



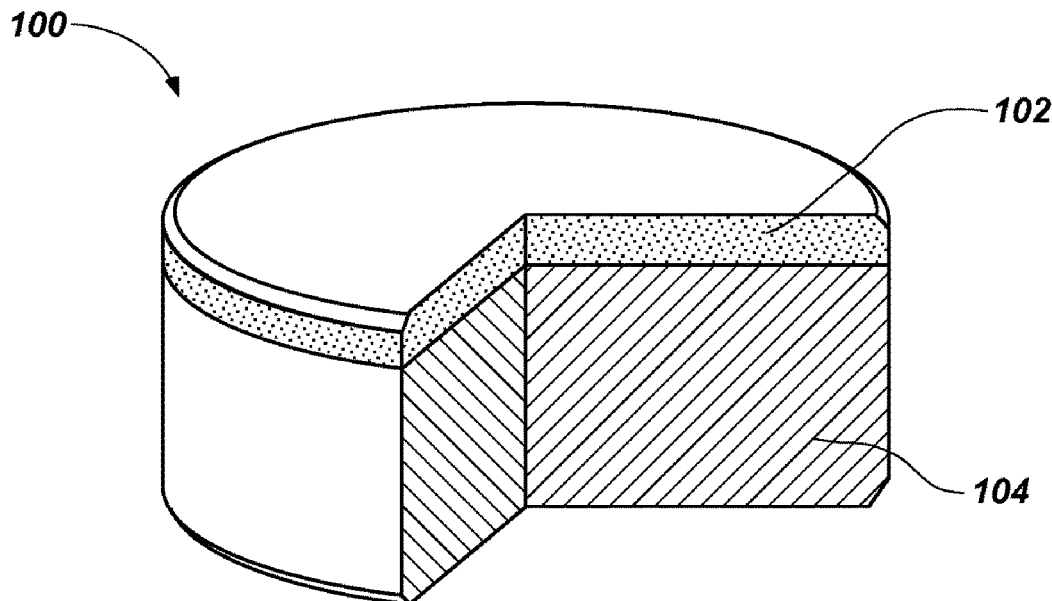
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(19) **United States**(12) **Patent Application Publication**
Bird(10) **Pub. No.: US 2017/0066110 A1**(43) **Pub. Date: Mar. 9, 2017**(54) **POLYCRYSTALLINE DIAMOND, METHODS
OF FORMING SAME, CUTTING ELEMENTS,
AND EARTH-BORING TOOLS**(52) **U.S. Cl.**CPC *B24D 18/0009* (2013.01); *B24D 3/06*
(2013.01); *E21B 10/54* (2013.01); *E21B 10/56*
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(57)

ABSTRACT

A method of forming polycrystalline diamond includes providing an alloy over at least portions of a plurality of diamond particles, and subjecting the plurality of diamond particles to a high-temperature, high-pressure process to form a polycrystalline diamond material having inter-granular bonds between adjacent diamond particles. The alloy includes iridium and nickel, and a volume of the diamond particles is at least about 92% of a total volume of the alloy and the diamond particles. The polycrystalline diamond material includes at least about 92% diamond by volume. A polycrystalline diamond compact includes grains of diamond bonded to one another by inter-granular bonds and an alloy disposed within interstitial spaces between the grains of diamond. The grains of diamond occupy at least 94% by volume of the polycrystalline diamond compact. An earth-boring tool may include a bit body and such a polycrystalline diamond compact.

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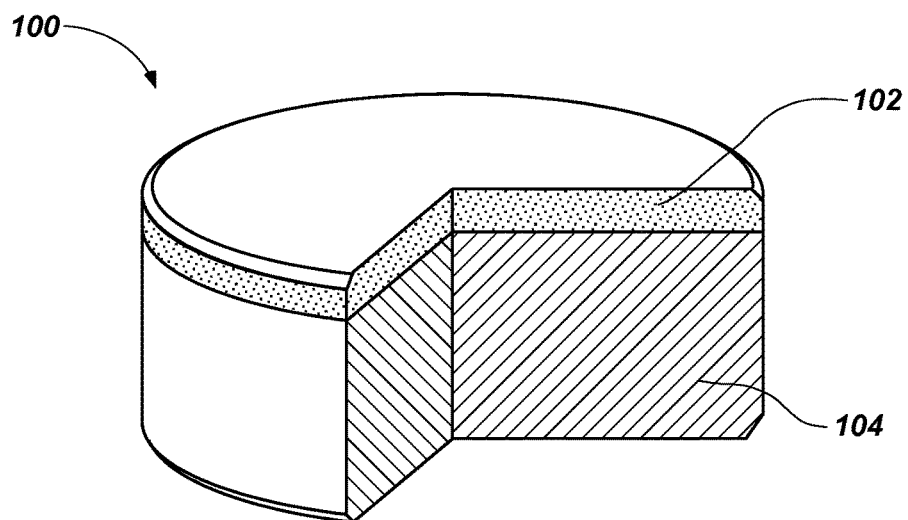


