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(54) **SUPERHARD CONSTRUCTIONS & METHODS OF MAKING**

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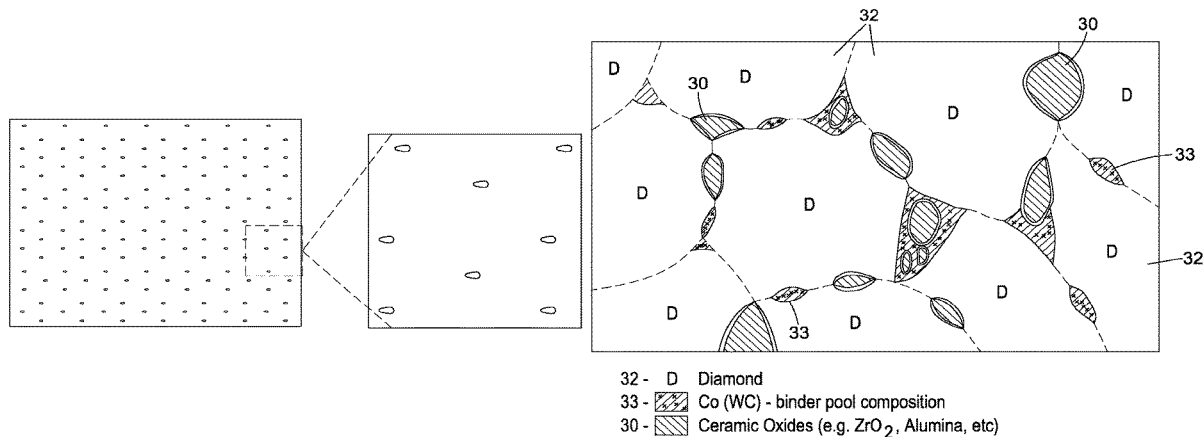
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**ABSTRACT**

A superhard polycrystalline construction comprises a body of polycrystalline superhard material comprising a superhard phase, and a non-superhard phase dispersed in the superhard phase, the superhard phase comprising a plurality of inter-bonded superhard grains. The non-superhard phase comprises particles or grains that do not chemically react with the superhard grains and form less than around 10 volume % of the body of polycrystalline superhard material. There is also disclosed a method of forming such a superhard polycrystalline construction.



