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(54) **SUPER HARD COMPONENTS AND POWDER METALLURGY METHODS OF MAKING THE SAME**

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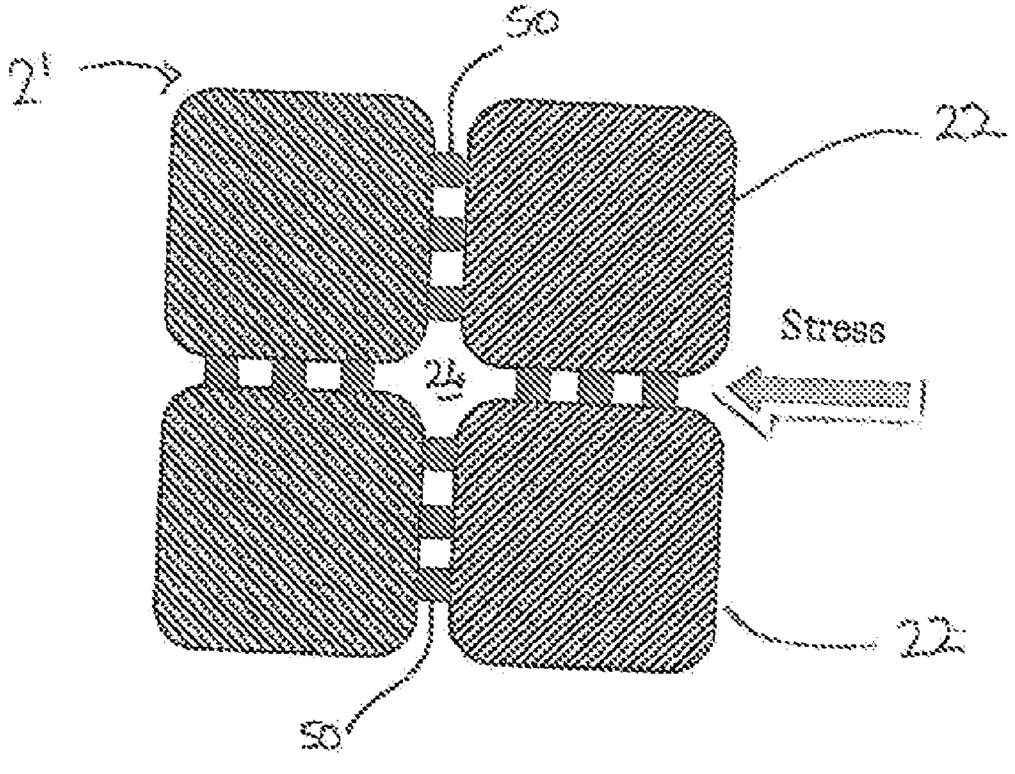
(57) **ABSTRACT**

A method of forming a super hard polycrystalline construction comprises forming a liquid suspension of nano-sized super hard particles and particles of super hard material having an average particle or grain size of 1 or more microns, dispersing the particles in the liquid suspension to form a substantially homogeneous suspension which is then dried and sintered to form a body of polycrystalline super hard material comprising a first and second fractions of super hard grains, the nano-sized particles forming the second fraction. The super hard grains in the first fraction are bonded along at least a portion of the peripheral surface(s) thereof to at least a portion of a plurality of nano-sized grains in the second fraction, the grains in the first fraction having a greater average grain size than that of the grains in the second fraction which is less than 999 nm, the average grain size of the first fraction being around 1 micron or more



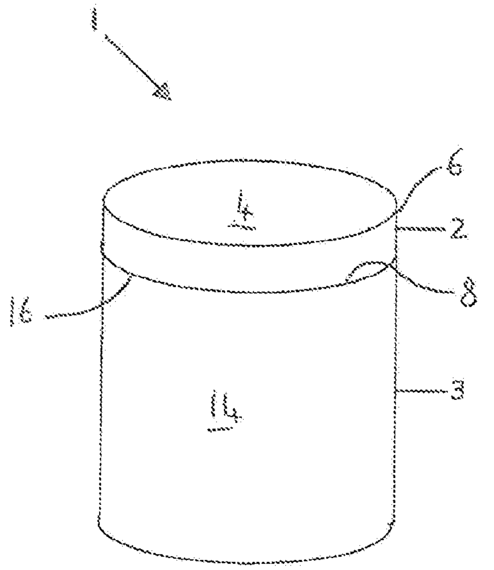


FIG 1

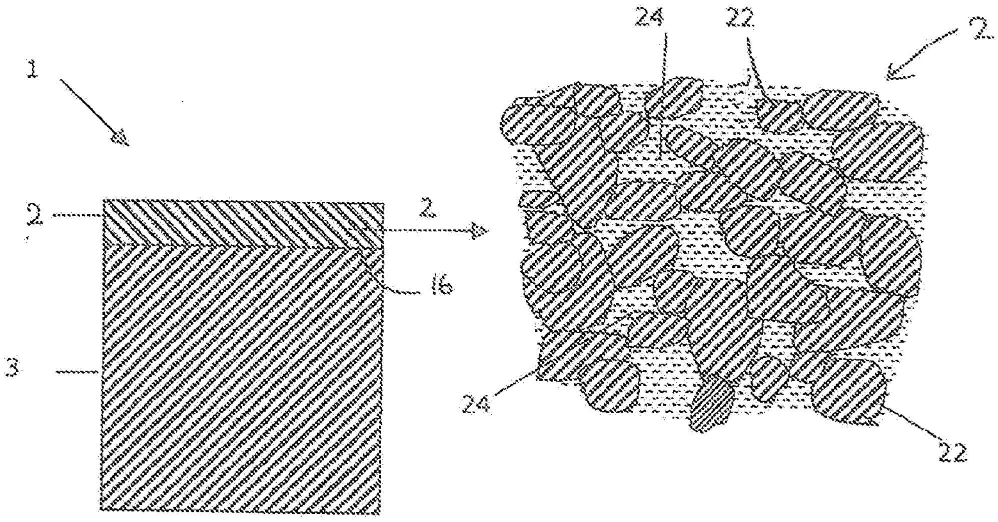


FIG 2

(prior art)

