(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
7 February 2013 (07.02.2013)

WIPO | PCT

(10) **International Publication Number**
WO 2013/017641 A1

(51) **International Patent Classification**:
B22F 3/14 (2006.01) ***E21B 10/567*** (2006.01)
C22C 26/00 (2006.01) ***B22F 7/06*** (2006.01)

(21) **International Application Number**:
PCT/EP2012/065082

(22) **International Filing Date**:
1 August 2012 (01.08.2012)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:

1113299.0	2 August 2011 (02.08.2011)	GB
61/514,414	2 August 2011 (02.08.2011)	US
1113391.5	3 August 2011 (03.08.2011)	GB
61/514,758	3 August 2011 (03.08.2011)	US
1116899.4	30 September 2011 (30.09.2011)	GB
61/553,722	31 October 2011 (31.10.2011)	US

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

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(54) **Title**: POLYCRYSTALLINE DIAMOND CONSTRUCTION AND METHOD FOR MAKING SAME

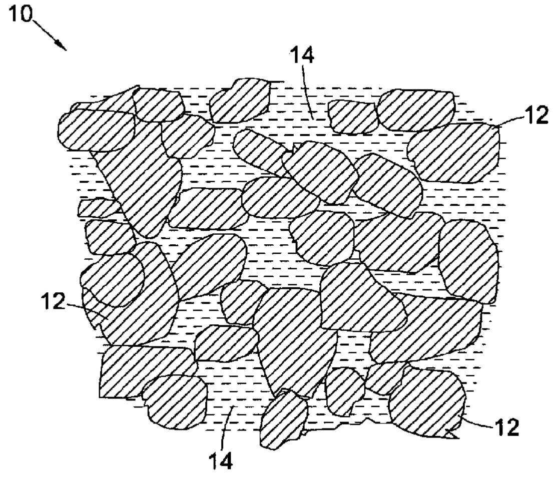

Fig. 1

(57) **Abstract**: A polycrystalline diamond construction comprising a body of polycrystalline diamond material is formed of a mass of diamond grains exhibiting intergranular bonding and defining a plurality of interstitial regions therebetween, and a non-diamond phase at least partially filling a plurality of the interstitial regions to form non-diamond phase pools, the non-diamond phase pools each having an individual cross-sectional area. The percentage of non- diamond phase in the total area of a cross-section of the body of polycrystalline diamond material and the mean of the individual cross-sectional areas of the non-diamond phase pools in the image analysed using an image analysis technique at a selected magnification is less than 0.7, or less than 0.340 microns squared, or between around 0.005 to 0.340 microns squared depending on the percentage of non-diamond phase in the total area of the cross-section of the polycrystalline diamond construction. There is also disclosed a method of making such a construction.

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TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

POLYCRYSTALLINE DIAMOND CONSTRUCTION AND METHOD FOR MAKING SAME

Field

This disclosure relates to a polycrystalline diamond construction formed of polycrystalline diamond (PCD) material, a method for making the same and tools comprising same, particularly but not exclusively for use in boring into the earth.

Background

Polycrystalline diamond (PCD) material comprises a mass of inter-bonded diamond grains and interstices between the diamond grains. A body of PCD material may be made by subjecting an aggregated mass of diamond grains to a high pressure and temperature in the presence of a sintering aid which is typically a metal such as cobalt, nickel, iron or an alloy containing one or more such metals and which may promote the inter-bonding of diamond grains. The sintering aid may also be referred to as a catalyst material for diamond and a binder material. Interstices within the sintered PCD material may be wholly or partially filled with residual catalyst material. PCD may be formed on a substrate, such as a cobalt-cemented tungsten carbide substrate, which may provide a source of cobalt catalyst material for the PCD.

PCD material may be used as an abrasive compact in a wide variety of tools for cutting, machining, milling, grinding, drilling or degrading hard or abrasive materials such as rock, metal, ceramics, composites and wood-containing materials. For example, tool inserts comprising PCD material 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 may become elevated as it engages rock or other workpieces or bodies. Mechanical properties of PCD material such as abrasion resistance, hardness and strength tend to deteriorate at elevated temperatures, which may be promoted by the residual catalyst material within the body of PCD material.

It is desirable to improve the abrasion resistance of a body of PCD material when used as an abrasive compact in tools such as those mentioned above, as this allows extended use of the cutter, drill or machine in which the abrasive compact is located. This is typically achieved by manipulating variables such as average diamond particle/grain size, overall binder content, particle density and the like.

For example, it is well known in the art to increase the abrasion resistance of an ultrahard composite by reducing the overall grain size of the component ultrahard particles. Typically, however, as these materials are made more wear resistant they become more brittle or prone to fracture.

Abrasive compacts designed for improved wear performance will therefore tend to have poor impact strength or reduced resistance to spalling. This trade-off between the properties of impact resistance and wear resistance makes designing optimised abrasive compact structures, particularly for demanding applications, inherently self-limiting.

Additionally, because finer grained structures will typically contain more solvent/catalyst or metal binder, they tend to exhibit reduced thermal stability when compared to coarser grained structures. This reduction in optimal behaviour for finer grained structures can cause substantial problems in practical applications where the increased wear resistance is nonetheless required for optimal performance.

Prior art methods to solve this problem have typically involved attempting to achieve a compromise by combining the properties of both finer and coarser ultrahard particle grades in various manners within the ultrahard abrasive layer.

Another conventional solution is to remove, typically by acid leaching, the catalyst/solvent or binder phase from the PCD material.

It is typically extremely difficult and time consuming to remove the bulk of a metallic catalyst/solvent effectively from a PCD table, particularly from the thicker PCD tables required by current applications. Achieving appreciable leaching depths can take so long as to be commercially unfeasible or require undesirable interventions such as extreme acid treatment or physical drilling of the PCD tables.

The development of an abrasive compact that can achieve improved properties of impact and fatigue resistance consistent with coarser grained materials, whilst still retaining good wear resistance and reduced incidence of cracking is highly desirable.

Summary

Viewed from a first aspect there is provided a polycrystalline diamond construction comprising a body of polycrystalline diamond material formed of:

a mass of diamond grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, and

a non-diamond phase at least partially filling a plurality of the interstitial regions to form non-diamond phase pools, the non-diamond phase pools each having an individual cross-sectional area,

wherein the percentage of non-diamond phase in the total area of a cross-section of the body of polycrystalline diamond material is between around 0 to 5 %, and the mean of the individual cross-sectional areas of the non-diamond phase pools in an analysed image of a cross-section through the body of polycrystalline material is less than around 0.7 microns squared when analysed using an image analysis technique at a magnification of around 1000 and an image area of 1280 by 960 pixels.

Viewed from a second aspect there is provided a polycrystalline diamond construction comprising a body of polycrystalline diamond material formed of:

a mass of diamond grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, and

a non-diamond phase at least partially filling a plurality of the interstitial regions to form non-diamond phase pools, the non-diamond phase pools each having an individual cross-sectional area,

wherein the percentage of non-diamond phase in the total area of a cross-section of the body of polycrystalline diamond material is between around 5 to 10 %, and the mean of the individual cross-sectional areas of the non-diamond phase pools in an analysed image of a cross-section through the body of polycrystalline diamond material is less than around 0.340 microns squared when analysed using an image analysis technique at a magnification of around 1000 and an image area of 1280 by 960 pixels.

Viewed from a third aspect there is provided a polycrystalline diamond construction comprising a body of polycrystalline diamond material formed of:

a mass of diamond grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, and

a non-diamond phase at least partially filling a plurality of the interstitial regions to form non-diamond phase pools, the non-diamond phase pools each having an individual cross-sectional area,

wherein the percentage of non-diamond phase in the total area of a cross-section of the polycrystalline diamond construction is between around 10 to 15 %, and

the mean of the individual cross-sectional areas of the non-diamond phase pools in an analysed image of a cross section through the body of polycrystalline material is less than around 0.340 microns squared when analysed using an image analysis technique at a magnification of around 3000 and an image area of 1280 by 960 pixels.

Viewed from a fourth aspect there is provided a polycrystalline diamond construction comprising a body of polycrystalline diamond material formed of:

a mass of diamond grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, and

a non-diamond phase at least partially filling a plurality of the interstitial regions to form non-diamond phase pools, the non-diamond phase pools each having an individual cross-sectional area,

wherein the percentage of non-diamond phase in the total area of a cross-section of the polycrystalline diamond construction is between around 15 to 30%, and

the mean of the individual cross-sectional areas of the non-diamond phase pools in an analysed image of a cross section through the body of polycrystalline material is between around 0.005 to 0.340 microns squared when analysed using an image analysis technique at a magnification of around 10000 and an image area of 1280 by 960 pixels.

In some embodiments, the body of polycrystalline diamond material has a largest dimension of around 6mm or greater.

In some embodiments, the body of polycrystalline diamond material has a thickness of around 0.3mm or greater.

Viewed from a fifth aspect there is provided a method for making a polycrystalline diamond construction, the method comprising:

providing a mass of diamond grains having a first average size;

arranging the mass of diamond grains to form a pre-sinter assembly with a body of material for forming a substrate; and

treating the pre-sinter assembly in the presence of a catalyst material for diamond at an ultra-high pressure of around 7GPa or greater and a temperature at which diamond is more thermodynamically stable than graphite to sinter together the diamond grains and a substrate bonded thereto along an interface to form an integral PCD construction; the diamond grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, a non-diamond phase at least partially filling a plurality of the interstitial regions to form non-diamond phase pools, the non-diamond phase pools each having an individual cross-sectional area,

wherein the percentage of non-diamond phase in the total area of a cross-section of the body of polycrystalline diamond material is between around 0 to 5 %, and the mean of the individual cross-sectional areas of the non-diamond phase pools in the image analysed is less than around 0.7 microns squared when analysed using an image analysis technique at a magnification of around 1000 and an image area of 1280 by 960 pixels; or

the percentage of non-diamond phase in the total area of a cross-section of the body of polycrystalline diamond material is between around 5 to 10 %, and the mean of the individual cross-sectional areas of the non-diamond phase pools in the image analysed is less than around 0.340 microns squared when analysed using an image analysis technique at a magnification of around 1000 and an image area of 1280 by 960 pixels; or

the percentage of non-diamond phase in the total area of a cross-section of the polycrystalline diamond construction is between around 10 to 15 %, and the mean of the individual cross-sectional areas of the non-diamond phase pools in the image analysed is less than around 0.340 microns squared when analysed using an image analysis technique at a magnification of around 3000 and an image area of 1280 by 960 pixels; or the percentage of non-diamond phase in the total area of a cross-section of the polycrystalline diamond construction is between around 15 to 30 %, and the mean of the individual cross-sectional areas of the non-diamond phase pools in the image analysed is between around 0.005 to 0.340 microns squared when analysed using an image analysis technique at a magnification of around 10000 and an image area of 1280 by 960 pixels.