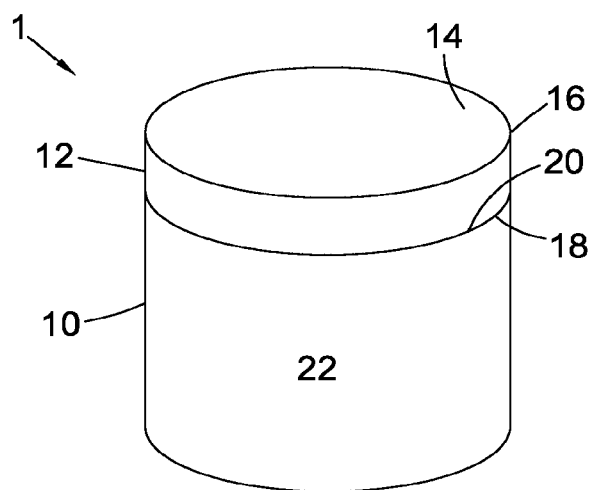


Fig. 1

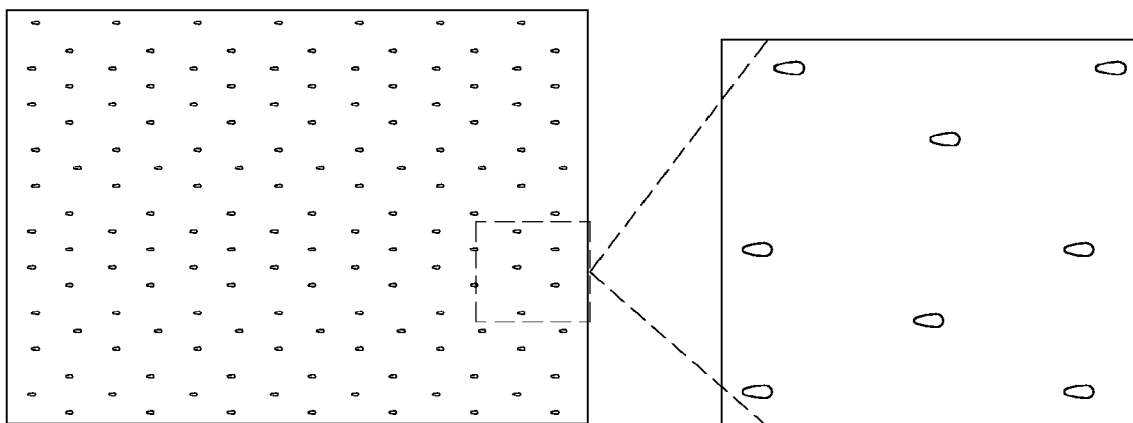


Fig. 2a

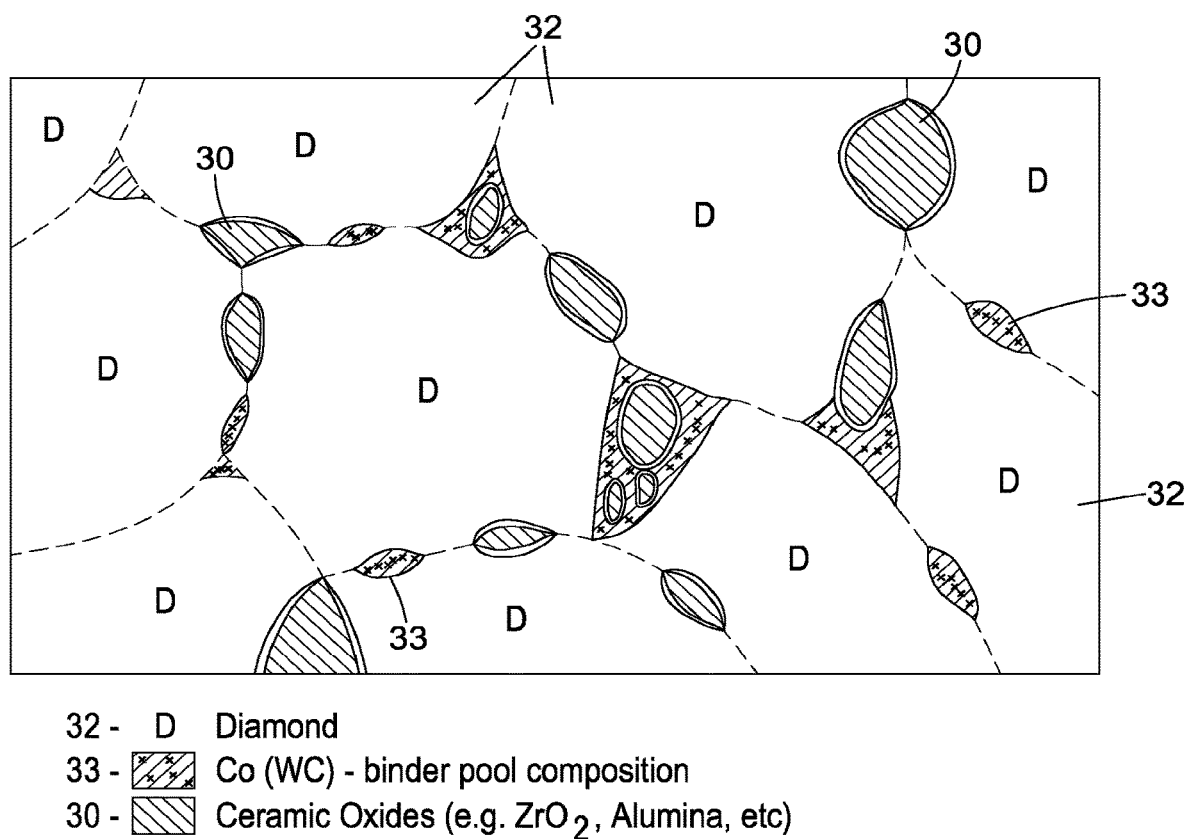


Fig. 2b

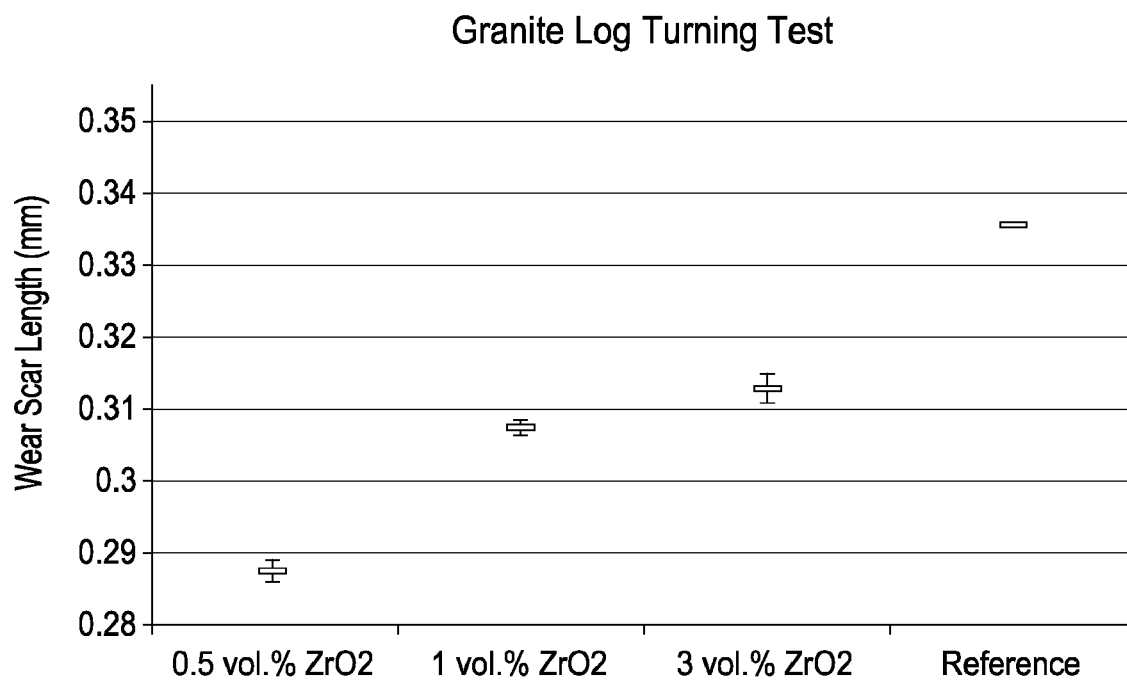


Fig. 3

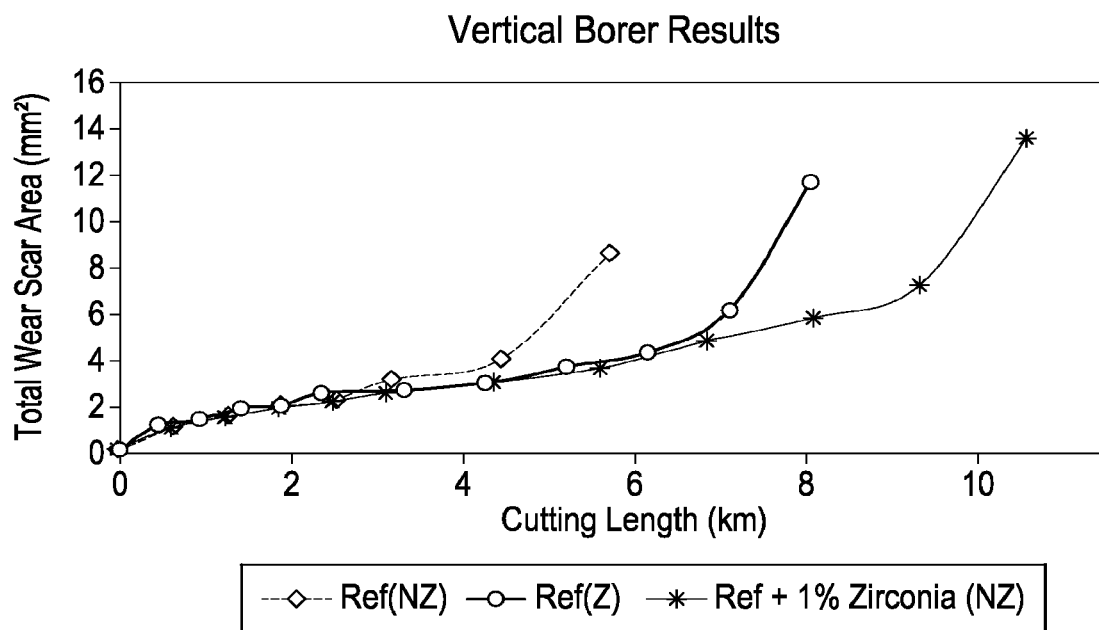
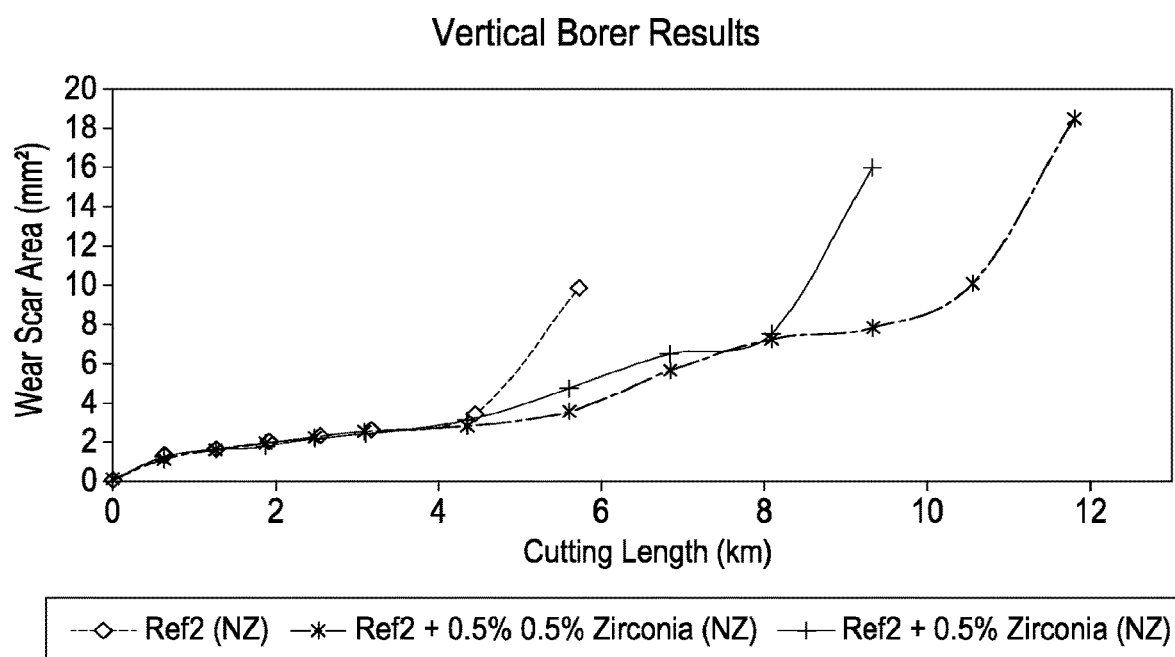


Fig. 4



**Fig. 5**

## SUPERHARD CONSTRUCTIONS & METHODS OF MAKING

### FIELD

**[0001]** This disclosure relates to superhard constructions and methods of making such constructions, particularly but not exclusively to constructions comprising polycrystalline diamond (PCD) structures 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 superhard materials, such as polycrystalline diamond (PCD) and polycrystalline cubic boron nitride (PCBN) 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), polycrystalline cubic boron nitride (PCBN) or a thermally stable product TSP material such as thermally stable polycrystalline diamond.

**[0004]** Polycrystalline diamond (PCD) is an example of a superhard material (also called a superabrasive 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 inter-growth 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 to 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 often 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 superhard material layer such as PCD or PCBN, diamond particles or grains or CBN 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 or CBN grains occurs, forming a polycrystalline superhard diamond or polycrystalline CBN layer.

**[0007]** In some instances, the substrate may be fully cured prior to attachment to the superhard 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 superhard 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 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 superhard polycrystalline construction comprising:

[0015] a body of polycrystalline superhard material, the body of polycrystalline superhard material comprising:

[0016] a superhard phase, and a non-superhard phase dispersed in the superhard phase, the superhard phase comprising a plurality of inter-bonded superhard grains;

[0017] wherein the non-superhard phase comprises particles or grains that do not chemically react with the superhard grains and form less than around 10 volume % of the body of polycrystalline superhard material.