FIG. 1

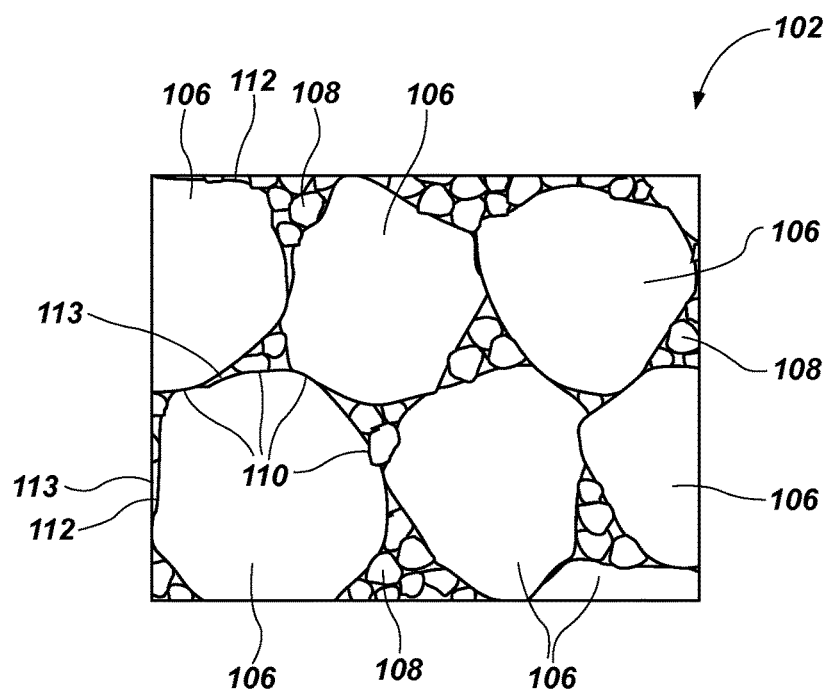


FIG. 2

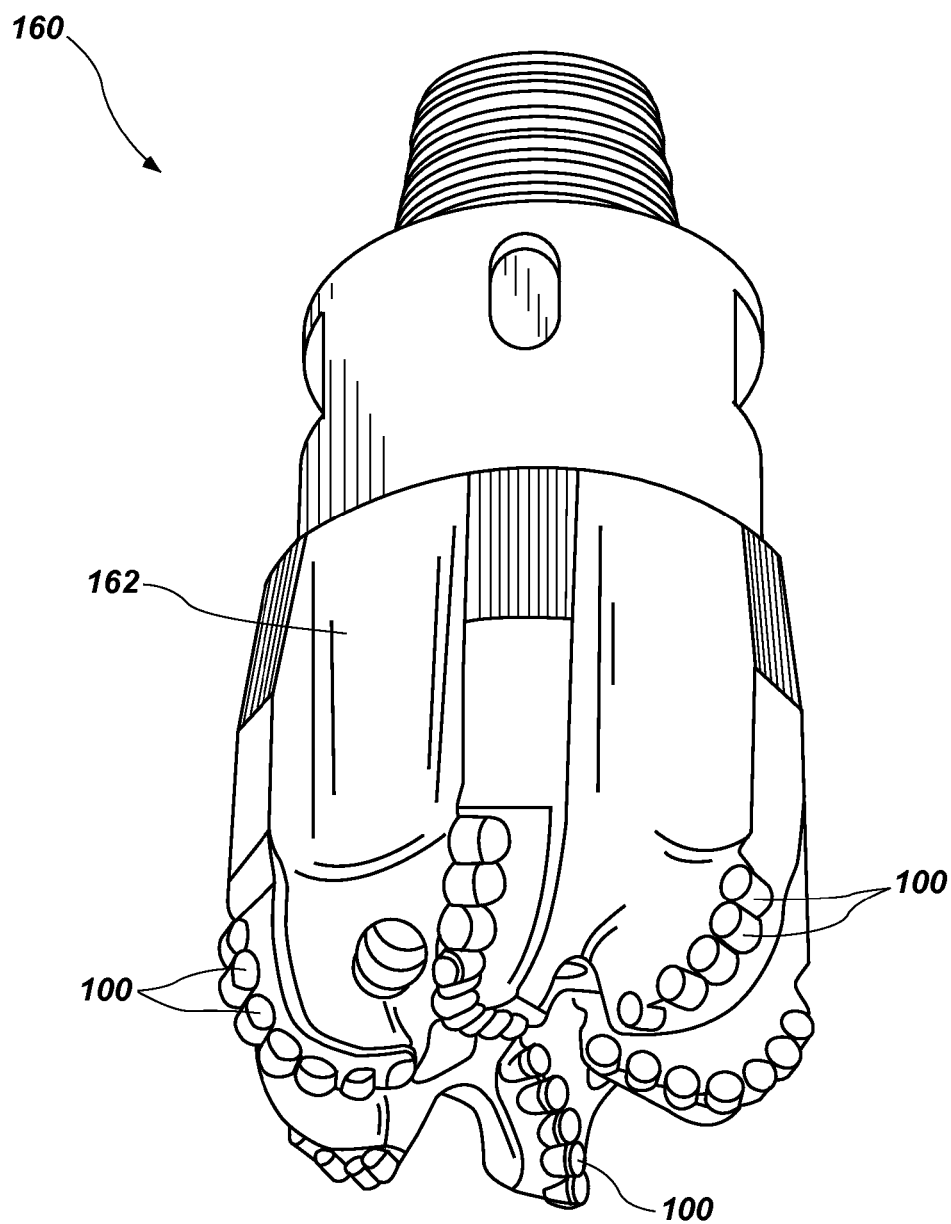


FIG. 3

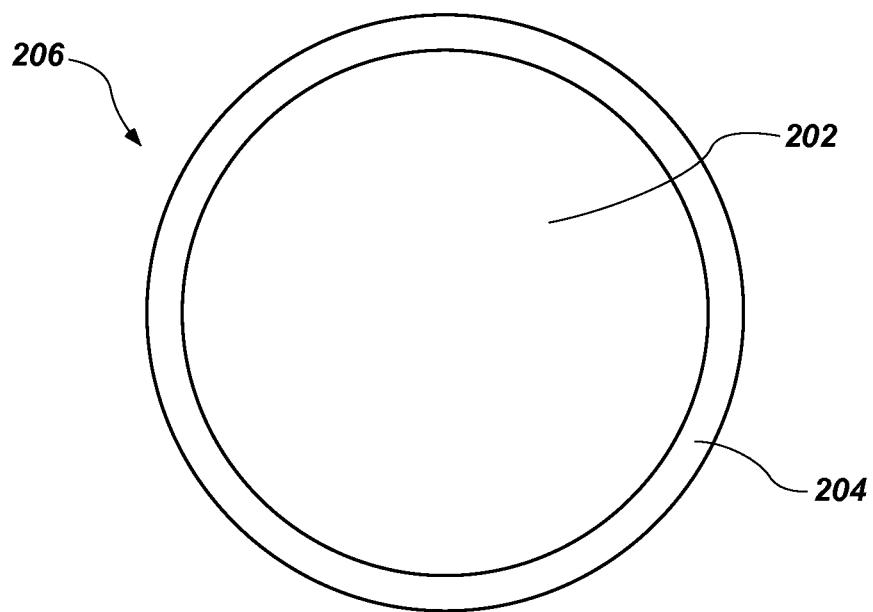


FIG. 4

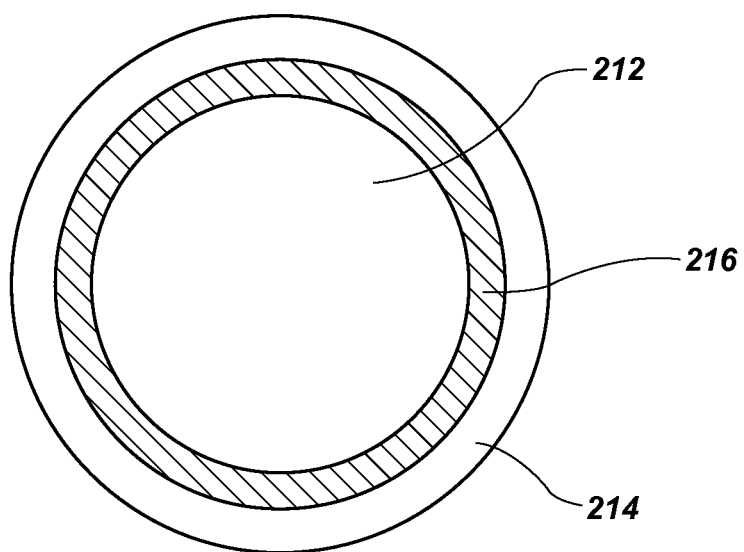


FIG. 5

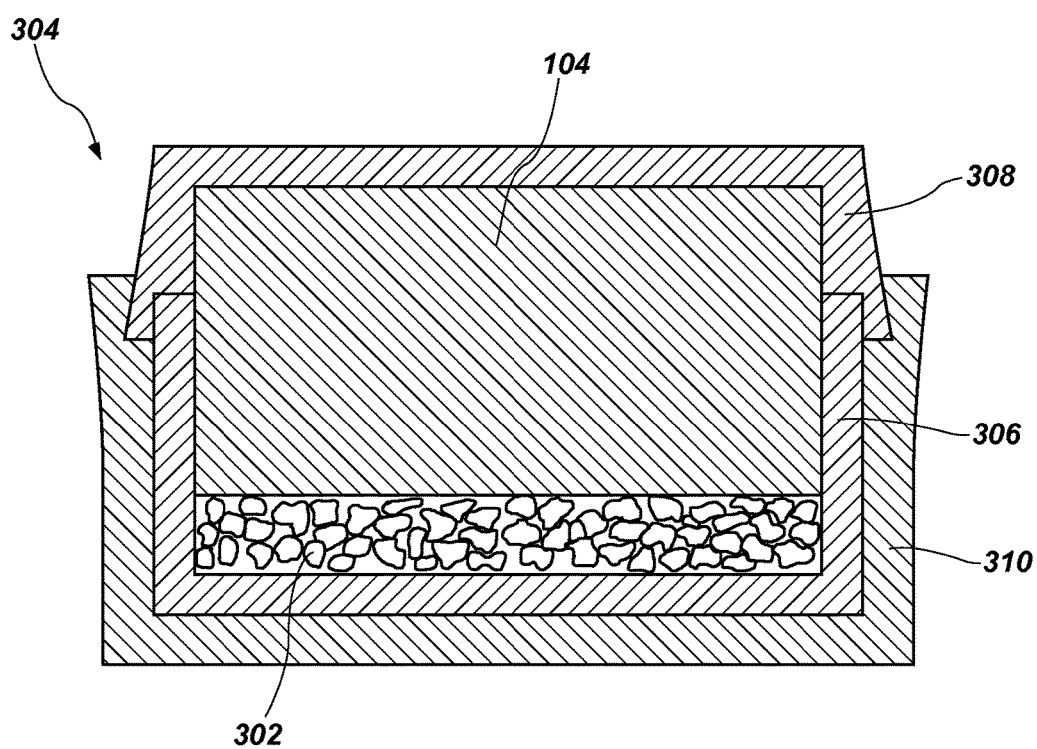
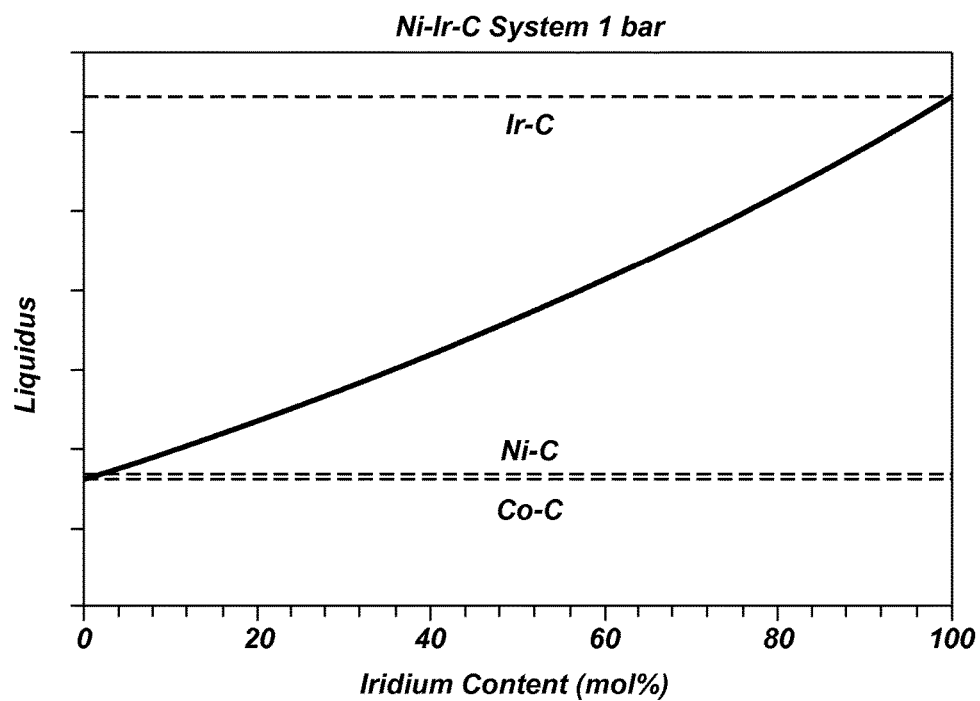
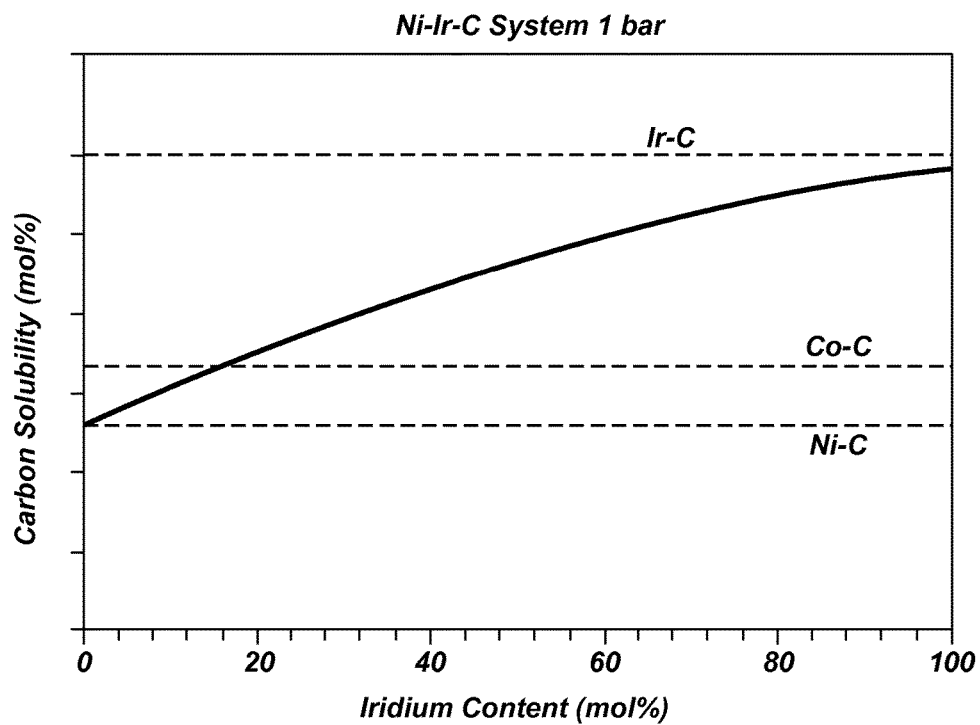


FIG. 6



POLYCRYSTALLINE DIAMOND, METHODS OF FORMING SAME, CUTTING ELEMENTS, AND EARTH-BORING TOOLS

FIELD

[0001] Embodiments of the present disclosure relate generally to polycrystalline diamond, cutting elements, earth-boring tools, and method of forming such materials, cutting elements, and tools.

BACKGROUND

[0002] Earth-boring tools for forming wellbores in subterranean earth formations may include a plurality of cutting elements secured to a body. For example, fixed-cutter earth-boring rotary drill bits (also referred to as “drag bits”) include a plurality of cutting elements that are fixedly attached to a bit body of the drill bit. Similarly, roller-cone earth-boring rotary drill bits include cones that are mounted on bearing pins extending from legs of a bit body such that each cone is capable of rotating about the bearing pin on which the cone is mounted. A plurality of cutting elements may be mounted to each cone of the drill bit.

[0003] The cutting elements used in earth-boring tools often include polycrystalline diamond compact (often referred to as “PDC”) cutters, which are cutting elements that include a polycrystalline diamond (PCD) material. Such polycrystalline diamond cutting elements are formed by sintering and bonding together relatively small diamond grains or crystals under conditions of high pressure and high temperature, typically in the presence of a catalyst (such as cobalt, iron, nickel, or alloys or mixtures thereof), to form a layer of polycrystalline diamond material on a cutting element substrate. These processes are often referred to as high-pressure, high-temperature (or “HPHT”) processes. Catalyst material is mixed with the diamond grains to reduce the amount of oxidation of diamond by oxygen and carbon dioxide during an HPHT process and to promote diamond-to-diamond bonding.