Brief Description of Drawings

Non-limiting embodiments will now be described by way of example and with reference to the accompanying drawings 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 side view of an example assembly comprising first and second structures;

Figure 4 is a schematic diagram of part of an example pressure and temperature cycle for making a super-hard construction;

Figures 5 to 9 are schematic diagrams of parts of example pressure and temperature cycles for making a PCD construction; and

Figures 10a and 10b are processed images of a micrograph of a polished section of an embodiment of a body of PCD material at different diamond densities.

Detailed description

As used herein, “polycrystalline diamond” (PCD) material comprises a mass of diamond grains, a substantial portion of which are directly inter-bonded with each other and in which the content of diamond is at least about 80 volume percent of the material. In one embodiment of PCD material, interstices between the diamond gains may be at least partly filled with a binder material comprising a catalyst for diamond. As used herein, “interstices” or “interstitial regions” are regions between the diamond grains of PCD material. In embodiments of PCD material, interstices or interstitial regions may be substantially or partially filled with a material other than diamond, or they may be substantially empty. Embodiments of PCD material may comprise at least a region from which catalyst material has been removed from the interstices, leaving interstitial voids between the diamond grains.

As used herein, a “PCD structure” comprises a body of PCD material.

As used herein, a “metallic” material is understood to comprise a metal in unalloyed or alloyed form and which has characteristic properties of a metal, such as high electrical conductivity.

As used herein, “catalyst material” for diamond, which may also be referred to as solvent / catalyst material for diamond, means a material that is capable of promoting the growth of diamond or the direct diamond-to-diamond inter-growth between diamond grains at a pressure and temperature condition at which diamond is thermodynamically stable.

A filler or binder material is understood to mean a material that wholly or partially fills pores, interstices or interstitial regions within a polycrystalline structure.

A multi-modal size distribution of a mass of grains is understood to mean that the grains have a size distribution with more than one peak, each peak corresponding to a respective “mode”. Multimodal polycrystalline bodies may be made by providing more than one source of a plurality of grains, each source comprising grains having a substantially different average size, and blending together the grains or particles from the sources. In one embodiment, the PCD structure may comprise diamond grains having a multimodal distribution.

As used herein, the term ‘total binder area’ is expressed as the percentage of non-diamond phase(s) in the total cross-sectional area of a polished cross section of the body of PCD material being analysed.

With reference to Figure 1, a body of PCD material 10 comprises a 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.

Figure 2 shows an embodiment of a PCD composite compact 20 for use as a cutter comprising a body of PCD material 22 integrally bonded at an interface 24 to a substrate 30. The substrate 30 may be formed of, for example, 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 22 during formation of the compact 20.

An example of a method for producing the PCD compact 20 comprising the body of PCD material 22, as shown in Figures 1 and 2, is now described with reference to Figures 3 to 9. As shown in Figure 3, a PCD structure (the second structure) 200 is disposed adjacent a cemented carbide substrate (the first structure) 300, a thin layer or film 400 of binder material comprising Co connecting opposite major surfaces of the PCD structure 200 and the substrate 300 to comprise an assembly encased in a housing 100 for an ultra-high pressure, high temperature press (not shown). The CTE of the PCD material comprised in the PCD structure 200 is in the range from about 2.5 X

10-6 per degree Celsius to about 4 X 10-6 per degree Celsius and the CTE of the cobalt-cemented tungsten carbide material comprised in the substrate 300 is in the range from about 5.4 X 10-6 per degree Celsius to about 6 X 10-6 per degree Celsius (the CTE values are for 25 degrees Celsius). In this example, the substrate 300 and the PCD structure 200 contain binder material comprising Co. It is estimated that PCD material would have a Young's modulus from about 900 gigapascals to about 1,400 gigapascals depending on the grade of PCD and that the substrate would have a Young's modulus from about 500 gigapascals to about 650 gigapascals depending largely on the content and composition of the binder material.

Figure 4 shows a schematic phase diagram of carbon in terms of pressure p and temperature T axes, showing the line D-G of thermodynamic equilibrium between diamond and graphite allotropes, diamond being the more thermally stable in region D and graphite being the more thermally stable in region G of the diagram. The line S-L shows schematically the temperature at which the binder material melts or solidifies at various pressures, this temperature tending to increase with increasing pressure. Note that this temperature is likely to be different from that for the binder material in a pure form because the presence of carbon from the diamond and or some dissolved WC is expected to reduce this temperature, since the presence of carbon in solution is expected to reduce the melting point of cobalt and other metals. The assembly described with reference to Figure 3 may be under a first pressure P1 of about 7.5 gigapascals to about 8 gigapascal and at a temperature of about 1,450 degrees Celsius to about 1,800 degrees Celsius, at a condition at which the PCD material has been formed by sintering an aggregation of diamond grains disposed adjacent the substrate. There may be no substantial interruption between the formation of the PCD in situ at the sinter pressure and sinter temperature on the one hand and subjecting the assembly to the first pressure P1 on the other; it is the subsequent relationship between the reduction of the pressure and the temperature at stages I and II that is the more relevant aspect of the method. At the sinter temperature, the Co binder material will be molten and expected to promote the direct inter-growth sintering of the diamond grains to form the PCD material, the diamond comprised in the PCD material being thermodynamically substantially more stable than graphite at the sinter temperature and sinter pressure.

With further reference to Figure 4, the pressure and temperature of the assembly may be reduced to ambient levels in stages I, II and III. In a particular example, the pressure may be reduced in stage I from the first pressure P1 to a second pressure P2 of about 5.5 gigapascals to about 6 gigapascals while reducing the temperature to about 1,350 degrees Celsius to about 1,500 degrees Celsius to ensure that the pressure-temperature condition remains such that diamond is more thermodynamically stable than graphite and that the binder material remains substantially molten. In stage II, the temperature may then be reduced to about 1,100 degrees Celsius to a temperature in the range of about 1,200 degrees Celsius while maintaining the pressure above the line D-G in the diamond-stable region D to solidify the binder material; and in stage III the pressure and temperature may be reduced to ambient levels in various ways. The PCD construction can then be removed from the press apparatus. Note that the stages I, II and III are used merely to explain Figure 4 and there may not be clear distinction between these stages in practice. For example these stages may flow smoothly into one another with no substantial period of maintaining pressure and temperature conditions at the end of a stage. Alternatively, some or all of the stages may be distinct and the pressure and temperature condition at the end of a stage may be maintained for a period.

In some examples, a pre-sinter assembly for making a PCD or PCBN construction, for example, may be prepared and provided in situ at the first pressure P1 as follows. A cup may be provided into which an aggregation comprising a plurality of diamond or CBN grains and a substrate may be assembled, the interior shape of the cup being generally that of the desired shape of the PCD or PCBN structure (having regard to likely distortion during the sintering step). The aggregation may comprise substantially loose diamond or CBN grains or diamond- or CBN-containing pre-cursor structures such as granules, discs, wafers or sheets. The aggregation may also include catalyst material for diamond, matrix material for PCBN, or pre-cursor material for catalyst or matrix material, which may be admixed with the diamond or CBN grains and or deposited on the surfaces of the diamond or CBN grains. The diamond or CBN grains may have a mean size of at least about 0.1 micron and or at most about 75 microns and may be substantially mono-modal or multi-modal. The aggregation may also contain additives for reducing abnormal diamond or CBN grain growth or the aggregation may be substantially free of catalyst material or additives. Alternatively or additionally, another source of catalyst or matrix material such as cobalt may be provided, such as the binder material in a cemented carbide substrate. A sufficient quantity of the aggregation may be placed into the cup and then the substrate may inserted into the cup with a proximate end pushed against the aggregation. The pre-sinter assembly comprising the aggregation and the substrate may be encased within a metal jacket comprising the cup, subjected to a heat treatment to burn off organic binder that may be comprised in the aggregation, and encapsulated within a housing (which may be referred to as a capsule) suitable for an ultra-high pressure press. The housing may be placed in a suitable ultra-high pressure press apparatus and subjected to a sinter pressure and sinter temperature to form the assembly comprising a PCD or PCBN structure adjacent the substrate, connected by a thin film of molten binder comprising cobalt. In examples such as these, the sinter pressure may be regarded as the first pressure P1.

In an example arrangement, a pre-sinter assembly for making a PCD or PCBN construction may be prepared and provided in a press apparatus at the first pressure P1 as follows. A PCD or PCBN structure may be provided pre-sintered in a previous ultra-high pressure, high temperature process. The

PCD or PCBN structure may contain binder or matrix material comprising cobalt, located in interstitial regions between the diamond or CBN grains comprised in the PCD or PCBN material. In the case of PCD material, the PCD structure may have at least a region substantially free of binder material. For example, the PCD structure may have been treated in acid to remove binder material from the interstices at least adjacent a surface of the PCD structure or throughout substantially the entire volume of the PCD structure (or variations between these possibilities), leaving at least a region that may contain pores or voids. In some examples, voids thus created may be filled with a filler material that may or may not comprise binder material. The PCD or PCBN structure may be placed against a substrate and the resulting pre-construction assembly may be encased within a housing suitable for an ultra-high pressure press. The housing may be placed in a suitable ultra-high pressure press apparatus and the subjected to the first pressure P1 at a temperature at which the binder material is in the liquid state (at a condition in region D of Figure 4).

