



(51) International Patent Classification:

B22F 3/14 (2006.01) *C22C 29/08* (2006.01)
B22F 7/06 (2006.01) *E21B 10/573* (2006.01)
B23B 27/14 (2006.01) *B22F 5/00* (2006.01)
C22C 26/00 (2006.01)

(21) International Application Number:

PCT/EP2024/087078

(22) International Filing Date:

18 December 2024 (18.12.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/615,103 27 December 2023 (27.12.2023) US

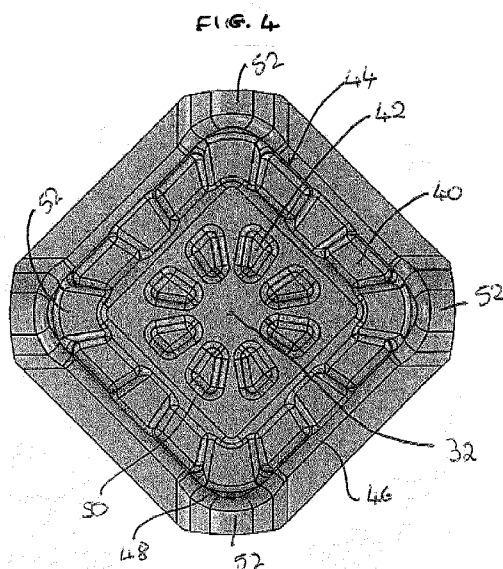
(71) Applicant: **ELEMENT SIX (UK) LIMITED** [GB/GB];
Global Innovation Centre Fermi Avenue, Harwell Oxford,
Didcot Oxfordshire OX11 0QR (GB).

(72) Inventor: **ROTHER, Mitchell August**; Element Six US
Corporation, 24900 Pitkin Road, Suite 250, Spring, Texas
77386 (US).

(74) Agent: **REEVE, Anna Elizabeth** et al.; Global Innova-
tion Centre Fermi Avenue, Harwell Campus, Didcot Ox-
fordshire OX11 0QR (GB).

(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, CV, CZ, DE, DJ, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG,
KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY,

(54) Title: METHOD OF MAKING A SUPER HARD CONSTRUCTION



(57) Abstract: A method of forming a superhard polycrystalline construction includes providing a substrate having an interface surface with one or more projections arranged in a first array having a non-circular peripheral outline, the outline having two or more linear sections, adjacent linear sections being spaced by a respective arcuate surface section extending therebetween. The substrate has a non-circular cross-section in a plane perpendicular to a plane through which its longitudinal axis extends. The substrate is placed in a canister having an internal peripheral wall having a non-circular outline matching the peripheral side surface of the substrate. An aggregated mass of particles or grains of superhard material is placed into the canister over the interface surface to form a pre-sinter assembly. The canister is sealed and the pre-sinter assembly subjected to a pressure of greater than 5.5 GPa at a temperature of at least 1250 degrees Celsius to form the superhard construction.

MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, 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, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, 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))*
- *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

METHOD OF MAKING A SUPER HARD CONSTRUCTION

Field

This disclosure relates to a method of making super hard constructions, particularly but not exclusively to constructions comprising polycrystalline diamond (PCD) structures attached to a substrate and for use as cutter inserts or elements for drill bits for boring into the earth.

Background

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

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

Polycrystalline diamond (PCD) is an example of a super hard material (also called a superabrasive material) comprising a mass of substantially inter-grown diamond grains, forming a skeletal mass defining interstices between

the diamond grains. PCD material typically comprises at least about 80 volume % of diamond and is conventionally made by subjecting an aggregated mass of diamond grains to an ultra-high pressure of greater than about 5 GPa, and temperature of at least about 1,200°C, for example. A material wholly or partly filling the interstices may be referred to as filler or binder material.

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

Cemented tungsten carbide which may be used to form a suitable substrate is formed from carbide particles being dispersed in a cobalt matrix by mixing tungsten carbide particles/grains and cobalt together then heating to solidify. To form the cutting element with a super hard material layer such as PCD or PCBN, diamond particles or grains or CBN grains are placed adjacent the cemented tungsten carbide body in a refractory metal enclosure such as a niobium enclosure and are subjected to high pressure and high temperature

so that inter-grain bonding between the diamond grains or CBN grains occurs, forming a polycrystalline super hard diamond or polycrystalline CBN layer.

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

Cobalt has a significantly different coefficient of thermal expansion to that of diamond and, as such, for constructions where the super hard material is a polycrystalline diamond (PCD) material, upon heating of the polycrystalline diamond material during use, the cobalt in the substrate to which the PCD material is attached expands and may cause cracks to form in the PCD material, resulting in the deterioration of the PCD layer.

To reduce the residual stresses created at the interface between the substrate and the super hard layer, interface surfaces on substrates are known to have been formed with a plurality concentric annular rings projecting from the planar interface surface. Due to the difference in the coefficients of thermal expansion of the substrate and the super hard material layer, these layers contract at different rates when the cutting element is cooled after HTHP sintering. Tensile stress regions are formed on the upper surfaces of the rings, whereas compressive stress regions are formed on/in the valleys between such rings. Consequently, when a crack begins to grow in use, it may grow annularly along the entire upper surface of the annular ring where it is exposed to tensile stresses, or may grow along the entire annular valley between the projecting rings where it is exposed to compressive stresses, leading to the early failure of the cutting element.

It is also known for cutting element substrate interfaces to comprise a plurality of spaced apart projections, the projections having relatively flat upper surfaces projecting from a planar interface surface.

Common problems that affect cutting elements are chipping, spalling, partial fracturing, and cracking of the super hard material layer. Another problem is cracking along the interface between the super hard material layer and the substrate and the propagation of the crack across the interface surface.