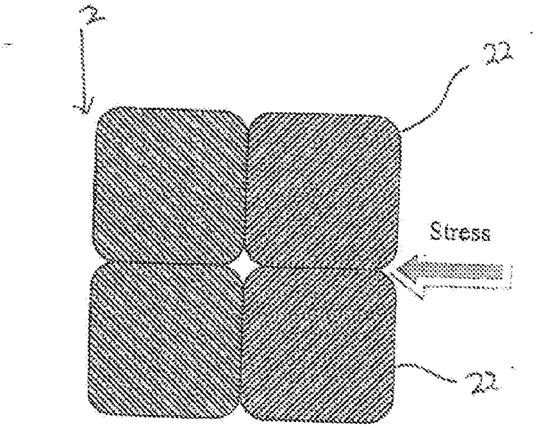


FIG.3 (prior art)

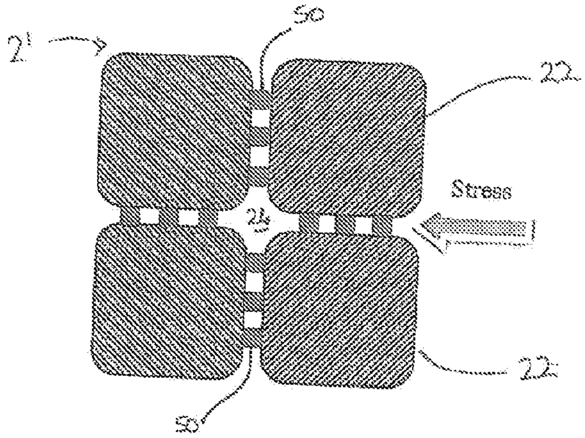


FIG. 4

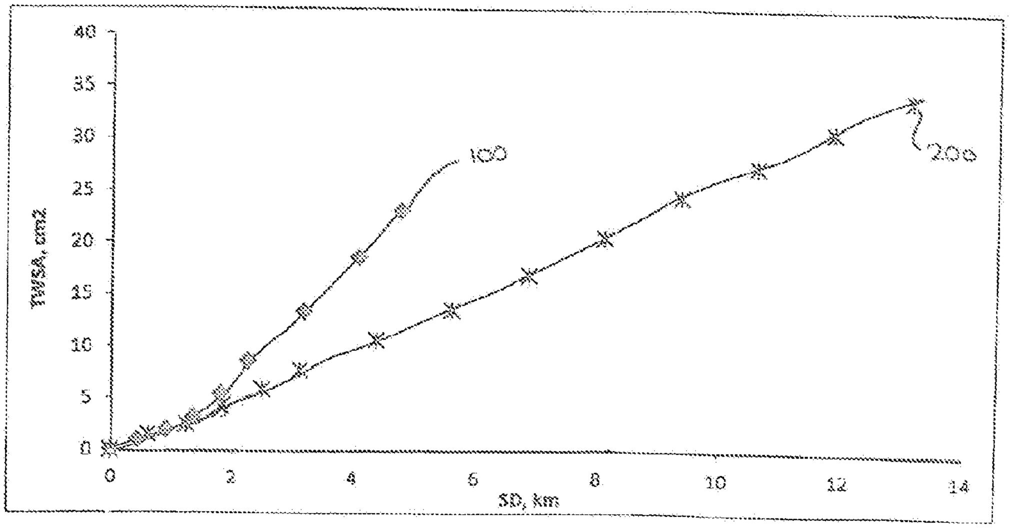


FIG. 5

SUPER HARD COMPONENTS AND POWDER METALLURGY METHODS OF MAKING THE SAME

FIELD

[0001] This disclosure relates to super hard constructions and methods of making such constructions, particularly but not exclusively to constructions comprising polycrystalline diamond (PCD) structures which may or may not be attached to a substrate, and tools comprising the same, particularly but not exclusively for use in rock degradation or drilling, or for boring into the earth.

BACKGROUND

[0002] Polycrystalline super hard materials, such as polycrystalline diamond (PCD) may be used in a wide variety of tools for cutting, machining, drilling or degrading hard or abrasive materials such as rock, metal, ceramics, composites and wood-containing materials. In particular, tool inserts in the form of cutting elements comprising PCD material are widely used in drill bits for boring into the earth to extract oil or gas. The working life of super hard tool inserts may be limited by fracture of the super hard material, including by spalling and chipping, or by wear of the tool insert.

[0003] Cutting elements such as those for use in rock drill bits or other cutting tools typically have a body in the form of a substrate which has an interface end/surface and a super hard material which forms a cutting layer bonded to the interface surface of the substrate by, for example, a sintering process. The substrate is generally formed of a tungsten carbide-cobalt alloy, sometimes referred to as cemented tungsten carbide and the super hard material layer is typically polycrystalline diamond (PCD), or a thermally stable product TSP material such as thermally stable polycrystalline diamond.

[0004] Polycrystalline diamond (PCD) is an example of a super hard material (also called a super abrasive material or ultra hard material) comprising a mass of substantially inter-grown diamond grains, forming a skeletal mass defining interstices between the diamond grains. PCD material typically comprises at least about 80 volume % of diamond and is conventionally made by subjecting an aggregated mass of diamond grains to an ultra-high pressure of greater than about 5 GPa, and temperature of at least about 1,200° C., for example. A material wholly or partly filling the interstices may be referred to as filler or binder material.

