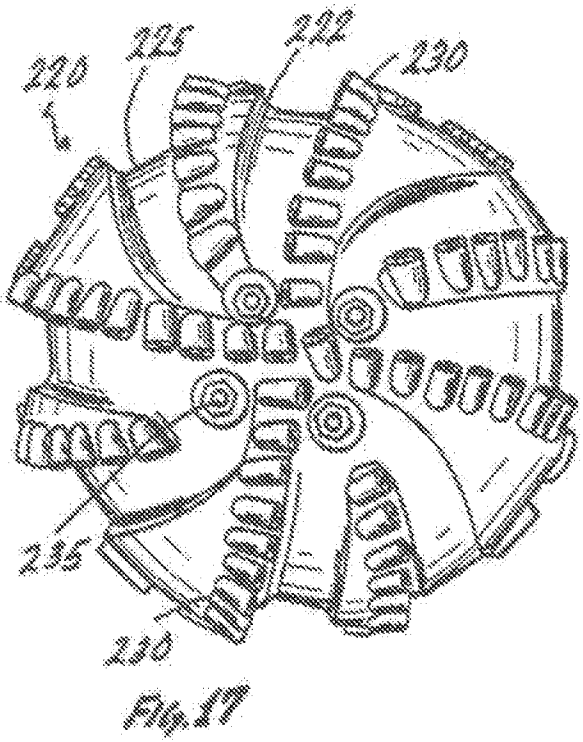
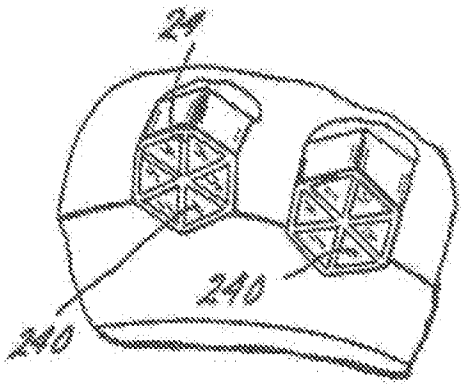


Fig. 17

Fig. 18



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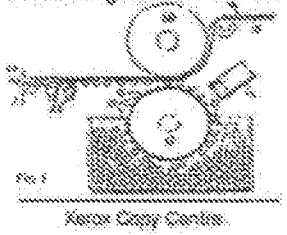
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(54) Abrasive sheeting having individually positioned abrasive granules.

(57) Abrasive sheeting can produce fine finishes at surprisingly high cutting rates when its abrasive granules are individually positioned in a predetermined pattern, with an uncoated portion of virtually every granule protruding from the surface of the binder layer. Each of the abrasive granules preferably is a spherical composite of a large number of abrasive grains in a binder. For example, abrasive grains having a mean dimension of about 4 µm can be bonded together to form spherical abrasive granules of virtually identical diameters, preferably within a range of from 25 to 100 µm.



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ABRASIVE SHEETING HAVING INDIVIDUALLY POSITIONED ABRASIVE GRANULES

Background of the Invention

Field of the Invention

The invention concerns abrasive sheeting or coated abrasives of the type having a backing which usually is flexible and carries abrasive grains or granules embedded in a binder layer and usually is flexible.

Description of the Related Art

At least as early as 1905, as taught in U.S. Patent No.794,495 (Gonton), it was discovered that unbroken "abrading surfaces soon become clogged and gummed by the fine grit and minute particles worn from the abrading surface and from the metal-work (or other work) being held to the abrading-surface" and that these materials can be carried away more effectively by applying the abrasive grit in a dot pattern. In U.S. Patent No. 1,867,784 (Bergstrom), a dot pattern is obtained by applying a binder to a backing, applying abrasive grains or granules to the binder, and then scraping off portions of the binder and adhered abrasive granules. More commonly, an adhesive is applied in a dot pattern so that the abrasive granules adhere only in that pattern. In U.S. Patent No. 4,317,660 (Kramis et al.), the adhesive dot pattern is obtained by applying the adhesive through stencil holes. After attracting a large number of abrasive granules to each dot, the abrasive granules are covered with a size coat.

In abrasive sheeting that has appeared on the market with such a dot pattern, there is a heap or a pile of abrasive granules at each dot, and that heap of granules is covered with a size coat. Because the height of each heap is more or less random, the individual heaps and the individual granules of each heap are loaded differently and hence produce uneven cutting. The size coat interferes with the cutting action of the abrasive granules and also results in uneven cutting due to variations in the extent to which the size coat covers the abrasive granules.

Uneven cutting of prior abrasive sheetings also emanates from irregular sizes and shapes of their abrasive granules. This effect has been minimized by using spherical granules of equal size. Another type of spherical abrasive granule consists of a large number of abrasive grains in either an organic or inorganic matrix. Because of their uniformity, such composite granules renew themselves as they wear away, thus maintaining relatively uniform abrasive cutting action for longer periods of time than has been possible when using abrasive sheeting coated with irregular abrasive granules. Such composite abrasive granules are disclosed in U.S. Pats. No. 3,916,584 (Howard et al.); No. 4,113,831 (Howard); and No. 4,541,842 (Rostoker). U.S. Pat. No. Re. 28,808 (Wagner) shows hollow balls consisting of abrasive grains bonded onto the outer surface of a friable matrix. Even though Fig. 1 of the Wagner patent shows those spheres uniformly positioned in a binder layer, the patent says that the hollow balls "are mixed with a bonding material and brought into the shape of the grinding body, after which the bonding material is allowed to harden out, and during the production of an abrasive belt the hollow bodies are bonded in the usual manner to a base material" (col. 6, lines 43-48). In Example 1, ready-prepared abrasive grain balls are uniformly strewn onto a layer of resin on a cotton twill fabric.

Even when prior abrasive sheetings employ composite spherical granules of equal size, sheetings made at one time tend to have different cutting rates than do those made at other times due to variables in their manufacture. Accordingly, when prior abrasive sheetings have been used under numerical or robotic control, it has been necessary to test the cutting rate of each jumbo roll before putting it to use.

Abrasive sheeting ordinarily is manufactured in great lengths that are wound into rolls for storage and shipment. Eventually, the sheeting is die-cut into desired sizes and shapes. For example, it may be cut to form disky pads that are used to polish lenses. In doing so, the die contacts the abrasive particles which cause its cutting edge to become dull and to require resharpening within a short period of time.

Other Prior Art

Abrasive tools are often made by handsetting abrasive granules such as diamonds, but such granules are quite large. It is believed that handsetting has never been employed in abrasive sheeting that has appeared in the market.

U.S. Pat No. 4,539,195 (Ishikawa) concerns a method of making grinding stones, the abrasive grains of which are distributed in a controlled manner so that the load working on each grain is even, making the stone more efficient and of longer life. In a first variation of the Ishikawa method, an electrically conductive pattern is formed on a resinous binder sheet which is then immersed into an electroplating path containing metallic ions mixed with abrasive grains that are attracted to the pattern. The electrically conductive pattern may be formed by photoetching or printing techniques. A number of the abrasive-bearing sheets are placed in layers and molded into a grinding stone by warm or hot pressure molding. Another variation is the same as the first except that the sheet is metallic and a surface is masked so that the abrasive grains are attracted only to the unmasked areas. An example of distribution of abrasive grains on the surface of a grinding stone is shown in Fig. 15 wherein the grains are located in rows and uniformly spaced from adjacent grains.

Summary of the Invention

The invention provides abrasive sheeting or coated abrasive that can produce finer finishes at faster cutting rates than could be attained in the prior art. Furthermore, the novel abrasive sheeting is believed to provide a more predictable cutting rate, thus minimizing the need to test its cutting rate before using it in robotic or numerically controlled machines.

Briefly, the abrasive sheeting of the invention has a backing carrying a binder in which abrasive granules are strongly bonded and lie substantially in a plane and at a predetermined lateral spacing. The granules should be of substantially equal size, i.e., the mean dimension of 90% of the granules should differ by less than 2:1. Each of the abrasive granules should pass a screen with 300 um openings, because substantially larger granules would not provide the fine finishes desired in uses for which the novel abrasive sheeting is intended.

The granules preferably are in a predetermined pattern (or patterns when using granules of differing sizes or types) that provides spaces between the granules of sufficient width to carry off detritus. In a preferred pattern, single granules are uniformly spaced and aligned in rows extending both longitudinally and transversely (i.e., in the X and Y directions). In another preferred pattern, abrasive sheeting having circular rows of uniformly spaced granules can be cut into discs, the centers of which are concentric with the circular rows.

Preferably the abrasive granules are equiax, and the diameter of substantially every granule is within 10% of the mean diameter so that the granules protrude from the surface of the binder layer to substantially the same extent and so can be loaded equally upon contacting a workpiece, thus providing an extraordinarily uniform finish. By "equiax" is meant that each granule has approximately the same thickness in every direction. An equiax granule can be considered to have a diameter, whether or not it is spherical.

The abrasive granules can have various populations at various areas of the novel abrasive sheeting in order to remove material at differing rates from selected faces of a workpiece. In one technique for determining the populations required to accomplish this, the wear of abrasive sheets of uniform density is studied, and the novel abrasive sheeting is made to have increased granule population at areas showing the most wear. The predetermined granule pattern also can be selected to leave the novel abrasive sheeting free from abrasive granules in areas to be die-cut, thus allowing the die to remain sharp much longer than has heretofore been possible. This also minimizes waste.

The invention also concerns a novel method of making abrasive sheeting by the sequential steps of

1) attracting small abrasive granules only to dots in a predetermined pattern on a carrier,

2) while advancing a backing that carries a tacky binder layer in synchronism with said carrier, transferring the attracted granules into the binder layer in said pattern, and

3) cindering the binder nontacky.

When the carrier is at the surface of a rotating cylinder, this 3-step method can produce abrasive sheeting of almost unlimited length which can be wound up in roll form for convenient storage and shipment. In such a roll, the predetermined pattern of abrasive granules repeats many times. Such a roll can be converted into a variety of articles such as discs, daisies, sheets, and belts.

When the abrasive granules have irregular shapes, the 3-step method causes the major axis of each

granule to lie substantially in a plane parallel to the backing. Hence, when irregular granules are of substantially the same size, they tend to protrude from the binder to substantially the same extent and to abrade uniformly to afford uniform finishes.

Preferably the binder is selected so that subsequent to step 2) is an additional step of softening the binder, usually by being heated, to form a meniscus at each granule, thus enhancing the bonding of each granule to the backing. Doing so should make it unnecessary to overcoat the granules, thus leaving the cutting surface of each granule free from material that could otherwise interfere with its abrasive function. When heat is used to form menisci, the extent to which the abrasive granules protrude from the binder can be controlled by adjusting the time and temperature at which the menisci are formed. When a meniscus is to be formed at each abrasive granule, the pressure applied in step 2) can be very light, just enough to tack the granules to the binder layer.

Instead of, or in addition to, forming a meniscus at each granule, a size coat can be applied over the novel abrasive sheeting to enhance the bonding of the abrasive granules. Usually this is unnecessary, unless the abrasive granules are rather large, e.g., are retained by a screen with 100 µm openings. When the abrasive granules are expensive, e.g., diamonds, a size coat may be desirable to ensure that they are not dislodged and lost.

Although the individual abrasive granules that lie in a predetermined pattern should be of substantially equal size, selected areas of the novel abrasive sheeting can have abrasive granules of one size in one predetermined pattern while other areas have granules of a different size in another predetermined pattern, each to provide a desired rate of cutting and degree of finish at a particular area of a workpiece. For the same reason, the novel abrasive sheeting may employ abrasive granules of two or more different types, each type being individually positioned in a predetermined pattern. In order to make abrasive sheeting having two sizes or two types of abrasive granules, steps 1) and 2) are repeated with the second size or type of granule prior to step 3).

Detailed Description

Each of the abrasive granules of the novel sheeting preferably is an equiax composite of a large number of abrasive grains in an inorganic or organic binder matrix. For example, abrasive grains having a mean dimension of about 4 µm can be bonded together to form spheres of virtually identical diameters, preferably within a range of from 25 to 100 µm. Because of their uniform diameter, each equiax granule can be positioned to protrude to the same extent from the binder layer. By individually positioning the equiax granules to be spaced equally from adjacent granules, the granules each bear the same load and hence wear at substantially identical rates and tend to continue to be equally effective as long as uncoated portions protrude from the binder layer. Consequently, workpieces continue to be polished uniformly, in contrast to the tendency of prior abrasive sheeting to provide uneven polishing upon becoming worn.

Preferably the thickness of the binder layer of the novel abrasive sheeting is from 25 to 150 µm. Thicknesses above that range may be uneconomical, while thicknesses below that range may not bind the abrasive granules as strongly as desired. When the binder layer is coated from solution or emulsion, it may be difficult to obtain uniform layers much greater than 50 µm.

A carrier that can be used in the above-outlined 3-step process is a printing plate marketed by Toray Industries as "Toray Waterless Plate." It has a flexible sheet of aluminum bearing a layer of photosensitive material covered with a layer of silicone rubber. Upon exposure to light through a half-tone screen, the silicone rubber of a positive-acting plate causes the photosensitive material to bind itself firmly to the silicone rubber in areas where the light strikes, after which the silicone rubber in unexposed areas can be brushed off, leaving silicone rubber dots in the predetermined pattern provided by the light exposure. The printing plate is then wrapped onto a cylinder, and the cylinder is rotated through a fluidized bed of abrasive granules. The granules are attracted to the printing plate only where the silicone rubber remains and not to the ink-receptive areas. Upon moving a binder-carrying backing in synchronism with the rotating printing plate, the granules are picked up by and become embedded into the binder layer in the pattern of the printing plate. That pattern repeats many times when the backing is long.

When a "Toray Waterless Plate" is used in the above-outlined 3-step process and the tacky binder layer would stick to the silicone rubber of the printing plate, a transfer roll can be positioned between the binder layer and the printing plate. The surface of the transfer roll should be selected to cause the abrasive granules to transfer from the silicone rubber of the printing plate, while acting as a release surface in relation to the tacky binder.

For most applications of the novel sheet, the breadth of the dots formed in step 1) of the above 3-step

process should be small enough that only one abrasive granule is attracted to each position, but when each dot is large enough to make it fairly certain that there will be a granule at every dot, it can be expected two or possibly three granules will be deposited side by side at a few positions. When only one abrasive granule per dot is desired, each dot preferably is roughly circular and has a diameter within the range of 30 to 80% of the mean dimension of the abrasive granules. When using spherical abrasive granules 80 um in diameter, good results have been attained with dots 62 um in diameter. When the diameter of each dot substantially exceeds the diameter of an abrasive granule, a monolayer of several granules may be attracted to each dot.

The use of a printing plate mounted on a cylinder in the above-outlined 3-step process may result in a seam that may produce discontinuities in the pattern of abrasive granules. Abrasive sheeting of the invention, that has no seam in its pattern, can be made by sequentially coating onto a cylinder formulations that provide a cylindrical printing plate, preferably including a silicone rubber layer. Preferred sequential coating formulations are those of U.S. Pat. No. 3,511,178 (Curtin).

If a seam in the pattern is not objectionable, step 1) of the above-outlined 3-step process for making abrasive sheeting of the invention can use a carrier prepared by the steps of

1) coating one face of a sheet of metal foil with rubber and the other face with a photoresist,

2) exposing the photoresist to light in a predetermined pattern,

3) removing areas of the photoresist corresponding to said pattern, and

4) etching away the metal foil in said areas to expose the rubber in said predetermined pattern.

It is also preferred, particularly if the abrasive granules would be attracted to the remaining photoresist, to include after the etching step the step

5) removing the remaining photoresist.

Among classes of binders that can be used in the novel abrasive sheeting are thermoplastic resins such as ethylene/acrylic acid copolymer, polyethylene, and poly(ethylmethylacrylic) acid, which is available from E.I. duPont Company under the trade designation "Surlyn". Another useful class of binders is acrylic pressure-sensitive adhesives which cure to a nontacky state. Also useful are thermosetting binders which have a tacky state such as epoxy resins, phenolics, and polyurethanes.

The backing of the novel abrasive sheeting can be fabric (e.g., woven or non-woven fabric such as paper) which may be saturated with a filled binder material, a polymer film such as that formed of oriented heat-set polypropylene or poly(ethylene terephthalate) which may be first primed, if needed, with a priming material, or any other conventional backing material.

In the novel abrasive sheeting, the addition of a grinding aid over the surface of the abrasive granules may provide improved grinding performance. Grinding aids may also be added to the size coat or as particulate material. The preferred grinding aid is KBF_4, although other grinding aids are also believed to be useful. Other useful grinding aides include NaCl, sulfur, K_2TiF_6, polyvinyl chloride, polyvinylidene chloride, cryolite and combinations and mixtures thereof. The preferred amount of grinding aid is on the order of 50 to 300 g, preferably 80 to 160 g, per square meter of coated abrasive product.

The Drawing

The invention may be more understandable by reference to the drawing wherein:

Fig. 1 schematically shows a method of printing abrasive granules onto a binder layer carried by a flexible backing, thus providing preferred abrasive sheeting of the invention;

Fig. 2 is an electronmicrograph showing abrasive granules having been attracted to a tackified binder layer using apparatus illustrated in Fig. 1;

Fig. 3 is an electronmicrograph showing a fragment of abrasive sheeting of the invention made by heating the intermediate product of Fig. 2 to form a binder meniscus at each granule; and

Fig. 4 schematically shows a fragment of an abrasive sheeting of the invention after it has been cut to form daisy pads.

In Fig. 1, attached to a rotatable, heated metal cylinder 10 is a printing plate 12, the outer surface of which has been developed to leave roughly circular rubber dots 13. The cylinder is rotated through a fluidized bed of spherical abrasive granules 14, each of uniform diameter somewhat larger than the diameter of the rubber dots. After removing excess granules by suction at 15, substantially one abrasive granule 14 adheres to each of the rubber dots 13. Moving at the same speed as the surface of the cylinder

10 is a flexible backing 16 carrying a heat-activatable binder layer 18 which is pressed against the printing plate 12 by a heated nip roll 20. Heat from the cylinder 10 and rubber-covered nip roll 20 tackify the binder layer 18 to permit the attracted granules 14 to be adhered superficially to the binder layer 18 in spaced rows extending in the X and Y directions as seen in Fig. 2. In the upper left corner of Fig. 2, a few abrasive granules have fallen out, leaving small craters in the binder layer. The abrasive granules have been deposited in the lower part of Fig. 2 at twice the density of the upper part. At most positions, only one abrasive granule has been deposited, but at a few dots, there are two granules side by side.

Referring again to Fig. 1, the granule-bearing backing 16 is passed across a bank of infrared lamps 22 by which the binder is heated to wet the surfaces of the abrasive granules, thus causing the binder layer to flow and form a meniscus 23 around the base of each granule as shown in the electronmicrograph of Fig. 3. This causes the abrasive granule to become strongly bonded to the flexible backing 16.

The resulting abrasive sheeting 24 of the invention contains abrasive granules 14 individually positioned to permit the sheeting to be die-cut into daisy pads 26 as shown in Fig. 4. The abrasive granules have been positioned in concentric rows such that their density in areas 28 adjacent the outer edges of each petal is twice the density at the central areas 30 of the daisy pad. The abrasive sheeting from which the daisy pads 26 were cut was left free from abrasive granules adjacent the phantom line 32 at the peripheries of the petals along which the sheeting 24 is to be die-cut so that the die does not contact any abrasive granules. By leaving the area 34 between the daisy pads free from abrasive granules, no granules have been wasted.

In the following examples, all parts are given by weight.

Example 1

Used to make abrasive sheeting of this example were:

1) a negative-acting "Toray Waterless Plate" which had been exposed to a half-tone screen to produce roughly circular dots, each about 63 µm in diameter and arranged in rows extending parallel to both the lengthwise and widthwise edges of the plate, 80 rows per inch (7.9 per cm) in both directions;

2) spherical abrasive granules, each 60 µm in diameter and made of 77 parts Al_2O_3 grains having a mean particle size of 4 µm in 23 parts of a matrix based on phenol-formaldehyde resin;

3) a long roll of biaxially oriented poly(ethyleneterephthalate) polyester film 0.05 mm in thickness bearing a 0.05 mm binder layer of ethylene/acrylic acid copolymer.

The dot-containing plate was mounted on the metal cylinder 10 of the apparatus shown in Fig. 1, and spherical abrasive granules 14 were fluidized by a mechanical vibrator and became attached to the silicone dots 13. Excess granules were removed by suction at 15. The binder layer 18 was heated by the rubber-covered nip roll 20 to about 70° C to become tacky so that the abrasive granules transferred to it, with a force of 79 N applied to the nip roll per cm of width. Additional heating by infrared lamps 22 caused the binder to form a meniscus around the base of each of the granules.

The exposed face of the polyester film backing of the resulting abrasive sheeting was laminated with a double-coated pressure-sensitive adhesive tape and this composite was die-cut into daisy pads 7.6 cm in diameter and similar in shape to the daisy pads 26 of Fig. 4 except having six petals. The pads were used as a second fining pad in the polishing of lenses formed of polycarbonate of the type commercially available from PPG under the trade designation CR39. A "Coburn" #606 cylinder machine was used at a load of 20 pounds (89 N) with a water flood on the high speed spindle setting. The test was conducted using two types of lapping tools, a 8.25/8.25 dioptral and a 2.12 dioptral. In both cases the amount of lens removed after two minutes was measured. The results are in Table I.

Examples 2-6

Abrasive sheetings of Examples 2-6 were made as in Example 1 except having different spacings of their rows in both directions as indicated in Table I. Also in Table I are results from using a "Control" daisy pad made with the same spherical abrasive granules coated from slurry in a manner used for current commercial production and having about 670 granules/cm². This granule density had been selected based upon extensive experimentation for general purpose use and was intermediate the granule densities of the abrasive sheetings of Examples 3 and 4.

TABLE I

Ex.	Rows per inch	Rows per cm	mm of lens removed in 2 mins	
			2.12 d. lens	6.25/6.25 d. lens
1	20	7.9	0.001	0.000
2	40	15.7	0.031	0.056
3	65	25.6	0.025	0.075
4	85	33.5	0.028	0.124
5	150	59.0	0.012	0.032
6	200	78.7	0.009	0.025
Control			0.028	0.056

Example 7

A negative-acting "Toray Waterless Plate" was exposed to produce 63 µm silicone rubber dots in rows extending in the X and Y directions at a density of 65 rows per inch (25.6 rows/cm). The plate was covered with the spherical abrasive granules of Example 1, and excess granules were then removed by turning the plate over and tapping it. Examination of the plate showed that there was at least one granule at each of the silicone dots. Against these granules was laid the binder layer of the polyester film backing of Example 1, and the composite was put through the nip of a heated two-roll laminator at about 73° C while a force of 70 N was applied to the nip roll per cm of width. The composite was then placed in an oven at 113° C for 10 minutes to cause the binder to form a meniscus around the base of each granule, resulting in abrasive sheeting of the invention.

Examples 8-11

A round-dot litho contact screen was exposed to form a pattern of spots, each 61 µm in diameter and equally spaced in rows extending in the X and Y directions. The number of rows of spots per unit distance within an inner circle 6.0 cm in diameter differed from the number of rows between that circle and an outer circle 15.24 cm in diameter. In other words, the spot population changed at the junction of the two circles as it does in Fig. 2. Several different combinations of populations were prepared in this manner as shown in Table II.

A negative-acting "Toray Waterless Plate" was exposed using each contact screen and developed in the usual manner. The developed plate was mounted on a metal cylinder and employed in the same way as in Example 1 to transfer spherical abrasive granules 63 µm in diameter from a fluidized bed to create 8-petal daisy pads, the centers of which coincided with the centers of the circles. The daisy pads were tested as in Example 1 with results in Table II in comparison to the same "Control".

TABLE II

Ex.	Inner Circle Rows/cm	Outer Circle Rows/cm	mm of lens removed	
			212 lens	625/625 lens
8	19.7	33.5	0.034	0.040
9	25.6	19.7	0.108	0.086
10	25.6	33.5	0.058	0.102
11	25.6	39.4	0.070	0.108
Control			0.025	0.056

Example 12

A round-dot litho contact screen was exposed to form an opaque spiral pattern using the standard formula $X = k\theta$ and $X = k\theta + 0.317$ mm, starting from a circle 2.1 cm in diameter and extending to a circle 18.2 cm in diameter. This produced opaque and transparent spiral areas of equal size between the two circles. Then using the developed contact screen as a mask, a laser was used to expose a negative-acting "Toray Waterless Plate" through the transparent areas of the mask to produce a pattern of dots 83 µm in diameter equally spaced in rows extending in the X and Y directions. There were 106 rows of silicone dots per inch (39.4 dots/cm) within a spiral pattern on the developed plate.

The developed plate was used as in Example 7 (except using abrasive granules 83 µm in diameter) to provide abrasive sheeting of the invention which was cut into a disc on which was centered the spiral pattern of abrasive granules in spaced rows.

Example 13

Abrasive sheeting was prepared as in Example 7 except as follows:

a) the abrasive granules were Al_2O_3 grains of irregular shape which had been screened to pass 100 mesh (150 µm openings) and retained on 120 mesh (125 µm openings);

b) there were 66 rows/inch (25.6 rows/cm) of silicone dots;

c) the abrasive sheeting, after being removed from the oven, was overcoated with a size coat of phenolformaldehyde resin which after curing in an oven had a dry weight of 80 g/m^2.

The backing of this abrasive sheeting was laminated with a double-coated pressure-sensitive adhesive tape and then die-cut to 3-inch (7.5 cm) discs. Each disc was adhered by its pressure-sensitive adhesive to a "Coburn" No. 807 cylinder machine using the following settings: spindle stroke set at 7, spindle speed 100%, cross stroke 0, and a load of 30 pounds (133 N). The workpiece was a 1018 mild steel ring 4.46 cm I.D. and 8.4 cm O.D. The ring was abraded in an operation normally called flat lapping after being mounted on a bracket that fixed its axis perpendicular to the abrasive surface as the machine oscillated the abrasive surface in a circular motion. The test was run in one minute cycles at a rate endpoint of 0.3 g/min. The total cut and surface finish at endpoint are given in Table III in comparison to a "Control" made in the same way except that the abrasive granules were coated from slurry to provide a binder layer containing approximately the same mass of granules (i.e., about 0.40g).

TABLE III

Example	Total Cut	R_a (µm)	R_t (µm)
13	2.84 g	0.30	2.87
Control	1.44 g	0.45	3.46
R_a = average surface roughness R_t = maximum peak-to-valley height			

Claims

1. Abrasive sheeting comprising a backing carrying a binder layer of substantially uniform thickness in which abrasive granules are bonded substantially in a plane and characterized by the abrasive granules lying at a predetermined lateral spacing and being of substantially equal size and passing a screen with 300 µm openings, and a portion of virtually every granule protruding from the surface of the binder layer.

2. Abrasive sheeting as defined in claim 1 further characterized by substantially every granule being equiax and of substantially the same diameter, and each granule protruding from the binder to substantially the same extent.

3. Abrasive sheeting as defined in claim 1 further characterized by single granules being aligned in uniformly spaced rows.

4. Abrasive sheeting as defined in claim 3, further characterized by a great length of which being wound upon itself in roll form, said granules being in a predetermined pattern that repeats a large number of times over the length of the sheet.

5. Abrasive sheeting as defined in claim 4 further characterized by said predetermined pattern leaving areas of the binder layer free from abrasive granules in positions to be contacted by a tool for cutting the sheeting into articles of desired shapes, thus protecting the cutting tool from contacting abrasive granules.

6. Abrasive sheeting as defined in claim 1 further characterized by additional abrasive granules of substantially equal size different from the size of the first-mentioned abrasive granules being individually positioned in a second predetermined pattern and an uncoated portion of virtually every of said additional granules protruding from the surface of the binder layer.

7. Method of making abrasive sheeting of claim 1 by the sequential steps of

1) attracting small abrasive granules only to dots laterally spaced in a predetermined pattern on a carrier,

2) while advancing a backing that carries a tacky binder layer in synchronism with said carrier, transferring the attracted granules into the binder layer in said pattern, and

3) rendering the binder nontacky.

8. Method as defined in claim 7, further characterized in step 2 of which the granules being pressed into the binder layer.

9. Method as defined in claim 7 further characterized by said carrier covering the cylindrical exterior of a rotating drum, and in step 1) the drum being rotated through a fluidized bed of said granules.

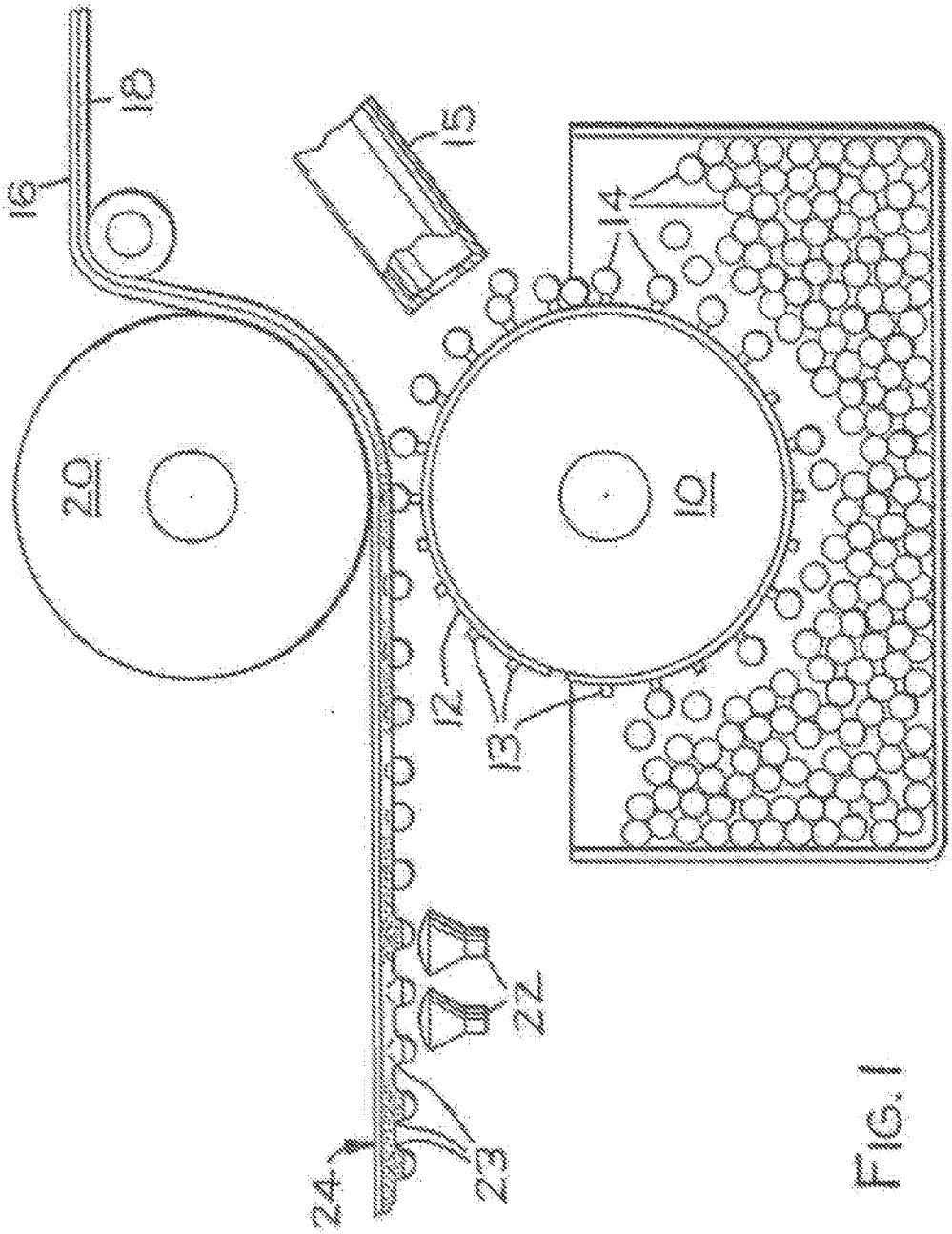


FIG. 1

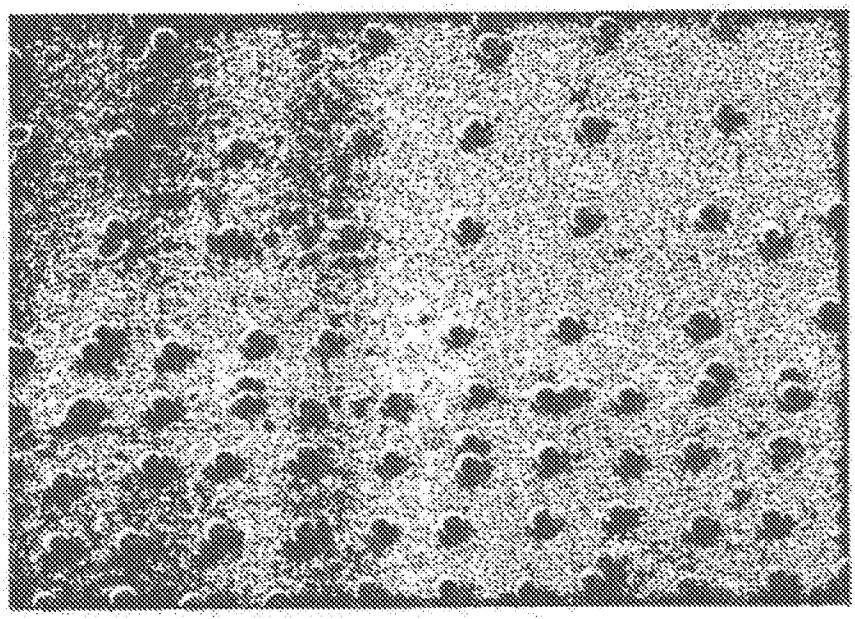


FIG. 2

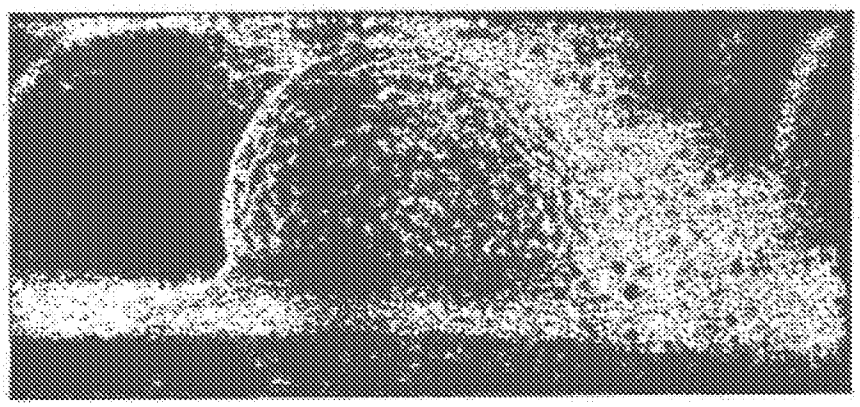


FIG. 3

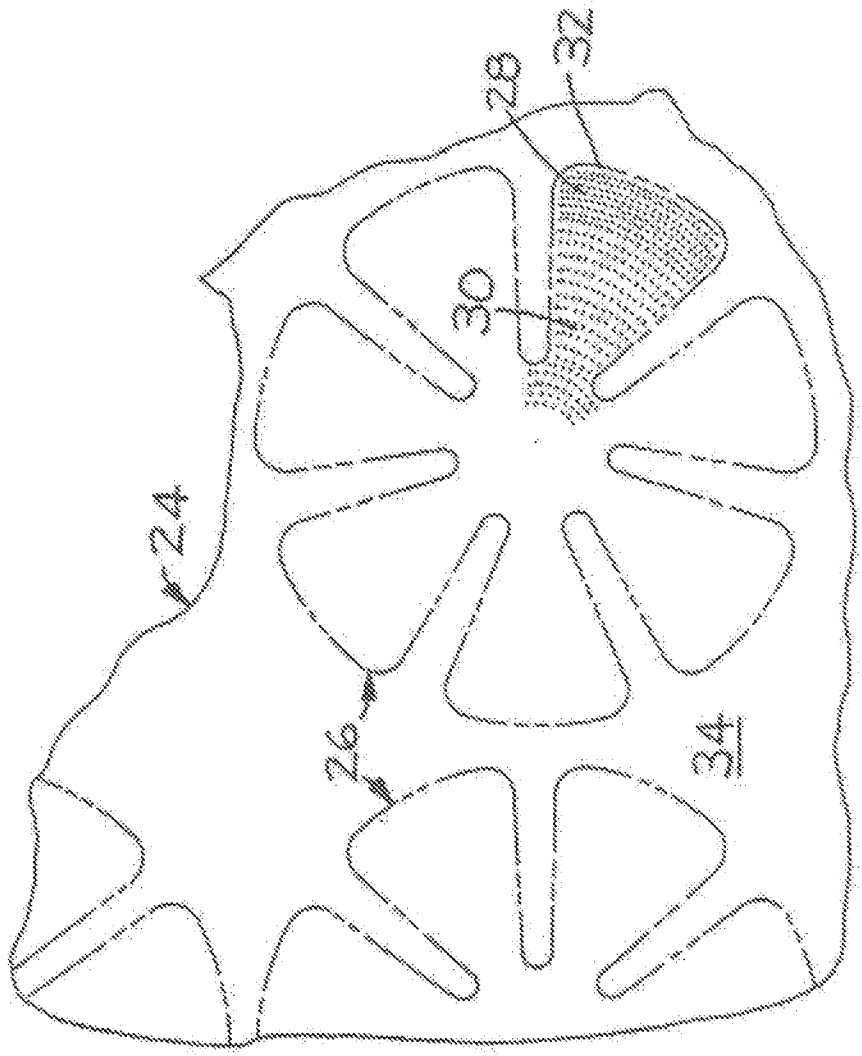


Fig. 4

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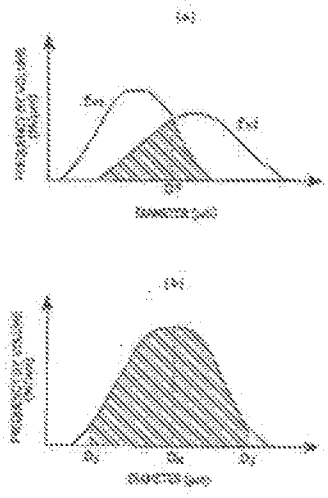
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(54) Diamond sinter, high-pressure phase boron nitride sinter, and processes for producing those sinters

(57) A powder of diamond or high-pressure phase boron nitride core particles is charged into a coating space as it is dispersed to a dispersity that is preset in accordance with the average diameter of those core particles and a precursor of a coat forming substance that is either gasified via the vapor phase or in a vapor-phase state is allowed to contact and/or impinge against the particles in said powder of core particles so that their surfaces are covered with the coat forming substance, thereby preparing coated diamond or high-pressure phase boron nitride particles, and these particles or mixtures containing them or mixtures of these particles with bonding materials are sintered under appropriate sintering conditions at a predetermined high temperature and pressure. The thusly produced diamond or high-pressure phase boron nitride sinter is composed of coated core particles of high performance that are superhard, uniform, dense and sintered firmly and which have a controlled microstructure. If sintering is done at pressures less than 3000 MPa, the invention offers the advantage of eliminating the constraint of the need to use equipment capable of creating ultrahigh pressures of at least 3000 MPa. The use of ultrahigh pressure HIP apparatus or other types of HIP apparatus offers the added advantage of enabling the production of shaped sinters, thereby presenting significant benefits to manufacture on an industrial scale.

FIG. 1



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Description

BACKGROUND OF THE INVENTION

This invention relates to a diamond sinter produced by sintering a mixture containing at least coated diamond particles having a coat forming substance formed on the surfaces of diamond particles and a high-pressure phase boron nitride sinter produced by sintering a mixture containing at least coated high-pressure phase boron nitride particles having a coat forming substance formed on the surfaces of high-pressure phase boron nitride particles. The invention also relates to processes for producing these sinters.

Diamond, with strong covalent bonding, has many excellent properties. On the other hand, because of the covalent bonding, diamond has such a small self-diffusion coefficient that it is very difficult to sinter. Another problem with diamond is that it is thermodynamically stable only under ultrahigh pressures so that it will experience a phase transition to graphite if the pressure is insufficient under elevated temperatures. Therefore, without addition of bonding materials or sintering aids, strong sinters cannot be produced unless a ultrahigh pressure of about 9500 MPa is applied simultaneously with exposure to a very high temperature of about 2440 K.

High-pressure boron nitrides consist of cubic boron nitride and/or wurtzite boron nitride. Cubic boron nitride (c-BN) has similar characteristics to diamond; on account of strong covalent bonding, it has many excellent properties but, on the other hand, because of this covalent bonding, c-BN has such a small self-diffusion coefficient that it is very difficult to sinter. Further, c-BN is thermodynamically stable only under ultrahigh pressures and it will experience a phase transition to hexagonal boron nitride (h-BN) of a graphitic phase (if the pressure is insufficient under elevated temperatures.) Wurtzite boron nitride (w-BN) has generally the same properties as the cubic boron nitride; it is a difficult-to-sinter substance and it is thermodynamically stable only at ultrahigh pressures and will experience a phase transition to hexagonal boron nitride (h-BN) of a graphitic phase if the pressure is insufficient under elevated temperatures. It should be noted that if the wurtzite boron nitride is sintered under ultrahigh pressures and at elevated temperatures where the cubic boron nitride is thermodynamically stable, a phase transition to the cubic boron nitride occurs depending on the conditions, yielding in this case a sinter containing the cubic boron nitride or a sinter that is solely comprised of the cubic boron nitride. In either case, without addition of bonding materials or sintering aids, strong sinters cannot be produced unless a ultrahigh pressure of about 7000 MPa is applied simultaneously with exposure to a very high temperature of about 2000 K.

However, irrespective of whether diamond or high-pressure phase boron nitride is to be sintered, the sintering conditions set forth in the preceding paragraphs for the case where neither bonding materials nor sintering aids are added are extremely hostile and are not suitable for the purpose of producing diamond or high-pressure phase boron nitride sinters of high density on an industrial scale.

Therefore, in order to produce these high-density sinters, sintering must be done under industrially applicable conditions and to this end the addition of bonding materials and/or sintering aids is essential.

The first thing to be stated in this connection is that in recent years, a particular need exists for enhancing the performance of diamond or high-pressure phase boron nitride sinters of high density and to this end, it is required that diamond or high-pressure phase boron nitride particles such as those not larger than 10 μm be used as the starting material and sintered to produce a diamond or high-pressure phase boron nitride sinter of high density.

Conventionally, diamond or high-pressure phase boron nitride sinters have been produced mainly by a method in which bonding materials and/or sintering aids are added in a powder form. In this case, even if the bonding materials and/or sintering aids are of a fine particulate form, it is extremely difficult to insure ideal uniform addition or uniform dispersion in such a way that they cover all of the individual diamond or high-pressure phase boron nitride particles present. Even if such uniform dispersion is realized, the extent of "uniformity" that can be attained is limited since the bonding materials and/or sintering aids are added on a particle basis. It should particularly be noted that if the bonding materials or sintering aids are added in small quantities, the resulting sinter will inevitably contain those areas where the bonding materials or sintering aids are absent.

In many actual cases, those powder particles or the particles of the bonding material and/or sintering aid agglomerate to either form lumps in the sinter or occur unevenly in the sinter. Hence, particularly in those areas where diamond or high-pressure phase boron nitride particles agglomerate, the structure is essentially the same as what is produced without addition of bonding materials or sintering aids and unsintered portions will locally occur. In those areas where the bonding materials and/or sintering aids agglomerate, the microscopic structure contains portions where diamond or high-pressure phase boron nitride particles are absent from the sinter. Either phenomenon produces imperfections that cause marked deterioration in the performance of the produced diamond or high-pressure phase boron nitride sinter.

Therefore, in order to produce diamond or high-pressure phase boron nitride sinters of high performance that are free from the above-mentioned imperfections, it is necessary that the bonding material and/or sintering aid be positively distributed on individual diamond or high-pressure phase boron nitride particles and, to this end, it is strongly desired to produce diamond or high-pressure phase boron nitride sinters of high performance using coated diamond or high-pressure phase boron nitride particles which are prepared by coating uniformly a bonding material forming substance

and/or a sintering aid forming substance on the individual particles of diamond or high-pressure phase boron nitride, respectively.

Secondly, as already mentioned, both diamond and high-pressure phase boron nitride are substances that are extremely difficult to sinter and which are stable only under ultrahigh pressures and, hence, in order to prevent the diamond or high-pressure phase boron nitride from experiencing a phase transition to the lower-pressure phase (graphite or h-BN) and to produce a dense sinter of the diamond or high-pressure phase boron nitride, manufacturers have adopted the practice of using bonding materials and/or sintering aids under ultrahigh pressures in excess of 2000 MPa and at elevated temperatures. According to the report of T. Noma et al. (J. Mater. Sci., 19 (1984) 2319-2322), diamond is sintered at 6000 MPa (60 kb) and at 1300°C or above. Cubic boron nitride may be sintered at 4000 MPa (40 kb) and at 1200°C or above, as taught in Unexamined Published Japanese Patent Application (Kokai) Sho 60-35456. These sintering conditions refer to extreme states and they are both rigorous indeed in that they cannot be created without using a ultrahigh pressure apparatus such as of the girdle or belt type.

This constraint of using a ultrahigh pressure apparatus such as of the girdle or belt type for creating ultrahigh pressures in excess of 2000 MPa has made it difficult to achieve mass production of diamond or high-pressure phase boron nitride sinters and not only has the production cost been high but it has also been impossible to manufacture large shapes.

However, speaking of diamonds, Hall conducted an experiment under ultrahigh pressures and reported that when a diamond was thermodynamically metastable if not stable, it took such a long time for a phase transition to occur that it remained stable for practical purposes; he then drew line ② as shown in Fig. 33a to indicate the upper limit beyond which the diamond would no longer exist in a practically stable manner (H. T. Hall, Science, 169 (1970) 868-869). Hence, according to his report, even under low-pressure and high-temperature conditions that are not stable with respect to thermodynamic equilibrium line ① in Fig. 33a, a diamond will exist practically stable if it is at temperatures that do not exceed line ② in Fig. 33a, say, up to about 1400 K (ca. 1100°C), given a pressure of up to about 35 kb.

Speaking of high-pressure phase boron nitrides, Wakatsuki et al. conducted an experiment on a cubic boron nitride under ultrahigh pressures and reported that when the cubic boron nitride was thermodynamically metastable if not stable, it took such a long time for a phase transition to occur that it remained stable for practical purposes; they then drew line ② as shown in Fig. 33b to indicate the upper limit beyond which the cubic boron nitride would no longer exist in a practically stable manner (Wakatsuki, Ichise, Aoki and Maeda, Abstracts of the Lectures Read at the 14th Symposium on High-Pressure Technology (1973) p. 78). Hence, according to their report, even under low-pressure and high-temperature conditions that are not stable with respect to thermodynamic equilibrium line ① in Fig. 33b, a cubic boron nitride will exist practically stable if it is at temperatures that do not exceed line ② in Fig. 33b, say, not higher than 1200°C.

Based on these facts, one may conclude that if diamond sinters containing diamonds or high-pressure phase boron nitride sinters containing high-pressure phase boron nitrides at least one of which is a cubic boron nitride can be produced under the stable conditions mentioned above, he can effectively use a ultrahigh pressure apparatus such as a piston-cylinder (PC) type ultrahigh pressure apparatus that is capable of creating comparatively moderate ultrahigh pressures less than 2000 MPa, or a ultrahigh pressure HIP apparatus as a known technique capable of pressurization up to 1000 MPa, or hot isostatic press (HIP) apparatus excluding the ultrahigh pressure HIP apparatus, or a hot press (HP) apparatus.

Thusly, unlike in the case of ultrahigh pressure apparatus of such types as the aforementioned girdle and belt types that create ultrahigh pressures in excess of 2000 MPa, not only does it become easy to achieve mass production but it also becomes possible to produce sinters of large shapes.

In recent years, it is strongly desired that diamond or high-pressure phase boron nitride sinters of high density and performance that contain comparatively large amounts of diamond or high-pressure phase boron nitride particles such as those not larger than 10 μm should be manufactured in high volumes or in large shapes using a ultrahigh pressure apparatus such as the aforementioned piston-cylinder (PC) type ultrahigh pressure apparatus which is capable of creating comparatively moderate ultrahigh pressures less than 2000 MPa, or the ultrahigh pressure HIP apparatus capable of pressurization up to 1000 MPa, the hot isostatic press (HIP) apparatus excluding the ultrahigh pressure HIP apparatus, or the hot press (HP) apparatus.

In fact, however, it is not easy to assure that diamond or high-pressure phase boron nitride sinters containing fairly large amounts of diamond or high-pressure phase boron nitride, respectively, are effectively densified under those limited pressures.

Stated more specifically, this can be realized only when the bonding material which is added in the form of a feed powder for that material deforms or migrates during sintering to fill the gaps between diamond or high-pressure phase boron nitride particles so that the applied pressure will work effectively for the displacement and loss of pores or the voids which are surrounded by the bonding material and the diamond or high-pressure phase boron nitride particles. To this end, the bonding material and/or the feed powder for that material which reacts with diamond or high-pressure phase boron nitride to generate the bonding material must be present in such a way that they contact and surround the diamond or high-pressure phase boron nitride particles.

It should particularly be noted that under the sintering pressure and temperature conditions where the pressure is less than 2000 MPa and where diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable, there is little chance for the particles of diamond or high-pressure phase boron nitride to bind directly and, hence,

those portions of the diamond or high-pressure phase boron nitride particles in the resulting sinter where the feed powder for the bonding material is absent will remain unsintered. As a result, the performance of the sinters produced will deteriorate considerably. If the bonding material is added only in the form of a feed powder for that material, it is extremely difficult to insure ideal uniform addition or uniform dispersion in such a way that the particles of the feed powder cover all of the individual diamond or high-pressure phase boron nitride particles present even if the particles of the feed powder are fine. Even if such uniform dispersion is realized, the extent of "uniformity" that can be attained is limited since the feed powder for the bonding material is added on a particle basis. Thus, a serious problem is presented in the manufacture of diamond or high-pressure phase boron nitride sinters that contain large amounts of diamond or high-pressure phase boron nitride, respectively. Therefore, even in the case of mixing diamond or high-pressure phase boron nitride particles with the feed powder for the bonding material, one may compensate for the insufficiency by using coated diamond or high-pressure phase boron nitride particles which are prepared by coating the surfaces of bare diamond or high-pressure phase boron nitride particles with a bonding material forming substance that is of the same and/or different type from the feed powder for the bonding material, as a consequence, the distribution of the bonding material can be made sufficiently uniform. Hence, the coating method for preparing such coated diamond or high-pressure phase boron nitride particles bears technologically great importance.

Stated more specifically, irrespective of whether the bonding material is added in the form of a feed powder for bonding material forming substance or not, the bonding material and/or a substance that reacts with diamond or high-pressure phase boron nitride to form the bonding material is allowed to be present covering the surfaces of diamond or high-pressure phase boron nitride particles. Only by following this approach, one can assure that diamond or high-pressure phase boron nitride sinters of high density and performance that contain comparatively large amounts of diamond or high-pressure phase boron nitride particles are manufactured in high volumes or large shapes using a ultrahigh pressure apparatus such as the piston-cylinder (PC) type ultrahigh pressure apparatus which is capable of creating comparatively moderate ultrahigh pressures less than 2000 MPa, or the ultrahigh pressure HIP apparatus which is capable of pressurization up to 1000 MPa, or the hot isostatic press (HIP) apparatus excluding the ultrahigh pressure HIP apparatus, or the hot press (HP) apparatus.

While the foregoing description is directed to diamond or high-pressure phase boron nitride sinters that use the respective particles with a particle diameter not greater than 10 μm, it should be noted that if the sinters are to be used in definite applications, it is very effective to intentionally use diamond or high-pressure phase boron nitride particles of comparatively large particle diameters, say, in excess of 10 μm.

Consider, for example, a wear-resistant sinter that takes advantage of the ultrahigh hardness of diamond or high-pressure phase boron nitride. This sinter can be produced by sintering a dispersion of a comparatively large quantity of diamond or high-pressure phase boron nitride particles in excess of 10 μm in diameter and, in this case, using diamond or high-pressure phase boron nitride particles larger than 10 μm in diameter as a starting material is extremely important.

The diamond or high-pressure phase boron nitride sinter which has dispersed therein diamond or high-pressure phase boron nitride particles exceeding 10 μm in diameter is characterized in that the effect of dispersion of the dispersed particles is marked because these dispersed particles are sintered as they are closely bound to the surrounding microstructure without imperfections or pores. However, as already mentioned, both diamond and high-pressure phase boron nitride are extremely difficult to sinter and, therefore, it is essential to use a sintering aid or a bonding material that accelerate the sintering of the diamond or high-pressure phase boron nitride particles larger than 10 μm in diameter together with the surrounding microstructure.

Conventionally, such sintering aids and bonding materials have been added solely by the powder mixing method. However, the incorporation of impurities during mixing is unavoidable in this method; what is more, there is theoretically a limit on the extent to which a uniform structure can be realized. Even if the particles of a sintering aid or a bonding material are extremely fine, it is very difficult to insure ideal uniform mixing or uniform dispersion in such a way that the particles of a sintering aid or bonding material powder cover all of the diamond or high-pressure phase boron nitride particles present. Even if such uniform dispersion is realized, the extent of "uniformity" that can be attained is limited since the particles of the sintering aid or bonding material powder are mixed on a particle basis. Particularly in the case where these particles are used in relatively small amounts, an uneven distribution will occur inevitably.

In many actual cases, the dispersed diamond or high-pressure phase boron nitride particles lump together or the particles of the sintering aid or bonding material powder agglomerate, as a result, the diamond or high-pressure phase boron nitride particles will form lumps in the sinter or they occur unevenly in the diamond or high-pressure phase boron nitride sinter, eventually leading to marked deterioration in the performance of the sinters.