These problems may result in the early failure of the super hard material layer and thus in a shorter operating life for the cutting element. Accordingly, there is a need for a method of making a cutting element having an enhanced operating life in high wear or high impact applications, such as boring into rock, with a super hard material layer in which the likelihood of cracking, chipping, and fracturing is reduced or controllable.

Summary

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

a first stage; the first stage comprising providing a substrate, the substrate having an interface surface, a base surface, a longitudinal axis, and a peripheral side surface extending between the interface surface and the base surface, the interface surface comprising one or more projections arranged to project from the interface surface in a first array, the first array of one or more projections having a non-circular peripheral outline, the outline having two or more linear sections, adjacent linear sections being spaced by a respective arcuate surface section extending therebetween, the substrate having a non-circular cross-section in a plane perpendicular to a plane through which the longitudinal axis extends;

a second stage; the second stage comprising placing the substrate in a canister having an internal peripheral wall defining a recess for receiving the substrate, the internal peripheral wall having a non-circular outline matching the peripheral side surface of the substrate;

a third stage; the third stage comprising placing an aggregated mass of particles or grains of super hard material into the canister over the interface surface of the substrate to form a pre-sinter assembly;

a fourth stage; the fourth stage comprising sealing the cannister is sealed, and subjecting the pre-sinter assembly to a pressure of greater than around 5.5 GPa at a temperature of at least around 1250 degrees Celsius to sinter the particles or grains and form the super hard polycrystalline construction comprising a body of super hard polycrystalline material bonded to the substrate;

a fifth stage; the fifth stage comprising removing the super hard polycrystalline construction from the canister.

Viewed from a second aspect there is provided an earth-boring tool, comprising:

a body; and

at least one cutting element comprising the super hard polycrystalline construction formed according to the above defined method attached to the body.

Viewed from a third aspect there is provided an earth boring drill bit comprising the super hard polycrystalline construction formed by the above defined method and mounted thereon or therein as a cutter element.

Brief description of the drawings

Non-limiting examples will now be described with reference to the accompanying drawings in which:

Figure 1 is a schematic side view of a conventional cylindrical PCD cutter element;

Figure 2 is a schematic perspective view from above of a conventional substrate of the cutting element of Figure 1;

Figure 3 is a schematic perspective view from above of a substrate formed by an example method;

Figure 4 is a schematic plan view of the substrate of Figure 3;

Figure 5 is a schematic perspective view of a cutter element showing the substrate of Figures 3 and 4 with a body of super hard material bonded thereto formed by an example method; and

Figure 6 is a schematic diagram showing the stages of an example method.

Detailed description

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

As used herein, a “super hard construction” means a construction comprising a body of polycrystalline super hard material and a substrate attached thereto.

As used herein, polycrystalline diamond (PCD) is a type of polycrystalline super hard material (PCS) material comprising a mass of diamond grains, a substantial portion of which are directly inter-bonded with each other and in which the content of diamond is at least about 80 volume percent of the

material. In one example of PCD material, interstices between the diamond grains may be at least partly filled with a binder material comprising a catalyst for diamond. As used herein, "interstices" or "interstitial regions" are regions between the diamond grains of PCD material. In examples of PCD material, interstices or interstitial regions may be substantially or partially filled with a material other than diamond, or they may be substantially empty. PCD material may comprise at least a region from which catalyst material has been removed from the interstices, leaving interstitial voids between the diamond grains.

As used herein, PCBN (polycrystalline cubic boron nitride) material refers to a type of super hard material comprising grains of cubic boron nitride (cBN) dispersed within a matrix comprising metal or ceramic. PCBN is a further example of a super hard material.

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

The term "substrate" as used herein means any substrate over which the super hard material layer is formed. For example, a "substrate" as used herein may be a transition layer formed over another substrate. Additionally, as used herein, the terms "radial" and "circumferential" and like terms are not meant to limit the feature being described to a perfect circle.

The super hard construction 1 shown in the attached figures may be suitable, for example, for use as a cutter insert for a drill bit for boring into the earth.

Like reference numbers are used to identify like features in all drawings.

In a conventional cutter element as shown in Figure 1, the cutting element 1 includes a substrate 10 with a body of super hard material 11 formed on the substrate 10. The substrate 10 may be formed of a hard material such as cemented tungsten carbide. The body of super hard material 11 may be, for

example, be formed of polycrystalline diamond (PCD), polycrystalline cubic boron nitride (PCBN), or may be a thermally stable product such as thermally stable PCD (TSP) or a combination of the two in a multi-layer construction. In the construction shown in Figure 1, the body of super hard material 11 has a first layer 14 of thermally stable super hard material spaced from the interface 12 with the substrate 10 by a further layer 13 of super hard material.

The cutting element 1 may be mounted into a bit body such as a drag bit body (not shown). The exposed top surface 15 of the super hard material opposite the substrate 10 forms the cutting face, which is the surface which, along with its edge 16, performs the cutting in use.

At one end 12 of the substrate 10 is an interface surface 12 along which the layer of super hard material 11 is attached. In a conventional cutting element construction, the cutter element 1 including the substrate 10 is generally cylindrical and has a peripheral surface 20 and a peripheral top edge.

In the conventional cutter element 1 shown in Figures 1 and 2, the interface surface 12 includes a plurality of spaced-apart projections 22 that are arranged in a substantially annular discontinuous first array and are spaced from the peripheral surface 20 by a distance, and a second or inner substantially annular discontinuous array of projections 24 that are radially within the first array 22. The first and second arrays of projections 22, 24 typically have a circular peripheral outline.

A first substrate 30 formed by an example method is shown in Figures 3 and 4. The substrate 30 has a longitudinal axis 32, an interface surface 34, a base surface 36 and a peripheral side surface 38 extending between the interface surface 34 and the base surface 36. In this example, two arrays of projections 40, 42 extend from the interface surface 34. A first array 40, and a second array 42 located within the first array, are disposed around the central longitudinal axis 32 of the substrate 30 and are spaced from the peripheral

side surface 38 of the substrate 30. The first array 40 may include a single projection (not shown) or a plurality of discontinuous projections as shown in Figures 3 and 4. The first array 40 has a non-circular peripheral outline 44 with four linear sections 46, adjacent linear sections 46 being spaced by an arcuate section 48 extending therebetween.