[0005] PCD is typically formed in the presence of a sintering aid such as cobalt, which promotes the intergrowth of diamond grains. Suitable sintering aids for PCD are also commonly referred to as a solvent-catalyst material for diamond, owing to their function of dissolving, to some extent, the diamond and catalysing its re-precipitation. A solvent-catalyst for diamond is understood be a material that is capable of promoting the growth of diamond or the direct diamond-to-diamond inter-growth between diamond grains at a pressure and temperature condition at which diamond is thermodynamically stable. Consequently the interstices within the sintered PCD product may be wholly or partially filled with residual solvent-catalyst material. Most typically, PCD is formed on a cobalt-cemented tungsten carbide substrate, which provides a source of cobalt solvent-catalyst for the PCD. Materials that do not promote substantial coherent intergrowth between the diamond grains may themselves form strong bonds with diamond grains, but are not suitable solvent-catalysts for PCD sintering.

[0006] Cemented tungsten carbide, which may be used to form a suitable substrate, is formed from carbide particles being dispersed in a cobalt matrix by mixing tungsten carbide particles/grains and cobalt together then heating to solidify. To form the cutting element with a super hard material layer such as PCD, diamond particles or grains are placed adjacent the cemented tungsten carbide body in a refractory metal enclosure such as a niobium enclosure and are subjected to high pressure and high temperature so that inter-grain bonding between the diamond grains occurs, forming a polycrystalline super hard diamond layer.

[0007] In some instances, the substrate may be fully cured prior to attachment to the super hard material layer whereas in other cases the substrate may be green, that is, not fully cured. In the latter case, the substrate may fully cure during the HTHP sintering process. The substrate may be in powder form and may solidify during the sintering process used to sinter the super hard material layer.

[0008] Ever increasing drives for improved productivity in the earth boring field place ever increasing demands on the materials used for cutting rock. Specifically, PCD materials with improved abrasion and impact resistance are required to achieve faster cut rates and longer tool life.

[0009] Cutting elements or tool inserts comprising PCD material are widely used in drill bits for boring into the earth in the oil and gas drilling industry. Rock drilling and other operations require high abrasion resistance and impact resistance. One of the factors limiting the success of the polycrystalline diamond (PCD) abrasive cutters is the generation of heat due to friction between the PCD and the work material. This heat causes the thermal degradation of the diamond layer. The thermal degradation increases the wear rate of the cutter through increased cracking and spalling of the PCD layer as well as back conversion of the diamond to graphite causing increased abrasive wear.

[0010] Methods used to improve the abrasion resistance of a PCD composite often result in a decrease in impact resistance of the composite.

[0011] The most wear resistant grades of PCD usually suffer from a catastrophic fracture of the cutter before it has worn out. During the use of these cutters, cracks grow until they reach a critical length at which catastrophic failure occurs, namely, when a large portion of the PCD breaks away in a brittle manner. These long, fast growing cracks encountered during use of conventionally sintered PCD, result in short tool life.

[0012] Furthermore, despite their high strength, polycrystalline diamond (PCD) materials are usually susceptible to impact fracture due to their low fracture toughness. Improving fracture toughness without adversely affecting the material's high strength and abrasion resistance is a challenging task.

[0013] There is therefore a need for a polycrystalline super hard composite such as a PCD composite that has good or improved abrasion, fracture and impact resistance and a method of forming such composites.

SUMMARY

[0014] Viewed from a first aspect there is provided a method of forming a super hard polycrystalline construction, comprising:

- **[0015]** forming a liquid suspension of a first mass comprising nano-sized super hard particles and a mass of particles or grains of super hard material having an average particle or grain size of 1 or more microns;
- **[0016]** dispersing the first mass and mass of super hard particles or grains in the liquid suspension to form a substantially homogeneous suspension;
- **[0017]** drying the suspension to form an admix of the first mass and the super hard grains or particles;
- **[0018]** forming a pre-sinter assembly comprising the admix;
- **[0019]** treating the pre-sinter assembly in the presence of a catalyst/solvent material for the super hard grains at an ultra-high pressure of around 5 GPa or greater and a temperature to sinter together the grains of super hard material to form a body of polycrystalline super hard material comprising a first fraction of super hard grains and a second fraction of super hard grains, the super hard grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, the nano-sized particles forming the second fraction of super hard grains; wherein
- **[0020]** the super hard grains in the first fraction are bonded along at least a portion of the peripheral surface (s) thereof to at least a portion of a plurality of nano-sized grains in the second fraction;
- **[0021]** the super hard grains in the first fraction having a greater average grain size than the average grain size of the grains in the second fraction, the average grain size of the grains in the second fraction being less than around 999nm and the average grain size of the grains of superhard material in the first fraction being around 1 micron or more,

[0022] Viewed from a second aspect there is provided a method of forming a super hard polycrystalline construction, comprising:

- **[0023]** a body of polycrystalline super hard material comprising a first fraction of super hard grains and a second fraction of super hard grains, the first fraction having a greater average grain size than the super hard grains in the second fraction;
- **[0024]** the super hard grains in the first and second fraction having a peripheral surface; wherein
- **[0025]** the super hard grains in the first fraction are bonded along at least a portion of the peripheral surface to at least a portion of a plurality of super hard grains in the second fraction;
- **[0026]** the super hard grains in the second fraction being arranged to space one or more adjacent grains in the first fraction by a distance of less than around 999 nm; and wherein the average grain size of the super hard grains in the first fraction is around 1 micron or more.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] The present invention will now be described by way of example and with reference to the accompanying drawings in which:

[0028] FIG. **1** is a perspective view of an example super hard cutter element or construction for a drill bit for boring into the earth;

[0029] FIG. **2** is a schematic cross-section of a portion of a conventional POD micro-structure with interstices between the inter-bonded diamond grains filled with a non-diamond phase material;

[0030] FIG. **3** is a schematic cross-section of a portion of a conventional POD micro-structure;

[0031] FIG. **4** is a schematic cross-section of a portion of an example super hard micro-structure; and

[0032] FIG. **5** is a plot showing the results of a vertical borer test comparing a conventional POD cutter element and an example cutter element.