Therefore, it is necessary that the sintering aid or the bonding material be distributed positively to all individual diamond or high-pressure phase boron nitride particles exceeding 10 μm in diameter. Further, in order to assure that the diamond or high-pressure phase boron nitride particles are sintered as they are closely bound to the surrounding microstructure, it is required to provide a highly controlled uniform coating on the surfaces of the diamond or high-pressure phase boron nitride particles; the coating is uniform in that it leaves no surfaces of the individual diamond or high-pressure phase boron nitride particles left uncovered and it is highly controlled in that this uniform coating is applied to all individual diamond or high-pressure phase boron nitride particles. What is more, the greater the size of these

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particles, the more uniform this highly controlled coating should be in order to further reduce the uncovered portions of the particles.

Thus, the production of coated diamond or high-pressure phase boron nitride particles of desired diameters in which diamond or high-pressure phase boron nitride particles are covered with uniform coatings that are highly controlled in accordance with the particle diameter, as well as the manufacture of high-performance sinters using those coated particles are strongly desired.

While coat forming substances could be applied by various techniques such as vapor-phase processes and wet plating methods, the vapor-phase approach in which inorganic materials, metallic materials and other coat forming substances are applied to provide coatings as films and various other forms theoretically have major features that are unattainable by other coating techniques, such as: (1) easy control of the atmosphere; (2) the selection of coat forming substances is basically unlimited and various kinds of substances including elemental metallic substances (e.g. active metals), alloys, nitrides, carbides, borides and oxides can be applied; (3) the desired substance can be applied in high purity; and (4) the coating weight of the coat forming substance can be controlled freely.

However, for the reasons to be set forth below, none of the various coating apparatus and methods heretofore proposed as known techniques have been capable of forming the above-described highly controlled uniform coatings.

Particularly in the case of diamond or high-pressure phase boron nitride particles not larger than 10 μm, the diamond or high-pressure phase boron nitride particles to be coated are so fine that they are cohesive enough to have a great tendency to agglomerate together, whereby almost all single particles form agglomerates. Since these agglomerates cannot be disintegrated unless they are subjected to a special action greater than their cohesive force, they cannot be simply coated as such to insure that the surfaces of the individual particles are covered with the coating of a bonding material and/or sintering aid, eventually yielding coated agglomerates in which the surfaces of the agglomerates are covered with the coating of the bonding material and/or sintering aid. This has caused a problem with the individual diamond or high-pressure phase boron nitride particles forming the agglomerates in that the surfaces of the particles located on the surfaces of the agglomerates have large coating weights but suffer from uneven coating whereas the particles located within the agglomerates are not covered at all.

With a view to solving these problems, attempts have already been made to coat the particles in a dispersed state in order to assure the coating of the individual particles in the powder of the core particles to be coated. However, for the reasons stated below, none of the various coating apparatus and methods heretofore proposed as known techniques have been capable of forming the intended uniform coating.

For instance, Unexamined Published Japanese Patent Application (kokai) Sho 58-31075 teaches an apparatus and method, according to which a vessel placed in PVD equipment is charged with the particles in a powder of core particles and vibrated by an electromagnetic means so that the core particles in the vessel are rolled as they are coated by a PVD process. Unexamined Published Japanese Patent Application (kokai) Sho 61-30683 teaches an apparatus, according to which a vessel placed in PVD equipment is charged with the particles in a powder of core particles and vibrated by a mechanical means so that the core particles in the vessel are rolled as they are coated by a PVD process. However, in the actual practice with those apparatus or methods in which the vessel is vibrated so that the particles in the powder of core particles are rolled as they are provided with coatings, the necessary action for disintegrating the agglomerates of diamond or high-pressure phase boron nitride particles with an average diameter not greater than 10 μm by applying a force exceeding their cohesive force cannot be produced and, hence, the agglomerates cannot be disintegrated; to the contrary, a granulating action develops to form agglomerates that are greater in number or size than before the powder of core particles is supplied into the vessel. On the other hand, diamond or high-pressure phase boron nitride particles having an average diameter in excess of 10 μm are simply subjected to a sliding action as they form many layers in superposition and it has been impossible to achieve the desired coating of single separate particles.

Unexamined Published Japanese Patent Application (kokai) Hei 3-150364 teaches an apparatus and method, according to which a rotating vessel having barriers and/or ridges and grooves in the inner surface is charged with core particles and rotated as the surfaces of the particles are coated by an evaporation method. The problem with this apparatus and method is that the necessary action for disintegrating the agglomerates of diamond or high-pressure phase boron nitride particles with an average diameter not greater than 10 μm by applying a force exceeding their cohesive force cannot be produced and, hence, the agglomerates cannot be disintegrated and, what is more, an increased number or size of agglomerates will simply form. On the other hand, diamond or high-pressure phase boron nitride particles having an average diameter in excess of 10 μm are simply subjected to a gentle stirring action as many of them contact one another forming many layers in superposition and it has been impossible to achieve the desired coating of single separate particles.

Unexamined Published Japanese Patent Application (kokai) Sho 58-141375 teaches an apparatus in which the particles of a powder in a reactive gas atmosphere are suspended by the flow of the reactive gas under gravity and in which the surfaces of the particles are coated with the precipitating substance that forms by the chemical reaction involving the reactive gas. Unexamined Published Japanese Patent Application (kokai) Hei 3-43577 teaches a method in which particles placed under vacuum are fluidized as they are subjected to coating by a thermochemical reaction treatment. Unexamined Published Japanese Patent Application (kokai) Sho 64-60437 teaches a method in which the agglom-

erates of core particles in powder are disintegrated by a sound wave that is a composite of low and high frequency waves, so that the agglomerates are fluidized to improve the coating efficiency. However, these techniques which utilize the fluidized bed of the particles in a powder of core particles which is formed by a gas flow or vibrations have had the problem that with diamond or high-pressure phase boron nitride particles having an average diameter of no more than 10 μm, it is practically impossible to fluidize the separate individual particles, thus failing to disintegrate the agglomerates of these particles. On the other hand, with diamond or high-pressure phase boron nitride particles exceeding 10 μm in average diameter, it is practically impossible to insure that all of these particles are similarly and independently fluidized and suspended as single separate entities and one has been incapable of eliminating uneven coating of the particles which is due to the hiding of one particle by another.

Unexamined Published Japanese Patent Application (kokai) Sho 64-159789 teaches an apparatus in which a powder material is dropped within a vacuum vessel, where the metal vapor is generated to form a metal coating on the particles. Unexamined Published Japanese Patent Application (kokai) Sho 60-47004 teaches a method in which a monomer gas and the particles of a powder are introduced into a high-frequency plasma region in a vacuum vessel, where a coating film of an organic substance is formed by plasma-assisted polymerization. If diamond or high-pressure phase boron nitride particles with an average diameter of no more than 10 μm are simply introduced as in the techniques described above, agglomerates cannot be disintegrated. On the other hand, diamond or high-pressure phase boron nitride particles exceeding 10 μm in average diameter will simply drop while forming agglomerates which are not single separate particles and various problems occur, such as uneven coating due to the hiding of one particle by another, the total failure of the particles within an agglomerate to be coated, and differences in the coating weights of individual particles.

Unexamined Published Japanese Patent Application (kokai) Sho 64-60437 teaches a method in which the agglomerates of core particles in powder are disintegrated by a sound wave consisting of low and high frequency waves so that they are fluidized to improve the coating efficiency. However, this method which imparts vibrations to the fluidized bed has had the problem that with diamond or high-pressure phase boron nitride particles having an average diameter of no more than 10 μm, it is practically impossible to fluidize the separate individual particles, thus failing to disintegrate the agglomerates of these particles. On the other hand, with diamond or high-pressure phase boron nitride particles exceeding 10 μm in average diameter, it is practically impossible to insure that all of these particles are similarly and independently fluidized and suspended as single separate entities and one has been incapable of eliminating uneven coating of the particles which is due to the hiding of one particle by another.

Unexamined Published Japanese Patent Application (kokai) Sho 62-250172 teaches an apparatus and method, according to which a powder that has been preliminarily treated by jet milling is allowed to stay within a chamber for heat treatment under vacuum, where it is subjected to a heat treatment and thence dropped under gravity through a powder feeder into a cylindrical sputtering chamber equipped with a vertical target, whereby the particles in powder are provided with a coating. Unexamined Published Japanese Patent Application (kokai) Hei 2-153883 teaches an apparatus and method, according to which a powder that has been preliminarily treated by jet milling is allowed to stay within a chamber for heat treatment under vacuum, where it is subjected to a heat treatment and thence introduced through a powder feeder into a rotary vessel accommodating a sputter source within a sputtering chamber in the form of a powder (not as single particles), with sputtering being effected as the vessel is rotated. These techniques involve a heating step which is performed before coating so that the jet-milled powder of core particles is allowed to stay for heat treatment and because of this staying of the powder in the heating step, the diamond or high pressure phase boron nitride particles of any diameter will form agglomerates again which are not single particles and, eventually, such agglomerates will not revert to single particles in the coating step.

Thus, none of the so far proposed techniques have successfully solved the problems associated with the apparatus or method for providing coatings on the core particles in powder which are diamond or high-pressure phase boron nitride particles. In actual cases, diamond or high-pressure phase boron nitride particles having an average diameter of not more than 10 μm form agglomerates which cannot be disintegrated and, hence, no methods or apparatus have been available for producing coated diamond or high-pressure phase boron nitride particles in which said diamond or high-pressure phase boron nitride particles, being dispersed as single particles, are covered on their surfaces with coat forming substances including a bonding material forming substance and/or a sintering aid forming substance.

Speaking of diamond or high-pressure phase boron nitride particles exceeding 10 μm in average diameter, these particles are in actual cases subjected to a coating treatment in the form of agglomerates in which they remain in mutual contact and, hence, those portions which are blocked by other particles remain uncoated. As already mentioned, highly controlled uniform coatings are needed and although even the small cohesive force discussed above has been so much influential as to cause a very serious problem, no methods have been available for producing the satisfactory coated diamond or high-pressure phase boron nitride particles, nor have been apparatus for implementing such methods.

In short, irrespective of the diameter of starting diamond or high-pressure phase boron nitride particles, it has been impossible to prepare coated diamond or high-pressure phase boron nitride particles by providing each of those starting particles with a controlled uniform coat by vapor-phase coating techniques using coat forming substances including bonding material forming substances and/or sintering aid forming substances.

Hence, it has been impossible to manufacture diamond or high-pressure phase boron nitride sinters of high performance that are uniform, dense and firmly sintered and which have a highly controlled microstructure using small (e.g., ≤ 10 μm) coated diamond or high-pressure phase boron nitride particles. In addition, diamond or high-pressure phase boron nitride sinters of high density and performance that contain comparatively large amounts of diamond or high-pressure phase boron nitride based on those coated particles could not be manufactured in high volumes or large shapes. Further, diamond or high-pressure phase boron nitride sinters of high density and performance that contain comparatively large amounts of diamond or high-pressure phase boron nitride as derived from a mixture of those coated particles and a separately added bonding material could not be manufactured in high volumes or large shapes.

It has also been impossible to manufacture wear-resistant sinters that have dispersed therein comparatively large amounts of coated diamond or high-pressure phase boron nitride particles exceeding, for example, 10 μm in diameter.

BRIEF SUMMARY OF THE INVENTION

Under the circumstances described on the foregoing pages, it is strongly desired to develop and commercialize the following sinters and processes for producing them: a diamond or a high-pressure phase boron nitride sinter of high performance derived from coated diamond or high-pressure phase boron nitride particles in which the particles in a powder of core particles that are diamond or high-pressure phase boron nitride particles to be coated in practice having an average diameter of no more than 10 μm are coated on a single particle basis with a coat forming substance selected from the group consisting of a bonding material forming substance and a sintering aid forming substance, as well as processes for producing such diamond and high-pressure phase boron nitride sinters; a diamond or a high-pressure phase boron nitride sinter of high performance that contains a comparatively large amount of diamond or high-pressure phase boron nitride particles as produced by sintering the coated diamond or high-pressure phase boron nitride particles under pressure and temperature conditions where diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable, as well as processes for producing such diamond and high-pressure phase boron nitride sinters; a diamond or a high-pressure phase boron nitride sinter of high performance that is produced by sintering a mixture of the coated diamond or high-pressure phase boron nitride particles and a separately added bonding material under pressure and temperature conditions where diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable, as well as processes for producing such diamond and high-pressure phase boron nitride sinters; the production of coated diamond or high-pressure phase boron nitride particles in which bare diamond or high-pressure phase boron nitride particles in a powder of core particles exceeding 10 μm in average diameter are provided with a highly controlled uniform coating, which is uniform in that it leaves no surfaces of the individual diamond or high-pressure phase boron nitride particles left uncovered and which is highly controlled in that this uniform coating is applied to all individual diamond or high-pressure phase boron nitride particles, said highly controlled uniform coating being further characterized in that the greater the size of those particles, the more uniform it should be in order to further reduce the uncovered portions of the particles, as well as a diamond or a high-pressure phase boron nitride sinter that uses the thus coated diamond or high-pressure phase boron nitride particles, and processes for producing such diamond and high-pressure phase boron nitride sinters.

Thus, an object of the present invention is to provide a diamond or a high-pressure phase boron nitride sinter of high performance that are uniform, dense and firmly sintered and which have a highly controlled microstructure using coated diamond or high-pressure phase boron nitride particles in which diamond or high-pressure phase boron nitride particles that are either the particles in a powder of fine core particles or the particles in a powder of core particles the greater part of which is comprised of fine particles are coated on a single particle basis with a bonding material forming substance and/or a sintering aid forming substance.

Another object of the invention is to provide processes for producing said diamond or high-pressure phase boron nitride sinters of high performance.

A further object of the invention is to provide a diamond or a high-pressure phase boron nitride sinter that contain comparatively a large amount of diamond or high-pressure phase boron nitride particles comprised of high-performance fine particles, which are uniform, dense and firmly sintered and which have a highly controlled microstructure, which sinters are produced by sintering at pressures less than 20000 MPa and at temperatures not exceeding 1850°C those coated diamond or high-pressure phase boron nitride particles in which diamond or high-pressure phase boron nitride particles that are either the particles in a powder of fine core particles or the particles in a powder of core particles the greater part of which is comprised of fine particles are coated on a single particle basis with a coat forming substance selected from between a bonding material forming substance and a sintering aid forming substance, or a mixture containing said coated diamond or high-pressure phase boron nitride particles.

A still further object of the invention is to provide processes for producing said diamond or high-pressure phase boron nitride sinters.

Yet another object of the invention is to provide a diamond or a high-pressure phase boron nitride sinter that contains comparatively a large amount of diamond or high-pressure phase boron nitride particles comprised of high-performance fine particles, which are uniform, dense and firmly sintered and which have a highly controlled microstructure, which

sinters are produced by sintering, at pressures less than 2000 MPa and at temperatures not exceeding 1850°C under such pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable, a mixture of a bonding material and those coated diamond or high-pressure phase boron nitride particles in which diamond or high-pressure phase boron nitride particles that are either the particles in a powder of fine core particles or the particles in a powder of core particles the greater part of which is comprised of fine particles are coated on a single particle basis with coat forming substances comprising not only a bonding material forming substance and/or a sintering aid forming substance but also a surface modifier forming substance capable of controlling grain boundaries.

Still another object of the invention is to provide processes for producing such diamond and high-pressure phase boron nitride sinters.

A further object of the invention is to provide coated quasi-fine diamond or high-pressure phase boron nitride particles in which the particles in a powder of quasi-fine core particles that are quasi-fine diamond or high-pressure phase boron nitride particles or the particles in a powder of core particles the greater part of which is comprised of such quasi-fine particles are provided with a highly controlled uniform coating of a coat forming substance selected from between a bonding material forming substance and a sintering aid forming substance, which coating is uniform in that it leaves no surfaces of the individual diamond or high-pressure phase boron nitride particles left uncovered and which is highly controlled in that this uniform coating is applied to all individual diamond or high-pressure phase boron nitride particles, said highly controlled uniform coating being further characterized in that the greater the size of those particles, the more uniform it should be in order to further reduce the uncovered portions of the particles.

A still further object of the invention is to provide a diamond or a high-pressure phase boron nitride sinter using said coated quasi-fine diamond or high-pressure phase boron nitride particles.

A yet further object of the invention is to provide processes for producing said diamond and high-pressure phase boron nitride sinters.

In order to attain these objects, the present inventors conducted intensive studies and found the following: In order to insure that the particles in a powder of core particles which comprises diamond or high-pressure phase boron nitride particles are coated, on a single particle basis, with coat forming substances including a bonding material and/or a sintering aid, a mixture of a gas with a powder of highly dispersed core particles in which the particles in said powder of core particles are present in a gaseous atmosphere mainly in a single-particle state must be introduced into the coating start region of a coating space while the particles are in a highly dispersed state such that the dispersity β is at least 70%, 80%, 90%, 95%, 97% or 99% depending upon the diameter of the introduced particles and then a coating operation must be started on those particles.

Stated more specifically, the present invention has been accomplished on the basis of the finding of the following two facts: (i) In a mixture of a gas with a powder of highly dispersed core particles in which the particles in said powder of core particles are present in a gaseous atmosphere mainly in a single-particle state, those dispersed particles have a tendency to reagglomerate with the passage of time, chiefly due to turbulent agglomeration, even if they are not allowed to stay within a certain area and once they have formed reagglomerates, it is difficult to disintegrate the latter to a highly dispersed state, namely, to redisperse the agglomerated particles to separate single particles unless they are dispersed by a dispersing means having especially high dispersing performance (the situation is the same as with the agglomerates that formed before the treatment conducted to prepare the highly dispersed core particles) and, to this end, those particles have to be introduced into the coating start region of a coating space while the particles are in a highly dispersed state such that the dispersity β is at least 70%, 80%, 90%, 95%, 97% or 99% depending on the diameter of the introduced particles; and to this end, (ii) it is necessary to employ one or more dispersing means that have especially high dispersing performance such that the agglomerates composed of the powder of those core particles can be disintegrated and dispersed in a gaseous atmosphere to provide a very high dispersity in accordance with the specific diameter of the particles under treatment.

The present inventors also found that the coated diamond or high-pressure phase boron nitride particles described above behaved during sintering as if they were the particles of the aforementioned coat forming substances. Consequently, they found that such coated diamond or high-pressure phase boron nitride particles could be sintered in the presence of an added fibrous substance comprising at least one metal or compound that was capable of reinforcing diamond or high-pressure phase boron nitride sinters, which had a width of no more than 500 μm and which was of such a shape that the length to width ratio was at least two. The present invention has been accomplished on the basis of these findings.

According to the present invention, there is provided a process for producing a diamond or high-pressure phase boron nitride sinter comprising the step of preparing coated diamond or high-pressure phase boron nitride particles and sintering said coated diamond or high-pressure phase boron nitride particles or mixtures containing such particles or mixtures of coated diamond or high-pressure phase boron nitride particles with bonding material.

sintering said coated diamond or high-pressure phase boron nitride particles or said mixtures containing such particles at pressures no less than 2000 MPa and at elevated temperatures; or

sintering said coated diamond or high-pressure phase boron nitride particles or said mixtures containing such particles at pressures of less than 2000 MPa and at temperatures not exceeding 1850°C under such sintering pressure

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and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable; or

sintering said mixtures of coated diamond or high-pressure phase boron nitride particles with a bonding material in a volume ratio of (1 - 90):(99 - 10), said bonding material being sinterable to a density of at least 85% at pressures less than 2000 MPa and at temperatures not exceeding 1800°C under such conditions that diamond and/or high-pressure phase boron nitride particles are thermodynamically metastable, at pressures less than 2000 MPa and at temperatures not exceeding 1800°C under such sintering pressure and temperature conditions that diamond and/or high-pressure phase boron nitride is thermodynamically metastable if not stable.

wherein said coated diamond or high-pressure phase boron nitride particles are prepared by a method comprising the steps of charging a powder of diamond or high-pressure phase boron nitride core particles into a coating space and then permitting a precursor of a coat forming substance which is generated via the vapor phase and/or a precursor of a coat forming substance in a vapor-phase state to contact and/or impinge against the particles in said powder of core particles so that their surfaces are coated with the coat forming substance and

said coated diamond or high-pressure phase boron nitride particles are prepared by coating means comprising:

(A) a dispersing step in which the particles in the powder of core particles are dispersed by a group of means for high dispersion treatment of particles in a gaseous atmosphere to form a mixture of a gas and the particles in a powder of highly dispersed particles, the final treating means in said group of means for high dispersion treatment of particles being selected from between:

(a) dispersing means for dispersing the particles in the powder of core particles in a gaseous atmosphere; and
(b) means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles which comprises:

(b-1) means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles that separates a portion of the powder that is composed of less highly dispersed particles from the mixture of a gas and the particles in the powder of core particles in which the particles in the powder of core particles are dispersed in a gaseous atmosphere, thereby selecting a mixture of a gas and the particles in a powder of highly dispersed core particles in which the particles in the powder of core particles are present in the gaseous atmosphere mainly in a single-particle state; and
(b-2) feedback means by which the portion of the powder that is composed of less highly dispersed particles and which has been separated by said means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles is transported to the final dispersing means among the dispersing means in the group of means for high dispersion treatment of particles and/or treating means upstream of the final dispersing means; and

(B) a coating step in which the particles in the powder of core particles that have been dispersed in the dispersing step (A) start to be coated by being allowed to contact and/or impinge against the precursor of the coat forming substance in the coating start region of the coating space as they are dispersed to satisfy the following conditions:

the dispersity β should be at least 70% if those particles have an average diameter of no more than 10 μm in the frequency distribution by volume;

the dispersity β should be at least 87% if those particles have an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume;

the dispersity β should be at least 90% if those particles have an average diameter in excess of 20 μm but no more than 30 μm in the frequency distribution by volume;

the dispersity β should be at least 95% if those particles have an average diameter in excess of 50 μm but no more than 300 μm in the frequency distribution by volume;

the dispersity β should be at least 97% if those particles have an average diameter in excess of 300 μm but no more than 800 μm in the frequency distribution by volume; and

the dispersity β should be at least 99% if those particles have an average diameter in excess of 800 μm in the frequency distribution by volume, and wherein said sintering step is performed by

sintering said coated diamond or high-pressure phase boron nitride particles or said mixtures containing such particles at pressures no less than 2000 MPa and at elevated temperatures; or

sintering said coated diamond or high-pressure phase boron nitride particles or said mixtures containing such particles at pressures of less than 2000 MPa and at temperatures not exceeding 1800°C under such sintering pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable; or

sintering said mixtures of coated diamond or high-pressure phase boron nitride particles with a bonding material in a volume ratio of (1 - 90):(99 - 10), said bonding material being sinterable to a density of at least 85% at

pressures less than 2000 MPa and at temperatures not exceeding 1800°C under such conditions that diamond and/or high-pressure phase boron nitride particles are thermodynamically metastable, at pressures less than 2000 MPa and at temperatures not exceeding 1800°C under such sintering pressure and temperature conditions that diamond and/or high-pressure phase boron nitride is thermodynamically metastable if not stable.

Preferably, said coated diamond or high-pressure phase boron nitride particles are prepared through the following additional step(s):

a step of deagglomeration or otherwise size reduction in which lumps of the coated diamond and/or high-pressure phase boron nitride particles that form as a result of association of several particles that contact one another via the coat forming substance on the coated particles are deagglomerated and/or otherwise reduced in size; and/or

a step of selective separation in which the associating lumps of the coated diamond or high-pressure phase boron nitride particles are selectively separated from the coated diamond or high-pressure phase boron nitride particles on a primary particle basis.

Preferably, the particles in the powder of diamond and/or high-pressure phase boron nitride core particles to be coated with the coat forming substance are coated by a dip method using a molten salt bath with one or more layers of the coat forming substance that derives from the dip method.

Preferably, the dispersing step is performed by:

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter of no more than 10 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 70%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 80%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 20 μm but no more than 50 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 90%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 50 μm but no more than 300 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 95%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 300 μm but no more than 600 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 97%; and

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 600 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 99%; and

said coated diamond or high-pressure phase boron nitride particles being prepared by:

a method in which the mixture of a gas and the particles in the powder of highly dispersed core particles as formed by one of the means in said group of means for high dispersion treatment of particles is either discharged directly to the cooling step or transported thereto via at least one member indispensable to transport that is selected from the group consisting of a hollow member, an intermediate member composed of a member that forms a hollow portion, and a pipe and which is provided between the dispersing and cooling steps, as the mixture emerges from a discharge section that discharges said mixture of a gas and the particles; and/or

a method in which the mixture of a gas and the particles in the powder of highly dispersed core particles as formed by one of the means in said group of means for high dispersion treatment of particles is transported to the cooling step via at least one means selected from the group consisting of means for maintaining the dispersion in a gaseous atmosphere of the highly dispersed core particles in the mixture of a gas with the core particles which have been dispersed in the gaseous atmosphere to attain one of the dispersities set forth above, means for enhancing the dispersion in a

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gaseous atmosphere of the highly dispersed core particles in the mixture of a gas with the core particles which have been dispersed in the gaseous atmosphere to attain one of the dispersities set forth above, and means for separating a mixture of a gas and the particles in a powder of less highly dispersed core particles from said gas-particle mixture so as to select a mixture of a gas and the particles in a powder of highly dispersed core particles in which the core particles are present in the gaseous atmosphere mainly in a single-particle state.

Preferably, the dispersing step is performed by:

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter of no more than 10 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 70%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 80%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 20 μm but no more than 50 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 90%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 50 μm but no more than 300 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 95%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 300 μm but no more than 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 97%, and

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 99%, and

said coated diamond or high-pressure phase boron nitride particles being prepared by performing at least one part of the dispersing step in such a way that it shares one or more parts of the space with at least one part of the coating step.

Preferably, said coated diamond or high-pressure phase boron nitride particles are prepared with the coating start region of the coating space being located in either one of the following space regions that includes planes through which all particles in the powder of highly dispersed core particles as mixed with a gas will pass:

a space region in which a powder of core particles that have an average diameter of no more than 10 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 70%;

a space region in which a powder of core particles that have an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 80%;

a space region in which a powder of core particles that have an average diameter in excess of 20 μm but no more than 50 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 90%;

a space region in which a powder of core particles that have an average diameter in excess of 50 μm but no more than 300 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the

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group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 95%;

a space region in which a powder of core particles that have an average diameter in excess of 300 μm but no more than 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 97%; and

a space region in which a powder of core particles that have an average diameter in excess of 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 99%, or wherein

said coated diamond or high-pressure phase boron nitride particles are prepared with the coating start region of the coating space being located in either one of the following space regions that includes planes through which all particles to be recovered into the recovery section of the recovery means will pass:

a space region in which a powder of core particles that have an average diameter of no more than 10 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 70%;

a space region in which a powder of core particles that have an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 80%;

a space region in which a powder of core particles that have an average diameter in excess of 20 μm but no more than 50 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 90%;

a space region in which a powder of core particles that have an average diameter in excess of 50 μm but no more than 300 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 95%;

a space region in which a powder of core particles that have an average diameter in excess of 300 μm but no more than 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 97%; and

a space region in which a powder of core particles that have an average diameter in excess of 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 99%.

Preferably, the particles in the powder of core particles to be used have a size distribution of ($D_{90}/5$, $5D_{90}$, ≥ 90%) in terms of frequency distribution by volume, where D_{90} represents the average particle diameter.

According to another aspect of the present invention, there is provided a diamond or high-pressure phase boron nitride sinter that are produced by the processes for producing a diamond or high-pressure phase boron nitride sinter as recited above.

Thus, in accordance with the present invention, diamond or high-pressure phase boron nitride sinters are produced by one of the following methods: the particles in a powder of core particles that are diamond or high-pressure phase boron nitride particles and the surfaces of which are coated with a coat forming substance or mixtures containing such particles are sintered at a pressure of 2000 MPa or higher and at an elevated temperature; or those particles or mixtures containing them are sintered at a pressure less than 2000 MPa and at a temperature not exceeding 1550°C under such sintering pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable; or a mixture of the coated diamond or high-pressure phase boron nitride particles and a bonding material in a volume ratio of (1 - 90):(99 - 10), which bonding material is sinterable to a density of at least 85% at a

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pressure of less than 2000 MPa and at a temperature not exceeding 1800°C under such conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable, is sintered at a pressure of less than 3000 MPa and at a temperature not exceeding 1850°C under such sintering pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable. In the practice of this invention, the diamond or high-pressure phase boron nitride particles the surfaces of which are coated with the coat forming substance are prepared by the following method: a precursor for the coat forming substance that has just formed via the vapor phase by a vapor-phase process and/or a precursor for the coat forming substance in a vapor-phase state and a mixture of a gas with a powder of highly dispersed core particles that have been dispersed in a gaseous atmosphere by the first treating means in a group of means for high dispersion treatment of particles are allowed to combine with each other in the cooling start region of a cooling space while the particles in the mixture of a gas and the powder of highly dispersed core particles are in a dispersed state with their dispersity being adjusted to one of the values set forth in preceding paragraphs depending upon their diameter, whereupon the precursor and the mixture are allowed to contact and/or impinge against each other so that the surfaces of the diamond or high-pressure phase boron nitride particles are coated with the coat forming substance. By so doing, one can produce a heretofore unattainable diamond or high-pressure phase boron nitride sinter of high performance that has no surfaces of diamond or high-pressure phase boron nitride particles left unsintered, that is uniform, dense and firmly sintered and which has a highly controlled microstructure. The precursor for the coat forming substance which is to be used in preparing the coated core particles is in a vapor-phase state as comprised of atoms, molecules, ions, clusters, atomic clusters, molecular clusters, cluster ions, etc. or it has just formed via the vapor phase; having started to contact and/or impinge against the diamond or high-pressure phase boron nitride particles in the already-discussed highly dispersed state, the coat forming substance binds firmly to the surfaces of the individual core particles in the state of primary particles, thereby yielding coated diamond or high-pressure phase boron nitride particles in which those core particles in powder form are covered with the coat forming substance on a single particle basis.

As will be understood from the above description, when the coated diamond or high-pressure phase boron nitride particles are sintered at a pressure of 3000 MPa or above and at an elevated temperature under such sintering conditions that diamond or high-pressure phase boron nitride is thermodynamically stable, the coats on the diamond or high-pressure phase boron nitride particles are bursted by the pushing force from inside and any two contiguous diamond or high-pressure phase boron nitride particles will bind directly to each other, thereby yielding an extremely uniform and dense sinter.

The invention also contemplates the case where the coated diamond or high-pressure phase boron nitride particles, either taken alone or in combination with a bonding material, are sintered at a pressure less than 3000 MPa and at a temperature not exceeding 1850°C under such sintering pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable. In this case, the diamond or high-pressure phase boron nitride particles may contact each other but will not bind directly to each other; nevertheless, except in areas where the coated diamond or high-pressure phase boron nitride particles are in direct contact with each other, the coating substance which is to form a bonding material or a sintering aid is sure to surround those diamond or high-pressure phase boron nitride particles, and the resulting sinter has no part left unsintered, is uniform, dense and firmly sintered, and has an extremely highly controlled microstructure.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1a is a diagram showing the dispersity β of particles in a powder;
Fig. 1b is a diagram showing the frequency by volume vs diameter relationship of a powder 90% of the volume of which is occupied by particles with sizes in the range from D_1 - D_2;
Figs. 2a, 2b and 2c are block diagrams showing three basic arrangements of means for high dispersion treatment of particles;
Figs. 3a - 3g are block diagrams showing in greater detail the arrangements of means for high dispersion treatment of particles;
Figs. 4a - 4e are diagrams showing how the coating operation is started on core particles in powder;
Figs. 5a - 5g are block diagrams showing the compositions of various apparatus for producing coated diamond or high-pressure phase boron nitride particles;
Fig. 6 is a diagram showing the apparatus used in Example 1;
Fig. 7 is a partial enlarged view of the apparatus used in Example 1;
Fig. 8 is a scanning electron micrograph showing one of the coated diamond particles produced in Example 1;
Fig. 9 is an electron micrograph showing a polished surface of the sinter produced in Example 1;
Fig. 10 is an electron micrograph showing a polished surface of a commercial sintered diamond tool;
Fig. 11 is a diagram showing the apparatus used in Example 2;
Fig. 12 is a partial enlarged view of the apparatus used in Example 2;
Fig. 13 is a diagram showing the apparatus used in Example 3;

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Fig. 14 is a partial enlarged view of the apparatus used in Example 3;
Fig. 15 is a scanning electron micrograph showing one of the coated cubic boron nitride particles produced in Example 5-1;
Fig. 16 is a graph showing Vickers microhardness of the cubic boron nitride sinters;
Fig. 17 is an electron micrograph showing a polished surface of the sinter produced in Example 5-1;
Fig. 18 is an electron micrograph showing a polished surface of a commercial sintered cubic boron nitride tool;
Fig. 19 is a scanning electron micrograph showing one of the coated diamond particles produced in Example 6-1;
Fig. 20 is an electron micrograph showing a polished surface of the sinter produced in Example 6-1;
Fig. 21 is an electron micrograph showing a polished surface of a sinter comprising uncoated diamond particles;
Fig. 22 is a scanning electron micrograph showing one of the coated cubic boron nitride particles produced in Example 7-1;
Fig. 23 is an electron micrograph showing a polished surface of the sinter produced in Example 7-1;
Fig. 24 is an electron micrograph showing a polished surface of a sinter comprising uncoated cubic boron nitride particles;
Fig. 25 is a scanning electron micrograph showing one of the coated diamond particles produced in Example 8-1;
Fig. 26 is an electron micrograph showing a polished surface of the sinter produced in Example 8-1;
Fig. 27 is a scanning electron micrograph showing one of the coated cubic boron nitride particles produced in Example 9-1;
Fig. 28 is an electron micrograph showing a polished surface of the sinter produced in Example 9-1;
Fig. 29 is a scanning electron micrograph showing one of the coated diamond particles produced in Example 10-1;
Fig. 30 is an electron micrograph showing a polished surface of the sinter produced in Example 10-1;
Fig. 31 is a scanning electron micrograph showing one of the coated cubic boron nitride particles produced in Example 11-1;
Fig. 32 is an electron micrograph showing a polished surface of the sinter produced in Example 11-1;
Fig. 33a is a pressure-temperature diagram showing the region where diamond is stable; and
Fig. 33b is a pressure-temperature diagram showing the region where high-pressure phase boron nitride is stable.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is described below in detail. Before going into details of the invention, let us define the various terms, phrases and expressions that are used herein, and describe, if necessary, the specific implications of those terms, phrases and expressions, and then proceed to the description of the technical means for preparing diamond or high-pressure phase boron nitride particles coated with coat forming substances.

Coated Diamond or High-Pressure Boron Nitride Particles

The term "coated diamond particles" refers to the diamond particles to be described below which are provided with coats. The term "coated high-pressure phase boron nitride particles" refers to the high-pressure phase boron nitride particles to be described below which are provided with coats. To give one specific example, the terms refer to those coated particles in which diamond or high-pressure phase boron nitride core particles are provided with the coats of coat forming substances in the form of at least one type selected from among ultrafine particles, islands, continuous phase, uniform membranes, projections, etc.

Feed Powder Particles for Diamond or High-Pressure Boron Nitride Sinters

Natural and/or synthetic diamond powder particles are used as feed powder particles for diamond sinters in the present invention. On the other hand, cubic and/or wurtzite boron nitride particles are used as feed powder particles for high-pressure phase boron nitride sinters in the present invention.

To produce diamond or high-pressure phase boron nitride sinters of high performance which suit the purposes of the present invention, diamond or high-pressure phase boron nitride particles with diameters of no more than 10 μm are advantageously used as feed powders. However, in the case where wear resistance is of particular importance, particles exceeding 10 μm in average diameter are advantageous. Stated specifically, the particle diameter can be expressed in terms of frequency distribution by volume such that the average particle diameter D_{50} satisfies the relation ($[D_{50}/5, 5D_{50}]$, ≥ 90%). However, depending on use, diamond or high-pressure phase boron nitride particles of a comparatively narrow distribution which, when expressed in terms of frequency distribution by volume, satisfies the relation ($[D_{50}/3, 3D_{50}]$, ≥ 90%) can preferably be selected. More advantageously, one may select diamond or high-pressure phase boron nitride particles that have been controlled, by sieve classification or other techniques, in the diameter of diamond or high-pressure phase boron nitride particles to satisfy the relation ($[D_{50}/2, 2D_{50}]$, ≥ 90%) in terms of frequency distribution by volume.

If diamond or high-pressure phase boron nitride particles having such distributions are used as feed powder particles and, by sintering those diamond or high-pressure phase boron nitride particles or mixtures containing those coated diamond or high-pressure phase boron nitride particles, one can manufacture diamond or high-pressure phase boron nitride sinters of high performance that are uniform, dense and firmly sintered and which have an extremely highly controlled microstructure, those sinters being characterized in that the diamond or high-pressure phase boron nitride particles are sure to be surrounded by a bonding material and/or a sintering aid and/or a surface modifier except in areas where the coat forming substance is burned by the pushing force from inside and any two contiguous diamond or high-pressure phase boron nitride particles bind directly to each other and also characterized in that no part of the surfaces of the diamond or high-pressure phase boron nitride particles in the coated diamond or high-pressure phase boron nitride sinters is left uncoated.

It should be particularly noted when sintering is done under sintering pressure and temperature conditions where diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable, the diamond or high-pressure phase boron nitride is advantageously of as high purity as to inhibit a phase transition to the low-pressure phase (graphite or hBN). As for diamond, grades of ultrahigh purity can be selected from natural products; however, high-pressure phase boron nitride does not occur naturally. Hence, with synthetic products of diamond or high-pressure phase boron nitride, any substance that has a catalytic action and which is used during synthesis is advantageously removed thereafter as much as possible. Most advantageously, one can select, for example, a diamond or cubic boron nitride of ultrahigh purity that has been synthesized via the vapor phase by a suitable technique such as a physical vapor deposition (PVD) process or a chemical vapor deposition (CVD) process. When the synthesized product is in the form of a thin film, it is used after being reduced in size with care being taken to avoid contamination with impurities. If the synthesized product is in a particulate or powder form, it may be used as such. Another example of high-purity product that can be selected is a high-purity single-crystal one which has been grown over time. Alternatively, diamond or cubic boron nitride particles that have been positively freed of impurities may be selected.

Vapor-Phase Coating Method

The term "vapor-phase coating method" means a method in which coating is applied with the feed of a coat forming substance being passed at least once through a vapor-phase state that consists of at least one member selected from among a molecular stream, an ionic stream, a plasma, a gas, a vapor and an aerosol; alternatively, the term refers to a method in which coating is applied from the feed of a coat forming substance in either one of the vapor-phase states mentioned above.

Core Particles

The term "core particles" refers to those particles which are to be provided with coatings. Such particles may sometimes be referred to as "base particles", "feed particles" or "particles to be coated".

The core particles are diamond or high-pressure phase boron nitride particles and the high-pressure phase boron nitride particles consist specifically of cubic boron nitride particles and/or wurtzite boron nitride particles.

Powder of Core Particles

The term "powder of core particles" means a powder consisting of core particles. The phrase "the particles in a powder of core particles" refers to those particles which compose the powder of core particles. The particles in the powder of core particles to be coated which are used in the present invention range from fine particles the average diameter of which is not more than 10 μm in terms of frequency distribution by volume to those particles the average diameter of which exceeds 800 μm in terms of frequency distribution by volume.

Preferred particles are those which have such a particle size distribution that the average diameter D_M satisfies the relation ($(D_M/5, 5D_M)$, ≥ 90%) in terms of frequency distribution by volume.

With powders having such comparatively narrow distributions, their dispersion or cohesion characteristics are characterized by average particle diameter and the powders can be dispersed by operating a group of means for high dispersion treatment of particles under conditions that suit the specific value of D_M.

With a powder of core particles the particle size distribution of which is either broad or has a plurality of separate spaced peaks, a suitable selective separation treatment, say, classification may advantageously be performed and the individual classified powder portions are subjected to the coating treatment according to the invention. By so doing, coating can be started on the individual classified powder portions under the above-stated conditions in the coating start region of the coating space with the dispersity β adjusted to at least 70%, 80%, 90%, 95%, 97% or 99% depending on the average particle diameter, whereupon the individual particles in the powder of core particles can be provided with coatings.

Coat Forming Substance

The term "coat forming substance" means a substance that forms a coat on the particles to be coated. This may specifically be exemplified by those substances which provide the particles in the powder of core particles with coatings in the form of at least one kind selected from among ultrafine particles, islands, continuous phase, uniform membranes, projections, etc.

Particularly in the case where the coat forming substance assumes the form of ultrafine particles, their diameter may range from 0.0005 μm to 0.5 μm.

The coat forming substance may form a coating by itself or, alternatively, it reacts with the diamond or high-pressure phase boron nitride in the core particles and/or dissolves in the diamond or high-pressure phase boron nitride particles to form a solid solution and/or two or more coat forming substances may be reacted and/or alloyed with each other and/or dissolved in each other to form coatings. To this end, the coat forming substance is selected from among elemental substances and/or compounds that generate one or more of the desired inorganic compounds, alloys, intermetallic compounds, etc. to form such coatings, thereby serving as sintering aids and/or bonding materials which promote the sintering of the coated diamond or high-pressure phase boron nitride particles and/or as surface modifiers for the diamond or high-pressure phase boron nitride particles.

When sintering is done under sintering pressure and temperature conditions where diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable, the diamond or high-pressure phase boron nitride particles are to be coated with a coat forming substance that is selected from among those which will not promote the phase transition of diamond or high-pressure phase boron nitride to the lower-pressure phase (graphite or hBN). The coat forming substance is also selectable as a surface modifier which controls the grain boundaries of the diamond or high-pressure phase boron nitride particles. Various modifications may be performed as required and they include, for example: enhancing the chemical bonding between the diamond or high-pressure phase boron nitride particles and said sintering aid and/or bonding material; isolating the individual diamond or high-pressure phase boron nitride particles from a certain substance, thereby inhibiting the phase transition of diamond or high-pressure phase boron nitride to the lower-pressure phase (graphite or hBN); or inhibiting the reaction between diamond or high-pressure phase boron nitride with a certain substance. These methods contribute to an outstanding increase in the latitude in the selection of the coat forming substance as a sintering aid and/or bonding material, which certainly is a definite advantage for the purposes of the invention.

These coat forming substances can be those which contain at least one member selected from among metals, semiconductors, metalloids, rare earth metals and nonmetals of groups 1a, 2a, 3a, 4a, 5a, 6a, 7a, 1b, 2b, 3b, 4b, 5b, 6b, 7b and 8 of the periodic table, as well as oxides, nitrides, carbides, oxynitrides, oxycarbides, carbonitrides, oxycarbonitrides, borides and silicides thereof, as exemplified by the following: Al, B, Si, Fe, Ni, Co, Ti, Nb, V, Zr, Hf, Ta, W, Re, Cr, Cu, Mo, Y, La, TiAl, Ti_3Al, $TiAl_3$, TiNi, NiAl, Ni_3Al, SiC, TiC, ZrC, B_4C, WC, W_2C, HfC, VC, TaC, Ta_2C, NbC, Mo_2C, Cr_3C_2, Si_3N_4, TiN, ZrN, Si_2N_2O, AlN, HfN, VxN (x = 1 ~ 3), NbN, TaN, Ta_2N, TiB, TiB_2, ZrB_2, VB, VB_2, VB_2, NbB, NbB_2, TaB, TaB_2, MoB, MoB_2, MoB_4, Mo_2B, WB, W_2B, W_2B_5, LaB_6, $B_{13}P_2$, $MoSi_2$, BP, Al_2O_3, ZrO_2, $MgAl_2O_4$ (spinel) and $Al_6Si_2O_{13}$ (mullite).

The amounts in which the coat forming substances are added to form the coats on the surfaces of the coated diamond or high-pressure phase boron nitride particles are not limited in any particular way and suitable values can be selected that suit specific uses; advantageously, any desired values are selected as long as they are capable of densifying the diamond or high-pressure phase boron nitride sinters.

Uniform Coating

In the case where the coat forming substance takes the form of a uniform membrane, the term "uniform coating" means that the coating film is uniform in every portion of a single particle. In the case where the coat forming substance takes the form of an ultrafine particle, an island or a projection, the term "uniform coating" means that the coat forming substance in the form of an ultrafine particle, an island or a projection provides a coating of uniform distribution. It should be understood that any unevenness that is unavoidable in the process of generation of the coat forming substance will be embraced within the category of "uniformity".

Definition of "Charging into the Coating Space"

The phrase "charging into the coating space" means introducing the powder of core particles into the coating space by a certain method of filling such as free fall. In the case of charging by means of a carrier gas, the phrase means introducing the powder of core particles as it is carried in the direction of a mixture of a gas and the particles in the powder of core particles, or carried by a gas in the direction of its flow, or carried by a gas to change the direction of flow. Alternatively, the phrase means introduction under the action of a carrier gas, for example, through the wave motion, specifically, a nonlinear wave motion, of the carrier gas. Alternatively, the phrase means introduction into the coating

space by sound waves, ultrasonic waves, magnetic fields, electron beams, etc. in the gas. The phrase also means introduction in an applied field such as an electric field, a magnetic field or electron beams. Specifically, the powder particles may be charged or magnetized in an electric field, a magnetic field, by electron beams, etc. and introduced into the coating space by attractive or repulsive forces. Also contemplated by the phrase is introduction by aspiration under the back pressure of the gas or in vacuo.

Coating Space

The term "coating space" refers to a space in which the precursor of the coat forming substance which is generated from the feed of the coat forming substance via the vapor phase and/or the precursor of the coat forming substance in a vapor-phase state contacts and/or impinges against the particles in the powder of core particles. Alternatively, the term refers to a space region in which the surfaces of the particles in the powder of core particles are coated with the coat forming substance.

Coating Chamber

The term "coating chamber" means a compartment having the coating space in at least one part. More specifically, the coating chamber is a partitioned or generally partitioned (generally closed or semi-closed) compartment including the coating space and it is a compartment including the coating space in at least one part.

Within Gaseous Atmosphere

The expression "within a gaseous atmosphere" means within a space under vacuum or in a vapor-phase state. The term "vapor-phase state" as used herein means various states such as a molecular stream, an ionic stream, a plasma, a gas and a vapor. Technically speaking, the term "vacuum" refers to a state under reduced pressure. Strictly speaking, gases, molecules, atoms, ions, etc. are contained at any values of reduced pressure.

Precursor of the Coat Forming Substance

The term "precursor of the coat forming substance" means a precursor for the coat forming substance. More specifically, it refers to the feed per se of the coat forming substance in a vapor-phase state or, alternatively, it means a substance that is formed and/or synthesized from the feed of the coat forming substance via the vapor phase and which exists until just before it forms a coating on the core particles to be coated. The precursor of the coat forming substance is not limited to any state as long as it is formed and/or synthesized from the feed of the coat forming substance via the vapor phase. If the feed of the coat forming substance is in the vapor phase, the feed itself can be used as the precursor of the coat forming substance. The precursor of the coat forming substance may itself be in the vapor phase. If the precursor of the coat forming substance is a reactive substance, it may be prior to, or during or after the reaction. Specific examples of the precursor of the coat forming substance include ions, atoms, molecules, clusters, atomic clusters, molecular clusters, cluster ions, superfine particles, gases, vapors, aerosols, etc.

Feed of the Coat Forming Substance

The term "feed of the coat forming substance" refers to a feed material that passes through the vapor phase to become a coat forming substance. Specific examples of the state in which the feed of the coat forming substance may exist include solid lumps, powder particles, gases, liquids, etc.

Dispersity β

Dispersity β was proposed by Masuda, Gotoh et al. as an index for evaluating the dispersing performance of powder dispersing equipment [see KAGAKU KOGAKU, Summaries of Speeches and Lectures Delivered at the 23th Autumn Conference, p. 349 (1989)] and is defined as the proportion of the weight of particles in the state of apparent primary particles relative to the total weight of the particles present. The term "particles in the state of apparent primary particles" as used herein refers to the proportion of the overlap between the frequency distribution by mass of powder particles in a given state of dispersion $f_{m,2}$ and the frequency distribution by mass of completely dispersed powder particles $f_{m,1}$ and is expressed by β according to the following equation:

$$\beta = \int_0^{D_x} f_{m2}(D)dD + \int_{D_x}^{\infty} f_{m1}(D)dD$$

where

D: particle diameter (μm);
D_x: the particle diameter (μm) for the point of crossing between f_{m1} and f_{m2};
f_{m1}: the frequency distribution by mass (%/μm) representing the particle size distribution for complete dispersion;
f_{m2}: the frequency distribution by mass (%/μm) representing the particle size distribution of particles in a given state of dispersion; and
β: dispersity (%).

In the equation set forth above, the unit of measurement (μm) of the particle diameter is not limited to any particular value.

This equation evaluates dispersity on the basis of the particle size distribution as expressed by mass; however, dispersity should in principle be evaluated on the basis of the particle size distribution expressed by volume. But given the same density of powder particles, the particle size distribution as expressed by mass is equal to the particle size distribution expressed by volume. Therefore, in practice, the particle size distribution by mass which is easy to measure is determined and used as an equivalent of the particle size distribution by volume. Therefore, the dispersity β in the true sense of the term is expressed by the following equation and the area of the hatched portion shown in Fig. 1a.

$$\beta = \int_0^{D_x} f_{v2}(D)dD + \int_{D_x}^{\infty} f_{v1}(D)dD$$

where

D: particle diameter (μm);
D_x: the particle diameter (μm) for the point of crossing between f_{v1} and f_{v2};
f_{v1}: the frequency distribution by volume (%/μm) representing the particle size distribution for complete dispersion;
f_{v2}: the frequency distribution by volume (%/μm) representing the particle size distribution of particles in a given state of dispersion; and
β: dispersity (%).

In the equation set forth above, the unit of measurement (μm) of the particle diameter is not limited to any particular value.

In the following description, the distribution of the particles in the powder of core particles and their average diameter should, in principle, be based on volume unless otherwise noted.

Frequency Distribution by Volume

The frequency distribution by volume represents the distribution of particle diameter in terms of the relative volume of particles in a certain range of diameters.

Definition of ([D1,D2], x 90%)

A ([D1,D2], x 90%) distribution represents one in which particles from D1 to D2 (D1 and D2 each represent the particle diameter, provided that D1 < D2) account for at least 90% of the total volume of the particles present; a powder having this distribution is shown graphically in Fig. 1b, in which the hatched portion accounts for at least 90% of the area under the curve.

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Definition of Frequency Distribution by Volume ($(D_M/5, 50_{(\beta)}) \geq 90\%$)

A particle size distribution that is expressed by ($(D_M/5, 50_{(\beta)}) \geq 90\%$) in terms of frequency distribution by volume represents one in which particles ranging in diameter from one fifth of D_M to five times D_M (D_M is the average particle diameter by volume) account for at least 90% of the total volume of the particles present. Consider, for example, particles having an average diameter D_M of 10 μm on a volume basis; a particle size distribution that is expressed by ($(D_M/5, 50_{(\beta)}) \geq 90\%$) in terms of frequency distribution by volume represents one in which particles ranging in diameter from 2 μm to 50 μm account for at least 90% of the total volume of the particles present. The average particle diameter D_M on a volume basis is expressed by:

$$D_M = \frac{\int_0^\infty DF(D)dD}{\int_0^\infty F(D)dD}$$

where F(D) is the frequency distribution by volume. Or D_M is technically expressed by:

$$DM = \Sigma(V_i D_i)/\Sigma V_i$$

where V_i is the volume of a group of particles within a given interval of diameters $D_i \pm \Delta D_i/2$ (ΔD_i is the width of interval).

Coating Start Region

The region where coating is first started after the final treatment by the group of means for high dispersion treatment of particles is called the "coating start region". Therefore, prior to the final treatment by the group of means for high dispersion treatment of particles, no region is called the "coating start region" according to this definition even if coating is first started there.

Dispersity β in the Coating Start Region

In the present invention, the coating chamber is provided in such a way that the coating start region of the coating space is located in a region that satisfies one of the following conditions:

(1) a powder of core particles that have an average diameter of no more than 10 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 70%;

(2) a powder of core particles that have an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 80%;

(3) a powder of core particles that have an average diameter in excess of 20 μm but no more than 50 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 90%;

(4) a powder of core particles that have an average diameter in excess of 50 μm but no more than 300 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 95%;

(5) a powder of core particles that have an average diameter in excess of 300 μm but no more than 800 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group

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of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 97%; and

(6) a powder of core particles that have an average diameter in excess of 500 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 99%.

Given one of those dispersities in the coating start region of the coating space, one can disperse the particles in the powder of core particles to such a state that they are substantially single particles in a gaseous atmosphere, so that the precursor of the coat forming substance will uniformly contact and/or impinge against the surfaces of all particles in the powder of core particles that pass through the coating start region of the coating space, whereby the coat forming substance can be deposited on single particles in equal amounts.

In the present invention, dispersity β varies continuously with the average diameter of the particles in the powder of core particles but because of the difficulty involved in expressing it, the convenient stepwise expression is adopted.

Advantageously, the coating chamber is provided in such a way that the coating start region of the coating space is located in a space region that satisfies one of the following conditions.

(1) a powder of core particles that have an average diameter of no more than 10 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 80%;

(2) a powder of core particles that have an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 90%;

(3) a powder of core particles that have an average diameter in excess of 20 μm but no more than 50 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity of the particles in said powder of core particles should be adjusted to 95%;

(4) a powder of core particles that have an average diameter in excess of 50 μm but no more than 300 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to 97%; and

(5) a powder of core particles that have an average diameter in excess of 300 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 99%.

Given the coating chamber in which the coating start region of the coating space is located in such a way as to satisfy those conditions, the particles in the powder of core particles are at least free from areas that are substantially shaded by two adjacent core particles and it is possible to assure that the precursor of the coat forming substance is allowed to contact and/or impinge against the surfaces of individual particles from every direction, whereby coating with the coat forming substance can be accomplished more uniformly on a single particle basis and, accordingly, coating can be done to provide more uniform coating weights for the individual core particles.

The particles in a powder of core particles that have an average diameter exceeding 10 μm in the frequency distribution by volume are subjected to a cohesive action in a gaseous atmosphere, although not as intense as in the case of the particles in a powder of core particles that have an average diameter no more than 10 μm, and they contact and/or impinge against one another, causing unevenness in the distribution of the particles in the powder of highly dispersed core particles which form a mixture with a gas. However, if the coating of the particles in the powder of core particles is started as they are dispersed to provide one of the above-specified dispersities in accordance with their diameter, the particles in the powder of core particles or the particles in a powder that consists chiefly of the core particles can be coated with the coat forming substance more uniformly on a single particle basis and, accordingly, the individual particles can be coated with the coat forming substance in more uniform weights.