The second array 42 of projections is also formed of a plurality of discontinuous projections in the example of Figures 3 and 4 but could, in a further example, be formed of a single projection. The first and second arrays 40, 42 are substantially concentric about the longitudinal axis 32 in the example of Figures 3 and 4, and the projections in the first and second arrays 40, 42 are staggered relative to each other.

As shown in Figures 3 and 4, the second array has a peripheral outline 50 which is substantially parallel to the peripheral outline 44 of the first array 40.

In some examples, one or more of the surfaces of all or a majority of the projections in the first and/or second arrays 40, 42 extend in one or more planes which are not substantially parallel to the plane of the base 36 of the substrate 30 and/or in one or more planes which are not substantially parallel to a plane through which the longitudinal axis 32 of the substrate extends.

The substrate 30 may also have a recessed region 52 adjacent to and extending from the peripheral side surface 38 of the substrate 30 to the arcuate section 48 of the peripheral outline 44 of the first array 40 between adjacent planar sections 46. The substrate 30 of Figures 3 and 4 has four recessed regions 52 or notches adjacent to and extending from the peripheral side surface 38 of the substrate 30 to the arcuate section 48 of the peripheral outline 44 of the first array 40 between adjacent planar sections 46.

In this example, the first and second arrays 40, 42 have substantially square peripheral outlines 44 with each linear section 46 of the peripheral outline

being separated by a respective arcuate section 48. Additionally, the substrate 30 in this example has a substantially square cross-section with reflective symmetry along a plane through the central longitudinal axis 32. The peripheral outline 44 of the first array 40 is substantially parallel to the peripheral side surface 38 of the substrate 30, so the peripheral side surface of the substrate has four substantially planar surface regions 54, each planar surface region being separated by a respective arcuate surface region 56.

Figure 5 shows a polycrystalline diamond construction 60 having a body of PCD material 62 bonded to the substrate 30 shown in Figures 3 and 4 along the interface 34 formed according to an example method. The body of PCD material has an interface has a plurality of recesses (not shown), the projections in the first and second arrays 40, 42 projecting from the interface 34 of the substrate providing a matching fit with the recesses in the interface of the body of PCD material 62. The super hard material layer 62 may be attached to the substrate 30 by, for example, conventional brazing techniques or by sintering a body of diamond grains together with a pre-formed substrate 30 using a conventional high pressure and high temperature technique.

In some examples, the projections in the second array 42 may be positioned to radially align with the spaces between the projections in the first array 40. In further examples, the projections and spaces may be staggered, with projections in one array 40, 42 overlapping spaces in the other array 42, 40. This staggered or mis-aligned distribution of three-dimensional features on the interface surface 34 may assist in distributing compressive and tensile stresses and/or reducing the magnitude of the stress fields and/or arresting crack growth by preventing an uninterrupted path for crack growth.

As shown in Figures 3 and 4, in these examples, the interface surface 34 between the projections in the arrays 40, 42 is, for example, substantially planar and all or a majority of the projections in these arrays are shaped such that all or a majority of the surfaces of the projections are not substantially

parallel to the base surface 36 or to the plane through which the longitudinal axis 32 of the substrate extends.

The projections in the arrays 40, 42 may have a smoothly curving upper surface or may have a sloping upper surface. In some examples, the projections may be slightly trapezoidal or tapered in shape, being widest nearer the interface surface from which they project.

It is believed that such a configuration acts to disturb 'elastic' wave formation in the material and deflect cracks at the interface 34.

In Figures 3 and 4, the projections in the arrays 40, 42 are spaced substantially equally in/round the respective substantially annular array, with each projection within a given array having the same dimension. However, the projections may be formed in any desired shape, as described above, and spaced apart from each other in a uniform or non-uniform manner to alter the stress fields over the interface surface 34. In further examples, the projections in the outer array 40 may be larger in size than those in the inner array 42.

In the example shown in Figures 3 and 4, the outer array 40 includes the same number of projections as the inner array 42, for example eight projections. Additionally, in the example of Figures 3 to 5 where the cross-section of the substrate is substantially non-circular and has three or more planar peripheral surface regions 54 separated by a respective arcuate surface region with an associated notch or recess 52 therein, this configuration may permit the substrate 30 to have rotational symmetry. This may have a number of advantages including assisting in location of the end construction in an associated tool, and assisting in orienting the substrate when processing to achieve the end product shape and also may assist in enabling the end product to be rotated for re-use once a section of the product of which this forms the substrate has worn to its limit. The specific orientation

of the cutter in which this forms a substrate in the tool or drill bit in which it is to be used would easily be identified by the notches 52 or recesses which are visible in the end product.

The arrangement and shape of the projections in the arrays 40, 42 may affect the stress distributions in the substrate 30 and may act to improve resistance to crack growth in the end product in use, in particular crack growth along the interface surface 34, for example by arresting or diverting crack growth across the stress zones in, around and above the projections.

As shown in the example of Figure 6, the depth of super hard material in the region filling the recesses or notches 52 in the substrate 30 is greater than the depth of the super hard material at the centre of the super hard material layer 62. This may enable the depth of super hard material such as PCD (polycrystalline diamond material) at the working edge to be greater than the depth of the layer in the majority of the working surface to assist in keeping the wear scar in the super hard material for longer than conventional constructions having a substantially uniform depth across the working surface which may improve the lifespan of the cutter element 60.

