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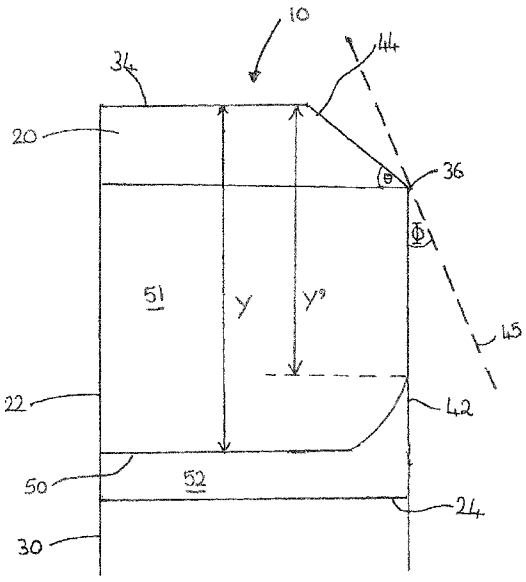


FIG. 3

(57) Abstract: A polycrystalline superhard construction comprises a body (20, 51, 52) of polycrystalline diamond material, a working surface (34), a first region (51) substantially free of a solvent/catalysing material, the first region extending a depth (Y) from the working surface into the body along a plane substantially perpendicular to the plane along which the working surface extends, and a second region (52) remote from the working surface that includes solvent/catalysing material in a plurality of interstitial regions. A substrate (30) is attached to the body along an interface (24) with the second region. A chamfer extends between the working surface and a peripheral side surface of the body. The depth of the first region tapers towards the working surface at the intersection of the first region with the peripheral side surface such that the depth (Y') of the first region at the peripheral side surface is less than the depth of the majority of the first region.

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A POLYCRYSTALLINE SUPER HARD CONSTRUCTION AND A METHOD OF MAKING SAME

FIELD

This disclosure relates to a polycrystalline super hard construction comprising a body of polycrystalline diamond (PCD) material and a method of making a thermally stable polycrystalline diamond construction

BACKGROUND

Cutter inserts for machining and other tools may comprise a layer of polycrystalline diamond (PCD) bonded to a cemented carbide substrate. PCD is an example of a super hard material, also called super abrasive material.

Components comprising PCD are 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. PCD comprises a mass of substantially inter-grown diamond grains forming a skeletal mass which defines interstices between the diamond grains. PCD material typically comprises at least about 80 volume % of diamond and may be made by subjecting an aggregated mass of diamond grains to an ultra-high pressure of greater than about 5 GPa, typically about 5.5 GPa, and temperature of at least about 1200°C, typically about 1440°C, in the presence of a sintering aid, also referred to as a catalyst material for diamond. Catalyst materials for diamond are understood to be materials that are capable of promoting direct inter-growth of diamond grains at a pressure and temperature condition at which diamond is thermodynamically more stable than graphite.

Catalyst materials for diamond typically include any Group VIII element and common examples are cobalt, iron, nickel and certain alloys including alloys of any of these elements. PCD may be formed on a cobalt-cemented tungsten carbide substrate, which may provide a source of cobalt catalyst material for the PCD.

During sintering of the body of PCD material, a constituent of the cemented-carbide substrate, such as cobalt in the case of a cobalt-cemented tungsten carbide substrate, liquefies and sweeps from a region adjacent the volume of diamond particles into interstitial regions between the diamond particles. In this example, the cobalt acts as a catalyst to facilitate the formation of bonded diamond grains. Optionally, a metal-solvent catalyst may be mixed with diamond particles prior to subjecting the diamond particles and substrate to the HPHT process. The interstices within PCD material may at least partly be filled with the catalyst material. The intergrown diamond structure therefore comprises original diamond grains as well as a newly precipitated or re-grown diamond phase, which bridges the original grains. In the final sintered structure, catalyst/solvent material generally remains present within at least some of the interstices that exist between the sintered diamond grains.

A problem known to exist with such conventional PCD compacts is that they are vulnerable to thermal degradation when exposed to elevated temperatures during cutting and/or wear applications. It is believed that this is due, at least in part, to the presence of residual solvent/catalyst material in the microstructural interstices which, due to the differential that exists between the thermal expansion characteristics of the interstitial solvent metal catalyst material and the thermal expansion characteristics of the intercrystalline bonded diamond, is thought to have a detrimental effect on the performance of the PCD compact at high temperatures. Such differential thermal expansion is known to occur at temperatures of about 400[deg.] C., and is believed to cause ruptures to occur in the diamond-to-diamond bonding, and eventually result in the formation of cracks and chips in the PCD structure. The chipping or cracking in the PCD table may degrade the mechanical properties of the cutting element or lead to failure of the cutting element during drilling or cutting operations thereby rendering the PCD structure unsuitable for further use.

Another form of thermal degradation known to exist with conventional PCD materials is one that is also believed to be related to the presence of the solvent metal catalyst in the interstitial regions and the adherence of the solvent metal catalyst to the diamond crystals. Specifically, at high temperatures, diamond grains may undergo a chemical breakdown or back-conversion with the solvent/catalyst. At extremely high temperatures, the solvent metal catalyst is believed to cause an undesired catalyzed phase transformation in diamond such that portions of diamond grains may transform to carbon monoxide, carbon dioxide, graphite, or combinations thereof, thereby degrading the mechanical properties of the PCD material and limiting practical use of the PCD material to about 750[deg.] C.

Attempts at addressing such unwanted forms of thermal degradation in conventional PCD materials are known in the art. Generally, these attempts have focused on the formation of a PCD body having an improved degree of thermal stability when compared to the conventional PCD materials discussed above. One known technique of producing a PCD body having improved thermal stability involves, after forming the PCD body, removing all or a portion of the solvent catalyst material therefrom using, for example, chemical leaching. Removal of the catalyst/binder from the diamond lattice structure renders the polycrystalline diamond layer more heat resistant.

Due to the hostile environment that cutting elements typically operate, cutting elements having cutting layers with improved abrasion resistance, strength and fracture toughness are desired. However, as PCD material is made more wear resistant, for example by removal of the residual catalyst material from interstices in the diamond matrix, it typically becomes more brittle and prone to fracture and therefore tends to have compromised or reduced resistance to spalling.

There is therefore a need to overcome or substantially ameliorate the above-mentioned problems to provide a PCD material having increased resistance to spalling and chipping.

SUMMARY

Viewed from a first aspect there is provided a polycrystalline super hard construction comprising a body of polycrystalline diamond (PCD) material comprising a plurality of interstitial regions between inter-bonded diamond grains forming the polycrystalline diamond material; the body of PCD material comprising:

a working surface positioned along an outside portion of the body;

a first region substantially free of a solvent/catalysing material; the first region extending a depth from the working surface into the body of PCD material along a plane substantially perpendicular to the plane along which the working surface extends; and

a second region remote from the working surface that includes solvent/catalysing material in a plurality of the interstitial regions;

a substrate attached to the body of PCD material along an interface with the second region;

a chamfer extending between the working surface and a peripheral side surface of the body of PCD material and defining a cutting edge at the intersection of the chamfer and the peripheral side surface; wherein:

the depth of the first region tapers towards the working surface at the intersection of the first region with the peripheral side surface such that the depth of the first region at the peripheral side surface is less than the depth of the majority of the first region.

Viewed from a second aspect there is provided a method for making a thermally stable polycrystalline diamond construction comprising the steps of:

machining a polycrystalline diamond body attached to a substrate along an interface, the polycrystalline diamond body comprising a plurality of interbonded

diamond grains and interstitial regions disposed therebetween, to form a chamfer extending between a working surface positioned along an outside portion of the body and a peripheral side surface of the body;

treating the PCD body to remove a solvent/catalyst material from a first region of the diamond body while allowing the solvent/catalyst material to remain in a second region of the diamond body;

the chamfer defining a cutting edge at the intersection of the chamfer and the peripheral side surface; wherein:

the step of treating further comprises masking the PCD body at a position between 0 microns to around 300 microns from the working surface; and

the step of removing solvent/catalyst from the interstitial regions in the first region comprises removing the solvent/catalyst to a depth in the first region that tapers towards the working surface at the intersection of the first region with the peripheral side surface such that the depth of the first region at the peripheral side surface is less than the depth of the majority of the first region.