Example methods for making an example PCD construction will be described below with reference to Figures 5 to 9. In each figure, only part of the pressure and temperature cycle is shown, the part beginning at respective first pressures P1, at which the PCD material comprised in the construction becomes formed by sintering, and ending after the temperature has been reduced sufficiently to solidify the binder material and the pressure has been reduced from the second pressure P2.

In some examples, a pre-sinter assembly may be provided, comprising an aggregation of a plurality of diamond grains located adjacent a surface of a substrate comprising cobalt-cemented tungsten carbide. The diamond grains may have a mean size in the range of about 0.1 to about 40 microns. The pre-sinter assembly may be encapsulated within a capsule for an ultra-high pressure press apparatus, into which the capsule may be loaded. The capsule may be pressurised at ambient temperature to a pressure of at least about 6.5 gigapascals and heated to a temperature in the range of about 1,500 to about 1,600 degrees Celsius, substantially greater than the melting point (at the pressure) of the cobalt-based binder material comprised in the substrate and causing the cobalt material to melt. At this temperature the pre-sinter assembly may be at a first pressure P1 in the range from about 7.5 to about 10 gigapascals (P1 may be somewhat higher than 7 gigapascals at least partly as a result of the increase in temperature). The first pressure P1 and the temperature may be substantially maintained for at least about 1 minute, or in any event sufficiently long to sinter together the diamond grains (in these examples, the sinter pressure will be substantially P1). The pressure may then be reduced from first pressure P1 through a second pressure P2 in the range from about 5.5 to about 8.5 gigapascals. The second pressure may be the pressure at which the binder material begins to solidify as the temperature is reduced through its solidification temperature.

The temperature of the pre-sinter assembly may be reduced simultaneously with pressure, provided that it remains greater than the temperature at which the cobalt-based binder material will have completely solidified. As the pressure is reduced from P2, the temperature may also be reduced through the solidification line of the cobalt-based binder material, resulting in the solidification of the binder material. In these particular examples, the pressure is substantially continuously reduced from the first pressure P1, through the second pressure P2 and through the pressure(s) at which the binder material solidifies, without substantial pause. The rate of reduction of the pressure and or temperature may be varied or the rate of the reduction of either or both may be substantially constant, at least until the cobalt-based binder material has solidified. The temperature may also be reduced substantially continuously at least until it is sufficiently low for substantially all the cobalt-based binder material to have solidified. The temperature and pressure may then be reduced to ambient conditions, the capsule removed from the ultra-high pressure press apparatus and the construction removed from the capsule.

The construction may comprise a sintered PCD structure formed joined to the substrate, the PCD structure having become joined to the substrate in the same general step in which the PCD material was formed by the sintering together of the plurality of diamond grains. A thin layer rich in cobalt will be present between the PCD structure and the substrate, joining together these structures.

In a particular example method illustrated in Figure 5, the first pressure P1 is about 7.6 gigapascals, the temperature at the first pressure being in the range of about 1,500 to about 1,600 degrees Celsius, and an example second pressure P2 is about 6.8 gigapascals.

In a particular example method illustrated in Figure 6, the first pressure P1 is about 7.7 gigapascals, the temperature at the first pressure being in the range of about 1,500 to about 1,600 degrees Celsius, and an example second pressure P2 is about 6.9 gigapascals.

In a particular example method illustrated in Figure 7, the first pressure P1 is about 7.8 gigapascals, the temperature at the first pressure being in the range of about 1,500 to about 1,600 degrees Celsius, and an example second pressure P2 is about 6.9 gigapascals.

In a particular example method illustrated in Figure 8, the first pressure P1 is about 7.9 gigapascals, the temperature at the first pressure being in the range of about 1,500 to about 1,600 degrees Celsius, and an example second pressure P2 is about 5.5 gigapascals.

In the example method illustrated in Figure 9, the first pressure P1 is about 9.9 gigapascals, the temperature at the first pressure being about 2,000 degrees Celsius, and an example second pressure P2 may be about 8.1 gigapascals.

Note that the line S-L in Figures 5 to 9, indicating the melting and solidification temperatures of cobalt-based binder material in the presence of carbon, was estimated based on a calculation using available data. In practice, it may be advisable not to rely completely on calculated values lying on S-L but to carry out trial and error experiments to discover the melting and solidification temperatures for the particular binder material and pressure being used.

The method used to measure the pressure and temperature cycles as illustrated in Figures 5 to 9 is measured using so-called K-type thermocouples and knowledge of the melting temperatures of copper (Cu) and silver (Ag). Data for the melting points of Cu and Ag measured using K-type thermocouples up at 60 kilobars was published by P.W. Mirwald and G.C. Kennedy in an article entitled “The melting curve of gold, silver and copper to 60-Kbar pressure – a reinvestigation”, published on 10 November 1979 in the Journal of Geophysical Research volume 84, number B12, pages 6750 to 6756, by The American Geophysical Union. A K-type thermocouple may also be referred to as a “chromel-alumel” thermocouple, in which the “chromel” component comprises 90 per cent nickel and 10 per cent chromium, and the “alumel” component comprises 95 per cent nickel, 2 per cent manganese, 2 per cent aluminium and 1 per cent silicon. The method includes inserting the junction of a first K-type thermocouple into a body consisting essentially of Cu and the junction of a second K-type thermocouple into a body consisting essentially of Ag, and positioning the two bodies proximate the pre-sinter assembly within the capsule. The readings from both thermocouples are recorded throughout at least a part of the pressure and temperature cycle and the readings processed and converted to pressure and temperature values according to the published data.

In some examples, the construction may comprise a polycrystalline cubic boron nitride (PCBN) structure joined to a cobalt cemented carbide substrate. In some example methods, an aggregation comprising cubic boron nitride (CBN) grains may be provided. The CBN grains may have a mean size of at least about 0.1 micron and at most about 30 microns. The aggregation may comprise tungsten carbide grains and or pre-cursor material for forming a matrix within which the CBN grains can dispersed in sintered PCBN material. In some examples, the aggregation may comprise a mixture of cubic boron nitride powder with a binder material containing Ti, Al, W or Co and the mixture cast into sheets using a plasticizer material. In some examples, the super-hard structure may comprise PCBN material substantially as described in international application number WO2007049140 and may be manufactured by a method including providing a powdered composition suitable for the manufacture of PCBN, the powder comprising at least 80 volume per cent CBN particles and a powdered binder material, and subjecting the powder composition to attrition milling. The composition may comprise CBN particles of more than one average particle size. In various examples, the average size of the CBN particles may be at most about 12 microns or at most 2 microns. The binder material may include one or more of phase(s) containing aluminium, silicon, cobalt, molybdenum, tantalum, niobium, nickel, titanium, chromium, tungsten, yttrium, carbon and iron. The binder material may include powder with uniform solid solution of more than one of aluminium, silicon, cobalt, nickel, titanium, chromium, tungsten, yttrium, molybdenum, niobium, tantalum, carbon and iron.

Various kinds of ultra-high pressure presses may be used, including belt-type, tetrahedral multi-anvil, cubic multi-anvil, walker-type or torroidal presses. The choice of press type is likely to depend on the volume of the super-hard construction to be made and the pressure and temperature desired for sintering the super-hard material. For example, tetrahedral and cubic presses may be suitable for sintering commercially viable volumes of PCD and PCBN material at pressures of at least about 7 gigapascals or at least about 7.7 gigapascals.

Some example methods may include subjecting a PCD or PCBN construction to a heat treatment at a temperature of at least about 500 degrees Celsius, at least about 600 degrees Celsius or at least about 650 degrees Celsius for at least about 5 minutes, at least about 15 minutes or at least about 30 minutes. In some embodiments, the temperature may be at most about 850 degrees Celsius, at most about 800 degrees Celsius or at most about 750 degrees Celsius. In some embodiments, the PCD structure may be subjected to the heat treatment for at most about 120 minutes or at most about 60 minutes. In one embodiment, the PCD or PCBN structure may be subjected to the heat treatment in a vacuum. For example, United States patent number 6,517,902 discloses a form of heat treatment for pre-form elements having a facing table of PCD bonded to a substrate of cemented tungsten carbide with a cobalt binder. The substrate includes an interface zone with at least 30 percent by volume of the cobalt binder in a hexagonal close packed crystal structure.

While wishing not to be bound by a particular theory, the method may result in a reduced likelihood or frequency of cracking of super-hard constructions because the residual stress within the construction is reduced.

Non-limiting examples are described in more detail below.

Example 1

A PCD insert for a rock-boring drill bit was made as described below.

A pre-sinter assembly was prepared, comprising an aggregation of a plurality of diamond grains disposed against a proximate end of a generally cylindrical cemented carbide substrate. The aggregation comprised a plurality of wafers comprising diamond grains dispersed within an organic binder material, the diamond grains having a mean size of at least about 15 microns and at most about 30 microns. The substrate comprised about 90 weight percent WC grains cemented together by a binder material comprising Co. The pre-sinter assembly was enclosed in a metal jacket and heated to burn off the organic binder comprised in the wafers, and the jacketed, pre-sinter assembly was encapsulated in a capsule for an ultra-high pressure, high temperature multi-anvil press apparatus.

The pre-sinter assembly was subjected to a pressure of about 7.7 gigapascals and a temperature of about 1,550 degrees Celsius to sinter the diamond grains directly to each other to form a layer of PCD material connected to the proximate end of the substrate by a film of molten binder material comprising cobalt from the substrate. The pressure was reduced to about 5.5 gigapascals and the temperature was reduced to about 1,450 degrees Celsius, maintaining conditions at which the diamond comprised in the PCD is thermodynamically stable (in relation to graphite, a softer allotrope of carbon) and at which the binder material is in the liquid phase. The temperature was then reduced to about 1,000 degrees Celsius to solidify the binder material and form a construction comprising the layer of PCD bonded to the substrate by the solidified binder material, and the pressure and temperature were then reduced to ambient conditions.