[0018] Viewed from a second aspect there is provided a method of forming a superhard polycrystalline construction, comprising:

[0019] providing a mass of particles or grains of superhard material;

[0020] providing a mass of non-superhard grains or particles comprising particles or grains of a material that does not chemically react with the superhard grains having a grain size of less than around 30% the grain size of the superhard material;

[0021] combining the mass of superhard material and the mass of non-superhard grains to form a pre-sinter assembly; and

[0022] treating the pre-sinter assembly in the presence of a catalyst/solvent material for the superhard grains at an ultra-high pressure of around 5.5 GPa or greater and a temperature at which the superhard material is more thermodynamically stable than graphite to sinter together the grains of superhard material to form a polycrystalline superhard construction, the superhard grains exhibiting intergranular bonding and defining a plurality of interstitial regions therebetween, the non-superhard phase being dispersed in the polycrystalline material and forming less than around 10 vol % of the body of polycrystalline superhard material, any residual catalyst/solvent at least partially filling a plurality of the interstitial regions.

[0023] Viewed from a further aspect there is provided a tool comprising the superhard polycrystalline construction defined above, the tool being for cutting, milling, grinding, drilling, earth boring, rock drilling or other abrasive applications.

[0024] The tool may comprise, for example, a drill bit for earth boring or rock drilling, a rotary fixed-cutter bit for use in the oil and gas drilling industry, or a rolling cone drill bit, a hole opening tool, an expandable tool, a reamer or other earth boring tools.

[0025] Viewed from another aspect there is provided a drill bit or a cutter or a component therefor comprising the superhard polycrystalline construction defined above.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0026] The present invention will now be described by way of example and with reference to the accompanying drawings in which:

[0027] FIG. 1 is a perspective view of an example PCD cutter element for a drill bit for boring into the earth;

[0028] FIG. 2a is a schematic cross-section of an example portion of a PCD micro-structure with a second dispersed non-reactive phase in the material;

[0029] FIG. 2b is an expanded view of a section of the schematic cross-section of the example PCD micro-structure of FIG. 2a;

[0030] FIG. 3 is a plot showing the results of a wear resistance test comparing the wear resistance of an embodiment with that of a conventional PCD material;

[0031] FIG. 4 is a plot showing the results of a vertical borer test comparing a conventional unleached PCD material, a conventional PCD material leached using an acid treatment, and an embodiment of PCD material prepared according to the described method; and

[0032] FIG. 5 is a plot showing the results of a vertical borer test comparing a conventional unleached PCD material, and a further embodiment of PCD material.

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

## DESCRIPTION

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

[0035] As used herein, a “superhard construction” means a construction comprising a body of polycrystalline superhard 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 superhard (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. In one embodiment of PCD material, interstices between the diamond grains may be at least partly filled with a binder material comprising a catalyst for diamond. As used herein, “interstices” or “interstitial regions” are regions between the diamond grains of PCD material. In embodiments 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 superhard material is capable of promoting the growth or sintering of the superhard material.

[0038] The term “substrate” as used herein means any substrate over which the superhard 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] In an embodiment as shown in FIG. 1, a cutting element 1 includes a substrate 10 with a layer of superhard material 12 formed on the substrate 10. The substrate 10 may be formed of a hard material such as cemented tungsten carbide. The superhard material 12 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 superhard material opposite the substrate forms the cutting face **14**, which is the surface which, along with its edge **16**, performs the cutting in use.

[0042] At one end of the substrate **10** is an interface surface **18** that forms an interface with the superhard material layer **12** which is attached thereto at this interface surface. As shown in the embodiment of FIG. 1, the substrate **10** is generally cylindrical and has a peripheral surface **20** and a peripheral top edge **22**.

[0043] 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.

[0044] 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  $K_{IC}$  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.

[0045] All of the PCD grades may comprise interstitial regions filled with material comprising cobalt metal, which is an example of catalyst material for diamond.

[0046] The PCD structure **12** may comprise one or more PCD grades.

[0047] FIGS. 2a and 2b are cross-sections through an embodiment of PCD material forming the superhard layer **12** of FIG. 1 showing, schematically, the PCD microstructure. A non-reactive phase comprising particles **30** formed of, for example, ceramic oxides is dispersed in the diamond phase matrix **32** to act as localised stress raisers and/or micro-defects. The diamond phase matrix **32** here refers to conventional PCD formed of diamond grains and a catalyst binder phase **33** dispersed therein. The non-reactive phase **30** may comprise an oxide, formed for example, of one or more oxides of alumina, zirconia, tantalum oxide and yttria. The grain size of the dispersed non-reactive phase particles **30** may, in some embodiments, not be greater than 30% of the size of diamond grains. The non-reactive phase particles **30** may be admixed with diamond powder and then the composite is sintered in the traditional way with, for example, cobalt infiltration at HPHT to provide the catalyst binder to form the intergranular bonds between the diamond grains. The non-reactive particles are non-reactive with respect to the superhard phase, for example, diamond, and may also be non-reactive with the binder phase such that

they are not soluble in the binder phase and do not adhere to the superhard (eg diamond) particles, that is, there is substantially no interfacial bonding between the superhard particles and the non-reactive particles which may be located, as shown in FIG. 2b between interbonded diamond grains and in a number of interstitial spaces between interbonded diamond grains, some of which spaces may be at least partially filled with residual binder phase.

[0048] In some embodiments, the non-reactive phase particles **30** comprise less than 5 volume % of the sintered PCD material. In other embodiments, the non-reactive phase particles **30** comprise less than 3 volume % of the sintered PCD material, or even, in some cases, less than 1 volume % of the sintered PCD material.

[0049] These disperse non-reactive phase particles **30** may be localized inside the binder pools or in between diamond grains, depending on the sizes.

[0050] The grains of superhard 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. In some embodiments, the coarse fraction may have, for example, an average particle/grain size ranging from about 10 to 60 microns. 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, for example between around 1/10 to 1/10 of the size of the coarse fraction, and may, in some embodiments, range for example between about 0.1 to 20 microns.

