ABSTRACT

The invention relates to a PCD composite compact element comprising a PCD structure integrally bonded at an interface to a cemented carbide substrate; the PCD structure comprising coherently bonded diamond grains having a mean size no greater than 15 microns; the cemented carbide substrate comprising carbide particles dispersed in a metallic binder, the carbide particles comprising a carbide compound of a metal; wherein the ratio of the amount of metallic binder to the amount of the metal at points in the substrate deviates from a mean value by at most 20 percent of the mean value. The invention further relates to a method for making a PDC compact element comprising a PCD structure integrally bonded to a substrate formed of cemented carbide; the method including introducing a source of excess carbon to the substrate at a bonding surface of the substrate to form a carburised substrate; contacting an aggregated mass of diamond grains with the carburised substrate; and sintering the diamond grains in the presence of a solvent/catalyst material for diamond; wherein the mean size of the diamond grains in the aggregated mass is no greater than 30 microns.
Figure 1
Figure 8

Figure 9
Figure 10
POLYCRYSTALLINE DIAMOND COMPOSITE COMPACT ELEMENT, TOOLS INCORPORATING SAME AND METHOD FOR MAKING SAME

FIELD

[0001] The invention relates to polycrystalline diamond (PCD) composite compacts comprising a PCD structure bonded to a cemented carbide substrate, tools incorporating same and methods for making same.

BACKGROUND

[0002] Polycrystalline diamond (PCD) is a super-hard material comprising a mass of inter-grown diamond grains and interstices between the diamond grains. PCD is typically made by subjecting an aggregated mass of diamond grains to an ultra-high pressure of at least about 5.5 GPa and temperature of at least about 1,400 degrees centigrade. As used herein, the term polycrystalline diamond, or PCD, is understood to mean a material that comprises at least 80 volume percent of diamond grains, a substantial portion of which are directly inter-bonded, alternatively referred to as coherently bonded. Material wholly or partly filling the interstices is referred to as filler material. PCD is typically formed in the presence of a sintering aid such as cobalt, which promotes the inter-growth of diamond grains. The sintering aid is commonly referred to as a solvent/catalyst material for diamond, owing to its function of dissolving diamond to some extent and catalysing its re-precipitation. A solvent/catalyst material for diamond is understood to be a material capable of promoting the growth of diamond and the formation of direct diamond-to-diamond bonds at a temperature and pressure at which diamond is thermodynamically stable. Generally preferred solvent/catalyst materials are Fe, Ni, Co and Mn, and alloys including any of these. Consequently the interstices within the sintered PCD product are wholly or partially filled with residual solvent/catalyst material. Typically, PCD is often formed on a cobalt-cemented tungsten carbide substrate, which provides a source of cobalt solvent/catalyst for the PCD.

[0003] PCD is 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. For example, PCD inserts are widely used within drill bits used for boring into the earth in the oil and gas drilling industry. In many of these applications the temperature of the PCD material becomes elevated as it engages a rock formation, workpiece or body with high energy. Unfortunately, mechanical properties of PCD such as hardness and strength tend to deteriorate at high temperatures, largely as a result of residual solvent/catalyst material dispersed within it.

[0004] U.S. Pat. No. 4,694,914 discloses an insert including at least one layering polycrystalline diamond and at least one transition layer between the polycrystalline diamond layer and the cemented carbide body. The transition layer comprises a composite material containing diamond crystals, cobalt and pre-cemented tungsten carbide particles.

[0005] U.S. Pat. No. 4,694,918 discloses inserts including a cemented metal carbide insert body, an outer layer of polycrystalline diamond, and at least one transition layer of a composite material. The composite material includes polycrystalline diamond and particles of pre-cemented metal carbide.

[0006] Delwiche et al. (Petroleum Division, v 40, and Drilling Technology 1992, 1992, p 51-60, American Society of Mechanical Engineers) disclose PCD inserts for oil and gas drilling, wherein a PCD layer is secured to a substrate comprising a back-up component containing coarse diamond grains dispersed within a matrix of cemented carbide.

[0007] There is a need to provide composite PCD compacts comprising a PCD structure, and particularly a PCD structure formed from fine or ultra-fine grains of diamond, bonded to a cemented carbide substrate and having reduced defects proximate the interface between the PCD structure and the cemented carbide substrate.

SUMMARY

[0008] According to a first aspect of the invention there is provided a PCD composite compact element comprising a PCD structure integrally bonded at an interface to a cemented carbide substrate; the PCD structure comprising coherently bonded diamond grains having a mean size no greater than about 30 microns, preferably no greater than about 20 microns, more preferably no greater than about 15 microns, even more preferably no greater than about 10 microns, yet more preferably no greater than about 5 microns, still more preferably no greater than about 2 microns, and even more preferably no greater than about 1 micron; the cemented carbide substrate comprising carbide particles dispersed in a matrix containing a carbide compound of a metal; wherein the ratio of the amount of metallic binder to the amount of the metal at points in the substrate deviates from a mean value by at most about 20 percent of the mean value.

[0009] In one embodiment the ratio of the amount of metallic binder to the amount of the metal at points in the substrate deviates from a mean value by at most about 20 percent of the mean value from the interface to a depth of at least 2 mm into the substrate.

[0010] Embodiments of this aspect of the invention have been found to exhibit reduced exaggerated grain growth proximate the interface between the PCD structure and the substrate, and are believed to be even more advantageous the lower the mean diamond grain size within the PCD structure.

[0011] In one embodiment of this aspect to the invention, the ratio of the amount of metallic binder to the amount of the metal at points in the substrate deviates from the mean value by at most about 10 percent of the mean value.

[0012] In some embodiments, the mean size of the diamond grains may be at least about 0.05 microns or at least about 0.1 microns.

[0013] In some embodiments the metal of the carbide particles may be a refractory metal such as W, or even Ti, Ta, or Cr, and in some embodiments the metallic binder comprises a solvent/catalyst for diamond, such as Co.