BRIEF DESCRIPTION OF THE DRAWINGS

Various examples will now be described in more detail, by way of example only, and with reference to the accompanying figures in which:

Figure 1 is a schematic drawing of the microstructure of a body of PCD material;

Figure 2 is a schematic drawing of a PCD compact comprising a PCD structure bonded to a substrate;

Figure 3 is a schematic cross-sections through a portion of the PCD structure of Figure 2 according to an example;

Figure 4 is a schematic cross-sectional view of the PCD cutter of Figure 2 being held in a support structure during a treatment process; and

Figure 5 is a plot of wear scar area against cutting length in a vertical borer test for an example.

DETAILED DESCRIPTION

With reference to Figures 1 to 3, a polycrystalline superhard construction 10 comprises a skeletal mass of directly inter-bonded diamond grains 12 and interstices 14 between the diamond grains 12, which may be at least partly filled with filler or binder material. The filler material may comprise, for example, cobalt, nickel or iron, and also, or in place of, may in some examples include one or more other non-diamond phase additions such as, for example, Titanium, Tungsten, Niobium, Tantalum, Zirconium, Molybdenum, Chromium, or Vanadium. As an example, the content of one or more of these within the filler material may be, for example about 1 weight % of the filler material in the case of Ti, and, in the case of V, the content of V within the filler material may be about 2 weight % of the filler material, and, in the case of W, the content of W within the filler material may be about 20 weight % of the filler material.

PCT application publication number WO2008/096314 discloses a method of coating diamond particles, to enable the formation of polycrystalline super hard abrasive elements or composites, including polycrystalline super hard abrasive elements comprising diamond in a matrix selected from materials selected from a group including VN, VC, HfC, NbC, TaC, Mo_2C, WC. PCT application publication number WO2011/141898 also discloses PCD and methods of forming PCD containing additions such as vanadium carbide to improve, inter alia, wear resistance.

Whilst wishing not to be bound by any particular theory, the combination of metal additives within the filler material may be considered to have the effect of better dispersing the energy of cracks arising and propagating within the PCD material in use, resulting in altered wear behaviour of the PCD material and enhanced

resistance to impact and fracture, and consequently extended working life in some applications.

In accordance with some examples, a sintered body of PCD material is created having diamond to diamond bonding and having a second phase comprising catalyst/solvent and WC (tungsten carbide) dispersed through its microstructure together with or instead of a further non-diamond phase carbide such as VC. The body of PCD material may be formed according to standard methods, for example as described in PCT application publication number WO2011/141898, using HpHT conditions to produce a sintered PCD table.

Figures 1 to 3 show an example of a polycrystalline composite construction 10 for use as a cutter insert for a drill bit (not shown) for boring into the earth. The polycrystalline composite compact or construction 10 comprises a body of super hard material 20 such as PCD material, integrally bonded at an interface 24 to a substrate 30. The substrate 30 may be formed of a hard material such as a cemented carbide material and may be, for example, cemented tungsten carbide, cemented tantalum carbide, cemented titanium carbide, cemented molybdenum carbide or mixtures thereof. The binder metal for such carbides may be, for example, nickel, cobalt, iron or an alloy containing one or more of these metals. Typically, this binder will be present in an amount of 10 to 20 mass %, but this may be as low as 6 mass % or less. Some of the binder metal may infiltrate the body of polycrystalline diamond material 20 during formation of the compact 10.

The super hard material may be, for example, polycrystalline diamond (PCD).

The cutting element 10 may be mounted in use into a bit body such as a drag bit body (not shown). The exposed top surface of the super hard material 20 opposite the substrate 30 forms the working surface 34, which is the surface which, along with its edge 36, performs the cutting in use.

The substrate 30 may be, for example, generally cylindrical and has a peripheral surface, a peripheral top edge and a distal free end.

The exposed surface of the cutter element 20 comprises the working surface 34 which also acts as a rake face in use. A chamfer 44 extends between the working surface 34 and the cutting edge 36, and at least a part of a flank or barrel 42 of the cutter, the cutting edge 36 being defined by the edge of the chamfer 44 and the flank 42.

The working surface or "rake face" 34 of the cutter is the surface or surfaces over which the chips of material being cut flow when the cutter is used to cut material from a body, the rake face 34 directing the flow of newly formed chips. This face 34 is commonly referred to as the top face or working surface of the cutter. As used herein, "chips" are the pieces of a body removed from the work surface of the body by the cutter in use.

As used herein, the "flank" 42 of the cutter is the surface or surfaces of the cutter that passes over the surface produced on the body of material being cut by the cutter and is commonly referred to as the side or barrel of the cutter. The flank 42 may provide a clearance from the body and may comprise more than one flank face.

As used herein, a "cutting edge" 36 is intended to perform cutting of a body in use.

As used herein, a "wear scar" is a surface of a cutter formed in use by the removal of a volume of cutter material due to wear of the cutter. A flank face may comprise a wear scar. As a cutter wears in use, material may be progressively removed from proximate the cutting edge, thereby continually redefining the position and shape of the cutting edge, rake face and flank as the wear scar forms. As used herein, it is understood that the term "cutting edge" refers to the actual cutting edge, defined functionally as above, at any particular stage or at more than one stage of the cutter wear progression up to failure of the cutter, including but not limited to the cutter in a substantially unworn or unused state.

With reference to Figure 3, the chamfer 44 is formed in the structure adjacent the cutting edge 36 and flank or barrel surface 42. The rake face 34 is therefore joined

to the flank 42 by the chamfer 44 which extends from the cutting edge 36 to the rake face 34, and lies in a plane at a predetermined angle θ to the plane perpendicular to the plane in which the longitudinal axis of the cutter extends. In some examples, this chamfer angle may be up to around 45 degrees. The vertical height of the chamfer 44 may be, for example, between around 200 μm and around 300 μm, or, for example, between around 350μm to around 450μm, such as around 400μm.

Figure 3 is a schematic representation of the PCD construction 10 which has been treated to remove residual solvent/catalyst from interstitial spaces between the diamond grains using the techniques described in detail below. The depth Y in the PCD layer 20 from the working surface 34 towards the interface 24 with the substrate 30 from which the solvent/catalyst has been substantially removed is known as the leach depth. According to examples, this depth Y tapers towards the working surface 34 at the intersection with the barrel 42 such that the leach depth at the longitudinal axis of the cutter is greater than the leach depth Y' at the barrel surface 42. It has been appreciated by the applicant that, surprisingly, this may assist in controlling spalling events during use of the PCD construction in applications. In some examples, the boundary 50 between the leached first region 51 and unleached second region 52 intersects the barrel 42 of the cutter 10 below the edge of the chamfer 44 that forms the cutting edge 36 in the new/unused condition.

Whilst not wishing to be bound by theory, it has been appreciated by the applicant that cracks have a tendency to propagate in the PCD along the interface 50 between leached and unleached regions 51, 52 of the PCD and therefore examples in which this boundary 50 tapers towards the working surface 34 such that the leach depth at the longitudinal axis of the cutter is greater than the leach depth at the barrel surface 42 may assist in managing the thermal wear events of the construction 10 in use and assist in managing the spalling by diverting cracks initiating at the leached/unleached boundary into the centre of the cutter 10 thereby

potentially delaying the onset of spalling and prolonging the working life of the construction 10. This is in contrast to conventional cutters where the leaching profile tends to be tapered away from the working surface and towards the distal free end of the substrate or the leach depth is substantially uniform across the diameter of the construction.

In some examples, the leach depth Y' at the barrel surface 42 is at least around 100 microns below the cutting edge 36, whilst in other examples it may be between around 50 to around 100 microns below the cutting edge 36, and in some examples it is less than around 50 microns and in others it intersects the chamfer surface 44 itself.

As used herein, the thickness of the body of PCD material 20 or the substrate 30 or some part of the body of PCD material or the substrate is the thickness measured substantially perpendicularly to the working surface 34. In some examples, the PCD structure, or body of PCD material 20 may have a generally wafer, disc or disc-like shape, or be in the general form of a layer. In some examples, the body of PCD material 20 may have a thickness of at least about 2.5 to at least 4.5 mm. In one example, the body of PCD material 20 may have a thickness in the range from about 2 mm to about 3.5 mm.

In some examples, the substrate 30 may have the general shape of a wafer, disc or post, and may be generally cylindrical in shape. The substrate 30 may have, for example, an axial thickness at least equal to or greater than the axial thickness of the body of PCD material 20 and may be for example at least about 1 mm, at least about 2.5 mm, at least about 3 mm, at least about 5 mm or even at least about 10 mm or more in thickness. In one example, the substrate 30 may have a thickness of at least 2 cm.