The construction was subjected to a heat treatment at 660 degrees Celsius for about 2 hours at substantially ambient pressure in a substantially non-oxidising atmosphere, and then cooled to ambient temperature. No cracks were evident in the PCD layer after the heat treatment.

The construction was processed by grinding and polishing to provide an insert for a rock-boring drill bit.

For comparison, a reference construction was made as follows. A pre-sinter assembly was prepared as described above in relation to the example pre-sinter assembly. The pre-sinter assembly was subjected to a pressure of about 7.7 gigapascal and a temperature of about 1,550 degrees Celsius to sinter the diamond grains directly to each other to form a layer of PCD material connected to the proximate end of the substrate by a film of molten binder material comprising cobalt from the substrate. The temperature was reduced to about 1,000 degrees Celsius to solidify the binder material and form a construction comprising the layer of PCD bonded to the substrate by the solidified binder material, and then the pressure and temperature were reduced to ambient conditions. The construction was subjected to a heat treatment at 660 degrees Celsius for about 2 hours at substantially ambient pressure in a substantially non-oxidising atmosphere, and then cooled to ambient temperature. Severe cracks were evident at the side of the PCD layer after the heat treatment.

Example 2

A PCD insert for a rock-boring drill bit was made as described below.

A pre-sinter assembly was prepared, comprising a PCD structure having a generally disc-like shape disposed against a proximate end of a generally cylindrical cemented carbide substrate. PCD structure had been made in a previous step involving sintering together an aggregation of a plurality of diamond grains at an ultra-high pressure of less than about 7 gigapascals and a high temperature (at which the diamond was thermodynamically more stable than graphite). The substrate comprised about 90 weight percent WC grains cemented together by a binder material comprising Co. The pre-sinter assembly was enclosed in a metal jacket and heated to burn off the organic binder comprised in the wafers, and the jacketed, pre-sinter assembly was encapsulated in a capsule for an ultra-high pressure, high temperature multi-anvil press apparatus.

The pre-sinter assembly was subjected to a pressure of about 7.7 gigapascals and a temperature of about 1,550 degrees Celsius to modify the microstructure of the PCD structure. The pressure was reduced to about 5.5 gigapascals and the temperature was reduced to about 1,450 degrees Celsius, maintaining conditions at which the diamond comprised in the PCD is thermodynamically stable (in relation to graphite, a softer allotrope of carbon) and at which the binder material is in the liquid phase. The temperature was then reduced to about 1,000 degrees Celsius to solidify the binder material and form a construction comprising the layer of PCD bonded to the substrate by the solidified binder material, and the pressure and temperature were then reduced to ambient conditions.

The construction was subjected to a heat treatment at 660 degrees Celsius for about 2 hours at substantially ambient pressure in a substantially non-oxidising atmosphere, and then cooled to ambient temperature. No cracks were evident in the PCD layer after the heat treatment.

The construction was processed by grinding and polishing to provide an insert for a rock-boring drill bit.

Certain terms and concepts as used herein will be briefly explained

As used herein, “super-hard” means a Vickers hardness of at least 25 gigapascal. Synthetic and natural diamond, polycrystalline diamond (PCD), cubic boron nitride (cBN) and polycrystalline cBN (PCBN) material are examples of super-hard materials. Synthetic diamond, which is also called man-made diamond, is diamond material that has been manufactured.

As used herein, PCBN material comprises grains of cubic boron nitride (cBN) dispersed within a matrix comprising metal and or ceramic material.

PCD material comprises a mass (an aggregation of a plurality) of diamond grains, a substantial portion of which are directly inter-bonded with each other and in which the content of diamond is at least about 80 volume per cent of the material. Interstices between the diamond grains may be at least partly filled with a binder material comprising a catalyst material for synthetic diamond, or they may be substantially empty. Catalyst material (which may also be referred to as solvent / catalyst material, reflecting the understanding that the material may perform a catalytic and or solvent function in promoting the growth of diamond grains and the sintering of diamond grains) for synthetic diamond is capable of promoting the growth of synthetic diamond grains and or the direct inter-growth of synthetic or natural diamond grains at a temperature and pressure at which synthetic or natural diamond is thermodynamically more stable than graphite. Examples of catalyst materials for diamond are Fe, Ni, Co and Mn, and certain alloys including these. Bodies comprising PCD material may comprise at least a region from which catalyst material has been removed from the interstices, leaving interstitial voids between the diamond grains. Various grades of PCD material may be made. As used herein, a PCD grade is a variant of PCD material characterised in terms of the volume content and size of diamond grains, the volume content of interstitial regions between the diamond grains and composition of material that may be present within the interstitial regions. Different PCD grades may have different microstructure and different mechanical properties, such as elastic (or Young's) modulus E, modulus of elasticity, transverse rupture strength (TRS), toughness (such as so-called K1C toughness), hardness, density and coefficient of thermal expansion (CTE). Different PCD grades may also perform differently in use. For example, the wear rate and fracture resistance of different PCD grades may be different.

Thermally stable PCD material comprises at least a part or volume of which exhibits no substantial structural degradation or deterioration of hardness or abrasion resistance after exposure to a temperature above about 400 degrees Celsius, or even above about 700 degrees Celsius. For example, PCD material containing less than about 2 weight percent of catalyst metal for diamond such as Co, Fe, Ni, Mn in catalytically active form (e.g. in elemental form) may be thermally stable. PCD material that is substantially free of catalyst material in catalytically active form is an example of thermally stable PCD. PCD material in which the interstices are substantially voids or at least partly filled with ceramic material such as SiC or salt material such as carbonate compounds may be thermally stable, for example. PCD structures having at least a significant region from which catalyst material for diamond has been depleted, or in which catalyst material is in a form that is relatively less active as a catalyst, may be described as thermally stable PCD.

Other examples of superhard materials include certain composite materials comprising diamond or cBN grains held together by a matrix comprising ceramic material, such as silicon carbide (SiC), or cemented carbide material, such as Co-bonded WC material (for example, as described in United States patents numbers 5,453,105 or 6,919,040). For example, certain SiC-bonded diamond materials may comprise at least about 30 volume percent diamond grains dispersed in a SiC matrix (which may contain a minor amount of Si in a form other than SiC). Examples of SiC-bonded diamond materials are described in United States patents numbers 7,008,672; 6,709,747; 6,179,886; 6,447,852; and International Application publication number WO2009/013713).

Young's modulus is a type of elastic modulus and is a measure of the uni-axial strain in response to a uni-axial stress, within the range of stress for which the material behaves elastically. A method of measuring the Young's modulus E is by means of measuring the transverse and longitudinal components of the speed of sound through the material using ultrasonic waves.

As used herein, the thickness of the PCD structure 22, 200 or the substrate 30, 300, or some part of the PCD structure or the substrate is the thickness measured substantially perpendicularly to the interface 24. In some embodiments, the PCD structure, or body of PCD material 22, 200 may have a generally wafer, disc or disc-like shape, or be in the general form of a layer. In some embodiments, the PCD structure 22, 200 may have a thickness of at least about 0.3 mm, at least about 0.5 mm, at least about 0.7 mm, at least about 1 mm, at least about 1.3 mm or at least about 2 mm. In one embodiment, the PCD structure 22, 200 may have a thickness in the range from about 2 mm to about 3 mm.

In some embodiments, the substrate 30, 300 may have the general shape of a wafer, disc or post, and may be generally cylindrical in shape. The substrate 30, 300 may have, for example, an axial thickness at least equal to or greater than the axial thickness of the body of PCD material 22, 200, 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 in thickness. In one embodiment, the substrate 30, 300 may have a thickness of at least 2 cm.

The PCD structure 22, 200 may be joined to the substrate 30, 300 for example only on one side thereof, the opposite side of the PCD structure not being bonded to the substrate 30, 300.

In some embodiments, the largest dimension of the body of PCD material 22, 200 is around 6 mm or greater, for example in embodiments 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 ultrahard particles used in the present process may be of natural or synthetic origin. The mixture of ultrahard 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 ultrahard 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 1, the bodies of polycrystalline diamond material produced by an embodiment additionally have a binder phase present. This binder material is preferably a catalyst/solvent for the ultrahard 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 ultrahard particles to bond to one another. Once manufactured, the PCD construction therefore comprises a coherent matrix of ultrahard (diamond) particles bonded to one another, thereby forming an ultrahard 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 ultrahard abrasive diamond material comprises one phase and the binder (non-diamond phase), the other.

In one form, the ultrahard 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, 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.

Figures 10a and 10b are an example of a processed SEM image of a polished section of a PCD material, for a diamond intensity of 0 (Figure 10a) and a diamond intensity of 15 (Figure 10b) showing the boundaries between diamond grains. These boundary lines were provided by image analysis software and were used to measure the total non-diamond phase (eg binder) surface area in a cross-section through the body of PCD material and surface area of the individual non-diamond phase (interstitial) regions which are indicated as dark areas. The cross-section through the body of PCD material may be at any orientation through the body of PCD material for the following analysis to be conducted and results to be achieved. The image analysis technique is described in more detail below.

As a non-limiting example, the cross section shown in Figures 10a and 10b may be exposed for viewing by cutting a section of the PCD composite compact 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 of the type shown in Figures 5a and 5b may be taken. Each of the images may be analysed by means of image analysis software to determine the total binder area and individual binder areas between the diamond grains. The values of the total binder area and individual binder area are determined by conducting a statistical evaluation on a large number of collected images taken on the scanning electron microscope.

The magnification selected for the microstructural analysis has a significant effect on the accuracy of the data obtained. Imaging at lower magnifications offers an opportunity to sample, representatively, larger particles or features in a microstructure but may tend to under-represent smaller particles or features as they are not necessarily sufficiently resolved at that magnification. By contrast, higher magnifications allow resolution and hence detailed measurement of fine-scale features but can tend to sample larger features such that they intersect the boundaries of the images and hence are not adequately measured. It has been appreciated that it is therefore important to select an appropriate magnification for any quantitative microstructural analysis technique. The appropriateness is therefore determined by the size of the features that are being characterised. The magnifications selected for the various measurements described herein are discussed in more detail below.