[0051] In some embodiments, the weight ratio of the coarse diamond fraction to the fine diamond fraction ranges from about 50% to about 97% coarse diamond and the weight ratio of the fine diamond fraction may be from about 3% to about 50%. In other embodiments, the weight ratio of the coarse fraction to the fine fraction will range from about 70:30 to about 90:10.

[0052] In further embodiments, the weight ratio of the coarse fraction to the fine fraction may range for example from about 60:40 to about 80:20.

[0053] In some embodiments, the particle size distributions of the coarse and fine fractions do not overlap and in some embodiments the different size components of the compact are separated by an order of magnitude between the separate size fractions making up the multimodal distribution.

[0054] Some embodiments consist of a wide bi-modal size distribution between the coarse and fine fractions of superhard material, but some embodiments may include three or even four or more size modes which may, for example, be separated in size by an order of magnitude, for example, a blend of particle sizes whose average particle size is 20 microns, 2 microns, 200 nm and 20 nm.

[0055] 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.

[0056] In embodiments where the superhard material is polycrystalline diamond material, the diamond grains used to form the polycrystalline diamond material may be natural or synthetic.



**[0057]** In some embodiments, 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 embodiments, the binder/catalyst/sintering aid may be Co.

**[0058]** The cemented metal carbide substrate may be conventional in composition and, thus, may 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 embodiments, the metal carbide is tungsten carbide.

**[0059]** The cutter of FIG. 1 having the microstructure of FIGS. 2a and 2b may be fabricated, for example, as follows.

**[0060]** As used herein, a “green body” is a body comprising grains to be sintered and a means of holding the grains together, such as a binder, for example an organic binder, together with the additional non-reactive phase 30.

**[0061]** Embodiments of superhard constructions may be made by a method of preparing a green body comprising grains or particles of superhard material, non-reactive phase and a binder, such as an organic binder. The green body may also comprise catalyst material for promoting the sintering of the superhard grains. The green body may be made by combining the grains or particles with the binder/catalyst and forming them into a body having substantially the same general shape as that of the intended sintered body, and drying the binder. At least some of the binder material may be removed by, for example, burning it off. The green body may be formed by a method including a compaction process, an injection process or other methods such as molding, extrusion, deposition modelling methods.

**[0062]** A green body for the superhard construction may be placed onto a substrate, such as a pre-formed cemented carbide substrate to form a pre-sinter assembly, which may be encapsulated in a capsule for an ultra-high pressure furnace, as is known in the art. The substrate may provide a source of catalyst material for promoting the sintering of the superhard grains. In some embodiments, the superhard grains may be diamond grains and the substrate may be cobalt-cemented tungsten carbide, the cobalt in the substrate being a source of catalyst for sintering the diamond grains. The pre-sinter assembly may comprise an additional source of catalyst material.

**[0063]** In one version, the method may include loading the capsule comprising a pre-sinter assembly into a press and subjecting the green body to an ultra-high pressure and a temperature at which the superhard material is thermodynamically stable to sinter the superhard grains. In some embodiments, the green body may comprise diamond grains and the pressure to which the assembly is subjected is at least about 5 GPa and the temperature is at least about 1,300 degrees centigrade.

**[0064]** A version of the method may include making a diamond composite structure by means of a method disclosed, for example, in PCT application publication number WO2009/128034 with the additional step of admixing with the diamond grains, prior to sintering, the grains/particles of non-reactive phase. A powder blend comprising diamond particles, non-reactive phase particles and a metal binder material, such as cobalt may be prepared by combining these particles and blending them together. An effective powder preparation technology may be used to blend the powders,

such as wet or dry multi-directional mixing, planetary ball milling and high shear mixing with a homogenizer. In one embodiment, the mean size of the diamond particles may be at least about 50 microns and they may be combined with other particles by mixing the powders or, in some cases, stirring the powders together by hand. In one version of the method, precursor materials suitable for subsequent conversion into binder material may be included in the powder blend, and in one version of the method, metal binder material may be introduced in a form suitable for infiltration into a green body. The powder blend may be deposited in a die or mold and compacted to form a green body, for example by uni-axial compaction or other compaction method, such as cold isostatic pressing (CIP). The green body may be subjected to a sintering process known in the art to form a sintered article. In one version, the method may include loading the capsule comprising a pre-sinter assembly into a press and subjecting the green body to an ultra-high pressure and a temperature at which the superhard material is thermodynamically stable to sinter the superhard grains.

**[0065]** After sintering, the polycrystalline super hard constructions may be ground to size and may include, if desired, a 45° chamfer of approximately 0.4 mm height on the body of polycrystalline super hard material so produced.

**[0066]** The sintered article may be subjected to a subsequent treatment at a pressure and temperature at which diamond is thermally stable to convert some or all of the non-diamond carbon back into diamond and produce a diamond composite structure. An ultra-high pressure furnace well known in the art of diamond synthesis may be used and the pressure may be at least about 5.5 GPa and the temperature may be at least about 1,250 degrees centigrade for the second sintering process.

**[0067]** A further embodiment of a superhard construction may be made by a method including providing a PCD structure and a precursor structure for a diamond composite structure, forming each structure into the respective complementary shapes, assembling the PCD structure and the diamond composite structure onto a cemented carbide substrate to form an unjoined assembly, and subjecting the unjoined assembly to a pressure of at least about 5.5 GPa and a temperature of at least about 1,250 degrees centigrade to form a PCD construction. The precursor structure may comprise carbide particles and diamond or non-diamond carbon material, such as graphite, non-reactive phase particles, and a binder material comprising a metal, such as cobalt. The precursor structure may be a green body formed by compacting a powder blend comprising particles of diamond or non-diamond carbon and particles of carbide material and compacting the powder blend.