In some examples, the largest dimension of the body of PCD material 20 is around 6 mm or greater, for example in examples where the body of PCD material is cylindrical in shape, the diameter of the body is around 6mm or greater.

In some versions of the method, prior to sintering, the aggregated mass of diamond particles/grains may be disposed against the surface of the substrate generally in the form of a layer having a thickness of least about 0.6 mm, at least about 1 mm, at least about 1.5 mm or even at least about 2 mm. The thickness of the mass of diamond grains may reduce significantly when the grains are sintered at an ultra-high pressure.

The super hard particles used in the present process may be of natural or synthetic origin. The mixture of super hard particles may be multimodal, that it is may comprise a mixture of fractions of diamond particles or grains that differ from one another discernibly in their average particle size. Typically the number of fractions may be:

- a specific case of two fractions
- three or more fractions.

By "average particle/grain size" it is meant that the individual particles/grains have a range of sizes with the mean particle/grain size representing the "average". Hence the major amount of the particles/grains will be close to the average size, although there will be a limited number of particles/grains above and below the specified size. The peak in the distribution of the particles will therefore be at the specified size. The size distribution for each super hard particle/grain size fraction is typically itself monomodal, but may in certain circumstances be multimodal. In the sintered compact, the term “average particle grain size” is to be interpreted in a similar manner.

As shown in Figure 2, the bodies of polycrystalline diamond material produced by an example additionally have a binder phase 14 present. This binder material 14 is preferably a catalyst/solvent for the super hard abrasive particles used. Catalyst/solvents for diamond are well known in the art. In the case of diamond, the binder is preferably cobalt, nickel, iron or an alloy containing one or more of these metals. This binder may be introduced either by infiltration into the mass of abrasive

particles during the sintering treatment, or in particulate form as a mixture within the mass of abrasive particles. Infiltration may occur from either a supplied shim or layer of the binder metal or from the carbide support. Typically a combination of the admixing and infiltration approaches is used.

During the high pressure, high temperature treatment, the catalyst/solvent material melts and migrates through the compact layer, acting as a catalyst/solvent and causing the super hard particles to bond to one another. Once manufactured, the PCD construction therefore comprises a coherent matrix of super hard (diamond) particles bonded to one another, thereby forming an super hard polycrystalline composite material with many interstices or pools containing binder material as described above. In essence, the final PCD construction therefore comprises a two-phase composite, where the super hard abrasive diamond material comprises one phase and the binder (non-diamond phase), the other.

In one form, the super hard phase, which is typically diamond, constitutes between 80% and 95% by volume and the solvent/catalyst material the other 5% to 20%.

The relative distribution of the binder phase, and the number of voids or pools filled with this phase, is largely defined by the size and shape of the diamond grains.

The binder (non-diamond) phase can help to improve the impact resistance of the more brittle abrasive phase, but as the binder phase typically represents a far weaker and less abrasion resistant fraction of the structure, and high quantities will tend to adversely affect wear resistance. Additionally, where the binder phase is also an active solvent/catalyst material, its increased presence in the structure can compromise the thermal stability of the compact.

The cutter of Figures 1 to 3 may be fabricated, for example, as follows.

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.

Examples of super hard constructions may be made by a method of preparing a green body comprising grains of super hard material and a binder, such as an organic binder. The green body may also comprise catalyst material for promoting the sintering of the super hard grains. The green body may be made by combining the grains with the binder 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, injection or other methods such as molding, extrusion, deposition modelling methods. The green body may be formed from components comprising the grains and a binder, the components being in the form of sheets, blocks or discs, for example, and the green body may itself be formed from green bodies.

One example of a method for making a green body includes providing tape cast sheets, each sheet comprising, for example, a plurality of diamond grains bonded together by a binder, such as a water-based organic binder, and stacking the sheets on top of one another and on top of a support body. Different sheets comprising diamond grains having different size distributions, diamond content or additives may be selectively stacked to achieve a desired structure. The sheets may be made by a method known in the art, such as extrusion or tape casting methods, wherein slurry comprising diamond grains and a binder material is laid onto a surface and allowed to dry. Other methods for making diamond-bearing sheets may also be used, such as described in United States patents numbers 5,766,394 and 6,446,740. Alternative methods for depositing diamond-bearing layers include spraying methods, such as thermal spraying.

A green body for the super hard construction may be placed onto a substrate, such as a 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 super hard grains. In some examples, the super hard 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.

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 super hard material is thermodynamically stable to sinter the super hard grains. In some examples, the green body comprises 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.

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 for making a super-hard enhanced hard-metal material. A powder blend comprising diamond 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 example, 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 super hard material is thermodynamically stable to sinter the super hard grains.

After sintering, the polycrystalline super hard constructions may be ground to size and may include, if desired, a chamfer of, for example, approximately 0.4mm height and an angle of 45º applied to the body of polycrystalline super hard material so produced.

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.

A further example of a super hard 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, 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.

The present disclosure may be further illustrated by the following examples which are not intended to be limiting.

The grains of super hard material, such as diamond grains or particles in the starting mixture prior to sintering 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 examples, 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 6/10 of the size of the coarse fraction, and may, in some examples, range for example between about 0.1 to 20 microns.

In some examples, 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 examples, the weight ratio of the coarse fraction to the fine fraction will range from about 70:30 to about 90:10.

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

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

The examples consists of at least a wide bi-modal size distribution between the coarse and fine fractions of super hard material, but some examples may include three or even four or more size modes which may, for example, be separated in size by an order of magnitude, for example, a blend of particle sizes whose average particle size is 20 microns, 2 microns, 200nm and 20nm.

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.

In examples where the super hard material is polycrystalline diamond material, the diamond grains used to form the polycrystalline diamond material may be natural or synthetic.

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

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

In some examples, both the bodies of, for example, diamond and carbide material plus sintering aid/binder/catalyst are applied as powders and sintered simultaneously in a single UHP/HT process. The mixture of diamond grains 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 example, the processing conditions generally involve the imposition for about 3 to 120 minutes of a temperature of at least about 1200 degrees C and an ultra-high pressure of greater than about 5 GPa.

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

In a further example, both the substrate and a body of polycrystalline super hard material are pre-formed. For example, the bimodal feed of super hard grains/particles with 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 super hard 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 super hard material and acts as a binder-catalyst to effect intergrowth in the layer and also serves to bond the layer of polycrystalline super hard material to the substrate. The sintering process also serves to bond the body of super hard polycrystalline material to the substrate.

The practical use of cemented carbide grades with substantially lower cobalt content as substrates for PCD inserts is limited by the fact that some of the Co is required to migrate from the substrate into the PCD layer during the sintering process in order to catalyse the formation of the PCD. For this reason, it is more difficult to make PCD on substrate materials comprising lower Co contents, even though this may be desirable.

An example of a super hard construction may be made by a method including providing a cemented carbide substrate, contacting an aggregated, substantially unbonded mass of diamond particles against a surface of the substrate to form an pre-sinter assembly, encapsulating the pre-sinter assembly in a capsule for an ultra-high pressure furnace and subjecting the pre-sinter assembly to a pressure of at least about 5.5 GPa and a temperature of at least about 1,250 degrees centigrade, and sintering the diamond particles to form a PCD composite compact element comprising a PCD structure integrally formed on and joined to the cemented carbide substrate. In some examples of the invention, the pre-sinter

assembly may be subjected to a pressure of at least about 6 GPa, at least about 6.5 GPa, at least about 7 GPa or even at least about 7.5 GPa.

The hardness of cemented tungsten carbide substrate may be enhanced by subjecting the substrate to an ultra-high pressure and high temperature, particularly at a pressure and temperature at which diamond is thermodynamically stable. The magnitude of the enhancement of the hardness may depend on the pressure and temperature conditions. In particular, the hardness enhancement may increase the higher the pressure. Whilst not wishing to be bound by a particular theory, this is considered to be related to the Co drift from the substrate into the PCD during press sintering, as the extent of the hardness increase is directly dependent on the decrease of Co content in the substrate.

In examples 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 examples 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.

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, electroless 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.

In one example of a method of the invention, 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:

$Co(NO_3)_2 + Na_2CO_3 \rightarrow CoCO_3 + 2NaNO_3$

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:

$CoCO_3 \rightarrow CoO + CO_2$

$CoO + H_2 \rightarrow Co + H_2O$

In another example, 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.