[0033] The same references refer to the same general features in all the drawings.

DESCRIPTION

[0034] As used herein, a "super hard material" is a material having a Vickers hardness of at least about 28 GPa. Diamond and cubic boron nitride (cBN) material are examples of super hard materials.

[0035] As used herein, a "super hard construction" means a construction comprising a body of polycrystalline super hard material. In such a construction, a substrate may be attached thereto or alternatively the body of polycrystalline material may be free-standing and unbacked.

[0036] As used herein, polycrystalline diamond (PCD) is a type of polycrystalline super hard (PCS) material comprising a mass of diamond grains, a substantial portion of which are directly inter-bonded with each other and in which the content of diamond is at least about 80 volume percent of the material. As used herein, "interstices" or "interstitial regions" are regions between the diamond grains of PCD material. In some examples of PCD material, interstices between the diamond grains may be at least partly filled with a binder material comprising a catalyst for diamond. In some examples of PCD material, interstices or interstitial regions may be substantially or partially filled with a material other than diamond, or they may be substantially empty. PCD material may comprise at least a region from which catalyst material has been removed from the interstices, leaving interstitial voids between the diamond grains.

[0037] A "catalyst material" for a super hard material is capable of promoting the growth or sintering of the super hard material.

[0038] The term "substrate" as used herein means any substrate over which the super hard material layer is formed. For example, a "substrate" as used herein may be a transition layer formed over another substrate.

[0039] As used herein, the term "integrally formed" regions or parts are produced contiguous with each other and are not separated by a different kind of material.

[0040] An example of a super hard construction is shown in FIG. **1** and includes a cutting element **1** having a layer of super hard material **2** formed on a substrate **3**. The substrate **3** may be formed of a hard material such as cemented tungsten carbide, The super hard material **2** may be, for example, polycrystalline diamond (PCD), or a thermally stable product such as thermally stable PCD (TSP). The cutting element **1** may be mounted into a bit body such as a drag bit body (not shown) and may be suitable, for example, for use as a cutter insert for a drill bit for boring into the earth.

[0041] The exposed top surface of the super hard material opposite the substrate forms the cutting face **4**, also known as the working surface, which is the surface which, along with its edge **6**, performs the cutting in use.

[0042] At one end of the substrate **3** is an interface surface **8** that forms an interface with the super hard material layer **2** which is attached thereto at this interface surface. As shown in the example of FIG. **1**, the substrate **3** is generally cylindrical and has a peripheral surface **14** and a peripheral top edge **16**.

[0043] The super hard material may be, for example, polycrystalline diamond (PCD) and the super hard diamond particles or grains may be of natural and/or synthetic origin.

[0044] The substrate **3** may be formed of a hard material such as a cemented carbide material and may be, for example, cemented tungsten carbide, cemented tantalum carbide, cemented titanium carbide, cemented molybdenum carbide or mixtures thereof. The binder metal for such carbides suitable for forming the substrate **3** may be, for example, nickel, cobalt, iron or an alloy containing one or more of these metals. Typically, this binder will be present in an amount of 10 to 20 mass %, but this may be as low as 6 mass % or less. Some of the binder metal may infiltrate the body of polycrystalline super hard material **2** during formation of the compact **1**.

[0045] As shown in FIGS. **2** and **3**, during formation of a conventional polycrystalline composite construction, the diamond grains are directly interbonded to adjacent grains and the interstices **24** between the grains **22** of super hard material such as diamond grains in the case of PCD, may be at least partly filled with a non-super hard phase material. This non-super hard phase material, also known as a filler material, may comprise residual catalyst/binder material, for example cobalt, nickel or iron. The typical average grain size of the diamond grains **22** is larger than 1 micron and the grain boundaries between adjacent grains is therefore typically between micron-sized diamond grains, as shown in FIGS. **2** and **3**.

[0046] The working surface or "rake face" **4** of the polycrystalline composite construction **1** is the surface or surfaces over which the chips of material being cut flow when the cutter is used to cut material from a body, the rake face **4** directing the flow of newly formed chips. This face **4** is commonly also referred to as the top face or working surface of the cutting element as the working surface **4** is the surface which, along with its edge **6**, is intended to perform the cutting of a body in use. It is understood that the term "cutting edge", as used herein, refers to the actual cutting edge, defined functionally as above, at any particular stage or at more than one stage of the cutter wear progression up to failure of the cutter, including but not limited to the cutter in a substantially unworn or unused state.

[0047] As used herein, "chips" are the pieces of a body removed from the work surface of the body being cut by the polycrystalline composite construction **1** in use.

[0048] As used herein, a "wear scar" is a surface of a cutter formed in use by the removal of a volume of cutter material due to wear of the cutter. A flank face may comprise a wear scar. As a cutter wears in use, material may progressively be removed from proximate the cutting edge, thereby continually redefining the position and shape of the cutting edge, rake face and flank as the wear scar forms.

[0049] As shown in FIG. **4**, in a polycrystalline composite construction according to a first example, the super hard material comprises a first fraction **22** of super hard grains or particles, and a second fraction **50** of super hard grains or particles. The first fraction **22** has a greater average grain size than that of the second fraction **50**. The grains of the first fraction **22** are bonded along at least a portion of their peripheral outer surface to a plurality of grains of the second fraction **50**.