**[0068]** In some embodiments, both the bodies of, for example, diamond and carbide material plus the non-reactive phase and sintering aid/binder/catalyst are applied as powders and sintered simultaneously in a single UHP/HT process. The mixture of diamond grains, non-reactive phase particles and mass of carbide 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 adjacent grains of abrasive particles and, optionally, the joining of sintered particles to the cemented metal carbide support. In one embodiment, 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.

**[0069]** In another embodiment, 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.

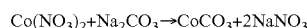
**[0070]** In a further embodiment, both the substrate and a body of polycrystalline superhard material are pre-formed. For example, the bimodal feed of ultrahard grains/particles with non-reactive phase particles and optional carbonate binder-catalyst also in powdered form are mixed together, and the mixture is packed into an appropriately shaped canister and is then subjected to extremely high pressure and temperature in a press. Typically, the pressure is at least 5 GPa and the temperature is at least around 1200 degrees C. The preformed body of polycrystalline superhard material is then placed in the appropriate position on the upper surface of the preform 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 superhard material and acts as a binder-catalyst to effect intergrowth in the layer and also serves to bond the layer of polycrystalline superhard material to the substrate. The sintering process also serves to bond the body of superhard polycrystalline material to the substrate.

**[0071]** In embodiments where the cemented carbide substrate does not contain sufficient solvent/catalyst for diamond, and where the PCD structure is integrally formed onto the substrate during sintering at an ultra-high pressure, solvent/catalyst material may be included or introduced into the aggregated mass of diamond grains from a source of the material other than the cemented carbide substrate. The solvent/catalyst material may comprise cobalt that infiltrates from the substrate in to the aggregated mass of diamond grains just prior to and during the sintering step at an ultra-high pressure. However, in embodiments where the content of cobalt or other solvent/catalyst material in the substrate is low, particularly when it is less than about 11 weight percent of the cemented carbide material, then an alternative source may need to be provided in order to ensure good sintering of the aggregated mass to form PCD.

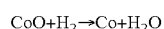
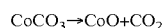
**[0072]** Solvent/catalyst for diamond may be introduced into the aggregated mass of diamond grains by various methods, including blending solvent/catalyst material in powder form with the diamond grains, depositing solvent/catalyst material onto surfaces of the diamond grains, or infiltrating solvent/catalyst material into the aggregated mass from a source of the material other than the substrate, either prior to the sintering step or as part of the sintering step. Methods of depositing solvent/catalyst for diamond, such as cobalt, onto surfaces of diamond grains are well known in the art, and include chemical vapour deposition (CVD), physical vapour deposition (PVD), sputter coating, electrochemical methods, electrodeless coating methods and atomic layer deposition (ALD). It will be appreciated that the advantages and disadvantages of each depend on the nature of the sintering aid material and coating structure to be deposited, and on characteristics of the grain.

**[0073]** Similarly, the non-reactive phase particles may be introduced by various means, for example, the diamond grains or particles could be coated with a non-reacting material prior to sintering.

**[0074]** In one embodiment, the binder/catalyst such as cobalt may be deposited onto surfaces of the diamond grains by first depositing a pre-cursor material and then converting the precursor material to a material that comprises elemental metallic cobalt. For example, in the first step cobalt carbonate may be deposited on the diamond grain surfaces using the following reaction:



**[0075]** The deposition of the carbonate or other precursor for cobalt or other solvent/catalyst for diamond may be achieved by means of a method described in PCT patent publication number WO/2006/032982. The cobalt carbonate may then be converted into cobalt and water, for example, by means of pyrolysis reactions such as the following:



**[0076]** In another embodiment, cobalt powder or precursor to cobalt, such as cobalt carbonate, may be blended with the diamond grains. Where a precursor to a solvent/catalyst such as cobalt is used, it may be necessary to heat treat the material in order to effect a reaction to produce the solvent/catalyst material in elemental form before sintering the aggregated mass.

**[0077]** In some embodiments, 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.

**[0078]** Embodiments are described in more detail below with reference to the following examples which are provided herein by way of illustration only and are not intended to be limiting.

#### Example 1

**[0079]** 0.5 g of Zirconia with an average grain size of 1 micron was added to 50 g of a bimodal diamond powder with an average grain size of 4 microns. The aggregated mass was ball milled in 60 ml of methanol with Co—WC milling balls. The ratio of milling balls:powder was 5:1 and milling was carried out for 1 hour at 90 rpm. 2.1 g of the mixture was placed on top of a pre-formed WC—Co substrate and sintered under high pressure high temperature HPHT conditions at 6.8 GPa and 1450° C. The PCD cutter was recovered, processed and analysed. The results are discussed below with reference to FIGS. 3 to 5.

#### Example 2

**[0080]** 1.5 g of Zirconia with an average grain size of 1 micron was added to 50 g of a bimodal diamond powder with an average grain size of 4 microns. The aggregated mass was ball milled in 60 ml of methanol with Co—WC milling balls. The ratio of milling balls:powder was 5:1 and milling was carried out for 1 hour at 90 rpm. 2.1 g of the

mixture was placed on top of a pre-formed WC—Co substrate and sintered under high pressure high temperature HPHT conditions at 6.8 GPa and 1450° C. The PCD cutter was recovered, processed and analysed.

[0081] The results are discussed below with reference to FIGS. 3 to 5.

#### Example 3

[0082] 0.25 g of Zirconia with an average grain size of 1 micron was added to 50 g of a unimodal diamond powder with an average grain size of 3 microns. The aggregated mass was ball milled in 60 ml of methanol with co-WC milling balls. The ratio of milling balls:powder was 5:1 and milling was carried out for 1 hour at 90 rpm. 2.1 g of the mixture was placed on top of a pre-formed WC—Co substrate and sintered under high pressure high temperature HPHT conditions at 6.8 GPa and 1450° C. The PCD cutter was recovered, processed and analysed.