In some examples, the cemented carbide substrate may be formed of tungsten carbide particles bonded together by the binder material, the binder material comprising an alloy of Co, Ni and Cr. The tungsten carbide particles may form at

least 70 weight percent and at most 95 weight percent of the substrate. The binder material may comprise between about 10 to 50 wt.% Ni, between about 0.1 to 10 wt.% Cr, and the remainder weight percent comprises Co. The size distribution of the tungsten carbide particles in the cemented carbide substrate in some examples has the following characteristics:

- fewer than 17 percent of the carbide particles have a grain size of equal to or less than about 0.3 microns;
- between about 20 to 28 percent of the tungsten carbide particles have a grain size of between about 0.3 to 0.5 microns;
- between about 42 to 56 percent of the tungsten carbide particles have a grain size of between about 0.5 to 1 microns;
- less than about 12 percent of the tungsten carbide particles are greater than 1 micron; and
- the mean grain size of the tungsten carbide particles is about 0.6±0.2 microns.

In some examples, the binder additionally comprises between about 2 to 20 wt.% tungsten and between about 0.1 to 2 wt.% carbon

A layer of the substrate adjacent to the interface with the body of polycrystalline diamond material may have a thickness of, for example, around 100 microns and may comprise tungsten carbide grains, and a binder phase. This layer may be characterised by the following elemental composition measured by means of Energy-Dispersive X-Ray Microanalysis (EDX):

- between about 0.5 to 2.0 wt% cobalt;
- between about 0.05 to 0.5 wt.% nickel;
- between about 0.05 to 0.2 wt.% chromium; and

- tungsten and carbon.

In a further example, in the layer described above in which the elemental composition includes between about 0.5 to 2.0 wt% cobalt, between about 0.05 to 0.5 wt.% nickel and between about 0.05 to 0.2 wt.% chromium, the remainder is tungsten and carbon.

The layer of substrate may further comprise free carbon.

The magnetic properties of the cemented carbide material may be related to important structural and compositional characteristics. The most common technique for measuring the carbon content in cemented carbides is indirectly, by measuring the concentration of tungsten dissolved in the binder to which it is indirectly proportional: the higher the content of carbon dissolved in the binder the lower the concentration of tungsten dissolved in the binder. The tungsten content within the binder may be determined from a measurement of the magnetic moment, σ, or magnetic saturation, $M_s = 4\pi\sigma$, these values having an inverse relationship with the tungsten content (Roebuck (1996), "Magnetic moment (saturation) measurements on cemented carbide materials", *Int. J. Refractory Met.,* Vol. 14, pp. 419-424.). The following formula may be used to relate magnetic saturation, Ms, to the concentrations of W and C in the binder:

$$M_s \propto [C]/[W] \times \text{wt.\% Co} \times 201.9 \text{ in units of } \mu T.m^3/kg$$

The binder cobalt content within a cemented carbide material may be measured by various methods well known in the art, including indirect methods such as such as the magnetic properties of the cemented carbide material or more directly by means of energy-dispersive X-ray spectroscopy (EDX), or a method based on chemical leaching of Co.

The mean grain size of carbide grains, such as WC grains, may be determined by examination of micrographs obtained using a scanning electron microscope (SEM) or light microscopy images of metallurgically prepared cross-sections of a

cemented carbide material body, applying the mean linear intercept technique, for example. Alternatively, the mean size of the WC grains may be estimated indirectly by measuring the magnetic coercivity of the cemented carbide material, which indicates the mean free path of Co intermediate the grains, from which the WC grain size may be calculated using a simple formula well known in the art. This formula quantifies the inverse relationship between magnetic coercivity of a Co-cemented WC cemented carbide material and the Co mean free path, and consequently the mean WC grain size. Magnetic coercivity has an inverse relationship with MFP.

As used herein, the "mean free path" (MFP) of a composite material such as cemented carbide is a measure of the mean distance between the aggregate carbide grains cemented within the binder material. The mean free path characteristic of a cemented carbide material may be measured using a micrograph of a polished section of the material. For example, the micrograph may have a magnification of about 1000x. The MFP may be determined by measuring the distance between each intersection of a line and a grain boundary on a uniform grid. The matrix line segments, Lm, are summed and the grain line segments, Lg, are summed. The mean matrix segment length using both axes is the "mean free path". Mixtures of multiple distributions of tungsten carbide particle sizes may result in a wide distribution of MFP values for the same matrix content. This is explained in more detail below.

The concentration of W in the Co binder depends on the C content. For example, the W concentration at low C contents is significantly higher. The W concentration and the C content within the Co binder of a Co-cemented WC (WC-Co) material may be determined from the value of the magnetic saturation. The magnetic saturation $4\pi\sigma$ or magnetic moment σ of a hard metal, of which cemented tungsten carbide is an example, is defined as the magnetic moment or magnetic saturation per unit weight. The magnetic moment, σ, of pure Co is 16.1 micro-Tesla times

cubic metre per kilogram ($\mu T.m^3/kg$), and the induction of saturation, also referred to as the magnetic saturation, $4\pi\sigma$, of pure Co is 201.9 $\mu T.m^3/kg$.

In some examples, the cemented carbide substrate may have a mean magnetic coercivity of at least about 100 Oe and at most about 145 Oe, and a magnetic moment of specific magnetic saturation with respect to that of pure Co of at least about 89 percent to at most about 97 percent.

A desired MFP characteristic in the substrate may be accomplished several ways known in the art. For example, a lower MFP value may be achieved by using a lower metal binder content. A practical lower limit of about 3 weight percent cobalt applies for cemented carbide and conventional liquid phase sintering. In an example where the cemented carbide substrate is subjected to an ultra-high pressure, for example a pressure greater than about 5 GPa and a high temperature (greater than about 1,400°C for example), lower contents of metal binder, such as cobalt, may be achieved. For example, where the cobalt content is about 3 weight percent and the mean size of the WC grains is about 0.5 micron, the MFP would be about 0.1 micron, and where the mean size of the WC grains is about 2 microns, the MFP would be about 0.35 microns, and where the mean size of the WC grains is about 3 microns, the MFP would be about 0.7 microns. These mean grain sizes correspond to a single powder class obtained by natural comminution processes that generate a log normal distribution of particles. Higher matrix (binder) contents would result in higher MFP values.

Changing grain size by mixing different powder classes and altering the distributions may achieve a whole spectrum of MFP values for the substrate depending on the particulars of powder processing and mixing. The exact values would have to be determined empirically.

In some examples, the substrate comprises Co, Ni and Cr.

The binder material for the substrate may include at least about 0.1 weight percent to at most about 5 weight percent one or more of V, Ta, Ti, Mo, Zr, Nb and Hf in solid solution.

In further examples, the polycrystalline diamond (PCD) composite compact element may include at least about 0.01 weight percent and at most about 2 weight percent of one or more of Re, Ru, Rh, Pd, Re, Os, Ir and Pt.

Some examples of a cemented carbide body may be formed by providing tungsten carbide powder having a mean equivalent circle diameter (ECD) size in the range from about 0.2 microns to about 0.6 microns, the ECD size distribution having the further characteristic that fewer than 45 percent of the carbide particles have a mean size of less than 0.3 microns; 30 to 40 percent of the carbide particles have a mean size of at least 0.3 microns and at most 0.5 microns; 18 to 25 percent of the carbide particles have a mean size of greater than 0.5 microns and at most 1 micron; fewer than 3 percent of the carbide particles have a mean size of greater than 1 micron. The tungsten carbide powder is milled with binder material comprising Co, Ni and Cr or chromium carbides, the equivalent total carbon comprised in the blended powder being, for example, about 6 percent with respect to the tungsten carbide. The blended powder is then compacted to form a green body and the green body is sintered to produce the cemented carbide body.

The sintering the green body may take place at a temperature of, for example, at least 1,400 degrees centigrade and at most 1,440 degrees centigrade for a period of at least 65 minutes and at most 85 minutes.

In some examples, the equivalent total carbon (ETC) comprised in the cemented carbide material is about 6.12 percent with respect to the tungsten carbide.

The size distribution of the tungsten carbide powder may, in some examples, have the characteristic of a mean ECD of 0.4 microns and a standard deviation of 0.1 microns.

Examples 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

A quantity of sub-micron cobalt powder sufficient to obtain 2 mass% in the final diamond mixture was initially de-agglomerated in a methanol slurry in a ball mill with WC milling media for 1 hour. A fine fraction of diamond powder with an average grain size of 2 microns was then added to the slurry in an amount to obtain 10 mass % in the final mixture. Additional milling media was introduced and further methanol was added to obtain suitable slurry; and this was milled for a further hour. A coarse fraction of diamond, with an average grain size of approximately 20 microns was then added in an amount to obtain 88 mass % in the final mixture. The slurry was again supplemented with further methanol and milling media, and then milled for a further 2 hours. The slurry was removed from the ball mill and dried to obtain the diamond powder mixture.