Figure 7 shows the various stages of an example method of forming a super hard polycrystalline construction 60 including an example substrate such as that shown in Figures 3 and 4 bonded to a body of super hard polycrystalline material 62 to form a construction shown for example in Figure 5. In a first stage 100, a substrate 30 is provided. The substrate is shaped to have an interface surface, a base surface and a peripheral side surface extending between the interface surface and the base surface. The interface surface has one or more projections arranged to project from the interface surface in a first array, the first array having a non-circular peripheral outline, the outline having two or more linear sections, adjacent linear sections being spaced by a respective arcuate surface section extending therebetween. Such a substrate is shown in Figures 3 and 4.

In a second stage 200 of the method, the substrate is placed in a canister having an internal peripheral wall defining the recess into which the substrate is placed, the internal peripheral wall having a non-circular outline and matching the outline of the peripheral side surface of the substrate. In a third stage 300, an aggregated mass of particles or grains of superhard material such as diamond grains or particles, are placed into the canister over the interface surface of the substrate to form a pre-sinter assembly.

In a fourth stage 400, the cannister is sealed and the pre-sinter assembly is then subjected to a pressure of greater than around 5.5 GPa in the presence of the sinter catalyst material for the grains of superhard material at a temperature sufficiently high for the catalyst material to melt, sintering the grains to form the super hard polycrystalline construction comprising a body of super hard polycrystalline material bonded to the substrate and having an outer peripheral surface corresponding to the shape defined by the internal peripheral wall of the cannister.

In a fifth stage 500 the super hard polycrystalline construction is removed from the canister. In some examples, the peripheral surface of the internal wall of the cannister in contact with the substrate and aggregated mass of grains of superhard material may be formed of, coated with or lined with a ceramic material that does not react chemically with the super hard material and/or a sinter catalyst material for the grains of super hard material, or the substrate or binder in the substrate. This may assist in the removal of the construction from the cannister.

In the fourth stage 400, the pre-sinter assembly may be mounted within a capsule for an HPHT furnace, as is known in the art. In some examples, the capsule may be subjected to a pressure of at least about 6.5 GPa and a

temperature of at least about 1,250 degrees Celsius or more for a period of between about 5 minutes to about several hours. After sintering, the substrate element will be bonded to a body of PCD material generated during the sintering process along the interface 34 to form a PCD construction.

In some examples, the pre-sinter assembly may be subjected to a pressure of at least about 7 GPa or even at least about 8 GPa or more.

In a sixth stage 600, the durability of the construction 60 may be further enhanced if the super hard material layer 62 is leached of catalyst material, either partially or fully, in subsequent processing, or subjected to a further high pressure high temperature sintering process. The leaching may be performed whilst the super hard material layer 32 is attached to the substrate 30 using conventional leaching techniques known in the art to remove residual catalyst binder from interstitial spaces between inter-bonded grains of the super hard polycrystalline material.

In some examples, the substrate may be formed of a cemented carbide material such as tungsten carbide (WC) including a binder phase. The binder phase may include, for example, any one or more of a solid solution of Re, carbon and W and/or any one of more of Fe, Co, and Ni. In some examples, the binder phase may have at least about 0.1 weight percent to at most about 5 weight percent of one or more of V, Cr, Ta, Ti, Mo, Zr, Nb and Hf in solid solution and/or in the form of carbide compounds. In some other examples, the material forming the substrate 30 may have at least about 0.01 weight percent and at most about 2 weight percent of one or more of Ru, Rh, Pd, Os, Ir and Pt.

An example of a cemented carbide material may be made by a method including milling a cemented carbide mixture containing WC with any one or

more of Re, Co, Ni and/or Fe and optionally grain growth inhibitors including V, Cr, Ta, Ti, Mo, Zr, Nb and Hf or their carbides and then pressing a cemented carbide article from the mixture. The article is then sintered at temperatures of above 1450°C in vacuum for 1 to 10 min and afterwards under pressure of Ar (HIP) for 5 to 120 min. The article is then cooled from the sintering temperatures to approximately 1300 degrees Celsius (°C) in an atmosphere comprising inert gases, nitrogen, hydrogen or a mixture thereof, or in a vacuum, at a cooling rate of approximately 0.2 to 2 degrees per minute.

In some examples, the substrate 30 may include excess carbon which is understood to be carbon that is in excess of the diamond of the diamond grains provided in an aggregated mass for sintering PCD which is to be bonded to the substrate in the formation of a super hard construction such as the cutter element of Figure 5, and is also in excess of the carbon included as the carbide of the cemented carbide (stoichiometric excess). A carburised substrate or carburised substrate assembly is therefore a substrate or substrate assembly including excess carbon.

Carbon may be introduced into the substrate 30 in any of a number of ways. In one example a substrate pre-form is prepared by a method including introducing diamond particles into the starting powders for making a cemented carbide to form a starting powder blend; forming the starting powder blend by means of compaction in a mould to form a green body; and sintering the green body at a temperature of greater than about 1,400 degrees Celsius at an applied pressure of less than about 1 GPa to produce a sintered substrate. At least some of the diamond particles are converted wholly or partially into graphite during this carbide sintering step, because the pressure is below that for diamond to be thermodynamically stable.

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

In some examples, carbon may be introduced into the substrate in the form of graphite powder.

In other examples, carbon may be introduced into the substrate in the form of carbonaceous gas, which is caused to permeate or infiltrate the substrate.

In still further examples, material comprising carbon may be sprayed onto a surface of the substrate. In particular, powder containing cobalt, carbon and tungsten may be deposited onto the substrate surface by means of thermal spraying.

In other examples, the substrate may be coated with a source of excess carbon, such as graphite.

In some examples, the substrate is prepared from starting carbide powder having a high content of carbon in the form of carbon black, for example.