[0004] The cutting element substrate may include a cermet material (i.e., a ceramic-metal composite material) such as cobalt-cemented tungsten carbide. In such instances, the cobalt (or other catalyst material) in the cutting element substrate may be drawn into the diamond grains or crystals during sintering and serve as a catalyst material for forming a diamond table from the diamond grains or crystals. In other methods, powdered catalyst material may be mixed with the diamond grains or crystals prior to sintering the grains or crystals together in an HPHT process.

[0005] Upon formation of a diamond table using an HPHT process, catalyst material may remain in interstitial spaces between the grains or crystals of diamond in the resulting polycrystalline diamond table. The presence of the catalyst material in the diamond table may contribute to thermal damage in the diamond table when the cutting element is heated during use, due to friction at the contact point between the cutting element and the formation.

[0006] Traditional PDC performance relies on the catalyst alloy which sweeps through the compacted diamond feed during HPHT synthesis. Traditional catalyst alloys are cobalt-based with varying amounts of nickel, tungsten, and chromium to facilitate diamond intergrowth between the compacted diamond material. However, in addition to facilitating the formation of diamond-to-diamond bonds during

HPHT sintering, these alloys also facilitate the formation of graphite from diamond during drilling. Formation of graphite can rupture diamond necking regions (i.e., grain boundaries) due to an approximate 57% volumetric expansion during the transformation. This phase transformation is known as “back-conversion” or “reverse graphitization,” and typically occurs at temperatures approaching 600° C. to 1,200° C., near cutting temperatures experienced during drilling applications. This mechanism, coupled with mismatch of the coefficients of thermal expansion of the metallic phase and diamond, is believed to account for a significant part of the general performance criteria known as “thermal stability.” From experimental wear conditions, back-conversion appears to dominate the thermal stability of a PDC, promoting premature degradation of the cutting edge and performance.