Unless otherwise stated herein, dimensions of total binder area and individual binder area within the body of PCD material refer to the dimensions as measured on a surface of, or a section through, a body comprising PCD material and no stereographic correction has been applied. For example, the measurements are made by means of image analysis carried out on a polished surface, and a Saltykov correction has not been applied in the data stated herein.

In measuring the mean value of a quantity or other statistical parameter measured by means of image analysis, several images of different parts of a surface or section (hereinafter referred to as samples) are used to enhance the reliability and accuracy of the statistics. The number of images used to measure a given quantity or parameter may be, for example between 10 to 30. If the analysed sample is uniform, which is the case for PCD, depending on magnification, 10 to 20 images may be considered to represent that sample sufficiently well.

The resolution of the images needs to be sufficiently high for the inter-grain and inter-phase boundaries to be clearly made out and, for the measurements stated herein an image area of 1280 by 960 pixels was used.

In the statistical analysis, 15 images were taken of different areas on a surface of a body comprising the PCD material, and statistical analysis was carried out on each image.

Images used for the image analysis were obtained by means of scanning electron micrographs (SEM) taken using a backscattered electron signal. The back-scatter mode was chosen so as to provide high contrast based on different atomic numbers and to reduce sensitivity to surface damage (as compared with the secondary electron imaging mode).

A number of factors have been identified as being important for image capturing. These are:

- SEM Voltage which, for the purposes of the measurements stated herein remained constant and was around 15kV;
- working distance which also remained constant and was around 8 mm
- image sharpness
- sample polishing quality,
- image contrast levels which were selected to provide clear separation of the microstructural features;

- magnification (should be varied according to different diamond grain size and is as stated below),
- number of images taken.

Given the above conditions, the image analysis software used was able to separate distinguishably the diamond and binder phases and the back-scatter images were taken at approximately 45° to the edge of the samples.

The magnification used in the image analysis should be selected in such a way that the feature of interest is adequately resolved and described by the available number of pixels. In PCD image analysis various features of different size and distribution are measured simultaneously and it is not practical to use a separate magnification for each feature of interest.

It is difficult to identify the optimum magnification for each feature measurement in the absence of a reference measurement result. It could vary from one operator to another. Therefore, a procedure is proposed for the selection of the magnification.

The size of a statistically significant number of diamond grains in the microstructure is measured and the average value taken.

As used herein in relation to grains or particles and unless otherwise stated or implied, the term “size” refers to the length of the grain viewed from the side or in cross section using image analysis techniques.

The number of pixels that describe this average length is determined and a range of pixel values are established to fix the magnification.

In the image analysis technique, the original image was converted to a greyscale image. The image contrast level was set by ensuring the diamond peak intensity in the grey scale histogram image occurred between 15 and 20.

As mentioned above, several images of different parts of a surface or section were taken to enhance the reliability and accuracy of the statistics. For measurements of total non-diamond phase (eg binder) area, the greater the number of images, the more accurate the results are perceived to be. For example, about 15000 measurements were taken, 1000 per image with 15 images.

The steps taken by the image analysis programme may be summarised in general as follows:

1. The original image was converted to a greyscale image. The image contrast level was set by ensuring the diamond peak intensity in the grey scale histogram image occurred between 10 and 20.

2. An auto threshold feature was used to binarise the image and specifically to obtain clear resolution of the diamond and binder phases.

3. The binder was the primary phase of interest in the current analysis.

4. The software, having the trade name analySIS Pro from Soft Imaging System® GmbH (a trademark of Olympus Soft Imaging Solutions GmbH) was used and excluded from the analysis any particles which touched the boundaries of the image. This required appropriate choice of the image magnification:

a. If too low then resolution of fine particles is reduced.

b. If too high then:

i. Efficiency of coarse grain separation is reduced.

ii. High numbers of coarse grains are cut by the boarders of the image and hence less of these grains are analysed.

iii. Thus more images must be analysed to get a statistically-meaningful result.

5. Each particle was finally represented by the number of continuous pixels of which it is formed.

6. The AnalySIS software programme proceeded to detect and analyse each particle in the image. This can be automatically repeated for several images.

7. A large number of outputs was available. The outputs may be post-processed further, for example using statistical analysis software and/or carrying out further feature analysis, for example the analysis described below for determining the mean of the total binder area for all images and the means of the individual binder areas.

If appropriate thresholding is used, the image analysis technique is unlikely to introduce further errors in measurements which would have a practical effect on the accuracy of those measurements, with the exception of small errors related to the rounding of numbers. In the current analysis, the statistical mean values of the total binder area and individual binder areas were used as, according to the Central Limitation Theorem, the distribution of an average tends to be normal as the sample size increases, regardless of the distribution from which the average is taken except when the moments of the parent distribution do not exist. All practical distributions in statistical engineering have defined moments, and thus the Central Limitation Theorem applies in the present case. It was therefore deemed appropriate to use the statistical mean values.

The individual non-diamond (eg binder or catalyst/solvent) phase areas or pools, which are easily distinguishable from that of the ultrahard phase using electron microscopy, were identified using the above-mentioned standard image analysis tools. The total non-diamond phase areas (in square microns) in the analysed cross-sectional images were determined by summing the individual binder pool areas within the entire microstructural image area that was analysed.

The collected distributions of this data were then evaluated statistically and an arithmetic average was then determined. Hence the mean total binder pool area in the surface of the microstructure being analysed was calculated

It is anticipated that microstructural parameters may alter slightly from one area of an abrasive compact to another, depending on formation conditions. Hence the microstructural imaging is carried out so as to representatively sample the bulk of the ultrahard composite portion of the compact.

Additional non-limiting examples are now described. Three sets of samples were produced as follows: a multimodal (trimodal) diamond powder mix with average diamond grain size of approximately 13 μm and 1 weight percent cobalt admix was prepared, in sufficient quantity to provide approximately 2g admix per sample. The admix for each sample was then poured into or otherwise arranged in a Niobium inner cup. A cemented carbide substrate of approximately 13 weight percent cobalt content and having a non-planar interface was placed in each inner cup on the powder mix. A titanium cup was placed in turn over this structure and the assembly sealed to produce a canister. The canisters were pre-treated by vacuum outgassing at approximately 1050ºC, and divided into three sets which were sintered at three distinct ultrahigh pressure and temperature conditions in the diamond-stable region, namely at approximately 5.5 GPa (Set 1), 6.8 GPa (Set 2), and 7.7 GPa (Set 3). Specifically the canisters were sintered at temperatures sufficient to melt the cobalt so as to produce PCD constructions with well-sintered PCD tables and well-bonded substrates. The technique described above in connection with Figures 3 to 9 was applied for the sintering of the canisters at 7.7GPa (set 3). The resulting superhard constructions were not subjected to any post-synthesis leaching treatment.

Image analysis was then conducted on each of these superhard constructions using the techniques described above and in particular the determination of appropriate magnification described above to determine the mean total binder area in a polished cross-section and mean cross-sectional binder area for each sample.

The experiments may be repeated for different diamond grain size compositions and the results are set out in Table 1.

TABLE 1

Grain Size microns		**Total Binder Area** %	**Binder Area** micron^2	**Magnification**
Mean	StdDev		0.01	
13.4600	2.2750	8.0699	0.4446	1000x
12.5755	3.1707	8.0223	0.2802	1000x
10.8800	1.8440	6.4004	0.2638	1000x
3.9700	0.7990	10.3135	0.1528	3000x

It was determined from the above experiments that, for a total non-diamond phase area (for example binder area) in the range of around 0 to 5 %, it is possible to achieve an associated individual non-diamond area of less than around 0.7 micon^2, as determined using an image analysis technique applying a magnification of around 1000 and analysing an image area of 1280x960 pixels, with the largest dimension of the body of PCD material being around 6mm or greater. The thickness of the body of PCD material in these embodiments may be, for example, around 0.3mm or greater.

Furthermore, for a total non-diamond phase area (for example binder area) in the range of around 5 to 10 %, it is possible to achieve an associated cross-sectional individual non-diamond phase area of less than around 0.340

micon^2, as determined using an image analysis technique applying a magnification of between around 1000 and analysing an image area of 1280x960 pixels, with the largest dimension of the body of PCD material being around 6mm or greater. The thickness of the body of PCD material in these embodiments may be, for example, around 0.3mm or greater.

Also, for a total non-diamond phase area (for example binder area) in the range of around 10 to 15 %, it is possible to achieve an associated cross-sectional individual non-diamond phase area of less than around 0.340 micon^2, as determined using an image analysis technique applying a magnification of between around 3000 and analysing an image area of 1280x960 pixels, with the largest dimension of the body of PCD material being around 6mm or greater. The thickness of the body of PCD material in these embodiments may be, for example, around 0.3mm or greater.

Also, for a total non-diamond phase area (for example binder area) in the range of around 15 to 30 %, it is possible to achieve an associated cross-sectional individual non-diamond phase area in the range of around 0.005 to around 0.340 micon^2, as determined using an image analysis technique applying a magnification of between around 10000 and analysing an image area of 1280x960 pixels, with the largest dimension of the body of PCD material being around 6mm or greater. The thickness of the body of PCD material in these embodiments may be, for example, around 0.3mm or greater.

Whilst not wishing to be bound by a particular theory, using the conditions described herein it was determined possible to achieve total binder areas in the ranges specified above together with the above-mentioned ranges of associated individual binder areas. These have been determined to assist generating a 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 embodiments described herein.

In addition, various arrangements and combinations are envisaged for the method by the disclosure, and examples of the method may further include one or more of the following non-exhaustive and non-limiting aspects in various combinations.