[0014] In some embodiments the carbide particles are dispersed within a surface region of the substrate or substantially throughout the entire substrate. In some embodiments, the content of the diamond particles within the surface region or within the substrate may be no greater than about 6 weight percent or no greater than about 5.5 weight percent of the material in the surface region or in the substrate as the case may be. In some embodiments, the content of the
diamond particles within the surface region or within the substrate may be at least about 0.1 weight percent or at least about 0.3 weight percent. The surface region of the substrate may extend from the interface to a depth of at least about 1 mm, at least about 2 mm, or even at least 3 mm. In some embodiments, the surface region extends from the interface and has a volume of at least 2 times that of the PCD structure or at least 3 times that of the PCD structure. In some embodiments the volume of the surface region extending from the interface may be at least ten times greater than the volume of the PCD structure.

[0015] In some embodiments, the diamond particles dispersed in the substrate or in the surface region of the substrate have mean size in the range from 0.1 to 100 microns, 0.1 to 50 microns or even 0.1 to 20 microns. In some embodiments the diamond particles may be substantially uniformly dispersed throughout the substrate or the surface region of the substrate. This may help reduce the occurrence of grain growth-related defects more uniformly over the interfacial area.

[0016] In some embodiments, the diamond content within the substrate or within the surface region of the substrate may be at least 1 volume percent, at least 2 volume percent and less than 20 volume percent, in the range from 1 to 15 volume percent, or in the range from 1 to 10 volume percent. It has been found that diamond content within these ranges may be sufficient to substantially reduce certain defects proximate the interface.

[0017] In some embodiments the PCD structure comprises a first and a second region, the mean size of the diamond grains of the first region being greater than that of the diamond grains in the second region; the first region being proximate the substrate and the second region being remote from the substrate. In one embodiment the second region defines a working surface. In some embodiments, the mean size of the diamond grains in the first region of the PCD structure may be greater than 2 microns and the mean size of the diamond grains in the second region of the PCD structure may be in the range from 0.01 micron to 1.5 microns or in the range from 0.01 micron to 1 micron. These embodiments may have substantially reduced incidence of grain growth defects proximate the interface between the PCD structure and the substrate in the case of very fine-grained PCD structures. Very fine-grained (less than about 2 microns) PCD structures may be desirable because they have certain desirable mechanical properties, such as increased toughness.

[0018] The PCD structure may have an axial thickness of at least 1 mm from an interface with the substrate.

[0019] The ratio of the amount of metallic binder to the amount of carbon at points in the PCD structure may be substantially constant about a mean value, from the interface to a depth of at least 0.5 mm, more preferably at least 0.75 mm and yet more preferably at least 1 mm into the PCD structure. In one embodiment, the ratio of the amount of metallic binder to the amount of carbon at points in the PCD structure deviates from the mean value by at most 20 percent of the mean value, more preferably at most about 10 percent from the mean value.

[0020] The substrate may have a thickness of at least 1 mm, at least 1.5 mm or at least 5 mm.

[0021] The diamond grains in PCD structure may have a multi-modal size distribution. In some embodiments the bonded diamond grains of the PCD structure have the size distribution characteristic that at least 50 percent of the grains have mean size greater than 5 microns, and at least 20 percent of the grains have mean size in the range from 10 to 15 microns. Embodiments of PCD structures having a multi-modal diamond grain size distribution and mean grain size within these ranges have been found to have sufficient strength to retain better their mechanical integrity and key properties after bonding to the substrate, such as by brazing.

[0022] In one embodiment a plurality of PCD or diamond-rich fingers extend from the PCD structure into the substrate, more preferably a plurality of PCD fingers extend from the PCD structure into the substrate, a finger being a generally elongate structure. In some embodiments, at least one of the PCD fingers has length at least 20 microns, at least 30 microns, or at least 40 microns.

[0023] Embodiments of a PCD composite compact element according to the invention may be made using an embodiment of the method according to an aspect of the invention.

[0024] Excess carbon is understood to be carbon that is in excess of the diamond of the diamond grains provided in the aggregated mass for sintering PCD, and is also in excess of the carbon included as the carbide of the cemented carbide (stoichiometric excess). A carburised substrate or carburised substrate assembly is therefore a substrate or substrate assembly including excess carbon.

[0025] A green body is a term known in the art and refers to an article intended to be sintered, but which has not yet been sintered. It is generally self-supporting and has the general form of the intended finished article. A green body is typically formed by combining a plurality of particles in a vessel and then compacting them to form self-supporting article.

[0026] Carbon may be introduced into the substrate in any of a number of ways. In one embodiment a substrate pre-form is prepared by a method including introducing diamond particles into the starting powders for making a cemented carbide to form a starting powder blend; forming the starting powder blend by means of compaction in a mould to form a green body; and sintering the green body at a temperature of greater than about 1,400 degrees centigrade at an applied pressure of less than about 0.5 GPa to produce a sintered substrate. At least some of the diamond particles are converted wholly or partially into graphite during this carbide sintering step, because the pressure is below that for diamond to be thermodynamically stable.

[0027] The sintering pressure at which diamond is thermodynamically stable is preferably at least about 5.5 GPa and the temperature is preferably at least about 1,400 degrees centigrade.

[0028] In some embodiments, carbon is introduced into the substrate in the form of graphite powder.

[0029] In some embodiments, carbon is introduced into the substrate in the form of carbonaceous gas, which is caused to permeate or infiltrate the substrate.

[0030] In some embodiments, material comprising carbon is sprayed onto a surface of the substrate. In particular, powder containing cobalt, carbon and tungsten may be deposited onto the substrate surface by means of thermal spraying.

[0031] In some embodiments, the substrate is coated with a source of excess carbon, such as graphite.
In some embodiments, the substrate is prepared from starting carbide powder having a high content of carbon in the form of carbon black, for example.