[0007] To reduce problems associated with different rates of thermal expansion and with back-conversion in polycrystalline diamond cutting elements, so-called “thermally stable” polycrystalline diamond (TSD) cutting elements have been developed. A TSD cutting element may be formed by leaching the catalyst material (e.g., cobalt) out from interstitial spaces between the diamond grains in the diamond table using, for example, an acid. Substantially all of the catalyst material may be removed from the diamond table. TSD cutting elements in which substantially all catalyst material has been leached from the diamond table have been reported to be thermally stable up to temperatures of about 1,200° C. It has also been reported, however, that fully leached diamond tables are relatively more brittle and vulnerable to shear, compressive, and tensile stresses than are non-leached diamond tables. In an effort to provide cutting elements having diamond tables that are more thermally stable relative to non-leached diamond tables, but that are also relatively less brittle and vulnerable to shear, compressive, and tensile stresses relative to fully leached diamond tables, cutting elements have been provided that include a diamond table in which only a portion of the catalyst material has been leached from the diamond table, for example, adjacent to a cutting face of the table, and from the cutting face along a side surface of the table.

BRIEF SUMMARY

[0008] In some embodiments, a method of forming polycrystalline diamond includes providing an alloy over at least portions of a plurality of diamond particles, and subjecting the plurality of diamond particles to a high-temperature, high-pressure process to form a polycrystalline diamond material having inter-granular bonds between adjacent diamond particles. The alloy comprises iridium and nickel, and a volume of the diamond particles is at least about 92% of a total volume of the alloy and the diamond particles. The polycrystalline diamond material comprises at least about 92% diamond by volume.

[0009] In other embodiments, a method of forming polycrystalline diamond includes providing an alloy over at least portions of a plurality of diamond particles, and subjecting the plurality of diamond particles to a pressure of at least 5 GPa and a temperature of at least 1,400° C. to form a porous polycrystalline diamond compact having inter-granular bonds between adjacent diamond particles. The alloy comprises nickel and at least about 10 mol % iridium.

[0010] In certain embodiments, a polycrystalline diamond compact includes grains of diamond bonded to one another

by inter-granular bonds and an alloy disposed within interstitial spaces between the grains of diamond. The alloy comprises iridium and nickel, and is from about 1 mol % iridium to about 99 mol % iridium. The grains of diamond occupy at least 94% by volume of the polycrystalline diamond compact. An earth-boring tool may include a bit body and such a polycrystalline diamond compact.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] While the specification concludes with claims particularly pointing out and distinctly claiming what are regarded as embodiments of the present disclosure, various features and advantages of embodiments of the disclosure may be more readily ascertained from the following description of example embodiments of the disclosure when read in conjunction with the accompanying drawings, in which:

[0012] FIG. 1 is a partially cut-away perspective view of an embodiment of a cutting element (i.e., a polycrystalline compact) including a volume of polycrystalline diamond on a substrate;

[0013] FIG. 2 is a simplified view illustrating how a microstructure of the polycrystalline diamond of the cutting element of FIG. 1 may appear under magnification;

[0014] FIG. 3 illustrates an earth-boring rotary drill bit comprising cutting elements as described herein;

[0015] FIG. 4 is a simplified drawing of a coated particle that may be used to form a cutting element like that of FIGS. 1 and 2 in accordance with some embodiments of methods described herein;

[0016] FIG. 5 is a simplified drawing of another coated particle that may be used to form a cutting element like that of FIGS. 1 and 2 in accordance with some embodiments of methods described herein;

[0017] FIG. 6 is a simplified cross-sectional view illustrating materials used to form the cutting element of FIG. 1 in a container in preparation for subjecting the container to an HPHT sintering process;

[0018] FIG. 7 is a plot of carbon solubility in alloys of iridium and nickel at 1 bar; and

[0019] FIG. 8 is a plot of the liquidus of alloys of iridium and nickel saturated with carbon at 1 bar.

DETAILED DESCRIPTION

[0020] The illustrations presented herein are not actual views of any particular cutting elements or tools, but are merely idealized representations that are employed to describe example embodiments of the present disclosure. Additionally, elements common between figures may retain the same numerical designation.

[0021] As used herein, the term “particle” means and includes any coherent volume of solid matter having an average dimension of about 500 μm or less, whether as grains, powder, or any other type of material. Grains (e.g., crystals) and coated grains are types of particles. As used herein, the term “nanoparticle” means and includes any particle having an average particle diameter of about 500 nm or less. Nanoparticles include grains in a polycrystalline diamond compact having an average grain size of about 500 nm or less.

[0022] As used herein, the term “inter-granular bond” means and includes any direct atomic bond (e.g., covalent, ionic, metallic, etc.) between atoms in adjacent grains of material.

[0023] As used herein, the terms “nanodiamond” and “diamond nanoparticles” mean and include any single or polycrystalline or agglomeration of nano crystalline carbon material comprising a mixture of sp-3 and sp-2 bonded carbon wherein the individual particle or crystal, whether singular or part of an agglomerate, is primarily made up of sp-3 bonds. Commercial nanodiamonds are typically derived from detonation sources (e.g., ultra-dispersed diamond or UDD) and crushed sources and can be naturally occurring or manufactured synthetically. Naturally occurring nanodiamond includes the natural lonsdaleite phase identified with meteoric deposits.

[0024] As used herein, the term “polycrystalline diamond” means and includes any material comprising a plurality of diamond grains or crystals bonded directly together by inter-granular diamond-to-diamond bonds. The crystal structures of the individual grains of polycrystalline diamond may be randomly oriented in space within the polycrystalline diamond.

[0025] As used herein, the term “polycrystalline diamond compact” means and includes any structure comprising a polycrystalline diamond comprising inter-granular bonds formed by a process that involves application of pressure (e.g., compaction) to the precursor material or materials used to form the polycrystalline diamond compact.

[0026] As used herein, the term “earth-boring tool” means and includes any type of bit or tool used for drilling during the formation or enlargement of a wellbore and includes, for example, rotary drill bits, percussion bits, core bits, eccentric bits, bi-center bits, reamers, mills, drag bits, roller-cone bits, hybrid bits, and other drilling bits and tools known in the art.

[0027] FIG. 1 illustrates a cutting element 100, which may be formed as disclosed herein. The cutting element 100 includes a polycrystalline diamond 102. Optionally, the cutting element 100 may also include a substrate 104 to which the polycrystalline diamond 102 may be bonded, or on which the polycrystalline diamond 102 is formed under the aforementioned HPHT conditions. For example, the substrate 104 may include a generally cylindrical body of cobalt-cemented tungsten carbide material, although substrates of different geometries and compositions may also be employed. The polycrystalline diamond 102 may be in the form of a table (i.e., a layer) of polycrystalline diamond 102 on the substrate 104, as shown in FIG. 1. The polycrystalline diamond 102 may be provided on (e.g., formed on or secured to) a surface of the substrate 104. In additional embodiments, the cutting element 100 may simply be a volume of the polycrystalline diamond 102 having any desirable shape, and may not include any substrate 104. The cutting element 100 may be referred to as “polycrystalline compact,” or, if the polycrystalline diamond 102 includes diamond, as a “polycrystalline diamond compact.”

[0028] As shown in FIG. 2, the polycrystalline diamond 102 may include interspersed and inter-bonded grains forming a three-dimensional network of diamond. Optionally, in some embodiments, the grains of the polycrystalline diamond 102 may have a multimodal (e.g., bi-modal, tri-modal, etc.) grain size distribution. For example, the polycrystalline diamond 102 may comprise a multi-modal grain size distribution as disclosed in at least one of U.S. Pat. No. 8,579,052, issued Nov. 12, 2013, and titled “Polycrystalline Compacts Including In-Situ Nucleated Grains, Earth-Boring Tools Including Such Compacts, and Methods of Forming Such Compacts and Tools”; U.S. Pat. No. 8,727,042, issued May

20, 2014, and titled “Polycrystalline Compacts Having Material Disposed in Interstitial Spaces Therein, and Cutting Elements Including Such Compacts”; and U.S. Pat. No. 8,496,076, issued Jul. 30, 2013, and titled “Polycrystalline Compacts Including Nanoparticulate Inclusions, Cutting Elements and Earth-Boring Tools Including Such Compacts, and Methods of Forming Such Compacts”; the disclosures of each of which are incorporated herein in their entireties by this reference.

