

- 1 -

COATED PARTICLES AND RELATED METHODS

PRIORITY CLAIM

This application claims the benefit of the filing date of United States Patent
5 Application Serial No. 13/166,557, filed June 22, 2011, for “Coated Particles and
Related Methods.”

TECHNICAL FIELD

Embodiments of the disclosure relate generally to coated particles, methods
10 of forming coated particles, and methods of forming polycrystalline compacts from
coated particles. Specifically, embodiments of the disclosure relate to particles of
superhard material that have nanoparticles coated thereon.

BACKGROUND

15 Superhard materials have proven to be useful in a wide variety of
applications. For example, cutting elements used in earth-boring tools often include
a polycrystalline diamond (PCD) material, which may be used to form
polycrystalline diamond cutters (often referred to as “PDCs”). Such polycrystalline
diamond cutting elements are conventionally formed by sintering and bonding
20 together relatively small diamond grains or crystals under conditions of high
temperature and high pressure in the presence of a catalyst (*e.g.*, cobalt, iron, nickel,
or alloys and mixtures thereof) to form a layer of polycrystalline diamond material
on a cutting element substrate. These processes are often referred to as high
temperature/high pressure (or “HTHP”) processes. The cutting element substrate
25 may comprise a cermet material (*i.e.*, a ceramic-metal composite material)
comprising a plurality of particles of hard material in a metal matrix, such as, for
example, cobalt-cemented tungsten carbide. In such instances, catalyst material in
the cutting element substrate may be drawn into the diamond grains or crystals
during sintering and catalyze formation of a diamond table from the diamond grains
30 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
HTHP process.

- 2 -

Earth-boring tools for forming wellbores in subterranean earth formations that may include a plurality of cutting elements secured to a body include, for example, fixed-cutter earth-boring rotary drill bits (also referred to as “drag bits”). Such fixed-cutter bits include a plurality of cutting elements that are fixedly attached
5 to a bit body of the drill bit, conventionally in pockets formed in blades and other exterior portions of the bit body. Other earth-boring tools may include rolling cone earth-boring drill bits, which include a plurality of cutters attached to bearing pins on legs depending from a bit body. The cutters may include cutting elements (sometimes called “teeth”) milled or otherwise formed on the cutters, which may
10 include hardfacing on the outer surfaces of the cutting elements, or the cutters may include cutting elements (sometimes called “inserts”) attached to the cutters, conventionally in pockets formed in the cutters. Cutting elements that include superhard materials increase the useful life of the earth-boring tools to which they are attached because the superhard materials increase the strength and abrasion
15 resistance of the tools.

Some superhard materials have desirable properties that render them useful in still other applications. For example, the high strength and abrasion resistance of such materials renders them useful in grinding, polishing, and machining applications. Increased thermal conductivity of some superhard materials renders
20 them useful as particles dispersed in lubricants, such as motor and pump oils, because such lubricants often serve to cool the parts they lubricate. Furthermore, increased electrical conductivity of some superhard materials renders them useful as fillers in polymers and elastomers, where increased electrical conductivity in at least some portion of the polymers and elastomers is desirable.

25 Some attempts have been made to enhance or alter the properties of superhard materials through layering other materials thereon. For example, *Core-Shell Diamond as a Support for Solid-Phase Extraction and High-Performance Liquid Chromatography*, 82 Analytical Chem. 4448 (June 1, 2010), by Gaurav Saini, David S. Jensen, Landon A. Wiest, Michael A. Vail,
30 Andrew Dadson, Milton L. Lee, V. Shutthanandan, and Matthew R. Linford discloses, among other things, layer-by-layer deposition of an amine-containing polymer and nanodiamond on an amine functionalized microdiamond.

BRIEF DESCRIPTION OF THE DRAWINGS

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

FIG. 1 is a cross-sectional view of a core particle;

FIG. 2 depicts a cross-sectional view of the core particle of FIG. 1 after being coated with a coating material;

FIG. 3 illustrates a cross-sectional view of the coated core particle of FIG. 2 after nanoparticles have been disposed on the coating material;

FIG. 4 is a cross-sectional view of the coated core particle of FIG. 3 after coating the nanoparticles with another coating;

FIG. 5 depicts a cross-sectional view of the coated core particle of FIG. 4 after other nanoparticles have been disposed on the other coating;

FIG. 6 illustrates a cross-sectional view of an alternative embodiment of the nanoparticles shown in FIG. 5;

FIG. 7 is a cross-sectional view of another embodiment of the coated core particle shown in FIG. 5 wherein the other nanoparticles are disposed directly on the first nanoparticles;