In some embodiments, a substrate with high carbon content is prepared by avoiding the removal of some carbon during the preparation of the green body for readiness for sintering. Typically, a green body is heat treated to remove binder, and to prepare aid mixture for the sintering, and carbon is removed during this process. In one embodiment, this process is not thoroughly completed, leaving at least some carbon of binder origin within the green body.

The size distribution of unbounded or free-flowing diamond grains is measured by means of a laser diffraction method, wherein the grains are suspended in a fluid medium and an optical diffraction pattern is obtained by directing a laser beam at the suspension. The diffraction pattern is interpreted by computer software and the size distribution is expressed in terms of equivalent circle diameter. In effect, the grains are treated as being spherical and the size distribution is expressed in terms of a distribution of equivalent diameters of spheres. A Mastersizer™ apparatus from Malvern Instruments Ltd., United Kingdom, may be used for this purpose.

A multi-modal size distribution of a mass of grains is understood to mean that the grains have a size distribution that is formed of more than one peak, each peak corresponding to a respective “mode”. Multimodal polycrystalline bodies are typically made by providing more than one source of a plurality of grains, each source comprising grains having a substantially different mean size, and blending together the grains from the sources. Measurement of the size distribution of the blended grains typically reveals distinct peaks corresponding to distinct modes. When the grains are sintered together to form the polycrystalline body, their size distribution is further altered as the grains are compacted against one another and fractured, resulting in the overall decrease in the sizes of the grains. Nevertheless, the multimodality of the grains is usually still clearly evident from image analysis of the sintered article.

In order to obtain a measure of the sizes of diamond grains within PCD, a method known as “equivalent circle diameter” is used. In this method, a scanning electron micrograph (SEM) image of a polished surface of the PCD material is used. The magnification and contrast should be sufficient for at least several hundred diamond grains to be identified within the image. The diamond grains can be distinguished from metallic phases in the image a circle equivalent in size for each individual diamond grain can be determined by means of conventional image analysis software. The collected distribution of these circles is then evaluated statistically. Wherever diamond mean grain size within PCD material is referred to herein, it is understood that this refers to the mean equivalent circle diameter.

“Binder pooling” refers to the existence of a region within the PCD structure adjacent the interface, the region having a substantially higher content of binder material (typically cobalt) than the mean or desired content within the PCD structure. The diamond content within the pooling region may be less than 50% in known PCD compacts, particularly those having a cemented carbide substrate thicker than about 1 millimetre and a PCD structure having thickness greater than about 0.6 millimetres. Pooling is a problem particularly in PCD compacts having relatively thick substrate and PCD structure. A corresponding region occurs within the substrate adjacent the interface, wherein the content of binder material is lower than the mean for the substrate. This is sometimes called a “binder denuded zone”. Binder pooling and depletion may be undesirable because it is associated with several related defects, including so-called “plume” defects and exaggerated diamond grain growth, and because it reduces the abrasion resistance of the compact in a region adjacent the interface. Reduced abrasion resistance at the interface may result in under-cutting of the PCD structure, which may be accelerated by the presence of erosion-promoting material in the environment.

Plume defects are relatively large grains of metal carbide formed within the PCD structure proximate the interface. While wanting not to be bound by theory, it is believed that plumes may be reduced in embodiments of the invention because material infiltrating from the substrate into the PCD during the sintering step has reduced tungsten content or is substantially free of tungsten.

Embodiments of the method of the invention may also result in reduced exaggerated grain growth of diamond within the PCD, which is more a problem the finer the diamond grains starting aggregated mass. For this reason the method is particularly advantageous where the mean grain size within the PCD is low. While wanting not to be bound by theory, when plumes of molten binder material, e.g. cobalt, invade the diamond layer and the plumes have a relatively low content of carbon, fine diamond grains readily dissolve and re-precipitate onto the larger grains, resulting in exaggerated grain diamond grain growth proximate the interface between the PCD structure and the substrate. The resulting grains can be an order of magnitude greater than the starting grain size. However, when the binder material contains relatively more carbon, as is the case where the source of excess carbon has been introduced into the substrate prior to the sintering step, then dissolution of finer grains is suppressed or retarded and instead, the carbon precipitates evenly onto all grains. Since this precipitation is spread out over many grains, there is little or reduced exaggerated grain growth.

Substantially constant is understood to mean that the ratio is a constant value with a statistical confidence interval of at least 68 percent, or even 90 or 95 percent.

The ratio of the amount of binder material in the substrate to the amount of carbide material within the substrate, and the ratio of amount of binder material to the amount of diamond within the PCD structure may be expressed as a weight ratio, volume ratio or other ratio indicative of the relative amounts of binder material and carbide material, or of binder material and diamond, respectively. The ratio may be expressed as a percentage value.

Where the substrate contains diamond particles in a region adjacent the interface with the PCD structure, it has been found that a type of “reverse pluming” occurs, where PCD “fingers” extend from the PCD structure into the region. It is hypothesised that these fingers may result in reduced internal stress proximate the interface and reduced incidence of delamination of the structure. The size of the fingers may be controlled by selecting the size of the diamond particles introduced into the substrate green body; the longer the fingers desired, the larger should be the diamond particles, in general. The number of fingers and to some extent their size is controlled by the number of diamond particles introduced into the substrate.
According to a second aspect to the present invention there is provided a method for making a polycrystalline diamond composite (PDC) compact element comprising a polycrystalline diamond (PCD) structure integrally bonded to a substrate formed of cemented carbide; the method including introducing a source of excess carbon to the substrate at or proximate a bonding surface of the substrate to form a carburised substrate or carburised substrate assembly adjacent or proximate the bonding surface to form an unbound assembly; and sintering the diamond grains in the presence of a solvent/catalyst material for diamond at a temperature and pressure at which diamond is thermodynamically stable to form PCD; wherein the mean size of the diamond grains in the aggregated mass is no greater than about 30 microns.