[0083] The results are discussed below with reference to FIGS. 3 to 5.

#### Example 4

[0084] 0.5 g of Zirconia with an average grain size of 1 micron was added to 50 g of a unimodal diamond powder with an average grain size of 3 microns. The aggregated mass was ball milled in 60 ml of methanol with Co—WC milling balls. The ratio of milling balls:powder was 5:1 and milling was carried out for 1 hour at 90 rpm. 2.1 g of the mixture was placed on top of a pre-formed WC—Co substrate and sintered under high pressure high temperature HPHT conditions at 6.8 GPa and 1450° C. The PCD cutter was recovered, processed and analysed.

[0085] The results are discussed below with reference to FIGS. 3 to 5.

#### Example 5

[0086] 1.5 g of Zirconia with an average grain size of 1 micron was added to 50 g of a unimodal diamond powder with an average grain size of 3 microns. The aggregated mass was ball milled in 60 ml of methanol with Co—WC milling balls. The ratio of milling balls:powder was 5:1 and milling was carried out for 1 hour at 90 rpm. 2.1 g of the mixture was placed on top of a pre-formed WC—Co substrate and sintered under high pressure high temperature HPHT conditions at 6.8 GPa and 1450° C. The PCD cutter was recovered, processed and analysed.

[0087] The results are discussed below with reference to FIGS. 3 to 5.

[0088] Various sample of PCD material were prepared and analysed by subjecting the samples to a number of tests. The results of these tests are shown in FIGS. 3 to 5.

[0089] The abrasive wear resistance of various PCD samples was analysed by subjecting the finished PCD samples to a conventional granite turning test for 3 minutes. The wear scar progression during the machining process was monitored. The results are shown in FIG. 3. The wear scar of the PCD compact formed according to example 1 above with 0.5 vol % zirconia in the finished PCD was compared with a reference sample (Ref 1) of conventional PCD without any zirconia additions in the PCD matrix. In addition, samples were prepared according to embodiments comprising 1 vol % zirconia in the PCD and 3 vol % zirconia in the PCD.

[0090] It will be seen from the results shown in FIG. 3 that the addition of small amounts of zirconia improves the wear resistance of PCD as the wear scar length is less than conventional PCD.

[0091] The PCD compact formed according to Example 1 was compared in a vertical boring mill test with both leached (Ref Z) and unleached (Ref NZ) commercially available polycrystalline diamond cutter elements. In this test, the wear flat area was measured as a function of the number of passes of the cutter element boring into the workpiece. The results obtained are illustrated graphically in FIG. 4. The results provide an indication of the total wear scar area plotted against cutting length. It will be seen that the PCD compact formed according to example 1 was able to achieve a greater cutting length and smaller wear scar area than that occurring in both leached and unleached conventional PCD compacts which were subjected to the same test for comparison. The conventional PCD compacts in this test comprised Ref 2 which was a bimodal mixture having an average diamond grain size of around 4 microns. Indeed, FIG. 4 shows a 96% improvement in cutting length was achieved in the embodiment of PCD compared to a conventional PCD without zirconia addition.

[0092] Further unleached (NZ) samples of PCD embodiments of Example 3 comprising 0.5 vol % zirconia were compared with a conventional unleached PCD sample formed of a unimodal diamond feed having an average diamond grain size of around 3 microns. The results are shown in FIG. 5. The test showed a 104% improvement in the life of the cutter compared to a conventional PCD without zirconia addition.

[0093] Whilst not wishing to be bound by a particular theory, it is believed that the fracture performance of PCD may be improved through the introduction of the micro-defects and/or stress raisers in a PCD matrix according to some embodiments described herein. The micro-defects and/or stress raisers are believed to promote crack bifurcation or multiple crack fronts in the PCD material in use, resulting in a redistribution of available strain energy or energy release rate (G) amongst the various crack tips. A material that is able to generate multiple cracks under loading would behave tougher than a material with only one major crack since multiple crack fronts ensures that the net energy supplied to the material is divided between several cracks, resulting in a much slower rate of crack growth through the material. The end result in application of the PCD material including such micro-defects is that, in use, the number of cracks initiated on the wear scar may be increased as compared to conventional PCD, thus reducing the strain energy available for each individual crack, hence slowing the growth rate, and the generation of shorter cracks. The ideal case is where the wear rate is comparable to the crack growth rate, in which case no cracks will be visible behind the wear scar thereby forming a smooth wear scar appearance with no chips or grains pulled out of the sintered PCD.

[0094] The addition of a ceramic non-reactive phase may also have the effect of increasing the thermal stability of the PCD through the resultant lower cobalt content in the material of the invention compared to conventional PCD.

[0095] The size, shape and distribution of these micro-defects may be tailored to the final application of the PCD material. It is believed possible to improve fracture resis-

tance without significantly compromising the overall abrasion resistance of the material, which is desirable for PCD cutting tools.

**[0096]** Thus, it is believed that embodiments may provide a means of toughening PCD material without compromising its high abrasion resistance. This may be achieved by engineering micro-defects into the PCD matrix. The concept works by enabling the creation of multiple crack-fronts or defects which help to redistribute or dissipate the available fracture energy. These defects may also promote crack bifurcations, which is another energy dissipation mechanism. The end result is that there is insufficient energy available to each individual crack to enable it to propagate quickly and hence this may significantly slow down the rate of crack growth.

**[0097]** The vertical borer test results of these engineered structures show a considerable increase in PCD cutting tool life compared to conventional PCD, and with no degradation in abrasion resistance.