There may be provided a method for making a super-hard construction comprising:

a first structure joined to a second structure, the first structure comprising first material having a first coefficient of thermal expansion (CTE) and a first Young's modulus, and the second structure comprising second material having a second CTE and a second Young's modulus; the first CTE and the second CTE being substantially different from each other and the first Young's modulus and the second Young's modulus being substantially different from each other; at least one of the first or second materials comprising super-hard material; the method including:

forming an assembly comprising the first material, the second material and a binder material arranged to be capable of bonding the first and second materials together, the binder material comprising metal; subjecting the assembly to a sufficiently high temperature for the binder material to be in the liquid state and to a first pressure at which the super-hard material is thermodynamically stable; reducing the pressure to a second pressure at which the super-hard material is thermodynamically stable, the temperature being maintained sufficiently high to maintain the binder material in the liquid state; reducing the temperature to solidify the binder material; and reducing the pressure and the temperature to an ambient condition to provide the super-hard construction.

In some embodiments, the CTE of one of the first or second materials is at least about 2.5 X 10-6 per degree Celsius and at most about 5.0 X 10-6 per degree Celsius and the CTE of the other of the first or second materials is at least about 3.5 X 10-6 per degree Celsius and at most about 6.5 X 10-6 per degree Celsius, at about 25 degrees Celsius.

In some embodiments, the Young's modulus of one of the first or second materials is at least about 500 gigapascals and at most about 1,300 gigapascals and the Young's modulus of the other of the first and second materials is at least about 800 gigapascals and at most about 1,600 gigapascals.

The Young's moduli of the first and second materials may, for example, differ by at least about 10%.

In some embodiments, the CTE of the first and second materials may, for example, differ by at least about 10%.

The method may further include sintering an aggregation of a plurality of grains of the super-hard material in the presence of sinter catalyst material at a sinter pressure and a sinter temperature to form the second structure.

The method may include disposing an aggregation of grains of super-hard material adjacent the first structure and in the presence of the binder material to form a pre-sinter assembly; subjecting the pre-sinter assembly to a sinter pressure and a sinter temperature to melt the binder material and sinter the grains of super-hard materials and form the second structure comprising polycrystalline super-hard material connected to the first structure by the binder material in the molten state.

In some embodiments, the first pressure is substantially the sinter pressure.

The method may further include providing the first structure, providing the second structure comprising polycrystalline super-hard material, disposing the first structure adjacent the second structure and forming a pre-construction assembly, and applying a pressure to the pre-construction assembly, increasing the pressure from ambient pressure to the first pressure.

The method may, for example, include subjecting an aggregation of a plurality of grains of super-hard material to a sinter pressure and a sinter temperature at which the super-hard material is capable of being sintered to form the second material, and reducing the pressure and temperature to an ambient condition to provide the second structure; the first pressure being substantially greater then the sinter pressure.

The second structure may comprise diamond material and the binder material comprises catalyst material for diamond.

The first and second structures may each comprise diamond material and the binder material comprises catalyst material for diamond.

In some embodiments, the difference between the second pressure and the first pressure is at least about 0.5 gigapascal.

The method may further include subjecting the super-hard construction to further heat treatment at a treatment temperature and a treatment pressure at which the super-hard material is thermodynamically meta-stable.

The super-hard material may comprise diamond material and the treatment temperature is at least about 500 degrees Celsius and the treatment pressure is less than about 1 gigapascal.

The method may include the step of reducing the pressure from the first pressure to an intermediate pressure for an holding period, and then further reducing the pressure from the intermediate pressure to the second pressure.

The first pressure may, for example, be at least about 7 gigapascal, the intermediate pressure may be, for example, at least about 5.5 gigapascals and less than about 10 gigapascals, the holding period may, for example, be at least about 1 minute and the second pressure may, for example, be at least about 5.5 gigapascals and at most about 7 gigapascals.

The pressure at which the binder material begins to solidify responsive to the reduction in temperature may, for example, be substantially equal to the second pressure in some embodiments.

In other embodiments, the pressure at which the binder material begins to solidify responsive to the reduction in temperature may be substantially less than the second pressure.

In some embodiments, the first structure comprises cobalt-cemented tungsten carbide material and the second material comprises PCD material, the CTE of the cemented carbide material being in the range of about 4.5 X 10-6 to about 6.5 X 10-6 per degree Celsius, the CTE of the PCD material being in the range of about 3.0 X 10-6 to about 5.0 X 10-6 per degree Celsius; the Young's modulus of the cemented carbide material being in the range of about 500 to about 1,000 gigapascals, and the Young's modulus of the PCD material being in the range of about 800 to about 1,600 gigapascals; the first pressure being in the range of about 6 to about 10 gigapascals, and the second pressure being in the range of about 5.5 to about 8 gigapascals.

In some embodiments, the pressure at which the cobalt-based binder material comprised in the cemented carbide material begins to solidify is equal to the second pressure.

The second pressure may, for example, be in the range of about 6.5 to about 7.5 gigapascals.

In some embodiments, the second structure comprises PCD material and the method includes subjecting the super-hard construction to further heat treatment for a treatment period in the range of about 30 to about 90 minutes at a treatment temperature in the range of about 550 to about 650 degrees Celsius.

The method may include processing the super-hard construction to provide a tool element. The super-hard construction may be suitable for an insert for a rock-boring drill bit, for an impact tool for degrading rock or pavement or for a machine tool.

Disclosed methods have the aspect of reducing the likelihood or frequency of cracking of super-hard constructions, particularly when subjected to heating in subsequent manufacturing steps or to elevated temperatures in use.

Claims:

1. A polycrystalline diamond construction comprising a body of polycrystalline diamond material formed of:

a mass of diamond grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, and

a non-diamond phase at least partially filling a plurality of the interstitial regions to form non-diamond phase pools, the non-diamond phase pools each having an individual cross-sectional area,

wherein the percentage of non-diamond phase in the total area of a cross-section of the body of polycrystalline diamond material is between around 0 to 5 %, and the mean of the individual cross-sectional areas of the non-diamond phase pools in an analysed image of a cross-section through the body of polycrystalline material is less than around 0.7 microns squared when analysed using an image analysis technique at a magnification of around 1000 and an image area of 1280 by 960 pixels.

2. A polycrystalline diamond construction comprising a body of polycrystalline diamond material formed of:

a mass of diamond grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, and

a non-diamond phase at least partially filling a plurality of the interstitial regions to form non-diamond phase pools, the non-diamond phase pools each having an individual cross-sectional area,

wherein the percentage of non-diamond phase in the total area of a cross-section of the body of polycrystalline diamond material is between around 5 to 10 %, and the mean of the individual cross-sectional areas of the non-diamond phase pools in an analysed image of a cross-section through the body of polycrystalline diamond material is less than around 0.340 microns squared when analysed using an image analysis technique at a magnification of around 1000 and an image area of 1280 by 960 pixels.

3. A polycrystalline diamond construction comprising a body of polycrystalline diamond material formed of:

a mass of diamond grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, and

a non-diamond phase at least partially filling a plurality of the interstitial regions to form non-diamond phase pools, the non-diamond phase pools each having an individual cross-sectional area,

wherein the percentage of non-diamond phase in the total area of a cross-section of the polycrystalline diamond construction is between around 10 to 15 %, and

the mean of the individual cross-sectional areas of the non-diamond phase pools in an analysed image of a cross section through the body of polycrystalline material is less than around 0.340 microns squared when analysed using an image analysis technique at a magnification of around 3000 and an image area of 1280 by 960 pixels.

4. A polycrystalline diamond construction comprising a body of polycrystalline diamond material formed of:

a mass of diamond grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, and

a non-diamond phase at least partially filling a plurality of the interstitial regions to form non-diamond phase pools, the non-diamond phase pools each having an individual cross-sectional area, wherein the percentage of non-diamond phase in the total area of a cross-section of the polycrystalline diamond construction is between around 15 to 30%, and

the mean of the individual cross-sectional areas of the non-diamond phase pools in an analysed image of a cross section through the body of polycrystalline material is between around 0.005 to 0.340 microns squared when analysed using an image analysis technique at a magnification of around 10000 and an image area of 1280 by 960 pixels.

5. A polycrystalline diamond construction according to any one of the preceding claims, wherein the body of polycrystalline diamond material has a largest dimension of around 6mm or greater.

6. A polycrystalline diamond construction according to any one of the preceding claims, wherein the body of polycrystalline diamond material has a thickness of around 0.3mm or greater.

7. The polycrystalline diamond construction according to any one of the preceding claims, further comprising a substrate bonded to the body of polycrystalline diamond material along an interface.

8. The polycrystalline diamond construction according to claim 7, wherein the interface between the substrate and the body of polycrystalline diamond material is substantially non-planar.

9. The polycrystalline diamond construction according to any one of claims 7 or 8, wherein the substrate comprises cemented carbide.

10. The polycrystalline diamond construction according to any one of claims 7 to 9, wherein the substrate has a thickness at least equal to or greater than the thickness of the body of polycrystalline diamond material.

11. A cutter for boring into the earth comprising the polycrystalline diamond construction according to any one of the preceding claims.

12. 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 diamond construction of any one of claims 1 to 10.

13. A drill bit or a component of a drill bit for boring into the earth, comprising a polycrystalline superhard construction according to any one of claims 1 to 10.

14. A method for making a polycrystalline diamond construction, the method comprising:

providing a mass of diamond grains having a first average size;

arranging the mass of diamond grains to form a pre-sinter assembly with a body of material for forming a substrate; and

treating the pre-sinter assembly in the presence of a catalyst material for diamond at an ultra-high pressure of around 7GPa or greater and a temperature at which diamond is more thermodynamically stable than graphite to sinter together the diamond grains and a substrate bonded thereto along an interface to form an integral PCD construction; the diamond grains exhibiting inter-granular bonding and defining a plurality of interstitial regions therebetween, a non-diamond phase at least partially filling a plurality of the interstitial regions to form non-diamond phase pools, the non-diamond phase pools each having an individual cross-sectional area,

wherein the percentage of non-diamond phase in the total area of a cross-section of the body of polycrystalline diamond material is between around 0 to 5 %, and the mean of the individual cross-sectional areas of the non-diamond phase pools in the image analysed is less than around 0.7 microns squared when analysed using an image analysis technique at a magnification of around 1000 and an image area of 1280 by 960 pixels; or

the percentage of non-diamond phase in the total area of a cross-section of the body of polycrystalline diamond material is between around 5 to

10 %, and the mean of the individual cross-sectional areas of the non-diamond phase pools in the image analysed is less than around 0.340 microns squared when analysed using an image analysis technique at a magnification of around 1000 and an image area of 1280 by 960 pixels; or

the percentage of non-diamond phase in the total area of a cross-section of the polycrystalline diamond construction is between around 10 to 15 %, and the mean of the individual cross-sectional areas of the non-diamond phase pools in the image analysed is less than around 0.340 microns squared when analysed using an image analysis technique at a magnification of around 3000 and an image area of 1280 by 960 pixels; or

the percentage of non-diamond phase in the total area of a cross-section of the polycrystalline diamond construction is between around 15 to 30 %, and the mean of the individual cross-sectional areas of the non-diamond phase pools in the image analysed is between around 0.005 to 0.340 microns squared when analysed using an image analysis technique at a magnification of around 10000 and an image area of 1280 by 960 pixels.