The mean size of the diamond grains in the aggregated mass may be no greater than about 20 microns, preferably no greater than about 15 microns, even more preferably no greater than about 10 microns, yet more preferably no greater than about 5 microns, still more preferably no greater than about 2 microns and even more preferably no greater than about 1 micron. Preferably, the mean size of the diamond grains in the aggregated mass is at least about 0.05 microns, more preferably at least about 0.1 microns.

Embodiments of the invention have been found to reduce exaggerated grain growth proximate the bonding surface, and may be even more advantageous the lower the mean diamond grain size.

In one embodiment, the method includes forming a carburised substrate, wherein source of excess carbon is included in or introduced into the volume of the substrate. In some embodiments the source of excess carbon is dispersed substantially throughout the entire volume of the carburised substrate. In other embodiments the source of excess carbon is dispersed in a surface region proximate or adjacent the bonding surface.

Preferably, the mean content of the source of excess carbon within a surface region of the carburised substrate or throughout substantially the entire carburised substrate is no greater than about 10 weight percent, more preferably no greater than about 6 weight percent and yet more preferably no greater than about 5.5 weight percent of the material in the surface region or the substrate. Preferably, the content of the source of excess carbons within the surface region or throughout the entire carburised substrate is at least about 0.1 weight percent and more preferably at least about 0.3 weight percent of the carbon in the region. In some embodiments the surface region extends to a depth of at least about 1 mm, at least about 2 mm, or even at least 3 mm from the bonding surface. In some embodiments, the surface region has a volume of at least 2 times that of the PCD structure or at least 3 times that of the PCD structure. In some embodiments the volume of the surface region may be at least ten times greater than the volume of the PCD structure.

The weight percent is expressed of the total substrate material within the region in which the carbon is introduced.

In one embodiment the diamond grains in the aggregated mass have a multi-modal size distribution. Preferably, the source of excess carbon is a carbonaceous material other than metal carbide, such as carbon black powder or graphite. In one embodiment the source of excess carbon may be derived from diamond that has been converted into a non-diamond material. Such materials may consist essentially of carbon and may not substantially introduce unwanted material into the substrate or PCD. In some embodiments the source of excess carbon may be in the form of organic molecules. In some embodiments the source of excess carbon may be introduced in the form of a gas, such as a gas of organic molecules such as methane.

In one embodiment, the method includes combining source of excess carbon in particulate or granular form with raw materials for the cemented carbide, forming the combination into a substantially self-supporting green body, and sintering the green body at a pressure at which diamond is not thermodynamically stable to form the carburised substrate. In some embodiments the raw materials for cemented carbide comprise grains of tungsten carbide and grains comprising cobalt.

The method may include combining diamond granules with raw materials for cemented carbide, forming the combination into a substantially self-supporting green body; subjecting the green body to a temperature of at least 500 degrees centigrade and a pressure at which diamond is not thermodynamically stable to form the carburised substrate. The diamond particles may be wholly or partly converted into a non-diamond material, particularly graphite. In one embodiment, substantially all of the converted diamond re-converts to diamond during the step of sintering the PCD. This embodiment has been found to result in PCD fingers extending into the substrate, which may result in improved bonding of the PCD to the substrate and reduced incidence of delamination.

In one embodiment of this aspect to the invention, the substrate is substantially free of diamond.

In embodiments where the substrate includes diamond particles formed from converted graphite, for example where the source of excess carbon is graphite, the diamond particles may have little or substantially no plastic deformation within at least a peripheral volume of each diamond particle. In some embodiments the diamond particles have substantially no plastic deformation.

In some embodiments, the source of excess carbon may be deposited onto a bonding surface of the substrate to form a carburised substrate or carburised substrate assembly. In some embodiments the source of excess carbon may be deposited onto the substrate bonding surface by means of a thermal or other spraying method. In one embodiment a disc or film comprising a refractory metal, such as tungsten may be placed over the deposited source of excess carbon to form a carburised substrate assembly.

The method may include introducing metal carbide or a precursor or precursors for metal carbide into the aggregated mass of diamond grains. More preferably, the method includes introducing refractory metal carbide particles, for example tungsten carbide, tantalum carbide, niobium carbide or vanadium carbide, into the aggregated mass of diamond grains. In some embodiments the method includes introducing a refractory metal precursor for metal carbide, for example tungsten, tantalum, niobium or vanadium in non-carbide compound or in elemental form, into the aggregated mass of diamond grains. In embodiments of the method where a source of excess carbon may be intro-
duced to or into the substrate, the introduction of metal carbide into the aggregated mass of diamond grains, directly or via the introduction of precursor or precursors, may significantly enhance the abrasion or erosion resistance of the sintered PCD structure.

[0057] In some embodiments the metal carbide or a precursor or precursors for metal carbide may be introduced in particulate form into the aggregated mass of diamond grains by blending the particles with the diamond grains.

[0058] In some embodiments the cemented carbide comprises grains of metal carbide cemented together by a metal binder, the metal binder comprising a solvent/catalyst material for diamond, such as cobalt. Such metal binder may inhibit the aggregated mass of diamond particles during the sintering step and function as a sintering aid for diamond.

[0059] Embodiments of the invention have been found to reduce or eliminate pooling of the metal binder material within the PCD adjacent the interface with the substrate and the corresponding depletion of metal binder material within the substrate adjacent the bonding surface/interface, and may reduce or eliminate certain defects associated with carbide or diamond grain growth proximate the bonding surface.

[0060] According a third aspect of the invention there is provided a PCD cutter insert for a drill bit, such as a drill bit for boring into the earth, the PCD cutter insert comprising a PCD composite compact element according to the invention.

[0061] According to a fourth aspect of the invention there is provided a drill bit for boring into the earth, the drill bit comprising a PCD cutter insert according to the invention.

[0062] Boring into the earth as carried out in the oil and gas drilling industry exerts high forces on a cutter insert and PCD cutter inserts according to the invention may exhibit reduced failure rate in use.