[0029] For example, in some embodiments, the polycrystalline diamond **102** may include larger grains **106** and smaller grains **108**. The larger grains **106** and/or the smaller grains **108** may have average particle dimensions (e.g., mean diameters) of less than 0.5 mm, less than 0.1 mm, less than 0.01 mm, less than 1 μm , less than 0.1 μm , or even less than 0.01 μm . That is, the larger grains **106** and smaller grains **108** may each include micron-sized particles (grains having an average particle diameter in a range from about 1 μm to about 500 μm (0.5 mm)), submicron-sized particles (grains having an average particle diameter in a range from about 500 nm (0.5 μm) to about 1 μm), and/or nanoparticles (particles having an average particle diameter of about 500 nm or less). In some embodiments, the larger grains **106** may be micron-sized diamond particles, and the smaller grains **108** may be submicron diamond particles or diamond nanoparticles. In some embodiments, the larger grains **106** may be submicron diamond particles, and the smaller grains **108** may be diamond nanoparticles. In other embodiments, the grains of the polycrystalline diamond **102** may have a monomodal grain size distribution. The polycrystalline diamond **102** may include direct inter-granular bonds **110** between the grains **106**, **108**, represented in FIG. 2 by dashed lines. If the grains **106**, **108** are diamond particles, the direct inter-granular bonds **110** may be diamond-to-diamond bonds. Interstitial spaces are present between the inter-bonded grains **106**, **108** of the polycrystalline diamond **102**. In some embodiments, some of these interstitial spaces may include voids **113** within the polycrystalline diamond **102** in which there is no solid or liquid substance (although a gas, such as air, may be present in the voids). An alloy material **112** may reside in a portion of the interstitial spaces unoccupied by the grains **106**, **108** of the polycrystalline diamond **102**, and may be in the form of a coating around the grains **106**, **108** of the polycrystalline diamond **102**.

[0030] As used herein, the term “grain size” means and includes a geometric mean diameter measured from a two-dimensional section through a bulk material. The geometric mean diameter for a group of particles may be determined using techniques known in the art, such as those set forth in Ervin E. Underwood, QUANTITATIVE STEREOLOGY, 103-105 (Addison-Wesley Publishing Company, Inc., 1970), the disclosure of which is incorporated herein in its entirety by this reference. As known in the art, the average grain size of grains within a microstructure may be determined by measuring grains of the microstructure under magnification. For example, a scanning electron microscope (SEM), a field emission scanning electron microscope (FE-SEM), or a transmission electron microscope (TEM) may be used to view or image a surface of a polycrystalline diamond **102** (e.g., a polished and etched surface of the polycrystalline diamond **102**). Commercially available vision systems are often used with such microscopy systems, and these vision systems are capable of measuring the average grain size of grains within a microstructure.

[0031] Referring again to FIG. 2, the alloy material **112** may include a material that promotes the formation of inter-granular bonds **110**, and in which carbon is soluble. For example, the alloy material may include iridium and nickel. An alloy of iridium and nickel may exhibit a higher carbon-solubility than nickel alone, and thus may promote the formation of inter-granular bonds **110** faster than nickel alone. A plot of carbon solubility in alloys of iridium and nickel at 1 bar is shown in FIG. 7. As the mole percentage of iridium increases (i.e., increasing along the x-axis of FIG. 7), the solubility of carbon in the alloy increases. The carbon solubility of carbon in some Ir—Ni alloys may be higher than the solubility of carbon in cobalt. For example, at 1 bar, Ir—Ni alloys having a mole percentage of iridium greater than about 15% may have a higher carbon solubility than cobalt.

[0032] An alloy of iridium and nickel may exhibit a liquidus (i.e., melting point) between the melting points of pure iridium (2,446° C.) and pure nickel (1,455° C.). For example, the alloy material **112** may be formulated to have a liquidus of less than about 2,000° C., less than about 1,800° C., or even less than about 1,600° C., such as about 1,550° C. or about 1,525° C. When the alloy material **112** contains carbon, the liquidus is depressed based on the concentration of carbon. For example, the liquidus of nickel saturated with carbon is about 1,326° C. at 1 bar. The liquidus of iridium saturated with carbon is about 2,286° C. at 1 bar. A plot of the liquidus of alloys of iridium and nickel saturated with carbon at 1 bar is shown in FIG. 8. As the mole percentage of iridium increases (i.e., increasing along the x-axis of FIG. 8), the liquidus of the alloy increases.

[0033] In some embodiments, the alloy material **112** may include carbon, iridium, and nickel. That is, carbon may be dissolved in the alloy material **112**. The alloy material **112** may also include other elements. The alloy material **112** may be formed by diffusing carbon into a precursor of the alloy material **112** during HPHT sintering, such as a binary mixture of iridium and nickel. Because iridium and nickel appear to be infinitely soluble in one another, the relative amounts of each may be selected to adjust the melting temperature (liquidus) of the alloy material **112**, the carbon content, carbon solubility, or any other property. By way of non-limiting example, the alloy material **112** may be formed from a mixture containing from about 1.0 mol % iridium to about 99.0 mol % iridium, from about 5 mol % iridium to about 40 mol % iridium, from about 10 mol % iridium to about 35 mol % iridium, such as about 22 mol % iridium. In some embodiments, the balance of the mixture used to form the alloy material may be substantially nickel. In other embodiments, other elements may also be included.

[0034] The alloy material **112** may have substantially similar compositions to those of the precursor described above, but for the presence of carbon that may have diffused into the alloy material **112** during HPHT sintering. The amount of carbon in the alloy material **112** may depend on the solubility of carbon in the alloy material **112** at HPHT conditions. For example, the alloy material **112** may contain up to about 15 mol % carbon, such as from about 10 mol % carbon to about 14 mol % carbon. The amount of carbon in the alloy material **112** may be higher than the carbon solubility of conventional metal solvent catalyst metals and alloys employed in the formation of polycrystalline diamond compacts. For example, cobalt, a common metal solvent catalyst for forming polycrystalline diamond, has a carbon

solubility of about 11.4 mol % carbon. In a volume of conventional polycrystalline diamond, the diamond typically occupies less than 100% of the total volume of the diamond table due to the inclusion of interstitial spaces. The polycrystalline diamond **102** described herein and shown in FIGS. **1** and **2**, having the alloy material **112** in interstitial spaces, may exhibit a relatively higher volume percentage of diamond than conventional polycrystalline diamond compacts. For example, the polycrystalline diamond **102** may include at least about 92% diamond by volume, as at least about 94% diamond by volume, at least about 95% diamond by volume, at least about 96% diamond by volume, at least about 97% diamond by volume, or even at least about 99% diamond by volume. In general, compacts having higher volume fractions of diamond may exhibit better wear resistance and improved resistance to thermal degradation.

[0035] Furthermore, the interstitial spaces may include one or more voids **113**, defined as volumes within the polycrystalline table in which there is no solid or liquid material. Thus the interstitial spaces may include the volume occupied by the alloy material **112** and the volume occupied by the voids **113**. The volume of the alloy material **112** may be less than about 50% of the interstitial spaces, such as less than about 30%, less than about 20%, or even less than about 10% of the interstitial spaces. In some embodiments, a majority of the voids **113** may be interconnected to form a three-dimensional open porous network that extends throughout the polycrystalline diamond **102**. In other embodiments, a majority of the voids **113** may be closed and isolated from one another.

[0036] Embodiments of cutting elements **100** (FIG. **1**) that include polycrystalline diamond **102** fabricated as described herein may be mounted to earth-boring tools and used to remove subterranean formation material. FIG. **3** illustrates a fixed-cutter earth-boring rotary drill bit **160**. The drill bit **160** includes a bit body **162**. One or more cutting elements **100** as described herein may be mounted on the bit body **162** of the drill bit **160**. The cutting elements **100** may be brazed or otherwise secured within pockets formed in the outer surface of the bit body **162**. The polycrystalline diamond **102** may or may not be leached before mounting on the bit body. Other types of earth-boring tools, such as roller cone bits, percussion bits, hybrid bits, reamers, etc., also may include cutting elements **100** as described herein.