More advantageously, in the coating start region of the coating space,

(1) a powder of core particles that have an average diameter of no more than 10 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final dispersing treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles; and the dispersity β of the particles in said powder of core particles should be adjusted to at least 90%, or

(2) a powder of core particles that have an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final dispersing treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 95%, or

(3) a powder of core particles that have an average diameter in excess of 20 μm but no more than 50 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final dispersing treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 97%, or

(4) a powder of core particles that have an average diameter in excess of 50 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final dispersing treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 99%.

If one of these dispersities is attained in the coating start region of the coating space, the core particles are practically free from agglomeration and practically uniform coating can be performed on all surfaces of the individual particles.

If, in a particular case, high-quality coating is desired at the sacrifice of the efficiency of treatment, the dispersity is preferably at least 95%. In this case, the throughput of the treatment of the particles in the powder of core particles may be reduced to a very small level, namely, the concentration by number of the particles in the powder of core particles in the gaseous atmosphere may be reduced so that the particles in the powder of core particles are dispersed completely, whereby uniform coating can thoroughly be accomplished on the entire surfaces of the individual particles.

Group of Means for High Dispersion Treatment of Particles

The group of means for high dispersion treatment of particles which is to be used in the present invention is such that: (A) it has at least one dispersing means; and (B) it has, as the final treating means,

(a) dispersing means for dispersing the particles in a powder of core particles in a gaseous atmosphere or
(b) means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles which comprises:

(b-1) means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles that separates a portion of the powder that is composed of less highly dispersed particles from the mixture of a gas and the particles in the powder of core particles in which the particles in the powder of core particles are dispersed in a gaseous atmosphere, thereby selecting a mixture of a gas and the particles in a powder of highly dispersed core particles in which the particles in the powder of core particles are present in the gaseous atmosphere mainly in a single particle state and
(b-2) feedback means by which the portion of the powder that is composed of less highly dispersed particles and which has been separated by the means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles is transported to the final dispersing means among the dispersing means in the group of means for high dispersion treatment of particles and/or treating means upstream of the final dispersing means.

Advantageously, the group of means for high dispersion treatment of particles has such dispersing performance that one of the following conditions is satisfied:

(1) a powder of core particles that have an average diameter of no more than 10 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 70%,
(2) a powder of core particles that have an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder

of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 80%;

(3) a powder of core particles that have an average diameter in excess of 20 μm but no more than 50 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 90%;

(4) a powder of core particles that have an average diameter in excess of 50 μm but no more than 300 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 95%;

(5) a powder of core particles that have an average diameter in excess of 300 μm but no more than 800 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 97%; and

(6) a powder of core particles that have an average diameter in excess of 800 μm in the frequency distribution by volume should be dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and the dispersity β of the particles in said powder of core particles should be adjusted to at least 99%.

By insuring that the group of means for high dispersion treatment of particles have dispersing capabilities comparable to or better than the various dispersities to be attained in the above-described coating start region and by providing them in correspondence to those dispersities, high-quality coating can be applied in the coating start region to comply with the respective dispersities.

Final Treating Means

If the final treating means in the group of means for high dispersion treatment of particles is a dispersing means, said dispersing means is referred to as the final treatment means in the group of means for high dispersion treatment of particles. If the final treating means in the group of means for high dispersion treatment of particles is a means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles which is equipped with a feedback means by which the portion that has been separated selectively on account of less highly dispersed state during the step of treatment for selecting the mixture of a gas and the particles in the powder of highly dispersed core particles is to be transported to the final dispersing means at the last stage of the means for high dispersion treatment of particles, or if said final treating means is a means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles which is equipped with a feedback means by which the portion that has been separated selectively on account of less highly dispersed state during the step of treatment for selecting the mixture of a gas and the particles in the powder of highly dispersed core particles is to be transported to a treating means upstream of the final dispersing means, said means for selecting a mixture of a gas and the particles in a powder of highly dispersed core particles is referred to as the final treating means in the group of means for high dispersion treatment of particles.

It should be noted here that any means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles that is provided upstream of the means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles that is equipped with a feedback means and which is the final treating means in the group of means for high dispersion treatment of particles ("upstream" may typically mean between the means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles that is equipped with a feedback means and the final dispersing means, or upstream of the final dispersing means) is a constituent element of the group of means for high dispersion treatment of particles and this is true irrespective of whether the feedback means is used or not.

Dispersing Means

The means used to disperse particles is named a dispersing means. Any mechanism that has even a small or slight dispersing effect is usable as a dispersing means and it is used as a dispersing means in the invention. Consider, for example, a rotary feeder and an injection feeder for pneumatic conveying which are commonly used as supply means ["Funtai Kogaku Binran (A Handbook of Particle Technology)", Ed. by Funtai Kogakukai (Society of Particle Technology), published by Nikkan Kogyo Shimbunsha in 1966, pp. 568 and 571]. These apparatus also have a dispersing effect and, hence, they are dispersing means if used as means to achieve dispersion. The dispersion maintaining and promoting means which are to be discussed later are also dispersing means if they are used to achieve dispersion (for increasing

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5). Such dispersing means may be a single apparatus or machine or it may be a complex of apparatus and machines; to cover all of these cases, the dispersing means is collectively referred to as the "group of means for high dispersion treatment of particles".

The group of means for high dispersion treatment of particles is such that it operates on at least one selected mechanism of dispersion, such as dispersing the particles in a powder of core particles by a gas stream which accelerates and/or places them in a velocity gradient, dispersing the particles in a powder of core particles by impingement against a static obstacle and/or an obstacle composed of a rotating body, and dispersing the particles in a powder of core particles by mechanical deagglomeration which consists of a fluidized bed and/or pulsation and/or a rotary drum and/or vibrations and/or scraping.

Specifically, the group of means for high dispersion treatment of particles is equipped with at least one selected dispersing means, such as an ejector-type disperser, a Venturi-type disperser, a disperser using a capillary, an agitator, and an obstacle in a gas stream, a disperser using a jet blow, a disperser using a spiral tube and rotating blades, a disperser using rotating pins (Kacty mill), a fluidized bed-type disperser, a disperser using pulsation, a disperser using a rotary drum, a disperser using vibrations, a disperser using a vibrating screen and the scraping action of a scraper, an SAEI Gonnet-type disperser, a Chujo-type disperser, a Roller-type disperser, an office-type disperser, a B.M. type disperser, a Timbrell-type disperser, and a Wright-type disperser ["Funtai Kogaku Binran (A Handbook of Particle Technology)", Ed. by Funtai Kogakukai (Society of Particle Technology), published by Nikkan Kogyo Shimbunsha in 1966, p. 430].

Also usable are the dispersers described in official gazettes and exemplified blow: the disperser using agitating blades which is described in Unexamined Published Japanese Patent Application (kokai) Sho 56-1038; the disperser using a high-speed gas stream and dispersing nozzles which is described in Unexamined Published Japanese Patent Application (kokai) Sho 58-163454; the disperser using the dispersing action of rotating blades and the dispersing action of plasma jets which is described in Unexamined Published Japanese Patent Application (kokai) Sho 59-199027; the disperser using the dispersing action of plasma jets which is described in Unexamined Published Japanese Patent Application (kokai) Sho 59-207318; the disperser using an ejector and the dispersing action of plasma jets which is described in Unexamined Published Japanese Patent Application (kokai) Sho 59-216616; the disperser using an ejector and the dispersing action of ion streams which is described in Unexamined Published Japanese Patent Application (kokai) Sho 59-225739; the disperser using the dispersing action of plasma jets which is described in Unexamined Published Japanese Patent Application (kokai) Sho 59-156845; the disperser using the dispersing action of dispersing blades and a pressure gas which is described in Unexamined Published Japanese Patent Application (kokai) Sho 62-155421; the disperser using linear or annular slit jet ports which is described in Unexamined Published Japanese Patent Application (kokai) Sho 62-176527; the disperser using mesh blades which is described in Unexamined Published Japanese Patent Application (kokai) Sho 63-221028; the disperser using the dispersing action of high-speed gas streams issuing from jet nozzles which is described in Unexamined Published Japanese Patent Application (kokai) Sho 63-1629; the disperser using many small holes which is described in Unexamined Published Utility Model Application (kokai) Sho 62-8215; the ejector-type disperser which is described in Unexamined Published Japanese Utility Model Application (kokai) Sho 62-156954; and the disperser using small holes and orifices which is described in Unexamined Published Japanese Utility Model Application (kokai) Sho 62-6034.

Dispersing means advantageous for use in the group of means for high dispersion treatment of particles include the apparatus that are described in Japanese Patent Application Sho 63-311258, Japanese Patent Application Hei 1-71071, Japanese Patent Application Hei 2-218587, etc.

Means for Selecting a Mixture of a Gas and the Particles in a Powder of Highly Dispersed Core Particles

The means for selecting a mixture of a gas and the particles in a powder of highly dispersed core particles is a means that separates a mixture of a gas and the particles in a powder of less highly dispersed core particles from the mixture of a gas and the particles in the powder of core particles so as to select a mixture of a gas and the particles in a powder of highly dispersed core particles that is chiefly composed of those particles which are in a single-particle state. Agglomerating particles which are association of primary particles have a greater apparent diameter than the primary particles and, hence, they can be separated by a suitable means such as dry classifying means. An example of the means for selecting a mixture of a gas and the particles in a powder of highly dispersed core particles is at least one dry classifying means selected from among the following: classifying means using gravity, classifying means using inertia force, classifying means using centrifugal force, classifying means using static electricity, classifying means using a fluidized bed, etc.

Specific examples of the means for selecting the mixture of a gas and the particles in a powder of highly dispersed core particles include: a gravity classifier, an inertia classifier, a centrifugal classifier, a cyclone, an air separator, a micron separator, a microplex, a multiplex, a zigzag classifier, an acu-cut, a conical separator, a turbo classifier, a super separator, a dispersion separator, an elbow jet, a fluidized bed classifier, a virtual impactor, an O-Sepa, a sieve, a vibrating

screen, a sifter ["Funtai Kogaku Binran (A Handbook of Particle Technology)", Ed. by Funtai Kogakukai (Society of Particle Technology), published by Nikkan Kogyo Shinbunsha in 1966, p. 514].

Mixture of a Gas and the Particles in a Powder of Core Particles

The mixture of a gas and the particles in a powder of core particles refers to (a) a homogeneous flow characterized in that the particles in a powder of core particles are suspended uniformly in a gaseous atmosphere (which may be called a "uniform suspension flow"), (b) a heterogeneous flow characterized in that the particles in a powder of core particles show a nonuniform distribution in certain regions of a gaseous atmosphere (which may be called an "inhomogeneous suspension flow"), (c) a flow involving a sliding layer of the particles in a powder of core particles (which may be called a "sliding flow"), or (d) a flow involving a stationary layer of the particles in a powder of core particles.

Mixture of a Gas and the Particles in a Powder of Less Highly Dispersed Core Particles

The mixture of a gas and the particles in a powder of less highly dispersed core particles refers to that portion of a mixture of a gas and the particles in a powder of core particles in which the powder particles are present in a gaseous atmosphere mainly in states other than the single particle state.

Mixture of a Gas and the Particles in a Powder of Highly Dispersed Core Particles

The mixture of a gas and the particles in a powder of highly dispersed particles refers to a mixture of a gas and the particles in a powder of core particles in which the powder particles are present in a gaseous atmosphere mainly in a single particle state. No matter how much high the degree of dispersion is, the mixture of a gas and the particles in a powder of highly dispersed core particles contains agglomerating particles in practice. The mixture of a gas and the particles in a powder of less highly dispersed particles contains non-agglomerating single particles in practice and can be selectively separated into a mixture of a gas and the particles in a powder of less highly dispersed particles and a mixture of a gas and the particles in a powder of highly dispersed particles. The mixture of a gas and the particles in a powder of less highly dispersed particles is converted to a mixture of a gas and the particles in a powder of highly dispersed particles by selective separation and/or redispersion of the agglomerating particles.

Recovery Means

The recovery means is a means for picking up the coated particles that have been prepared in the coating space. The part of the recovery means in which the recovery treatment is performed is called the "recovery section". The coated particles the coating on which has been provided by passage through the coating start region of the coating space are recovered by direct pickup from the gaseous atmosphere or after temporary storage following pickup from the gaseous atmosphere or together with a gas.

Usable as the recovery section of the recovery means is one of the following members: the recovery section of the recovery means that uses barriers (obstacles), the recovery section of the recovery means that uses gravity, the recovery section of the recovery means that uses inertia forces, the recovery section of the recovery means that uses centrifugal forces, the recovery section of the recovery means that uses coulombic attractive forces, the recovery section of the recovery means that uses thermophoretic forces, the recovery section of the recovery means that uses Brownian diffusion, the recovery section of the recovery means that uses the pulling force of the back pressure, evacuation, etc.

Advantageous examples of the recovery section of the recovery means include a gravity dust collector, an inertia dust collector, a centrifugal dust collector, a filtration dust collector, an electrostatic precipitator, a scrubbing dust collector, a particle packed layer, a cyclone, a bag filter, a ceramic filter, a scrubber, etc.

Bonding Material

The bonding material to be used to manufacture diamond or high-pressure phase boron nitride sinters in accordance with the invention is selected from among those bonding materials which can be sintered densely to a density of at least 80% by sintering at pressures less than 3000 MPa and at temperatures not exceeding 1850°C. Advantageously, those bonding materials are selected which will not promote the phase transition of diamond or high-pressure phase boron nitride to the lower pressure phase (graphite or hBN). Alternatively, those bonding materials are selected which, when sintered at pressures less than 3000 MPa and at temperatures not exceeding 1850°C, will react with diamond or boron nitride to yield dense reaction products that have densities of at least 95%. More preferably, those substances are selected which, when sintered at pressures less than 2000 MPa and at temperatures not exceeding 1850°C, will produce bonding materials that are dense (density ≥ 80%) and/or of high hardness (Vickers hardness ≥ 800). Feed powders which, when sintered at pressures less than 3000 MPa and at temperatures not exceeding 1850°C, will yield dense

bonding materials having densities of at least 80% are selected from powders or particles that contain at least one of the metals, semiconductors, metalloids and rare earth metals of groups 1a, 2a, 3a, 4a, 5a, 6a, 7a, 1b, 2b, 3b, 4b, 5b, 6b, 7b and 8 of the periodic table and/or at least one compound containing at least one of those metals, semiconductors, metalloids and rare earth metals. More specifically, such powders or particles can be those of at least one member which is selected from among B, Ti, Zr, Hf, Ta, Nb, V, SiC, TiC, ZrC, B_4C, WC, HfC, TaC, NbC, Si_3N_4, TiN, ZrN, AlN, HfN, TaN, TiB, TiB_2, ZrB_2, HfB, HfB_2, LaB_6 $MoSi_2$, BP, Al_2O_3, Al_2SiO_5 (mullite), ZrO_2 (PSZ: partially stabilized zirconia with Y_2O_3, MgO or CaO, or TZP: tetragonal zirconia polycrystalline compound), and $MgAl_2O_4$ (spinel). To take alumina as an example, a suitable example is a high purity, easily sintrable fine feed, such as the alumina described in Unexamined Published Japanese Patent Application (kokai) Sho 62-151618 which is produced by pyrolysis of an ammonium aluminum carbocate and that is prefered since it can be densified at a temperature of about 1400°C even by normal sintering at atmospheric pressure. Another suitable example is a fine, high-purity alumina powder that contains up to 10% by volume of magnesia (MgO) and/or titania (TiO_x, x = 1 - 2) which are effective in promoting the sintering of alumina and if this condition is met, high-purity aluminas other than the alumina described in Unexamined Published Japanese Patent Application (kokai) Sho 62-151618, supra may be used, as exemplified by high-purity (≥ 99%) and easily sintrable aluminas that are composed of fine (≤ 1 µm) particles and which are typically produced by the Bayer process, hydrolysis of organic aluminum, pyrolysis of aluminum alum, the ethylene chlorohydrin process, submerged arc discharge, etc.

Besides the aluminas mentioned above, zirconium oxides may also be selected and advantageous examples include the easily sintrable yttria partially stabilized zirconia (2-4 mol% Y_2O_3-ZrO_2) powder which is produced by coprecipitation, and an alumina-zirconia base powder [FC Report, 1(5) (1983) 13-17]. Also selectable is a titanium oxide or titania powder [TiO_2: Summaries of Lectures Read at the 19th Symposium on High-Pressure Technology (1978) p. 174].

Another example that can be selected is titanium nitride [TiN; Yamada et al., Yogyo Kyokaishi (Journal of The Ceramic Society of Japan, 89, (1981) 621-625].

In the next place, the group of means for high dispersion treatment of particles which is adopted to prepare the coated diamond or high-pressure phase boron nitride particles is described below with reference to accompanying drawings.

Description of the Drawings of the Group of Means for High Dispersion Treatment of Particles

Fig. 2a is a block diagram showing an example of the basic composition of the group of means for high dispersion treatment of particles as it is used to prepare coated diamond or high-pressure phase boron nitride particles. The group is composed of a final dispersing means A for dispersing the particles in a powder of core particles and a constituent element g of the group of means for dispersion treatment which is upstream of the final dispersing means. Shown by s is a mixture of a gas and the particles in a powder of highly dispersed core particles which are part of the particles in the powder of core particles and which are present in a gaseous atmosphere mainly in a single-particle state. Constituent element g may be any treating means such as dispersing means, supply means, and means for selecting a mixture of a gas and the particles in a powder of highly dispersed core particles, which may be used either individually or in combination. Constituent element g is optional and may be omitted. The group of means for high dispersion treatment of particles is advantageously of such a design that after treatment by the final treating means A, one of the following values of dispersity β can be realized: (1) at least 70% for a powder of core particles that have an average diameter of no more than 10 µm in the frequency distribution by volume; (2) at least 80% for a powder of core particles that have an average diameter in excess of 10 µm but no more than 20 µm in the frequency distribution by volume; (3) at least 90% for a powder of core particles that have an average diameter in excess of 20 µm but no more than 50 µm in the frequency distribution by volume; (4) at least 95% for a powder of core particles that have an average diameter in excess of 50 µm but no more than 300 µm in the frequency distribution by volume; (5) at least 97% for a powder of core particles that have an average diameter in excess of 300 µm but no more than 800 µm in the frequency distribution by volume; and (6) at least 99% for a powder of core particles that have an average diameter in excess of 800 µm in the frequency distribution by volume.

Fig. 2b is a block diagram showing a second example of the basic composition of the group of means for high dispersion treatment of particles as it is used to prepare coated diamond or high-pressure phase boron nitride particles. The group is composed of a final dispersing means A for dispersing the particles in a powder of core particles, final means B for selecting a mixture of a gas and the particles in a powder of highly dispersed core particles at the last stage which is equipped with feedback means C by which a mixture of a gas and the particles in a powder of less highly dispersed core particles η as separated from a mixture of a gas and the particles in a powder of highly dispersed core particles in which the powder particles are present in a gaseous atmosphere mainly in a single-particle state is fed back to the final dispersing means A, a constituent element g of the group of means for dispersion treatment which is upstream of the final dispersing means, and a constituent element g of the group of means for high dispersion treatment of particles which is provided between the final dispersing means and the final selecting means. As for the mixture s and the constituent element g, the explanation made in connection with Fig. 2a will apply and, hence, no detailed description is made. Constituent element g may be any treating means other than the dispersing means, such as supply means and

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selecting means, which may be used either individually or in combination. Constituent elements g and g are optional and may be omitted. The group of means for high dispersion treatment of particles is advantageously of such a design that after treatment by selecting means B which is the final treating means, the above-mentioned values of dispersity can be realized for powders of core particles having the above-mentioned average diameters.

Fig. 3c is a block diagram showing a third example of the basic composition of the group for high dispersion treatment of particles as it is used to prepare coated diamond or high-pressure phase boron nitride particles. The group is composed of a final dispersing means A for dispersing the particles in a powder of core particles, final means B for selecting a mixture of a gas and the particles in a powder of highly dispersed core particles at the last stage which is equipped with feedback means C by which a mixture of a gas and the particles in a powder of less highly dispersed core particles η as separated from a mixture of a gas and the particles in a powder of highly dispersed core particles in which the powder particles are present in a gaseous atmosphere mainly in a single-particle state is fed back to a treating means upstream of the final dispersing means A, a constituent element d of the group of means for high dispersion treatment of particles which is upstream of the final dispersing means, and a constituent element e of the group of means for high dispersion treatment of particles which is provided between the final dispersing means and the final selecting means. As for the mixture c, constituent elements d and e, and the group of means for high dispersion treatment of particles, the foregoing explanation will apply and no detailed description is made.

Having the construction described above, the group of means for high dispersion treatment of particles under discussion may include powder supply sources such as a supply vessel and core particle generating means. To take the case of Fig. 2c as an example, the group of means for high dispersion treatment of particles may of course adopt such a composition that the mixture η is fed back to a supply vessel by the feedback means C. It also goes without saying that the step of dispersion by the group of means for high dispersion treatment of particles may be preceded by a disintegrating step in which the particles in the powder of core particles are disintegrated and/or otherwise reduced in size.

Typical specific examples of these basic compositions of the group of means for high dispersion treatment of particles are described below in greater detail with reference to more detailed block diagrams.

Design 1

Fig. 3a is a block diagram illustrating a first specific design of the group of means for high dispersion treatment of particles as it is used to prepare coated diamond or high-pressure phase boron nitride particles and the drawing corresponds to Fig. 2a. The group shown in Fig. 3a is composed of a supply vessel 100 for supplying the powder of core particles to be coated, and the final dispersing means A for dispersing the powder of core particles to be coated.

Design 2

Fig. 3b is a block diagram illustrating a second specific design of the group of means for high dispersion treatment of particles as it is used to prepare coated diamond or high-pressure phase boron nitride particles and the drawing corresponds to Fig. 2a. The group shown in Fig. 3b is composed of a supply vessel 100 for supplying the powder of core particles to be coated, dispersing means a for dispersing the powder of core particles to be coated, and the final dispersing means A for dispersing the powder of core particles to be coated.

Design 3

Fig. 3c is a block diagram illustrating a third specific design of the group of means for high dispersion treatment of particles as it is used to prepare coated diamond or high-pressure phase boron nitride particles and the drawing corresponds to Fig. 2a. The group shown in Fig. 3c is composed of a supply vessel 100 for supplying the powder of core particles to be coated, dispersing means a for dispersing the powder of core particles to be coated, feedback means C by which a mixture of a gas and the particles in a powder of less highly dispersed core particles η as separated from a mixture of a gas and the particles in a powder of highly dispersed core particles in which the powder particles are present in a gaseous atmosphere mainly in a single-particle state is fed back from the mixture of a gas and the particles in the powder of core particles (which have been dispersed by the dispersing means a) to the dispersing means a, means b for selecting the mixture of a gas and the particles in a powder of highly dispersed particles, by which the mixture of a gas and the particles in a powder chiefly composed of highly dispersed core particles is introduced into the final dispersing means A, and the final dispersing means A for dispersing the powder of core particles to be coated.

Design 4

Fig. 3d is a block diagram illustrating a fourth specific design of the group of means for high dispersion treatment of particles as it is used to prepare coated diamond or high-pressure phase boron nitride particles and the drawing in Fig. 3d corresponds to Fig. 2b. The group shown in Fig. 3d is composed of a supply vessel 100 for supplying the powder

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of core particles to be coated, a final dispersing means A for dispersing the powder of core particles to be coated, feedback means C by which a mixture of a gas and the particles in a powder of less highly dispersed core particles is as separated from a mixture of a gas and the particles in a powder of highly dispersed particles in which the powder particles are present in a gaseous atmosphere mainly in a single-particle state is fed back from the mixture of a gas and the particles in the powder of core particles (which have been dispersed by the final dispersing means A) to the dispersing means A, and final means B for selecting the mixture of a gas and the particles in the powder of highly dispersed core particles at the final stage and which discharges the mixture of a gas and the particles in the powder of highly dispersed core particles.

Design 5

Fig. 3e is a block diagram illustrating a fifth specific design of the group of means for high dispersion treatment of particles as it is used to prepare coated diamond or high-pressure phase boron nitride particles and the drawing corresponds to Fig. 2b. The group shown in Fig. 3e is composed of a supply vessel 100 for supplying the powder of core particles to be coated, dispersing means a for dispersing the powder of core particles to be coated, a final dispersing means A for dispersing the powder of core particles to be coated, feedback means C by which a mixture of a gas and the particles in a powder of less highly dispersed core particles is as separated from a mixture of a gas and the particles in a powder of highly dispersed particles in which the powder particles are present in a gaseous atmosphere mainly in a single-particle state is fed back from the mixture of a gas and the particles in the powder of core particles (which have been dispersed by the final dispersing means A) to the dispersing means A, and final means B for selecting the mixture of a gas and the particles in the powder of highly dispersed core particles at the final stage and which discharges the mixture of a gas and the particles in the powder of highly dispersed core particles.

Design 6

Fig. 3f is a block diagram illustrating a sixth specific design of the group of means for high dispersion treatment of particles as it is used to prepare coated diamond or high-pressure phase boron nitride particles and the drawing corresponds to Fig. 2b. The group shown in Fig. 3f is composed of a supply vessel 100 for supplying the powder of core particles to be coated, means b for selecting a mixture of a gas and the particles in a powder of highly dispersed core particles, which rejects a mixture of a gas and the particles in a powder chiefly composed of less highly dispersed core particles from the mixture of a gas and the particles in the powder of core particles and which introduces into dispersing means A the mixture of a gas and the particles in a powder chiefly composed of highly dispersed core particles, final dispersing means A for dispersing the particles in the selectively separated powder of core particles, feedback means C by which a mixture of a gas and the particles in a powder of less highly dispersed core particles as separated from a mixture of a gas and the particles in a powder of highly dispersed particles in which the powder particles are present in a gaseous atmosphere mainly in a single-particle state is fed back from the mixture of a gas and the particles in the powder of core particles (which have been dispersed by the final dispersing means A) to the dispersing means A, and final means B for selecting the mixture of a gas and the particles in the powder of highly dispersed core particles at the final stage and which discharges the mixture of a gas and the particles in the powder of highly dispersed core particles.

Design 7

Fig. 3g is a block diagram illustrating a seventh specific design of the group of means for high dispersion treatment of particles as it is used to prepare coated diamond or high-pressure phase boron nitride particles and the drawing corresponds to Fig. 2b. The group shown in Fig. 3g is composed of a supply vessel 100 for supplying the powder of core particles to be coated, dispersing means a for dispersing the powder of core particles to be coated, a final dispersing means A for dispersing the powder of core particles to be coated, feedback means C by which a mixture of a gas and the particles in a powder of less highly dispersed core particles as separated from a mixture of a gas and the particles in a powder of highly dispersed particles in which the powder particles are present in a gaseous atmosphere mainly in a single-particle state is fed back from the mixture of a gas and the particles in the powder of core particles (which have been dispersed by the final dispersing means A) to the dispersing means A, and final means B for selecting the mixture of a gas and the particles in the powder of highly dispersed core particles at the final stage and which discharges the mixture of a gas and the particles in the powder of highly dispersed core particles.

To maintain the thus achieved high dispersive state of the particles, means for maintaining dispersion in a gaseous atmosphere may be added to the group of means for high dispersion treatment of particles. The term "means for maintaining dispersion in a gaseous atmosphere" as used herein refers to means that maintains a desired value of dispersity B by preventing reagglomeration of the particles in the powder of core particles that have been carried dispersively in a gaseous atmosphere. To promote the thus achieved high dispersive state of the core particles, means for promoting dispersion in a gaseous atmosphere may be added between the group of means for high dispersion treatment of particles

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and the coating chamber. The term "means for promoting dispersion in a gaseous atmosphere" as used herein refers to means which is primarily intended to promote the redispersion of that part of the particles in the powder of core particles carried dispersively in a gaseous atmosphere which have agglomerated again, thereby retarding the drop in the dispersive state of the powder; the term also refers to means that promotes redispersion in such a way that the state of dispersion that has dropped once can be restored to the initial high dispersive state.

Advantageous examples of said means for maintaining dispersion in a gaseous atmosphere or promoting dispersion in a gaseous atmosphere include a pipe vibrator, a pipe heater, a plasma generator, an electric charger, etc.

The pipe vibrator is means in which a pipe equipped with an oscillator is vibrated to provide the particles dispersed in a gaseous atmosphere with vibrations uncomparable to those imparted by dispersers, whereby reagglomeration is suppressed to maintain the high dispersive state or the dispersion of reagglomerating particles is promoted.

The pipe heater is means in which a heated pipe imparts heat to a carrier gas from outside, thereby expanding the carrier gas so that its flow velocity is accelerated to a level that is too fast to be comparable to that achieved by dispersers, whereby reagglomeration of the particles is suppressed while promoting the dispersion of reagglomerating particles.

The plasma generator is means in which a plasma is generated in the gaseous atmosphere which dispersively carries the powder of core particles, with the resulting plasma ions being allowed to impinge against the core particles, whereby reagglomeration is suppressed to maintain the high dispersive state or the dispersion of reagglomerating particles is promoted.

The electric charger is means in which corona discharge, electron beams, radiations or some other method is used to generate monopolar ions in the gaseous atmosphere which dispersively carries the powder of core particles, which are subsequently passed through the monopolar ion atmosphere to be charged to a single polarity, whereupon electrostatic repulsive forces either suppress reagglomeration to maintain the high dispersive state or promote the dispersion of reagglomerating particles.

The powder of core particles which have been rendered to assume a highly dispersive state in the manner described on the foregoing pages is sent to the coating chamber so that the surfaces of the particles are coated with the coat forming substance. The coating compartment is provided with the coating space including the coating start region.

The group of means for high dispersion treatment of particles is desirably coupled directly to the coating chamber. If necessary, they may be connected together by means of a hollow member and/or a pipe that are indispensable to transport. In this case, too, it is essential that the dispersity *fi* in the coating start region be adjusted to one of the values within the ranges set forth hereinabove.

If the group of means for high dispersion treatment of particles is coupled to the coating chamber located separately, the powder of core particles suffices to be introduced into the coating chamber as it maintains the state of dispersion that has been achieved by said group of means for high dispersion treatment of particles. To this end, means for maintaining dispersion in a gaseous atmosphere (which is a device for maintaining the state of dispersion of the powder of core particles) and/or means for promoting dispersion in a gaseous atmosphere (which is a device for enhancing the state of dispersion) and/or means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles (which separates the powder portion of less highly dispersed core particles from the mixture of a gas and the particles in the powder of core particles, thereby selecting a mixture of a gas and the particles in a powder of highly dispersed core particles, the major part of which comprises particles in a single-particle state) may be provided between the group of means for high dispersion treatment of particles and the coating chamber.

The invention also contemplates that when used to prepare coated diamond or high-pressure phase boron nitride particles, the group of means for high dispersion treatment of particles may share one or more portions of the space with (1) the coating chamber, (2) the coating space or (3) the coating start region.

For example, the group of means for high dispersion treatment of particles may share its dispersing space with the coating chamber, or with the coating space having the coating start region, or with the coating start region.

The term "coating start region" as used herein refers to the region where the precursor of the coat forming substance that has been generated via the vapor phase and/or the precursor of the coat forming substance in a vapor phase state contacts and/or impinges against the powder of highly dispersed core particles which has been transported in the state of dispersion that has one of the following values of dispersity *fi*, whereupon coating of the individual particles is started: (1) at least 70% for a powder of core particles that have an average diameter of no more than 10 μm in the frequency distribution by volume; (2) at least 80% for a powder of core particles that have an average diameter in excess of 10 μm but no more than 80 μm in the frequency distribution by volume; (3) at least 90% for a powder of core particles that have an average diameter in excess of 20 μm but no more than 60 μm in the frequency distribution by volume; (4) at least 95% for a powder of core particles that have an average diameter in excess of 60 μm but no more than 300 μm in the frequency distribution by volume; (5) at least 97% for a powder of core particles that have an average diameter in excess of 300 μm but no more than 600 μm in the frequency distribution by volume; and (6) at least 99% for a powder of core particles that have an average diameter in excess of 600 μm in the frequency distribution by volume. Five typical embodiments of the coating start region are shown schematically in Figs. 4a - 4e.

In Figs. 4a - 4e, the coating start region is indicated by numeral 2.

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In the case shown in Fig. 4a, the coating start region 2 of the coating space in which the coating of core particles is started as they are dispersed to one of the above-listed values of dispersity β in accordance with the average diameter of those core particles is provided in such a way that it surrounds the group of means for high dispersion treatment of particles or its discharge section 1.

In the case shown in Fig. 4b, the coating start region 2 of said coating space is provided in such a way that it is passed by all the particles 4 in the powder of core particles as they are discharged from the group of means for high dispersion treatment or its discharge section 1.

By adopting these arrangements, the particles in all powders of core particles can start to be coated as they are dispersed to the above-listed values of dispersity β.

In the case shown in Fig. 4c, the coating start region 2 of said coating space is provided in such a way that it is passed in all cases by those particles 4 in the powder of core particles which are discharged from the group of means for high dispersion treatment of particles or its discharge section 1 to enter the recovery section 5.

In the case shown in Fig. 4d, the coating start region 2 of said coating space is provided in such a way that it surrounds the recovery section 5.

In the case shown in Fig. 4e, the recovery section 5 is provided in a position that can be reached solely by the particles in the mixture of a gas and the particles in the powder of highly dispersed core particles. Hence, the region indicated by 6 in Fig. 4e is selection means using gravity. The coating start region 2 of said coating space is provided in the hatched area of Fig. 4e so that it is passed in all cases by those particles in the mixture of a gas and the particles in the powder of highly dispersed core particles which enter the recovery section. This arrangement insures that only the core particles that started to be coated as they were dispersed to the above-listed values of dispersity β can be recovered and there is no chance that the core particles that did not pass through the coating start region will intermingle with the coated particles which emerge from the coating start region.

As one can understand from the foregoing description, the apparatus for implementing the present invention are composed of the group of means for high dispersion treatment of particles and the coating chamber or, alternatively, the group of means for high dispersion treatment of particles, the coating chamber and the recovery means. The constituent elements of the apparatus can be contained in various manners and several designs of these apparatus are described below with reference to drawings.

Apparatus Design 1

Fig. 5a is a block diagram showing the construction of a first apparatus for producing coated diamond or high-pressure phase boron nitride particles. As shown, the apparatus is composed of the main body of the production equipment 2-A (coating apparatus), coating chamber 2-B1, coating space 2-B2, coating start region 2-B3, the group of means for high dispersion treatment of particles 2-C1, and recovery means 2-D. The group of means for high dispersion treatment of particles 2-C1 is coupled directly to the coating chamber 2-B1.

Apparatus Design 2

Fig. 5b is a block diagram showing the construction of a second apparatus for producing coated diamond or high-pressure phase boron nitride particles. As shown, the apparatus is composed of the main body of the production equipment 2-A (coating apparatus), coating chamber 2-B1, coating space 2-B2, coating start region 2-B3, the group of means for high dispersion treatment of particles 2-C1, indispensable hollow member 2-C2, and recovery means 2-D. The group of means for high dispersion treatment of particles 2-C1 is connected to the coating chamber 2-B1 via the indispensable hollow member 2-C2.

Apparatus Design 3

Fig. 5c is a block diagram showing the construction of a third apparatus for producing coated diamond or high-pressure phase boron nitride particles. As shown, the apparatus is composed of the main body of the production equipment 2-A (coating apparatus), coating chamber 2-B1, coating space 2-B2, coating start region 2-B3, the group of means for high dispersion treatment of particles 2-C1, means for maintaining dispersion in gaseous atmosphere 2-C3, and recovery means 2-D. The group of means for high dispersion treatment of particles 2-C1 is connected to the coating chamber 2-B1 via the means for maintaining dispersion in gaseous atmosphere 2-C3.

Apparatus Design 4

Fig. 5d is a block diagram showing the construction of a fourth apparatus for producing coated diamond or high-pressure phase boron nitride particles. As shown, the apparatus is composed of the main body of the production equipment 2-A (coating apparatus), coating chamber 2-B1, coating space 2-B2, coating start region 2-B3, the group of means

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for high dispersion treatment of particles 2-C1, and recovery means 2-D. The group of means for high dispersion treatment of particles 3-C1 shares space with the coating chamber 2-B1.

Apparatus Design 5

Fig. 5e is a block diagram showing the construction of a fifth apparatus for producing coated diamond or high-pressure phase boron nitride particles. As shown, the apparatus is composed of the main body of the production equipment 2-A (coating apparatus), coating chamber 2-B1, coating space 2-B2, coating start region 2-B3, the group of means for high dispersion treatment of particles 2-C1, and recovery means 2-D. The group of means for high dispersion treatment of particles 2-C1 is provided within the coating chamber 2-B1.

Apparatus Design 6

Fig. 5f is a block diagram showing the construction of a sixth apparatus for producing coated diamond or high-pressure phase boron nitride particles. As shown, the apparatus is composed of the main body of the production equipment 2-A (coating apparatus), coating chamber 2-B1, coating space 2-B2, coating start region 2-B3, the group of means for high dispersion treatment of particles 2-C1, and recovery means 2-D. The coating chamber 2-B1 is provided within the dispersing space of the group of means for high dispersion treatment of particles 2-C1.

Apparatus Design 7

Fig. 5g is a block diagram showing the construction of a seventh apparatus for producing coated diamond or high-pressure phase boron nitride particles. As shown, the apparatus is composed of the main body of the production equipment 2-A (coating apparatus), coating chamber 2-B1, coating space 2-B2, coating start region 2-B3, the group of means for high dispersion treatment of particles 2-C1, recovery means 2-D, and recoating supply means 2-E. The coated particles issuing from the recovery means 2-D can be transported by the recoating supply means 2-E to the group of means for high dispersion treatment of particles 2-C1 for performing repeated coating treatments.

Either one of the apparatuses of these designs can produce coated diamond or high-pressure phase boron nitride particles.

The coated particles in which the powder of core particles (diamond or high-pressure phase boron nitride particles) has its surface coated with the coat forming substance may be coated again with the coat forming substance or subjected to repeated recoating operations. In these cases, the coated particles are sent to the recoating supply means. The term "recoating supply means" as used herein refers to means for transporting the coated particles to the group of means for high dispersion treatment of particles to perform recoating. Specifically, the recoating supply means is furnished with (a) means for recovering the coated particles and (b) means for transporting said coated particles from the recovery means (a) to the group of means for high dispersion treatment of particles. Alternatively, the recoating supply means is furnished with (a) means for recovering the coated particles, (b) means for transporting said coated particles from the recovery means (a) to the group of means for high dispersion treatment of particles, and (c) means for classifying the coated particles. Given large coating weights, the particle size distribution of the coated particles will vary from that of the particles in the powder of uncoated core particles. Under these conditions, it is effective to perform the recoating operation after the particle size distribution of the coated particles is adjusted by the classifying means (a).

The recoating operation may be repeated depending on the need and the coating weight of the coat forming substance can be set to a desired level. If necessary, the coating operation may be repeated with the type of the coat forming substance varied and, thus, a substance of more than one component can be coated in multiple layers as the coat forming substance.

The equipment for producing coated particles that is to be used in the present invention is in no way limited as long as it is capable of applying the coat forming substance over the surfaces of the particles in the powder of core particles by vapor phase processes involving transition through the vapor phase. For example, chemical vapor deposition (CVD) equipment can be used, as exemplified by a thermal CVD apparatus, a plasma-assisted CVD apparatus, apparatus for CVD utilizing electromagnetic waves (i.e., visible light CVD, laser CVD, ultraviolet CVD, infrared CVD and far-infrared CVD) and a MOCVD apparatus. Alternatively, physical vapor deposition (PVD) equipment can be used, as exemplified by a vacuum evaporation apparatus, an ion sputtering apparatus and an ion plating apparatus. Stated more specifically, a suitable apparatus for producing coated particles is described in the official gazette of Unexamined Published Japanese Patent Application (Kokai) Hei 3-75502, entitled "Particles Coated with Superfine Grains on the Surfaces and A Process for Producing Such Coated Particles".

As described on the foregoing pages, the process of the present invention for producing coated diamond or high-pressure phase boron nitride comprises the steps of charging into the coating space the particles in the powder of core particles which are diamond or high-pressure phase boron nitride particles and then permitting the precursor of the coat forming substance which is generated via the vapor phase and/or the precursor of the coat forming substance in a vapor-

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phase state to contact and/or impinge against the particles in said powder of core particles so that their surfaces are coated with the coat forming substance. Five basic processes for coating the core particles with the coat forming substance are summarized below.

I. A coating method comprising:

(A) a dispersing step in which the particles in the powder of core particles are dispersed in a gaseous atmosphere by the group of means for high dispersion treatment of particles so as to make a mixture of a gas and the particles in a powder of highly dispersed core particles; and

(B) a coating step in which the core particles in said gas-particle mixture, as they have been dispersed with the dispersity β adjusted to the values within the ranges set forth above, are allowed to contact and/or impinge against the coat forming substance in the coating start region of the coating space, thereby starting the coating operation.

II. A coating method comprising:

(A) a dispersing step in which the particles in the powder of core particles are dispersed in a gaseous atmosphere by the group of means for high dispersion treatment of particles which realize the adjustment of dispersity β to the values within the ranges set forth above, thereby making a mixture of a gas and the particles in a powder of highly dispersed core particles; and

(B) a coating step in which the core particles in said gas-particle mixture, as they have been dispersed with the dispersity β adjusted to the values within the ranges set forth above, are allowed to contact and/or impinge against the coat forming substance in the coating start region of the coating space, thereby starting the coating operation.

III. A coating method comprising:

(A) a dispersing step in which the particles in the powder of core particles are dispersed in a gaseous atmosphere by the group of means for high dispersion treatment of particles which realize the adjustment of dispersity β to the values within the ranges set forth above, thereby making a mixture of a gas and the particles in a powder of highly dispersed core particles;

(B) a transport step in which the highly dispersed core particles in said gas-particle mixture are transported directly to a subsequent coating step; and

(C) the coating step in which the transported core particles in said gas-particle mixture, as they have been dispersed with the dispersity β adjusted to the values within the ranges set forth above, are allowed to contact and/or impinge against the coat forming substance in the coating start region of the coating space, thereby starting the coating operation.

IV. A coating method comprising:

(A) a dispersing step in which the particles in the powder of core particles are dispersed in a gaseous atmosphere by the group of means for high dispersion treatment of particles which realize the adjustment of dispersity β to the values within the ranges set forth above, thereby making a mixture of a gas and the particles in a powder of highly dispersed core particles;

(B) a transport step in which the highly dispersed core particles in said gas-particle mixture are transported via at least one member indispensable to transport that is selected from the group consisting of a hollow member, an intermediate member composed of a member that forms a hollow portion, and a pipe; and

(C) a coating step in which the transported core particles in said gas-particle mixture, as they have been dispersed with the dispersity β adjusted to the values within the ranges set forth above, are allowed to contact and/or impinge against the coat forming substance in the coating start region of the coating space, thereby starting the coating operation.

V. A coating method comprising:

(A) a dispersing step in which the particles in the powder of core particles are dispersed in a gaseous atmosphere by the group of means for high dispersion treatment of particles which realize the adjustment of dispersity β to the values within the ranges set forth above, thereby making a mixture of a gas and the particles in a powder of highly dispersed core particles;

(B) a transport step in which the highly dispersed core particles in said gas-particle mixture are transported to a subsequent coating step via at least one means selected from the group consisting of means for maintaining the dispersion in a gaseous atmosphere of the highly dispersed core particles in said gas-particle mixture, means for

enhancing the dispersion in a gaseous atmosphere of the highly dispersed core particles in said gas-particle mixture, and means for separating a mixture of a gas and the particles in a powder of less highly dispersed core particles from said gas-particle mixture so as to select a mixture of a gas and the particles in a powder of highly dispersed core particles in which the core particles are present in the gaseous atmosphere mainly in a single-particle state; and

(C) the coating step in which the transported particles in said mixture of a gas and the powder of highly dispersed core particles, as they have been dispersed with the dispersity β adjusted to the values within the ranges set forth above, are allowed to contact and/or impinge against the coat forming substance in the coating start region of the coating space, thereby starting the coating operation.

In each of the coating methods I - V, it is preferred that the coating start region of the coating space is located in either one of the following portions of the space region in which the dispersity β of the particles in the powder of highly dispersed core particles as mixed with a gas and which have been dispersed by the group of means for high dispersion treatment of particles is adjusted to the values within the ranges set forth above.

the space region that includes planes through which all particles in the powder of highly dispersed core particles as mixed with a gas will pass; or

the space region that includes planes through which all particles to be recovered into the recovery section of the recovery means will pass.

Alternatively, in each of the coating methods I and II, it is preferred that at least one part of the dispersing step, in which the particles in the powder of core particles are dispersed in a gaseous atmosphere by the group of means for high dispersion treatment of particles which realize the adjustment of dispersity β to the values within the ranges set forth above, thereby making a mixture of a gas and the particles in a powder of highly dispersed core particles, is performed sharing one or more parts of the space with at least one part of the coating step.

It should be noted here that the coated diamond or high-pressure phase boron nitride particles occasionally form lumps as a result of association of several particles that contact one another via the coat forming substance on the coated particles. Thus, the powder of the coated diamond or high-pressure phase boron nitride particles consists of coated particles in a single-particle state, lumps formed by the association of from several to several tens of such discrete coated particles as a result of contacting one another, and larger lumps formed by the association of more of such discrete coated particles as a result of contacting one another, and the shapes and sizes of the particles and lumps are nonuniform and irregular. The lumps which are the associations of the discrete coated particles are preferably deagglomerated and/or otherwise reduced in size before they are subjected to the shaping (molding) or sintering process. To deagglomerate and/or otherwise reduce in size the associating lumps of the coated diamond or high-pressure phase boron nitride particles, various deagglomerating means may be utilized, as exemplified by ball mills, vibrating ball mills, mortars and jet mills, etc. Alternatively, the discrete coated particles may be selectively separated from the associating lumps of such discrete coated particles, so that only the discrete coated particles can be subjected to the shaping or sintering process.

In accordance with the present invention, the thus coated diamond or high-pressure phase boron nitride particles or mixtures containing such particles are then sintered at pressures no less than 2000 MPa and at elevated temperatures, or at pressures of less than 2000 MPa and at temperatures not exceeding 1850°C under such sintering pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable.

Alternatively, the coated diamond or high-pressure phase boron nitride particles are mixed with a bonding material in volume ratios of (1 - 80):(99 - 10) that is sinterable to a density of at least 85% at pressures less than 2000 MPa and at temperatures not exceeding 1850°C under such pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable, and the mixture is then sintered at pressures less than 2000 MPa and at temperatures not exceeding 1850°C under such sintering pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable.

If an auxiliary agent, or a substance that develops another function, is to be added, the substance may be in a powder, plate or particulate form. More specifically, the substance may be selected from among powders and/or particles, etc. that are composed of at least one member selected from the group consisting of metals, semiconductors, metalloids, and rare earth metals of groups 1a, 2a, 3a, 4a, 5a, 6a, 7a, 1b, 2b, 3b, 4b, 5b, 6b, 7b and 8 of the periodic table, as well as oxides, nitrides, carbides, oxynitrides, oxycarbides, carbonitrides, oxycarbonitrides, borides and silicides of these elements, as exemplified below:

Al, B, Si, Fe, Ni, Co, Ti, Nb, V, Zr, Hf, Ta, W, Re, Cr, Cu, Mo, TiAl, Ti_3Al, $TiAl_3$, TiB, NiAl, Nb_3Al, SiC, B_4C, Cr_3C_2, TiC, ZrC, WC, W_2C, HfC, TaC, Ta_2C, NbC, VC, Mo_2C, Si_3N_4, TiN, ZrN, Si_2N_2O, AlN, HfN, VxN (x = 1 ~ 3), NbN, TaN, Ta_2N, TiB, TiB_2, ZrB_2, VB, V_3B_2, VB_2, NbB, NbB_2, TaB, TaB_2, MoB, Mo_2B_4, MoB_4, Mo_2B, WB, W_2B, W_2B5, LaB_6, BP, $B_{13}P_2$, $MoSi_2$, Al_2O_3, ZrO_2 (PSZ: partially stabilized zirconia with the addition of Y_2O_3, MgO or CaO, or TZP: tetragonal zirconia polycrystalline compound), $MgAl_2O_4$ (spinel) and Al_6SiO_2 (mullite).

The auxiliary agent may be a fibrous substance. The fibrous substance to be mixed with the coated diamond or high-pressure phase boron nitride particles is composed of at least one of elemental metals and compounds and has such a morphology that the width is no more than 500 μm, with the length to width ratio being at least 2. The fibrous

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substance comprises bar- or rod-like substances having widths of no more than 500 μm, with the length to width ratio being at least 2, and/or filaments which are continuous fibers formed by melt spinning and/or short fibers produced by crystals themselves to give shape and/or whiskers produced by unidirectional crystal growth into a fibrous form. The whiskers comprise intrinsic whiskers which, according to the definition, are formed without experiencing any phase transition or any phenomenon such as chemical reactions that affect the overall volume and/or whiskers in the broad sense of the term which refer to single crystals that are formed as long needles by the growth of only one crystal face of the crystal that is created by a phase transition or a chemical change that affects the overall volume and/or other whiskers that are single crystals having cross sectional areas of no more than 8×10^{-6} in^2, with the length being at least 10 times the average diameter.

The fibrous substance to be used may be those which contain at least one compound containing at least one member of the group consisting of metals, semiconductors, metalloids, rare earth metals and nonmetals of groups 1a, 2a, 3a, 4a, 5a, 6a, 7a, 1b, 3b, 4b, 5b, 6b, 7b and 8 of the periodic table and which have widths of no more than 500 μm, with the length to width ratio being at least 2. More specifically, the fibrous substances to be used are those which are composed of at least one member selected from the group consisting of metals, semiconductors, metalloids, and rare earth metals of groups 1a, 2a, 3a, 4a, 5a, 6a, 7a, 1b, 3b, 5b, 4b and 8 of the periodic table, as well as oxides, nitrides, carbides, oxynitrides, oxycarbides, carbonitrides, oxycarbonitrides, borides and silicides and which have widths of no more than 500 μm, with the length to width ratio being at least 2. Preferably, the following fibrous substances may be selected: those which are composed of at least member one selected from the group consisting of Al, B, Si, Fe, Ni, Co, Ti, Nb, V, Zr, Hf, Ta, W, Re, Cr, Cu, Mo, TiAl, Ti_3Al, $TiAl_3$, TiNi, NiAl, Ni_3Al, SiC, B_4C, Cr_3C_2, TiC, ZrC, WC, W_2C, HfC, TaC, Ta_2C, NbC, VC, Mo_2C, Si_3N_4, TiN, ZrN, Si_2N_2O, AlN, HfN, VxN (x = 1 ~ 8), NbN, TaN, Ta_2N, TiB, TiB_2, ZrB_2, VB, V_3B_2, VB_2, MoB, NbB_2, TaB, TaB_2, MoB, MoB_2, MoB_4, Mo_2B, WB, W_2B, W_2B5, LaB_6, SP, $B_{13}P_2$, $MoSi_2$, Al_2O_3, ZrO_2 (PSZ: partially stabilized zirconia with the addition of Y_2O_3, MgO or CaO; or TZP: tetragonal zirconia polycrystalline compound), $MgAl_2O_4$ (spinel), Al_2SiO_5 (mullite), etc., and which have widths of no more than 500 μm, with the length to width ratio being at least 2.

As described above, the coated diamond or high-pressure phase boron nitride particles to be used in the present invention have their surfaces coated with the coat forming substance by vapor-phase processes and, hence, the coat forming substance that can be used is basically unlimited. While materials design of diamond or high-pressure phase boron nitride sinters can be made in any suitable manners depending on their use, the coating of diamond or high-pressure phase boron nitride particles with the coat forming substance may be preceded by preliminary coating of the surfaces of those surfaces with a similar and/or dissimilar coat forming substance by a similar and/or dissimilar coating technique.

Take, for example, the case where the surfaces of diamond or high-pressure phase boron nitride particles are to be eventually provided with coats formed of a desired metal carbide. In this case, those particles may be preliminarily coated with carbon. While the preliminary coating technique is not limited in any particular way, suitable examples include not only the molten salt dip method which is described in Unexamined Published Japanese Patent Application (kokai) Hei 2-252060 and the molten salt disproportionation method which is described in Unexamined Published Japanese Patent Application (kokai) Hei 1-207680 but also electroplating, electroless plating, cladding, physical vapor deposition processes (e.g., sputtering and ion plating) and chemical vapor deposition processes. The metals in the metal components to be eventually coated are not limited to any particular types as long as they are within the class of substances that can be applied as bonding materials and/or sintering aids for the purpose of the invention.

The coating films formed by the molten salt dip method are composed of dense substances having high hardness and melting point and, having typically the capability of isolating diamond or high-pressure phase boron nitride particles from other substances, these films offer the advantage of markedly increasing the latitude in the choice of binders. The diamond or high-pressure phase boron nitride particles provided with coating films by the molten salt dip method are difficult to sinter densely by the conventional process for producing diamond or high-pressure phase boron nitride sinters at pressures less than 2000 MPa under such sintering pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable. However, if diamond or high-pressure phase boron nitride particles that are coated with the films of high-hardness and high-melting substances which have been formed by the molten salt dip method are coated by the vapor-phase coating techniques of the invention with one or more layers in suitable amounts of substances that can be applied as bonding materials that are sinterable to assure satisfactory density and high hardness, favorable results are obtained that are advantageous for the purpose of promoting sintering.

In accordance with the present invention, coated diamond or high-pressure phase boron nitride particles which have the coat forming substance applied to the surfaces of bare diamond or high-pressure phase boron nitride particles by vapor phase processes may be mixed with a bonding material or, alternatively, the mixture of the coated diamond or high-pressure phase boron nitride particles and the bonding material may be mixed with the aforementioned auxiliary substance in a powder, plate or particulate form and/or the fibrous substance also mentioned above which has a width of no more than 500 μm, with the length to width ratio being at least 2, and either mixture may be sintered in a powder form or after being shaped into a compact.