DRAWING CAPTIONS

[0063] Non-limiting embodiments will now be described with reference to the accompanying drawings of which:

[0064] FIG. 1 shows (a) a schematic drawing of a perspective view of an embodiment of a PCD composite compact element, as well as longitudinal side cross-sectional views of two embodiments, (b) and (c).

[0065] FIGS. 2 to 7 are schematic drawings of perspective views of embodiments of PCD composite compact elements.

[0066] FIG. 8 shows a graph of number of grains versus equivalent circle diameter grain size for a fine-grained bi-modal size distribution of diamond grains within an embodiment of PCD material.

[0067] FIG. 9 shows a graph of number of grains versus equivalent circle diameter grain size for diamond grains within an embodiment of PCD material.

[0068] FIG. 10 shows a schematic graph of binder content as well as the carbon content in the PCD and the substrate as a function of depth from the PCD working surface in the case of a prior art PCD composite compact as well as in the case of an embodiment of the invention.

[0069] FIG. 11 is a graph showing the ratio of cobalt to tungsten content as a function of distance into the substrate from the interface with the PCD structure, in the case of an embodiment of the invention (data shown as filled squares) and a control according to the prior art (data shown as unfilled diamonds).

[0070] FIG. 12 is a graph showing the ratio of cobalt to carbon content as a function of distance into the PCD structure from the interface with the substrate, in the case of an embodiment of the invention (data shown as filled squares) and a control according to the prior art (data shown as unfilled diamonds).

[0071] FIG. 13 shows a scanning electron micrograph of a cross-section of a bonding interface between a PCD structure and a cobalt-cemented WC substrate enhanced with diamond.

DETAILED DESCRIPTION OF EMBODIMENTS

[0072] With reference to FIG. 1, an embodiment of a polycrystalline diamond composite compact (PCD) element, 100, comprises a PCD structure, 110, integrally bonded to a cemented carbide substrate, 120, at an interface, 125. In some embodiments the interface between the embodiment shown in (a) The PCD structure, 110, has an axial thickness \( t_{PCD} \) and the substrate, 120, has an axial thickness \( t_{w_c} \) the axial thickness being measured from an interface, 125, between the PCD structure, 110, in an axial direction indicated by the line marked “axial”. In an embodiment shown in (b), the interface, 125, is substantially planar, and in an embodiment shown in (c), the interface, 125, is non-planar and the PCD structure, 110, has at least two thicknesses, \( t_{PCD,1} \) and \( t_{PCD,2} \).

[0073] With reference to FIG. 2, an embodiment of a polycrystalline diamond composite compact (PCD) element, 100, comprises a PCD structure, 110, integrally bonded to a cemented carbide substrate, 120, at an interface, 125, and the PCD structure comprises a first region, 112, and a second region, 111, the mean size of the diamond grains of the first region, 112, being greater than that of the diamond grains in the second region, 111; the first region, 112, being proximate the substrate, 120, and the second region, 111, being remote from the substrate, 120.

[0074] With reference to FIG. 3, an embodiment of a polycrystalline diamond composite compact (PCD) element, 100, comprises a PCD structure, 110, integrally bonded to a cemented carbide substrate, 120, at an interface, 125, wherein the substrate, 120, includes diamond particles dispersed within a surface region, 221, extending from the interface to a depth. The remaining region, 122, of the substrate, 120, is substantially free of diamond. In some embodiments the depth is at least 1 millimetre, at least 2 millimetres or at least 3 millimetres. In some embodiments the surface region, 121, of the substrate has a volume of at least 2 times that of the PCD structure, 110, at least 3 times that of the PCD structure, 110, or even at least ten times greater than the volume of the PCD structure, 110.

[0075] With reference to FIG. 4, an embodiment of the method of the invention includes introducing a source of excess carbon to the substrate, 220, at or proximate a bonding surface, 225, to form a carburised substrate assembly, 250; contacting an aggregated mass, 210, of diamond grains with the carburised substrate assembly, 250, adjacent or proximate the bonding surface, 225, to form an unbonded assembly, 200, wherein the source of excess carbon is in the form of graphite dispersed in a surface region, 221, of the substrate, 220, the surface region extending from proximate the bonding surface, 225, to a depth. In some embodiments the depth is at least 1 millimetre, at least 2 millimetres or at least 3 millimetres. With reference to FIG. 5, the source of
excess carbon is in the form of graphite dispersed substantially throughout the entire volume of the substrate, 220.

[0076] With reference to FIG. 6, an embodiment of the method of the invention includes introducing a source of excess carbon to the substrate, 220, at or proximate a bonding surface, 225, to form a carburised substrate assembly, 250; contacting an aggregated mass, 210, of diamond grains with the carburised substrate assembly, 250, adjacent or proximate the bonding surface, 225, to form an unbonded assembly, 200; wherein the source of excess carbon, 230, is deposited onto a bonding surface, 125, of the substrate. With reference to FIG. 7, an embodiment of the method of the invention includes placing a disc or film, 240, comprising tungsten over the deposited source of excess carbon, 230.

[0077] For example, FIG. 8 shows a graph of number of grains versus equivalent circle diameter grain size for a fine-grained bi-modal size distribution of diamond grains within an embodiment of PCD material; and FIG. 9 shows a graph of number of grains versus equivalent circle diameter grain size for diamond grains within an embodiment of a multi-modal PCD material.

[0078] The PCD material having the diamond grain size distribution shown in FIG. 8 is an example of an embodiment of PCD material that may benefit particularly well from the invention, wherein the mean size of the diamond grains within the sintered PCD is in the range from about 1.5 to about 6 microns and the size distribution can be resolved into at least two distinct peaks. FIG. 8 shows the distribution of equivalent circle diameters, with no Saltykov correction having been applied to convert the size distribution obtained from the two-dimensional image data to a grain size distribution in three dimensions.