[0050] In some examples, the average grain size of the second fraction **50** is nano-sized, that is, less than around 1 micron and the average grain size of the first fraction.

[0051] Non-super hard phase material **24** such as residual catalyst/binder may remain in a number of the interstices between adjacent super hard grains **22**, **50** and the average binder pool size of these interstices may be smaller than in conventional PCD such as that shown in FIGS. **2** and **3**.

[0052] As used herein, a PCD grade is a PCD material characterised in terms of the volume content and size of diamond grains, the volume content of interstitial regions between the diamond grains and composition of material that may be present within the interstitial regions. A grade of PCD material may be made by a process including providing an aggregate mass of diamond grains having a size distribution suitable for the grade, optionally introducing catalyst material or additive material into the aggregate mass, and subjecting the aggregated mass in the presence of a source of catalyst material for diamond to a pressure and temperature at which diamond is more thermodynamically stable than graphite and at which the catalyst material is molten. Under these conditions, molten catalyst material may infiltrate from the source into the aggregated mass and is likely to promote direct intergrowth between the diamond grains in a process of sintering, to form a PCD structure. The aggregate mass may comprise loose diamond grains or diamond grains held together by a binder material and said diamond grains may be natural or synthesised diamond grains,

[0053] Different PCD grades may have different microstructures and different mechanical properties, such as elastic (or Young's) modulus E, modulus of elasticity, transverse rupture strength (TRS), toughness (such as so-called K_1C toughness), hardness, density and coefficient of thermal expansion (CTE). Different PCD grades may also perform differently in use. For example, the wear rate and fracture resistance of different PCD grades may be different.

[0054] All of the PCD grades may comprise interstitial regions filled with material comprising cobalt metal, which is an example of catalyst material for diamond.

[0055] The PCD structure **2'** of examples, as shown in FIG. **3**, may comprise two or more PCD grades.

[0056] The grains of super hard material may be, for example, diamond grains or particles. In the starting mixture prior to sintering they may be, for example, bimodal, that is, the feed comprises a mixture of a coarse fraction of diamond grains and a fine fraction of diamond grains having a smaller average grain size than the coarser fraction. By "average particle or grain size" it is meant that the individual particles/grains have a range of sizes with the mean particle/grain size representing the "average". The average particle/grain size of the fine fraction is less than the size of the coarse fraction.

[0057] Some examples may comprise a wide bi-modal size distribution between the coarse and fine fractions of super hard material, and some examples may include three or even four or more size modes which may, for example, be separated in size by an order of magnitude.

[0058] Sizing of diamond particles/grains into fine fraction, coarse fraction, or other sizes in between, may be through known processes such as jet-milling of larger diamond grains and the like.

[0059] In some examples, the binder catalyst/solvent may comprise cobalt or some other iron group elements, such as iron or nickel, or an alloy thereof. Carbides, nitrides, borides, and oxides of the metals of Groups IV-VI in the periodic table are other examples of non-diamond material that might be added to the sinter mix. In some examples, the binder/catalyst/sintering aid may be Co.

[0060] The cemented metal carbide substrate may be conventional in composition and, thus, may be include any of the Group IVB, VB, or VIB metals, which are pressed and sintered in the presence of a binder of cobalt, nickel or iron, or alloys thereof. In some examples, the metal carbide is tungsten carbide.

[0061] The cutter of FIG. **1** having the microstructure of FIG. **4** may be fabricated, for example, as follows.

[0062] A mass of nanodiamond grains having an average grain size of less than around 999 nm, for example, less than around 500 nm, or less than around 250 nm or less than around 100 nm are thoroughly dispersed in a liquid, such as deionized water or an organic solvent, for example ethanol, with or without surfactants using a sonication process by inserting an ultrasonic probe into the liquid. Micron sized diamond grits having an average grain size of greater than 1 micron are added to the mixture and a sintering agent such as cobalt may also be added. The mixture is then subjected to a further sonication process by applying the ultrasonic probe into the mixture for a further period of time to form a homogeneous mixture. The resulting mixture is then dried using a fast drying process to maintain the homogeneity. A fast drying process such as freeze drying using, for example, liquid nitrogen, or spray drying, or spray granulation may be used to form an admix powder. The admix powder is then sintered under conventional diamond sintering conditions, for example at a pressure of around 6.8 GPa, and temperature of around 1300 degrees C., in some examples with a preformed WC substrate, to form a PCD structure such as that shown in FIG. **4**.

[0063] Whilst not wishing to be bound by a particular theory, it is believed that the thorough dispersion of the nanodiamond and diamond grits in the initial dispersion mixture prior to drying, such that when dried, the nanodiamonds coat, at least in part, the surface of the micron sized diamond particles or grains, may assist in achieving the desired microstructure in which the grains of the first fraction **22** are bonded along a portion of their peripheral outer surface to plurality of grains of a fraction **50** formed from the nanodiamond grains or particles. Various techniques may be used to achieve this dispersed homogenous mixture including, for example, ultrasonic dispersing, ball milling, homogenization, and jet milling techniques.

[0064] Also, it is believed that a fast drying process to dry the nanodiamond/diamond suspension without agglomeration may also assist in achieving the desired microstructure in the sintered product. Suitable drying techniques to assist in inhibiting agglomeration of the nanodiamond/diamond materials during drying may include, for example, freeze drying, spray freeze drying, spray drying, and spray granulation or spray freeze granulation.

[0065] In the example in which a spray drying technique is used, a suitable inlet temperature may be, for example, around 120 deg C., and an outlet temperature of around 50-56 deg C., and a feeding rate of around 5.8 ml/min may be used.