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Diamond or high-pressure phase boron nitride is thermodynamically stable only at ultrahigh pressures and if the pressure is inadequate under elevated temperatures, they will experience a phase transition to the lower-pressure phase (graphite or hexagonal boron nitride (hBN)).

Therefore, in order to prevent the phase transition of diamond or high-pressure phase boron nitride to the lower-pressure phase (graphite or hBN) and to insure sintering to high density, the sinters containing diamond or high-pressure phase boron nitride are produced at ultrahigh pressures exceeding 2000 MPa and at elevated temperatures under such conditions that diamond or high-pressure phase boron nitride is thermodynamically stable.

Therefore, if one selects those sintering pressure and temperature conditions where the pressure is at least 2000 MPa and where diamond or high-pressure phase boron nitride is thermodynamically stable, the temperature is limited by pressure in accordance with the thermodynamic equilibrium line in the phase diagram of diamond or high-pressure phase boron nitride. However, if one selects those sintering pressure and temperature conditions where the pressure is at least 2000 MPa and where diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable, temperatures will suffice if they deviate slightly from the region that is limited by pressure in accordance with the thermodynamic equilibrium line in the phase diagram of diamond or high-pressure phase boron nitride.

On the other hand, if one selects those sintering pressure and temperature conditions where the pressure is less than 2000 MPa and where diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable, one should note that there is a pressure-dependent temperature in the region where diamond or high-pressure phase boron nitride is thermodynamically metastable.

Stated more specifically, in the case of selecting those sintering pressure and temperature conditions where diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable, the upper limit of the sintering temperature will vary with the quality of the diamond or high-pressure phase boron nitride particles to be sintered.

Take, for example, the case of diamonds; Hall conducted an experiment under ultrahigh pressures and reported that when a diamond was thermodynamically metastable if not stable, it took such a long time for a phase transition to occur that it remained stable for practical purposes; he then indicated the temperature 1100°C as the upper limit beyond which the diamond would no longer exist in a practically stable manner (see H.T. Hall, Science, 169 (1970) 868-869, as well as Fig. 15a). Speaking of high-pressure phase boron nitrides, Wakatsuki et al. conducted an experiment on a cubic boron nitride under ultrahigh pressures and reported that when the cubic boron nitride was thermodynamically metastable if not stable, it took such a long time for a phase transition to occur that it remained stable for practical purposes; they then indicated the temperature 1200°C as the upper limit beyond which the cubic boron nitride would no longer exist in a practically stable manner (see Wakatsuki, Ichise, Aoki and Maeda, Abstracts of the Lectures Read at the 14th Symposium on High-Pressure Technology (1972) p. 78, as well as Fig. 83b).

Therefore, if high-purity diamonds (e.g. natural products of high quality synthetic diamonds produced via the vapor phase by means of PVD or CVD processes, or diamonds synthesized by application of ultrahigh pressures over a long time) are especially selected and if they are sintered either by HIP, optionally under ultrahigh pressures, as they are confined within a degassed, pressure-transmitting capsule or by PC or HP under vacuum or in an inert gas, diamonds will actually exist up to 1950°C which is much higher than 1100°C, or the temperature reported by Hall, even if they are not in a thermodynamically stable state. However, if the temperature exceeds 1850°C, the diamonds will turn to the graphite phase in a short time. Generally speaking, synthesis catalysts or the like will sometimes remain as impurities in synthetic diamonds. However, if synthetic diamonds are such that impurities have been removed positively to achieve high purity, the diamond will exist up to 1700°C by application of similar sintering techniques and this is the same as in the case of natural diamonds. Alternatively, with known diamonds that do not contain fine grains smaller than 1 μm, preferably those which are at least 3 μm and whose size is within the class contemplated by the present invention, the diamond will exist up to 1900°C irrespective of whether they are natural or synthetic products. It should also be noted that in the case of known diamonds of comparatively high purity, both natural and synthetic products will exist up to 1800°C. However, with commonly known types of synthetic diamonds, the suitable temperature is up to 1400°C. Therefore, the upper limit of sintering temperatures is 1850°C.

Speaking of high-pressure phase boron nitrides, if those of high purity (e.g. cubic boron nitrides of ultrahigh purity that are produced via the vapor phase by means of PVD or CVD processes, or cubic boron nitrides of ultrahigh purity that are synthesized by application of ultrahigh pressures over a long time) are especially selected and if they are sintered either by HIP (hot isostatic pressing), optionally under ultrahigh pressures, as they are confined within a degassed, pressure-transmitting capsule or by PC (piston-cylinder) or HP (hot pressing) under vacuum or in an inert gas, cubic boron nitrides will actually exist up to 1950°C which is much higher than 1200°C, or the temperature reported by Wakatsuki et al., even if they are not in a thermodynamically stable state. However, if the temperature exceeds 1850°C, the cubic boron nitrides will turn to a graphitic phase in a short time. If conventionally known cubic boron nitrides are used after impurities have been removed positively to achieve high purity, the cubic boron nitride will exist up to 1700°C by application of similar sintering techniques. Alternatively, with known cubic boron nitrides that do not contain fine grains, preferably those which are at least 3 μm in size, the cubic boron nitride will exist up to 1900°C by application of similar sintering techniques. It should also be noted that in the case of known cubic boron nitrides of comparatively high purity, the cubic boron nitride will exist up to 1800°C by application of similar sintering techniques. However, in the case where

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commonly known types of cubic boron nitrides or wurtzitic boron nitrides are contained, the suitable temperature is up to 1400°C.

Consequently, if one selects those sintering pressure and temperature conditions where the pressure is less than 2000 MPa and where diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable, the upper limit of sintering temperatures is 1800°C. It should be remembered that the temperature at which the diamond or high-pressure phase boron nitride is not in a thermodynamically stable state but exists stably for practical purposes varies with the quality of the diamond or high-pressure phase boron nitride to be used and that, therefore, the sintering temperature must be set in accordance with the quality of the feed of diamond or high-pressure phase boron nitride. If it is necessary that the sintering temperature be set to a value that is close to the right temperature which matches the quality of the feed of diamond or high-pressure phase boron nitride, said sintering temperature must be controlled with close tolerance.

The diamond or high-pressure phase boron nitride sinters of the present invention are produced by sintering processes that adopt two kinds of conditions with different pressures. To produce diamond or high-pressure phase boron nitride sinters by performing sintering for a suitable period of time at ultrahigh pressures of 2000 MPa or above and at elevated temperatures, any conventional equipment that produces ultrahigh pressures can be applied without particular limitations, as exemplified by the cubic, tetragonal, girdle, and belt type ultrahigh pressure apparatus.

Known apparatus and methods may be applied without any particular limitations to produce dynamic ultrahigh pressures (≥ 2000 MPa) and elevated temperatures and they include: an explosive charge lens (planar explosion generator) ... a cylindrical explosion generator, a method involving collision with a flying object, a magnetic implosion method, a Mach explosion method, an excessive explosion method, a conical implosion method, a single-action shock gun, a double-action light gas gun, etc. According to these apparatus and methods which generate dynamic ultrahigh pressures and elevated temperatures, the pressure that can be produced is at least 10 GPa (10,000 MPa), preferably at least 40 GPa and, therefore, they can be selected as preferred examples in cases where particularly high pressures need be exerted for short periods of time.

Depending on the object, for example, in the case where samples need be pressurized while giving results with good reproducibility, the above-mentioned cubic apparatus and various other types of equipment that are capable of generating ultrahigh temperatures in a static manner may be used to produce pressures of 2000 MPa and above. The sintering temperature condition may deviate slightly from the region where diamond or high-pressure phase boron nitride is thermodynamically stable.

But, more preferably, one may select those sintering pressure and temperature conditions where the pressure is at least 2000 MPa and where diamond or high-pressure phase boron nitride is thermodynamically stable.

To produce diamond or high-pressure phase boron nitride sinters by performing sintering for a suitable period of time at pressures less than 2000 MPa and at temperatures not exceeding 1800°C under such sintering pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable, any conventional equipment can be applied without particular limitations, as exemplified by PC (piston-cylinder) type ultrahigh pressure apparatus, ultrahigh pressure HIP (hot isostatic pressing) apparatus, HIP apparatus and HP (hot pressing) apparatus.

If the PC type ultrahigh pressure apparatus is to be used, pressures less than 2000 MPa may be applied but, considering the durability of this apparatus, the pressure does not preferably exceed 1600 MPa. Conventionally known technologies concerning the production of pressures include ultrahigh pressure HIP apparatus which is capable of operating at HIP pressures up to 1000 MPa, as well as HIP apparatus (excluding the ultrahigh pressure HIP apparatus) and HP apparatus which are each capable of operating at pressures up to 200 MPa.

The diamond or high-pressure phase boron nitride sinters produced by the methods described above have high performance with highly controlled microstructures. While their most common use is as machine parts, it is possible to manufacture diamond or high-pressure phase boron nitride sinters that are superhard, with the Vickers hardness (Hv) being preferably at least 800, and which are dense, with the density being at least 85%. Preferably, it is possible to manufacture diamond or high-pressure phase boron nitride sinters that are superhard, with the Vickers hardness (Hv) being preferably at least 800, and/or which are dense, with the density being at least 90%. More preferably, considering the application to highly wear-resistant machine parts, superhard (Hv ≥ 1000) diamond or high-pressure phase boron nitride sinters can be manufactured by both increasing the relative content of diamond or high-pressure phase boron nitride and sintering to high density. For use in tools and other applications that require even higher levels of wear resistance, diamond or high-pressure phase boron nitride sinters having Vickers hardness values of at least 2000 can be manufactured by further increasing the content of diamond or high-pressure phase boron nitride while sintering to high density.

In a typical case, a diamond sinter may be produced from a diamond powder feed in the following manner using a cubic apparatus to produce ultrahigh pressures. First, the particles in the diamond powder are coated with a suitable coat forming substance on the surfaces. The coated diamond particles are then shaped into a pellet by stamping. The pellet is surrounded by a shaped hexagonal boron nitride (h-BN) part which, in turn, is enclosed with a graphite tubular heater. Provided around the heater as a solid pressure transmitting medium is pyrophyllite from which the walls of

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crystallization has been removed by heat treatment at 700°C. The sample thus prepared is placed in the cubic apparatus; the pressure is increased to a predetermined level and, then, the temperature is also elevated to a predetermined level and sintering is effected for a suitable time. Thereafter, the temperature is lowered and the pressure is also reduced. The pressure-transmitting medium is taken out of the cubic ultrahigh pressure apparatus and the sample is then recovered from the medium. In this way, one can produce a diamond sinter of high performance that is composed of diamond and which is characteristic in that it has a controlled distribution of the bonding material and/or sintering aid and/or surface modifier, that is uniform and dense, and that it has a highly controlled microstructure.

As described in detail on the foregoing pages, a powder of fine diamond or high-pressure phase boron nitride core particles having an average diameter of no more than 10 μm in terms of frequency distribution by volume was dispersed in a gaseous atmosphere and the core particles thus dispersed to a dispersity β of at least 70% were allowed to contact or impinge against a precursor of a coat forming substance, whereby the core particles were covered on their surfaces with the coat forming substance in a single-particle state. In accordance with the invention, the thus coated core particles or mixtures containing them were sintered at ultrahigh atmospheres of at least 2000 MPa and at elevated temperatures, whereby coated diamond or high-pressure phase boron nitride sinters of high performance were produced that had uniform, dense, firmly sintered and highly controlled microstructures.

According to another aspect of the invention, said core particles or mixtures containing them or mixtures of said core particles with bonding materials are sintered at pressures less than 2000 MPa and at temperatures not exceeding 1650°C under such sintering pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable, whereby one can produce coated diamond or high-pressure phase boron nitride sinters of high performance that have uniform, dense, firmly sintered and highly controlled microstructures. This offers the advantage of eliminating the constraint of the need to use equipment capable of creating ultrahigh pressures of at least 2000 MPa. It should be particularly noted that the use of ultrahigh pressure HIP apparatus or other types of HIP apparatus offers the added advantage of enabling the production of complexly shaped sinters, thereby presenting significant benefits to manufacture on an industrial scale.

According to yet another aspect of the invention, even pseudo-fine diamond or high-pressure phase boron nitride particles having an average diameter greater than 10 μm in terms of frequency distribution by volume may be covered with coat forming substances after being dispersed to a dispersity as determined by their average diameter. By sintering the thus coated pseudo-fine particles, one can produce sinters that are substantially free from graphite or a graphitic phase and which have the same features as fine particulate sinters having an average particle diameter of no more than 10 μm.

EXAMPLES

The diamond or high-pressure phase boron nitride sinters of the present invention, as well as the processes for their production are described below with reference to examples.

Example 1

Diamond particles having an average diameter (D_{50}) of 1 μm and a frequency distribution by volume of ($D_{50}/2 \leq 3D_{50}/2$), $\alpha \geq 80\%$) were coated with elemental silicon.

The construction of the apparatus used is shown in Fig. 6 and Fig. 7 which is a partial enlarged view of Fig. 6; the apparatus is a specific example of the design shown in Fig. 3a.

As shown, the apparatus comprises: a plasma torch 3-A including a plasma chamber 3-a, a vessel 3-B for coating a coat forming substance precursor generating chamber 3-b, a coating chamber coating vessel 3-C in the narrow sense of the term, a coating chamber 3-c in the narrow sense of the term, a vessel 3-D for coating a coated particle coating chamber 3-d, a supply unit 3-E1 on the side where the feed of the coat forming substance is supplied, an agitating disperser 3-F1 and an ejector-type disperser 3-H1 which are on the side where a powder of core particles is supplied, a capillary disperser 107, and a coated particle recovery section 3-G. The supply unit 3-E1 is coupled to a feeder 112 equipped with a vessel for supplying the feed powder of the coat forming substance, and the agitating disperser 3-F1 is coupled to a feeder 111 equipped with a vessel for supplying the powder of core particles. According to the definition, the coating chamber used in Example 1 is composed of the plasma chamber 3-a, the coat forming substance precursor generating chamber 3-b, the coating chamber 3-c in the narrow sense of the term, and the coated particle coating chamber 3-d. These make up the coating chamber in the broad sense of the term and the chamber 3-c where most part of the coating operation is performed is referred to as the "coating chamber in the narrow sense of the term".

The group of means for high dispersion treatment of particles c used in Example 1 is composed of the feeder 111 equipped with a supply vessel, agitating disperser 3-F1, ejector-type disperser 3-H1, and the capillary disperser 107 which is made of a stainless steel pipe having an inside diameter of 4 mm. The basic concept of the group is shown in Fig. 2a and it is a specific example of the group of means for high dispersion treatment of particles that is of the design shown in Fig. 3b. The group is designed in such a way that it can realize an output value β of at least 70% (β ≥ 70%).

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given the particles in a powder of diamond core particles that are characterized by (D_{50}/5, SD_{50}) ≥ 90%) where D_{50} = 1 μm. The capillary disperser 107 which is the final means of treatment in the group of means for high dispersion treatment of particles is coupled directly to the coating chamber 3-c and designed in such a way as to realize β ≥ 70% in the coating start region 3-L1 of the coating space 3-L3.

A gas jet port 101 is provided on top of the plasma torch 3-A and an argon gas is supplied from a supply source 102 through this port at a rate of 30 L/min. The supplied argon gas is turned into a plasma by applied high-frequency waves, thereby forming a plasma flame in the plasma chamber 3-a within the plasma torch 3-A.

A silicon powder comprising particles with an average diameter of 10 μm serves as the feed of the coat forming substance and is supplied from the feeder 112 equipped with a vessel for supplying the feed powder of the coat forming substance. The supplied silicon powder is carried by a carrier gas 103 flowing at a rate of 5 L/min so that it is introduced into the plasma flame at a rate of 0.2 g/min via an inlet 104 provided at the bottom of the plasma torch 3-A. Being evaporated by the heat of the plasma flame, the silicon powder goes through the vapor phase to become the precursor of the coat forming substance in the precursor generating chamber 3-b.

The diamond core particles with an average diameter of 1 μm are supplied at a rate of 1.2 g/min from the feeder 111 equipped with a supply vessel of the core particles and they are dispersed with the agitating disperser 3-F1 while being carried by a carrier gas 105 that is supplied at a rate of 5 L/min. The particles are then dispersed to a dispersity (β) of 82% by means of the ejector-type disperser 3-H1 and the capillary disperser 107 with the aid of a dispersing gas 106 that is supplied at a flow rate of 10 L/min. The thusly dispersed core particles are introduced into the coating chamber.

The highly dispersed diamond particles entering the coating start region 3-L1 of the coating space 3-L2 start to contact and/or impinge against the precursor of the coat forming substance as they maintain the dispersity β at 82%.

Thus, the diamond particles are given the coat of the coat forming substance on their surfaces and they descend down the coated particle cooling chamber 3-d together with the gas, eventually reaching the recovery section 3-G. The product comprising the coated particles is separated from the gas 109 by means of a filter 110 and collected for recovery.

The recovered fine diamond particles having silicon coats on the surfaces were examined with a scanning electron microscope. As Fig. 8 shows, all of these particles were uniformly coated with superfine silicon particles of about 0.005 μm in size. The silicon coating weight was 20% by volume.

The resulting powder of diamond particles coated with 20 vol% silicon was stamped into a pellet having an outside diameter of 6 mm and a height of 2 mm. The pellet was buried in a pressure-transmitting medium surrounded by a shaped hexagonal boron nitride (h-BN) and it was vacuum-dried overnight at 800°C and at 10^{-3} torr to remove low-boiling impurities. The pellet was then set in a cubic ultrahigh pressure apparatus, the pressure was raised to 5.5 GPa at room temperature, then the temperature was elevated to 1450°C, which was held for 30 min, thereafter, the temperature was lowered and the pressure reduced.

The resulting sinter was examined by X-ray diffractometry, the elemental silicon reacted with the diamond to change to both diamond and SiC while the elemental silicon disappeared. Quantification by X-ray analysis showed that the volume proportions of the diamond sinter and SiC were about 78% and 22%, respectively.

The surface of the sinter was polished with a diamond paste and its Vickers microhardness (Hv) was measured. The diamond sinter synthesized in Example 1 was superhard with the Hv (0.5/10) being about 12,000 and this value was comparable to or higher than that of a commercial cutting tool made of sintered diamond. Furthermore, the hardness of the sinter of Example 1 was uniform over the entire surface subjected to the hardness measurement and it was substantially free from variations.

The polished surface of the sinter resulting of the example 1 was coated with a gold film by a customary evaporation technique and examined with an electron microscope. The result is shown in the Fig. 9 electron micrograph (X5000), from which one can see that the sinter had a relative density of at least 90%. In addition, the sinter had no portion left unsintered. In areas where diamond particles contacted each other via a thin layer of the coat forming substance, the latter was bonded by the contiguous diamond particles, which hence were coupled directly as a result of sintering. In all other areas, SiC was distributed to surround the diamond particles, rendering the sinter to be characteristic in that it was dense, uniform and had the bonding material distributed provide a highly controlled microstructure. It should also be noted that the diamond particles in the sinter did not grow at all compared to the particles in the feed powder and that the coating on the diamond was formed by chemical reaction between the diamond and the elemental silicon which served as the coat forming substance; these facts combined together to offer the characteristic feature that the diamond particles in the sinter were finer than those in the feed although they were coated with silicon. This is very favorable and, hence, ideal for the mechanical characteristics of the sinter. The differences can be clearly seen by comparing Fig. 9 with Fig. 10 which is an electron micrograph (X5000) of a polished surface of the above-mentioned commercial cutting tool that was made of sintered diamond and which was coated with a gold film by a customary evaporation technique for examination. Obviously, the bonding material and the sintering aid were distributed irregularly in the diamond sinter of the commercial cutting tool to form lumps in certain areas. On the other hand, the number of areas that were devoid of the necessary sintering aid and bonding material was by no means small and unsintered portions were found there. Another major difference from the sinter of Example 1 was that every diamond particle in the cutting tool was coarse.

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Diamond is the most difficult to sinter of all substances that exist on the earth. In spite of this fact, the coated particles in a diamond powder that were synthesized in Example 1 in accordance with the invention behaved as if they were comparatively easy-to-sinter particles under industrially feasible ultrahigh pressures and elevated temperatures, thereby forming a dense, rigid and superhard structure.

Example 2

Cubic boron nitride particles having an average diameter (D_{50}) of 1 μm and a frequency distribution by volume of ($D_{90}/2$, $3D_{90}/2$), α (90%) were coated with alumina.

The construction of the apparatus used is shown in Fig. 11 and Fig. 12 which is a partial enlarged view of Fig. 11; the apparatus is a specific example of the design shown in Fig. 5d.

As shown, the apparatus comprises: a plasma torch 5-A including a plasma chamber 5-a, a vessel 5-B for cooling a coat forming substance precursor generating chamber 5-b, a coating chamber cooling vessel 5-C in the narrow sense of the term, a coating chamber 5-c in the narrow sense of the term, a vessel 5-D for cooling a coated particle cooling chamber 5-d, a supply unit 5-E1 on the side where the feed of the coat forming substance is supplied, an agitating disperser 5-F1 which is on the side where a powder of core particles is supplied, a capillary disperser 211 and a disperser 5-H2 that utilizes an impingement plate, and a coated particle recovery section 5-G. That part of this apparatus which was to generate the precursor of the coat forming substance was of the same design as in Example 1. The group of means for high dispersion treatment of particles α was composed of a feeder 214 equipped with a supply vessel, the agitating disperser 5-F1, the capillary disperser 211, and the disperser 5-H2 that utilizes an impingement plate. The basic concept of the group α is shown in Fig. 3a and it is a specific example of the group of means for high dispersion treatment of particles that is of the design shown in Fig. 3b. The capillary disperser 211 is made of a stainless steel pipe having an inside diameter of 4 mm. The disperser 5-H2 is the final means of treatment in the group of means for high dispersion treatment of particles α and it consists of a 5-G impingement plate 213 supported by a stainless steel holder 212. The disperser 5-H2 is contained in the coating chamber 5-c in the narrow sense of the term, which shares the space with the group of means for high dispersion treatment of particles α. A coating space 5-L1 and the coating start region 5-L2 of the coating space are also contained in the coating chamber 5-c in the narrow sense of the term. The group of means α in the apparatus of Example 2 has such performance that the particles in a powder of core particles having an average diameter (D_{50}) of 1 μm and a frequency distribution by volume of ($D_{90}/2$, $3D_{90}/2$), α (90%) can be dispersed to a dispersity (β) of at least 70% (β ≥ 70%) right after impingement against the plate 213 in the disperser 5-H2 at the last stage of dispersion treatment. Therefore, coating of the core particles starts with the dispersity β held at 70% and above.

A gas jet port 201 is provided on top of the plasma torch 5-A and an argon gas is supplied from a supply source 202 through this port at a rate of 20 L/min. The supplied argon gas is turned into a plasma by applied high-frequency waves, thereby forming a plasma flame in a plasma chamber 5-a within the plasma torch 5-A.

An alumina powder comprising particles with an average diameter of 2 μm serves as the feed of the coat forming substance and is supplied at a rate of 1.0 g/min from a feeder 315 equipped with a vessel for supplying the feed powder of the coat forming substance. The supplied alumina powder is carried by a carrier gas 203 flowing at a rate of 5 L/min so that it is introduced into the plasma flame via an inlet 304 of the feed of the coat forming substance provided at the bottom of the plasma torch 5-A. Being evaporated by the heat of the plasma flame, the alumina powder goes through the vapor phase to become the precursor of the coat forming substance in a coat forming substance precursor generating chamber 5-b.

The core particles of cubic boron nitride are supplied at a rate of 0.7 g/min from the feeder 214 equipped with a vessel for supplying the powder of core particles and they are dispersed with the agitating disperser 5-F1 while being carried by a carrier gas 206 that is supplied at a rate of 20 L/min. The particles then pass through the capillary disperser 211 to enter the disperser 5-H2 with the impingement plate in the coating chamber, in which they are dispersed in a gaseous atmosphere to a dispersity (β) of 82%.

The highly dispersed core particles of cubic boron nitride, entering the coating start region 5-L1 of the coating space 5-L2 start to contact and/or impinge against the precursor of the coat forming substance as they maintain the dispersity β of 82%.

Thus, the cubic boron nitride particles are given the coat of the coat forming substance on their surfaces and they descend down a coated particle cooling chamber 5-d together with the gas, eventually reaching a coated particle recovery section 5-G. The product comprising the coated cubic boron nitride particles is separated from the gas 309 by means of a filter 210 and collected for recovery. The recovered cubic boron nitride particles had alumina coats in an amount of 60% by volume.

The recovered fine cubic boron nitride particles having alumina coats on their surfaces were examined with a scanning electron microscope. All of those particles were uniformly coated with superfine alumina particles of about 0.005 μm in size.

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The resulting cubic boron nitride particles with 30 vol% alumina were stamped into a pellet having a diameter of 8 mm and a thickness of 6 mm. The pellet was put into a Pyrex glass capsule of generally the same design as in Example 1 and sealed after degassing by heating.

Thereafter, the encapsulated pellet was set in a ultrahigh pressure HIP apparatus and sintered by holding at a temperature of 1200°C and at a pressure of 1030 MPa for 3 h.

The sinter of Example 2 was checked for its crystalline phase by powder X-ray diffraction and no diffraction peaks were observed except for the cubic boron nitride and α-form alumina.

As Table 4 shows, the sinter was considerably dense, with a density of 98.8%, and at the same time it was superhard, with the Vickers microhardness being Hv (0.5/10) = 3750.

It should also be mentioned that the cubic boron nitride particles in the sinter were surrounded by alumina to provide a uniform distribution and a highly controlled microstructure.

Example 3

Quasi-fine diamond particles having an average diameter (DM) of 17 μm and a frequency distribution by volume of ([DM/2, 3DM/2], ≥ 80%) were coated with metallic zirconium.

The construction of the apparatus used is shown in Fig. 13 and Fig. 14 which is a partial enlarged view of Fig. 16; the apparatus is a specific example of the design shown in Fig. 5b.

As shown, the apparatus comprises: a plasma torch 6-A including a plasma chamber 6-a, a vessel 6-B for cooling a coat forming substance precursor generating chamber 6-b, a coating chamber cooling vessel 6-C in the narrow sense of the term, a coating chamber 6-c in the narrow sense of the term, a vessel 6-D for cooling a coated particle cooling chamber 6-d, a supply unit 6-E1 on the side where the feed of the coat forming substance is supplied, an agitating disperser 6-F1, a cyclone 6-I, a hopper 6-J and a rotary valve 6-K which are on the side where a powder of core particles is supplied, a pipe 307 inevitable to transport, and a coated particle recovery section 6-G. That part of this apparatus which was to generate the precursor of the coat forming substance was of the same design as in Example 1. The group of means for high dispersion treatment of particles α was composed of a feeder 312 equipped with a supply vessel, the agitating disperse 6-F1 which is dispersing means, and the cyclone 6-I which is means for selecting a mixture of a gas and the particles in a powder of highly dispersed core particles. The basic concept of the group α is shown in the Fig. 3b block diagram. The section of cyclone 6-I discharging the mixture of a gas and the particles in a powder of highly dispersed core particles is connected to the coating chamber 6-c in the narrow sense of the term by means of the pipe 307 inevitable to transport, whereas the section of cyclone 6-I discharging the powder portion consisting of less highly dispersed core particles is connected to the agitating disperser 6-F1 by means of a transport pipe 310 via the hopper 6-J and the rotary valve 6-K. Using the group of means α in the apparatus of Example 3, the particles in a powder of core particles having an average (DM) of 17 μm and a frequency distribution by volume of ([DM/2, 3DM], ≥ 80%) can be dispersed to a dispersity (β) of at least 85% in the section of cyclone 6-I (i.e., the means of final treatment) discharging the powder stream of highly dispersed particles. As shown, the coating space 6-L2 and the coating start region 6-L1 of this coating space are contained in the coating chamber 6-c in the narrow sense of the term. Because of the constraint by the flange portion coupling a coating chamber cooling vessel 6-C in the narrow sense of the term with the vessel 6-D for cooling the coated particle cooling chamber 6-d, the pipe 307 was indispensable to transport, but the resulting drop in dispersity β could be held at a reduced level. Hence, coating of the core particles starts with the dispersity β held at 80% and above in the coating start region.

A gas jet port 301 is provided on top of the plasma torch 6-A and an argon gas is supplied from a supply vessel 302 through this port at a rate of 40 L/min. The supplied argon gas is turned into a plasma by applied high-frequency waves, thereby forming a plasma flame in the plasma chamber 6-a within the plasma torch 6-A.

A zirconium powder serving as the feed of the coat forming substance is supplied at a rate of 0.8 g/min from a feeder 314 equipped with a vessel for supplying the feed powder of the coat forming substance. The supplied zirconia powder is carried by a carrier gas 303 flowing at a rate of 5 L/min so that it is introduced into the plasma flame via an inlet 304 the feed of the coat forming substance provided at the bottom of the plasma torch 6-A. Being evaporated by the heat of the plasma flame, the zirconia powder goes through the vapor phase to become the precursor of the coat forming substance in the coat forming substance precursor generating chamber 6-b.

Diamond core particles are supplied at a rate of 2.0 g/min from the feeder 313 equipped with a vessel for supplying the powder of core particles and they are dispersed with the agitating disperser 6-F1 while being carried by a carrier gas 305 that is supplied at a rate of 15 L/min. The particles then pass through a pipe 308 and thence enter the cyclone 6-I. The cyclone 6-I is adjusted in such a way that the fines produced will have a maximum particle diameter of 20 μm; a mixture of the gas and the particles in a powder of highly dispersed (β = 85%) core particles which are mostly single particles passes through the pipe 307 which is indispensable to transport, so that it is discharged into the coating chamber 6-c in the narrow sense of the term via a discharge port 306. On the other hand, the powder portion consisting of less highly dispersed core particles which have been selectively separated by cyclone 6-I passes through hopper 6-J and

rotary valve 6-K to be transported through a pipe 310 by a carrier gas 309 flowing at a rate of 10 L/min so that it is fed back to the agitating disperser 6-F1.

The highly dispersed diamond particles entering the coating start region 6-L1 of the coating space 6-L3 start to contact and/or impinge against the precursor of the coat forming substance as they maintain the disperstty (β) of 80%.

Thus, the diamond particles are given the coat of the coat forming substance on their surfaces and they descend down a coated particle cooling chamber 6-d together with the gas, eventually reaching a coated particle recovery section 6-G. The product comprising the coated diamond particles is separated from the gas 311 by means of a filter 312 and collected for recovery.

The recovered diamond particles having zirconium coats on the surfaces were examined with a scanning electron microscope. All of these particles were uniformly coated with superfine zirconium particles of about 0.005 μm in size. The zirconium coating weight was 10% by volume.

To provide a bonding material for binding the resulting zirconium-coated diamond particles, another lot of diamond particles were coated with titanium carbide under generally the same conditions as those used to produce the zirconium-coated diamond particles, thereby producing a coated diamond powder in which fine diamond particles of diameters ranging from 0.5 to 2 μm (average diameter = 1 μm) were coated with 15 vol% of titanium carbide. Thirty percent by volume of the previously prepared zirconium-coated diamond particles were wet mixed in acetone with seventy percent by volume of the thus prepared titanium carbide coated diamond particles. The mixture was stamped to a pellet having an outside diameter of 6 mm and a height of 2 mm. The pellet was buried in a pressure-transmitting medium surrounded by a shaped hexagonal boron nitride (h-BN) part and it was vacuum-dried overnight at 200°C and at 10^{-3} torr to remove low-boiling impurities. The pellet was then set in a cubic ultrahigh pressure apparatus, the pressure was raised to 5.5 GPa at room temperature, then the temperature was elevated to 1430°C, which was held for 30 min; thereafter, the temperature was lowered and the pressure reduced.

The resulting sinter was examined by X-ray diffractometry and only diamond, zirconium carbide and titanium carbide were found in it. The sinter was dense with a relative density of at least 99%. Quantification by X-ray analysis showed that the volume proportions of diamond, zirconium carbide and titanium carbide were about 86%, 3% and 11%, respectively.

The sinter was dense and rigid, forming a very highly controlled microstructure.

Example 4

Coated diamond particles were prepared by coating the bare diamond particles of Example 1 with various coat forming substances using apparatus of the same types as used in Examples 1 - 3. The names of the coat forming substances used to prepare the coated diamond particles and their coating weights (relative proportions by vol%), as well as the specific types of the apparatus used and the conditions for their use (coating operation) are shown in Table 1 together with the data for Example 1.

The coated diamond particles thus obtained were examined with a scanning electron microscope. All of the particles prepared in Runs 4-1 and 4-2 were uniformly covered with superfine particles of coat forming substances in sizes of about 0.005 μm.

The apparatus used in Run 4-1 was of the same type as used in Example 2, a metallic zirconium powder having an average diameter of 12 μm was supplied as a feed of coat forming substance from the feeder 215 at a rate of 0.6 g/min, and the core diamond particles were supplied from the feeder 214 at a rate of 1.2 g/min. The other conditions in Run 4-1 were the same as in Example 2.

The apparatus used in Run 4-2 was of the same type as used in Example 3, the group of means for high dispersion treatment of particles in this apparatus was to treat core diamond particles having an average diameter D_{sv} of 1 μm and a distribution by volume of ($[D_{sv}/6, SD_{sv}] \geq 90\%$), so the particles in the powder of core particles could be dispersed to a disperstty of 75% or more (β ≥ 75%) at the discharge section of cyclone 6-I, making it possible to start the coating operation at a disperstty of 70% or more (β ≥ 70%) in the coating start region. In Run 4-2, a metallic titanium powder was supplied as a feed of coating forming substance from the feeder 314 at a rate of 0.9 g/min and the core diamond particles were supplied from the feeder 313 at a rate of 1.2 g/min; the cyclone 6-I was adjusted in such a way that the fines produced would have a maximum particle diameter of 1.5 μm and the disperstty that could be attained in the discharge section was 85% (β = 85%) whereas the disperstty attainable in the coating start region was 82% (β = 82%); the other conditions in Run 4-2 were the same as in Example 3.

The apparatus used in Runs 4-7 and 4-8 were both of the same type as used in Example 1 and operated under generally the same conditions as in Example 1 except that aluminum and metallic nickel were deposited in that order to give a total coating weight of 15% in Run 4-7 as calculated for NiAl (Al to Ni molar ratio being 1:1) and 20% in Run 4-8 for Ni_3Al (Al to Ni molar ratio being 1:3).

The thus prepared powders of coated diamond particles or mixtures thereof with silicon carbide whiskers (addition aids) were shaped as in Example 1 and set in a cubic ultrahigh pressure apparatus; the pressure was raised to 5.5 GPa

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at room temperature, then the temperature was elevated to 1450 - 1460°C, which was held for 30 min; thereafter, the temperature was lowered and the pressure reduced.

In Runs 4-9 and 4-10, 30% by volume of the titanium carbide and silicon carbide coated diamond particles prepared in Runs 4-4 and 4-6, respectively, were wet mixed in acetone with 10% by volume of silicon carbide whiskers as a fibrous substance (SiC: width = 0.3 μm; average length = 30 μm) and subsequently vacuum dried to produce dry blends.

Each of the sinters thus produced was entirely free from pores, could be densified to a relative density of 100% and had no portion left unsintered. As in Example 1, the surfaces of the sinters were polished with a diamond paste and their Vickers microhardness Hv (0.5/10) values were measured. The results are shown in Table 1 together with the sintering conditions including the data for Example 1.

The crystalline phases of the sinters were examined by powder X-ray diffraction. In Run 4-1, only diamond and ZrC were observed and quantification by X-ray analysis showed that the volume proportions of diamond and ZrC were about 78% and 22%, respectively. In Run 4-2, only diamond and TiC were observed and quantification by X-ray analysis showed that the volume proportions of diamond and TiC were about 76% and 24%. In Runs 4-3 to 4-8, only diamond and the coat forming substances used (TiC, TiC, SiC, SiC, NiAl and Ni_3Al, respectively) were observed. In Run 4-9, only diamond and TiC were observed in addition to SiC. In Run 4-10, only diamond and SiC were observed.

All of the sinters thus produced were superhard, dense, uniform and had a uniform distribution of bonding materials to establish highly controlled microstructures. In particular, the composite sinters produced in Runs 4-9 and 4-10 had highly controlled microstructures in which the TiC bonding material (Run 4-9) or SiC bonding material (Run 4-10) and the SiC whiskers were dispersed uniformly between coated diamond particles.

Table 1

Run No.	Raising Promotion			Coating Solution			Sintering Conditions			Sinter		
	Core Reaction Element	Core Forming Substance		Coating Agent	Coating Solution Concentration (Approximate Value)		Pressure	Temperature	Time	Kind	Density	Average Size
		Name	Amount									
				Kind	Ex. or Com. No.		GPa	°C	min		%	nm
1	60	S1	20	-	1	1	5.2	1450	30	CB	100	12000
4-1	60	S1	20	-	2	4-1	5.5	1450	30	CB	100	11500
4-2	60	S1	20	-	3	4-2	5.2	1450	30	CB	100	11500
4-3	60	S1C	10	-	1	1	5.5	1450	30	CB	100	12000
4-4	60	S1C	20	-	1	4-3	5.5	1450	30	CB	100	11800
4-5	60	S1C	20	-	1	4-4	5.5	1450	30	CB	100	12000
4-6	10	S1C	30	-	2	4-5	5.5	1450	30	CB	100	11800
4-7	60	S1AL	10	-	1	1	5.5	1450	30	CB	100	1800
4-8	60	S1AL	20	-	1	4-2	5.3	1450	20	CB	100	4300
4-9	72	S1C	18	10	1	4-4	5.5	1450	20	CB	100	3650
4-10	72	S1C	18	10	1	4-6	5.5	1450	20	CB	100	3400

CB: Cubic silicon nitride presence apparatus

Example 5

Using apparatus of the same types as used in Examples 1 - 3, high-pressure phase boron nitride powder particles, or cubic boron nitride (cBN) particles of the same type as used in Example 2 that had an average diameter (D_{50}) of 1 μm and a frequency distribution by volume of ($D_{90}/2$, $3D_{10}/2$), ≥ 90%) were covered with various coat forming substances. The names of the coat forming substances used to prepare the coated cubic boron nitride particles and their coating weights (relative proportions by vol%), as well as the specific types of the coating apparatus used and the conditions for their use (generally the same) are shown in Table 2.

The apparatus used in Run 5-1 was of the same type as used in Example 1; a metallic zirconium powder having an average diameter of 12 μm was supplied as a feed of coat forming substance from the feeder 112 at a rate of 0.8 g/min, and the cubic boron nitride core particles were supplied from the feeder 111 at a rate of 1.2 g/min. The other conditions in Run 5-1 were the same as in Example 1. The apparatus used in Run 5-2 was of the same type as used in Example 2; a metallic titanium powder having an average diameter of 25 μm was supplied as a feed of coat forming substance at a rate of 0.4 g/min whereas the core particles were supplied at a rate of 1.2 g/min; the other conditions in Run 5-2 were the same as in Example 2.

The apparatus used in Run 5-3 was of the same type as used in Example 3. Notwithstanding the difference in the core particles used (diamond or cubic boron nitride), the values of dispersity (β) attained in the discharge section of cyclone 6-1 and in the coating start region were the same as in Run 4-2 and titanium nitride as a feed of coat forming substance was supplied at a rate of 0.6 g/min whereas the core particles were supplied at a rate of 2.0 g/min. The other conditions in Run 5-3 were the same as in Example 3.

The coated cubic boron nitride particles thus prepared were examined with a scanning electron microscope. All of the particles prepared in Runs 5-1 to 5-3 were uniformly covered with superfine particles (ca. 0.005 μm) of coat forming substances as Fig. 15 shows (particularly for the case of Run 5-1).

The coating with NiAl in Run 5-14 and with Ni_3Al in Run 5-13, as well as the production of mixtures with SiC whiskers in Runs 5-15 and 5-16 were performed as in Runs 4-7 to 4-10, respectively.

The thus prepared powders of coated cubic boron nitride particles or mixtures thereof with SiC whiskers were shaped as in Example 1 and set in a cubic ultrahigh pressure apparatus; the pressure was raised to 5.1 - 5.6 GPa at room temperature, then the temperature was elevated to 1450 - 1500°C, which was held for 30 min; thereafter the temperature was lowered and the pressure reduced.

Each of the thus produced sinters was entirely free from pores, could be densified to a relative density of 100% and had no portion left unsintered. As in Example 1, the surfaces of the sinters were polished with a diamond paste and their Vickers microhardness Hv (0.5/10) values were measured. The results are shown in Table 2 together with the sintering conditions.

The crystalline phases of the sinters were examined by powder X-ray diffraction. In Run 5-1, Zr reacted with the cubic boron nitride, whereupon metallic Zr disappeared, changing to cubic boron nitride, ZrN and ZrB_2 which were found to be present in respective volume proportions of about 77%, 14% and 9% according to quantification by X-ray analysis. In the sinter of Run 5-2, only cubic boron nitride, TiN and TiB_2 were observed and their respective volume proportions were about 74%, 15% and 11%. In Runs 5-3 to 5-14, only the cubic boron nitride and the coating forming substances used (TiN, TiN, AlN, AlN, α- and β-Si_3N_4, α- and β-Si_3N_4, α-Al_2O_3, α-Al_2O_3, Co, Co, Ni_3Al and NiAl, respectively) were observed; in Runs 5-15 and 5-16, only TiN and α- and β-Si_3N_4, respectively, were observed in addition to the old SiC and the cubic boron nitride core particles. It should be noted that the sinter produced in Run 5-11 and 5-12 were entirely free from the peak of metallic Co.

Fig. 16 is a graph showing the Hv (0.5/10) value of the cubic boron nitride sinter of Run 5-1 in comparison with the hardness data of four typical commercial cutting tools made from cubic boron nitride sinters using ceramic bonding materials or sintering aids. The sinter produced in Run 5-1 was superhard with the Hv (0.5/10) being about 6500 and this value was comparable to or higher than those of the commercial cutting tools made of sintered cubic boron nitride. Furthermore, the hardness of the sinter of Run 5-1 was uniform over the entire surface subjected to the hardness measurement and it was substantially free from variations.

The polished surface of the sinter of Run 5-1 was coated with a gold film by a customary evaporation technique and examined with an electron microscope. The result is shown in the Fig. 17 electron micrograph (X5000), in which the dark area represents the cubic boron nitride and the light area the ZrN-ZrB_2 base substance. As one can see from Fig. 17, the sinter was entirely free from pores and could be sintered to a relative density of 100%. In addition, it had no portion left unsintered. In areas where cubic boron nitride particles contacted each other via a thin layer of the coat forming substance, the latter was bursted by the contiguous cubic boron nitride particles, which hence were coupled directly as a result of sintering. In all other areas, the ZrN-ZrB_2 base material was distributed to surround the cubic boron nitride particles, rendering the sinter to be characteristic in that it was dense, uniform and had the bonding material distributed to provide a highly controlled microstructure. It should also be noted that the cubic boron nitride particles in the sinter did not grow at all compared to the particles in the feed powder and that the coating on the cubic boron nitride was formed by chemical reaction between the cubic boron nitride and the metallic zirconium which served as the coat

forming substance; these factors combined together to offer the characteristic feature that the cubic boron nitride particles in the sinter were finer than those in the feed although they were coated zirconium. This is very favorable and, hence, ideal for the mechanical characteristics of the sinter. The differences can be clearly seen by comparing Fig. 17 with Fig. 18 which is an electron micrograph (X5000) of a polished surface of one of the above-mentioned commercial cutting tools that was made of sintered cubic boron nitride and which was coated with a gold film by a customary evaporation technique for examination. Obviously, the bonding material and the sintering aid were distributed irregularly in the cubic boron nitride sinter of the commercial cutting tool to form lumps in certain areas. On the other hand, the number of areas that were devoid of the necessary sintering aid and bonding material was by no means small and unsintered portions were found there. Another major difference from the sinter of Run 5-1 was that every cubic boron nitride particle in the cutting tool was coarse.

The cubic boron nitride is inherently very difficult to sinter. In spite of this fact, the coated particles in a cubic boron nitride powder that were produced in Example 5 in accordance with the invention behaved as if they were comparatively easy-to-sinter particles under industrially feasible ultrahigh pressures and elevated temperatures, thereby forming dense, rigid and superhard structures.

The sinters thus produced were similar to those produced in Examples 1 and 4 in that they were sinters or composite sinters that were superhard and which had dense, uniform and highly controlled microstructures with substantially uniform distributions of the bonding materials.

Table 2

Run No.	Relative proportions (vol %)				Coating apparatus Ex. No.	Coating Conditions (Approximate Ex. of Run. No.)	Sintering Conditions			Silver appearance	Density %	Hardness Hv
	Core Particle	Coat Forming Substance		Moisture etc			Pressure atm	Temperature °C	Time min			
	CBN	Name	Amount									
S-1	60	Zr	20	-	1	S-1	5.5	1450	30	CB	100	3500
S-2	60	Ti	20	-	2	S-2	5.1	1440	30	CB	100	3605
S-3	60	SiN	15	-	3	S-3	5.3	1480	30	CB	100	4000
S-4	60	TiN	30	-	1	S-1	5.2	1460	28	CB	100	3900
S-5	60	AlN	20	-	1	S-1	5.4	1490	30	CB	100	3800
S-6	70	AlN	30	-	1	S-3	5.4	1495	30	CB	100	3500
S-7	40	Si_3N_4	20	-	1	S-1	5.2	1430	30	CB	100	3300
S-8	20	Si_3N_4	30	-	1	S-7	5.3	1470	30	CB	100	3140
S-9	85	Al_2O_3	15	-	2	S-2	5.5	1480	30	CB	100	4141
S-10	80	Al_2O_3	20	-	2	S-3	5.4	1460	30	CB	100	3920
S-11	30	C	10	-	1	S-1	5.3	1450	30	CB	100	3000
S-12	70	Co	30	-	1	S-1	5.5	1480	30	CB	100	2870
S-13	80	PtAl	18	-	1	S-1	5.1	1430	30	CB	100	4200
S-14	80	WAl	20	-	1	S-13	5.1	1460	30	CB	100	3950
S-15	72	TiN	18	18	1		5.3	1500	30	CB	100	3800
S-16	72	SiAl	18	18	1		5.3	1470	30	CB	100	3100

CB: Cubic ultrahigh pressure apparatus

Example 6

Coated diamond particles were prepared by coating the bare diamond particles of Example 1 with various coat forming substances using apparatus of the same types as used in Examples 1 - 3. The names of the coat forming substances used to prepare the coated diamond particles and their coating weights (relative proportions by vol%) are shown in Table 3.

The apparatus used in Run 6-1 was of the same type as used in Example 1; an alumina powder having an average diameter of 2 μm was supplied as a feed of coat forming substance from the feeder 112 at a rate of 1.5 g/min and the core diamond particles were supplied from the feeder 111 at a rate of 0.3 g/min. The other conditions in Run 6-1 were the same as in Example 1. The apparatus used in Run 6-2 was of the same type as used in Example 2; an alumina powder having an average diameter of 2 μm was supplied as a feed of coat forming substance at a rate of 1.0 g/min and the diamond particles were supplied at a rate of 0.7 g/min. The other conditions in Run 6-2 were the same as in Example 2. The apparatus used in Run 6-3 was of the same type as in Example 3; the values of dispersity (δ) attained in the discharge section of cyclone 6-1 and in the coating start region were the same as in Run 4-2 and an alumina powder was supplied at a rate of 0.6 g/min whereas the diamond particles were supplied at a rate of 1.5 g/min. The other conditions in Run 6-3 were the same as in Example 3.

The apparatus used in Run 6-4 was of the same type as used in Example 1 and operated to perform the coating operation under generally the same conditions as in Run 6-1. In Runs 6-5 to 6-9, inorganic salts consisting of KCl, $BaCl_2$ and NaF were mixed with TiO_2 and ferroalloy (Fe-Ti) to prepare an immersing bath. In this bath, diamond powder particles (up to 3 μm in diameter) were dipped for 1 h by the molten salt disproportionation method with the bath being melted at 900°C. As a result, the surfaces of the diamond powder particles were coated with TiC in such a way that the amount of internal addition would be 5% by volume. The surfaces of diamond particles were further coated with the apparatus of Example 1 under generally the same conditions as in Run 6-1.

The coated diamond particles thus prepared were examined with a scanning electron microscope. All of the particles prepared in Runs 6-1 to 6-3 were uniformly covered with superfine particles (ca. 0.005 μm) of coat forming substances as Fig. 19 shows (particularly for the case of Run 6-1).

In Runs 6-10 and 6-11, the powders of alumina-coated diamond particles prepared in Runs 6-1 and 6-2, respectively, were wet mixed with SiC whiskers at a volume ratio of 80:10 in acetone for 3 h in an alumina ball mill. In Run 6-12, a powder of diamond particles was coated with 32% by volume of alumina using the apparatus of Example 1 under generally the same conditions as in Run 6-1 and then wet mixed with SiC whiskers at a volume ratio of 85:15 in acetone for 3 h in an alumina ball mill. The SiC whiskers had their surfaces coated with the target TiC by sputtering in a coating weight of 33% by volume in terms of internal addition. The mixtures was vacuum dried at 10^{-4} torr at 800°C to make dry blends.

The coated diamond particles thus prepared or mixtures thereof with SiC whiskers were stamped into disks having a diameter of 16 mm and a thickness of 5 mm in Runs 6-1 and 6-10 and into disks having a diameter of 8 mm and a thickness of 5 mm in Runs 6-2 and 6-11. The disks were placed into Pyrex glass capsules packed with a h-BN powder, degassed to 10^{-6} torr at 400°C over 12 h and then sealed. The sealed capsules were set in a HIP or a ultrahigh pressure HIP apparatus using an argon gas as a pressure-transmitting medium and sintering was performed under the conditions shown in Table 3. In Runs 6-3 to 6-12, the coated diamond particles or mixtures thereof with whiskers were stamped into pellets having a diameter of 10 mm and a thickness of 8 mm and the pellets were buried in a pyrophyllite pressure-transmitting medium surrounded by a h-BN shaped part; the assemblies were set in a piston-cylinder (PC) ultrahigh pressure apparatus and sintering was performed under the conditions shown in Table 3. Following furnace cooling, the pressure was opened to atmosphere and the sinters were recovered.

The recovered sinters were measured for their density and Vickers microhardness Hv (0.5/10) as in Example 1 and the results are shown in Table 3.

The sinters of Runs 6-1 to 6-4 were checked for their crystalline phases by powder X-ray diffraction and no diffraction peaks were observed except for the diamond and α-form alumina. Similar results were obtained in the other runs: only diffraction peaks for diamond, titanium carbide and α-form alumina were observed in Runs 6-5 to 6-7; only diffraction peaks for diamond, titanium carbide and the monoclinic and tetragonal zirconium oxide each composing the PSZ were observed in Runs 6-8 and 6-9; only diffraction peaks for diamond, α-form alumina and silicon carbide were observed in Runs 6-10 and 6-11; and only diffraction peaks for diamond, α-form alumina, silicon carbide and titanium carbide were observed in Run 6-12. No other diffraction peaks were observed.

The surface of the sinter produced in Run 6-1 was polished with a diamond paste; the polished surface was coated with a gold film by a customary evaporation technique and examined with an electron microscope. The result is shown in the Fig. 20 micrograph (X5000), in which the dark area represents the diamond and the light area the alumina bonding material.

For comparison, bare diamond particles of the same type as used in Example 6 were mixed with an alumina powder at a ratio of 70:30 in volume percent and the mixture was sintered under the same conditions as in Example 6. The resulting sinter had a density of 92% and a Vickers microhardness of 2550. The difference is clearly visible by comparing

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Fig. 20 with Fig. 21 which is an electron micrograph (X3000) of a polished surface of the comparative sinter that was coated with a gold film by a customary evaporation technique for examination. Obviously, the bonding material and the sintering aid were distributed irregularly in the comparative sinter to form lumps in certain areas. On the other hand, the number of areas that were devoid of the necessary sintering aid and bonding material was by no means small and unsintered portions were found there. Thus, the sinter produced in Run 6-1 in accordance with the invention was significantly superior to the comparative sinter in terms of density, hardness and microstructure.

Each of the sinters produced in Runs 6-5 to 6-7 presented considerable difficulty in forming a polished surface for the hardness measurement and this fact shows that these sinters had high wear resistance, which was probably due to the formation of the titanium carbide coating film by dip coating.

The foregoing data, when considered with particular reference to Figs. 20 and 21, demonstrate that the sinters produced in Example 6 were entirely free from unsintered portions, pores, defects, etc., highly dense, superhard and comprised of highly controlled microstructures in which the diamond particles were surrounded by uniform distributions of the bonding material(s), i.e., α-form alumina, the combination of titanium carbide and α-form alumina, or the combination of titanium carbide and PSZ, or in which these coated diamond particles were further surrounded with a uniform dispersion of SiC.

Table 3

Run No.	Relative Proportions (vol%)						Sintering Conditions			Sintex	
	Coated Diamond Particles		Fibrous Substance			Pressure	Temperature	Time	Apparatus	Density	Hardness
	Diamond	Coat, Forming Substance		Whisker	Coating Substance						
		TiC	Al_2O_3	TaC	SiC	ZrC	MPa	°C	Hr.		Hs
E-1	20	-	20	-	-	-	150	1200	1	HIP1	96.0	2240
E-2	30	-	30	-	-	-	1000	1200	1	HIP2	99.0	2350
E-3	50	-	50	-	-	-	4800	1200	1	PC	98.2	3000
E-4	60	-	60	-	-	-	1500	1300	1	PC	99.5	2400
E-5	55	5	40	-	-	-	1800	1400	4	PC	94.6	2670
E-6	50	5	45	-	-	-	1800	1100	1	PC	95.0	3200
E-7	60	5	35	-	-	-	1500	1300	6	PC	99.6	2230
E-8	55	5	-	40	-	-	1500	1300	4	PC	99.3	2060
E-9	30	5	-	45	-	-	1500	1300	1	PC	99.4	1120
E-10	72	-	63	-	10	-	150	1200	3	HIP1	94.8	2080
E-11	42	-	42	-	10	-	1000	1200	3	HIP2	99.0	3220
E-12	40	-	48	-	10	2	1300	1300	3	PC	98.1	3170

HIP1: HIP apparatus incapable of producing ultrahigh pressures

HIP2: Superhigh pressure HIP apparatus

PC: Piston-cylinder (PC) ultrahigh pressure apparatus

Example 7

Cubic boron nitride (cBN) particles of the same type as used in Example 2 were coated with various coat forming substances using apparatus of the same types as used in Examples 1 - 3. The names of the coat forming substances used to prepare the coated cubic boron nitride particles and their coating weights (relative proportions by vol%) are shown in Table 4.