[0079] With reference to FIG. 9, the relative (e.g. weight percent) content of cobalt, 200, within a prior art PCD composite compact, 210, and a PCD composite compact according to an embodiment of the invention, 220, are compared in respect of qualitative features. In some embodiments of the invention binder pooling is substantially reduced. In some embodiments the incidence of plume defects is substantially reduced. Also shown in FIG. 9 are the corresponding relative content of carbon, 400, within a prior art PCD composite compact, 410, and a PCD composite compact according to an embodiment of the invention, 420, are compared in respect of qualitative features. The region of the graphs indicated by 110 corresponds to the PCD structure and the region indicated by 121 corresponds to the carbide substrate.

[0080] FIG. 10 is a graph showing the ratio of cobalt to tungsten as a function of axial distance into the substrate from the interface with the PCD structure, in the case of an embodiment of the invention (data shown as filled squares) and a control according to the prior art (data shown as unfilled diamonds). The interface corresponds to zero micrometres. In an embodiment of the invention, the ratio (shown as filled squares) remains substantially constant from the interface into the bulk of the substrate, the standard deviation of the data being less than about 5 percent of the mean value, M. The upper and lower standard deviations are indicated as SU and SL, respectively. The upper and lower percent limits or M(1+20%) and M(1−20%), are shown as LU and LL, respectively. In the case of a control material, made according to the prior art, the mean ratio of cobalt to tungsten is substantially lower within a depth of approximately 1.5 micrometres is substantially and systematically less than the mean value in the bulk of the substrate, and is less than the lower limit M(1−20%) within a depth of about 1 millimetre from the interface. This is called the "depleted zone".

[0081] FIG. 11 is a graph showing the ratio of cobalt to carbon as a function of axial distance into the PCD structure from the interface with the substrate, in the case of an embodiment of the invention (data shown as filled squares) and a control according to the prior art (data shown as unfilled diamonds). The interface corresponds to zero micrometres. In an embodiment of the invention, the ratio (shown as filled squares) remains substantially constant from the interface into the bulk of the PCD structure, even within the first 0.2 micrometres from the interface, where the ratio in the control material increases dramatically to greater than M(1+20%), corresponding to binder pooling within the PCD structure adjacent the interface.

[0082] With reference to FIG. 12, an SEM micrograph of the region straddling an interface between a PCD structure, 40, and a cemented carbide substrate, 50, of a PCD composite compact according to an embodiment of the invention is shown. The substrate, 50, contains particles of diamond, 46. A “finger”, 45, comprising contiguous polycrystalline diamond and having a length in the range of about 30 to 50 microns extends from the PCD structure, 40, into the substrate, 50.

[0083] As previously noted, embodiments of the invention may comprise relatively thick PCD caps and substrates without the need for using higher temperatures in the sintering step. In general, the thicker the PCD layer, the higher must be the sintering temperature in order to urge molten solvent/catalyst material from the substrate to infiltrate the entire PCD layer. A serious consequence of this not occurring is the presence of “soft spot” defects wherein the diamond grains remote from the interface have not adequately sintered. Unfortunately, higher sintering temperatures result in excessive dissolution of diamond proximate the interface and may result in plume defects in the form of exaggerated large acicular metal carbide grains. On the other hand, higher sintering temperatures tend to promote exaggerated diamond grain growth, which is also undesirable. This is less of a problem where the PCD structure is relatively thin, since the minimum sintering temperature for the avoidance of soft spots is lower the thinner the PCD structure. However, many applications require that the PCD structure is several millimetres thick and that the substrate is tens of millimetres thick. In particular, PCD compacts used for boring into earth and rock in the oil and gas industry comprise relatively thick PCD caps and substrates.

[0084] The invention will now be described with reference to the following non-limiting examples.

Example 1

[0085] A first substrate element for use as the surface region of a substrate for a PCD compact was manufactured by blending together diamond particles, tungsten carbide (WC) powder and cobalt powder, forming the blended mixture into a compacted green body, and subjecting the green body to a conventional carbide sintering process. The diamond particles had mean size in the range of 0.75 to 1.5 microns, and constituted 3 weight percent of the blended mixture. The WC powder and the cobalt powder had been pre-mixed, the cobalt constituting 13 weight percent of the
WC-Co pre-mix and the WC particles having a mean size in the range from about 1 to 4 microns. About 2 weight percent organic pressing aid was included in the WC-Co mix. The blended powder mix was uniaxially compacted at ambient temperature to form a substantially cylindrical green body, which was conventionally sintered at a temperature of 1,400 degrees centigrade for 2 hours to form a sintered article. By the end of the sintering process, the diamond particles had completely converted into graphite. The substrate had a diameter of about 17.4 millimetres and a height of about 6 millimetres after final machining.

[0086] A second substrate element for use as a region of a substrate substantially free of diamond was manufactured in the same way and using the same raw materials as the first substrate element, except that no diamond was introduced and the height of the second substrate element was about 7 millimetres.

[0087] The first substrate element was placed on top of the second substrate element, the first and second substrate elements being substantially in registration, to form a substrate assembly, having an upper surface being the exposed end surface of the first substrate element.

[0088] A layer comprising an unbounded aggregated mass of diamond grains was deposited onto the upper surface of the substrate assembly end surface of the sintered article to form an unbounded assembly. The diamond grains had mean size of about 0.5 microns and were coated with cobalt, which constituted 5 weight percent of the aggregated mass. The coated grains were then subjected to heat treatment in a hydrogen rich atmosphere at 850 degrees centigrade in order to terminate the surfaces with hydrogen.

[0089] The unbounded assembly was mounted within a capsule for an ultra-high pressure furnace, as is known in the art. The capsule was subjected to a pressure of about 5.5 GPa and a temperature of about 1,400 degrees centigrade for a period of about 5 minutes. After sintering, the first and second substrate elements had sintered together and the PCD composite compact element was processed in the usual way to form an insert having a diameter of about 1.7 to 2.1 millimetres.