15. A method of forming the polycrystalline diamond construction of any one of claims 1 to 10.

16. A polycrystalline diamond construction substantially as hereinbefore described with reference to any one embodiment as that embodiment is illustrated in Figures 3 to 10b of the accompanying drawings.

17. A method of forming the polycrystalline diamond construction substantially as hereinbefore described with reference to any one embodiment as that embodiment is illustrated in Figures 3 to 10b of the accompanying drawings.

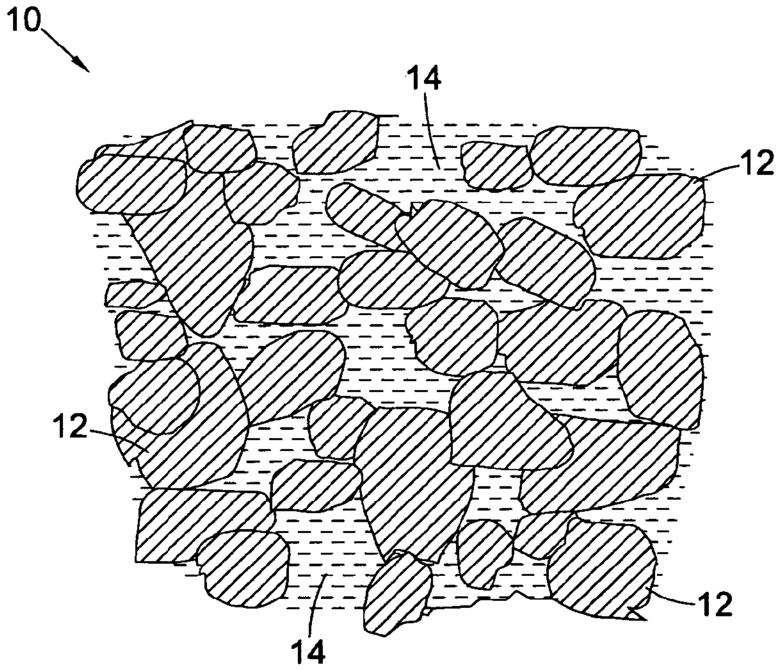


Fig. 1

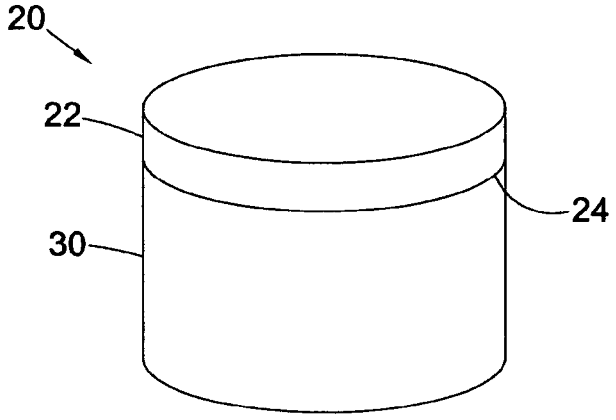


Fig. 2

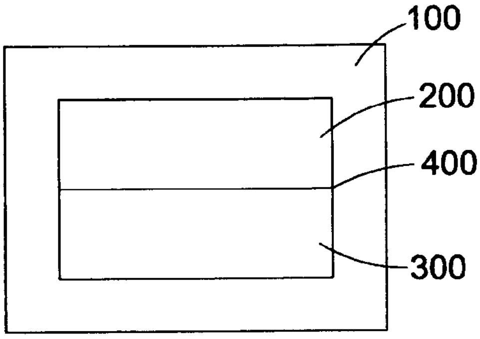


Fig. 3

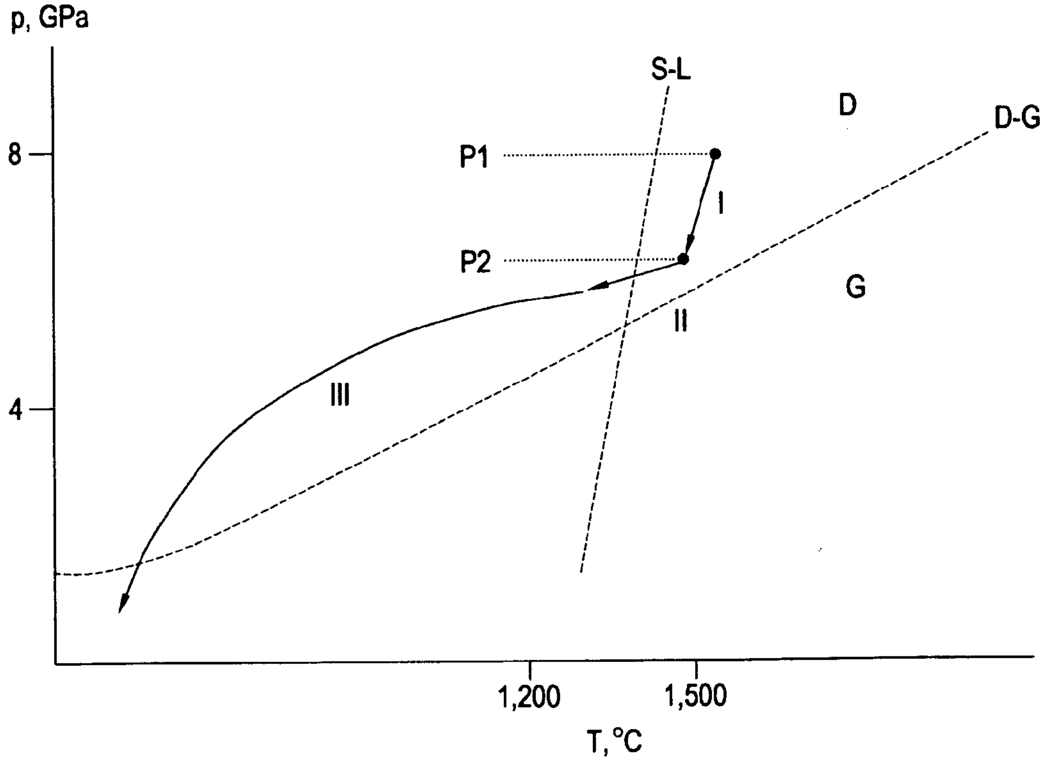


Fig. 4

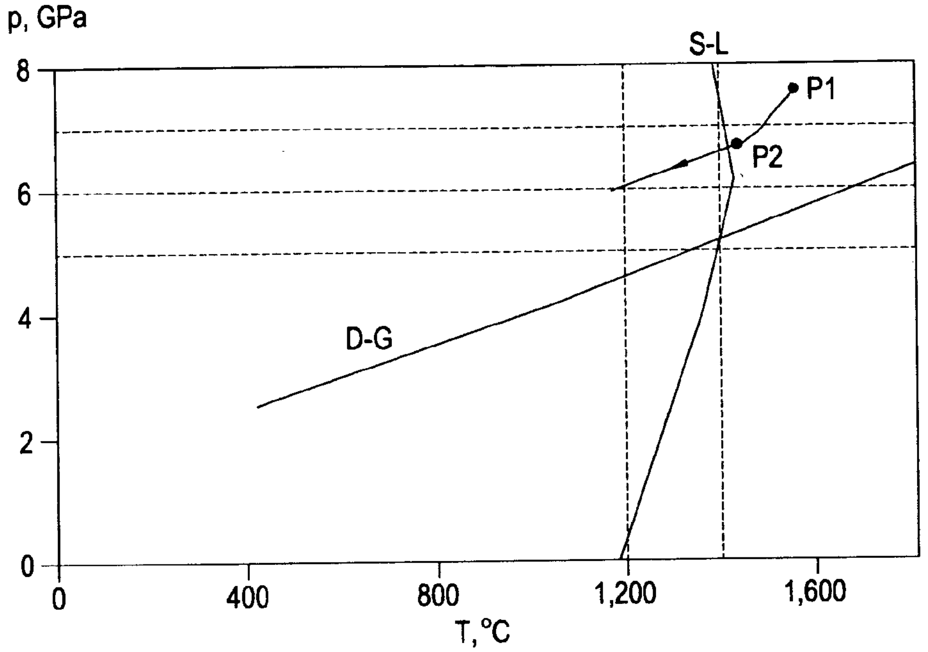
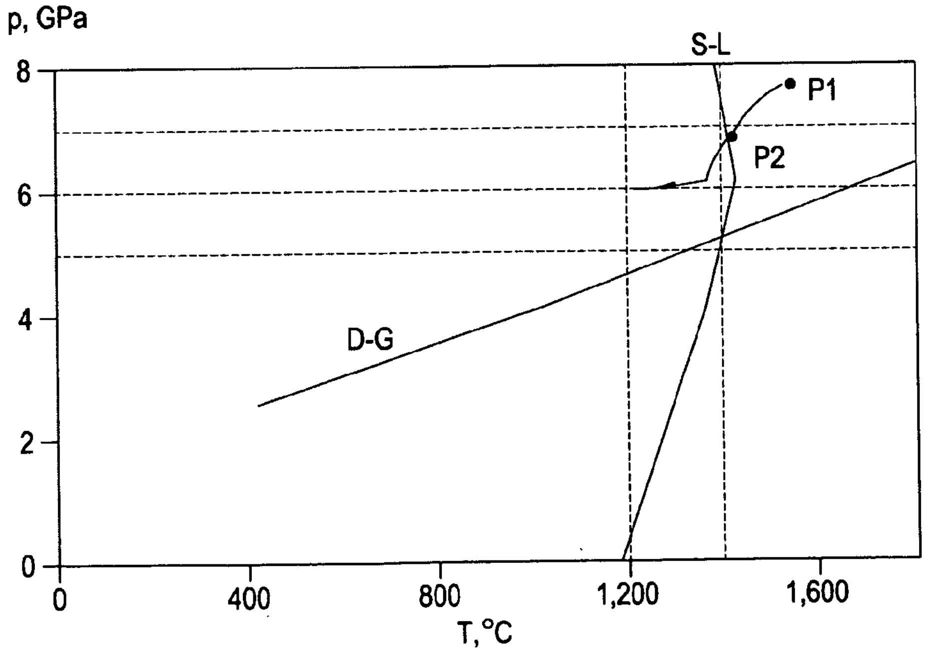