[0066] In the example in which a freeze drying technique is used, the admix may be in the form of a homogeneous paste which is frozen using liquid nitrogen, and is then placed into a freeze dryer for several days until the paste is thoroughly dried. The freeze drying conditions may be optimized for different solvents, for example, for deionized water, the preferred operation temperature is −55 deg C. plus/minus 5 deg C., and the preferred pressure is between around 50 to 500 microbar.

[0067] In some examples, the catalyst binder, for example cobalt, may instead be added to the dried admix powder rather than be included in the liquid suspension.

[0068] In some examples, a stabilizer such as a polymeric stabiliser, for example a surfactant, may be added to the suspension mixture. The surfactant may be, for example, a non-ionic or cationic surfactant. Also, a binding material such as polyvinyl alcohol may be added to the suspension mixture to assist in inhibiting agglomeration.

[0069] The micron-sized diamond particles or grains may be subjected to a heat treatment or acid treatment prior to adding these to the suspension mixture to clean the particles or grains by removing impurities. A suitable heat treatment temperature for micron-sized diamond grits may be, for example, between around 1000 to around 1300 deg C., or between around 1100 to around 1300 deg C., or between around 1200 to around 1300 deg C.

[0070] In some examples the admix material comprising the nano and micron-sized diamond admix, and the carbide material for forming the substrate plus any additional sintering aid/binder/catalyst may be applied as powders and sintered simultaneously in a single UHP/HT process. In such an example, the admix of nano and micron sized diamond grains, and mass of carbide powder material are placed in an HP/HT reaction cell assembly and subjected to HP/HT processing. The HP/HT processing conditions selected are sufficient to effect intercrystalline bonding between the diamond grains as well as, optionally, the joining of sintered particles to the cemented metal carbide support. In one example, the processing conditions generally involve the imposition for about 3 to 120 minutes of a temperature of at least about 1200 degrees C. and an ultra-high pressure of greater than about 5 GPa.

[0071] In another example, the substrate may be pre-sintered in a separate process before being bonded together in the HP/HT press during sintering of the ultrahard polycrystalline material.

[0072] In a further example, both the substrate and a body of polycrystalline super hard material are pre-formed. The preformed body of polycrystalline super hard material is then placed in the appropriate position on the upper surface of the preformed carbide substrate (incorporating a binder catalyst), and the assembly is located in a suitably shaped canister. The assembly is then subjected to high temperature and pressure in a press, the order of temperature and pressure being again, at least around 1200 degrees C. and 5 GPa respectively. During this process the solvent/catalyst migrates from the substrate into the body of super hard material and acts as a binder-catalyst to effect intergrowth in the layer and also serves to bond the layer of polycrystalline super hard material to the substrate.

[0073] In some examples, the cemented carbide substrate may be formed of tungsten carbide particles bonded together by the binder material, the binder material comprising an alloy of Co, Ni and Cr. The tungsten carbide particles may form at least 70 weight percent and at most 95 weight percent of the substrate. The binder material may comprise between about 10 to 50 wt. % Ni, between about 0.1 to 10 wt. % Cr, and the remainder weight percent comprises Co.

[0074] The PCD construction **1** described with reference to FIGS. **1** and **4**, may be further processed after sintering. For example, catalyst material may be removed from a region of the PCD structure adjacent the working surface or the side surface or both the working surface and the side surface. This may be achieved by treating the PCD structure with acid to leach out catalyst material from between the diamond grains, or by other methods such as electrochemical methods. A thermally stable region, which may be substantially porous, extending a depth of at least about 50 microns or at least about 100 microns from a surface of the PCD structure, may thus be formed which may further enhance the thermal stability of the PCD element.

[0075] Furthermore, the PCD body in the structure of FIG. **1** comprising a PCD structure bonded to a cemented carbide support body may be treated or finished by, for example, grinding, to provide a PCD element which is substantially cylindrical and having a substantially planar working surface, or a generally domed, pointed, rounded conical or frusto-conical working surface. The PCD element may be suitable for use in, for example, a rotary shear (or drag) bit for boring into the earth, for a percussion drill bit or for a pick for mining or asphalt degradation.

[0076] In addition, after sintering, the polycrystalline super hard construction may be ground to size and may include, if desired, a chamfer, for example of around 45 degrees and of approximately 0.4 mm height measured parallel to the longitudinal axis of the construction.

[0077] Some versions are discussed in more detail below with reference to the following example, which is not intended to be limiting.

EXAMPLE

[0078] 5 g of diamond powder having an average grain size of 250 nm was cleaned in HCl acid to remove metal contaminants and the cleaned powder was then suspended in 30 ml of deionised water together with 1 g of polyvinyl alcohol to form a suspension. The suspension was then treated with an ultrasonic probe set at 95% power for at least around 10 minutes until a well or fully dispersed diamond suspension was achieved. 2 g of SP cobalt was added into the suspension and a further sonication process applied for around 5 minutes using the ultrasonic probe to disperse the materials and form a nanodiamond suspension.

[0079] In a separate beaker, 63 g of diamond grains having an average grain size of around 22 microns (Grade 22) and 32 g of diamond grains having an average grain size of around 2 microns (Grade 2) and 2 g SP cobalt were mixed together with 30 ml of ethanol, and this mixture was treated with an ultrasonic probe (set at 95% power) for 3 minutes. The nanodiamond suspension was then introduced into the mixture and the resultant mixture subjected to a further **5** minutes of sonication process to form a final admix suspension. The final admix suspension was spray dried with a BUCHI Mini-290 spray dryer to remove liquids and form an admix powder. The spray dryer conditions were:

[0080] Atomization Pressure: 3 Bar

[0081] Inlet temperature: 120° C.