In other examples, a substrate with high carbon content may be prepared by avoiding the removal of some carbon during the preparation of the green body for readiness for sintering. Typically, a green body is heat treated to remove binder or pressing aid material prior to sintering, and carbon is removed during this process. In one example, this process is not thoroughly completed, leaving at least some carbon of binder origin within the green body.

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

In some examples, the mean content of the source of excess carbon within a surface region of an example carburised substrate or throughout substantially the entire carburised substrate is no greater than about 10 weight percent, more preferably no greater than about 6 weight percent and yet more preferably no greater than about 5.5 weight percent of the material in the surface region or the substrate. For example, the content of the source of excess carbon within the surface region or throughout the entire carburised substrate may be at least about 0.1 weight percent or at least about 0.3 weight percent of the material in the region. In some examples, such a surface region may extend to a depth of at least about 1 mm, at least about 2 mm, or even at least 3 mm from the interface surface 34.

In some examples, the source of excess carbon is a carbonaceous material other than metal carbide, such as carbon black powder or graphite. In one example, the source of excess carbon may be derived from diamond that has been converted into a non-diamond material.

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

examples the raw materials for cemented carbide comprise grains of tungsten carbide and grains comprising cobalt.

The method of forming an example substrate may include combining diamond grains with raw materials for cemented carbide, forming the combination into a substantially self-supporting green body; subjecting the green body to a temperature of at least 500 degrees Celsius and a pressure at which diamond is not thermodynamically stable to form the carburised substrate. The diamond particles may be wholly or partly converted into a non-diamond material, particularly graphite.

A first substrate element for use as the surface region of a substrate for a PCD compact may be manufactured by blending together diamond particles, tungsten carbide (WC) powder and cobalt powder, forming the blended mixture into a compacted green body, and subjecting the green body to a conventional carbide sintering process. The diamond particles may, for example, have a mean size in the range of 0.75 to 1.5 microns, and constitute 3 weight percent of the blended mixture in one example. The WC powder and the cobalt powder may be pre-mixed, the cobalt constituting 13 weight percent of the WC-Co pre-mix and the WC particles having a mean size in the range from about 1 to 4 microns. About 2 weight percent organic pressing aid may be included in the WC-Co mix in such an example. The blended powder mix may be uniaxially compacted at ambient temperature to form a substantially cylindrical green body, which may be conventionally sintered at a temperature of 1,400 degrees Celsius for 2 hours to form a sintered article. By the end of the sintering process, the diamond particles may have completely converted into graphite.

In one or more of the above-described examples, the projections in the arrays 40, 42 on the interface surface 34 may be formed integrally whilst the

substrate 30 is being formed, through use of an appropriately shaped mold into which the particles of material to form the substrate are placed. Alternatively, the projections in the arrays 40, 42 may be created after the substrate 30 has been created or part way through the creation process, for example by a conventional machining process such as EDM or by laser ablation.

In an example where the substrate 30 includes Re, an example method of manufacture may be as follows. A mass of tungsten carbide powder having WC grains having an average grain size of about 0.6 μm with a carbon content of 6.13 wt.%, may be milled with 5.5%Re powder and 3.7%Co powder. The Co grains may have an average grain size of about 1 μm . The powder mixture may be produced by milling the powders together for 24 hours using a ball mill in a milling medium comprising hexane with 2 wt.% paraffin wax, and using a powder-to-ball ratio of 1:6. After milling 0.35 wt.% carbon black may be added and additional milling performed for 1 hr. After drying the mixture, green bodies may be pressed and sintered at 1540°C for 60 min (30 min vacuum + 30 min HIP in Ar at a pressure of 50 Bar). After the sintering at 1540°C the bodies may be cooled down to 1300°C at a rate of 0.5 degrees per min and afterwards at an uncontrolled rate down to room temperature.

In some examples, as described above, the cemented carbide material forming the substrate may comprise between around 2 to around 9 wt.% Re, and around 3 to around 9 wt.%Co, with the remainder being WC.

Although the examples shown in Figures 3 to 5 are shown as having a substantially square cross-section, example substrates may have another non-cylindrical cross-section shape such as substantially rectangular, or substantially triangular, for example with rounded corners in each case.

To achieve the final desired dimensions or surface finish, the substrate and/or body of super hard polycrystalline material may be machined such as through application of a lapping process, or laser ablated or polished.

Claims:

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

a first stage; the first stage comprising providing a substrate, the substrate having an interface surface, a base surface, a longitudinal axis, and a peripheral side surface extending between the interface surface and the base surface, the interface surface comprising one or more projections arranged to project from the interface surface in a first array, the first array of one or more projections having a non-circular peripheral outline, the outline having two or more linear sections, adjacent linear sections being spaced by a respective arcuate surface section extending therebetween, the substrate having a non-circular cross-section in a plane perpendicular to a plane through which the longitudinal axis extends;

a second stage; the second stage comprising placing the substrate in a canister having an internal peripheral wall defining a recess for receiving the substrate, the internal peripheral wall having a non-circular outline matching the peripheral side surface of the substrate;

a third stage; the third stage comprising placing an aggregated mass of particles or grains of super hard material into the canister over the interface surface of the substrate to form a pre-sinter assembly;

a fourth stage; the fourth stage comprising sealing the cannister is sealed, and subjecting the pre-sinter assembly to a pressure of greater than around 5.5 GPa at a temperature of at least around 1250 degrees Celsius to sinter the particles or grains and form the super hard polycrystalline construction comprising a body of super hard polycrystalline material bonded to the substrate;

a fifth stage; the fifth stage comprising removing the super hard polycrystalline construction from the canister.