p, GPa
8
6
4
2
0
S-L
P1
P2
D-G
0
400
800
1,200
1,600
T,°C

Fig. 5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4
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P1
P2
D-G
0
400
800
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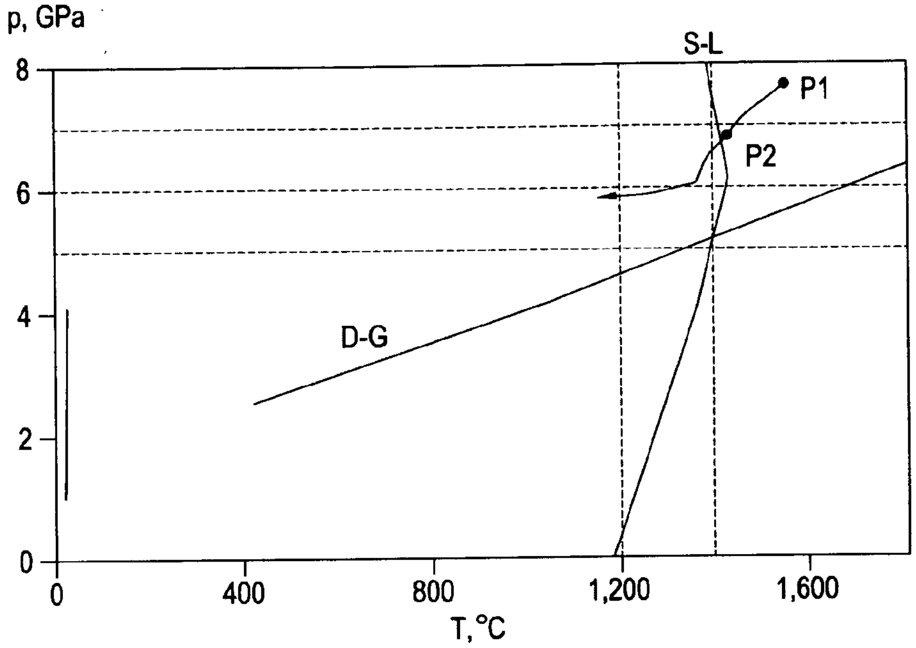
T,°C

Fig. 6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P2
D-G
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T,°C

Fig. 7

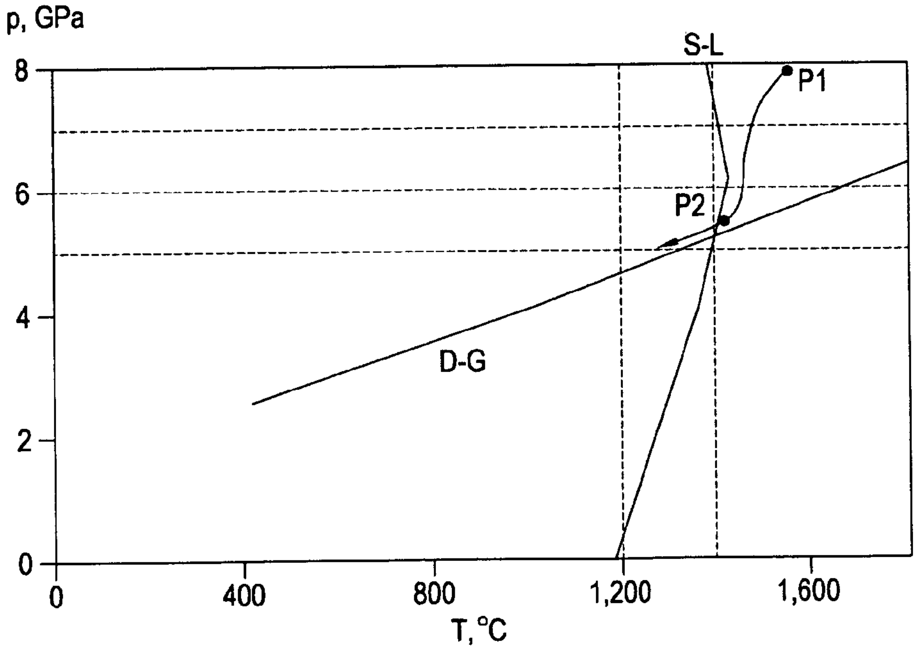
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Fig. 8

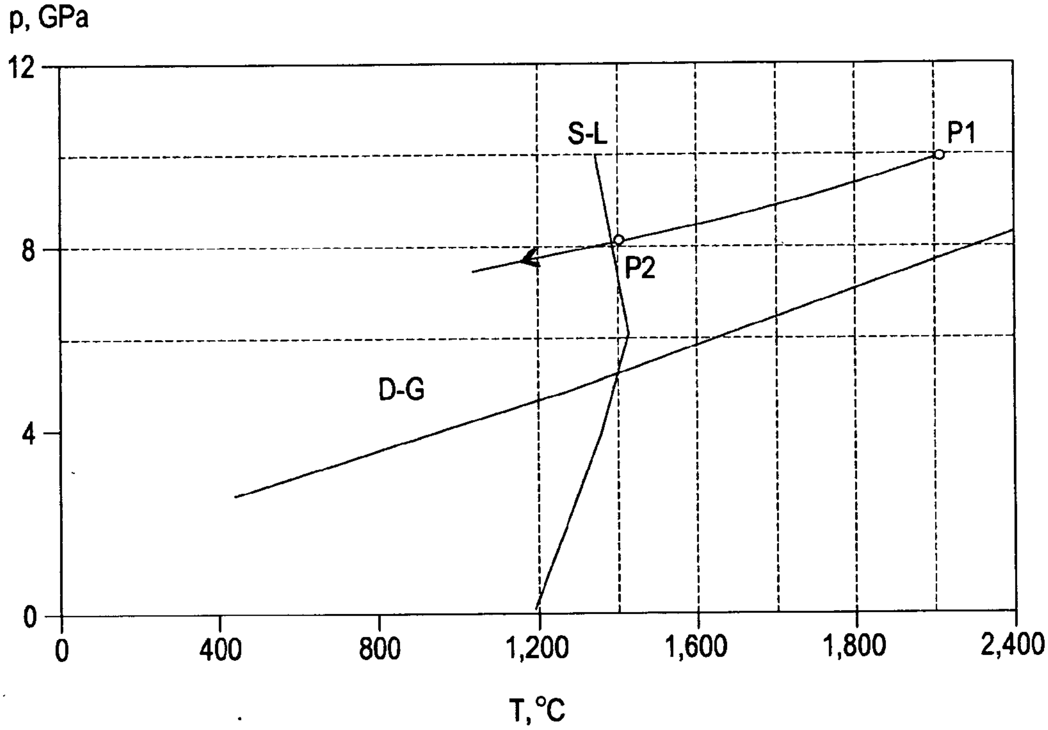
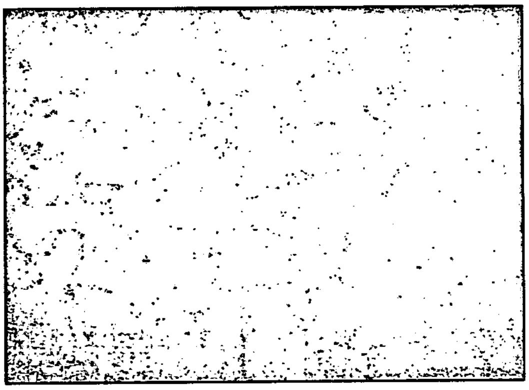


Fig. 9

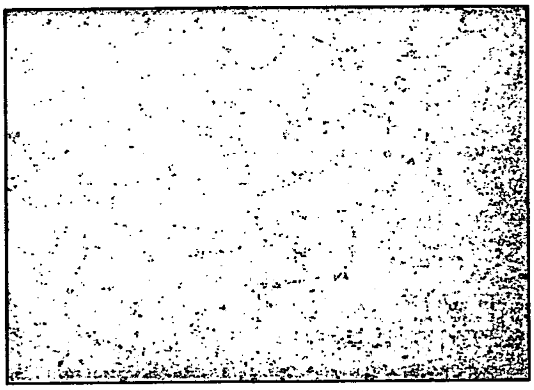
Contrast Level - Same criteria threshold

[IN NEGATIVE]



Diamond intensity: 0

Fig. 10(a)



Diamond intensity: 15

Fig. 10(b)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/065082

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F3/14 C22C26/00 E21B10/567 B22F7/06
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)
B22F C22C E21B

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, COMPENDEX, INSPEC, 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 2011/024201 A1 (SCOTT DANNY EUGENE [US] ET AL) 3 February 2011 (2011-02-03) examples -----	1-17
X	US 2010/300764 A1 (NAIDOO KAVESHINI [ZA] ET AL) 2 December 2010 (2010-12-02) examples -----	1-17

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 2 November 2012	Date of mailing of the international search report 12/11/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Morra, Valentina

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/065082

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011024201 A1	03-02-2011	NONE	
US 2010300764 A1	02-12-2010	NONE	