[0082] Outlet temperature: 50~56° C.

[0083] Feeding rate: 5.8 ml/min

[0084] 2.1 g of the admix powder was then placed into a canister with a pre-formed cemented WC substrate to form a pre-sinter assembly, which was then loaded into a press and subjected to an ultra-high pressure and a temperature at which the super hard material is thermodynamically stable to sinter the super hard grains. The pressure to which the assembly was subjected was about 6.8 GPa and the temperature was at least about 1,200 degrees centigrade. The sintered PCD construction was then removed from the canister.

[0085] In another example, the 5 g of diamond powder comprised of clusters of polycrystalline nanodiamond having an average cluster size of around 25 microns and the PCD sample was prepared in the same manner described above.

[0086] A conventional PCD cutter construction formed of the same mixture of diamond grain sizes (grades) as set out in the above example, but without adding nanodiamond grains, was prepared in a conventional manner for forming PCD by mixing the grains using conventional milling and mixing techniques and the mixture was then sintered under the same conditions as above for the example containing the nanodiamond additions, with a pre-formed cemented carbide substrate.

[0087] The prepared PCD constructions formed according to the above methods were compared in a vertical boring mill test. The results are shown in FIG. **5**.

[0088] The first PCD construction tested was that formed of the conventional diamond grain mixture (without any nanodiamond additions) and the results are shown in FIG. **5** by line **100**. The second PCD construction tested was a first example formed with the nanodiamond additions described above and the results are shown in FIG. **5** by line **200**.

[0089] In this test, the wear flat area was measured as a function of the number of passes of the construction boring into the workpiece and the results obtained are illustrated graphically in FIG. **5**.

[0090] The results provide an indication of the total wear scar area plotted against cutting length. It will be seen that the POD construction formed according to the example (line **200**) was able to achieve a significantly greater cutting length than that occurring in the conventional POD compact (shown by line **100** in FIG. **5**) which was subjected to the same test for comparison and the POD construction formed according to the example (line **200**) was able to achieve a significantly smaller wear scar area than that occurring in the conventional POD compact (shown by line **100** in FIG. **5**).

[0091] Thus it will be seen from FIG. **5** that the POD construction formed with the inclusion of nanodiamond in the admix prior to sintering in the manner described above from a homogeneously distributed solution to enable the nanodiamonds to coat the larger diamond grains as shown in FIG. **4**, showed a significant improvement in both cutting distance and abrasion resistance over the conventional POD construction (line **100**).

[0092] Thus, examples of a POD material may be formed having a combination of high abrasion and fracture performance which is surprising considering the reduction in diamond contiguity in those POD constructions which is shown schematically in FIG. **4**.

[0093] Diamond contiguity is an important performance indicator, as it indicates the degree of intergrowth or bonding between the diamond particles and, all else being equal, the higher the diamond contiguity the better the cutter performance. Higher diamond contiguity is normally associated with high diamond content which in turn results in lower binder content, as the high diamond content translates into low porosity and therefore low binder content, as the binder occupies the pores.

[0094] According to classic materials science of composite materials, low binder content results in low fracture toughness, as it is normally the hard grains (in this case diamond) that imparts hardness to the composite material, and the more ductile binder (in POD, normally Co-WC) that imparts toughness to the composite material.

[0095] Therefore, high diamond content and low binder content are expected to be associated with increased hardness and decreased toughness, so that failure due to fracture or spalling of the PCD is expected to increase.

[0096] It was therefore surprising to find that PCD with improved wear performance may be obtained, as is evidenced by the results of an analysis of the wear performance of the PCD material shown in FIG. **5**, by adding nanodiamond in the starting mixture in such a manner that enables it to substantially retain its size in the sintered product, which is believed to be due to one or more of the presintering steps described above, and bridges the surfaces of at least some of the adjacent larger diamond grains.

[0097] Using a nanodiamond additive in this way results in an unusual combination of diamond content, binder content and diamond contiguity, which, whilst resulting in a decrease in diamond contiguity combined with a decrease in the binder pool sizes, may result in improved wear performance without compromising toughness. It is further believed that these nanodiamond bridges between the larger diamond grains may assist in arresting cracks which may attempt to propagate through the material in use.

[0098] The microstructure of the PCD constructions formed according to one or more of the above described example methods may be determined using conventional image analysis techniques such as scanning electron micrographs (SEM) taken using a backscattered electron signal.

[0099] The homogeneity or uniformity of the PCD structure may be quantified by conducting a statistical evaluation using a large number of micrographs of polished sections.

[0100] The distribution of the filler phase, which is easily distinguishable from that of the diamond phase using electron microscopy, can then be measured in a method similar to that disclosed in EP 0 974 566 (see also WO2007/110770). This method allows a statistical evaluation of the average thicknesses of the binder phase along several arbitrarily drawn lines through the microstructure. This binder thickness measurement is also referred to as the “mean free path” by those skilled in the art.

[0101] While various versions have been described with reference to a number of examples, those skilled in the art will understand that various changes may be made and equivalents may be substituted for elements thereof and that these examples are not intended to limit the particular examples or versions disclosed.

[0102] For example, in some embodiments of the method, the POD material may be sintered for a period in the range from about 1 minute to about 30 minutes, in the range from about 2 minutes to about 15 minutes, or in the range from about 2 minutes to about 10 minutes.

[0103] In some examples of the method, the sintering temperature may be in the range from about 1,200 degrees centigrade to about 2,300 degrees centigrade, in the range from about 1,400 degrees centigrade to about 2,000 degrees centigrade, in the range from about 1,450 degrees centigrade to about 1,700 degrees centigrade, or in the range from about 1,450 degrees centigrade to about 1,650 degrees centigrade.