2. The method of claim 1, wherein the substrate is formed of a cemented carbide material comprising a binder material; and wherein the second stage further comprises placing the substrate in the canister wherein the peripheral wall of the cannister is formed of a ceramic material that does not react chemically with the super hard material and/or a sinter catalyst material for the grains of super hard material and/or the material from which the substrate is formed or the binder in the material from which the substrate is formed.
3. The method of claim 1, wherein the substrate is formed of a cemented carbide material comprising a binder material; and wherein the second stage further comprises placing the substrate in the canister wherein the peripheral wall of the cannister is coated with a ceramic material that does not react chemically with the super hard material and/or a sinter catalyst material for the grains of super hard material and/or the material from which the substrate is formed or the binder in the material from which the substrate is formed.
4. The method of claim 1, wherein the substrate is formed of a cemented carbide material comprising a binder material; and wherein the second stage further comprises lining the canister prior to placing the substrate in the canister; the step of lining comprising lining the peripheral wall of the cannister with a ceramic material that does not react chemically with the super hard material and/or a sinter catalyst material for the grains of super hard material and/or the material from which the substrate is formed or the binder in the material from which the substrate is formed.
5. The method of any one of the preceding claims, wherein the fourth stage comprises subjecting the pre-sinter assembly to a pressure a pressure of at least about 6.5 GPa to around 9 GPa for a period of between about 5 minutes to about 3 hours.
6. The method of any one of the preceding claims, wherein the third stage of placing an aggregated mass of particles or grains of super hard material into the canister comprises placing a mass of diamond particles into the canister.

7. The method of claim 6, wherein the fourth stage of subjecting the pre-sinter assembly to a pressure comprises subjecting the pre-sinter assembly to a temperature and pressure such that the diamond grains exhibit intergranular bonding and define a plurality of interstitial regions therebetween, any residual catalyst solvent at least partially filling a plurality of the interstitial regions, the body of super hard polycrystalline material bonded to the substrate comprising a body of polycrystalline diamond material.

8. The method of claim 7, further comprising a sixth stage, the sixth stage comprising treating at least a portion of the body of polycrystalline diamond material to remove residual catalyst solvent from the interstitial regions to form a region substantially free of the catalyst solvent material for the PCD material, said portion forming a thermally stable region extending a depth from a working surface of the body of polycrystalline diamond material towards the interface with the substrate.

9. The method of any one of the preceding claims, wherein the first stage of providing a substrate comprises providing a substrate comprising a cemented carbide material.

10. The method of claim 9, wherein the cemented carbide material comprises tungsten carbide.

11. The method of any one of claims 9 or 10, wherein the first stage of providing a substrate comprises providing a substrate comprising tungsten carbide particles bonded together by a binder material, the binder material comprising an alloy of Co, Ni and Cr.

12. The method of claim 11, wherein the binder material further comprises one or more of V, Ta, Ti, Mo, Zr, Nb and Hf in solid solution.

13. The method of any one of claims 11 or 12, wherein the first stage of providing a substrate comprises providing a substrate further comprising one or more of Re, Ru, Rh, Pd, Re, Os, Ir and Pt.

14. The method of any one of the preceding claims, wherein the first stage of providing a substrate comprises providing a substrate comprising free carbon.

15. The method of any one of the preceding claims, wherein the first stage of providing a substrate comprises providing a substrate in which the peripheral outline of the first array is substantially parallel to the peripheral side surface of the substrate.

16. The method of any one of the preceding claims, wherein the first stage comprising providing a substrate comprises providing a substrate with a substantially square cross-section.

17. The method of any one of claims 1 to 15, wherein the first stage comprising providing a substrate comprises providing a substrate with a substantially rectangular cross-section.

18. The method of any one of claims 1 to 15, wherein the first stage comprising providing a substrate comprises providing a substrate with a substantially triangular cross-section.

19. The method of any one of the preceding claims, wherein the first stage comprises providing a substrate comprising a recessed region adjacent to and extending from the peripheral side surface of the substrate to the arcuate section of the peripheral outline of the first array between adjacent planar sections.