The apparatus used in Runs 7-1 and 7-2 were of the same types as used in Examples 1 and 3, respectively, an alumina powder having an average diameter of 2 µm was supplied as a feed of coat forming substance at respective rates of 1.5 and 8.1 g/min and the cubic boron nitride core particles were supplied at respective rates of 0.3 and 1.5 g/min. The other conditions in Runs 7-1 and 7-2 were the same as in Example 1 and Run 6-2, respectively. The apparatus used in Runs 7-3 and 7-4 was of the same type as used in Example 1 and the other conditions were the same as in Run 7-1. In Runs 7-5, 7-6 and 7-8, the procedures of Runs 6-6, 6-7 and 6-9 were repeated, except that the surfaces of cubic boron nitride particles were dip coated with the combination of titanium nitride (TiN) and titanium diboride (TiB_2) in place of titanium carbide and, further, alumina or PSZ coating was performed using the same apparatus as in Example 1 under generally the same conditions as in Run 7-1. In Run 7-7, the apparatus of Example 1 was used and coating was performed under generally the same conditions as in Run 7-1, except that alumina was replaced by PSZ. In Runs 7-9 and 7-10, the alumina coated cubic boron nitride particles as prepared in Run 7-1 and Example 2, respectively, were each mixed with SiC whiskers as in Runs 6-10 and 6-11. In Run 7-11, cubic boron nitride particles were coated with 93% alumina using the apparatus of Example 1 under generally the same conditions as in Run 7-1 and then mixed with TiC coated SiC whiskers that were prepared as in Run 6-12.

The coated cubic boron nitride particles thus prepared were examined with a scanning electron microscope. All of the particles prepared in Runs 7-1 to 7-3 were uniformly covered with superfine particles (ca. 0.005 µm) of coat forming substances as Fig. 22 shows (particularly for the case of Run 7-1).

The powders of coated cubic boron nitride particles thus prepared in Runs 7-1 to 7-8 or the mixtures thereof with SiC whiskers which were prepared in Runs 7-9 to 7-11 were shaped by stamping as in Runs 6-1, 6-3 to 6-12, respectively, and sintered with the sinter apparatus shown in Table 4 under the sintering conditions shown in Table 4.

The sinters thus produced were measured for their density and Vickers microhardness Hv (0.5/10) as in Example 1 and the results are shown in Table 4.

The crystalline phases of the sinters were examined by powder X-ray diffraction as in Runs 6-1 to 6-12, no diffraction peaks were observed except for the cubic boron nitride (core particles), the bonding materials or coat forming substances (α-alumina, titanium nitride, titanium diboride, as well as the PSZ composing monoclinic and tetragonal zirconium oxide), and whiskers (silicon carbide) and the titanium carbide coating thereon.

The polished surface of the sinter of Run 7-1 was coated with a gold film by a customary evaporation technique and examined with an electron microscope. The result is shown in the Fig. 23 electron micrograph (X5000), in which the dark area represents the cubic boron nitride and the light area the bonding material alumina. As one can see from Fig. 23, the sinter was entirely free from unsintered portions, pores, defects, etc. and it was comprised of a highly controlled microstructure in which the bonding material alumina was distributed uniformly around the cubic boron nitride particles.

For comparison, bare cubic boron nitride particles of the same type as used in Run 7-1 were mixed with an alumina powder at a ratio of 70:30 in volume percent and the mixture was sintered under the same conditions as in Run 7-1. The resulting sinter had a density of 94% and a Vickers microhardness of 2300. From an electron micrograph (X5000) of a polished surface of the comparative sinter that was coated with a gold film by a customary evaporation technique for examination, obviously, the bonding material and the sintering aid were distributed irregularly in the comparative sinter to form lumps in certain areas. On the other hand, in the comparative sinter, the number of areas that were devoid of the necessary sintering aid and bonding material was by no means small and unsintered portions were found there.

In Runs 7-5, 7-6 and 7-9, the TiN-TiB_2 coating film formed by dip coating were found to be as effective as the TiC coating film formed by dip coating in Runs 6-5 to 6-7.

Thus, the sinters produced in Example 7 were entirely free from unsintered portions, pores, defects, etc., highly dense, superhard and comprised of highly controlled microstructures in which the cubic boron nitride particles were surrounded by uniform distributions of the bonding material(s), i.e., α-alumina, PSZ, the combination of TiN-TiB_2 and α-alumina, or the combination of TiN-TiB_2 and PSZ, or in which these coated cubic boron nitride particles were further surrounded with a uniform dispersion of SiC as whiskers.

Table 4

Run No.	Relative Proportions (vol%)					Blistering Conditions			Glaze		
	Coated High-Pressure Boron Nitride Particles			Fibrous Substance		Pressure kg/cm²	Temperature °C	Time hr.	Appearance	Density %	Hardness Hv
	BN	Cost Forming Substance		Whisker	Coating Substance						
		TiB-TiB2	Al2O3	TiB	SiC						
2	30	-	30	-	-	1000	1100	1	NUP2	99.4	3230
2-1	30	-	30	-	-	150	1200	1	NUP1	97.1	2900
2-2	30	-	30	-	-	1300	1200	1	PC	99.3	3830
2-3	30	-	30	-	-	1300	1300	1	PC	99.8	3970
2-4	40	-	40	-	-	1300	1300	1	PC	99.2	4100
2-5	50	1	38	-	-	1300	1300	1	PC	99.0	4030
2-6	40	1	38	-	-	1300	1200	1	PC	98.5	4100
2-7	40	-	-	40	-	1300	1200	1	PC	99.8	4300
2-8	30	1	2	45	-	1300	1200	1	PC	99.8	3900
2-9	27	-	63	-	10	150	1200	1	NUP1	96.0	2780
2-10	45	-	45	-	10	1000	1200	1	NUP3	98.0	3540
2-11	40	-	45	-	15	1300	1200	1	PC	98.2	3600

NUP1: NUP apparatus incapable of producing ultrahigh pressures

NUP3: Specified pressure NUP apparatus

PC: Plate-cylinder (BC) ultrahigh pressure apparatus

Example 8

Coated diamond particles were prepared by coating the bare diamond particles of Example 1 with various coat forming substances using apparatus of the same type as used in Examples 1 - 3. The names of the coat forming substances used to prepare the coated diamond particles and their coating weights (relative proportions by vol%) are shown in Table 8.

The apparatus used in Runs 8-1, 8-2 and 8-4 were of the same types as used in Examples 1, 2 and 3, respectively; a titanium carbide powder having an average diameter of 2 µm was supplied as a feed of coat forming substance at a rate of 0.4 g/min and the core diamond particles were supplied at a rate of 2.0 g/min; the other conditions in Runs 8-1, 8-2 and 8-4 were generally the same as in Example 1 and Runs 4-1 and 4-2, respectively. In each of those runs, 10% titanium carbide coated diamond particles were obtained. In Runs 8-5 and 8-6, an apparatus of the same type as used in Example 1 was operated under generally the same conditions as in Run 8-1 to produce 10% titanium carbide coated diamond particles; in Runs 8-7 and 8-8, the same procedure was repeated to produce 10% metallic titanium coated diamond particles; in Runs 8-9 and 8-10, the same procedure was repeated to yield 20% titanium carbide coated diamond particles; in Run 8-3, the 10% titanium carbide coated particles prepared in Run 8-2 were used.

The coated diamond particles thus prepared were examined with a scanning electron microscope. All of the particles prepared in Runs 8-1 to 8-4 were uniformly covered with superfine particles (ca. 0.005 µm) of coat forming substances as Fig. 25 shows (particularly for the case of Run 8-1).

The thus prepared powders of coated diamond particles and powders of bonding materials having the various formulations shown in Table 8 were added in the various proportions shown in Table 8 and wet mixed in acetone for 2 h in an alumina ball mill. Thereafter, the mixtures were vacuum dried at 10^{-3} torr and at 200°C to produce dry blends. The bonding material powder used in Runs 8-1 to 8-4 was easily sinterable alumina of high purity (i.e., the alumina powder described in the official gazette of Unexamined Published Japanese Patent Application (kokai) Sho 63-151616); in Runs 8-5 and 8-6, PSZ was used as a bonding material powder, and in Runs 8-7 to 8-10, TiC was used. Take, for example, Run 8-1; in this run, 85 vol% of 10% TiC coated diamond particles were mixed with 45.4 vol% of easily sinterable alumina of high purity as a bonding material powder, and with sintering aids for the alumina powder which were 0.6 vol% and 1.0 vol%, respectively, of magnesia (MgO) and titania (TiO_x; x = 1 - 2).

In Runs 8-11 and 8-12, 90 vol% of the mixtures prepared in Runs 8-4 and 8-5, respectively, were mixed with 10 vol% of SiC whiskers and the mixtures thus prepared were used as sinter feeds.

The thus prepared mixtures of coated diamond particles with bonding material powders were stamped into disks having a diameter of 10 mm and a thickness of 6 mm in Runs 8-1, 8-7, 8-8 and 8-10. The disks were buried in a pyrophyllite pressure-transmitting medium surrounded by a h-BN shaped part and the assemblies were set in a piston-cylinder (PC) ultrahigh pressure apparatus, and sintering was performed under the conditions set forth in Table 8. In the other runs, the same mixtures of coated diamond particles with bonding material powders, or mixtures further containing SiC whiskers were stamped into disks having a diameter of 18 mm and a thickness of 6 mm. The disks were placed in a Pyrex glass capsule packed with a h-BN shaped part and the assemblies were degassed to 10^{-3} torr by heating at 400°C for 12 h and sealed. Thereafter, the capsules were set in a HIP or ultrahigh pressure HIP apparatus using an argon gas as a pressure-transmitting medium and sintering was performed under the conditions set forth in Table 8. Subsequently, the temperature was lowered and the pressure reduced for recovering the sinters.

The recovered sinters were measured for their density and Vickers microhardness Hv (0.5/10); the results are shown in Table 8 together with the sintering conditions and the types of sintering apparatus used.

The sinters were also checked for their crystalline phases by powder X-ray diffraction. In Example 8, no diffraction peaks were observed except for the diamond, coat forming substances (coating materials) and the bonding material powders or whisker SiC. Take, for example, Runs 8-1 to 8-4; in these cases, the only diffraction peaks observed were those for diamond, TiC and α-alumina. In the other runs, the only diffraction peaks observed were those for the following: diamond, TiC and PSZ composing monoclinic and tetragonal zirconium oxide (Runs 8-5 and 8-6); diamond, the TiC that was generated by the reaction between the coating metallic titanium and the diamond, as well as TiN (Runs 8-7 and 8-8); diamond and TiC (Run 8-9 and 8-10); diamond, TiC, α-alumina and SiC (Run 8-11); diamond, TiC, the PSZ composing monoclinic and tetragonal zirconium oxide, and SiC (Run 8-12).

The surface of the sinter produced in Run 8-1 was polished with a diamond paste and coated with a gold film by a customary evaporation technique and examined with an electron microscope. The result is shown in the Fig. 26 electron micrograph (X6000), in which the dark area represents the diamond and the light area the alumina-base bonding material.

As one can see from Fig. 26, all the sinters of Example 8 were entirely free from unsintered portions, pores, defects, etc., highly dense, superhard and comprised of highly controlled microstructures in which the diamond particles were surrounded by uniform distributions of the coating materials, the bonding materials (TiC, TiN, α-alumina and PSZ) and the SiC whiskers, if any.

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Table 5

Run No.	Relative Proportions (vol%)									Sintering Conditions				Binder	
	Diamond	Coating Material		Bonding Material Powder					Balance	Pressure	Temperature	Time	Apparatus	Density	Hardness
		TiC	TiN	Si	WSi$_2$	TiN	Al$_2$O$_3$	MgO	ZrO$_2$	SiC	MPa	°C	hr		g/cm^3	Hv
E-1	50.0	3.0	-	-	-	-	43.4	0.6	3.0	-	1300	1300	1	HP	99.2	4110
E-2	30.0	3.0	-	-	-	-	63.4	0.6	3.0	-	130	1300	1	HP1	98.8	3130
E-3	40.0	4.0	-	-	-	-	51.4	0.6	4.0	-	1300	1300	1	HP2	99.4	3380
E-4	20.0	2.0	-	-	-	-	76.4	0.6	1.0	-	130	1300	1	HP1	97.8	2810
E-5	30.0	3.0	-	3	67.0	-	3	-	-	-	130	1300	1	HP1	99.5	1010
E-6	45.0	4.5	-	-	50.5	-	-	-	-	-	130	1300	1	HP1	98.8	1030
E-7	20.0	-	-	2.0	-	76.0	-	-	-	-	1300	1300	3	HP	99.1	2660
E-8	40.0	-	-	1.0	-	56.0	-	-	-	-	1300	1300	1	HP	97.8	3330
E-9	20.0	-	4.0	-	-	76.0	-	-	-	-	1300	1200	3	HP2	99.0	2640
E-10	40.0	-	8.0	-	-	52.0	-	-	-	-	1300	1300	3	HP	99.2	3400
E-11	18.0	1.8	-	-	-	-	68.9	0.3	0.9	10.2	130	1300	3	HP1	99.4	2880
E-12	27.0	2.7	-	-	60.3	-	-	-	-	10.0	130	1300	3	HP1	98.9	1880

HP1: HIP apparatus incapable of producing ultrahigh pressures

HP2: Ultrahigh pressure HIP apparatus

HP: Belt-cylinder (DC) ultrahigh pressure apparatus

Example 9

Coated cubic boron nitride particles were prepared by coating the bare cubic boron nitride (cBN) particles of Example 1 with various coat forming substances using the apparatus employed in Examples 1 - 8. The names of the coat forming substances used to prepare those coated cubic boron nitride particles and their coating weights (relative proportions by vol%) are shown in Table 6.

The apparatus used in Runs 9-1, 9-2 and 9-3 were of the same types as used in Examples 1, 2 and 3, respectively; a titanium nitride powder having an average diameter of 2 µm was supplied as a feed of coat forming substance at a rate of 0.3 g/min and the cubic boron nitride core particles were supplied at a rate of 1.5 g/min; the other conditions in Runs 9-1, 9-2 and 9-3 were generally the same as in Example 1, Runs 4-2 and 4-3, respectively. In each of those runs, 10% titanium nitride coated cubic boron nitride particles were obtained. In Runs 9-4 and 9-5, an apparatus of the same type as used in Example 1 was operated under generally the same conditions as in Run 9-1 to produce 10% titanium nitride coated cubic boron nitride particles; in Runs 9-6 and 9-7, the same procedure was repeated to produce 10% metallic titanium coated cubic boron nitride particles; and in Runs 9-8 and 9-9, the same procedure was repeated to yield 20% titanium nitride coated cubic boron nitride particles.

The coated cubic boron nitride particles thus prepared were examined with a scanning electron microscope. All of the particles prepared in Runs 9-1 to 9-9 were uniformly covered with superfine particles (ca. 0.005 µm) of coat forming substances as Fig. 27 shows (particularly for the case of Run 9-1).

The thus prepared powders of coated cubic boron nitride particles and powders of bonding materials having the various formulations shown in Table 6 were added in the various proportions shown in Table 6. Those powders were wet mixed in acetone for 8 h in an alumina ball mill as in Example 8. Thereafter, the mixtures were vacuum dried at 10^{-3} torr and at 800°C to produce dry blends. The bonding material powders used in Example 9 were the same as those used in Example 8, i.e., easily sinterable alumina of high purity, PSZ, and TiN. As in Example 8, the use of easily sinterable high-purity alumina with an average particle diameter of 0.2 µm as a bonding material powder was accompanied by the use of sintering aids for the alumina powder which were magnesia (MgO) and titania (TiO_x; $x \approx 1 \sim 2$).

In Runs 9-10 and 9-11, 80 vol% of the mixtures prepared in Runs 9-3 and 9-4, respectively, were mixed with 10 vol% of SiC whiskers and the mixtures thus prepared were used as sinter feeds.

The thus prepared mixtures of coated cubic boron nitride particles with bonding material powders were stamped into disks in Runs 9-1, 9-6, 9-7 and 9-9 as in Run 8-1; in the other runs, the same mixtures of coated cubic boron nitride particles with bonding material powders, or mixtures further containing SiC whiskers were stamped into disks as in Run 8-2. The disks were then sintered with the sinter apparatus listed in Table 6 under the sinter conditions also set forth in Table 6. Thereafter, the temperature was lowered and the pressure reduced for recovering the sinters.

The recovered sinters were measured for their density and Vickers microhardness Hv (0.5/10); the results are shown in Table 6 together with the sintering conditions and the types of sintering apparatus used.

The sinters were also checked for their crystalline phases by powder X-ray diffraction. In Example 9, no diffraction peaks were observed except for the cubic boron nitride, coat forming substances (coating materials) and the bonding materials or whisker SiC. Take, for example, Runs 9-1 to 9-3; in these cases, the only diffraction peaks observed were those for cubic boron nitride, TiN and α-alumina. In the other runs, the only diffraction peaks observed were those for the following: cubic boron nitride, TiN and the PSZ composing monoclinic and tetragonal zirconium oxide (Runs 9-4 and 9-5); cubic boron nitride, the TiB_2 that was generated by the reaction between the coating metallic titanium and cubic boron nitride, as well as TiN (Runs 9-6 and 9-7); cubic boron nitride and TiN (Runs 9-8 and 9-9); cubic boron nitride, TiC, α-alumina and SiC (Run 9-10); and cubic boron nitride, TiC, the PSZ composing monoclinic and tetragonal zirconium oxide, and SiC (Run 9-11).

Quantification by X-ray analysis showed that the sinter of Run 9-6 consisted of cubic boron nitride, TiB_2 and TiN in proportions of 19.5%, 1.0% and 79.5%, respectively, by volume whereas the sinter of Run 9-7 had relative volume proportions of 30.1%, 2.0% and 68.0%.

The surface of the sinter produced in Run 9-1 was polished with a diamond paste and coated with a gold film by a customary evaporation technique and examined with an electron microscope. The result is shown in the Fig. 28 electron micrograph (X5000), in which the dark area represents the cubic boron nitride and the light area the alumina base bonding material.

As one can see from Fig. 28, all the sinters of Example 9 were entirely free from unsintered portions, pores, defects, etc., highly dense, superhard and comprised of highly controlled microstructures in which the cubic boron nitride particles were surrounded by uniform distributions of the coating materials, the bonding materials (TiN, TiB_2, α-alumina and PSZ) and the SiC whiskers, if any.

Table 6

Run No.	Relative Proportions (vol %)								Sintering Conditions			Sinter	
	cBN	Coating Material	Bonding Material Powder					Whisker SiC	Pressure	Temperature	Time	Apparatus	Density	Hardness
		TiN	Ti	PSZ	TiN	Al_2O_3	MgO	Y_2O_3	MPa	°C	hr.		g	Hv
E-1	10.0	2.0	-	-	-	42.4	0.6	1.0	-	1500	1300	1	EC	97.8	4030
E-2	40.0	4.0	-	-	-	54.4	0.6	1.0	-	1000	1300	2	HIP2	98.1	3330
E-3	20.0	2.0	-	-	-	76.4	0.6	1.0	-	150	1300	3	HIP1	98.3	2870
E-4	30.0	3.0	-	62.0	-	-	-	-	-	150	1300	1	HIP1	98.6	1030
E-5	48.0	4.0	-	32.3	-	-	-	-	-	150	1300	2	HIP1	98.0	2010
E-6	20.0	-	2.0	-	78.0	-	-	-	-	1500	1300	3	EC	98.3	2890
E-7	40.0	-	4.0	-	56.0	-	-	-	-	1500	1300	1	EC	98.0	3430
E-8	20.0	4.0	-	-	76.0	-	-	-	-	1000	1300	3	HIP2	98.0	2900
E-9	40.0	6.0	-	-	54.0	-	-	-	-	1500	1300	1	EC	96.4	3310
E-10	10.0	1.6	-	-	-	86.8	0.2	0.8	10.0	150	1300	1	HIP1	99.8	2700
E-11	22.0	2.2	-	60.3	-	-	-	-	10.0	150	1300	3	HIP1	98.1	1940

HIP1: HIP apparatus incapable of producing ultrahigh pressures

HIP2: Superhigh pressure HIP apparatus

EC: Belt-cylinder (EC) ultrahigh pressure apparatus

Examples 10 and 11

Using the apparatus employed in Examples 1 - 3, pseudo-fine diamond particles (Example 10) or pseudo-fine particles in a high-pressure phase boron nitride powder (Example 11) were covered with various coat forming materials. The pseudo-fine diamond particles were the same as those used in Example 8; the pseudo-fine particles in a high-pressure phase boron powder were pseudo-fine cubic boron nitride (cBN) particles that had an average diameter (D_{50}) of 17 μm and a frequency distribution by volume of ($[D_{50}/2, 3D_{50}/2]$, ≥ 90%). The names of the coat forming substances used to prepare the pseudo-fine coated diamond and cubic boron nitride particles and their coating weights (relative proportions by vol%), as well as the specific types of the coating apparatus used and the conditions for their use (generally the same) are shown in Tables 7 and 8 together with the data for Example 3.

The apparatus used in Runs 10-1 and 11-1 was of the same type as used in Example 1; the group of means for high dispersion treatment of particles in this apparatus was to treat the pseudo-fine particles of either a diamond powder or a cubic boron nitride powder, in which the core particles had an average diameter of 17 μm and a frequency distribution by volume of ($[D_{50}/3, 5D_{50}]$, ≥ 90%) and, hence, said group of means was designed in such a way that it could realize an output dispersity (β) value of at least 80% (β ≥ 80%) for the core particles in those powders while, at the same time, the coating operation could be started with a dispersity (β) of at least 80% (β ≥ 80%) in the coating start region. A titanium carbide powder (Run 10-1) or a titanium nitride powder (Run 11-1) that were feeds for coat forming substances and which had an average particle diameter of 2 μm were supplied from the feeder 112 at a rate of 0.3 g/min whereas the pseudo-fine diamond or cubic boron nitride core particles were supplied from the feeder 111 at a rate of 3.0 g/min and introduced into the coating chamber after being dispersed to a dispersity (β) of 80%, and the dispersity (β) in the coating start region 3-L1 was 80%. The other conditions in Examples 10 and 11 were the same as in Example 1. The coating weights of titanium carbide and titanium nitride were each 5% by volume.

The apparatus used in Runs 10-2 and 11-2 was of the same type as used in Example 2; the dispersity (β) value attainable in these runs was the same as in Runs 10-1 and 11-1; a metallic titanium powder having an average particle diameter of 25 μm was supplied as a feed for coat forming substance from the feeder 215 at a rate of 0.5 g/min, and the pseudo-fine diamond or cubic boron nitride core particles were supplied from the feeder 214 at a rate of 2.5 g/min; the other conditions in Runs 10-2 and 11-2 were the same as in Example 2. The apparatus used in Run 11-3 was of the same type as used in Example 3; a zirconium powder having an average particle diameter of 28 μm was supplied as a feed for coat forming substance from the feeder 314 at a rate of 0.5 g/min and the pseudo-fine cubic boron nitride core particles were supplied from the feeder 313 at a rate of 2.0 g/min; the other conditions in Run 11-3 were the same as in Example 3. In Runs 10-2, 11-2 and 11-3, the coating weights of metallic titanium and zirconium were each 10% by volume.

The apparatus used in Runs 10-3, 10-4, 11-4 and 11-5 was of the same type as used in Example 1 and operated under generally the same conditions as in Example 1 to prepare the following in the respective runs: pseudo-fine diamond particles first coated with 6 vol% TiC, then with 50 vol% alumina; pseudo-fine diamond particles coated with 10 vol% TiC; pseudo-fine cubic boron nitride particles coated with 50 vol% alumina; and pseudo-fine cubic boron nitride particles coated with 10 vol% TiN.

The coated pseudo-fine diamond and cubic boron nitride particles were examined with a scanning electron microscope. All of the particles prepared in Examples 10 and 11 were uniformly covered with superfine particles (ca. 0.005 μm) of coat forming substances (TiC, TiN, Ti and Zr) as in Example 3 and as Fig. 29 (for the particular case of Run 10-1) and Fig. 30 (for the particular case of Run 11-1) show.

The thus prepared powders of pseudo-fine coated diamond or cubic boron nitride particles, or mixtures thereof with the bonding materials listed in Table 7 or 8 were shaped, set in the various types of sinter apparatus shown in Tables 7 and 8, and sintered under the various sintering conditions also set forth in Tables 7 and 8. Thereafter, the temperature was lowered and the pressure reduced for recovering the sinters. The specific procedures were as follows.

In Runs 10-1 and 10-2, 60% by volume of the powders of pseudo-fine diamond particles coated with TiC and Ti, respectively, were wet mixed in acetone with 40% by volume of bonding materials that were the powders of fine coated diamond particles as prepared by coating fine diamond particles of 0.5 - 2 μm in diameter (average diameter = 1 μm) with 15 vol% of TiC under generally the same conditions. In Runs 11-1, 11-2 and 11-3, 80% by volume of the powders of pseudo-fine cubic boron nitride particles coated with TiN, Ti and Zr, respectively, were wet mixed in acetone with 40% by volume of bonding materials that were the powders of fine coated cubic boron nitride particles as prepared by coating fine cubic boron nitride particles of 0.5 - 2 μm in diameter (average diameter = 1 μm) with 15 vol% of TiC under generally the same conditions. Thereafter, the resulting wet mixtures were shaped, vacuum dried and sintered with a cubic ultrahigh pressure apparatus as in Example 3.

In Runs 10-3 and 11-4, the powder of TiC and alumina coated pseudo-fine diamond particles and the powder of alumina coated fine cubic boron nitride particles, respectively, were stamped into disks having a diameter of 8 mm and a thickness of 5 mm; the disks were placed in Pyrex glass capsules packed with a h-BN powder. After degassing at 10^{-6} torr by heating at 600°C for 12 h, the capsules were sealed, set in a HIP apparatus using an argon gas as a pressure-transmitting medium and sintered under the conditions set forth in Tables 7 and 8.

In Runs 10-4 and 11-5, the powder of TiC coated pseudo-fine diamond particles and the powder of TiN coated fine cubic boron nitride particles were respectively wet mixed in 40% by volume as in Run 9-2 with the associated bonding materials that were 83.4%, 0.8% and 1.0% by volume of the high-purity and easily sinterable alumina, magnesia (MgO) and titania (TiO_x; x = 1 ~ 8) which were used in Run 9-1. The mixtures were vacuum dried, shaped into disks, placed into capsules, degassed, sealed, set in a HIP apparatus and sintered under the conditions set forth in Tables 7 and 8.

The sinters thus produced were measured for their density and Vickers microhardness Hv (0.5/10). The results are shown in Tables 7 and 8 together with the sintering conditions and the types of sinter apparatus used.

As for the Vickers microhardness Hv (0.5/10) measurement of the sinters of the coated pseudo-fine particles, the hardness values obtained by the measurement were the values of the pseudo-fine particles and not the values of the sinters, since particles sizes of the pseudo-fine particles were larger than those of the fine particles and the hardness values of the sinters could not be measured. Therefore, in Tables 7 and 8 the Vickers microhardness values of the sinters were not shown.

The sinters were also checked for their crystalline phases by powder X-ray diffraction. In Examples 10 and 11, no diffraction peaks were observed except for the core particles (diamond or cubic boron nitride), coating materials (TiC, TiN and α-alumina), the products of reaction between the core particles and the metallic coating materials (TiC, ZrC, TiN, TiB_2, ZrN and ZrB_2) and the bonding materials (the diamond or cubic boron nitride in the core particles, TiC or TiN and α-alumina as the coating materials). Take, for example, Runs 10-1 and 10-2; in these cases, the only diffraction peaks observed were those for diamond and TiC. In the other runs, the only diffraction peaks observed were those for the following: diamond, TiC and α-alumina (Runs 10-3 and 10-4); cubic boron nitride and TiN (Run 11-1); cubic boron nitride, TiN and TiB_2 (Run 11-2); cubic boron nitride, TiN, ZrN and ZrB_2 (Run 11-3); cubic boron nitride and α-alumina (Run 11-4); and cubic boron nitride, TiN and α-alumina (Run 11-5). Quantification by X-ray analysis showed that the sinter of Run 10-3 consisted of 87% diamond and 13% TiC, the sinter of Run 11-2 consisted of cubic boron nitride, TiN and TiB_2 in proportions of about 87%, 10% and 3%, respectively, by volume; and the sinter of Run 11-3 consisted of cubic boron nitride, ZrN, ZrB_2 and TiN in proportions of about 88%, 8%, 1% and 11%, respectively, by volume.

The polished surface of the sinter of Run 10-1 was coated with a gold film by a customary evaporation technique and examined with an electron microscope. The result is shown in the Fig. 31 electron micrograph (X5000), in which the dark area represents the diamond and the light area TiC. As one can see from Fig. 31, the sinter was entirely free from pores and could be sintered to a relative density of 99%. In addition, it had no portion left unsintered. In areas where pseudo-fine diamond particles and/or fine diamond particles contacted each other via a thin layer of the coat forming substance, the latter was bursted by the contiguous pseudo-fine diamond particles and/or fine diamond particles, which hence were coupled directly as a result of sintering. In all other areas, TiC was distributed uniformly around the pseudo-fine diamond particles, rendering the sinter to be characteristic in that the coated pseudo-fine diamond particles had a dense, uniform and extremely highly controlled distribution. The diamond particles in the sinter were also characterized in that they did not grow at all compared to the particles in the feed powder. It has heretofore been impossible to produce sinters having such an extremely highly controlled microstructure. Fig. 32 is an electron micrograph (X3000) showing a polished surface of the sinter of Run 11-1 and this was taken by the same method as used to prepare Fig. 31. Again, this sinter had established therein a microstructure in which pseudo-fine cubic boron nitride particles and/or fine cubic boron nitride particles and TiN as the coat forming substance were distributed uniformly, densely and in an extremely highly controlled manner.

Thus, in spite of the fact that diamonds and cubic boron nitrides are inherently very difficult to sinter, the coated pseudo-fine diamond and high-pressure phase boron nitride particles prepared in accordance with the invention behaved as if they were comparatively easy-to-sinter particles under industrially feasible ultrahigh pressures and elevated temperatures, thereby forming dense, rigid and superhard structures.

The sinters thus produced in Examples 10 and 11 were similar to that produced in Example 9 in that they were sinters or composite sinters that were superhard and which had dense, uniform and highly controlled microstructures with substantially uniform distributions of the bonding materials.

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Table 1

Ex. or Ref. No.	Relative Proportions (vol %)										Sintering Conditions			Sinter Density g/cm³
	Core particle size	Coating Material				Bonding Material Powder					Pressure GPa	Temperature °C	Time min	Sintered Appearance	
	Diamond	2nd	1st	Zr	Al_2O_3	Core particle size	Coating material	TiC	Al_2O_3	mol% ZrO_2					
						diamond									
1	22	-	24	3	-	10.3	-	10.3	-	-	5.5	1450	30	CB	3.99
10-1	22	3	-	-	-	11	1	-	-	-	5.5	1450	30	CB	3.99
10-2	24	-	6	-	-	11	1	-	-	-	5.5	1350	30	CB	3.99
10-3	19	3	-	-	50	-	-	-	-	-	6.15	1200	180	BBPL	3.99
10-4	18	4	-	-	-	-	-	33.1	0.4	0.5	6.15	1300	180	BBPL	3.99

Table 6

Run No.	Pulsation Conditions (cont.)										Sintering Conditions			Others
	Core material	Coating material				Bonding material Powder					Pressure	Temperature	Time	Atmosphere	Density
						Core material	Coating material								
	CBN	TiN	Ti	Si	Al_2O_3	CBN	TiN	Al_2O_3	Mo/TiO$_2$	GPa	°C	min		%
11-1	47	3	-	-	-	34	6	-	-	5.5	1350	20	Ar	100
11-2	53	-	4	-	-	24	6	-	-	5.5	1420	30	Ar	100
11-3	41	-	-	3	-	43.3	10.3	-	-	5.5	1450	30	Ar	100
11-4	40	-	-	-	30	-	-	-	-	6.33	1400	180	Ar	100
11-5	30	4	-	-	-	-	-	33.3	6.67	5.16	1300	180	Ar	100

Claims

1. A process for producing a diamond or high-pressure phase boron nitride sinter comprising the step of preparing coated diamond or high-pressure phase boron nitride particles and sintering said coated diamond or high-pressure phase boron nitride particles or mixtures containing such particles or mixtures of coated diamond or high-pressure phase boron nitride particles with bonding material,

sintering said coated diamond or high-pressure phase boron nitride particles or said mixtures containing such particles at pressures no less than 2000 MPa and at elevated temperatures, or

sintering said coated diamond or high-pressure phase boron nitride particles or said mixtures containing such particles at pressures of less than 2000 MPa and at temperatures not exceeding 1850°C under such sintering pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable; or

sintering said mixtures of coated diamond or high-pressure phase boron nitride particles with a bonding material in a volume ratio of (1 ~ 99):(99 ~ 10), said bonding material being sinterable to a density of at least 85% at pressures less than 2000 MPa and at temperatures not exceeding 1850°C under such conditions that diamond and/or high-pressure phase boron nitride particles are thermodynamically metastable, at pressures less than 2000 MPa and at temperatures not exceeding 1850°C under such sintering pressure and temperature conditions that diamond and/or high-pressure phase boron nitride is thermodynamically metastable if not stable,

wherein said coated diamond or high-pressure phase boron nitride particles are prepared by a method comprising the steps of charging a powder of diamond or high-pressure phase boron nitride core particles into a coating space and then permitting a precursor of a coat forming substance which is generated via the vapor phase and/or a precursor of a coat forming substance in a vapor-phase state to contact and/or impinge against the particles in said powder of core particles so that their surfaces are coated with the coat forming substance and

said coated diamond or high-pressure phase boron nitride particles are prepared by coating means comprising:

(A) a dispersing step in which the particles in the powder of core particles are dispersed by a group of means for high dispersion treatment of particles in a gaseous atmosphere to form a mixture of a gas and the particles in a powder of highly dispersed particles, the final treating means in said group of means for high dispersion treatment of particles being selected from between:

(a) dispersing means for dispersing the particles in the powder of core particles in a gaseous atmosphere; and

(b) means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles which comprises:

(b-1) means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles that separates a portion of the powder that is composed of less highly dispersed particles from the mixture of a gas and the particles in the powder of core particles in which the particles in the powder of core particles are dispersed in a gaseous atmosphere, thereby selecting a mixture of a gas and the particles in a powder of highly dispersed core particles in which the particles in the powder of core particles are present in the gaseous atmosphere mainly in a single-particle state; and

(b-2) feedback means by which the portion of the powder that is composed of less highly dispersed particles and which has been separated by said means for selecting a mixture of a gas and the particles in a powder of highly dispersed particles is transported to the final dispersing means among the dispersing means in the group of means for high dispersion treatment of particles and/or treating means upstream of the final dispersing means; and

(B) a coating step in which the particles in the powder of core particles that have been dispersed in the dispersing step (A) start to be coated by being allowed to contact and/or impinge against the precursor of the coat forming substance in the coating start region of the coating space as they are dispersed to satisfy the following conditions:

the dispersity β should be at least 70% if those particles have an average diameter of not more than 10 μm in the frequency distribution by volume;

the dispersity β should be at least 60% if those particles have an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume;

the dispersity β should be at least 50% if those particles have an average diameter in excess of 20 μm but no more than 50 μm in the frequency distribution by volume;

the dispersity β should be at least 35% if those particles have an average diameter in excess of 50 μm

but no more than 300 μm in the frequency distribution by volume;

the dispersity β should be at least 97% if those particles have an average diameter in excess of 300 μm but no more than 600 μm in the frequency distribution by volume; and

the dispersity β should be at least 98% if those particles have an average diameter in excess of 600 μm in the frequency distribution by volume, and wherein said sintering step is performed by

sintering said coated diamond or high-pressure phase boron nitride particles or said mixtures containing such particles at pressures no less than 3000 MPa and at elevated temperatures; or

sintering said coated diamond or high-pressure phase boron nitride particles or said mixtures containing such particles at pressures of less than 3000 MPa and at temperatures not exceeding 1650°C under such sintering pressure and temperature conditions that diamond or high-pressure phase boron nitride is thermodynamically metastable if not stable; or

sintering said mixtures of coated diamond or high-pressure phase boron nitride particles with a bonding material in a volume ratio of (1 - 90):(99 - 10), said bonding material being sintrable to a density of at least 95% at pressures less than 2000 MPa and at temperatures not exceeding 1850°C under such conditions that diamond and/or high-pressure phase boron nitride particles are thermodynamically metastable, at pressures less than 2000 MPa and at temperatures not exceeding 1850°C under such sintering pressure and temperature conditions that diamond and/or high-pressure phase boron nitride is thermodynamically metastable if not stable.

2. A process for producing a diamond or high-pressure phase boron nitride sinter according to claim 1 wherein said coated diamond or high-pressure phase boron nitride particles are prepared through the following additional step(s):

a step of disagglomeration or otherwise size reduction in which lumps of the coated diamond and/or high-pressure phase boron nitride particles that form as a result of association of several particles that contact one another via the coat forming substance on the coated particles are disagglomerated and/or otherwise reduced in size; and/or

a step of selective separation in which the associating lumps of the coated diamond or high-pressure phase boron nitride particles are selectively separated from the coated diamond or high-pressure phase boron nitride particles on a primary particle basis.

3. A process for producing a diamond or high-pressure phase boron nitride sinter according to claim 1 wherein the particles in the powder of diamond and/or high-pressure phase boron nitride core particles to be coated with the coat forming substance are coated by a dip method using a molten salt bath with one or more layers of the coat forming substance that derives from the dip method.

4. A process for producing a diamond or high-pressure phase boron nitride sinter according to claim 1, wherein the dispersing step is performed by:

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter of no more than 10 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 70%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 80%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 20 μm but no more than 30 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 90%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 30 μm but no more than 200 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 95%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a

powder of core particles having an average diameter in excess of 300 μm but no more than 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 97%; and

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 99%; and

said coated diamond or high-pressure phase boron nitride particles being prepared by:

a method in which the mixture of a gas and the particles in the powder of highly dispersed core particles as formed by one of the means in said group of means for high dispersion treatment of particles is either discharged directly to the coating step or transported thereto via at least one member indispensable to transport that is selected from the group consisting of a hollow member, an intermediate member composed of a member that forms a hollow portion, and a pipe and which is provided between the dispersing and coating steps, as the mixture emerges from a discharge section that discharges said mixture of a gas and the particles; and/or

a method in which the mixture of a gas and the particles in the powder of highly dispersed core particles as formed by one of the means in said group of means for high dispersion treatment of particles is transported to the coating step via at least one means selected from the group consisting of means for maintaining the dispersion in a gaseous atmosphere of the highly dispersed core particles in the mixture of a gas with the core particles which have been dispersed in the gaseous atmosphere to attain one of the dispersities set forth above, means for enhancing the dispersion in a gaseous atmosphere of the highly dispersed core particles in the mixture of a gas with the core particles which have been dispersed in the gaseous atmosphere to attain one of the dispersities set forth above, and means for separating a mixture of a gas and the particles in a powder of less highly dispersed core particles from said gas-particle mixture so as to select a mixture of a gas and the particles in a powder of highly dispersed core particles in which the core particles are present in the gaseous atmosphere mainly in a single-particle state.

8. A process for producing a diamond or high-pressure phase boron nitride sinter according to claim 1 wherein the dispersing step is performed by:

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter of no more than 10 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 70%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 80%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 20 μm but no more than 50 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 90%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 50 μm but no more than 300 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 95%;

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 300 μm but no more than 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 97%; and

a group of means for high dispersion treatment of particles that has such dispersing performance that a powder of core particles having an average diameter in excess of 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 99%; and

said coated diamond or high-pressure phase boron nitride particles being prepared by performing at least one part of the dispersing step in such a way that it shares one or more parts of the space with at least one part of the coating step.

8. A process for producing a diamond or high-pressure phase boron nitride sinter according to claim 1 wherein said coated diamond or high-pressure phase boron nitride particles are prepared with the coating start region of the coating space being located in either one of the following space regions that includes planes through which all particles in the powder of highly dispersed core particles as mixed with a gas will pass:

a space region in which a powder of core particles that have an average diameter of no more than 10 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 70%;

a space region in which a powder of core particles that have an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 80%;

a space region in which a powder of core particles that have an average diameter in excess of 20 μm but no more than 50 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 90%;

a space region in which a powder of core particles that have an average diameter in excess of 50 μm but no more than 300 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 95%;

a space region in which a powder of core particles that have an average diameter in excess of 300 μm but no more than 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 97%; and

a space region in which a powder of core particles that have an average diameter in excess of 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 99%, or wherein

said coated diamond or high-pressure phase boron nitride particles are prepared with the coating start region of the coating space being located in either one of the following space regions that includes planes through which all particles to be recovered into the recovery section of the recovery means will pass:

a space region in which a powder of core particles that have an average diameter of no more than 10 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 70%;

a space region in which a powder of core particles that have an average diameter in excess of 10 μm but no more than 20 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by said group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 80%;

a space region in which a powder of core particles that have an average diameter in excess of 20 μm but no more than 50 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles

in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 90%.

a space region in which a powder of core particles that have an average diameter in excess of 50 μm but no more than 500 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 95%;

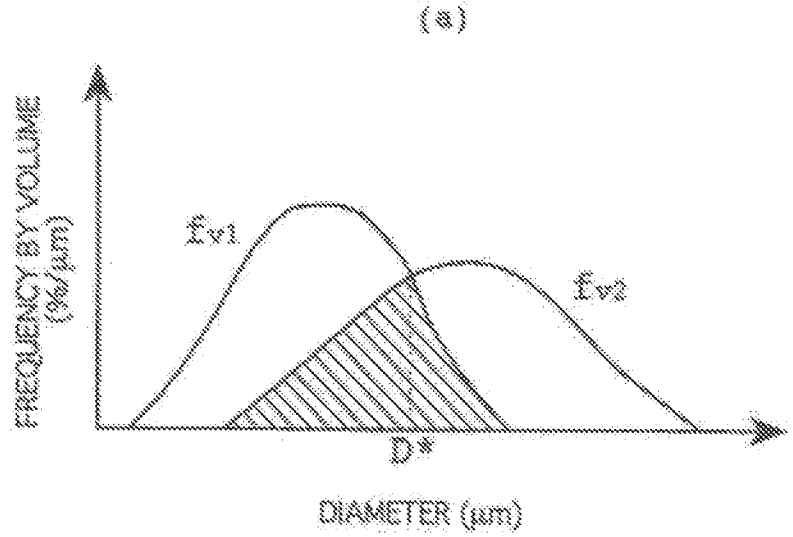
a space region in which a powder of core particles that have an average diameter in excess of 300 μm but no more than 800 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 97%; and

a space region in which a powder of core particles that have an average diameter in excess of 600 μm in the frequency distribution by volume is dispersed in a gaseous atmosphere by the final treatment by the group of means for high dispersion treatment of particles, thereby forming a mixture of a gas and the particles in the powder of highly dispersed core particles and that the dispersity β of the particles in said powder of core particles is adjusted to at least 99%.

7. A process for producing a diamond or high-pressure phase boron nitride sinter according to claim 1 wherein the particles in the powder of core particles to be used have a size distribution of (D_{50}/3, 3D_{50}) ≥ 80%) in terms of frequency distribution by volume, where D_{50} represents the average particle diameter.

8. A diamond or high-pressure phase boron nitride sinter that is produced by either one of the processes for producing a diamond or high-pressure phase boron nitride sinter as recited in claims 1 - 7.

FIG.1


(a)
FREQUENCY BY VOLUME (%/μm)
f_{v1}
f_{v2}
D*
DIAMETER (μm)

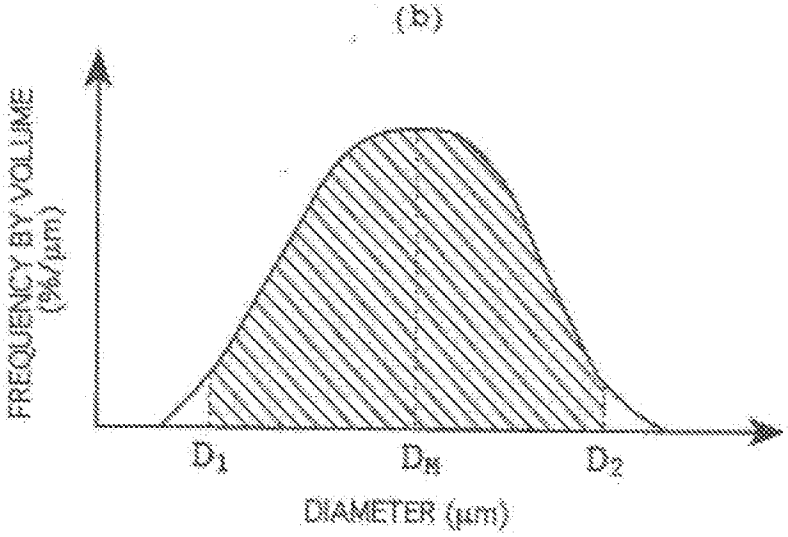
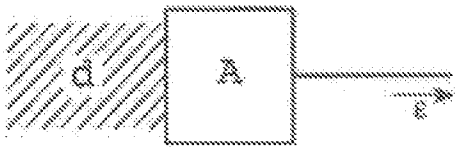
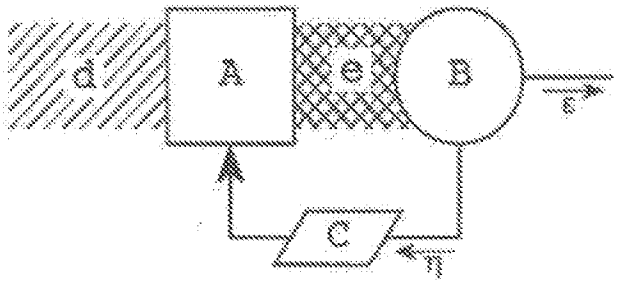

(b)
FREQUENCY BY VOLUME (%/μm)
D_1
D_M
D_2
DIAMETER (μm)

FIG. 2

(a)



(b)



(c)

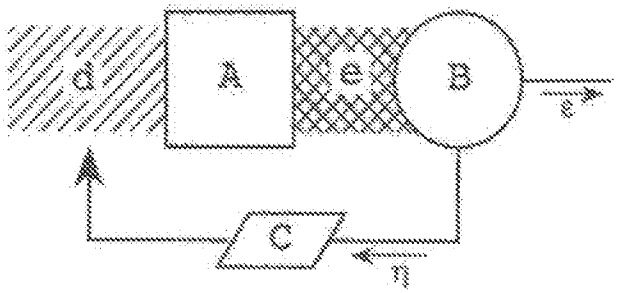


FIG. 3

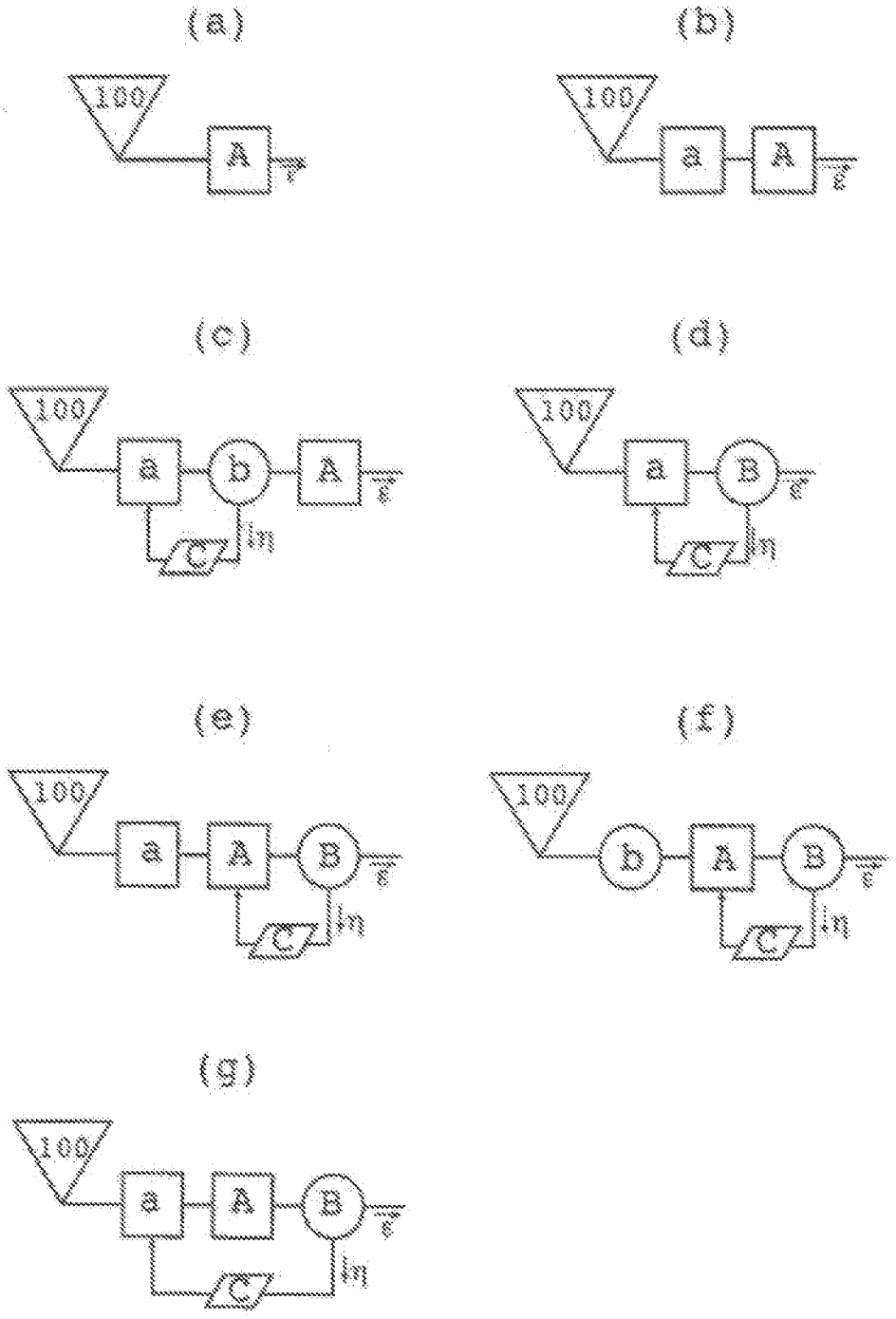

(a)
100
A
(b)
100
a
A
(c)
100
a
b
A
C
(d)
100
a
B
C
(e)
100
a
A
B
C
(f)
100
b
A
B
C
(g)
100
a
A
B
C