[0090] The insert was analysed using scanning electron micrography (SEM). The Analysis of the material was carried out at several points on a polished cross-section longitudinally through the interface between the PCD structure and the substrate. The contents of tungsten (W) and cobalt (Co) were measured within the substrate at several different points from proximate the interface into the bulk of the substrate, and the contents of carbon (C) and cobalt (Co) were measured within the PCD structure at several different points from proximate the interface into the bulk of the PCD structure. The results of these measurements are shown as ratios as functions of distance from the interface in FIGS. 11 and 12, respectively. Particularly noteworthy was the absence of substantial “pooling” of cobalt binder adjacent the interface between the PCD and the substrate, which is a typical feature of known inserts, especially those having relatively thick PCD and substrate. The sample displayed an abrupt compositional transition between the carbide of the substrate and the PCD. In addition, no substantial exaggerated diamond or WC grains were observed within the PCD layer proximate the interface, as occur in known inserts.

Example 2

[0091] A substrate a PCD compact was manufactured by blending together diamond particles, tungsten carbide (WC) powder and cobalt powder, forming the blended mixture into a compacted green body, and sintering the green body to a conventional carbide sintering process. The diamond particles had mean size of about 2 microns and constituted about 1 to 4 microns. About 2 weight percent organic pressing aid was included in the WC-Co mix. The blended powder mix was uniaxially compacted at ambient temperature to form a substantially cylindrical green body, which was conventionally sintered at a temperature of 1,400 degrees centigrade for 2 hours to form a sintered article. By the end of the sintering process, the diamond particles had completely converted into graphite. The substrate had a diameter of about 17.4 millimetres and a height of about 13 millimetres after final machining.

[0092] A layer comprising an unbounded aggregated mass of diamond grains was deposited onto the upper surface of the substrate of the sintered article to form an unbounded assembly. Raw material diamond powder for the aggregated mass was prepared by blending diamond grains from three sources, each source having a different average grain size distribution.

[0093] The unbounded assembly was mounted within a capsule for an ultra-high pressure furnace, as is known in the art. The capsule was subjected to a pressure of about 5.5 GPa and a temperature of about 1,400 degrees centigrade for a period of about 5 minutes. After sintering, the first and second substrate elements had sintered together and the PCD composite compact element was processed in the usual way to form an insert having a diameter of about 15.9 millimetres and a PCD structure with thickness in the range of about 1.7 to 2.1 millimetres.

[0094] The insert was analysed using scanning electron micrography (SEM). The Analysis of the material was carried out at several points on a polished cross-section longitudinally through the interface between the PCD structure and the substrate. The contents of tungsten (W) and cobalt (Co) were measured within the substrate at several different points from proximate the interface into the bulk of the substrate, and the contents of carbon (C) and cobalt (Co) were measured within the PCD structure at several different points from proximate the interface into the bulk of the PCD structure. The results of these measurements are shown as ratios as functions of distance from the interface in FIGS. 11 and 12, respectively. Particularly noteworthy was the absence of substantial “pooling” of cobalt binder adjacent the interface between the PCD and the substrate, which is a typical feature of known inserts, especially those having relatively thick PCD and substrate. The sample displayed an abrupt compositional transition between the carbide of the substrate and the PCD. In addition, substantially no exaggerated diamond or WC grains were observed within the PCD layer proximate the interface, as occur in known inserts.

Example 3

[0095] A substrate a PCD compact was manufactured as in example 2, except that the diamond particles had mean size of about 2 microns and constituted about 2.7 weight percent of the blended mixture. A layer comprising an unbounded aggregated mass of diamond grains as described in example 2 was deposited onto the upper surface of the substrate of the sintered article to form an unbounded assembly, which was sintered as in example 2 to form a PCD composite compact element.

[0096] As in example 2, the absence of substantial “pooling” of cobalt binder adjacent the interface between the PCD and the substrate was observed, and substantially no exag-
gerated diamond or WC grains were observed within the PCD layer proximate the interface.

Example 4

[0097] A substrate for a PCD compact was manufactured in the same way and using the same raw materials as the first substrate element of example 1, except that the height of the substrate was 13 millimetres. In other words, the whole substrate had substantially the same composition, shape and diameter as the first substrate element described in example 1.

[0098] A layer of unbonded aggregated mass of diamond grains was deposited onto an end surface of the substrate to form an unbonded assembly. The diamond grains had an ultra-fine bi-modal distribution, having a mean size in the range from about 0.1 to 1 micrometre and were coated with cobalt, which constituted 5 weight percent of the aggregated mass. The coated grains were then subjected to heat treatment in a hydrogen rich atmosphere at 850 degrees centigrade in order to terminate the surfaces with hydrogen.

[0099] The unbonded assembly was mounted within a capsule for an ultra-high pressure furnace, as is known in the art. The capsule was subjected to a pressure of about 5.5 GPa and a temperature of about 1,400 degrees centigrade for a period of about 5 minutes. After sintering, the PCD composite was processed in an assembly to form an insert having a diameter of about 15.9 millimetres and a PCD structure with thickness in the range of about 1.7 to 2.1 millimetres.

[0100] The insert was analysed using scanning electron micrography (SEM). Particularly noteworthy was the absence of discernable pooling of cobalt binder adjacent the interface between the PCD and the substrate. The sample displayed an abrupt transition between the cemented carbide of the substrate and the PCD. In addition, no substantial exaggerated diamond or WC grains were observed within the PCD layer proximate the interface, as occur in known inserts.

Example 5

[0101] A substrate for a PCD compact was manufactured in the same way and using the same raw materials as the first substrate element of example 1, except that the height of the substrate was 13 millimetres. In other words, the whole substrate had substantially the same composition, shape and diameter as the first substrate element described in example 1.