The diamond powder mixture was then placed into a suitable HpHT vessel, adjacent to a tungsten carbide substrate and sintered at a pressure of around 6.8 GPa and a temperature of about 1500 deg.C.

Example 2

A quantity of sub-micron cobalt powder sufficient to obtain 2.4 mass% in the final diamond mixture was initially de-agglomerated in a methanol slurry in a ball mill with WC milling media for 1 hour. A fine fraction of diamond powder with an average grain size of 2 microns was then added to the slurry in an amount to obtain 29.3 mass % in the final mixture. Additional milling media was introduced and further methanol was added to obtain a suitable slurry; and this was milled for a further hour. A coarse fraction of diamond, with an average grain size of approximately 20 microns was then added in an amount to obtain 68.3 mass % in the final mixture. The slurry was again supplemented with further methanol and

milling media, and then milled for a further 2 hours. The slurry was removed from the ball mill and dried to obtain the diamond powder mixture.

The diamond powder mixture was then placed into a suitable HpHT vessel, adjacent to a tungsten carbide substrate and sintered at a pressure of around 6.8 GPa and a temperature of about 1500 deg.C.

The diamond content of the sintered diamond structure is greater than 90 vol% and the coarsest fraction of the distribution is greater than 60 weight % and preferably greater than weight 70%.

In polycrystalline diamond material, individual diamond particles/grains are, to a large extent, bonded to adjacent particles/grains through diamond bridges or necks. The individual diamond particles/grains retain their identity, or generally have different orientations. The average grain/particle size of these individual diamond grains/particles may be determined using image analysis techniques. Images are collected on a scanning electron microscope and are analysed using standard image analysis techniques. From these images, it is possible to extract a representative diamond particle/grain size distribution.

Generally, the body of polycrystalline diamond material will be produced and bonded to the cemented carbide substrate in a HPHT process. In so doing, it is advantageous for the binder phase and diamond particles to be arranged such that the binder phase is distributed homogeneously and is of a fine scale.

The homogeneity or uniformity of the sintered structure is defined by conducting a statistical evaluation of a large number of collected images. The distribution of the binder phase, which is easily distinguishable from that of the diamond phase using electron microscopy, can then be measured in a method similar to that disclosed in EP 0974566. This method allows a statistical evaluation of the average thicknesses of the binder phase along several arbitrarily drawn lines through the microstructure. This binder thickness measurement is also referred to as the "mean free path" by those skilled in the art. For two materials of similar overall composition or binder

content and average diamond grain size, the material which has the smaller average thickness will tend to be more homogenous, as this implies a "finer scale" distribution of the binder in the diamond phase. In addition, the smaller the standard deviation of this measurement, the more homogenous is the structure. A large standard deviation implies that the binder thickness varies widely over the microstructure, i.e. that the structure is not even, but contains widely dissimilar structure types.

The sintered construction is then subjected to a post-synthesis treatment to assist in improving thermal stability of the sintered structure, by removing catalysing material from a region of the polycrystalline layer adjacent an exposed surface thereof, namely the working surface opposite the substrate. It has been found that the removal of non-binder phase from within the PCD table, conventionally referred to as leaching, is desirable in various applications. The residual presence of solvent/catalyst material in the microstructural interstices is believed to have a detrimental effect on the performance of PCD compacts at high temperatures as it is believed that the presence of the solvent/catalyst in the diamond table reduces the thermal stability of the diamond table at these elevated temperatures. Therefore leaching is desired to enhance thermal stability of the PCD body. However, leaching solvent/catalyst material from a PCD structure is known to reduce its fracture toughness and strength by between 20 to 30%. The present applicants have surprisingly determined that, contrary to conventional expectations, ensuring the depth Y tapers towards the working surface 34 at the intersection with the barrel 42 such that the leach depth Y at the longitudinal axis of the cutter and/or the leach depth of the majority of the first region is greater than the leach depth Y' at the barrel surface 42 may assist in controlling spalling events during use of the PCD construction in applications as cracks have a tendency to propagate in the PCD along the interface 50 between leached and unleached regions 51, 52 of the PCD and therefore examples in which this boundary 50 tapers towards the working surface 34 such that the leach depth in the majority of the first region 51 is greater than the leach depth Y' at the barrel surface 42 may assist in managing the thermal

wear events of the construction 10 in use and assist in managing the spalling by diverting cracks initiating at the leached/unleached boundary 50 into the centre of the cutter 10 thereby potentially delaying the onset of spalling and prolonging the working life of the construction 10.

Removal of the catalysing material may be carried out using methods known in the art such as electrolytic etching, acid leaching or evaporation techniques. However, the tapered leaching profiles of the examples described above and shown in Figure 3 may be obtained by, for example, the additional steps set out below.

In some examples, a protective layer, or mask is applied to the body of PCD material that extends either up to the working surface 36 and down the chamfer surface 44 and may also extend down the barrel 42 depending on the leaching technique to be applied and the fixtures holding the construction during the leaching process. In some examples the mask extends from 0 microns to around 150 microns from the working surface 36 down the chamfer surface 44, and in other examples the mask extends from around 150 microns to around 300 microns from the working surface 36 down the chamfer surface 44. The protective layer or mask is designed to prevent the leaching solution from chemically damaging certain portions of the body of PCD material and/or the substrate 30 attached thereto during leaching and the positioning of the mask or layer close to or at the working surface 36 has been determined to effect the leaching profile shown in Figure 3 as it enables selective leaching of the body of PCD material, which may be beneficial. Following leaching, the protective layer or mask may be removed.

The interstitial material which may include, for example, the metal-solvent/catalyst and one or more additions in the form of carbide additions, may be leached from the interstices 14 in the body of PCD material 20 by exposing the PCD material to a suitable leaching solution.

Control of the where the PCD element is leached may be important for a number of reasons. Firstly, it may be desirable not to remove the catalyst from all areas of the

PCD, such as regions that are not exposed to such extreme heat or that may benefit from the mechanical strength conferred by the catalyst. Secondly, the substrate is typically made of a material such as tungsten carbide whose resistance to harsh leaching conditions is far less than that of the diamond matrix. Accordingly, exposure of the substrate to the leaching mixture may cause serious damage to the substrate, often rendering the PCD element as a whole useless. Thirdly, the presence of the catalyst in the PCD near the substrate may be useful to assist in strengthening the region of the interface between the substrate and the PCD so that the PCD body does not separate from the substrate during use of the element. It may therefore be important to protect the interface region from the leaching mixture.

Various systems for protecting non-leached portions of a PCD element and providing a mask are known to include, for example, encasing the PCD element in a protective material and removing the masking material from the regions to be leached, or coating the portion of the element to not be leached with a masking material.

In an alternative method, a leaching system such as that shown in Figure 4 may be used. The leaching system 400 includes a support 420 comprising a cup portion 440 having an upper rim 460 defining an aperture into which is located the PCD construction 470 to be leached. A sealing element 480 such as an elastomeric o-ring seal is located on a flange adjacent the rim of the cup portion 440 or may be locatable in a groove in the inner peripheral wall defining the aperture in the support and acts to extend around a portion of the PCD element 100 to be leached to separate the portion 520 of the PCD to be leached from the portion of the PCD element which is not to be leached, including the substrate 300 bonded thereto. The support 420 is shaped to leave exposed the region of the PCD element which is to be subjected to the leaching mixture during the treatment process. The cup 440 and sealing element 480 shown in Figure 4 are therefore designed to encapsulate the desired surfaces of the substrate 300 and part of the PCD construction 470 which are not to be leached.

As shown in Figure 4 the support 420 is configured as having a cylindrical cup portion 440 with an inside surface diameter that is sized to fit concentrically around the outside surface of the PCD construction 470 to be processed. The groove or flange in or on which is located the sealing element 480 extends circumferentially around an inner rim positioned adjacent to an end of the cup portion 440. In an alternative example (not shown), the support 420 may be configured without a groove and a suitable seal may simply be interposed between the opposed respective PCD construction 470 and support 420 outside and inside diameter surfaces. When placed around the outside surface of the PCD construction 470, the seal 480 operates to provide a leak-tight seal between the PCD element 100 and the support 420 to prevent unwanted migration of the leaching agent therebetween.