FIG. 4

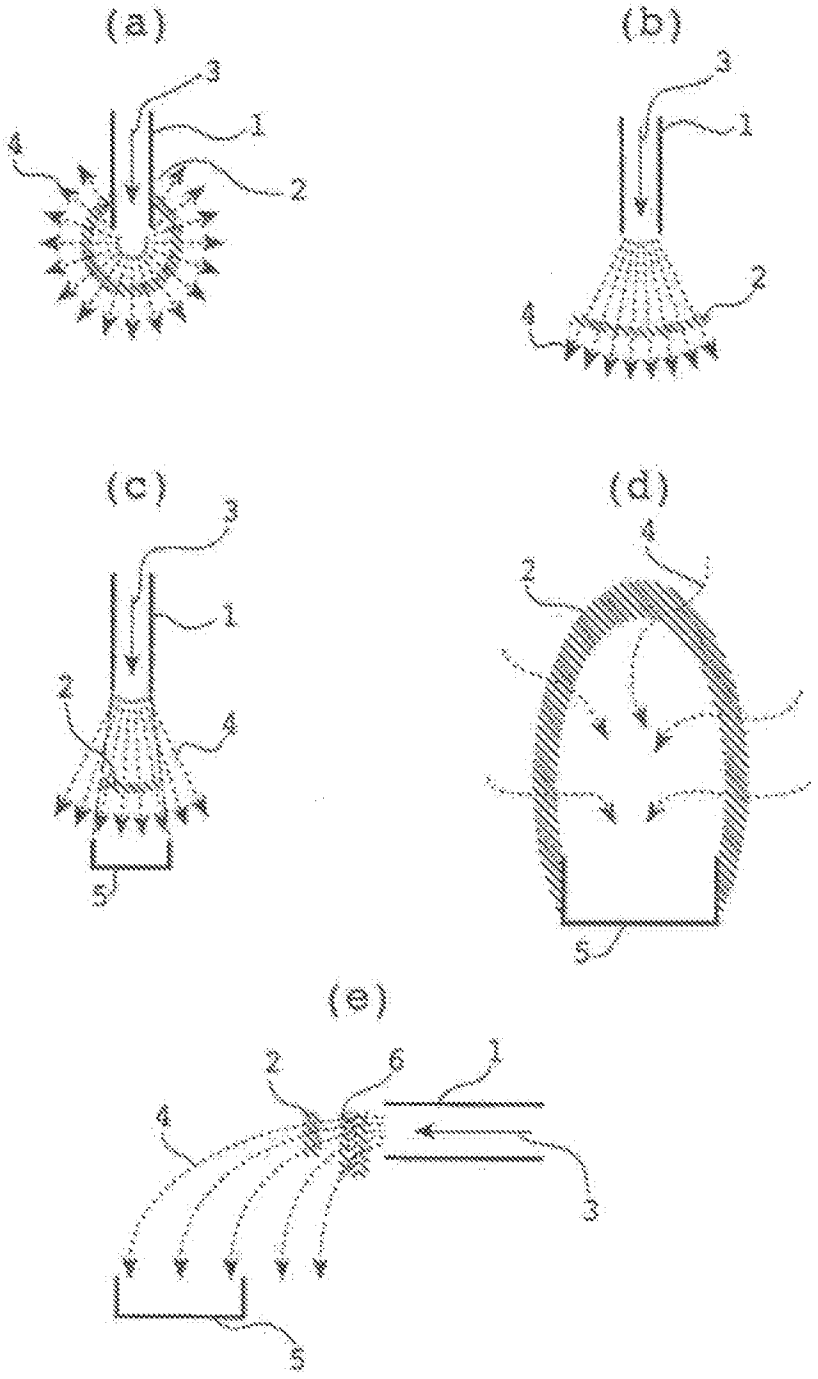
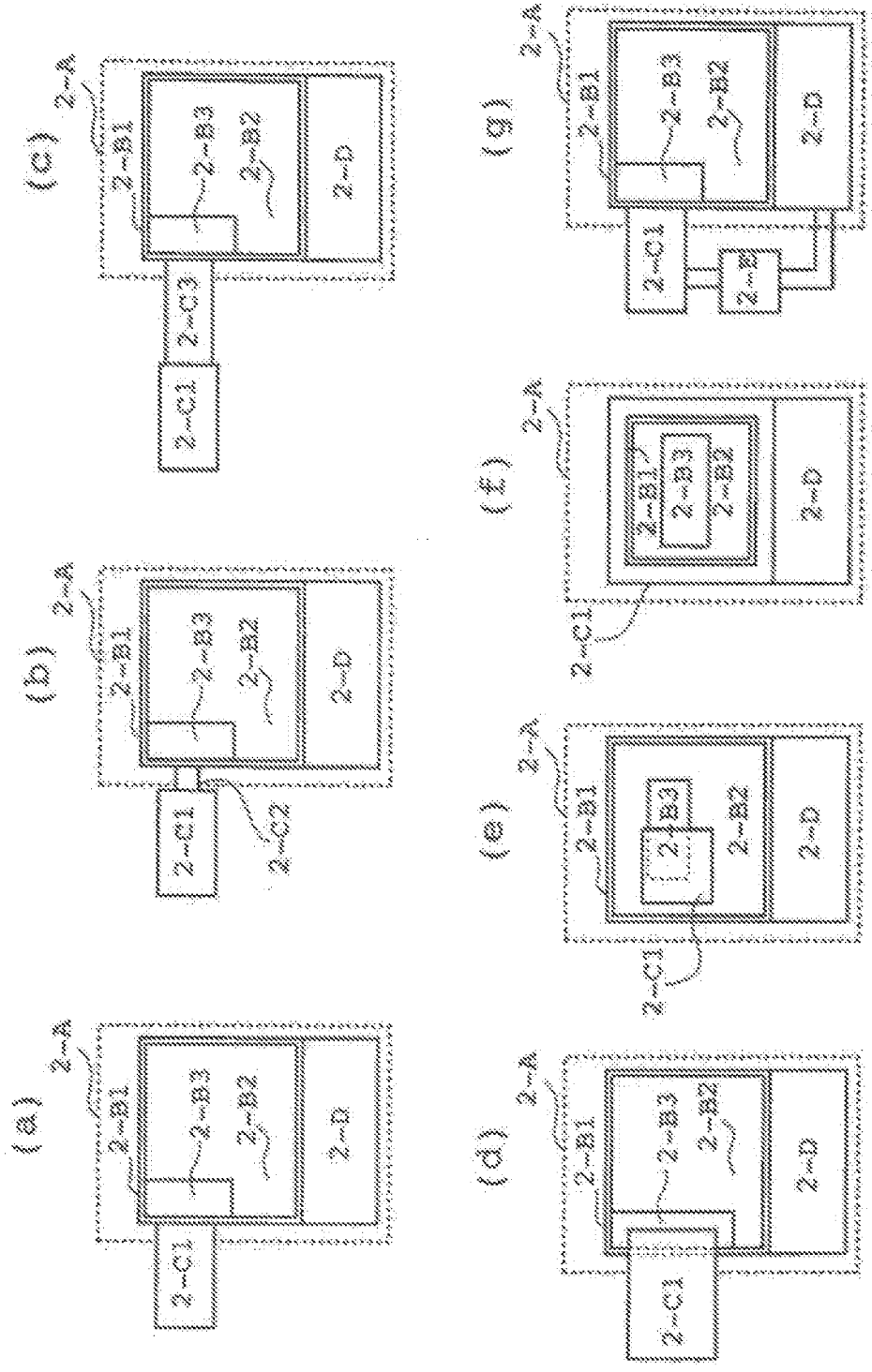


FIG. 5



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FIG. 6

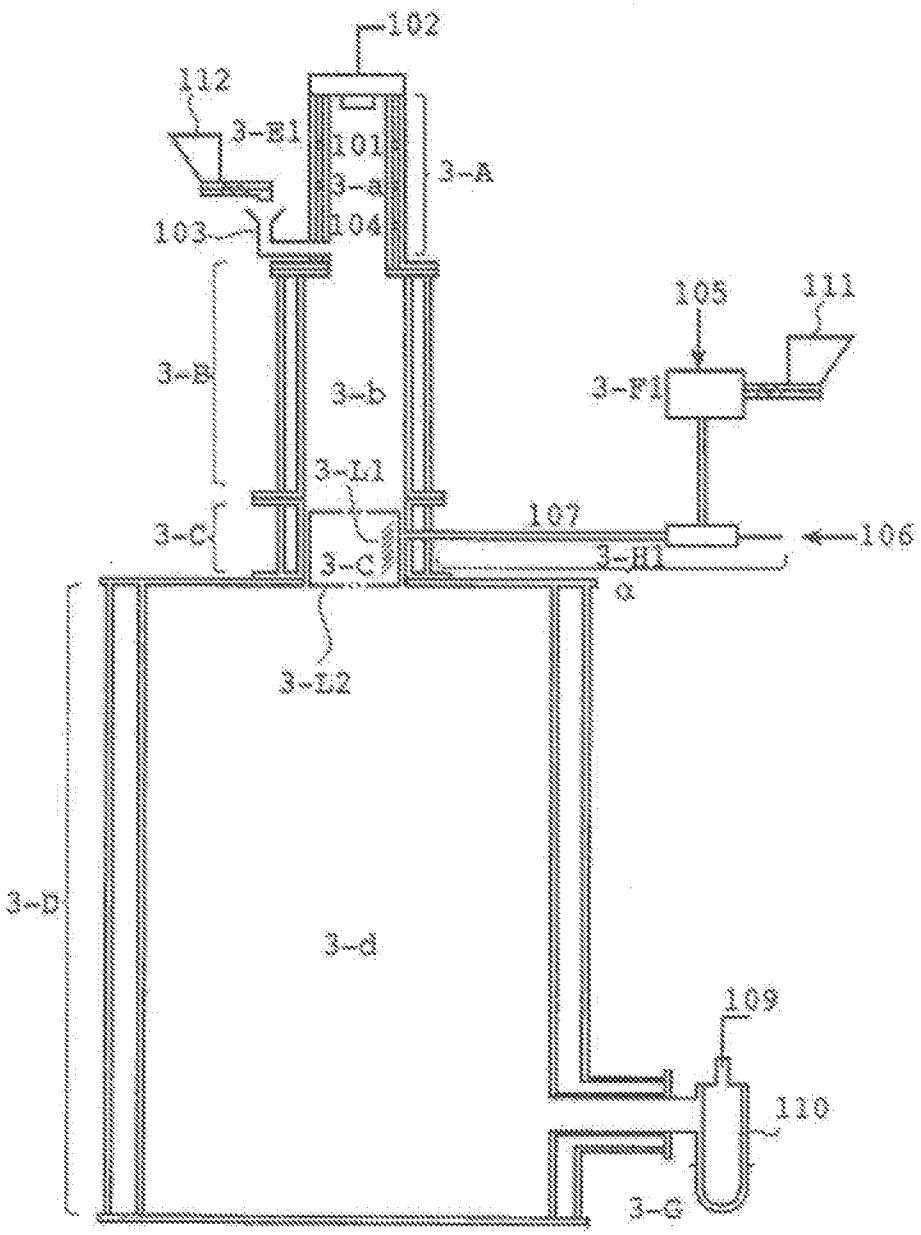

102
112
3-E1
101
3-a
104
3-A
103
105
111
3-B
3-b
3-F1
3-L1
107
106
3-c
3-C
3-H1
Q
3-L2
3-D
3-d
109
110
3-G

FIG. 7

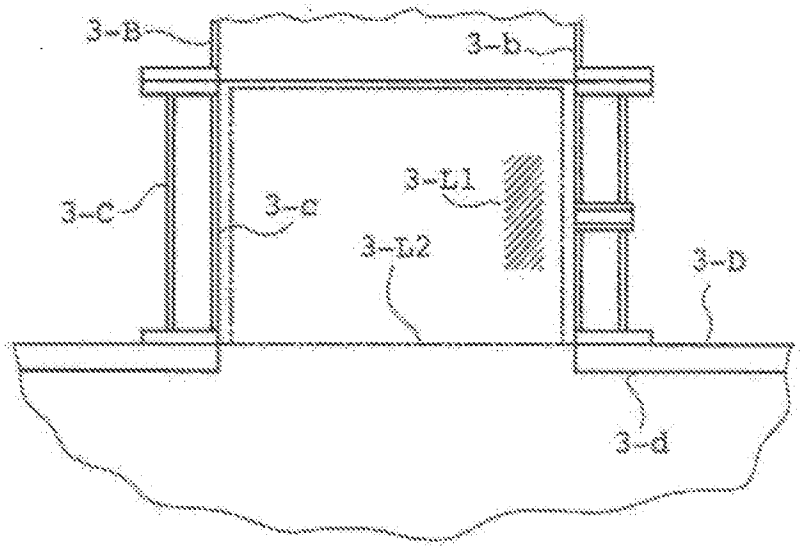


FIG. 8



FIG. 9

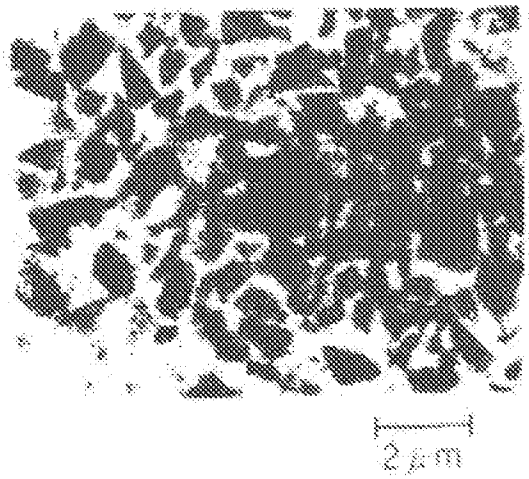


FIG. 10

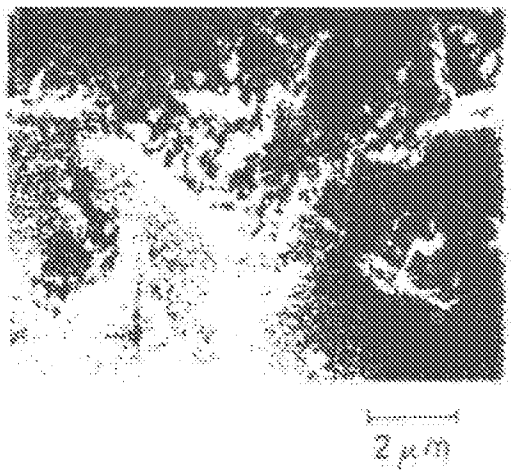


FIG. 11

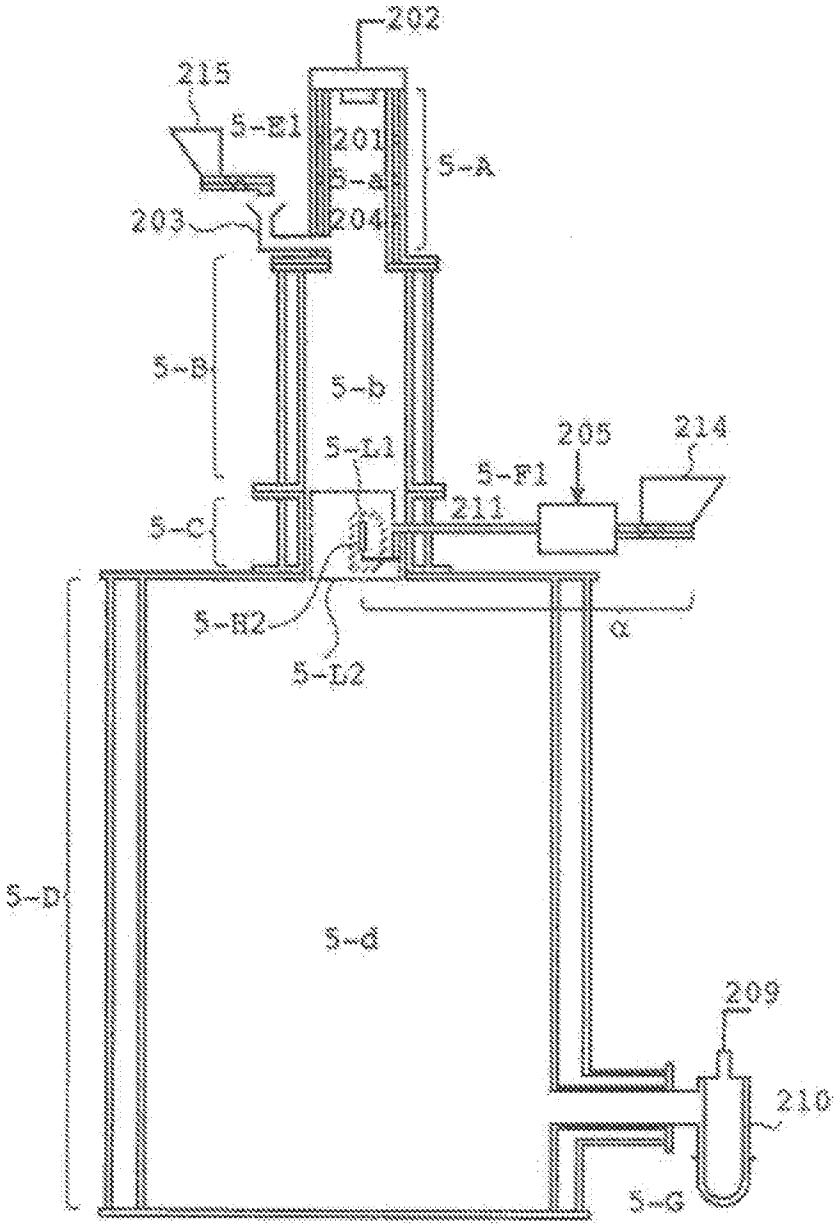

202
215
S-E1
201
S-A
203
204
S-B
S-b
205
214
S-F1
S-C
211
S-E2
S-E2
Q
S-D
S-d
209
210
S-G

FIG.12

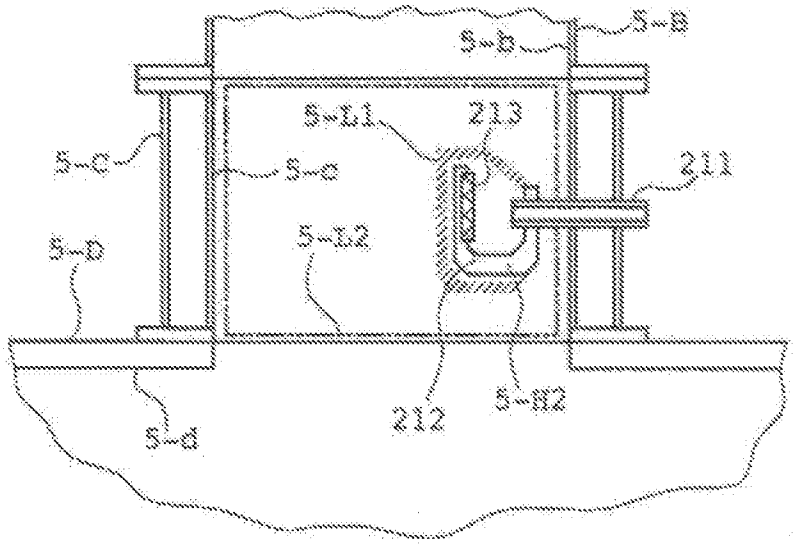


FIG. 13

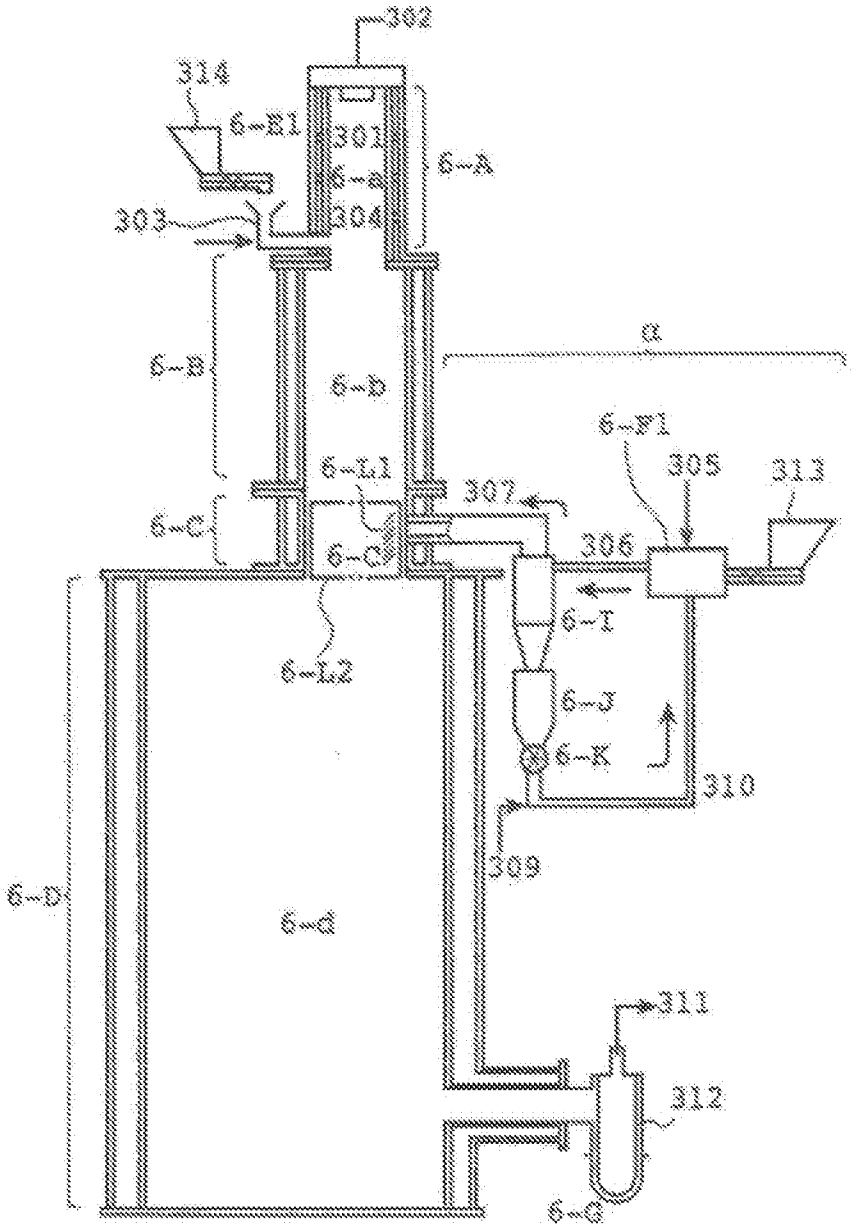

302
314
6-B1
301
6-A
303
304
α
6-B
6-b
6-F1
305
313
6-L1
307
6-C
6-c
306
6-I
6-L2
6-J
6-K
310
309
6-D
6-d
311
312
6-G

FIG. 14

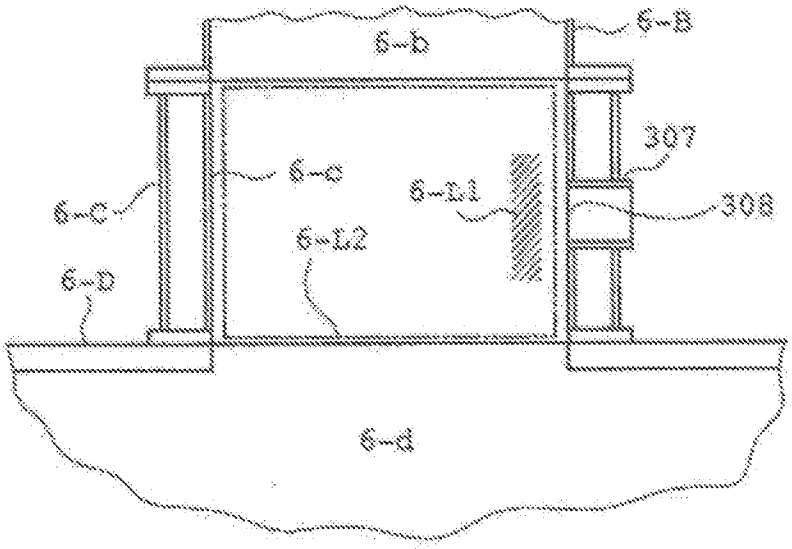


FIG. 15



FIG.16

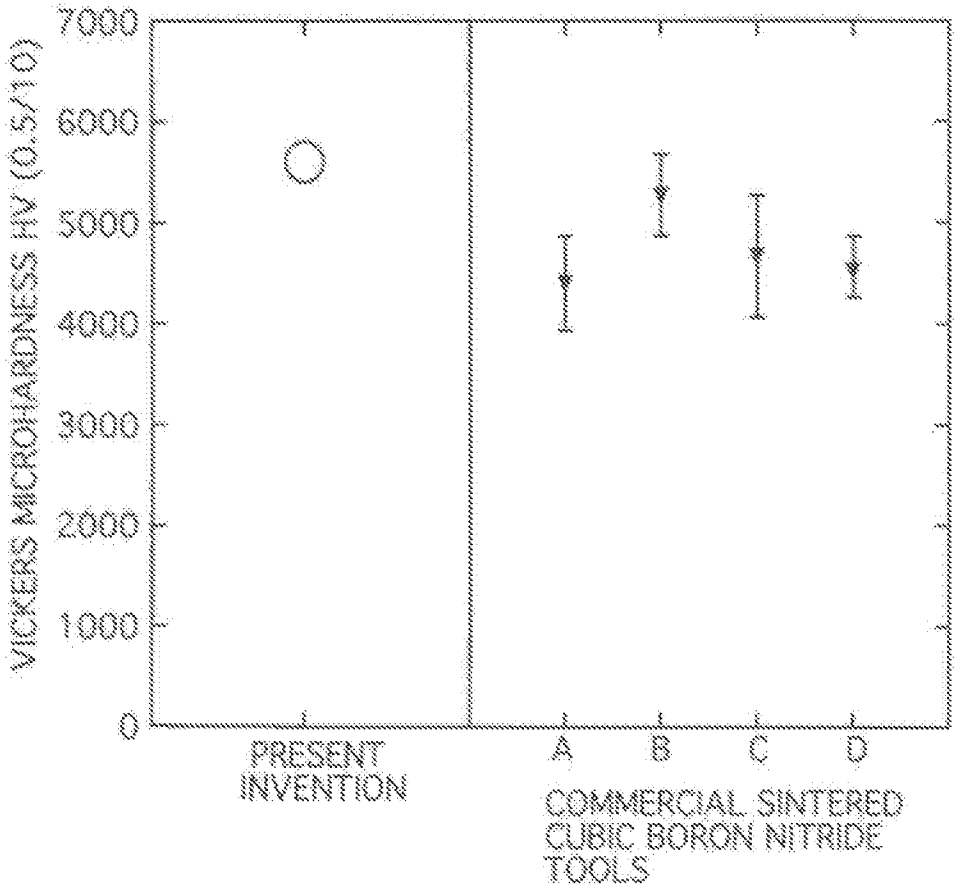

VICKERS MICROHARDNESS HV (0.5/10)
7000
6000
5000
4000
3000
2000
1000
0
PRESENT INVENTION
A
B
C
D
COMMERCIAL SINTERED CUBIC BORON NITRIDE TOOLS

FIG. 17

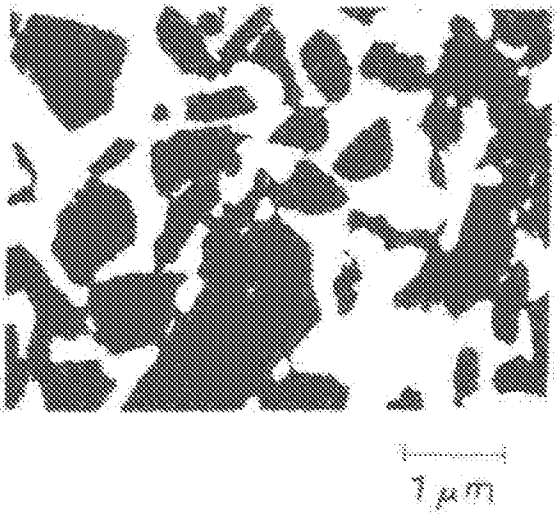


FIG. 18

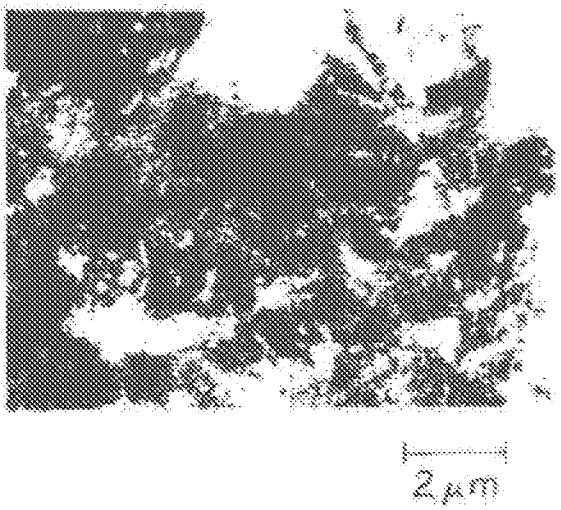


FIG.19



FIG.20

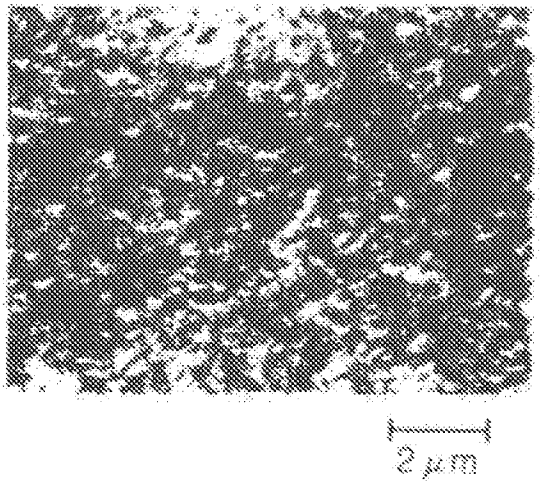


FIG.21

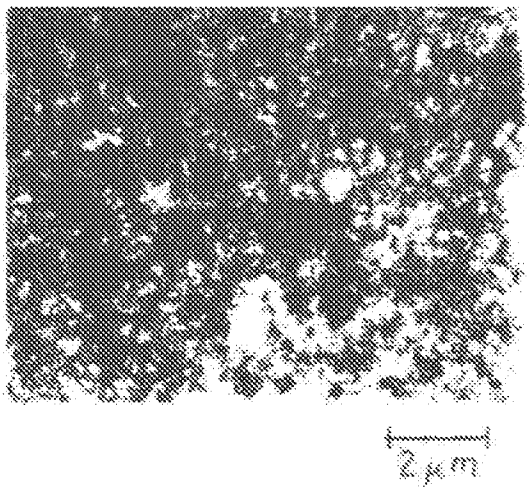


FIG. 22



FIG. 23

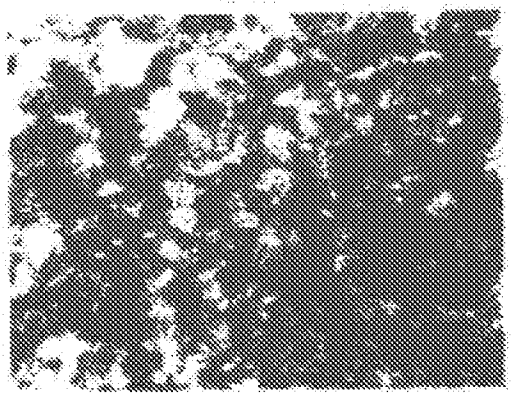


FIG. 24

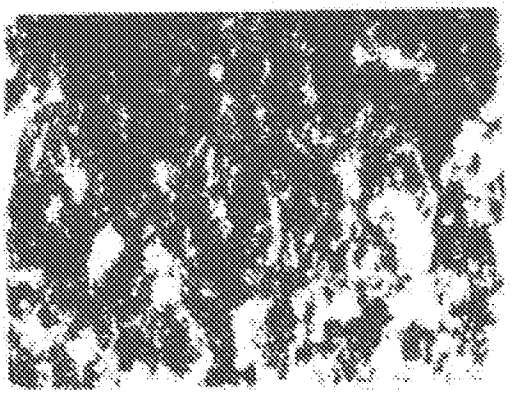


FIG.25

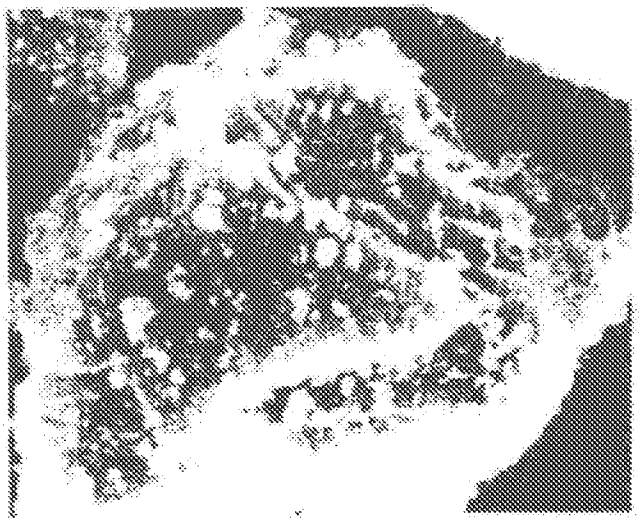


FIG.26

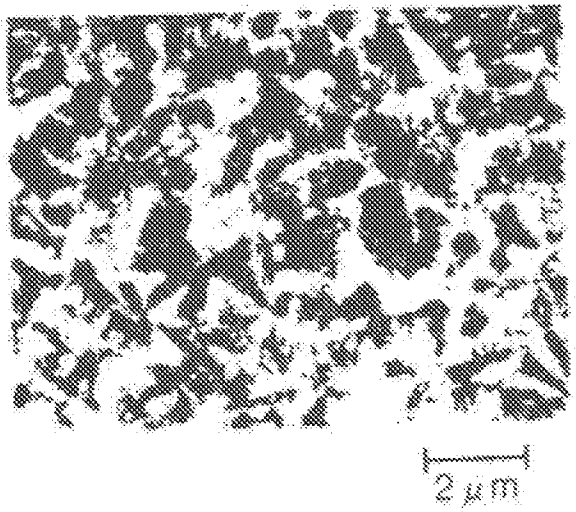


FIG.27



FIG.28

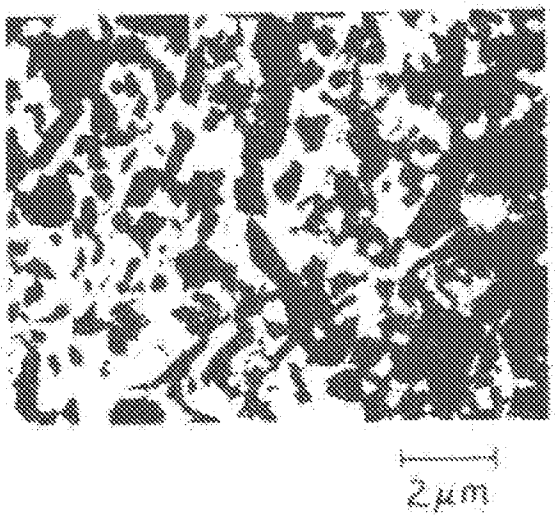


FIG. 29

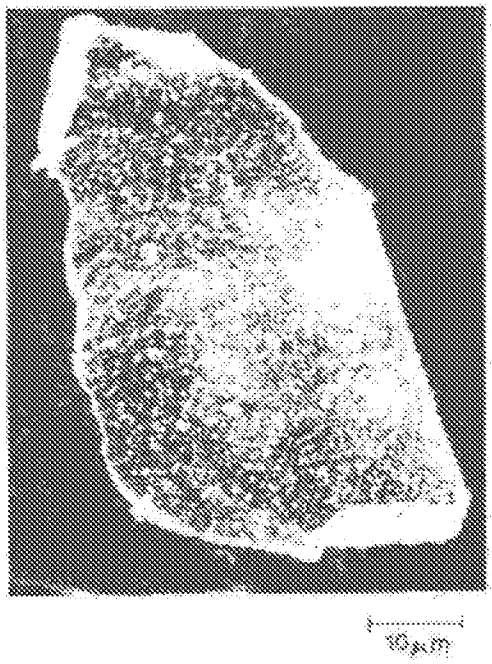


FIG. 30

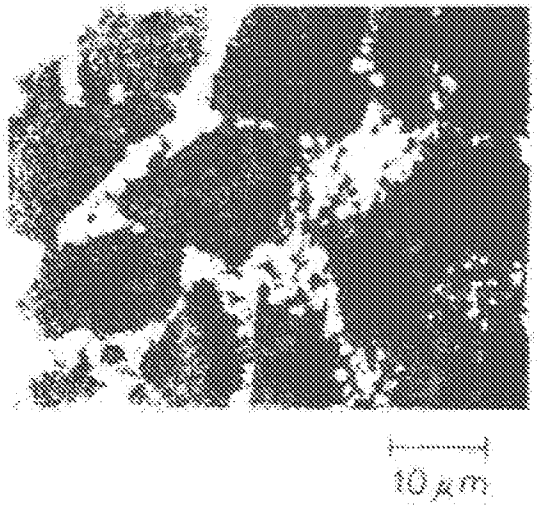


FIG. 31



FIG. 32

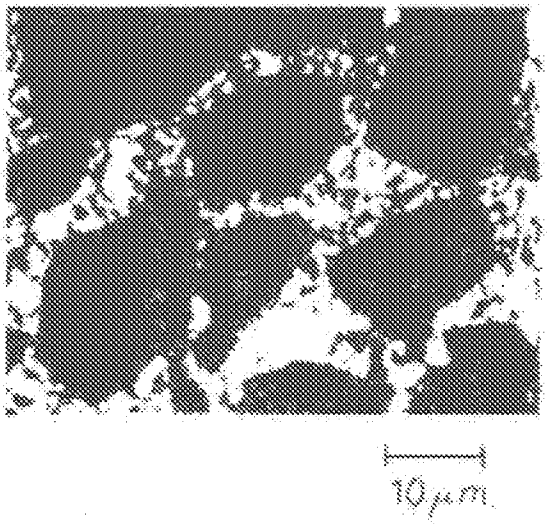


FIG.33a

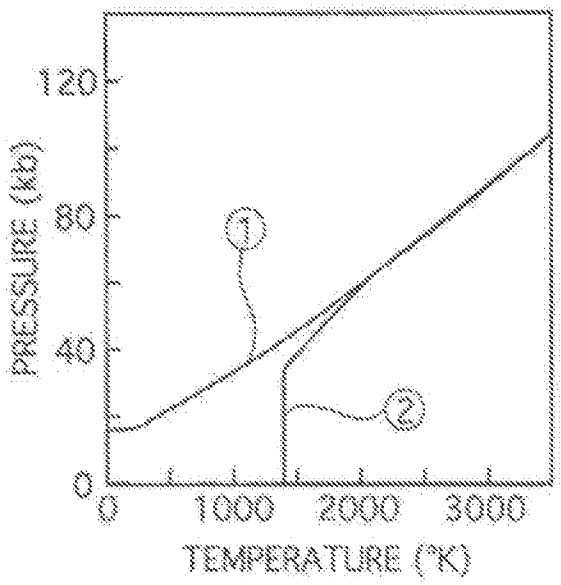
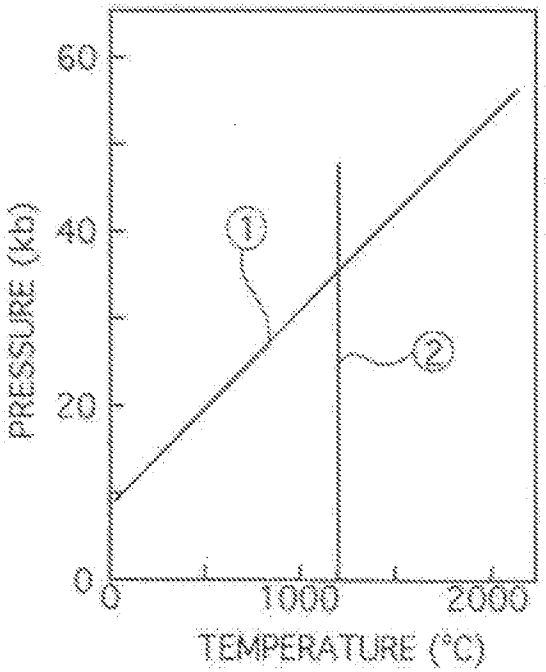


FIG.33b



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 11 8222

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 273 573 (QA TECHNOLOGIES INC) 6 July 1988 * page 3, line 3 - line 29 *	1,2,4-8	C23C14/22
X	GB-A-2 214 196 (INCO LTD) 31 August 1989 * page 4, line 21 - page 5, line 31 *	1,2,4-8	
A,D	GB-A-2 242 443 (NISSHIN FLOUR MILLING CO) 2 October 1991 * example 4 *	1-8	
A,D	PATENT ABSTRACTS OF JAPAN vol. 014 no. 282 (C-0713) ,25 April 1990 & JP-A-02 043177 (SEIJI MOROOKA;OTHERS: 01) 13 February 1990, * abstract *	1-8	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 April 1995	Schruers, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EX1058, Page 804

(12) UK Patent Application (19) GB (11) 2 239 011 (13) A

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(51) INT CL5
C01B 31/06

(52) UK CL (Edition K)
C1A A42

(56) Documents cited
EP 0288820 A

(58) Field of search
UK CL (Edition K) C1A A42
INT CL5 C01B
Online database: WPI; CLAIMS

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(54) Single-crystal diamond of very high thermal conductivity

(57) Single-crystal diamond consisting of isotopically pure carbon-12 or carbon-13 has been found to have a thermal conductivity higher than that of any substance previously known, typically at least 40% higher than that of naturally occurring IIA diamond. It may be prepared by a method comprising comminution of diamond of high isotopic purity, such as that obtained by low pressure chemical vapor deposition employing an isotopically pure hydrocarbon in combination with hydrogen, followed by conversion of the comminuted diamond to single-crystal diamond by diffusion under high pressure through a metallic catalyst-solvent material to a region containing a diamond seed crystal.

GB 2 239 011 A

SINGLE-CRYSTAL DIAMOND OF VERY HIGH THERMAL CONDUCTIVITY

This invention relates to the preparation of single crystal diamond of extremely high thermal conductivity.

Diamond substances with high thermal conductivity are known in the art. For example, type IIA natural diamond, characterized by a very high degree of purity, has a thermal conductivity at 25°C (298°K) on the order of 21 watts/cm.°K, the highest of any material known prior to the present invention. Its electrical conductivity, on the other hand, is so low as to be negligible.

These properties make diamond an excellent material for conducting heat away from heat-generating objects or units. It may be used as a heat sink or as a conductor/spreader to conduct heat from the heat-generating object or unit to a heat sink of some other material.

Various areas exist in which heat conductors of very high thermal conductivity are necessary. One example is in repeating stations for fiber optic networks. Signals are transmitted by laser light over the fibers of such networks for very great distances. Since these signals decrease substantially in intensity over several kilometers, it is necessary to construct "repeating stations" periodically along the network, for the purpose of increasing the intensity of the light transmitted along the network. In a typical repeating station of this type, a photodetector is employed to convert the weakened signal transmitted by fiber optics to an electrical signal, which is then magnified, reconverted to a light signal by a light-emitting diode, and transmitted in turn along the next segment of the network.

In order to minimize the requisite number of repeating stations, optimum magnification of the signal in any station is desirable. However, the amount of radiant energy of any kind generated electrically is proportional to the fourth power of the current employed. While a portion of such radiant energy is in the form of light, the remainder thereof is lost as heat. In any individual station, therefore, very large amounts of heat are generated, requiring efficient heat conductors to maintain the operativeness of the repeating station.

The use of natural type IIA diamond as a conductor of heat in these areas has not been foreclosed despite its very high cost since the operative heat-conducting units are very small, typically about 1 mm. on a side. When larger heat-conducting elements are required, expense considerations become important and the use of natural diamond may accordingly be foreclosed.

Conventionally produced high-pressure synthetic diamond of gem quality is lower in cost than natural diamond. However, synthetic diamond of this type having high thermal conductivity cannot effectively be produced directly from graphite because a profound contraction in volume occurs in the conversion and introduces imperfections into the crystalline structure. For the most part, diamond prepared by low-pressure chemical vapor deposition (hereinafter sometimes "CVD") processes are not single crystal diamond and have substantially lower thermal conductivities, typically on the order of 12 watts/cm.°K at about 300°K (hereinafter sometimes "room temperature conductivity").

In U.S. Patent 3,895,313, there are disclosed various diamond materials which allegedly have very high thermal conductivities, and which allegedly are useful as optical elements for very high-power laser beams. In particular, it is stated that synthetic diamond grown from

isotopically pure carbon-12 or carbon-13 would be useful in this way, with room temperature conductivity values in the range of 10-20 watts/cm.°K being mentioned. This is, of course, the order of magnitude of natural type IIA diamond and also of diamond produced by chemical vapor deposition. It is further suggested that at a temperature of 70°K (-203°C), below the temperature of liquid nitrogen, a thermal conductivity exceeding 200 watts/cm.°K may be obtained, perhaps in diamond which has high isotopic purity and "relevant properties which closely approach the limits predicted by the theory of the perfect solid state" (i.e., are in single-crystal form). However, no methods for the preparation of such diamond are suggested, and the state of the art has hitherto been inadequate to put them in the possession of the public.

The present invention provides a method for preparing single-crystal diamond of very high chemical and isotopic purity. The raw material for such diamond is itself diamond, which eliminates the volume contraction encountered in the high-pressure conversion of graphite to diamond. The thermal conductivity of the diamond so produced has been found to be higher than that of any substance presently known including natural type IIA diamond, and also higher than the values in the aforementioned U.S. Patent 3,895,313. Accordingly, it is eminently suitable for use as a conductor of heat and also in numerous other areas.

In one of its aspects, the invention is a method for preparing single-crystal diamond of high isotopic purity which comprises the steps of:

(A) preparing diamond consisting of isotopically pure carbon-12 or carbon-13; and

(B) converting said diamond to single-crystal diamond by diffusion under high pressure through a metallic

catalyst-solvent material to a region containing a diamond seed crystal.

An essential feature of the method of this invention is the employment of isotopically pure carbon-12 or carbon-13. As explained hereinafter, it has been found that the increase in thermal conductivity resulting from the employment of chemically and isotopically pure carbon is vastly greater than would be expected based on theoretical considerations. In general, the isotopic purity of the hydrocarbon should be at least 99.2% by weight; that is, the other isotope should be present in a maximum amount of 8 parts per 1000. An isotopic purity of at least 99.9% by weight is preferred. The hydrocarbon should also have a high degree of chemical purity.

Various methods may be employed in step A for the preparation of diamond in isotopically pure form. For example, a gaseous carbon compound such as carbon monoxide may be separated into carbon-12 and carbon-13 species via differences in diffusivity and then converted to solid carbon by art-recognized means, such as combustion in a reducing flame in the case of carbon monoxide. The carbon thus formed may then be converted to diamond under conventional conditions, including high temperature and high pressure conditions or CVD conditions.

Alternatively, other methods may be employed including shock formation and CVD processes under conditions which produce a mixture of diamond and graphite. In processes of the latter type, the carbon-13 species will concentrate in the diamond phase and the carbon-12 species in the graphite phase. Other diamond precursors which may be employed in enriched form include pyrolytic graphite, amorphous or glassy carbon, liquid hydrocarbons and polymers.

It is usually found that conventional methods of CVD diamond formation are most convenient for the preparation of isotopically pure diamond. In such methods, a layer of diamond is deposited on at least one substrate. Any substrate material suitable for diamond deposition thereon may be employed; examples of such materials are boron, boron nitride, platinum, graphite, molybdenum, copper, aluminum nitride, silver, iron, nickel, silicon, alumina and silica, as well as combinations thereof. Metallic molybdenum substrates are particularly suitable under many conditions and are often preferred.

The method of chemical vapor deposition of diamond on a substrate is known, and the details need not be repeated herein. In brief, it requires high-energy activation of a mixture of hydrogen and a hydrocarbon, typically methane, whereupon the hydrogen gas is converted to atomic hydrogen which reacts with the hydrocarbon to form elemental carbon. Said carbon then deposits on the substrate in the form of diamond. Activation may be achieved by conventional means involving high-energy activation which produces atomic hydrogen from molecular hydrogen; such means include thermal means typically involving heated filaments, flame means, D.C. discharge means and radiation means involving microwave or radio-frequency radiation or the like.

Thermal and especially filament methods, employing one or more resistance heating units including heated wires or filaments, are often preferred for the purposes of this invention. In such methods, the filaments are typically of metallic tungsten, tantalum, molybdenum and rhenium; because of its relatively low cost and particular suitability, tungsten is often preferred. Filament diameters of about 0.2-1.0 mm. are typical, with about 0.8 mm. frequently being preferred. Distances from filaments to substrate(s) are generally on the order of 5-10 mm.

Said filaments are typically heated at temperatures of at least 2000°C and the optimum substrate temperature is in the range of 900-1000°C. The pressure in the deposition vessel is maintained up to about 760 torr, typically on the order of 10 torr. The hydrogen-hydrocarbon mixture generally contains hydrocarbon in an amount up to about 2% by volume based on total gases. For a description of illustrative CVD methods of diamond preparation, reference is made to copending, commonly owned applications U.S. Serial Nos. 07/389,210 and 07/389,212.

Isotopically pure hydrocarbon is employed in the CVD method, when used. In order to avoid contamination thereof, it is essential to employ equipment which does not contain natural carbon as an impurity. For this purpose, the CVD chamber should be constructed of materials substantially incapable of dissolving carbon. Typical materials of this type are quartz and copper.

As between carbon-12 and carbon-13, the former is usually preferred for various reasons. In the first place, carbon-12 is present in nature in much higher proportions than carbon-13, the latter typically occurring in amounts no higher than about 1% by weight; therefore, the use of carbon-12 involves minimum expense. In the second place, thermal conductivity is inversely proportional to the square of the mass number of the isotope, and diamond prepared from carbon-12 can therefore be expected to have a thermal conductivity about 17% greater than those prepared from carbon-13. In some applications, however, carbon-13 is preferred and its preparation and use are part of the invention.

The thickness of the CVD diamond layer deposited on the substrate is not critical. In general, it is convenient to deposit at least as much diamond as will be needed to produce a single crystal of the desired size. Of course, the

production of a larger amount of CVD diamond for use to make several crystals is also contemplated.

It is possible to convert the product of the CVD process directly to diamond of high thermal conductivity by high pressure means, as described hereinafter, employing the same in the form of a slab, sheet or broken pieces thereof. However, the method of this invention is most efficiently conducted if the isotopically pure diamond is first comminuted.

Comminution may be achieved by art-recognized means such as crushing and powdering. The particle size thereof is not critical so long as a sufficient degree of comminution is attained; the form known in the art as "grit diamond" is suitable.

Step B, the production of single crystal diamond, is conventional except that the isotopically pure diamond produced in step A is the raw material employed. Two things are achieved by using diamond rather than graphite or some other allotrope of carbon as the raw material: an easily obtained isotopically pure material may be employed, and the contraction in volume encountered in the conversion of graphite and other allotropes to diamond is avoided, permitting production of a single crystal of regular structure and high quality.

The process for producing single-crystal diamond under high pressure is also known in the art, and a detailed description thereof is not deemed necessary. Reference is made, for example, to Encyclopedia of Physical Science & Technology, vol. 6, pp. 492-506 (Academic Press, Inc., 1987); Strong, The Physics Teacher, January 1975, pp. 7-13; and U.S. Patents 4,073,380 and 4,082,185, for general descriptions of the process. It generally involves diffusion of the carbon employed as a source material through a liquid bath of a metallic catalyst-solvent material, at pressures on the order

of 50,000-60,000 atmospheres and temperatures in the range of about 1300-1500°C. A negative temperature gradient, typically of about 50°C, is preferably maintained between the material being converted and the deposition region, which contains a diamond seed on which crystal growth can begin.

Catalyst-solvent materials useful in step B are known in the art. They include, for example, iron; mixtures thereof with nickel, aluminum, nickel and cobalt, nickel and aluminum, and nickel, cobalt and aluminum; and mixtures of nickel and aluminum. Iron-aluminum mixtures are frequently preferred for the production of single-crystal diamond, with a material consisting of 95% (by weight) iron and 5% aluminum being particularly preferred for the purposes of the invention.

Following preparation of the single-crystal diamond by the method of this invention, it is often preferred to remove the portion attributable to the seed crystal by polishing. This is particularly true if the seed crystal is not isotopically pure.

Studies on single-crystal diamond prepared according to the invention and having various degrees of isotopic purity have shown that at carbon-12 purity levels of 99.2%, 99.5% and 99.9% by weight, the room temperature conductivities are, respectively, 10%, 25% and 40% greater than that of natural type IIA diamond. At lower temperatures, even higher differences in thermal conductivity are to be expected. Such thermal conductivities are higher than those of any material previously known. Single-crystal diamond of this type is another aspect of the invention, as is diamond prepared by the method described herein.

The reasons for the extremely high thermal conductivity of the single-crystal diamond of this invention are not fully understood. It is assumed, however, that the phenomenon is principally a function of the mean free path of

the phonons (i.e., lattice vibration modes) in the diamond crystals. Thermal conductivity is directly proportional to specific heat, sound velocity in and phonon mean free path of the crystal, and isotope effects on specific heat and sound velocity are negligible.

In a simplified calculation, the reciprocal of the phonon mean free path can be considered as equal to the sums of the reciprocals of the mean free paths attributable to phonon-phonon scattering and to isotope effects. It has been calculated that the isotope-related mean free path is 34,000 Angstroms and the phonon scattering-related path is 1900 Angstroms; consequently, the isotope effect would account for a decrease in mean free path on the order of only about 5.2%. One possible reason for the substantially greater observed isotope effect on thermal conductivity is that contrary to theory, the isotopic constitution of the diamond has a direct effect on the mean free path attributable to phonon-phonon scattering. This effect has apparently not been previously recognized.

By reason of the aforementioned high thermal conductivity value and essentially non-existent electrical conductivity, the isotopically pure single crystal diamond of the present invention is singularly useful as a conductor of heat from electronic devices and similar heat-generating sources. Articles comprising such a source in contact with said diamond as a thermal conductor are another aspect of the invention.

A further aspect is abrasive articles comprising said diamond. Such articles can be expected to have extraordinarily long life by reason of their ability to dissipate frictional heat generated during their use. Typical areas of application include abrasive grit, diamond compacts, wire drawing dies, saw blades, scribing tools, drills, tool sharpeners, and polishing tools for optical

items, stone and precious stones including diamonds and articles made therefrom.

Still another aspect is light-filtering articles comprising said diamond with a pinhole aperture therein. They are useful, for example, as spatial filters for laser beams and the like. Articles of this type fabricated from natural diamond are subject to radiation-induced damage, probably thermal in nature. The substantially higher thermal conductivity of the diamond of this invention may be expected to greatly minimize damage of this kind.

The invention is illustrated by an example in which a layer of CVD diamond was first deposited on a molybdenum substrate in a chamber constructed of quartz and copper, neither of which dissolves substantial amounts of carbon. The substrate was vertically disposed in a plane parallel to and 8-9 mm. distant from the plane of a tungsten filament about 0.8 mm. in diameter. The vessel was evacuated to a pressure of about 10 torr, the filament was heated to about 2000°C by passage of an electric current and a mixture of 98.5% (by volume) hydrogen and 1.5% methane was passed into the vessel. The methane employed was substantially impurity-free and 99.9% thereof contained the carbon-12 isotope. Upon removal and mass spectroscopic analysis of the diamond thus obtained, it was found that 99.91% of the carbon therein was carbon-12.

Thermal conductivity of the isotopically pure CVD diamond was measured by the mirage detection of thermal waves generated by a modulated argon-ion beam impinging on the diamond crystals, in accordance with a conventional method. The room temperature conductivity was shown to be about 12 watts/cm.°K. A control sample of similar CVD diamond prepared from methane having the naturally occurring isotope distribution (98.96% C-12, 1.04% C-13) had essentially the same conductivity.

The isotopically pure CVD diamond was crushed and powdered, and was used as a source of carbon for the growth of a single-crystal diamond under high pressure and high temperature conditions. Specifically, a conventional belt apparatus was employed at 52,000 atmospheres and 1400°C, employing a catalyst-solvent mixture of 95% (by weight) iron and 5% aluminum. A small (0.005 carat) single-crystal diamond seed of normal isotopic distribution was used to initiate growth, and a negative temperature gradient of about 50°C was maintained between the CVD diamond and the seed crystal. The process was continued until a single crystal of 0.95 carat had been produced. It was shown by analysis that 99.93% of the carbon therein was the C-12 isotope.

The diamond was polished on a standard diamond scaife to remove the seed crystal, and its room temperature conductivity was compared with those of several other materials, including a control single-crystal diamond prepared from the CVD diamond with normal isotope distribution. The results were as follows, all values being in watts/cm.°K:

Isotopically pure C-12 diamond (this invention)	31.5
Control	21.18
Naturally occurring type IIA diamond	21.2
CVD diamond	12.0
Cubic boron nitride	7.8
Silicon carbide	4.9
Copper	4.0
Beryllium oxide	3.7
Boron phosphide	3.6
Aluminum nitride	3.2
Silicon	1.6
Aluminum oxide	0.3

Thus, the room temperature conductivity of the diamond of this invention is 48.7% greater than that of the control. It is also much higher than the room temperature conductivity of any other diamond or non-diamond material which has been measured.