**[0098]** Observation of the wear scar development during testing showed the material's ability to generate large wear scars without exhibiting brittle-type micro-fractures (e.g. spelling or chipping), leading to a longer tool life. A 100% improvement in cutter tool life, i.e., double the life of conventional untreated PCD of same average diamond grain size, was noted during testing.

**[0099]** Thus, embodiments of a PCD material may be formed having that a combination of high abrasion and fracture performance.

**[0100]** The PCD element **10** described with reference to FIG. **1** 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 done 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 provided which may further enhance the thermal stability of the PCD element.

**[0101]** Furthermore, the PCD body in the structure of FIG. **1** comprising a PCD structure bonded to a cemented carbide support body may be created 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.

**[0102]** While various embodiments 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 embodiments disclosed. For example, the micro-defects in the form of the non-reactive phase particles may be introduced into the PCD in various ways and, in some embodiments, they may be introduced by modifying the HPHT sintering conditions such that micro-defects are introduced along diamond grain boundaries through partial sintering of the PCD. These dispersed non-reactive phase particles may

be localized inside the binder pools or in between diamond grains, depending on the sizes.

1. A superhard polycrystalline construction comprising:
  - a body of polycrystalline superhard material, the body of polycrystalline superhard material comprising:
    - a superhard phase, and a non-superhard phase dispersed in the superhard phase, the superhard phase comprising a plurality of inter-bonded superhard grains;
  - wherein the non-superhard phase comprises particles or grains that do not chemically react with the superhard grains and form less than around 10 volume % of the body of polycrystalline superhard material.
2. A superhard polycrystalline construction according to claim **1**, wherein the superhard grains comprise natural and/or synthetic diamond grains, the superhard polycrystalline construction forming a polycrystalline diamond construction.
3. A superhard polycrystalline construction according to claim **1**, wherein the non-superhard phase further comprises a binder phase.
4. A superhard polycrystalline construction according to claim **3**, 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.
5. A superhard polycrystalline construction according to claim **3**, wherein the particles or grains that do not chemically react with the superhard grains are such that they do not dissolve in the binder phase material and thereby remain unsintered in the body of polycrystalline material and form defects in the polycrystalline material.
6. A superhard polycrystalline construction according to claim **1**, wherein the particles or grains that do not chemically react with the superhard grains comprise any one or more of an oxide material, such as an oxide of alumina, zirconia, yttria, silica, or tantalum oxide, or any combination thereof.
7. A superhard polycrystalline construction according to claim **1**, wherein the particles or grains that do not chemically react with the superhard grains have a grain size of around 30% or less of the grain size of the superhard grains.
8. A superhard polycrystalline construction according to claim **1**, wherein the particles or grains that do not chemically react with the superhard grains form between around 0.5 to around 5 volume % of the body of polycrystalline superhard material.
9. A superhard polycrystalline construction according to claim **1**, wherein the particles or grains that do not chemically react with the superhard grains form between around 0.5 to around 2 volume % of the body of polycrystalline superhard material.
10. A superhard polycrystalline construction according to claim **1**, wherein at least a portion of the body of superhard material is substantially free of a catalyst material for diamond, said portion forming a thermally stable region.
11. A superhard polycrystalline construction as claimed in claim **10**, wherein the thermally stable region comprises at most 2 weight percent of catalyst material for diamond.
12. A method of forming a superhard polycrystalline construction, comprising:
  - providing a mass of particles or grains of superhard material;

providing a mass of non-superhard grains or particles comprising particles or grains of a material that does not chemically react with the superhard grains having a grain size of less than around 30% the grain size of the superhard material;

combining the mass of superhard material and the mass of non-superhard grains to form a pre-sinter assembly; and

treating the pre-sinter assembly in the presence of a catalyst/solvent material for the superhard grains at an ultra-high pressure of around 5.5 GPa or greater and a temperature at which the superhard material is more thermodynamically stable than graphite to sinter together the grains of superhard material to form a polycrystalline superhard construction, the superhard grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, the non-superhard phase being dispersed in the polycrystalline material and forming less than around 10 vol % of the body of polycrystalline superhard material, any residual catalyst/solvent at least partially filling a plurality of the interstitial regions.

**13.** A method according to claim **12**, wherein the step of providing a mass of grains of superhard material comprises providing a mass of diamond grains.

**14.** A method according to claim **13**, wherein the step of providing a mass of diamond grains comprises providing a mass of grains having a first fraction having a first average size and a second fraction having a second average size, the first fraction having an average grain size ranging from

about 10 to 60 microns, and the second fraction having an average grain size less than the size of the coarse fraction.

**15.** The method of claim **12**, wherein the average grain size of the first fraction is between around 10 to 60 microns, and the average grain size of the second fraction is between about 0.1 to 20 microns.

**16.** The method of claim **14**, wherein the weight ratio of the first fraction to the second fraction ranges from about 50% to about 97%, the weight ratio of the second fraction ranging from about 3% to about 50 weight %.

**17.** The method of claim **12**, wherein the step of providing a mass of non-superhard grains or particles comprising particles or grains of a material that does not chemically react with the superhard grains comprises providing a mass of material comprising any one or more of an oxide, a carbide, zirconia, alumina, yttria, and tantalum oxide.

**18.** The method of claim **12**, wherein the step of combining the masses of particles or grains comprises admixing the particles or grains.

**19.** The method of claim **12**, wherein the step of combining the masses of particles or grains comprises coating the superhard grains or particles with the particles or grains of non-superhard material which does not chemically react with the particles or grains of superhard material.

**20.** The method of claim **12**, wherein the step of providing the mass of material that does not chemically react with the superhard grains comprises providing grains or particles to form between around 0.5 to 5 vol % of the body of polycrystalline superhard material.

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