In preparation for treatment, the support 420 is positioned axially over the PCD construction 470 and the PCD construction 470 is located into the support 420 with the working surface of the PCD construction 470 protruding from the cup portion 440 and projecting a desired distance outwardly from sealed engagement with the inside wall of the cup portion 440. Positioned in this manner within the support 420, the working surface of the PCD construction 470 is freely exposed to make contact with the leaching agent. As mentioned above in the context of masking using a protective coating, to achieve the desired leaching profile shown in Figure 3, the seal 480 is positioned either adjacent the working surface 360 of the PCD construction 470, or between around 0 to around 300 microns from the working surface sealing the chamfer portion 42 of the PCD construction 470.

The PCD construction 470 and support fixture 420 form an assembly 400 that are then placed into a suitable container (not shown) that includes a desired volume of the leaching agent. In some examples, the leaching vessel may be a pressure vessel.

In some examples, the level of the leaching agent within the container is such that the working surface of the PCD construction 470 that is exposed within the support fixture is completely immersed into the leaching agent.

In some examples, the PCD construction 470 and support fixture 420 may be first placed in a leaching vessel and then the leaching agent may be added, or the leaching agent may be added to the leaching vessel before the PCD construction 470 is placed in the leaching vessel. This step may be performed by hand or using an automated system, such as a robotic system.

The leaching agent may be any chemical leaching agent. In particular examples, it may be a leaching agent as described herein.

The leaching process may be aided by stirring the leaching agent or otherwise agitating it, for example by ultrasonic methods, vibrations, or tumbling.

Leaching may take place over a time span of a few hours to a few months. In particular examples, it may take less than one day (24 hours), less than 50 hours, or less than one week. Leaching may be performed at room temperature or at a lower temperature, or at an elevated temperature, such as the boiling temperature of the leaching mixture.

The duration and conditions of the leaching treatment process may be determined by a variety of factors including, but not limited to, the leaching agent used, the depth to which the PCD construction 470 is to be leached, and the percentage of catalyst to be removed from the leached portion of the PCD construction 470.

In some examples, the sealing element 480 may be formed from a polyketone based plastics materials such as PEEK or another protective elastomer material.

In most instances, the PCD construction 470 may be inserted into and removed from the support fixture 420 by hand but this operation could be automated.

The PCD construction 470 may be any type of element to be leached, including a cutter as shown in Figures 1 and 3.

According to some examples, the body of PCD material 20 may be exposed to the leaching solution at an elevated temperature, for example to a temperature at which the acid leaching mixture is boiling. Exposing the body of PCD material 20 to an elevated temperature during leaching may increase the depth to which the PCD material 20 may be leached and reduce the leaching time necessary to reach the desired leach depth. In some examples, the leaching process may also be conducted at an elevated pressure.

Additionally, in some examples, at least a portion of the body of PCD material 20 and the leaching solution may be exposed to at least one of an electric current, microwave radiation, and/or ultrasonic energy to increase the rate at which the body of PCD material 20 is leached.

In some examples, the leaching depth Y may be less than 0.05 mm, less than 0.1 mm, less than 1 mm, less than 2 mm, or less than 3 mm, or greater than 0.4mm. In some examples, at least 85%, at least 90%, at least 95%, or at least 99% of the catalyst may be removed to the leaching depth from the leached portion of the PDC element. The leaching depth and amount of catalyst removed may be selected based on the intended use of the PCD element 100. Thus, chemical leaching may be used to remove the metal-solvent catalyst and any additions from the body of super hard material 20 either up to a desired depth from an external surface of the body of PCD material or from substantially all of the super hard material 20 whilst maintaining the leaching profile shown in Figure 3. Following leaching, the body of super hard material 20 may therefore comprise a first volume that is substantially free of a metal-solvent catalyst. However, small amounts of catalyst may remain within interstices that are inaccessible to the leaching process. Additionally, following leaching, the body of super hard material 20 may also comprise a volume that contains a metal-solvent catalyst. In some examples, this further volume may be remote from one or more exposed surfaces of the body of super hard material 20.

The thermally stable region, which may be substantially porous, may extend, for example, a depth of at least about 50 microns or at least about 100 microns from a surface of the PCD structure. Some examples may have a leach depth greater than around 250 microns or up to or greater than around 650 microns and in some examples substantially all of the catalysing material may be removed from the body of polycrystalline material whilst maintaining the leaching profile of Figure 3.

It is to be understood that the exact depth of the thermally stable region can be selected to and will vary depending on the desired particular end use drilling and or cutting applications.

Once leached to the desired depth, the PCD construction 470 and support fixture 420 are removed from the leaching vessel. This may occur prior to or after removal of the leaching agent from the leaching vessel. After removal, the PCD construction 470 may optionally be washed, cleaned, or otherwise treated to remove or neutralize residual leaching agent. Finally, the PCD construction 470 is removed from the support fixture 420.

All of these steps may also be performed by hand or using an automated system, such as a robotic system.

HF-HNO3 may be an effective media for the removal of tungsten carbide (WC) from a sintered PCD table. Alternatively, HCl and other similar mineral acids are easier to work with at high temperatures than HF-HNO3 and are aggressive towards the catalyst/solvent, particularly cobalt (Co). HCl, for example, may remove the bulk of the catalyst/solvent from the PCD table in a reasonable time period, depending on the temperature, typically in the region of 80 hours.

According to some examples, the leaching solution may comprise one or more mineral acids and diluted nitric acid. The body of PCD material may be exposed to such a leaching solution in any suitable manner, including, for example, by

immersing at least a portion of the body of PCD material 20 in the leaching solution for a period of time.

Examples of suitable mineral acids may include, for example, hydrochloric acid, phosphoric acid, sulphuric acid, hydrofluoric acid, and/or any combination of the foregoing mineral acids.

The polycrystalline super hard layer 20 to be leached by examples of the method may, but not exclusively, have a thickness of about 1.5 mm to about 3.5 mm.

After leaching, leached depths of the PCD table may be determined for various portions of the PCD table, through conventional x-ray analysis. Furthermore, the profile of boundary 50 between the leached and unleached regions in the PCD construction 10 may be determined by a number of techniques including non-destructive x-ray analysis wherein the cutter is x-rayed after leaching, SEM imaging techniques wherein a polished section of the construction is obtained by means of a wire EDM. The cross section may be polished in preparation for viewing by a microscope, such as a scanning electron microscope (SEM) and a series of micrographic images may be taken. Each of the images may be analysed by means of image analysis software to determine the profile of the cross-section.

The construction may be processed by grinding and polishing as a post-synthesis treatment to provide an insert for a rock-boring drill bit.

In order to test the wear resistance of the sintered polycrystalline products formed according to the above methods, PCD constructions were produced and leached having the leaching profile of Figure 3. A further control cutter was formed having the same composition as the PCD construction but having a leaching profile having a substantially uniform leach depth extending across the diameter of the construction rather than the tapered leaching profile of Figure 3 for comparison. The diamond layers were then polished and a subjected to a vertical boring mill test. 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 Figure 5. The results provide an indication of the total wear scar area plotted against cutting length.

It will be seen that the PCD compacts formed according to an example having the leaching profile of Figure 3 (CG-B cutter 5 and CG-B cutter 11 in Figure 5) were able to achieve a significantly greater cutting length and smaller wear scar area than the control cutter denoted by CG-A cutter 3 in Figure 5.

Whilst not wishing to be bound by a particular theory, using the conditions described herein it was determined possible to achieve a mechanically stronger and more wear-resistant body of PCD material which, when used as a cutter, may significantly enhance the durability of the cutter produced according to some examples described herein.

The preceding description has been provided to enable others skilled the art to best utilize various aspects of the examples described by way of example herein. This description is not intended to be exhaustive or to be limited to any precise form disclosed. Many modifications and variations are possible. In particular, the method described is equally applicable to the effective leaching of PCD with other acid combinations such as mineral acids and/or complexing agents. Furthermore, whilst the use of the support fixture shown in Figure 4 has been described as being particularly effective for use with the described method, it will be appreciated that the shape of the fixture illustrated and described should not be taken to be limiting as other shapes of fixture will be appreciated.

CLAIMS:

1. A polycrystalline super hard construction comprising a body of polycrystalline diamond (PCD) material comprising a plurality of interstitial regions between inter-bonded diamond grains forming the polycrystalline diamond material; the body of PCD material comprising:

a working surface positioned along an outside portion of the body;

a first region substantially free of a solvent/catalysing material; the first region extending a depth from the working surface into the body of PCD material along a plane substantially perpendicular to the plane along which the working surface extends; and

a second region remote from the working surface that includes solvent/catalysing material in a plurality of the interstitial regions;

a substrate attached to the body of PCD material along an interface with the second region;

a chamfer extending between the working surface and a peripheral side surface of the body of PCD material and defining a cutting edge at the intersection of the chamfer and the peripheral side surface; wherein:

the depth of the first region tapers towards the working surface at the intersection of the first region with the peripheral side surface such that the depth of the first region at the peripheral side surface is less than the depth of the majority of the first region.