[0037] In some embodiments, methods of forming polycrystalline diamond may include HPHT sintering of diamond particles and an alloy material to form inter-granular bonds between the diamond particles. The diamond and alloy material may be placed into contact with one another before sintering. For example, the alloy material may be provided over grains or particles of diamond (e.g., as a coating) before sintering. Referring now to FIG. **4**, a grain **202** of diamond may be at least partially coated with an alloy material **204** to form a coated grain **206**. Though depicted in FIG. **4** as completely encapsulating the grain **202**, the alloy material **204** may cover only a portion of an exterior surface of the grain **202**. A plurality of grains **202** may be uniformly coated. In some embodiments, grains **202** may have a distribution of an amount of the alloy material **204** thereon. For example, the alloy material **204** may cover an average of at least about 30% of the surface area of grains **202** in a particle mixture to be sintered. In some embodiments, the alloy material **204** may cover an average from about 70% to about 100% of the surface area of grains **202** in a particle

mixture to be sintered, or at least about 90% of the surface area of grains **202**. The alloy material **204** may be in a continuous formation over each grain **202**, such that even if the alloy material **204** does not coat the entire grain **202**, there may be few or no “islands” of alloy material **204** disconnected from the remainder of the alloy material **204** on the grain **202**.

[0038] The alloy material **204** may be formed to have any selected thickness, although relatively thin and uniform coatings may be desirable. For example, the alloy material **204** may have an average thickness from about 1 nanometer (nm) to about 50 nm, from about 5 nm to about 20 nm, or from about 10 nm to about 15 nm.

[0039] The coated grains **206** may be formed by, for example, sputtering, physical vapor deposition (PVD), chemical vapor deposition (CVD), electroplating, or any other process known in the art. In some embodiments, the coated grains **206** may be formed by a PVD coating process. The PVD process may control the composition and thickness of the alloy material **204** better than other coating processes. Furthermore, coating by a PVD process may provide a high-purity alloy material **204** on the grains **202** without damaging the grains **202** or the alloy material **204**. The alloy material **204** may be provided to a PVD system as prealloyed material or as individual commercially pure metals (e.g., powders, billets, etc.). The PVD system may deposit the alloy material **204** in a substantially uniform thickness over the grains **202** (e.g., the thickness of alloy material **204** may vary less than about 50%, less than about 20%, less than about 10%, or even less than about 5%).

[0040] PVD processes may occur under an initial high vacuum, such as at a pressure of less than about 10^{-7} torr. Working pressures may be varied by increasing or decreasing argon or other inert gas flow rates. In this manner, the deposition rates of materials (e.g., prealloyed material or individual commercially pure elements) may be varied as desired to control compositions and/or thickness. If the alloy material to be deposited is provided in powder form, a continuously rotating apparatus may be used in-situ during deposition for promoting uniform coating thickness, alloy composition, and powder surface coverage. For example, grains **202** may be placed in a ball mill with grinding media or in autogenous mill without grinding media. The mill may be subjected to a vacuum, and the alloy material **204** may be deposited onto the grains **202** while the mill rotates.

[0041] In some embodiments, and as shown in FIG. **5**, a diamond grain **212** may include a non-diamond carbon coating **216** or layer, which may be referred to as a carbon shell. The non-diamond carbon coating **216** may include, for example, graphite, graphene, fullerenes, amorphous carbon, or any other carbon phase or morphology. The alloy material **204** may be formed over the non-diamond carbon coating **216**. The alloy material **204** may be formed as described above with respect to FIG. **4**. Although the non-diamond carbon coating **216** and the alloy material **204** are depicted in FIG. **5** as completely encapsulating the diamond grain **212**, in other embodiments, the non-diamond carbon coating **216** and/or the alloy material **204** may only partially coat the diamond grain **212**. The diamond grain **212** may include a single diamond crystal or a cluster of diamond crystals.

[0042] The non-diamond carbon coating **216** may react with the alloy material **204** to form the alloy material **112** shown in FIG. **2**. In some embodiments, at least a portion of the non-diamond carbon coating **216** may undergo a change

in atomic structure during or prior to sintering. Some carbon atoms in the non-diamond carbon coating **216** may diffuse to and enter the diamond crystal structure of the diamond grain **212** (i.e., contribute to grain growth of the diamond grain **212**). For example, carbon atoms from the non-diamond carbon coating **216** may form “necks” of diamond material between adjacent diamond grains **106**, **108** (FIG. 2) during sintering (i.e., non-diamond carbon may be converted to diamond). Some carbon atoms in the non-diamond carbon coating **216** may diffuse to and enter the alloy material **204**, some of which may then be converted to diamond.

[0043] In some embodiments, grains **202** (FIG. 4) or and/or grains **212** (FIG. 5) may be tumbled with an inert media to break down aggregates and promote uniform coating. Additionally, grains **202**, **212** may be pretreated to reduce aggregation and improve the flow of grains **202**, **212** during coating processes. For example, grains **202**, **212** may be pretreated with hydrogen to remove oxygen-, nitrogen- and water-bearing surface impurities and/or to functionalize the surfaces with methyl or methylene groups. Additional functionalization, such as long-alkyl-chain or fluorine compounds, may be employed for nano-diamond particles. Coated grains **202**, **212** may include monomodal nanometer- or micron-diamond feed or composite blends of nano- and micron-diamond feed having nano-diamond compositions from about 1% by weight to about 99% by weight. Grains coated by PVD processes may have relatively uniform coating thicknesses across a wide particle-size range, which may more evenly distribute the alloy material **204** to locations where the alloy material **204** is beneficial during sintering (i.e., at the contact point between adjacent grains). Additional multimodal nanodiamond or multimodal micron-diamond feed may also be coated and subsequently dry-blended, forming composite blends. The final coated feed product may be sintered at HPHT conditions, as discussed in more detail below.

[0044] Referring to FIG. 6, particles **302** of diamond having an alloy material thereon may be positioned within a container **304** (e.g., a metal canister). The particles **302** may include, for example, grains or crystals of diamond (e.g., diamond grit), which will ultimately form the grains **106**, **108** in the sintered polycrystalline diamond **102** (FIG. 2). The particles **302** may include, for example, the coated grains **202**, **212** (FIGS. 4 & 5) having the alloy material **204** formed thereon. The container **304** may include an inner cup **306** in which the particles **302** may be provided. In some embodiments, a substrate **104** (e.g., as shown in FIG. 1) optionally may also be provided in the inner cup **306** over or under the particles **302**, and may ultimately be encapsulated in the container **304**. The container **304** may further include a top cover **308** and a bottom cover **310**, which may be assembled and bonded together (e.g., swage bonded) around the inner cup **306** with the particles **302** and the optional substrate **104** therein.

[0045] In the container **304**, the particles **302** may have a packing fraction from about 45% to about 99% (i.e., with a void space of between about 55% and about 1% of the total volume), such as from about 50% to about 70% (i.e., with a void space of between about 50% and about 30% of the total volume).

[0046] The container **304** with the particles **302** therein may be subjected to an HPHT process to form a polycrystalline diamond (e.g., the polycrystalline diamond **102** shown in FIG. 1). For example, the container **304** may be

subjected to a pressure of at least about 5.5 GPa and a temperature of at least about 1,000° C. In some embodiments, the container **304** may be subjected to a pressure of at least about 6.0 GPa, or even at least about 6.5 GPa. For example, the container **304** may be subjected to a pressure from about 5.5 GPa to about 10.0 GPa, or from about 6.5 GPa to about 8.0 GPa. The container **304** may be subjected to a temperature of at least about 1,600° C., at least about 1,800° C., at least about 2,000° C., or even at least about 2,500° C.

[0047] During the sintering process, the alloy material **204** deposited on the grains **202**, **212** may melt into a liquid phase. The alloy material **204** may behave as a metal-solvent catalyst material to promote the formation of inter-granular (e.g., diamond-to-diamond) bonds between the grains **202**, **212** so as to form a polycrystalline compact from the grains **202**, **212**. Upon completion of the sintering process and cooling below the sintering temperature, the alloy material **204** solidify in interstitial spaces between the grains **202**, **212** in the polycrystalline diamond **102**.