At 70°K, below the boiling point of liquid nitrogen, the diamond of the present invention is theoretically predicted to have a conductivity of about 2675 watts/cm.°K, more than 13 times the minimum value predicted in the aforementioned U.S. Patent 3,895,313.

CLAIMS

1. A method for preparing single-crystal diamond of high isotopic purity which comprises the steps of:

(A) preparing diamond consisting of isotopically pure carbon-12 or carbon-13; and

(B) converting said diamond to single-crystal diamond by diffusion under high pressure through a metallic catalyst-solvent material to a region containing a diamond seed crystal.

2. A method as claimed in claim 1 wherein the carbon in the hydrocarbon is carbon-12.

3. A method as claimed in claim 1 or claim 2 wherein the product of step A is comminuted.

4. A method as claimed in any of the preceding claims wherein the carbon in the hydrocarbon is at least 99.2% isotopically pure.

5. A method as claimed in any of the preceding claims wherein the diamond of step A is prepared by chemical vapor deposition.

6. A method as claimed in any of the preceding claims wherein the equipment employed in step A is constructed of materials substantially incapable of dissolving carbon.

7. A method as claimed in claim 4 wherein the particle size achieved by comminution is that of grit diamond.

8. A method as claimed in claim 7 or claim 6 wherein step A is conducted at a filament temperature of at least 2000°C, a substrate temperature in the range of 900-1000°C and a pressure of about 10 torr.

9. A method as claimed in claim 7 or claim 8 wherein the filaments are of tungsten and the substrate is molybdenum.

10. A method as claimed in claim 6 wherein the carbon in the hydrocarbon is at least 99.9% isotopically pure.

11. A method asclaimed in claim 10 wherein the catalyst-solvent material employed in step B is an iron-aluminum mixture.

12. A method as claimed in claim 11 wherein a negative temperature gradient is maintained in step B between the material being converted and the deposition region.

13. A method as claimed in claim 12 wherein the catalyst-solvent material employed in step B is a mixture of 95% iron and 5% aluminum by weight.

14. A method as claimed in claim 13 wherein the temperature gradient is about 50°C.

15. A method as claimed in claim 12 wherein the pressure in step B is in the range of 50,000-60,000

atmospheres and the temperature is in the range of 1300-1500°C.

16. A method as claimed in claim 13 wherein the seed crystal is single-crystal diamond of normal isotopic distribution.

17. A method as claimed in claim 16 wherein the portion of the product diamond attributable to the seed crystal is removed by polishing.

18. Single-crystal diamond consisting of at least 99.2% by weight isotopically pure carbon-12 or carbon-13, said diamond having a thermal conductivity at 300°K at least 10% greater than that of natural type IIA diamond.

19. Diamond as claimed in claim 18 which consists of carbon-12.

20. An article comprising a heat-generating source in contact with the diamond of claim 18 as a thermal conductor.

21. An abrasive article comprising the diamond of claim 18.

22. A light-filtering article comprising the diamond of claim 18 with a pinhole aperture therein.

23. Single-crystal diamond consisting of at least 99.5% by weight isotopically pure carbon-12 or carbon-13, said diamond having a thermal conductivity at 300°K at

least 25% greater than that of natural type IIA diamond.

26. Single-crystal diamond consisting of at least 99.9% by weight isotopically pure carbon-12 or carbon-13, said diamond having a thermal conductivity at 300°K at least 40% greater than that of natural type IIA diamond.

29. Single-crystal diamond prepared by the method of claim 1.

28. Single-crystal diamond prepared by the method of claim 2.

27. Single-crystal diamond prepared by the method of claim 4.

28. Single-crystal diamond prepared by the method of claim 10.

29. Single-crystal diamond prepared by the method of claim 17.

30. A method as claimed in claim 1 substantially as hereinbefore described in any one of the examples.

31. A single crystal diamond as claimed in claim 18 substantially as hereinbefore described in any one of the examples.

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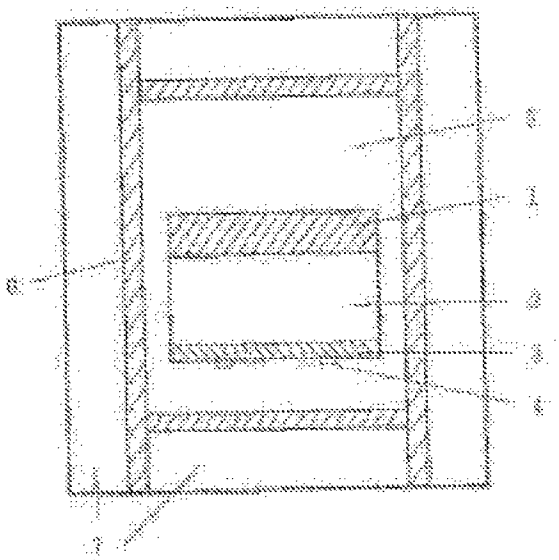
Bibliographic data: JP6182184 (A) — 1994-07-05

SYNTHESIS OF SINGLE CRYSTAL DIAMOND

Inventor(s):	SUMIYA HITOSHI; SATO SHUICHI +
Applicant(s):	SUMITOMO ELECTRIC INDUSTRIES +
Classification:	- **International:** *B01J3/06; C01B31/06; C30B29/04;* (IPC1-7): B01J3/06 - **European:**
Application number:	JP19920341940 19921222
Priority number (s):	JP19920341940 19921222
Also published as:	JP3259384 (B2)

Abstract of JP6182184 (A)

PURPOSE:To advantageously produce a colorless, transparent high-quality single-crystal diamond in the synthesis thereof employing temp. difference process by a method where Ti, etc., are added to a solvent metal as nitrogen getter, a metal plate such as made of Cu is interposed between the solvent metal and seed crystal and, in this condition, the synthesis of the diamond is started. CONSTITUTION:In the synthesis of a single crystal diamond employing temp. difference process, one or more metals selected as nitrogen getter from among Ti, Zr, Hf, V, Nb and Ta are added to a solvent metal 2, a metal plate 3 consisting of one or more metals selected from among Cu, Ag, Au, Zn and Cd is interposed between the solvent metal 2 and the seed crystal 4 and, in this condition, the diamond synthesis is started.; Since, in this way, a colorless, transparent high quality IIa type diamond almost free from inclusion can be synthesized inexpensively and stably, a synthetic diamond useable in accessory or optical part application can be produced advantageously.



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(43)公開日　平成6年(1994)7月5日

(51)Int.Cl.'	識別記号	庁内整理番号	FI	技術表示箇所
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審査請求　未請求　請求項の数4(全 5 頁)

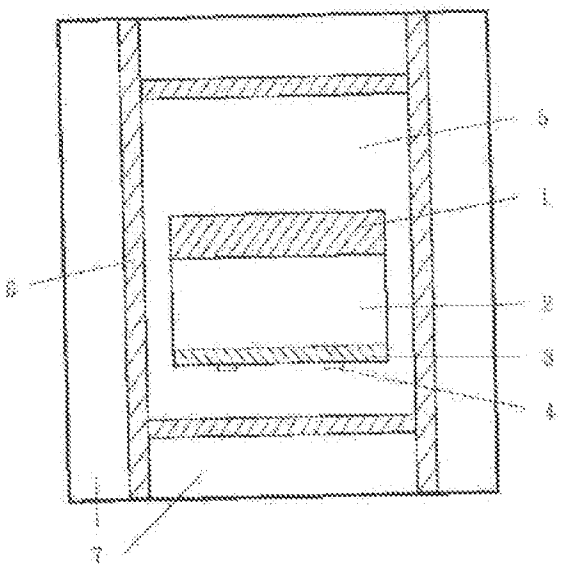
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(54)【発明の名称】　ダイヤモンド単結晶の合成方法

(57)【要約】
【目的】　装飾用途や光学部品などに用いることができる無色透明で良質なダイヤモンド単結晶の新規な合成方法を提供する。
【構成】　温度差法によるダイヤモンド単結晶合成において、溶媒金属に窒素ゲッターとしてTi，Zr，Hf，V，Nb，Taから選ばれる一種もしくは二種以上の金属を添加し、かつ、前記溶媒金属と融結晶との間にCu，Ag，Au，Zn，Cdから選ばれる一種もしくは二種以上からなる金属板を配置した状態でダイヤモンドの合成を開始することを特徴とする。これにより、無色透明でインクルージョンの発生しない良質なIIa型ダイヤモンド結晶を安価に且つ安定に合成できるので、装飾用途や光学部品に供し得る合成ダイヤモンドの有利な製法である。



【特許請求の範囲】
【請求項１】　温度差法によるダイヤモンド結晶合成において、溶媒金属に窒素ゲッターとしてＴｉ，Ｚｒ，Ｈｆ，Ｖ，Ｎｂ，Ｔａから選ばれる一種もしくは二種以上の金属を添加し、かつ、前記溶媒金属と種結晶との間にＣｕ，Ａｇ，Ａｕ，Ｚｎ，Ｃｄから選ばれる一種もしくは二種以上からなる金属板を配置した状態でダイヤモンドの合成を開始することを特徴とするダイヤモンド単結晶の合成方法。
【請求項２】　前記の溶媒金属と種結晶との間に配置される金属板の厚みは０．０１ｍｍ以上、１ｍｍ以下であることを特徴とする請求項１記載のダイヤモンド単結晶の合成方法。
【請求項３】　前記窒素ゲッターとして用いられるＴｉ，Ｚｒ，Ｈｆ，Ｖ，Ｎｂ，Ｔａから選ばれる一種もしくは二種以上の金属の含有量が、溶媒金属に対して０．２～１０重量％であることを特徴とする請求項１または２記載のダイヤモンド単結晶の合成方法。
【請求項４】　前記溶媒金属は、Ｆｅ，Ｃｏ，Ｎｉ，Ｍｎ，Ｃｒの中から選ばれる一種もしくは二種以上からなり、且つ０．１～５．０重量％の炭素を含むことを特徴とする請求項１または２または３記載のダイヤモンド単結晶の合成方法。
【発明の詳細な説明】
【０００１】
【産業上の利用分野】本発明は装飾用途や光学部品などに用いられる無色で透明なダイヤモンド単結晶の合成方法に関するものである。
【０００２】
【従来の技術】現在市販されている装飾用ダイヤモンドは、主に南アフリカ、ロシアより産出されるものの中から、無色透明で内部欠陥の少ないものを選別して用いられている。天然装飾用ダイヤモンドは宝石の中でも最も販売量が多い。また、ダイヤモンドを用いた光学部品として、レーザー窓やＩＲアンビルセルなどがあるが、いずれも天然原石の中から赤外領域に光の吸収のない透明なダイヤモンド（ＩＩａ型と呼ばれる）が選ばれて用いられている。しかし、透明無色な原石の産出は極めて少なく、安定供給や価格に問題がある。一方、人工合成によるダイヤモンドは通常、超高圧高温下で合成する際に溶媒中の窒素が結晶格子内に取り込まれるために黄色く着色してしまうが、溶媒中に窒素ゲッターを添加することで無色透明のダイヤモンドを得ることができる。この窒素ゲッターとしては、たとえば、The Journal of Physical Chemistry, vol.79, No.12 (1975) p1338 に示されているように、Ａｌがよく知られている。具体的には、米国特許第４０３４０６５号明細書には、Ｆｅ溶媒にＡｌを３～５重量％添加することにより宝石級の無色透明なダイヤモンド単結晶が得られると記載されている。Ａｌ以外の窒素ゲッターを用いた例として、たとえば無機材質研究所研究報告書第３９号、ｐ１６～にＴｉやＺｒを溶媒金属に添加することで結晶中の窒素が除去されたという報告がある。
【０００３】
【発明が解決しようとする課題】しかし、特に無色透明の合成ダイヤモンドは合成コストが天然ダイヤモンドよりはるかに高くなるため工業生産は行われていない。この理由は、合成には高価で特殊な装置が必要である上に、Ａｌなどを窒素ゲッターとして添加した場合、その添加量の増加に従って溶媒が結晶中に取り込まれ（以下インクルージョンと呼ぶ）て、不良結晶となることが多くなるため、良質な結晶とするためには成長速度を大幅に下げる必要があるからである。とくにＴｉやＺｒを窒素ゲッターとして用いた場合は合成中に溶媒中に生成したＴｉＣやＺｒＣなどの炭化物が原因でより多くのインクルージョンが結晶中に取り込まれるようになる。
【０００４】本発明者らが行った実験による結果では、窒素ゲッターとしてＡｌを用い、溶媒金属に均一混合した場合、無色透明なダイヤモンド結晶を合成するためには、その添加量は溶媒に対し少なくとも４重量％（約１２体積％）必要であるが、この場合インクルージョンの巻き込みなしに結晶成長させるためには成長速度を１ｍｇ／ｈｒ以下にする必要があった。この成長速度では、たとえば１カラット（２００ｍｇ）の結晶を合成するには２００時間以上の合成時間を要し、製造コストは膨大なものとなる。また、Ｔｉ，Ｚｒなど、Ａｌより窒素との反応性の高い物質を窒素ゲッターとして溶媒に均一添加した場合、添加量は１重量％でも無色透明な結晶となる。しかし、これらは炭化物を形成しやすく、成長速度を大幅に低下させたとしてもＴｉＣやＺｒＣなどの炭化物の影響で、良質な結晶は殆ど得られない。本発明はかかる問題点を解決し、無色透明でインクルージョンのほとんどない結晶を、安価にしかも安定して合成できる方法を提供し、人工合成ダイヤモンドの装飾用途又は光学部品用途への使用を可能とするものである。
【０００５】
【課題を解決するための手段】本発明者らは、ＴｉやＺｒを窒素ゲッターとして溶媒に添加して成長させたダイヤモンド結晶を観察したところ、インクルージョンのほとんどは種結晶を起点として連続して結晶中に取り込まれていることがわかった。さらに、詳細に調べると成長初期に種結晶直上に生成したＴｉＣやＺｒＣなどの炭化物がインクルージョン起点となっていることがわかった。そこで本発明者らは、成長初期に種結晶上に炭化物生成を防ぐため溶媒と種結晶の間にあらかじめＣｕ，Ａｇ，Ａｕ，Ｚｎ，Ｃｄなど、それ自体炭化物を作らず、加えて、ＴｉＣやＺｒＣやＮｂＣなどのＩＶａ族もしくはＶａ族元素の炭化物を分解する働きのある金属箔を配置したところ、種結晶上にほとんど炭化物を生成しないことを見いだした。その結果、炭化物を起点としたインクル

ージョンの巻き込みを防ぐことができ、このため、従来の２倍以上の早い成長速度でも、良質なＩＩａ結晶が得られることを確認した。

【０００６】本発明は温度差法によるダイヤモンド結晶合成において、溶媒金属に、窒素ゲッターとしてＴｉ、Ｚｒ、Ｈｆ、Ｖ、Ｎｂ、Ｔａから選ばれる一種もしくは二種以上の金属を添加し、さらに前記溶媒金属と種結晶との間にＣｕ、Ａｇ、Ａｕ、Ｚｎ、Ｃｄから選ばれる一種もしくは二種以上からなる金属板を配置した状態でダイヤモンドの合成を開始することを特徴とするものである。本発明において溶媒金属と種結晶との間に配置される金属板の厚みは０．０１ｍｍ以上、１ｍｍ以下であることが好ましい。また、窒素ゲッターとして用いられるＴｉ、Ｚｒ、Ｈｆ、Ｖ、Ｎｂ、Ｔａから選ばれる一種もしくは二種以上の金属の含有量は、溶媒金属に対して０．２～１０重量％であることが好ましい。窒素ゲッターとしてのこれら金属は、他の金属、例えば、Ａｌ、Ｃｕ、Ｓｉ、Ｓｎ等との合金の形で添加することもできる。また、溶媒金属は、Ｆｅ、Ｃｏ、Ｎｉ、Ｍｎ、Ｃｒの中から選ばれる一種もしくは二種以上からなり、且つ０．１～６．０重量％の炭素を含むことが好ましい。

【０００７】図１は本発明の一具体例であってダイヤモンド結晶合成用の試料室構成を示す縦断面図である。溶媒金属２には窒素ゲッターとしてＴｉ、Ｚｒ、Ｈｆ、Ｖ、Ｎｂ、Ｔａが添加され、この溶媒金属と種結晶４の間にＣｕ、Ａｇ、Ａｕ、Ｚｎ、Ｃｄから選ばれる金属板３が配置される。１は炭素源、５は絶縁体、６は黒鉛ヒーター、７は圧力媒体である。この金属板３の厚みは０．０１ｍｍ未満では効果は不十分で、１ｍｍをこえるとＣｕ、Ａｇ、Ａｕ、Ｚｎ、Ｃｄなどの金属がダイヤモンドの結晶成長に悪影響を及ぼし、結晶が多結晶化したり、煤の残しのある不良結晶となってしまう。また溶媒２に窒素ゲッターとして添加するＴｉ、Ｚｒ、Ｈｆ、Ｖ、Ｎｂ、Ｔａの添加量としては、０．２重量％未満では窒素は十分に除去されず、合成されたダイヤモンドは黄色み帯びた結晶となる。一方、１０重量％をこえると多結晶化や自発核発生が多くなり、良質なダイヤモンド結晶が得られなくなる。

【０００８】ここで、２の溶媒金属はＦｅ、Ｃｏ、Ｎｉ、Ｍｎ、Ｃｒの中から選ばれる一種もしくは二種以上からなる金属であり、種結晶溶解防止のための０．１～６．０重量％の炭素をあらかじめ添加しておくのが好ましい。炭素添加量が０．１重量％未満もしくは炭素を含まない溶媒金属を用いた場合、種結晶上にＰｔなどの種結晶溶解防止材を配置する必要があるが、このような種結晶溶解防止材を配置することは、多結晶化やインクルージョンの巻き込みの原因となり好ましくない。また、炭素添加量が６重量％をこえると、自然核発生がおこりやすくなり、種結晶以外の部分より結晶成長するため結晶同士が干渉し、良質の結晶が得られなくなる。

【０００９】【作用】本発明ではＴｉ、Ｚｒ、Ｈｆ、Ｖ、Ｎｂ、Ｔａなど、窒素との反応性の高い元素を窒素ゲッターとするため、少量の添加でほとんど窒素を含まない無色透明なＩＩａ型のダイヤモンド結晶が得られ、また、溶媒と種結晶の間に、炭化物生成防止のために、Ｃｕ、Ａｇ、Ａｕ、Ｚｎ、Ｃｄの金属板をあらかじめ配置した状態で合成を開始する構成になっているため、インクルージョンの混入を大幅に抑えることができる。その結果、従来よりかなり速い成長速度でも良質なＩＩａ型ダイヤモンド結晶が得られるようになる。また、本発明に用いる種結晶、炭素源等はこの種の技術分野で公知のものを用いることができる。また、温度差法による合成の条件等は適宜選択することができる。

【００１０】【実施例】以下実施例により本発明をさらに詳細に説明する。

実施例１

溶媒の原料として粒径５０～１００ミクロンの高純度Ｆｅ粉末、Ｃｏ粉末、グラファイト粉末を用い、

Ｆｅ：Ｃｏ：Ｃ＝６０：４０：４．５（重量比）

となるように配合した。これに、さらに窒素ゲッターとして平均粒径５０ミクロンのＴｉ粉末を１．５重量％添加し、十分に混合した。この混合粉末を型押し成形し、脱ガス、焼成したもの（直径２０ｍｍ、厚み１０ｍｍ）を溶媒とした。図１に示す試料室構成で炭素源１にはダイヤモンドの粉末、種結晶４には直径５００ミクロンのダイヤモンド結晶３個を用いた。種結晶４と溶媒２の間に配置する金属板３としては厚み０．３ｍｍのＣｕ板を用いた。そして、炭素源１と種結晶４部に約３０℃の温度差がつくように加熱ヒーター６内にセットした。これを超高圧発生装置を用いて、圧力５．５ＧＰａ、温度１３００℃で７０時間保持し、ダイヤモンドの合成を行った。その結果０．７～０．９カラットの無色透明な、インクルージョンのほとんどない良質なＩＩａ型のダイヤモンド結晶が得られた。ＥＳＲにより、結晶中の窒素濃度を測定するといずれも０．１ｐｐｍ以下であった。磁気天秤によりインクルージョン量を測定するといずれも０．３重量％以下であった。

【００１１】実施例２

種結晶４と溶媒２の間に配置する金属板３に厚み０．５ｍｍのＣｕ板を用いた他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

実施例３

種結晶４と溶媒２の間に配置する金属板３に厚み０．２ｍｍのＡｇ板を用いた他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

実施例４

種結晶４と溶媒３の間に配置する金属板３に厚み０．３ｍｍのＡｕ板を用いた他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

【００１２】実施例５

種結晶４と溶媒３の間に配置する金属板３に厚み０．０５ｍｍのＡｕ板を用いた他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

実施例６

種結晶４と溶媒３の間に配置する金属板３に厚み０．２ｍｍのＺｎ板を用いた他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

実施例７

溶媒２に添加する窒素ゲッターに粒径４４ミクロン以下（平均１０ミクロン）のＺｒ粉末を溶媒に対し３重量％添加した他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

【００１３】実施例８

溶媒２に添加する窒素ゲッターに粒径４４ミクロン以下（平均１０ミクロン）のＡｌＴｉ合金粉末を溶媒に対し３重量％添加した他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

実施例９

溶媒２に添加する窒素ゲッターとしてＡｌＴｉ合金粉末の代わりに、ＣｕＴｉ、ＳｎＴｉ又はSi_3Ti_5合金粉末を用いた他は実施例８と同様にしてダイヤモンドの合成を行った。その結果、いずれの場合も、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

実施例１０

溶媒の原料として粒径５０～１００ミクロンの高純度Ｆｅ粉末、Ｎｉ粉末、Ｃｏ粉末、グラファイト粉末を用い、

Ｆｅ：Ｎｉ：Ｃｏ：Ｃ＝６０：３０：１０：４．２（重量比）

となるように配合した他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

【００１４】実施例１１

溶媒の原料として粒径５０～１００ミクロンの高純度Ｆｅ粉末、Ｎｉ粉末、Ｍｎ粉末、グラファイト粉末を用い、

Ｆｅ：Ｎｉ：Ｍｎ：Ｃ＝６０：３０：１０：４（重量比）

となるように配合した他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

実施例１２

溶媒の原料として粒径５０～１００ミクロンの高純度Ｆｅ粉末、Ｎｉ粉末、グラファイト粉末を用い、

Ｆｅ：Ｎｉ：Ｃ＝７０：３０：３．５（重量比）

となるように配合した他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

実施例１３

溶媒の原料として粒径５０～１００ミクロンの高純度Ｃｏ粉末、グラファイト粉末を用い、

Ｃｏ：Ｃ＝１００：４．７（重量比）

となるように配合した他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

【００１５】実施例１４

溶媒の原料として粒径５０～１００ミクロンの高純度Ｎｉ粉末、グラファイト粉末を用い、

Ｎｉ：Ｃ＝１００：４．２（重量比）

となるように配合した他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、実施例１とほとんど同じ良質なＩＩａ型ダイヤモンド結晶が得られた。

【００１６】比較例１

溶媒と種結晶の間に金属板を配置せずに、他は実施例１と同様にダイヤモンドの合成を試みた。窒素含有量の少ない（約０．１ｐｐｍ）結晶が得られたが、インクルージョンの巻き込み量は約１．５重量％と多く、良質な結晶は得られなかった。

実施例１５

溶媒と種結晶の間に配置するＣｕ板の厚みを２ｍｍとした他は実施例１と同様にダイヤモンドの合成を試みた。成長したダイヤモンド結晶は表面に溶け残しのない単結晶となった。

実施例１６

窒素ゲッターとして溶媒に添加するＴｉの量を１５重量％とした他は実施例１と同様にダイヤモンドの合成を試みた。種結晶から成長した結晶は多結晶化していた。

【００１７】実施例１７

溶媒の原料として粒径５０～１００ミクロンの高純度Ｆｅ粉末、Ｎｉ粉末、Ｃｏ粉末を用い、

Ｆｅ：Ｎｉ：Ｃｏ＝６０：３０：１０（重量比）

となるように配合し、グラファイトを添加しなかった他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、種結晶は溶媒中に完全に溶解してしまい、ダイヤモンドの成長は不充分であった。

実施例１８

溶媒の原料として粒径５０～１００ミクロンの高純度Ｆｅ粉末、Ｎｉ粉末、Ｃｏ粉末、グラファイト粉末を用い、

Ｆｅ：Ｎｉ：Ｃｏ：Ｃ＝６０：３０：１０：７（重量

比）
となる比率に配合した他は実施例１と同様にしてダイヤモンドの合成を行った。その結果、種結晶以外の所よりダイヤモンドが多数自然発生し、このため結晶同士が干渉し、良質なダイヤモンド結晶はほとんど得られなかった。

【００１８】

【発明の効果】以上説明したように、本発明によれば、無色透明でインクルージョンのほとんどないダイヤモンド結晶を、安価に安定して合成できる。本方法によって合成ダイヤモンドを装飾用途、光学部品などに利用することが可能なものとなる。

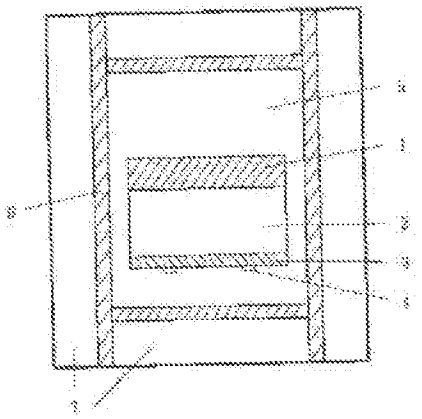
【図面の簡単な説明】

【図１】図１は本発明の一具体例であって、結晶合成用の試料室構成を示す概略断面図である。

【符号の説明】

１：炭素源
２：溶媒金属（窒素ゲッター含む）
３：金属板
４：種結晶
５：絶縁体
６：黒鉛ヒーター
７：圧力媒体

【図１】



Espacenet

Bibliographic data: JP10128654 (A) — 1998-05-19

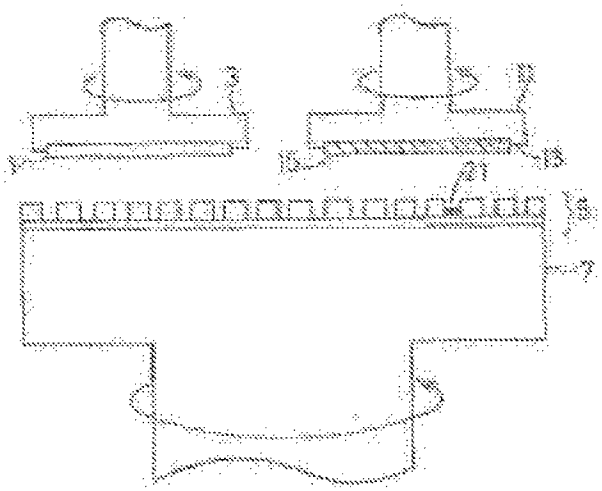
CMP DEVICE AND ABRASIVE CLOTH CAPABLE OF BEING USED IN THIS CMP DEVICE

Inventor(s):	KATO NOBUHIRO; MURAKAMI SATOSHI; WATANABE TOMOJI ±	
Applicant(s):	TOSHIBA CORP ±	
Classification:	**- International:**	***B24B37/00; B24B37/04; B24B49/18; B24B53/007; H01L21/304;*** (IPC1-7): B24B37/00; H01L21/304
	- European:	B24B49/18; B24B53/017
Application number:	JP19960290397 19961031	
Priority number (s):	JP19960290397 19961031	
Also published as:	US6059921 (A) TW423043 (B)	

Abstract of JP10128654 (A)

PROBLEM TO BE SOLVED: To provide a CMP device and an abrasive cloth capable of being used in the CMP device, which can suppress deterioration of polishing performance of the abrasive cloth and easily detect a limit of use. SOLUTION: In a CMP device polishing a semiconductor substrate 1, a diamond dresser 11 is provided with a material 15 capable of mechanically removing a diamond abrasive grain coming off onto an abrasive cloth 5 inside a diamond abrasive grain electrocoating surface 13, and, by the material 15, simultaneously with dressing, the diamond abrasive grain on the cloth 5 is removed. Further, the cloth 5 is provided with a use limit detection part 21 with a work amount of dimple work or the like less than of the other part, and, by polishing the semiconductor substrate 1, the point of time exposing a surface of the use limit detection part 21 is detected as a use limit.

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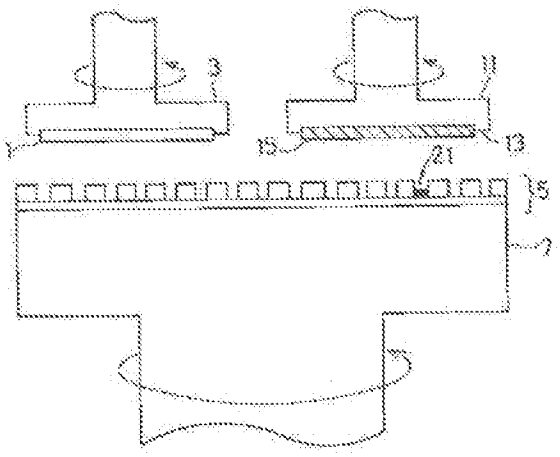
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(54)【発明の名称】　ＣＭＰ装置及び該ＣＭＰ装置に用いることのできる研磨布

(57)【要約】
【課題】　研磨布の研磨性能の劣化を抑制し、かつ、使用限界を容易に検出することができるＣＭＰ装置及び該ＣＭＰ装置に用いることのできる研磨布を提供することを課題とする。
【解決手段】　半導体基板１の研磨を行うＣＭＰ装置で、ダイヤモンドドレッサー１１はダイヤモンド砥粒電着面１３の内側に研磨布５上に散布したダイヤモンド砥粒を機械的に除去することが可能な材料１９を備え、材料１９によりドレッシングを同時に研磨布５上のダイヤモンド砥粒を除去する。さらに、研磨布５は、ティンプル加工等の加工量が他の部分よりも多い使用限界検出部２１を備え、半導体基板１の研磨により使用限界検出部２１が表面に露出した時点を使用限界として検出する。



【特許請求の範囲】
【請求項１】　底面開口部に設けられたダイヤモンド砥粒電着面により研磨布表面のドレッシングを行うダイヤモンドドレッサーを有するＣＭＰ装置において、
前記ダイヤモンドドレッサーがドレッシングの際に前記ダイヤモンド砥粒電着面から前記研磨布表面に脱落するダイヤモンド砥粒を除去する手段を具備することを特徴とするＣＭＰ装置。
【請求項２】　底面開口部に設けられたダイヤモンド砥粒電着面により研磨布表面のドレッシングを行うダイヤモンドドレッサーを有するＣＭＰ装置において、
前記ダイヤモンドドレッサーは、前記ダイヤモンド砥粒電着面の内側に前記研磨布上に脱落したダイヤモンド砥粒を機械的に除去することが可能の材料を備え、前記材料によりドレッシングと同時に該ドレッシングの際に前記ダイヤモンド砥粒電着面から前記研磨布上に脱落した前記ダイヤモンド砥粒を除去することを特徴とするＣＭＰ装置。
【請求項３】　前記材料は、ナイロンブラシであることを特徴とする請求項２記載のＣＭＰ装置。
【請求項４】　前記材料は、スポンジであることを特徴とする請求項２記載のＣＭＰ装置。
【請求項５】　前記材料は、モヘアブラシであることを特徴とする請求項２記載のＣＭＰ装置。
【請求項６】　表面に凹部が形成された研磨布により基板の研磨を行うＣＭＰ装置において、
前記研磨布の該研磨布の使用限界を目視により確認することができる使用限界検出手段を具備することを特徴とするＣＭＰ装置。
【請求項７】　表面に凹部が形成された研磨布により基板の研磨を行うＣＭＰ装置において、
前記研磨布は、前記凹部内に使用限界検出部を備え、前記基板の研磨により前記使用限界検出部が前記研磨布表面に露出した時点を使用限界として検出することを特徴とするＣＭＰ装置。
【請求項８】　前記使用限界検出部は、前記凹部内で他の部分よりも浅く加工された部分であることを特徴とする請求項７記載のＣＭＰ装置。
【請求項９】　前記凹部を通して研磨布全面に供給されることを特徴とする請求項６乃至請求項８のいずれか１項に記載のＣＭＰ装置。
【請求項１０】　表面に凹部が形成され、基板の研磨に用いられる研磨布において、
前記凹部内に他の部分よりも浅く加工された部分を使用限界検出部として備え、前記基板の研磨により前記使用限界検出部が前記研磨布表面に露出した時点を使用限界と検出することを特徴とする研磨布。
【請求項１１】　前記凹部は、研磨布全面に研磨液を供給するために設けられたものであることを特徴とする請求項１０記載の研磨布。

【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明はＬＳＩ製造工程における平坦化技術として用いられるＣＭＰ装置及び該ＣＭＰ装置に用いることのできる研磨布に関し、特に、研磨布の研磨特性の劣化を抑制し、かつ、使用限界を容易に検出することができるＣＭＰ装置及び該ＣＭＰ装置に用いることのできる研磨布に関する。
【０００２】
【従来の技術】近年、ＬＳＩ（Large Scale Integrated Circuit）の高集積化が多層化するのに伴い、層間絶縁膜の平坦化技術が非常に重要となってきているが、その技術として現在最も注目されているものが化学的機械研磨（chemical mechanical polishing ：ＣＭＰ）技術である。
【０００３】図５は、上記ＣＭＰ技術を実現する一般的なＣＭＰ装置の構成を示す図である。同図に示すように、このＣＭＰ装置は半導体基板１を固定し、半導体基板１を回転させるトップリング３と、半導体基板１の表面を研磨する研磨布５と、研磨布５を固定し、研磨布５を回転させるターンテーブル７とを少なくとも有し、所定の製造工程を経て凹凸状態となっている半導体基板１の表面を研磨布５に押し付け、研磨剤９を供給しながらトップリング３とターンテーブル７をそれぞれ回転させ、化学反応を生じさせながら機械的に半導体基板１表面を研磨布５で研磨することにより半導体基板１表面の平坦化を図るものである。
【０００４】上述したようなＣＭＰ装置においては、研磨布の研磨性能維持のためにドレッシング（dressing）と呼ばれる作業が必要である。ドレッシングとは硬くなった研磨布の目を再び鋭くする目立てのことであり、半導体基板の処理枚数の増加に伴って鋭くなっていく研磨布の目を再び鋭くすることにより、研磨布の研磨性能を維持するのである。このドレッシングは例えば次のようなダイヤモンドドレッサーにより実施される。図６は、ドレッシングを行う際のダイヤモンドドレッサーと研磨布を示す図であり、ドレッシングはダイヤモンドドレッサー１１をターンテーブル７上に固定された研磨布５の表面に押し付け、ダイヤモンドドレッサー１１とターンテーブル７をそれぞれを回転させることにより行われる。また、ダイヤモンドドレッサー１１自体を揺動させる場合もある。図７は、上記ダイヤモンドドレッサー１１の拡大図であり、ダイヤモンドドレッサー１１の底面周辺にはダイヤモンド砥粒を電着して形成したダイヤモンド砥粒電着面１３が設けられ、このダイヤモンド砥粒電着面１３を研磨布表面に当てることにより上記ドレッシングが行われる。なお、ドレッシングは上述した半導体基板の研磨と同時に、または、その研磨前、研磨後に行われる。
【０００５】また、図８は、図５と同様に一般的なＣＭ

Ｐ装置の概略を示す図であるが、図８に示すように、ＣＭＰ装置に用いられる研磨布５の表面は実際には砥液９の導溝布５全面に行き渡るようにディンプル加工や格子状の溝加工が施されている。この研磨布５により上述したように半導体基板１の表面を研磨した場合、半導体基板１の処理枚数の増加に伴って研磨布５は磨耗し導くなるが、研磨布５の使用限界を越えた場合には研磨速度や研磨量の面内均一性の値が悪化してしまう。そのため、実際に上記ＣＭＰ装置により半導体基板１を研磨する場合には、その直前に予め測定された使用限界検出用のテスト基板を予め研磨し、そのテスト基板を評価することにより研磨速度や研磨量の面内均一性の値を算出し、その算出結果に基づいて研磨布５が使用限界に達しているか否かを判断し、使用限界に達していないと判断した場合にのみ本来の半導体基板１の研磨を行い、使用限界に達していると判断した場合には研磨布５の交換が行われる。

【０００６】

【発明が解決しようとする課題】しかしながら、従来のＣＭＰ装置には次のような問題があった。

【０００７】それは、上述したドレッシングの際に、ダイヤモンド電着電着面からダイヤモンド砥粒が研磨布表面に脱落し、その脱落したダイヤモンド砥粒がその後の研磨の際に半導体基板表面にキズをつけてしまうということである。図９は、図７のダイヤモンド砥粒電着面１３の断面図であるが、図９（ａ）に示すように、ダイヤモンド砥粒電着面１３は、ダイヤモンド砥粒１７をニッケル層１９に埋め込み、露出しているダイヤモンド砥粒１７により研磨布のドレッシングを行うものであるが、同図（ｂ）に示すように、ドレッシング時の研磨布との摩擦によりニッケル層１９からダイヤモンド砥粒１７が脱落し、研磨布に脱落してしまうのである。さらに、ドレッサー１１の使用と共にニッケル層１９が磨耗りし、新たにニッケル層１９表面に露出するダイヤモンド砥粒１７やニッケル層１９への埋まり具合が浅くなってくるものもあり、上述したダイヤモンド砥粒１７の脱落は次々と起こり得るのである。

【０００８】また、研磨布の使用限界を検出するために半導体基板の研磨前後にテスト研磨が行われるが、その時用いられるテスト基板は再利用することはできず、廃棄しなければならない。一方、半導体基板の径は、そのサイズの拡大と共に益々に上昇している。従って、部材コストの増大を招くのは必至である。さらに、テスト研磨及びテスト基板の評価に要する時間は量産ラインにおいて生産効率を向上させる上で非常に問題である。

【０００９】本発明は上記事情に鑑みて成されたものであり、その目的は、ドレッシングの際にダイヤモンド砥粒電着面から研磨布表面に脱落したダイヤモンド砥粒をその後の研磨の時までに除去することにより半導体基板表面にキズをつけることのないＣＭＰ装置を提供することにある。また、その他の目的は、研磨布の使用限界をテスト研磨することなく容易に判断することができるＣＭＰ装置及び研磨布を提供することにある。

【００１０】

【課題を解決するための手段】上記の目的を達成するために本発明の第１の手段は、底面周辺部に設けられたダイヤモンド砥粒電着面により研磨布表面のドレッシングを行うダイヤモンドドレッサーを有するＣＭＰ装置において、前記ダイヤモンドドレッサーがドレッシングの際に前記ダイヤモンド砥粒電着面から前記研磨布表面に脱落するダイヤモンド砥粒を除去する手段を具備することである。

【００１１】ここで、前記手段は、具体的には、前記ダイヤモンド砥粒電着面の内側に配置される前記研磨布上に摺接したダイヤモンド砥粒を機械的に除去することが可能な材料であり、例えば、ナイロンブラシ、スポンジである。また、ナイロンブラシに比べて毛先の柔らかいモヘアブラシを用いれば、押し付け圧にあまり影響されることなく良好な除去効果を得ることができる。なお、上記材料の外径は、少なくともＣＭＰ処理を行う基板の外径以上であることが必要である。さらに、ドレッシングの際にダイヤモンドドレッサー自体を揺動させる場合には、少なくとも、研磨布表面の内で研磨に使用される領域全体に上記材料が接触することが可能な外径であることが必要である。

【００１２】上記構成によれば、ダイヤモンドドレッサーとナイロンブラシ等の材料を一体化させることにより、ドレッシングの際にダイヤモンド砥粒電着面から研磨布上に脱落するダイヤモンド砥粒の除去をドレッシングと同時に行うことができる。従って、その後の研磨においてダイヤモンド砥粒による基板表面のキズを減らすことができる。

【００１３】本発明の第２の手段は、表面に凹部が形成された研磨布により基板の研磨を行うＣＭＰ装置において、前記研磨布が前記研磨布の使用限界を目視により確認することができる使用限界検出手段を具備することである。

【００１４】ここで、前記使用限界検出手段は、好ましくは、前記凹部の加工量を調節してその他の部分よりも浅く加工された部分であり、前記凹部の形成により前記浅く加工された部分が表面に露出した時点を使用限界と検出するものである。なお、前記浅く加工された部分の深みは研磨の基板の研磨速度と研磨量の面内均一性の値が悪化する時期に研磨布表面に露出して目視で確認することができるよう設定する。

【００１５】上記構成によれば、使用限界検出手段が研磨布の表面に露出し目視で確認できた時点を研磨布の交換時期とするので、従来のようなテスト研磨を行う必要が無くなり、また、その際無駄に消費されていたテスト基板も不要となる。従って、コストの低減を図ることが

できる。

【００１６】

【発明の実施の形態】以下、本発明の実施の形態について図面を用いて説明する。図１は、本発明の実施の形態に係るＣＭＰ装置の構成を示す図である。なお、従来例と同一部分には同一符号が付してある。

【００１７】同図に示すように、このＣＭＰ装置は半導体基板１を固定し、半導体基板１を回転させるトップリング３と、半導体基板１の表面を研磨する研磨布５と、研磨布５を固定し、研磨布５を回転させるターンテーブル７とを有し、所定の製造工程を経て凹凸状態となっている半導体基板１の表面を研磨布５に押し付け、砥液Ｑを供給しながらトップリング３とターンテーブル７をそれぞれ回転させ、化学反応を生じさせながら機械的に半導体基板１表面を研磨布５で研磨することにより半導体基板１表面の平坦化を図るものである。また、ドレッシングを行うダイヤモンドドレッサー１１を有し、ダイヤモンドドレッサー１１をターンテーブル７に固定された研磨布５の表面に押し付け、ダイヤモンドドレッサー１１とターンテーブル７それぞれを回転させることにより、半導体基板１の処理枚数の増加に伴って粗くなっていく研磨布５の目を再び整え、その研磨性能を維持するものである。

【００１８】図２は、図１に示すダイヤモンドドレッサー１１の拡大図である。なお、従来例と同一部分には同一符号が付してある。

【００１９】図２に示すように、本実施の形態に係るダイヤモンドドレッサー１１は、ダイヤモンド電着電着面１３の内縁に、研磨布上に脱落したダイヤモンド砥粒を機械的に除去することが可能な材料、例えば、ナイロンブラシを配置することにより、ドレッシング時に研磨布表面上に脱落するダイヤモンド砥粒を研磨布表面から除去し、あるいは、研磨布表面の内で半導体基板の研磨に使用されない領域へ除外することにより従来では問題となったダイヤモンド砥粒による半導体基板表面のキズを無くすことができる。また、かかるダイヤモンド砥粒を上記ナイロンブラシに取り込むことにより除去することも可能である。

【００２０】さらに、ダイヤモンドドレッサー自体にナイロンブラシ等の材料が内蔵されているので、従来と同じドレッシング時間だけでドレッシングと同時にダイヤモンド砥粒の除去も行うことができる。従って、全体の処理時間を短くすることができる。

【００２１】ここで、研磨布上に脱落したダイヤモンド砥粒を機械的に除去することが可能な材料としては、ナイロンブラシ以外にスポンジでも同様な効果を得ることができる。また、ナイロンブラシに比べて毛先の柔らかいモヘアブラシを用いることにより、押し付け圧により影響されることなく良好な除去効果を得ることができる。また、上記材料の外径は、少なくともＣＭＰ処理を行う半導体基板の外径以上であることが必要である。さらに、ドレッシングの際にダイヤモンドドレッサー自体を揺動させる場合には、少なくとも、研磨布表面の内で研磨に使用される領域全体に上記材料が接触することが可能な外径であることが必要である。

【００２２】図３は、図１に示す研磨布５の拡大図であり、図３（ａ）がその平面図、図３（ｂ）がそのＡ－Ａ´における断面図である。なお、従来例と同一部分には同一符号が付してある。

【００２３】図３に示すように、本実施の形態に係る研磨布５は、例えば従来例と同様にディンプル加工あるいは格子状の溝加工をすることで表面に凹部が形成されているが、さらに、その加工量を測定してその他の部分よりも深く加工された部分を形成し、その深く加工された部分を研磨布５の使用限界サイン２１として用いる構成としたものである。このような構成とすることにより、この研磨布５で半導体基板１の表面を研磨した場合に半導体基板１の処理枚数の増加に伴って研磨布５は徐々に薄くなると使用限界サイン２１が徐々に表面に現れることとなるが、その出現確認によって研磨布５の使用限界を容易に検知することができるのである。従って、従来では研磨布５の使用限界を検知するために必要であったテスト研磨が不要となり、その際無駄に消費されていたテスト基板も必要なくなる。なお、使用限界サイン２１は研磨布５の円部内に形成されてもよいが、上述した溝り円部内で深く加工された部分を使用限界サイン２１として用いることで使用限界サイン２１を研磨布５の素材と同材質から簡易に得ることができ、好ましい。

【００２４】図４は、図３に示す研磨布５を用いて実際に半導体基板を研磨した結果を示す図であり、図４（ａ）が半導体基板が酸化膜を０．６μｍ堆積したシリコン基板である場合、図４（ｂ）がポリシリコン膜を０．５μｍ堆積したシリコン基板である場合である。また、図４（ａ）及び（ｂ）それぞれの横軸は研磨した半導体基板の枚数であり、縦軸は研磨速度及び研磨量の面内均一性である。なお、ここで用いた研磨布５はポリウレタン材料の研磨布であり、その厚みを約１．３μｍ、使用限界サイン２１の厚みを０．５μｍとしたものである。

【００２５】図４（ａ）に示すように、酸化膜を０．６μｍ堆積したシリコン基板を研磨した場合には、約６００枚研磨した辺りで急激に研磨速度は減少すると共に研磨量の面内均一性が悪化していることが分かる。この時、研磨布５表面には使用限界サイン２１が目視で確認され、それにより、容易に研磨布５が交換時期であることを検知することができた。また、図４（ｂ）に示すように、ポリシリコン膜を０．５μｍ堆積したシリコン基板を研磨した場合には、約９００枚研磨した辺りで急激に研磨速度は減少すると共に研磨量の面内均一性が悪化していることが分かる。この時も同様に、研磨布５表面

には使用限界サイン２１が目視で確認され、それにより、容易に研磨布９が交換時期であることを検知することができた。

【００２６】ここで、研磨布９の材料としてポリウレタンを用いて説明したが、サイロン、レーヨン等の半導体基板を研磨するために用いられる研磨布材料全てに適用することが可能である。また、使用限界サインの厚みは所望の半導体基板の研磨速度と研磨量の面内均一性の値が劣化する時期に研磨布表面に現れて使用限界サインを目視で確認することができるような厚さに適宜設定する。なお、研磨する半導体基板として酸化膜、ポリシリコン膜を成膜したシリコン基板について説明したが、本実施の形態はこれらの研磨に使用されるのみではなく、一般的にＬＳＩ製造工程で用いられる成膜材料。例えば、高融点金属（Ｓｉ、Ｍｏ、Ｗ、Ｔｉ、Ｔａ等）並びにそれら高融点金属の窒化物、登化物及びシリサイド、金属配線用材料（Ａｌ、Ｃｕ、Ａｌ－Ｓｉ－Ｃｕ、Ａｌ－Ｃｕ等）の研磨においても適用され得る。

【００２７】

【発明の効果】以上説明したように本発明によれば、ドレッシングを行う際同時に研磨布上に付着したダイヤモンド砥粒を除去することができるので、従来問題であった付着したダイヤモンド砥粒による基板表面のキズを無くすことができる。また、ダイヤモンドドレッサーに研磨布上に付着したダイヤモンド砥粒を除去するナイロンブラシ等の材料を一体化させることにより、ドレッシングとダイヤモンド砥粒の除去を同時に行うことができるので、処理時間の低減を図ることができ、さらに、装置の点からコストの低減を行うことができる。

【００２８】また、研磨布の使用限界を目視で容易に検出することができるので、従来必要であったテスト研磨が不要となり、事前に準備されていたテスト基板を無くすことができる。従って、全体の処理時間は短縮され、コストの低減にもつながる。

【図面の簡単な説明】

【図１】本発明の実施の形態に係るＣＭＰ装置の構成を示す図である。

【図２】図１に示すダイヤモンドドレッサーの拡大図である。

【図３】図１に示す研磨布の拡大図である。

【図４】図３に示す研磨布を用いて実際に半導体基板を研磨した結果を示す図である。

【図５】一般的なＣＭＰ装置の構成を示す図である。

【図６】ドレッシングを行う際のダイヤモンドドレッサーと研磨布を示す図である。

【図７】図６に示すダイヤモンドドレッサーの拡大図である。

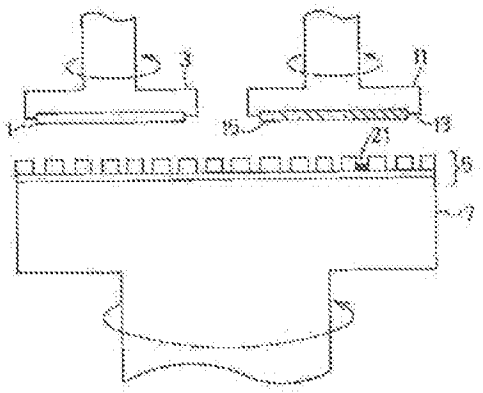
【図８】他の一般的なＣＭＰ装置の構成を示す図である。

【図９】図７に示すダイヤモンド砥粒電着面の断面図である。

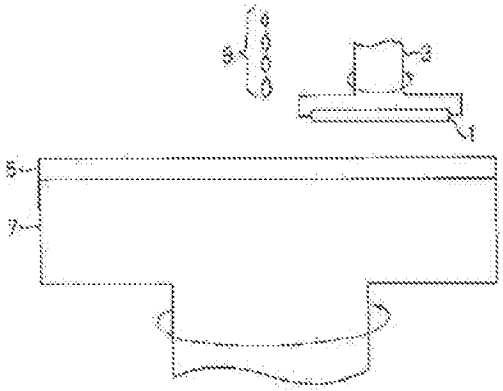
【符号の説明】

１　半導体基板
３　トップリング
５　研磨布
７　ターンテーブル
９　研磨布
１１　ダイヤモンドドレッサー
１３　ダイヤモンド砥粒電着面
１５　ナイロンブラシ
１７　ダイヤモンド砥粒
１９　ニッケル膜
２１　使用限界サイン

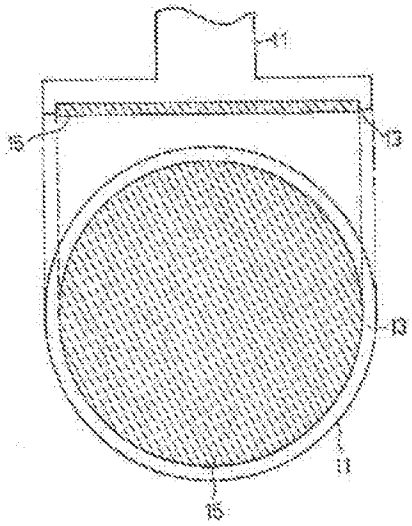
【図１】



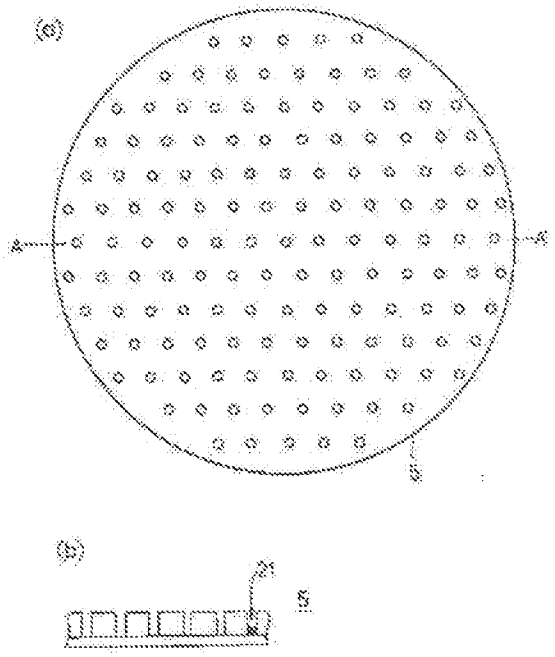
【図５】



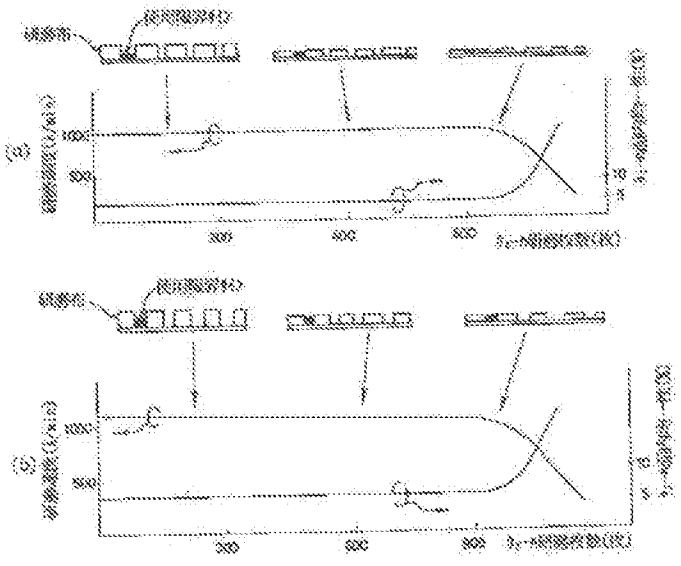
【図2】



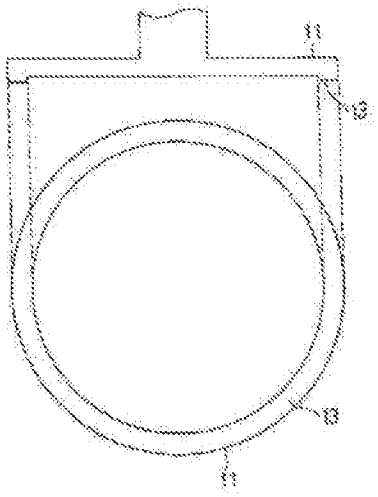
【図3】



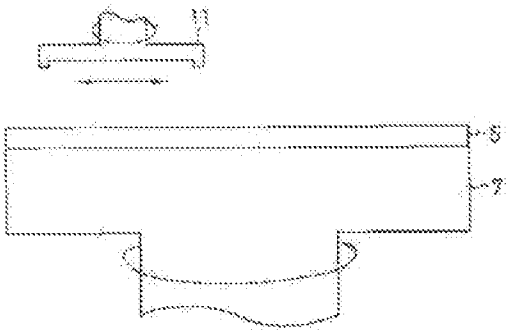
【図4】



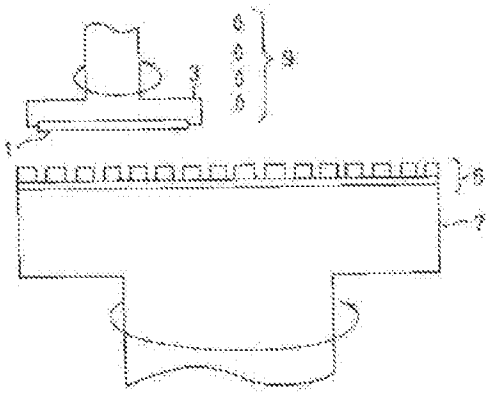
【図7】



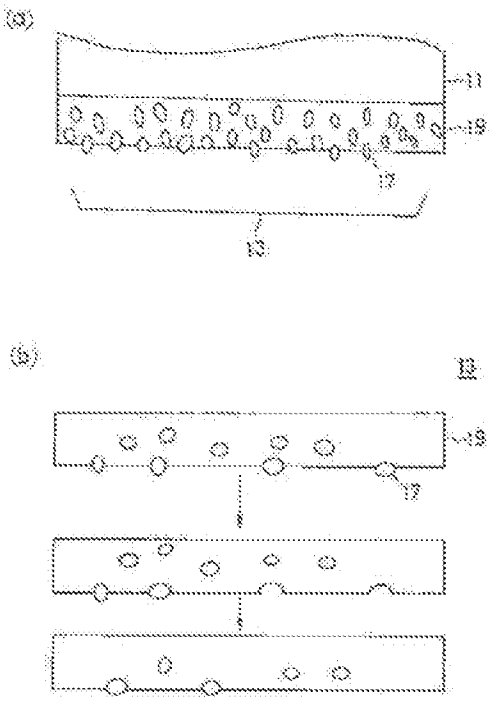
【図６】



【図８】



【図９】



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Espacenet

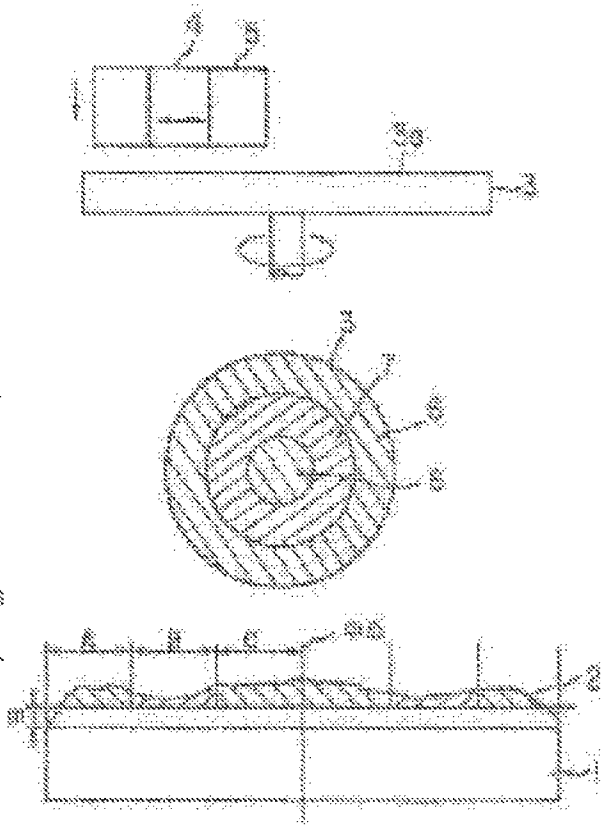
Bibliographic data: JP10180618 (A) — 1998-07-07

GRINDING PAD ADJUSTING METHOD FOR CMP DEVICE

Inventor(s):	TAKEUCHI NOBUYOSHI ±
Applicant(s):	NIPPON KOKAN KK ±

Classification:	- **international:**	***B24B37/00; H01L21/304;*** (IPC1-7): B24B37/00; H01L21/304
	- **European:**	
Application number:	JP19960343567 19961224	
Priority number (s):	JP19960343567 19961224	

Abstract of JP10180618 (A)



PROBLEM TO BE SOLVED: To maintain the flatness of the device surface of a semiconductor substrate to be ground by dividing the surface of a pad according to the film thickness distribution of the device surface before grinding where the pad surface of the grinding pad is pressed, and adjusting each surface roughness of the pad surface to each different roughness with a plurality of grinding wheels different in hardness. SOLUTION: The film thickness distribution of a film 2 deposited on the device surface of a semiconductor substrate 1 takes a shape having a doughnut- like recess. According to this film thickness distribution, the inside of a pad surface 3a is divided into, for instance areas A, B and C. A grinding pad 3 needs to adjust surface roughness such that an outer peripheral pad surface part 6 and a center pad surface part 8 for grinding the areas A and C have grinding amounts larger than that of an inner peripheral pad surface part 7 for grinding the area B. Accordingly, a diamond grinding wheel 4 having hardness for reducing a grinding amount more than that of a diamond grinding wheel 5 is loaded, pressed to the pad surface 3a and, then by rotating the grinding pad 3, surface roughness is formed on the pad surface 3a.