FIG. 8 depicts a cross-sectional view of the coated core particle of FIG. 5 after coating the other nanoparticles with yet another coating;

FIG. 9 illustrates a cross-sectional view of the coated core particle of FIG. 8 after still other nanoparticles have been disposed on the yet other coating;

FIG. 10 is a cross-sectional view of the coated core particle of FIG. 9 after coating the still other nanoparticles have been coated in a final coating;

FIG. 11 depicts a cross-sectional view of a mold that may be used to form a cutting element;

FIG. 12 illustrates a partial cutaway perspective view of a cutting element that may be attached to an earth-boring tool; and

- 4 -

FIG. 13 is a perspective view of an earth-boring tool to which cutting elements may be attached.

MODE(S) FOR CARRYING OUT THE INVENTION

5 The illustrations presented herein are not meant to be actual views of any particular particle, cutting element, or earth-boring tool, but are merely idealized representations that are employed to describe the embodiments of the disclosure. Thus, the drawings are not necessarily to scale and relative dimensions may have been exaggerated for the sake of clarity. Additionally, elements common between
10 figures may retain the same or similar numerical designation.

Embodiments of the disclosure relate to particles of superhard material that have nanoparticles coated thereon. In some embodiments, a coating material comprising an amine terminated group may be successively interposed between the particles and/or the nanoparticles.

15 The terms “earth-boring tool” and “earth-boring drill bit,” as used herein, mean and include any type of bit or tool used for drilling during the formation or enlargement of a wellbore in a subterranean formation and include, for example, fixed-cutter bits, rolling cone bits, impregnated bits, core bits, eccentric bits, bicenter bits, hybrid bits as well as reamers, mills, and other drilling bits and tools known in
20 the art.

As used herein, the term “polycrystalline material” means and includes any structure comprising a plurality of grains (*i.e.*, crystals) of material (*e.g.*, superhard material) that are bonded directly together by inter-granular bonds. The crystal structures of the individual grains of the material may be randomly oriented in space
25 within the polycrystalline material.

As used herein, the terms “inter-granular bond” and “interbonded” mean and include any direct atomic bond (*e.g.*, covalent, metallic, *etc.*) between atoms in adjacent grains of superabrasive material.

As used herein, the term “superhard material” means and includes any
30 material having a Knoop hardness value of about 3,000 Kg_f/mm² (29,420 MPa) or more. Superhard materials include, for example, diamond and cubic boron nitride. Superhard materials may also be characterized as “superabrasive” materials.

- 5 -

As used herein, the terms “nanoparticle” and “nanoscale” mean and include any particle, such as, for example, a crystal or grain, having an average particle diameter of between about 1 nm and 500 nm.

As used herein, the term “tungsten carbide” means any material composition
5 that contains chemical compounds of tungsten and carbon, such as, for example, WC, W₂C, and combinations of WC and W₂C. Tungsten carbide includes, for example, cast tungsten carbide, sintered tungsten carbide, and macrocrystalline tungsten carbide.

Referring to FIG. 1, a cross-sectional view of a core particle 100 is shown.
10 The core particle 100 is shown having a circular cross-section for the sake of simplicity, but core particles 100 in practice may have cross-sections of any shape, including irregular shapes. The core particle 100 may comprise a superhard material. For example, the core particle 100 may comprise synthetic diamond, natural diamond, cubic boron nitride, or any superhard material known in the art.
15 Thus, the core particle 100 may comprise a single grain of diamond, for example. The core particle 100 may comprise an average diameter of between 1 μm and 500 μm. The core particle 100 may be provided as one of a plurality of similar core particles 100. Such a plurality of core particles 100 may be free of nanoscale particles.

20 An outer surface 102 of the core particle 100 may be modified by a surface treatment in some embodiments. For example, the outer surface 102 of the core particle 100 may be derivatized to exhibit a net negative charge or a net positive charge. Thus, a net charge may be imparted to the outer surface 102 of the core particle 100. Surface treatment may be accomplished using, for example, corona
25 treatment, plasma treatment, chemical vapor treatment, wet etch, ashing, primer treatment (*e.g.*, polymer-based or organosilane primer treatments), and other surface treatments known in the art.