[0048] Use of an alloy material **204** as described herein may impart certain benefits to polycrystalline diamond **102** (FIGS. 1 & 2). For example, the alloy material **204** (including iridium and nickel) may have a higher carbon solubility than conventional cobalt-based alloys. Without being bound to any particular theory, a higher concentration of carbon in the alloy material may correspond to faster or more uniform formation of inter-granular bonds **110**. Thus, HPHT sintering may be performed for shorter periods of time or at lower pressures than sintering with conventional catalysts. During sintering, non-diamond forms of carbon may be converted to diamond, adding to the inter-granular bonds **110**.

[0049] Furthermore, because the alloy material **204** may be coated onto individual grains **202**, **212**, the alloy material **204** need not diffuse through the entire polycrystalline diamond **102** during sintering. Thus, the mean diffusion distance (i.e., the mean distance from any individual grain to the alloy material **204** during sintering) may be reduced from, for example 1 mm (e.g., a significant fraction of the thickness of the polycrystalline diamond **102**), to about 1 μ m or even less. In some embodiments, the mean diffusion distance may about 100 nm or less.

[0050] Furthermore, use of an alloy material **204** as described herein may allow the alloy material **204** to be provided where needed most—at the points where individual grains contact one another. Thus, volumes that are free of grains or the alloy material **204** may become voids **113** within the polycrystalline diamond **102**, and leaching may not be required to form such voids **113**. Thus, the polycrystalline diamond **102** formed may have a lower concentration of metal than conventional unleached sintered polycrystalline diamond compacts. Because the alloy material **204** may be placed near the point where it is needed to form intergranular bonds, the grains **202**, **212** may be packed more tightly without negatively affecting the sintering process. The volume fraction of diamond may be relatively higher than in conventional materials at least in part because the interstitial spaces may be formed relatively smaller than in conventional materials. The polycrystalline diamond **102** may be porous when fully sintered because the amount of alloy material **204** provided over the grains **202**, **212** may be lower than the amount of alloy material in conventional polycrystalline materials.

[0051] One advantage of using iridium as a component of the alloy material **204** is that iridium may promote fine-grained microstructures, which may facilitate the deposition of coatings that are of thin and uniform thickness. Quality control (i.e., thickness and uniformity) may be relatively easier for alloys containing iridium than for other alloys. For example, diamond particles having grain sizes from about 10 nm to about 0.5 μm may be coated tougher relatively uniformly through PVD with an alloy material **204** that includes iridium or an iridium alloy. The power, gas pressure (plasma), and deposition time may be controlled to produce a selected composition and thickness of the alloy material **204**.

[0052] By providing the alloy material **112** or a precursor thereof as a coating over the grains **106**, **108**, the time and distance required to sweep the alloy material **112** through the grains **106**, **108** may be reduced. Thus, the grains **106**, **108** may be provided with a lower mean free path and therefore a higher packing fraction. This may result in relatively higher final (post-sintered) density of the polycrystalline diamond **102**. For example, the mean free path through the grains **106**, **108** may be on the order of the diameter of the grains **106**, **108** (e.g., from about 1 nm to about 20 μm) of the microstructure of the polycrystalline diamond **102**, rather than the order of the thickness of the polycrystalline diamond **102** (e.g., from about 1 mm to 3.5 mm) without negatively affecting the ability of the alloy material **112** to fill the interstitial spaces. Furthermore, the alloy material **112** may be formulated to avoid oxidation in air. Conventional diamond grains may undergo back-conversion starting at temperatures of about 750° C. in air or about 1,200° C. in an inert atmosphere. Providing at least some of the grains **106**, **108** with a coating material thereon may limit the time during which the grains **106**, **108** are exposed to air or other gases in the HPHT process, thus limiting the time during which the grains **106**, **108** may degrade (e.g., by conversion from diamond to carbon). Furthermore, the grains **106**, **108** may be more uniformly coated with the alloy material **112**, and thus may be relatively more resistant to degradation than conventional polycrystalline materials.

[0053] Additional non limiting example embodiments of the disclosure are described below.

[0054] Embodiment 1: A method of forming polycrystalline diamond, comprising providing an alloy over at least portions of a plurality of diamond particles; and subjecting the plurality of diamond particles to a high-temperature, high-pressure process to form a polycrystalline diamond material having inter-granular bonds between adjacent diamond particles. The alloy comprises iridium and nickel, and a volume of the diamond particles is at least about 92% of a total volume of the alloy and the diamond particles. The polycrystalline diamond material comprises at least about 92% diamond by volume.

[0055] Embodiment 2: The method of Embodiment 1, wherein providing an alloy over at least portions of a plurality of diamond particles comprises covering at least 30% of a surface area of the diamond particles with the alloy.

[0056] Embodiment 3: The method of Embodiment 2, wherein providing an alloy over at least portions of a plurality of diamond particles comprises covering at least 75% of a surface area of the particles with the alloy.

[0057] Embodiment 4: The method of any of Embodiments 1 through 3, wherein providing an alloy over at least portions of a plurality of diamond particles comprises form-

ing a layer of the alloy having a thickness from about 1 nm to about 50 nm over the diamond particles.

[0058] Embodiment 5: The method of Embodiment 4, wherein providing an alloy over at least portions of a plurality of diamond particles comprises forming a layer of the alloy having a thickness from about 2 nm to about 5 nm over the diamond particles.

[0059] Embodiment 6: The method of any of Embodiments 1 through 5, wherein providing an alloy over at least portions of a plurality of diamond particles comprises providing the alloy comprising about 5 mol % iridium to about 40 mol % iridium.

[0060] Embodiment 7: The method of Embodiment 6, wherein providing an alloy over at least portions of a plurality of diamond particles comprises providing the alloy comprising about 10 mol % iridium to about 35 mol % iridium.

[0061] Embodiment 8: The method of any of Embodiments 1 through 7, wherein providing an alloy over at least portions of a plurality of diamond particles comprises formulating the alloy to consist essentially of iridium and nickel.

[0062] Embodiment 9: The method of any of Embodiments 1 through 8, wherein providing an alloy over at least portions of a plurality of diamond particles comprises formulating the alloy to exhibit a liquidus of less than about 1,600° C. at atmospheric pressure.

[0063] Embodiment 10: The method of any of Embodiments 1 through 9, wherein providing an alloy over at least portions of a plurality of diamond particles comprises providing the alloy over a plurality of diamond particles having a multi-modal particle size distribution.

[0064] Embodiment 11: The method of any of Embodiments 1 through 10, wherein providing an alloy over at least portions of a plurality of diamond particles comprises providing the alloy over a plurality of diamond nanoparticles.

[0065] Embodiment 12: The method of any of Embodiments 1 through 11, wherein subjecting the plurality of diamond particles to a high-temperature, high-pressure process comprises subjecting the plurality of diamond particles to a temperature of at least about 1,400° C. and a pressure of at least about 5.0 GPa.

[0066] Embodiment 13: The method of any of Embodiments 1 through 12, wherein subjecting the plurality of diamond particles to a high-temperature, high-pressure process comprises subjecting the plurality of diamond particles to a pressure between about 6.5 GPa and 10 GPa.

[0067] Embodiment 14: The method of any of Embodiments 1 through 13, wherein providing an alloy over at least portions of a plurality of diamond particles comprises providing an alloy over at least portions of a plurality of diamond particles by a physical vapor deposition process.

[0068] Embodiment 15: The method of any of Embodiments 1 through 14, wherein subjecting the plurality of diamond particles to a high-temperature, high-pressure process comprises forming the polycrystalline diamond material defining at least one void without leaching the alloy therefrom.

[0069] Embodiment 16: A method of forming polycrystalline diamond, comprising providing an alloy over at least portions of a plurality of diamond particles, and subjecting the plurality of diamond particles to a pressure of at least 5 GPa and a temperature of at least 1,400° C. to form a porous polycrystalline diamond compact having inter-granular

bonds between adjacent diamond particles. The alloy comprises nickel and at least about 10 mol % iridium.