[0104] In one example, the method may include removing residual metallic catalyst/binder material for diamond from interstices between the diamond grains of the POD material. In some examples, the POD structure may have a region adjacent a surface comprising at most about 2 volume percent of catalyst material for diamond. In further examples, the POD structure may additionally have a region remote from the surface comprising greater than about 2 volume percent of catalyst material for diamond. In some such examples, the region adjacent the surface may extend to a depth of at least about 20 microns, at least about 80 microns, at least about 100 microns or even at least about 400 microns from the surface, or greater.

What is claimed is:

1. A method of forming a super hard polycrystalline construction, comprising:

forming a liquid suspension of a first mass comprising nano-sized super hard particles and a mass of particles or grains of super hard material having an average particle or grain size of 1 or more microns;

dispersing the first mass and mass of super hard particles or grains in the liquid suspension to form a substantially homogeneous suspension;

drying the suspension to form an admix of the first mass and the super hard grains or particles;

forming a pre-sinter assembly comprising the admix;

treating the pre-sinter assembly in the presence of a catalyst/solvent material for the super hard grains at an ultra-high pressure of around 5 GPa or greater and a temperature to sinter together the grains of super hard material to form a body of polycrystalline super hard material comprising a first fraction of super hard grains and a second fraction of super hard grains, the super hard grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, the nano-sized particles forming the second fraction of super hard grains; wherein

the super hard grains in the first fraction are bonded along at least a portion of the peripheral surface(s) thereof to at least a portion of a plurality of nano-sized grains in the second fraction;

the super hard grains in the first fraction having a greater average grain size than the average grain size of the grains in the second fraction, the average grain size of the grains in the second fraction being less than around 999 nm and the average grain size of the grains of superhard material in the first fraction being around 1 micron or more.

2. The method of claim **1**, wherein the step of providing a mass of super hard material comprises providing a mass of natural and/or synthetic diamond grains, the super hard polycrystalline construction forming a polycrystalline diamond (PCD) construction, the nano-sized particles or grains comprising nanodiamond.

3. (canceled)

4. The method of claim **1**, further comprising treating the super hard construction to remove at least a portion of residual binder/catalyst from at least a portion of interstitial spaces between interbonded super hard grains.

5. The method of claim **1**, wherein the step of forming the liquid suspension comprises dispersing the nano-sized particles or grains and the super hard particles or grains in deionized water.

6. The method of claim **1**, wherein the step of forming a liquid suspension of a first mass of nano-sized particles or grains and a mass of particles or grains of super hard material comprises dispersing the particles or grains in an organic solvent.

7. The method of claim **6**, wherein the organic solvent comprises ethanol.

8. The method of claim **1**, wherein the step of forming a liquid suspension further comprises adding a surfactant to the liquid suspension.

9. The method of claim **8**, wherein the surfactant comprises a non-ionic or cationic surfactant.

10. The method of claim **1**, wherein the step of dispersing the super hard particles or grains in the liquid suspension to form a substantially homogeneous suspension comprises applying to the liquid suspension one or more of:

a sonication process;

an ultrasonic dispersion process;

a homogenization process; and/or

a jet milling process.

11. The method of claim **1**, wherein the step of drying the suspension to form an admix of the grains or particles comprises one or more of drying the suspension using freeze drying spray freeze drying, spray drying, spray granulation, and/or spray freeze granulation.

12. The method of claim **1**, wherein the average grain size of the nano-sized grains or particles in the admix is around 999 nm or less, or around 500 nm or less, or around 250 nm or less, or around 100 nm or less.

13. The method of claim **1**, wherein the first mass comprises polycrystalline nano-diamond material.

14. A super hard polycrystalline construction comprising:

a body of polycrystalline super hard material comprising a first fraction of super hard grains and a second fraction of super hard grains, the first fraction having a greater average grain size than the super hard grains in the second fraction;

the super hard grains in the first and second fraction having a peripheral surface; wherein

the super hard grains in the first fraction are bonded along at least a portion of the peripheral surface to at least a portion of a plurality of super hard grains in the second fraction;

the super hard grains in the second fraction being arranged to space one or more adjacent grains in the first fraction by a distance of less than around 999 nm; and

wherein the average grain size of the super hard grains in the first fraction is around 1 micron or more.

15. (canceled)

16. The super hard polycrystalline construction of claim **1**, wherein the grains in the first and second fraction comprise natural and/or synthetic diamond grains, the super hard polycrystalline construction forming a polycrystalline diamond (PCD) construction.

17. The super hard polycrystalline construction of claim **16**, wherein the PCD construction further comprises a non-super hard phase comprising a binder phase located in interstitial spaces between the inter-bonded diamond grains.

18. The super hard polycrystalline construction according to claim **17**, wherein the binder phase comprises cobalt, and/or one or more other iron group elements, such as iron or nickel, or an alloy thereof, and/or one or more carbides, nitrides, borides, and oxides of the metals of Groups IV-VI in the periodic table.

19-21. (canceled)

22. The super hard polycrystalline construction according to claim **14**, wherein at least a portion of the body of super hard material is substantially free of a catalyst material for diamond, said portion forming a thermally stable region.

23. The super hard polycrystalline construction as claimed in claim **22**, wherein the thermally stable region comprises at most 2 weight percent of catalyst material for diamond.

24. The super hard polycrystalline construction of claim **14**, wherein the first fraction comprises a mass of super hard abrasive grains having two or more different average grain sizes.

25. The super hard polycrystalline construction of claim **14**, wherein the super hard grains in the second fraction are arranged to space one or more adjacent grains in the first fraction by a distance of less than around 500 nm, or less than around 250 nm, or less than around 100 nm.

26-32. (canceled)

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