Referring to FIG. 2, a cross-sectional view of the core particle 100 of FIG. 1 after being coated with a coating material 104 is shown. Though the coating
30 material 104 is shown as a coating of uniform thickness covering the entire outer surface 102 of the core particle 100, the coating material 104 may be of non-uniform thickness and may cover only a portion of the outer surface 102 of the core

- 6 -

particle 100 in practice. The coating material 104 may carry a net charge opposite the net charge of the outer surface 102 of the core particle 100, which may facilitate adhesion of the coating material 104 to the outer surface 102 of the core particle 100, for example, by adsorption. The coating material 104 may comprise an amine terminated group. For example, the coating material 104 may comprise polyallylamine, polyethylenimine, polyethylenamine. As continuing examples, the coating material 104 may comprise a polyamine prepared by the polymerization of aziridene and including polyethylemeamines and polyethylenimines having a branched structure derived from aziridene and tris(aminoethyl)amine, a hyperbranched or dendrimeric polyamine such as polyamidoamine (PAMAM) dendrimer, a polyaminoacrylate such as poly(N,N-dimethylaminoethyl-(meth)acrylate), a copolymer thereof with an alkyl or aralkyl (meth)acrylate such as methyl (meth)acrylate, ethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, (meth)acrylonitrile, poly(N,N-dimethylaminoethyl-(meth)acrylate)-co-(methyl (meth)acrylate), and combinations comprising at least one of these. As a specific example, the coating material 104 may comprise polyethylenimine, which carries a net positive charge and is water soluble.

The coating material 104 may be disposed on the outer surface 102 of the core particle 100 by any of several well-known processes. For example, the coating material 104 may be disposed on the outer surface 102 of the core particle 100 by wet chemistry processes (*e.g.*, dip coating, solid-gel processing, *etc.*), physical deposition processes (*e.g.*, sputtering, also known as physical vapor deposition (PVD), *etc.*), chemical deposition processes (*e.g.*, chemical vapor deposition (CVD), atomic layer deposition (ALD), *etc.*), or combinations of these. As a specific example, a plurality of core particles 100 that have been surface treated using a corona treatment to impart a net negative charge to the outer surfaces 102 of particles of the plurality of core particles 100 may be disposed in an aqueous solution of polyallylamine, which carries a net positive charge, and the polyallylamine may adhere to the outer surfaces 102 of particles of the plurality of core particles 100.

Referring to FIG. 3, a cross-sectional view of the coated core particle 100 of FIG. 2 after a plurality of nanoparticles 106 has been disposed on the coating

- 7 -

material 104 is shown. Though the plurality of nanoparticles 106 is depicted as having a circular cross-section for the sake of simplicity, the plurality of nanoparticles 106 may comprise any shape, and specifically may have irregular shapes, in practice. In addition, though the plurality of nanoparticles 106 is depicted as being disposed on the coating material 104 at fairly regular intervals over the entire coating material 104, the plurality of nanoparticles 106 may be disposed on the coating material 104 at irregular intervals and/or over only a portion of the coating material 104. The plurality of nanoparticles 106 may comprise, for example, surface modified nanodiamonds, oxidized nanodiamonds, carbon nanotubes, nanographite, nanographene, other nanoscale non-diamond allotropes of carbon (*e.g.*, amorphous carbon, fullerenes, carbon nanobuds, Lonsdaleite, *etc.*), nanoscale particles of BeO, and nanoscale particles comprising a Group VIIIA element (*e.g.*, iron, cobalt, nickel, *etc.*), known in the art as catalyst materials. Thus, the material of the plurality of nanoparticles 106 may be the same as the material of the core particle 100 in some embodiments. In other embodiments, the plurality of nanoparticles 106 may comprise a different material from the material of the core particle 100. In some embodiments, the plurality of nanoparticles 106 may comprise at least some nanoparticles 106 of one material (*e.g.*, graphite), and at least some other nanoparticles 106 of another material (*e.g.*, a Group VIIIA element catalyst material).

Prior to being deposited onto the coating material 104, the plurality of nanoparticles 106 may be modified by a surface treatment in some embodiments. For example, the outer surface 108 of the plurality of nanoparticles 106 may be derivatized to exhibit a net charge opposite a net charge of the coating material 104, which may be a net negative charge or a net positive charge. Surface treatment may be accomplished using, for example, any of the surface treatments described previously in connection with the core particle 100 and other surface treatments known in the art. By alternating the net charge carried by the successive components of the coated core particle 100, each successive component (*e.g.*, the core particle 100, the coating material 104, and the plurality of nanoparticles 106) may be adhered to its adjacent components using non-covalent intermolecular interactions (*e.g.*, van der Waals forces) and mechanical interference.