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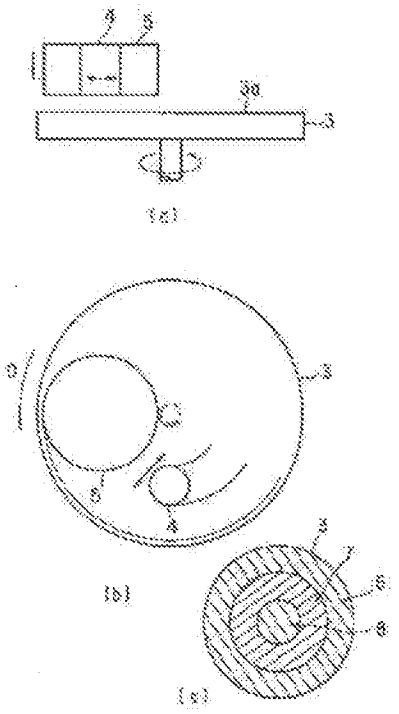
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(74)代理人　弁理士　花輪　義男　（外1名）

(54)【発明の名称】　CMP装置の研磨パッドの調整方法

(57)【要約】
【課題】従来の研磨パッドの調整は、パッド面に単一的な表面荒れを形成していたため、半導体装置のデバイス面の凸部に押し付けられたパッド面が削られ、平坦性がなくなり、表面荒れに研磨の能力の差が生じていた。
【解決手段】本発明は、研磨する半導体基板のデバイス面の膜厚分布を研磨前に測定し、その膜厚分布に対応して、硬度が異なる複数のダイヤモンド砥石を用いて、パッド面内を区分して表面荒れの粗さをそれぞれ調整し、パッド面内での研磨量を変化させることにより、研磨パッドの平坦性を維持させ、研磨される半導体基板のデバイス面の平坦化するCMP装置の研磨パッドの調整方法である。



【特許請求の範囲】
【請求項１】　半導体基板の回路素子を形成するデバイス面を平坦化する化学的機械研磨（ＣＭＰ）装置に用いる研磨パッドの研磨を行うパッド面の調整方法において、
前記研磨パッドのパッド面を研磨前のデバイス面の段差分布に応じて、該パッド面内を区分して、硬度の異なる複数の砥石で、該パッド面の表面荒れを異なる粗さにそれぞれ調整することを特徴とするＣＭＰ装置の研磨パッドの調整方法。
【請求項２】　前記ＣＭＰ装置の研磨パッドの調整方法において、
前記デバイス面が平坦化されるまでの研磨量に比例して、そのデバイス面部分に押し付けるパッド面部分の表面荒れが粗くなるように調整することを特徴とする請求項１記載のＣＭＰ装置の研磨パッドの調整方法。
【請求項３】　前記ＣＭＰ装置の研磨パッドの調整方法において、
硬度が異なる砥石を回転する研磨パッドの動径方向にそれぞれ配置して、前記パッド面に押し付け、パッド面を区分してそれぞれ研磨し、異なる粗さの表面荒れに調整することを特徴とする請求項１記載のＣＭＰ装置の研磨パッドの調整方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、半導体デバイスの製造工程において、半導体基板表面の平坦化を行う化学的機械研磨（ＣＭＰ：Chemical Mechanical Polishing）技術に係り、特にＣＭＰ装置における研磨パッドの調整方法に関する。
【０００２】
【従来の技術】近年、処理時間の高速化や微細化の要求に伴い半導体デバイスの回路素子は積み上げられて多層化し、配線層も多層化されている。
【０００３】このような回路素子等の多層化は、半導体基板上で回路素子を形成した領域と未形成の領域との間に段差を生じさせ、さらに積み上げる毎にそれらの段差が加算される。この結果、上層膜では、フォトリソグラフィ工程のマスク露光の際に、焦点深度を越えたり、エッチング困難な場合が生じる。さらに、例えばビアホールにメタル配線を形成した場合、段差によりビアホールの深さに違いが生じ、ビアホール抵抗のばらつきの原因にもなっている。
【０００４】そこで、多層に回路素子を形成する際に、半導体基板表面の平坦化を図る技術が求められていた。
【０００５】従来の平坦化技術としては、エッチバック技術やＳＯＧ（Spin On Glass）技術が知られている。これらの技術は、段差近傍のローカルな平坦化には有用であった。しかし、半導体デバイスの多層化や大型化が進むと半導体基板全体を平坦化する技術が必要である。
【０００６】エッチバック技術による平坦化は、オーバーエッチングの管理が難しく、半導体基板のデバイス面全体を平坦化させるには、容易でなかった。さらに、層間絶縁膜のような同一材料が全表面を覆った面を平坦化するには問題がないが、例えばＡｌ等を含有する配線のようにエッチングされにくい材料を使用した配線等が含まれる構成であれば、エッチングにより平坦化することは難しい。
【０００７】また、ＳＯＧ技術においては、ＳＯＧ膜をスピンコーティングして塗布し、段差の平坦化を実現していたが、ＳＯＧ膜自体のクラック耐性が乏しく、半導体基板全体を平坦化させる膜厚までは形成できない問題があり、さらに塗布により平坦化させるためには、回路素子の表面形状や配置に工夫を施さねばならなかった。このため、多層化された回路素子や多層化配線には、十分な平坦化を提供できる技術ではなくなった。
【０００８】そこで新たな平坦化技術として、インゴットからスライスカットされたシリコンウエハの平面研磨を行うポリッシング研磨技術と化学研磨技術の特徴を併せ持たせ、半導体デバイスの平坦化に応用したＣＭＰ技術が注目されている。
【０００９】このＣＭＰ技術は、図４に示すように、ポリッシング研磨における研磨剤として、アルミナやシリカ等の研磨粒子に過酸化水素水等の化学物質を併せた研磨剤（スラリー液）２１を用いて、定盤２２上に軟質若しくは、粘弾性を有する材料からなる研磨パッド２３を張り付け、化学反応を伴う機械研磨によりデバイス面を物理的に研磨して段差を無くし、表面を平坦化するものである。
【００１０】この機械において、駆動可能なテーブル２４に真空吸着により固定された半導体基板２５は、そのデバイス面２５ａを対向し回転する研磨パッド２３に押しつけられ、研磨剤２１が注ぎされて研磨される。デバイス面が平坦化される。このＣＭＰ技術は、研磨レートが小さいため高精度の研磨が可能であり、研磨された面に加工変質を残すおそれが少ない特徴がある。
【００１１】
【発明が解決しようとする課題】前述したＣＭＰ技術において、研磨に用いられる研磨パッドの表面は、砥石例えば、ダイヤモンド砥石で削られ、適当な表面荒れが設けられている。この研磨パッドの表面荒れにより、デバイス面上に積層形成された絶縁膜又は金属膜を研磨を行っているが、ダイヤモンド砥石自らの表面も削られるため、表面荒れの削り取られて研磨能力が劣化する。
【００１２】そこで、研磨パッドは、予め定めた処理回数（割った量）毎に、その表面を再度、ダイヤモンド砥石で削り直し、適当な表面荒れが保たれるように調整を行っている。
【００１３】通常、研磨前のデバイス面は、いわゆるｎａｋｅｄの状態にあり、その膜厚分布は下地の平坦さによ

る影響と、成膜装置の特性に依存する面内膜厚分布の偏在性がある。ＣＭＰ技術において研磨パッドによる研磨を行った場合、研磨後の研磨パッドもこの凹形状に依存して平坦な表面の形状が変化する。つまり、膜なりに削れていくのである。

【００１４】例えば、図５に示すようなデバイス面では、凸形状の部分２５ｂに押しつけられた研磨パッド部分２３ｂは多く削れ、表面荒れの部分も削り取られる。また、凹形状の部分２５ｃを押し付けられた研磨パッド部分２３ｃはあまり削れないため、表面荒れの部分も残っている。

【００１５】この削れ具合の差により、研磨後の研磨パッド表面は、削った凹形状に変化し、且つ研磨パッド内で研磨の能力の差が生じている。従って、このように表面形状が変化していく研磨パッドで、引き続きデバイス面を研磨すると、半導体基板の表面も平坦にならない場合が生じる。

【００１６】また従来の研磨パッドの調整は、研磨パッド表面の平坦化維持を考慮したものではなく、単一的な表面荒れを形成することを目的としているため、研磨パッドの表面全体を１つのダイヤモンド砥石で均一的に削るだけであった。

【００１７】よって、研磨パッドの表面荒れの均一性を持たせる管理を難しくして、研磨パッドのパッド面の平坦性を維持させ、研磨された半導体基板のデバイス面の平坦化を維持させるために、研磨パッドの交換回数や調整回数が多くなり、生産効率の低下を招き、結果的にコストアップとなる。

【００１８】そこで本発明は、半導体基板のデバイス面の膜厚分布に応じて、研磨パッドのパッド面内を区分して表面荒れの粗さをそれぞれ調整し、研磨量の平坦性と研磨された半導体基板のデバイス面の平坦化を維持させるＣＭＰ研磨パッドの調整方法を提供することを目的とする。

【００１９】

【課題を解決するための手段】本発明は上記目的を達成するために、半導体基板の回路素子を形成するデバイス面を平坦化する化学的機械研磨（ＣＭＰ）装置に用いる研磨パッドの研磨を行うパッド面の調整方法において、前記研磨パッドのパッド面を押し付ける研磨前のデバイス面の膜厚分布に応じて、該パッド面内を区分して、硬度の異なる複数の砥石で、該パッド面の表面荒れを異なる粗さにそれぞれ調整するＣＭＰ装置の研磨パッドの調整方法を提供する。

【００２０】以上のようなＣＭＰ研磨パッドの調整方法は、研磨前の半導体基板のデバイス面の膜厚分布に対応して、硬度が異なる複数の砥石により、デバイス面の膜の研磨量に比例して、そのデバイス面に押し付けられるパッド面の表面荒れが粗くなるように研磨して、パッド面内での研磨量を変化させることにより、研磨される半導体基板のデバイス面の平坦化を維持する。

【００２１】

【発明の実施の形態】以下、図面を参照して本発明の実施の形について詳細に説明する。

【００２２】まず、本発明によるＣＭＰの研磨パッドの調整方法の概要について説明する。図２（ａ）には、半導体基板上に回路素子を形成するための絶縁膜や金属膜をＣＶＤ（Chemical Vapor Deposition）装置やスパッタリング装置を用いて半導体基板上に形成した場合の膜厚分布の一例を示す。

【００２３】この半導体基板１のデバイス面上に堆積された膜厚２の膜厚分布の形状は、同心円状で、半導体基板１の中心で厚く、エッヂ方向に向かって一旦薄くなるが、次第に厚くなり、再度エッヂで薄くなる。すなわち、ドーナツ形状の凹みを有した形状である。

【００２４】このような膜厚分布を持つ半導体基板をＣＭＰ技術により平坦化させる場合、図２（ｂ）に示すように、斜線で示すＡ領域及びＣ領域の膜厚が近似し、仮に膜厚ｍに平坦化するものとすると、Ａ領域及びＣ領域は、研磨量を多くし、Ｂ領域は、研磨量を少なくすることにより、効率的に平坦化できる。

【００２５】従って、半導体基板１のデバイス面に押し付けられ研磨を行う研磨パッドのパッド面（研磨面）は、膜厚分布と逆の研磨具合の調整が必要となる。つまり後述する図１（ｃ）に示すように、堆積膜の厚いＡ領域及びＣ領域に押し付けられるパッド面部分５及びパッド面部分８は、表面荒れを粗くして研磨レートを上げるように調整し、堆積膜が薄く研磨量が少ないＢ領域に押し付けられるパッド面部分７は、その表面荒れを研磨パッド部分６に比べて、粗くせずに研磨レートを下げるように調整する。

【００２６】このような調整を行うためには研磨パッドのパッド面内を区分して、それぞれの表面荒れの粗さに調整する必要がある。

【００２７】図１（ａ），（ｂ）に示すように、図２（ｂ）に示したような膜厚分布に対応する、少なくとも硬度が異なる２つのダイヤモンド砥石４、５を研磨パッド３の円周方向の上に配置して、研磨パッドのパッド面３ａの表面荒れを調整する。少なくともダイヤモンド砥石４は浮動可能に備えられている。

【００２８】この膜厚分布は、予め成膜装置毎に膜厚分布の形状に関するデータを取って、パーソナルコンピュータ等に記憶させておき、研磨の際に読み出して利用してもよいし、その都度、半導体基板のデバイス面の膜厚分布を計測してもよい。

【００２９】本実施形態では、図２（ｂ）に示した堆積膜の膜厚分布を例とすると、研磨パッド３は、図１（ｃ）に示すように半導体基板１のＡ領域及びＣ領域を研磨する外周部のパッド面部分６及び中心部のパッド面部分８が、Ｂ領域を研磨する内周部のパッド面部分７よ

りも研磨量が多くなるように、表面荒れの粗さを調整する必要がある。

【００３０】その調整方法は、ダイヤモンド砥石５に比べて、研磨量が低い硬度のダイヤモンド砥石４を装着してパッド面３ａに押し付け、研磨パッド３を回転させて、パッド面３ａに表面荒れを形成する。

【００３１】本実施形態の研磨パッドの調整方法によれば、ＣＭＰ装置に装着して、半導体基板のデバイス面を平坦化する研磨パッド内の表面荒れの粗さを、デバイス面の膜厚分布（研磨すべき量）に基づき、研磨量の多い部分ほど粗くなるように調整することにより、パッド面の平坦化を維持し、且つ同時に膜厚分布の傾向を持つデバイス面を研磨する処理回数（研磨量）を増やすことができる。

【００３２】また、表面荒れの粗さは、研磨量や研磨剤や研磨被膜及び研磨を行う装置の特質や経験方法により異なるため、経験的にあわせて決定する。

【００３３】次に図３を参照して、本発明による第２の実施形態としてのＣＭＰ研磨パッドの調整方法について説明する。

【００３４】前述した第１の実施形態では、硬度が異なる２つのダイヤモンド砥石により、研磨パッドを調整したため、２種類の粗さの表面荒れが形成されたが、図２（ｂ）に示した堆積膜２の膜厚分布で、例えば、Ｃ領域の膜厚がＡ領域の膜厚より、さらに厚かった場合には、Ｃ領域の堆積膜の研磨量をＡ領域よりも多くする必要がある。そこで、図３（ａ）、（ｂ）に示すように、硬度が異なる３つのダイヤモンド砥石１１，１２，１３を研磨パッド３の径方向に配置し、研磨パッド３の表面荒れの調整を行う。このダイヤモンド砥石１１、１２、１３の取り付け機構においては、砥石の支持や研磨パッドに対する研磨位置の移動が可能な構成になっているものとする。

【００３５】この調整は、図３（ｃ）に示すような半導体基板１の膜厚分布において、堆積膜２を膜厚ｂに平坦化する際に、Ｃ’領域の研磨量ｑがＡ’領域の研磨量ｐよりも２倍程度ある場合など、半導体基板の外周部と中心部の膜厚に差があり、前述した第１の実施形態による硬度が２種類のダイヤモンド砥石では、十分な平坦化が実現されない膜厚分布に対応する。このような調整において、砥石の配置は、ダイヤモンド砥石１２、ダイヤモンド砥石１１、ダイヤモンド砥石１３の順に研磨量が多くなる硬度ものを配置する。

【００３６】以上のことから本実施形態は、第１の実施形態に比べて、パッド面内の表面荒れの粗さをさらに調整でき、研磨する膜厚の膜厚分布に依らず、平坦化が実現でき、第１の実施形態と同様な効果が得られる。

【００３７】本実施形態では、硬度が異なる２若しくは３個のダイヤモンド砥石を用いて説明したが、これらに限定されるものではなく、半導体基板の径やデバイス面の膜厚分布、膜の材質により、自由に硬度の選択と配置をしてもよく、また、砥石側を回転させてパッド面を押し付け研磨してもよい。

【００３８】尚、従来、ＣＭＰ装置の研磨機構では研磨パッドだけでなく、研磨を施す半導体基板側も回転させ、且つ半導体基板支持体を揺動方向に揺動する研磨機構もあり、半導体基板のエッヂ領域近傍は、研磨パッドの外周側と内周側とで研磨されるが半導体基板中心部は揺動中心近くで研磨されている。このような研磨装置では、半導体基板の外周部が中心部分よりも、研磨量が多くなっていたが、本実施形態の調整方法を利用して、研磨パッドの表面荒れを調整し、中心部分の研磨量を多くすることにより、この問題を解決できる。

【００３９】

【発明の効果】以上詳述したように本発明によれば、半導体基板のデバイス面の膜厚分布に応じて、研磨パッドのパッド面内を区分して表面荒れの粗さをそれぞれ調整し、研磨面の平坦性と研磨された半導体基板のデバイス面の平坦化を維持させるＣＭＰ研磨パッドの調整方法を提供することができる。

【図面の簡単な説明】

【図１】本発明による第１の実施形態としてのＣＭＰ研磨パッドの調整方法を実施するための研磨パッドと砥石の配置の構成例を示す図である。

【図２】成膜装置を用いて形成した時の堆積膜の膜厚分布の一例を示す図である。

【図３】本発明による第２の実施形態としてのＣＭＰ研磨パッドの調整方法を実施するための研磨パッドと砥石の配置の構成例を示す図である。

【図４】ＣＭＰ装置の概略的な構成を示す図である。

【図５】従来の半導体基板と研磨パッドの研磨状態を説明するための図である。

【符号の説明】

１…半導体基板

２…堆積膜

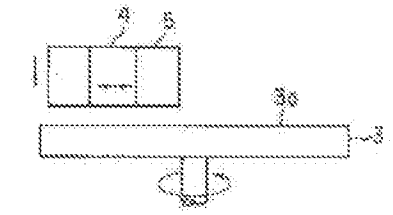
３…研磨パッド

３ａ…パッド面

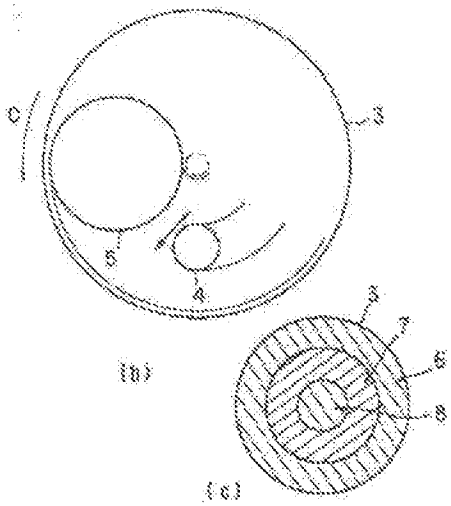
４，５…ダイヤモンド砥石

６，７，８…研磨パッド部分

【図1】

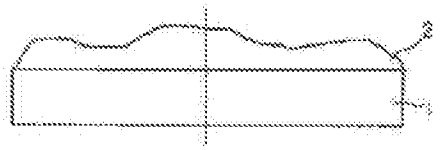


(a)

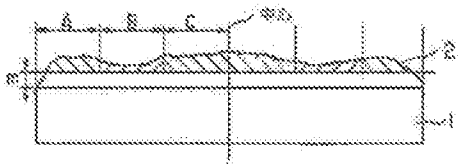


(b) (c)

【図2】

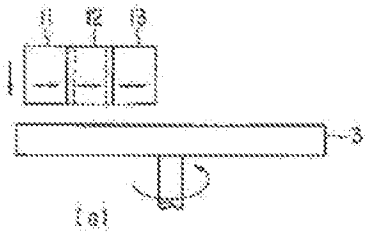


(a)

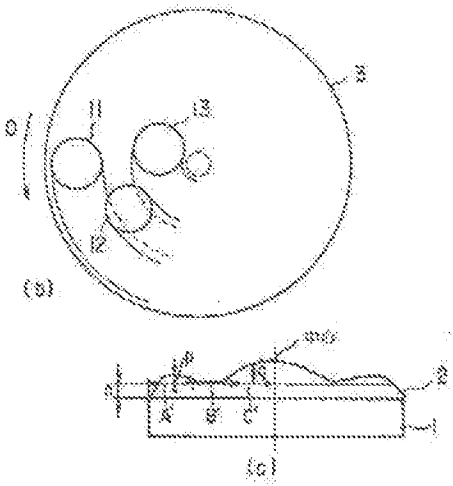


(b)

【図3】

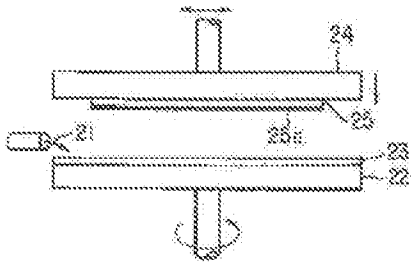


(a)

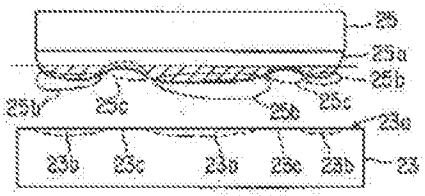


(b) (c)

【図4】



【図5】



Espacenet

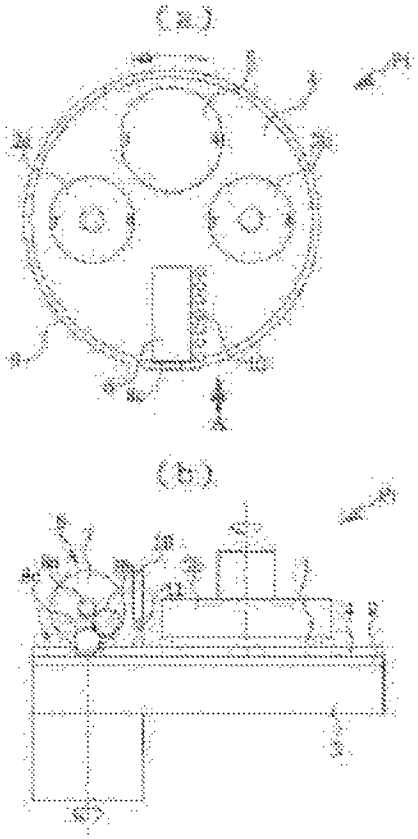
Bibliographic data: JP11048122 (A) — 1999-02-23

CHEMICAL-MECHANICAL POLISHING DEVICE, AND MANUFACTURE OF SEMICONDUCTOR INTEGRATED CIRCUIT DEVICE USING SAME

Inventor(s):	KIMURA TAKESHI; ITO HIDEFUMI; SATO KIYOHIKO; NEZU HIROKI; OKUYA KEN ±
Applicant(s):	HITACHI LTD ±
Classification:	- ***B24B37/00; H01L21/304***; (IPC1-7): B24B37/00; H01L21/304 - **European:**
Application number:	JP19970208874 19970804
Priority number (s):	JP19970208874 19970804

Abstract of JP11048122 (A)

PROBLEM TO BE SOLVED: To provide a polishing pad of long life in a chemical-mechanical polishing(CMP) technique, as well as to polish uniformly a whole surface of a polished film on a semiconductor wafer at stable polishing speed. SOLUTION: After a surface of a polishing pad 4 is ground by the first dressor 5 with embedded diamond particles to achieve flatness, a surface of a polished film on a semiconductor wafer 1 is polished, and a sodding grain on a surface of the polishing pad 4 is set up simultaneously by the second dressor 6 composed of a cylindrical brush 7 while supplying a polishing abrasive solution through a supplying nozzle 10 so as to restore an original coarse sodding grain.



Last updated: 14.03.2012 Worldwide Database 6.7.38; 93p

(19)日本国特許庁（JP）　(12)公開特許公報（A）　(11)特許出願公開番号
特開平11－48122
(43)公開日　平成11年(1999)2月23日

(51)Int.Cl.⁶	識別記号	FI	
B24B 37/00		B24B 37/00	A
H01L 21/304	321	H01L 21/304	321E

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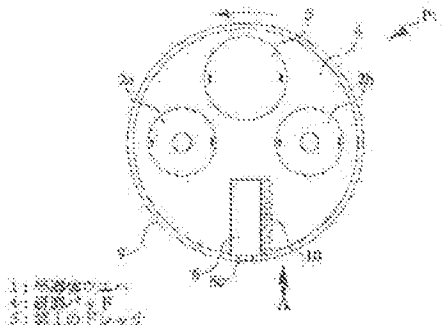
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(54)【発明の名称】　化学的機械研磨装置およびこれを用いた半導体装置の製造方法

(57)【要約】
【課題】　CMP技術において、寿命の長い研磨パッドを得ると同時に、安定した研磨速度で半導体ウエハ上の絶縁膜の全面を均一に研磨する。
【解決手段】　ダイヤモンド粒子が埋め込まれた第1のドレッサ5で研磨パッド4の表面を切削して平坦度を出した後、半導体ウエハ1上の絶縁膜の研磨を開始すると同時に、供給ノズル10から研磨砥粒液11を供給しながら円盤状のブラシによって構成される第2のドレッサ6で研磨パッド4の表面の溝を立たせて、元の荒い溝を復元する。

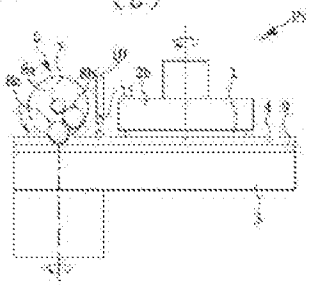
図 1

(a)



1：半導体ウエハ
3：研磨パッド
5：第1のドレッサ
6：第2のドレッサ

(b)



【特許請求の範囲】
【請求項１】　研磨定盤上に貼り付けられた研磨パッドに半導体ウエハを押し付けて前記半導体ウエハ上に設けられた各種膜の表面を研磨する化学的機械研磨装置であって、前記研磨パッドの表面を整形するドレッサが、少なくとも２種類設けられていることを特徴とする化学的機械研磨装置。
【請求項２】　請求項１記載の化学的機械研磨装置において、前記研磨パッドの表面を整形するドレッサとして、少なくとも前記研磨パッドの表面を平坦化する第１のドレッサと、前記研磨パッドの表面の荒さを復元させる第２のドレッサとが設けられていることを特徴とする化学的機械研磨装置。
【請求項３】　請求項２記載の化学的機械研磨装置において、前記第１のドレッサはダイヤモンド粒子が埋め込まれたドレッサであり、前記第２のドレッサはポリマー繊維からなるブラシによって構成されたドレッサであることを特徴とする化学的機械研磨装置。
【請求項４】　請求項３記載の化学的機械研磨装置において、前記半導体ウエハ上に設けられた各種膜の表面を研磨すると同時に、前記研磨パッドの表面に研磨砥粒液を供給しながら、前記第２のドレッサを前記研磨パッドの表面に押さえ付けて間欠的または連続的に回動させることを特徴とした化学的機械研磨装置。
【請求項５】　請求項４記載の化学的機械研磨装置において、前記第２のドレッサの前記研磨パッドに対する回動方向が、少なくとも前記半導体ウエハの回動方向とはほぼ逆方向の成分を有していることを特徴とする化学的機械研磨装置。
【請求項６】　請求項４記載の化学的機械研磨装置において、前記研磨砥粒液の供給口が前記第２のドレッサに内蔵されていることを特徴とする化学的機械研磨装置。
【請求項７】　請求項２～６のいずれか１項に記載の化学的機械研磨装置において、前記第２のドレッサが前記研磨パッドの研磨面に対して平行な回転軸を有する円筒状のドレッサであることを特徴とする化学的機械研磨装置。
【請求項８】　請求項７記載の化学的機械研磨装置において、前記第２のドレッサが強制的に回転されることを特徴とする化学的研磨装置。
【請求項９】　請求項７又は８に記載の化学的機械研磨装置において、前記第２のドレッサの円周速度は、前記研磨パッドが貼り付けられた研磨定盤の最外周部の円周速度よりも速いことを特徴とする化学的機械研磨装置。
【請求項１０】　請求項１～９のいずれか１項に記載の化学的機械研磨装置を用いた半導体集積回路装置装置の製造方法であって、前記第１のドレッサおよび前記第２のドレッサで整形される前記研磨パッドによって、半導体ウエハ上に設けられた各種膜の表面を平坦に加工する工程を有することを特徴とする半導体集積回路装置の製造方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、半導体集積回路装置の製造技術に関し、特に、半導体ウエハ上に堆積された絶縁膜または金属膜の表面の凹凸を化学的機械研磨（Chemical Mechanical Polishing ；CMP）装置を用いて平坦に加工する技術に関するものである。
【０００２】
【従来の技術】従来のCMP装置P_1の要部断面の模式図を図５に示す。図において、５１は半導体ウエハ、５２は調性表、５３は弾性体の合成樹脂から成る加圧用パッド、５４は調性表５２にその厚み方向に貫通設けられた通気孔、５５は弾性表５２に設けられた通気孔５４と一致する如く加圧用パッド５３に配列された通気孔、５６は加圧ヘッド、５７は研磨パッド、５８は研磨パッドが貼り付けられた研磨定盤、５９は半導体ウエハ５１が研磨中に加圧ヘッド５６から外れないように設けられたストッパである。
【０００３】半導体ウエハ５１は、調性表５２および加圧用パッド５３にそれぞれ設けられた通気孔５４、５５からの真空吸引により加圧ヘッド５６に装着された後、研磨パッド５７上に押し付けられる。研磨時の圧力は加圧ヘッド５６、調性表５２、加圧用パッド５３を介して半導体ウエハ５１に加えられる。半導体ウエハ５１は加圧ヘッド５６と共に回転し、同じく回転する研磨定盤５８に貼り付けられた研磨パッド５７に押さえつけながら研磨される。
【０００４】次に、前記CMP装置P_1を用い、半導体ウエハ上に堆積された絶縁膜または金属膜の表面の凹凸を平坦化する製造工程の一例を図６（ａ）～（ｆ）を用いて説明する。
【０００５】これらの図において、６０は半導体基板、６１は第１層目の配線、６２は層間絶縁膜、６３は層間絶縁膜６２に開孔されたスルーホール、６４は金属膜、６５は第２層目の配線である。
【０００６】まず、半導体基板６０上に、例えばトランジスタ等の半導体素子、電荷蓄積用容量素子または抵抗素子（いずれも図示せず）などを形成した後、これらを互いに電気的に接続する第１層目の配線６１を形成する（工程（ａ））。この際、半導体基板６０の表面には第１層目の配線６１の厚み分の凹部が生ずる。
【０００７】次に、ＣＶＤ（Chemical Vapor Deposition）法を用いて酸化シリコン膜または窒化シリコン膜などによって構成される層間絶縁膜６２を半導体基板６０上に堆積させて、上記第１層目の配線６１を層間絶縁膜６２で覆う（工程（ｂ））。この際、ほぼ前記第１層目の配線６１の厚み分の段差が層間絶縁膜６２の表面に残存する。次いで、前記CMP装置P_1を用いて、層間絶

絶縁膜６２の表面を研磨して平坦に加工する（工程（ｃ））。

【０００８】次に、第１層目の配線６１に達するスルーホール６３を層間絶縁膜６２に設けた後、ＣＶＤ法またはスパッタリング法などによって半導体基板６０上に金属膜６４を堆積し（工程（ｄ））、次いで、前記ＣＭＰ装置Ｐ１を用いて層間絶縁膜６２の表面に堆積された金属膜６４を研磨除去する。これによって、スルーホール６３に金属膜６４を埋め込む（工程（ｅ））。

【０００９】次に、半導体基板６０上に金属膜（図示せず）を堆積した後、この金属膜をパターニングすることによって第２層目の配線６５を形成する（工程（ｆ））。第１層目の配線６１と第２層目の配線６５とはスルーホール６３に埋め込まれた金属膜６４を介して電気的に接続される。また、上記工程（ａ）～（ｆ）を同様に繰り返すことにより所望の多層配線を有する半導体集積回路装置を形成することができる。

【００１０】ところで、上記工程（ｃ）での層間絶縁膜６２の表面の平坦化および上記工程（ｅ）での金属膜６４の表面の平坦化で要求される研磨技術の基本的性能としては、被研磨膜の面内の平坦度、研磨量の均一性、スループットおよび研磨速度の安定性が挙げられる。これらのうち、被研磨膜の面内の平坦度は使用する研磨パッドの機械的特性、研磨量の均一性はウエハ加圧方式によってほぼ決定されるのに対し、スループットおよび研磨速度の安定性は、研磨砥粒の作用、加圧力または摺動速度などの研磨条件に加えて、研磨パッドの表面状態に強く依存する。

【００１１】特に、本発明者の実験により、研磨速度の安定性は研磨パッドの表面の荒さの変化と強い相関関係があることが明らかとなった。図７は、本発明者の実験結果の一例であり、半導体ウエハの処理枚数に対する半導体ウエハ上の被研磨膜の研磨速度の変化および研磨パッドの表面の荒さの変化を示すグラフ図である。

【００１２】図に示すように、半導体ウエハの処理枚数が増加するに従い、研磨速度は初期に急激に低下し、その後、なだらかに低下した後、ほぼ一定の速度に安定する。また、研磨速度の変化と同様に、研磨パッドの表面の荒さも半導体ウエハの処理枚数が増加するに従い減少した後、ほぼ一定の荒さに落ち着く。

【００１３】この理由は、研磨パッドの表面の荒さが減少すると研磨剤は液の保持力が低下して研磨パッドの表面に供給された研磨砥粒液が半導体ウエハの摺動により半導体ウエハの外周部で掻き出されてしまい、半導体ウエハ上の研磨面と研磨パッド面との間に存在する研磨砥粒の量が減少して、研磨速度が低下するものと考えられる。なお、研磨パッドの表面の荒さが減少する理由は、研磨パッドの表面の凹凸の構造が、研磨中に繰り返し受ける半導体ウエハへの研磨圧力によって潰れてしまうためである。

【００１４】そこで、研磨中における研磨パッドの表面状態の経時変化を防ぎ、半導体ウエハの表面の研磨速度を一定に保つために、半導体ウエハ上の被研磨膜を研磨する加圧ヘッドとは別に、ダイヤモンド粒子を埋め込んだ円盤（以下、ドレッサと称す）を研磨作業後または研磨作業中に研磨パッド上に摺動させて、研磨パッドの表面を整形するドレッシングが研磨パッドに施されている。

【００１５】図８および図９に従来の研磨パッドのドレッシング方法の概略図を示す。図８に示すドレッシング方法は、大型のドレッサ６６に回転と揺動を加えながら研磨パッド５７の表面を整形する方法であり、図９に示すドレッシング方法は、アーム揺動６７を用いて小型のドレッサ６８を研磨パッド５７の全面に均等に揺動させて、研磨パッド５７の表面を整形する方法である。これらのドレッシング方法には、半導体ウエハ上の被研磨膜の研磨と研磨パッドの表面のドレッシングとを同時に行う同時ドレッシング、または半導体ウエハ上の被研磨膜の研磨前後の半導体ウエハを搬送する空き時間に研磨パッドの表面のドレッシングを行う間欠ドレッシングがある。

【００１６】なお、ＣＭＰ装置のドレッシング方法については、例えばソリッド・ステート・テクノロジ（Solid State Technology, 日本版,Dec. 1994. Iqbal Ali et al., "層間絶縁膜の化学的機械研磨に関する概観"）などに記載されている。

【００１７】

【発明が解決しようとする課題】しかしながら、前記ドレッシング方法には、以下の問題点があることを本発明者は見いだした。

【００１８】すなわち、まず、同時ドレッシングでは、研磨パッドの表面が常にドレッシングされるので安定な研磨速度が得られるが、研磨パッドの表面が常にドレッサによって削り取られるため研磨パッドの寿命が著しく低下する。また、間欠ドレッシングでは、研磨パッドの寿命は長いが、半導体ウエハ上の被研磨膜の研磨中に研磨速度が低下して安定な研磨速度が得られず、さらに、ドレッシングに要する時間が単独で必要なためにＣＭＰ装置のスループットが低下する。

【００１９】これらの問題を解決する方法の一つとして、研磨パッドに対するドレッサの押圧力を低下させる方法がある。この方法を採用すれば、研磨速度をある程度安定化させ、研磨パッドの寿命を長くすることができる。

【００２０】しかし、ドレッシングには、研磨パッドの表面の荒さを一定に保ち研磨速度を安定化させる目的の他に、研磨パッドの全面をドレッシングでの切削によって整形し、研磨パッドの表面の平坦度を得ることにより半導体ウエハ上の被研磨膜の全面の均一性を確保する目的があり、研磨パッドに対するドレッサの押圧力を低下

させると研磨パッドの表面の平坦度を維持することが難しく、半導体ウエハ上の被研磨膜の全面を均一に研磨することができない問題がある。

【００２１】本発明の目的は、ＣＭＰ技術において、寿命の長い研磨パッドを得ると同時に、安定した研磨速度で半導体ウエハ上の被研磨膜の全面を均一に研磨することができる技術を提供することにある。

【００２２】本発明の前記ならびにその他の目的と新規な特徴は、本明細書の記述および添付図面から明らかになるであろう。

【００２３】

【課題を解決するための手段】本願において開示される発明のうち、代表的なものの概要を簡単に説明すれば、次のとおりである。

【００２４】すなわち、本発明のＣＭＰ装置は、研磨定盤上に貼り付けられた研磨パッドの表面を整形するドレッサとして、少なくとも、ダイヤモンド粒子が埋め込まれ、研磨パッドの表面を平坦化する第１のドレッサと、ポリマ繊維からなるブラシによって掻き出され、研磨パッドの表面の荒さを復元させる第２のドレッサとを有しており、上記第１のドレッサにより研磨パッドの表面を切削した後、第１のドレッサを後退させ、次いで、加圧ヘッドに装着された半導体ウエハを研磨パッドの表面に押さえ付けて半導体ウエハ上の被研磨膜の表面を研磨すると同時に、研磨パッドの表面に研磨剤含有液を供給しながら上記第２のドレッサを断続的または連続的に研磨パッドの表面に押さえ付けて、研磨パッドの表面の荒めを立たせる方向に揺動させるものである。

【００２５】上記した手段によれば、第２のドレッサによるドレッシングによって、研磨パッドの表面を切削することなく、半導体ウエハ上の被研磨膜の表面を研磨することによって潰れた研磨パッドの表面の荒めを立たせて、比較的容易に元の荒い荒めに復元できるので、研磨パッドの寿命を大幅に長くできると同時に、半導体ウエハ上の被研磨膜の研磨速度を安定化することができる。さらに、研磨パッドに対する第１のドレッサの押圧力を低下させる必要がないので、研磨パッドの表面の平坦度が確保できて、半導体ウエハ上の被研磨膜の全面を均一に研磨することができる。

【００２６】

【発明の実施の形態】以下、本発明の実施の形態を図面に基づいて詳細に説明する。

【００２７】なお、実施の形態を説明するための全図において同一機能を有するものは同一の符号を付し、その繰り返しの説明は省略する。

【００２８】本発明の一実施の形態であるＣＭＰ装置Ｐ$_1$が有する研磨パッドのドレッシング方法を図１に示す模式図を用いて説明する。図１（ａ）は、ＣＭＰ装置Ｐ$_1$の上面図であり、図１（ｂ）は、図１（ａ）中に記載のＡ方向から見たＣＭＰ装置Ｐ$_1$の側面図である。１は半導体ウエハ、２ａ，２ｂは加圧ヘッド、３は研磨定盤、４は研磨パッド、５は第１のドレッサ、６は第２のドレッサ、７はブラシ、８ａ，８ｂ，８ｃは歯車、９はギア、１０は供給ノズル、１１は研磨剤含有液である。

【００２９】被研磨材料である半導体ウエハ１は、加圧ヘッド２ａ，２ｂに装着され、回転する研磨定盤３上に張り付けられた研磨パッド４の表面に加圧ヘッド２ａ，２ｂを介して押さえ付けられて、その表面は研磨される。なお、研磨時の加圧ヘッド２ａ，２ｂおよび研磨定盤３の回転数は、例えば共に３０回／分であり、半導体ウエハ１および研磨定盤３の直径は、例えばそれぞれ８インチおよび６００ｍｍである。半導体ウエハ１は、例えば３００ｇｒ／ｃｍ^{2}の圧力で研磨パッド４の表面に押さえ付けられている。

【００３０】研磨パッド４の表面は、第１のドレッサ５および第２のドレッサ６を用いてドレッシングされる。第１のドレッサ５にはダイヤモンド粒子が埋め込まれており、第１のドレッサ５は研磨パッド４の表面を切削して平坦度を出すために用いられる。第２のドレッサ６は研磨パッドの研磨面に対して平行な回転軸を有する円筒状のブラシ７と歯車８ａ，８ｂ，８ｃとによって構成されており、研磨パッド４の表面の荒めを立たせて元の荒い荒めを復元するために用いられる。

【００３１】第２のドレッサ６の歯車８ｃを研磨定盤３の外周端面に形成したギアと噛み合わせて研磨定盤３を回転させることにより、歯車８ｂを介して歯車８ａと一体のブラシ７を強制的に回転駆動させる。この際、第２のドレッサ６の研磨パッド４に対する揺動方向は、半導体ウエハ１の揺動方向とは逆方向の成分を有している。また、ブラシ７の円周速度は研磨定盤３の最外周部の円周速度より約１．５倍速くなるように、歯車８ｃのギア比とブラシ７の径は選ばれる。ブラシ７には、例えば線径１００μｍ、長さ５ｍｍのナイロンブラシを使用した。

【００３２】まず、第１のドレッサ５を用いて研磨パッド４の表面を切削した後、第１のドレッサ５を後退させ、次いで、半導体ウエハ１上の被研磨膜の表面を研磨すると同時に、第２のドレッサ６を断続的または連続的に研磨パッド４上で揺動させて、研磨パッド４の表面を整形する。この際、第２のドレッサ６の近傍に設置した供給ノズル１０から研磨剤含有液１１が約２００ｍｌ／分の速度で研磨パッド４上に供給される。研磨剤含有液１１の供給口は第２のドレッサ６に内蔵してもよい。

【００３３】図２に、本実施の形態である前記ＣＭＰ装置Ｐ$_1$を用いて、半導体ウエハ上にプラズマＣＶＤ法で堆積された酸化シリコン膜の表面を研磨した際の酸化シリコン膜の研磨速度と半導体ウエハの研磨枚数との関係を示す。図において、四角印は前記本実施の形態のドレッシング、白丸印は従来の同時ドレッシング、黒丸印は従来の間欠ドレッシングを採用した際のそれぞれの酸化

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シリコン膜の研磨速度を示す。

【００３４】いずれの場合も一つの研磨定盤に対して２つの加圧ヘッドを有し、２枚の半導体ウエハを同時に研磨した結果であり、図中には２枚の半導体ウエハで得られたそれぞれの酸化シリコン膜の研磨速度の平均値を１点で示してある。半導体ウエハ上の酸化シリコン膜の研磨時間は５分である。

【００３５】本実施の形態のドレッシングでは、半導体ウエハ１上の酸化シリコン膜の研磨前の第１のドレッサ５によるドレッシング時間は３分であり、半導体ウエハ１上の酸化シリコン膜の研磨中は第２のドレッサ６でドレッシングを行っている。研磨パッドには厚さが１．２ｍｍの発泡ポリウレタン性のＩＣ１０００（米国ロデール社）を用いた。なお、従来の間欠ドレッシングのドレッシング時間は２分である。

【００３６】図から明らかなように、従来の間欠ドレッシングの研磨速度は他のドレッシングの研磨速度と比べて約１０％低く、また、±５％以上の研磨速度の変動がある。しかし、本実施の形態のドレッシングでは半導体ウエハの研磨枚数が２５枚まで従来の同時ドレッシングとほぼ同じ研磨速度が得られ、また、±２％以下の研磨量の均一性（図示せず）が得られる。

【００３７】図３に、本実施の形態である前記ＣＭＰ装置Ｐ，を用いて、半導体ウエハ上に堆積された酸化シリコン膜を研磨した際の研磨パッドの厚さと半導体ウエハの研磨枚数との関係を示す。図において、四角印は前記本実施の形態のドレッシング、白丸印は従来の同時ドレッシング、黒丸印は従来の間欠ドレッシングを採用した際のそれぞれの研磨パッドの厚さを示す。

【００３８】なお、本発明者の実験から、研磨パッドをその厚さが初期の厚さ（例えば１．２ｍｍ）の半分になるまで研磨すると、半導体ウエハ上の被研磨膜の研磨速度の安定性または半導体ウエハ上の被研磨膜の研磨量均一性に顕著な劣化が認められることが明らかになっており、このことから、研磨パッドの厚さが半分となった時点を研磨パッドの寿命と称す。

【００３９】図に示すように、従来の同時ドレッシングでは約１００枚の半導体ウエハを研磨するだけで研磨パッドは寿命に達し、従来の間欠ドレッシングでも約２５０枚の半導体ウエハを研磨すると研磨パッドは寿命に達する。これに対し、本実施の形態のドレッシングでは、約４０００枚の半導体ウエハを研磨すると研磨パッドが寿命に達する。

【００４０】次に、本実施の形態の前記ＣＭＰ装置Ｐ，を用いたＤＲＡＭ（Dynamic Random Access Memory）のメモリ回路の製造方法を図４を用いて説明する。なお、ＤＲＡＭの周辺回路部はｎチャネル型ＭＩＳＦＥＴ（Metal Insulator Semiconductor Field Effect Transistor）Ｑｎの製造方法のみを記載する。

【００４１】まず、ｐ－型シリコン単結晶からなる半導体基板１２の主面上に周知の方法でｐ型ウエル１３、フィールド絶縁膜１４およびゲート絶縁膜１５を順次形成する。

【００４２】次に、図示はしないが、半導体基板１２上に堆積された酸化シリコン膜、タングステンシリサイド（ＷＳｉ$_2$）膜および多結晶シリコン膜からなる積層膜を順次エッチングすることにより、ＷＳｉ$_2$膜および多結晶シリコン膜からなるメモリセルのメモリセル選択用ＭＩＳＦＥＴのゲート電極１６および周辺回路部のｎチャネル型ＭＩＳＦＥＴＱｎのゲート電極１６を形成する。

【００４３】なお、上記ゲート電極１６を構成するメタルシリサイド膜にＷＳｉ$_2$膜を用いたが、その他のメタルシリサイド膜、例えばモリブデンシリサイド（ＭｏＳｉ$_2$）膜、チタンシリサイド（ＴｉＳｉ$_2$）膜、タンタルシリサイド（ＴａＳｉ$_2$）膜などを用いてもよい。

【００４４】次に、レジストパターンならびに上記酸化シリコン膜、ＷＳｉ$_2$膜および多結晶シリコン膜からなる積層膜をマスクにして、周辺回路部のｐ型ウエル１３にｎ型不純物、例えばリン（Ｐ）をイオン注入し、ｎチャネル型ＭＩＳＦＥＴＱｎのｎ型半導体領域（ソース領域、ドレイン領域）１７を、ゲート電極１６に対して自己整合で形成する。

【００４５】その後、半導体基板１２上に堆積された酸化シリコン膜をＲＩＥ（Reactive Ion Etching）法などの異方性エッチングで加工することによって、ゲート電極１６の側壁にサイドウォールスペーサを形成し、ゲート電極１６を酸化シリコン膜からなる絶縁膜１８で覆う。

【００４６】なお、上記サイドウォールスペーサを形成した後、周辺回路部のｐ型ウエル１３に高濃度のｎ型不純物、例えば砒素（Ａｓ）をイオン注入することにより、ｎチャネル型ＭＩＳＦＥＴＱｎのソース領域、ドレイン領域をＬＤＤ（Lightly Doped Drain）構造としてもよい。

【００４７】次に、半導体基板１２上に酸化シリコン膜１９および第１のＢＰＳＧ（Boron-doped Phospho Silicate Glass）膜２０をＣＶＤ法によって堆積した後、９００～９５０℃のリフロー処理により上記第１のＢＰＳＧ膜２０の表面を平坦化する。

【００４８】その後、レジストパターンをマスクにして第１のＢＰＳＧ膜２０、酸化シリコン膜１９およびゲート絶縁膜１５と同一層の絶縁膜を順次エッチングすることにより、メモリセル選択用ＭＩＳＦＥＴの一方の後に形成されるｎ型半導体領域２１上に第１のコンタクトホール２２を形成する。

【００４９】次いで、上記第１のコンタクトホール２２内にＰが導入された多結晶シリコン膜２３からなる第１プラグ電極を形成する。なお、この多結晶シリコン膜２３に導入されたＰの拡散によってメモリセル選択用ＭＩ