[0102] A first diamond layer formed of an unbonded aggregated mass of diamond grains was deposited onto an end surface of the substrate, and a second diamond layer formed of an unbonded aggregated mass of diamond grains was deposited onto the first layer to form an unbonded assembly. The first diamond layer had a mean thickness of about 0.5 millimetres and the second diamond layer had a mean thickness of about 2.5 millimetres. The first diamond layer being sandwiched between the substrate and the second diamond layer. The diamond grains of the first diamond layer had a fine-grain bi-modal distribution and the diamond grains of the second diamond layer had an ultra-fine-grain distribution. The diamond grains of the second diamond layer had been coated with cobalt, which constituted 5 weight percent of the aggregated mass, and had then been subjected to heat treatment in a hydrogen rich atmosphere at 850 degrees centigrade in order to terminate the surfaces with hydrogen.

[0103] The unbonded assembly was mounted within a capsule for an ultra-high pressure furnace, as is known in the art. The capsule was subjected to a pressure of about 5.5 GPa and a temperature of about 1,400 degrees centigrade for a period of about 5 minutes. After sintering, the PCD composite was processed in the usual way to form an insert having a diameter of about 15.9 millimetres and a PCD structure with thickness in the range of about 2.2 millimetres.

[0104] The insert was analysed using scanning electron micrography (SEM). Particularly noteworthy was the absence of discernable pooling of cobalt binder adjacent the interface between the PCD and the substrate. The sample displayed an abrupt transition between the cemented carbide of the substrate and the PCD. In addition, no substantial exaggerated diamond or WC grains were observed within the PCD layer proximate the interface, as occur in known inserts.

Example 6

[0105] As example 2, except that the capsule was subjected to a pressure of about 6.8 GPa and a temperature of about 1,500 degrees centigrade for a period of about 5 minutes.

[0106] Although the foregoing description of consolidated superhard materials, production methods, and various applications of them contain many specific embodiments, these should not be construed as limiting the scope of the present invention, but merely as providing illustrations of some exemplary embodiments. Similarly, other embodiments of the invention may be devised which do not depart from the spirit or scope of the present invention. The scope of the invention is, therefore, indicated and limited only by the appended claims and their legal equivalents, rather than by the foregoing description. All additions, deletions, and modifications to the invention, as disclosed herein, which fall within the meaning and scope of the claims are to be embraced.

1. A polycrystalline diamond (PCD) composite compact element comprising a PCD structure integrally bonded at an interface to a cemented carbide substrate, the PCD structure comprising coherently bonded diamond grains having a mean size no greater than about 15 microns; the cemented carbide substrate comprising carbide particles dispersed in a metallic binder, the carbide particles comprising a carbide compound of a metal; wherein the ratio of the amount of metallic binder to the amount of the metal at points in the substrate deviates from a mean value by at most about 20 percent of the mean value.

2. A PCD composite compact element according to claim 1, wherein the metal of the carbide particles is a refractory metal selected from the group consisting of W, Ti, Ta, and Cr.

3. A PCD composite compact element according to either one of claims 1 and 2, wherein the substrate has a surface region extending from the interface to a depth of at least 1 mm, the region containing diamond particles dispersed within it.

4. A PCD composite compact element according to any one of claims 1 to 3, wherein the PCD structure comprises a first and a second region, the mean size of the diamond grains of the first region being greater than the mean size of
the diamond grains in the second region; the first region being proximate the substrate and the second region being remote from the substrate.

5. A PCD composite compact element according to any one of claims 1 to 4, wherein the ratio of the amount of metallic binder to the amount carbon at points in the PCD structure deviates from a mean value by at most 20 percent of the mean value, from the interface to a depth of at least 0.5 mm into the PCD structure.

6. A method for making a polycrystalline diamond composite (PDC) compact element comprising a polycrystalline diamond (PCD) structure integrally bonded to a substrate formed of cemented carbide; the method including introducing a source of excess carbon to the substrate at or proximate a bonding surface of the substrate to form a carburised substrate or carburised substrate assembly; contacting an aggregated mass of diamond grains with the carburised substrate or carburised substrate assembly adjacent or proximate the bonding surface to form an unbonded assembly; and sintering the diamond grains in the presence of a solvent/catalyst material for diamond at a temperature and pressure at which diamond is thermodynamically stable to form PCD; wherein the mean size of the diamond grains in the aggregated mass is no greater than about 30 microns.

7. A method according to claim 6, including introducing at least 0.1 weight percent source of excess carbon to the substrate at or proximate the bonding surface of the substrate wherein the weight percent is expressed as of the total substrate material within the region in which the carbon is introduced.

8. A method according to any one of claims 6 and 7, including forming the aggregated mass from diamond grains having a multi-modal size distribution.

9. A method according to any one of claims 6 to 8, wherein the source of excess carbon is in the form of carbon black powder or graphite.

10. A method according to any one of claims 6 to 9, including introducing diamond to the substrate at or proximate the bonding surface of the substrate and converting at least some of the diamond into graphite to serve as a source of excess carbon.

11. A method according to any one of claims 6 to 10, including combining source of excess carbon in particulate or granular form with raw materials for the cemented carbide, forming the combination into a substantially self-supporting green body, and sintering the green body at a pressure at which diamond is not thermodynamically stable.

12. A method according to any one of claims 6 to 11, including combining diamond grains with raw materials for cemented carbide, forming the combination into a substantially self-supporting green body; subjecting the green body to a temperature of at least 500 degrees centigrade and a pressure at which diamond is not thermodynamically stable.

13. A method according to any one of claims 6 to 12, including introducing refractory metal carbide particles into the aggregated mass of diamond grains, the refractory metal carbide particles being selected from the group consisting of tungsten carbide, tantalum carbide, niobium carbide and vanadium carbide and/or introducing a refractory metal precursor for metal carbide into the aggregated mass of diamond grains, the refractory metal being selected from the group consisting of tungsten, tantalum, niobium and vanadium in non-carbide compound or in elemental form.

14. A PCD cutter insert for a drill bit, the PCD cutter insert comprising a PCD composite compact element according to any one of claims 1 to 5.

15. A drill bit for boring into the earth comprising a PCD cutter insert according to claim 14.

* * * * *