2. The polycrystalline super hard construction of claim 1, wherein the first region intersects the peripheral side surface at a position on the chamfer.

3. The polycrystalline super hard construction of claim 1, wherein the first region intersects the peripheral side surface at a position at least around 100 microns from the cutting edge.

4. The polycrystalline super hard construction of claim 1, wherein the first region intersects the peripheral side surface at a position between around 50 to 100 microns from the cutting edge.

5. The polycrystalline super hard construction of claim 1, wherein the first region intersects the peripheral side surface at a position less than around 50 microns from the cutting edge.

6. The polycrystalline super hard construction of any one of the preceding claims, wherein a majority of the diamond grains in the body within a depth of between around 250 microns to around 650 microns from the working surface have a surface which is substantially free of catalyzing material, the remaining grains contacting catalyzing material.

7. The polycrystalline super hard construction of any one of the preceding claims, wherein the interface between the substrate and the second region is substantially planar; or is substantially non-planar and comprises one or more features protruding into or extending from one or other of the body of PCD material or substrate.

8. The polycrystalline super hard construction of any one of the preceding claims, wherein the first and/or second regions comprise diamond grains of two or more diamond grain sizes.

9. The polycrystalline super hard construction according to any one of the preceding claims, wherein the diamond grains comprise natural and/or synthetic diamond grains.

10. The polycrystalline super hard construction according to any one or more of the preceding claims wherein the solvent/catalyst in the second region 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.

11. The polycrystalline super hard construction according to any one of the preceding claims wherein the solvent catalyst in the second region is the solvent catalyst used in sintering the PCD body when forming the PCD construction.

12. A polycrystalline super hard construction according to any one of the preceding claims, wherein the body of polycrystalline diamond material has a thickness of around 2.5 mm to around 3.5 mm or greater.

13. A polycrystalline super hard construction according to any one of the preceding claims, wherein the PCD body comprises at least between around 90 to 95 percent by volume diamond based on the total volume of the diamond body.

14. A cutter for boring into the earth comprising the polycrystalline super hard construction according to any one of the preceding claims.

15. A PCD element for a rotary shear bit for boring into the earth, for a percussion drill bit or for a pick for mining or asphalt degradation, comprising the polycrystalline super hard construction of any one of claims 1 to 13.

16. A drill bit or a component of a drill bit for boring into the earth, comprising a polycrystalline super hard construction according to any one of claims 1 to 13.

17. A method for making a thermally stable polycrystalline diamond construction comprising the steps of:

machining a polycrystalline diamond body attached to a substrate along an interface, the polycrystalline diamond body comprising a plurality of interbonded diamond grains and interstitial regions disposed therebetween, to form a chamfer

extending between a working surface positioned along an outside portion of the body and a peripheral side surface of the body;

treating the PCD body to remove a solvent/catalyst material from a first region of the diamond body while allowing the solvent/catalyst material to remain in a second region of the diamond body;

the chamfer defining a cutting edge at the intersection of the chamfer and the peripheral side surface; wherein:

the step of treating further comprises masking the PCD body at a position between 0 microns to around 300 microns from the working surface; and

the step of removing solvent/catalyst from the interstitial regions in the first region comprises removing the solvent/catalyst to a depth in the first region that tapers towards the working surface at the intersection of the first region with the peripheral side surface such that the depth of the first region at the peripheral side surface is less than the depth of the majority of the first region.

18. The method of claim 17, wherein the step of removing solvent/catalyst from the interstitial regions in the first region comprises removing the solvent/catalyst to a depth in the first region such the first region intersects the peripheral side surface at a position on the chamfer.

19. The method of claim 17, wherein the step of removing solvent/catalyst from the interstitial regions in the first region comprises removing the solvent/catalyst to a depth in the first region such the first region intersects the peripheral side surface at a position at least around 100 microns from the cutting edge.

20. The method of claim 17, wherein the step of removing solvent/catalyst from the interstitial regions in the first region comprises removing the solvent/catalyst to a depth in the first region such the first region intersects the peripheral side surface at a position between around 50 to 100 microns from the cutting edge.

21. The method of claim 17, wherein the step of removing solvent/catalyst from the interstitial regions in the first region comprises removing the solvent/catalyst to a depth in the first region such the first region intersects the peripheral side surface at a position less than around 50 microns from the cutting edge.

22. The method of any one of claims 17 to 21, wherein the step of removing solvent/catalyst from the interstitial regions in the first region comprises removing the solvent/catalyst such that a majority of the diamond grains in the body within a depth of between around 250 microns to around 650 microns from the working surface have a surface which is substantially free of catalyzing material, the remaining grains contacting catalyzing material.

23. The method of any one of claims 17 to 22, wherein the step of masking the PCD construction protects the substrate and the peripheral side surface from exposure to a treating agent used during the step of treating.

24. The method of any one of any one of claims 17 to 23, wherein prior to the step of treating, forming the PCD construction, the step of forming comprising:

providing a mass of diamond grains;

arranging the mass of diamond grains to form a pre-sinter assembly; and

treating the pre-sinter assembly in the presence of catalyst/solvent material for the diamond grains at an ultra-high pressure of around 5.5 GPa or greater and a temperature at which the diamond material is more thermodynamically stable than graphite to sinter together the grains of diamond material to form a polycrystalline diamond construction.

25. The method of any one of claims 17 to 24, wherein prior to the step of treating, the method further comprising machining the polycrystalline diamond body to a final dimension.

26. The method of any one of claims 17 to 24, wherein after the step of treating, the method further comprising machining the polycrystalline diamond body to a final dimension.

27. A polycrystalline super hard construction substantially as hereinbefore described with reference to any one example as that example is illustrated in Figure 3 of the accompanying drawings.

28. A method of making a thermally stable polycrystalline diamond construction substantially as hereinbefore described with reference to any one example as that example is illustrated in the accompanying drawings.