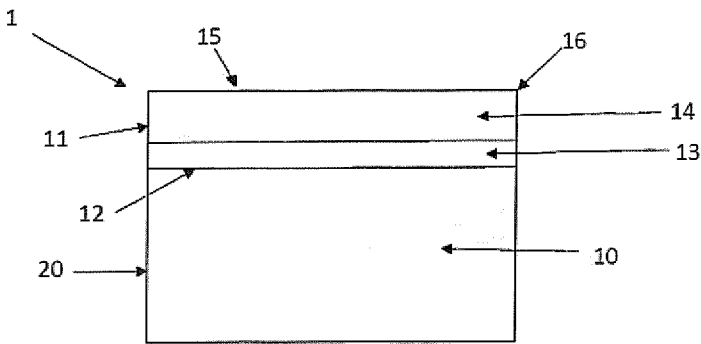


Figure 1 PRIOR ART

FIG. 2
PRIOR ART

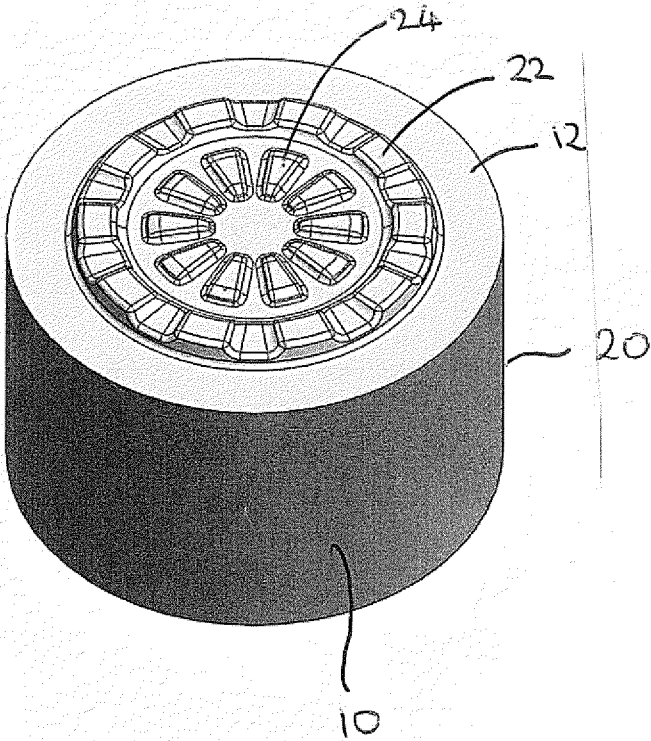


FIG. 3

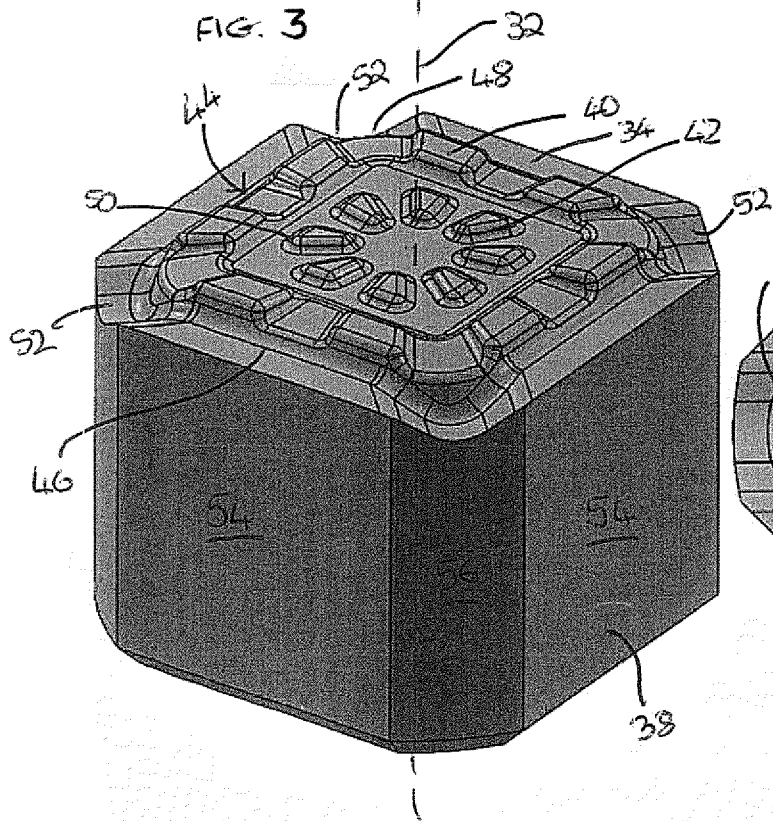


FIG. 4

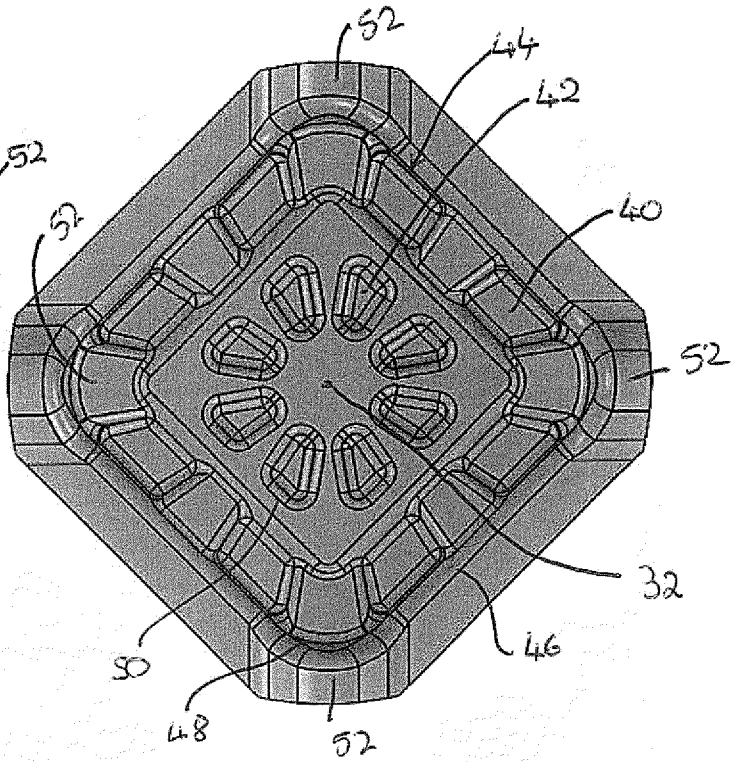


FIG. 5

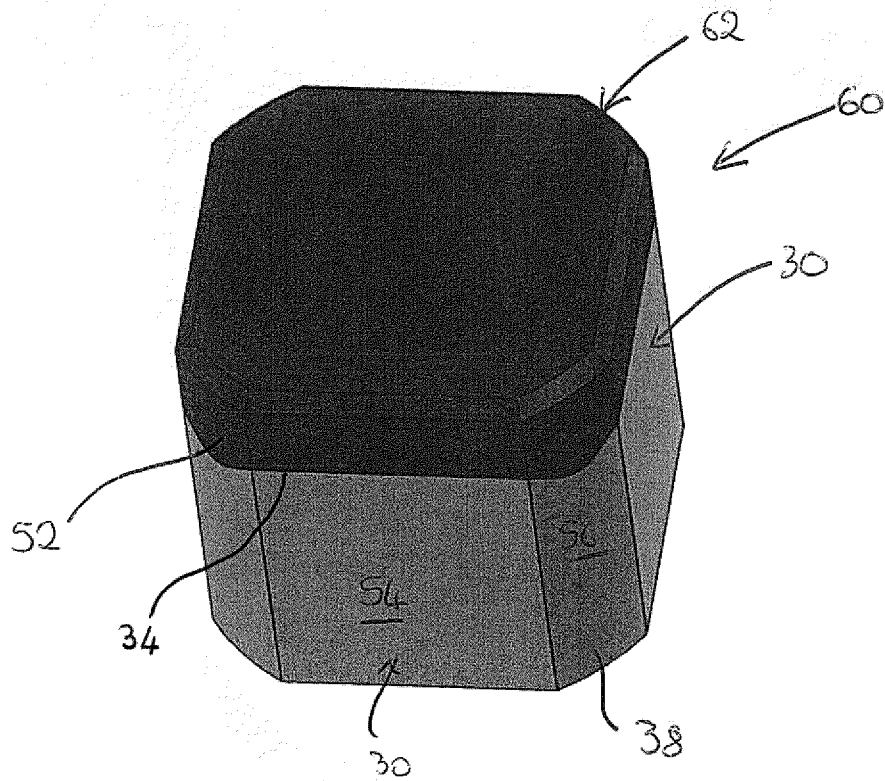
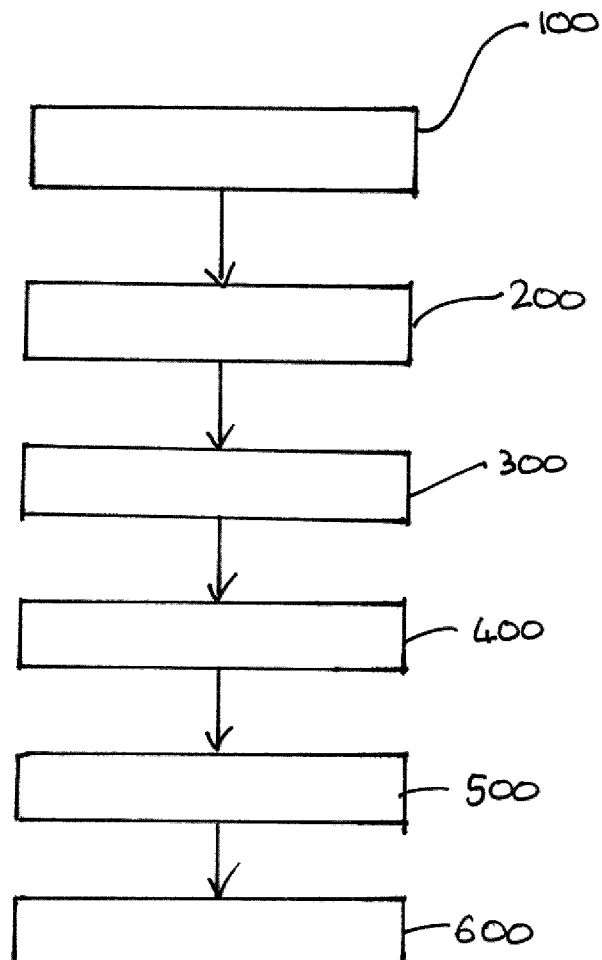


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/087078

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	B22F3/14	B22F7/06
	E21B10/573	
ADD.	B22F5/00	
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 B32B C22C C23C E21B B23G B23B		
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		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2014/238753 A1 (NELMS DEREK L [US] ET AL) 28 August 2014 (2014-08-28) paragraphs [0036], [0041], [0054] figures 1-14, 16	1 - 19
A	US 2007/062737 A1 (HALL DAVID R [US] ET AL) 22 March 2007 (2007-03-22) paragraphs [0020], [0023], [0027] figures 2-9	1 - 19
A	EP 2 467 559 B1 (SMITH INTERNATIONAL [US]) 25 October 2017 (2017-10-25) paragraphs [0005], [0022], [0048] figures 4-16	1 - 19
	- / - -	
☒ Further documents are listed in the continuation of Box C.		
☒ 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		
"E" earlier application or patent but published on or after the international filing date		
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		
"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		Date of mailing of the international search report
7 March 2025		13/03/2025
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 Traon, Nicolas