- 8 -

The plurality of nanoparticles 106 may be disposed on the coating material 104 by, for example, dispersing the plurality of nanoparticles 106 in a continuous phase material to form a dispersion. The resulting dispersion may be, for example, a suspension, a colloid, or a solution, depending on the type of continuous phase material used and the material of the plurality of nanoparticles 106. As a specific example, the plurality of nanoparticles 106 may comprise carbon nanotubes suspended in water. The plurality of nanoparticles 106 shown disposed on the coating material 104 in FIG. 3 may represent only a small proportion of an overall plurality of nanoparticles 106 in the dispersion to ensure that a sufficient quantity of nanoparticles 106 is present for adhering to the coating material 104. A plurality of core particles 100 at least partially coated with the coating material 104 may then be exposed to the dispersed plurality of nanoparticles 106 by disposing the plurality of coated core particles 100 in the dispersion. In some embodiments, the dispersion may then be agitated to circulate the plurality of coated core particles 100 and the plurality of nanoparticles 106 and increase the likelihood that at least some of the plurality of nanoparticles 106 may adhere to the coating material 104 disposed on the coated core particles 100. As a result, at least some nanoparticles of the plurality of nanoparticles 106 may be disposed on and adhered to the coating material 104, which is disposed on and adhered to the plurality of core particles 100.

The plurality of nanoparticles 106 may impart desirable characteristics to the core particle 100. Where the core particle 100 comprises diamond and the plurality of nanoparticles 106 comprises nanographite, for example, the plurality of nanoparticles 106 may increase the ability to lubricate, increase the electrical insulation, and increase the thermal insulation of the resulting coated core particle 100 as compared to the core particle 100 without any nanoparticles 106 coated thereon. Such a combination of characteristics may be desirable in, for example, a lubricant in which the coated core particles 100 may be dispersed. Thus, the core particles 100, the coating materials 104, and the nanoparticles 106 used will depend on the application for which they are intended and the properties of each. In some embodiments, a single application of coating material 104 and nanoparticles 106 may be sufficient. In other embodiments, the coated core particle 100 may undergo subsequent processing.

Referring to FIG. 4, a cross-sectional view of the coated core particle 100 of FIG. 3 is shown after the plurality of nanoparticles 106 has been coated with a second coating material 104'. Though the second coating material 104' is shown as a coating of uniform thickness covering the entire exposed outer surface 108 of the plurality of nanoparticles 106 and the underlying coating material 104, the second coating material 104' may be of non-uniform thickness and may cover only a portion of the exposed outer surfaces of components (*e.g.*, the underlying coating material 104 and the plurality of nanoparticles 106) of the coated core particle 100 in practice. The second coating material 104' may carry a net charge opposite the net charge of the outer surface 108 of the plurality of nanoparticles 106, which may facilitate adhesion of the second coating material 104' to the outer surface 108 of the plurality of nanoparticles 106, for example, by adsorption. The second coating material 104' may comprise an amine terminated group, such as, for example, any of the amine terminated group materials described previously in connection with the underlying coating material 104. The second coating material 104' may comprise the same material as the underlying coating material 104 in some embodiments. In other embodiments, the second coating material 104' may comprise a different material from the underlying coating material 104.

The second coating material 104' may be disposed on the coated core particle 100 by any of several well-known processes. For example, the second coating material 104' may be disposed on the coated core particle 100 by any of the processes described previously in connection with the underlying coating material 104. As a specific example, a plurality of coated core particles 100 having a coating material 104 interposed between and adhered to each core particle 100 and a plurality of nanoparticles 106 that have been surface treated using a corona treatment to impart a net negative charge to the outer surface 108 of the plurality of nanoparticles 106 may be disposed in an aqueous solution of polyallylamine, which carries a net positive charge, and the polyallylamine may thereby be disposed on and adhered to the outer surface 108 of the plurality of nanoparticles 106.

Referring to FIG. 5, a cross-sectional view of the coated core particle 100 of FIG. 4 is shown after a second plurality of nanoparticles 106' has been disposed on the second coating material 104'. Though the second plurality of nanoparticles 106'

- 10 -

is depicted as having a circular cross-section for the sake of simplicity, the second plurality of nanoparticles 106' may comprise any shape, and specifically may have irregular shapes, in practice. In addition, though the second plurality of nanoparticles 106' is depicted as being disposed on the second coating material 104' at fairly regular intervals over the entire second coating material 104', the second plurality of nanoparticles 106' may be disposed on the second coating material 104' at irregular intervals over only a portion of the second coating material 104'. The second plurality of nanoparticles 106' may comprise any of the materials described previously in connection with the first plurality of nanoparticles 106. Thus, the material of the second plurality of nanoparticles 106' may be the same as the material of the core particle 100 and the material of the first plurality of nanoparticles 106 in some embodiments. In other embodiments, the second plurality of nanoparticles 106' may comprise a different material from one or both of the materials of the core particle 100 and the first plurality of nanoparticles 106. In some embodiments, the second plurality of nanoparticles 106' may comprise at least some nanoparticles 106' of one material (*e.g.*, graphite), and at least some other nanoparticles 106' of another material (*e.g.*, a Group VIIIA element catalyst material). As a specific, non-limiting example, the core particle 100 shown in FIG. 5 may comprise a diamond crystal, the first plurality of nanoparticles 106 may comprise nanographite, and the second plurality of nanoparticles 106' may comprise nanographene.