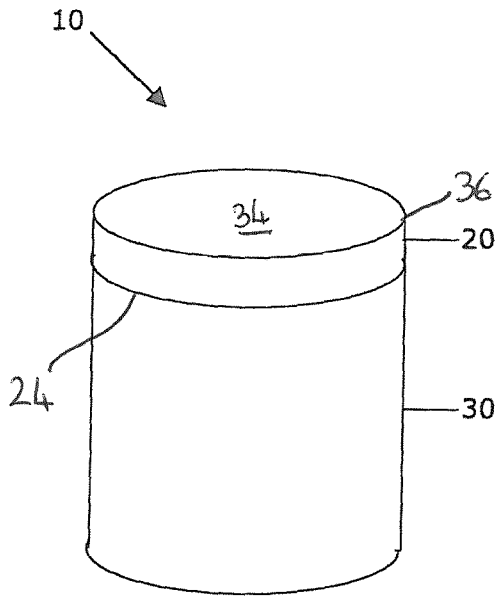


FIG 1

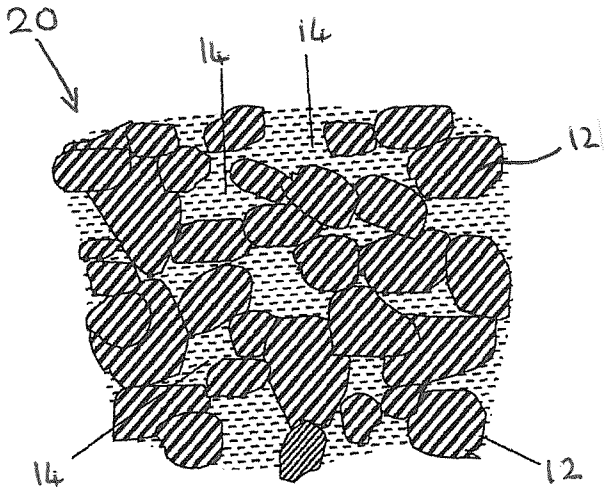


FIG. 2

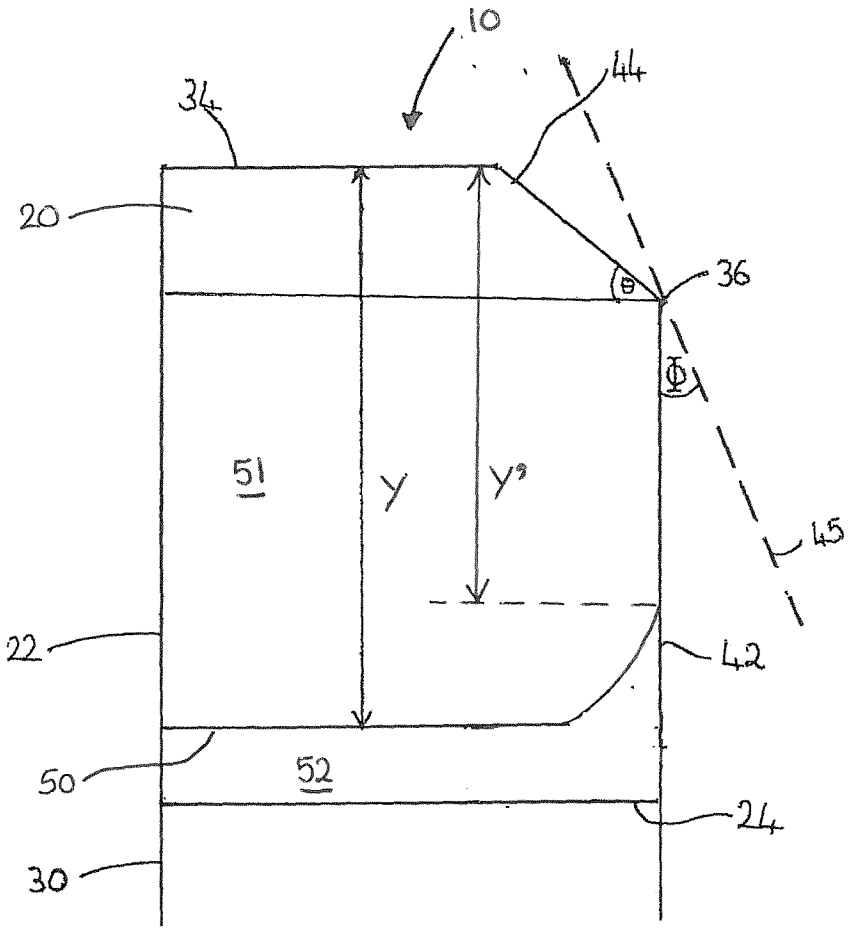


FIG. 3

FIG. 4

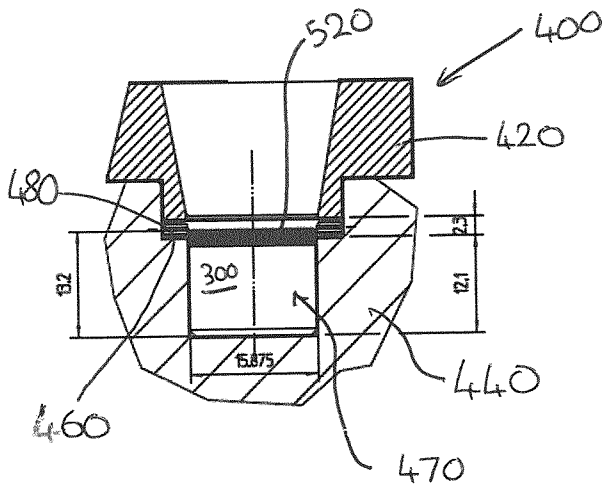
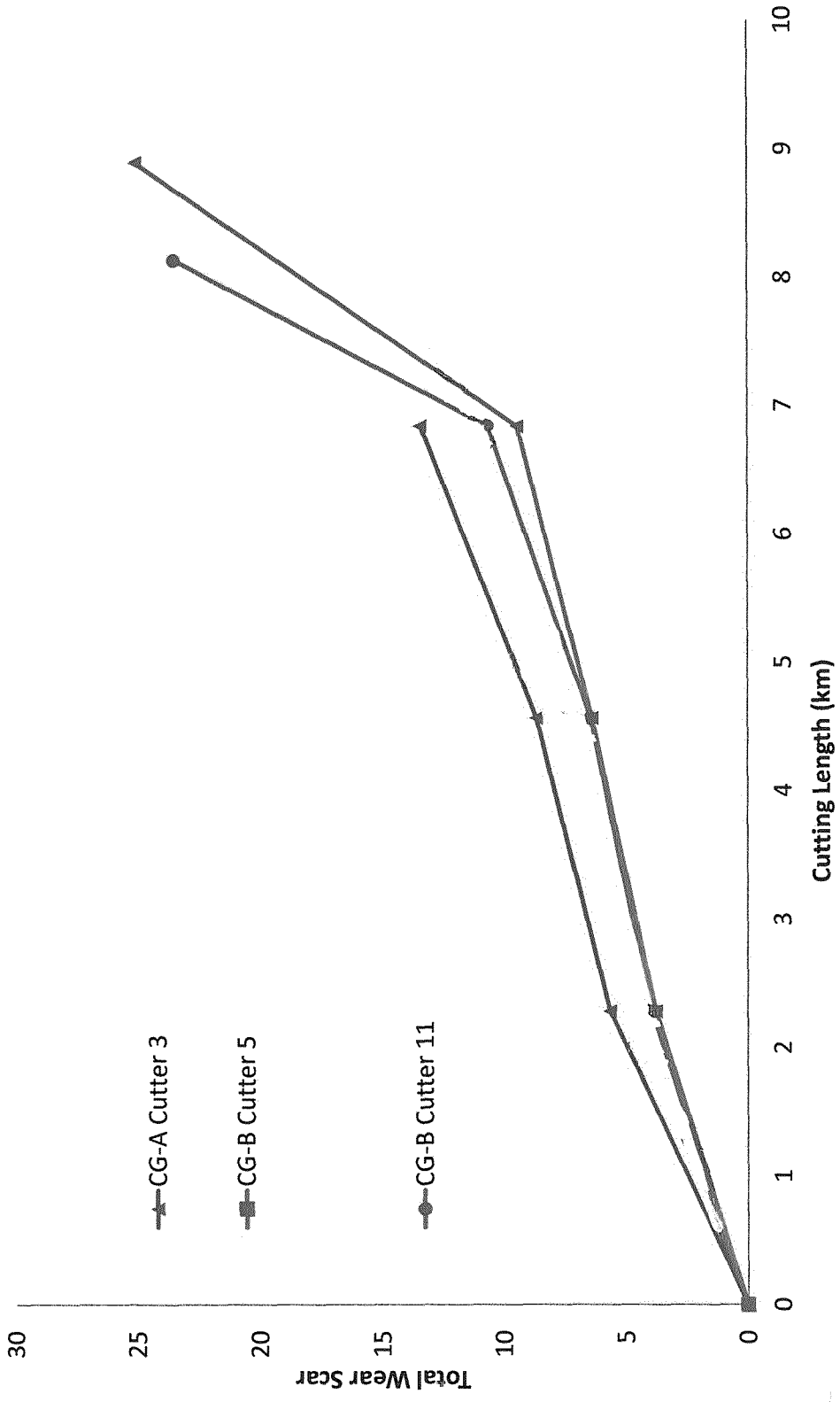


FIG.5


Total Wear Scar
0
5
10
15
20
25
30
Cutting Length (km)
0
1
2
3
4
5
6
7
8
9
10
CG-A Cutter 3
CG-B Cutter 5
CG-B Cutter 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/077433

A. CLASSIFICATION OF SUBJECT MATTER
INV. E21B10/573
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
E21B C04B C22C B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 8 596 387 B1 (SANI MOHAMMAD N [US] ET AL) 3 December 2013 (2013-12-03) figure 1B column 4, lines 11-30	1-28
A	US 2009/133938 A1 (HALL DAVID R [US] ET AL) 28 May 2009 (2009-05-28) figures 21a-f paragraphs [0007], [0009], [0044], [0050] - [0052], [0060]	1,17

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search	Date of mailing of the international search report
13 March 2015	26/03/2015

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/077433

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BILLY PLEMONS ET AL: "New Cutter Technology for Faster Drilling in Hard/Abrasive Formations", SOCIETY OF PETROLEUM ENGINEERS, 10 June 2010 (2010-06-10), XP055173339, https://www.onepetro.org/conference-paper/SPE-132143-MS?sort=&start=0&q=leaching+and+TSP&from_year=&peer_reviewed=&published_between=&fromSearchResults=true&to_year=&rows=10#&event-fire=false pages 1-2	1,17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/077433

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		US 8925655 B1	06-01-2015
US 2009133938 A1	28-05-2009	NONE	