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/087078

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 571 891 B1 (SMITH REDD H [US] ET AL) 3 June 2003 (2003-06-03) column 4, line 55 - column 6, line 12 figures 2-16 column 2, lines 58-65 -----	1 - 19
A	US 2016/303709 A1 (BOWES DAVID CHRISTIAN [GB]) 20 October 2016 (2016-10-20) paragraphs [0011], [0049] figures 1, 2 -----	1 - 19
A	US 2016/311689 A1 (NILEN ROGER WILLIAM NIGEL [GB] ET AL) 27 October 2016 (2016-10-27) paragraphs [0011], [0046] figures 1-3 -----	1 - 19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/087078

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2014238753 A1	28-08-2014	US 2014238753 A1	28-08-2014
		WO 2014134390 A1	04-09-2014
US 2007062737 A1	22-03-2007	NONE	
EP 2467559 B1	25-10-2017	EP 2467559 A2	27-06-2012
		US 2011036642 A1	17-02-2011
		WO 2011022372 A2	24-02-2011
US 6571891 B1	03-06-2003	BE 1014395 A5	07-10-2003
		BE 1016089 A3	07-03-2006
		BE 1016090 A3	07-03-2006
		BE 1016091 A3	07-03-2006
		GB 2364082 A	16-01-2002
		IT TO20010609 A1	25-12-2002
		US 6571891 B1	03-06-2003
		US 2003116361 A1	26-06-2003
US 2016303709 A1	20-10-2016	CN 106068360 A	02-11-2016
		GB 2528728 A	03-02-2016
		US 2016303709 A1	20-10-2016
		US 2020353590 A1	12-11-2020
		WO 2015091682 A2	25-06-2015
		ZA 201604006 B	27-09-2017
US 2016311689 A1	27-10-2016	CN 106068362 A	02-11-2016
		US 2016311689 A1	27-10-2016
		US 2019366442 A1	05-12-2019
		US 2022144646 A1	12-05-2022
		WO 2015091672 A2	25-06-2015
		ZA 201604008 B	28-11-2018