[0070] Embodiment 17: The method of Embodiment 16, wherein providing an alloy over at least portions of a plurality of diamond particles comprises sputtering the alloy over the plurality of diamond particles.

[0071] Embodiment 18: The method of Embodiment 16 or Embodiment 17, wherein providing an alloy over at least portions of a plurality of diamond particles comprises covering at least 30% of a surface area of the diamond particles with the alloy.

[0072] Embodiment 19: The method of Embodiment 18, wherein providing an alloy over at least portions of a plurality of diamond particles comprises covering at least 75% of a surface area of the particles with the alloy.

[0073] Embodiment 20: The method of any of Embodiments 16 through 19, wherein providing an alloy over at least portions of a plurality of diamond particles comprises forming a layer of the alloy having a thickness from about 1 nm to about 20 nm over the diamond particles.

[0074] Embodiment 21: The method of Embodiment 20, wherein providing an alloy over at least portions of a plurality of diamond particles comprises forming a layer of the alloy having a thickness from about 2 nm to about 5 nm over the diamond particles.

[0075] Embodiment 22: The method of any of Embodiments 16 through 21, wherein providing an alloy over at least portions of a plurality of diamond particles comprises providing the alloy exhibiting a liquidus of less than about 1,600° C. at atmospheric pressure.

[0076] Embodiment 23: The method of any of Embodiments 16 through 22, wherein providing an alloy over at least portions of a plurality of diamond particles comprises providing the alloy over the plurality of diamond particles having a multi-modal particle size distribution.

[0077] Embodiment 24: The method of any of Embodiments 16 through 23, wherein subjecting the plurality of diamond particles to a pressure of at least 5 GPa and a temperature of at least 1,400° C. comprises forming a polycrystalline diamond material defining at least one void, wherein the at least one void occupies from about 1% to about 5% of a volume of the polycrystalline diamond compact.

[0078] Embodiment 25: The method of Embodiment 24, wherein forming a polycrystalline diamond material defining at least one void comprises forming a polycrystalline diamond material defining at least one void without leaching the alloy therefrom.

[0079] Embodiment 26: The method of any of Embodiments 16 through 25, wherein providing an alloy over at least portions of a plurality of diamond particles comprises forming a substantially uniform layer of the alloy over the plurality of diamond particles.

[0080] Embodiment 27: A polycrystalline diamond compact, comprising a plurality of grains of diamond bonded to one another by inter-granular bonds and an alloy disposed within interstitial spaces between the grains of diamond. The alloy comprises iridium and nickel, and is from about 1 mol % iridium to about 99 mol % iridium. The grains of diamond occupy at least 92% by volume of the polycrystalline diamond compact.

[0081] Embodiment 28: The polycrystalline diamond compact of Embodiment 27, wherein the alloy exhibits a liquidus of less than about 1,600° C. at atmospheric pressure.

[0082] Embodiment 29: The polycrystalline diamond compact of Embodiment 27 or Embodiment 28, wherein the grains of diamond comprise nanodiamond.

[0083] Embodiment 30: The polycrystalline diamond compact of any of Embodiments 27 through 29, wherein the alloy is substantially free of iron and cobalt.

[0084] Embodiment 31: The polycrystalline diamond compact of any of Embodiments 27 through 30, wherein the polycrystalline diamond compact comprises at least 94% diamond by volume.

[0085] Embodiment 32: The polycrystalline diamond compact of Embodiment 31, wherein the polycrystalline diamond compact comprises at least 94% diamond by volume.

[0086] Embodiment 33: The polycrystalline diamond compact of any of Embodiments 27 through 32, wherein the alloy occupies from about 10% to about 90% of a total volume of the interstitial spaces.

[0087] Embodiment 34: The polycrystalline diamond compact of any of Embodiments 27 through 33, wherein the grains of diamond exhibit a multimodal particle size distribution.

[0088] Embodiment 35: An earth-boring tool comprising a bit body and the polycrystalline diamond compact of any of Embodiments 27 through 34.

[0089] While the present invention has been described herein with respect to certain illustrated embodiments, those of ordinary skill in the art will recognize and appreciate that it is not so limited. Rather, many additions, deletions, and modifications to the illustrated embodiments may be made without departing from the scope of the invention as hereinafter claimed, including legal equivalents thereof. In addition, features from one embodiment may be combined with features of another embodiment while still being encompassed within the scope of the invention as contemplated by the inventors. Further, embodiments of the disclosure have utility with different and various types and configurations of tools and materials.

What is claimed is:

1. A method of forming polycrystalline diamond, comprising:

providing an alloy over at least portions of a plurality of diamond particles, wherein the alloy comprises iridium and nickel, and wherein a volume of the diamond particles is at least about 92% of a total volume of the alloy and the diamond particles; and

subjecting the plurality of diamond particles to a high-temperature, high-pressure process to form a polycrystalline diamond material having inter-granular bonds between adjacent diamond particles, wherein the polycrystalline diamond material comprises at least about 92% diamond by volume.

2. The method of claim 1, wherein providing an alloy over at least portions of a plurality of diamond particles comprises covering at least 30% of a surface area of the diamond particles with the alloy.

3. The method of claim 1, wherein providing an alloy over at least portions of a plurality of diamond particles comprises forming a layer of the alloy having a thickness from about 1 nm to about 50 nm over the diamond particles.

4. The method of claim 1, wherein providing an alloy over at least portions of a plurality of diamond particles comprises providing the alloy comprising about 5 mol % iridium to about 40 mol % iridium.

5. The method of claim 4, wherein providing an alloy over at least portions of a plurality of diamond particles comprises providing the alloy comprising about 10 mol % iridium to about 35 mol % iridium.

6. The method of claim 1, wherein providing an alloy over at least portions of a plurality of diamond particles comprises formulating the alloy to consist essentially of iridium and nickel.

7. The method of claim 1, wherein providing an alloy over at least portions of a plurality of diamond particles comprises formulating the alloy to exhibit a liquidus of less than about 1,600° C. at atmospheric pressure.

8. The method of claim 1, wherein providing an alloy over at least portions of a plurality of diamond particles comprises providing the alloy over a plurality of diamond particles having a multi-modal particle size distribution.

9. The method of claim 1, wherein providing an alloy over at least portions of a plurality of diamond particles comprises providing the alloy over a plurality of diamond nanoparticles.

10. The method of claim 1, wherein subjecting the plurality of diamond particles to a high-temperature, high-pressure process comprises subjecting the plurality of diamond particles to a temperature of at least about 1,400° C. and a pressure of at least about 5.0 GPa.

11. The method of claim 1, wherein subjecting the plurality of diamond particles to a high-temperature, high-pressure process comprises subjecting the plurality of diamond particles to a pressure between about 6.5 GPa and 10 GPa.

12. The method of claim 1, wherein providing an alloy over at least portions of a plurality of diamond particles comprises providing an alloy over at least portions of a plurality of diamond particles by a physical vapor deposition process.

13. The method of claim 1, wherein subjecting the plurality of diamond particles to a high-temperature, high-pressure process comprises forming the polycrystalline diamond material defining at least one void without leaching the alloy therefrom.

14. A polycrystalline diamond compact, comprising:

a plurality of grains of diamond bonded to one another by inter-granular bonds, wherein the grains of diamond occupy at least 92% by volume of the polycrystalline diamond compact; and

an alloy disposed within interstitial spaces between the grains of diamond, the alloy comprising iridium and nickel, wherein the alloy comprises from about 1 mol % iridium to about 99 mol % iridium.

15. The polycrystalline diamond compact of claim 14, wherein the alloy exhibits a liquidus of less than about 1,600° C. at atmospheric pressure.

16. The polycrystalline diamond compact of claim 14, wherein the alloy is substantially free of iron and cobalt.

17. The polycrystalline diamond compact of claim 14, wherein the alloy occupies from about 10% to about 90% of a total volume of the interstitial spaces.

18. The polycrystalline diamond compact of claim 14, wherein the alloy further comprises carbon.

19. The polycrystalline diamond compact of claim 14, wherein the polycrystalline diamond compact is unleached.

20. An earth-boring tool comprising:
a bit body; and

the polycrystalline diamond compact of claim 14.

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