Prior to being deposited onto the second coating material 104', the second plurality of nanoparticles 106' may be modified by a surface treatment in some embodiments. For example, the outer surface 110 of the second plurality of nanoparticles 106' may be derivatized to exhibit a net charge opposite a net charge of the second coating material 104', which may be a net negative charge or a net positive charge. Surface treatment may be accomplished using, for example, any of the surface treatments described previously in connection with the core particle 100 and other surface treatments known in the art. By alternating the net charge carried by the successive components of the coated core particle 100, each successive component (*e.g.*, the core particle 100, the first coating material 104, the first

- 11 -

plurality of nanoparticles 106, the second coating material 104', and the second plurality of nanoparticles 106') may be adhered to its adjacent components.

The second plurality of nanoparticles 106' may be disposed on the second coating material 104' by, for example, dispersing the second plurality of nanoparticles 106' in a continuous phase material to form a dispersion. The resulting dispersion may be, for example, a suspension, a colloid, or a solution, depending on the type of continuous phase material used and the material of the second plurality of nanoparticles 106'. As a specific example, the second plurality of nanoparticles 106' may comprise nanoscale particles of cobalt suspended in water. The second plurality of nanoparticles 106' shown disposed on the second coating material 104' in FIG. 5 may represent only a small proportion of an overall second plurality of nanoparticles 106' in the dispersion to ensure that a sufficient quantity of nanoparticles 106' is present for adhering to the second coating material 104'. A plurality of coated core particles 100, such as that shown in FIG. 4, may then be exposed to the dispersed second plurality of nanoparticles 106' by disposing the plurality of coated core particles 100 in the dispersion. In some embodiments, the dispersion may then be agitated to circulate the plurality of coated core particles 100 and the second plurality of nanoparticles 106' and increase the likelihood that at least some of the second plurality of nanoparticles 106' may adhere to the second coating material 104' disposed on the coated core particles 100. As a result, at least some of the second plurality of nanoparticles 106' may be disposed on and adhered to the second coating material 104'.

Referring to FIG. 6, a cross-sectional view of an alternative embodiment of the second plurality of nanoparticles 106' of FIG. 5 is shown. Specifically, the core particle 100 shown in FIG. 6 may comprise a diamond crystal, the first plurality of nanoparticles 106 may comprise nanographite, and the second plurality of nanoparticles 106' may comprise nanoscale particles of cobalt. Such a coated particle may be used as a precursor in a process for making a polycrystalline diamond material of a PDC cutting element. By locating nanoparticles comprising carbon allotropes and catalyst material proximate one another and proximate a larger core diamond particle, such a coated core particle 100 may facilitate the *in situ* nucleation of diamond grains. For example, the catalyst material of the coated core

- 12 -

particle 100 may more easily access and catalyze *in situ* nucleation of diamond grains from the nanographite particles because the catalyst material does not have to flow, as from a cobalt-cemented carbide substrate, through the often tortuous path to the presence of the nanographite. U.S. Application Publication No. 2011/0031034, published February 10, 2011, to DiGiovanni et al., discloses that *in situ* nucleation of diamond grains may result in a stronger and more abrasion resistant polycrystalline diamond material.

Referring to FIG. 7, a cross-sectional view of another alternative embodiment of the coated core particle 100 shown in FIG. 5 is shown. In this embodiment, the second plurality of nanoparticles 106' is adhered directly to the first plurality of nanoparticles 106. To facilitate adhesion, the second plurality of nanoparticles 106' may be modified by a surface treatment. For example, the outer surface 110 of the second plurality of nanoparticles 106' may be derivatized to exhibit a net charge opposite a net charge of the outer surface 108 of the first plurality of nanoparticles 106, which may be a net negative charge or a net positive charge. Surface treatment may be accomplished using, for example, any of the surface treatments described previously in connection with the core particle 100 and other surface treatments known in the art. In embodiments where particles are adhered directly to one another, coating materials, such as, for example, the second coating material 104' shown in FIGS. 5 and 6 may be omitted. Thus, any of the coating materials 104 and 104' described previously and any of those described subsequently herein may optionally be omitted where alternating net charge carried by the outer surface or other factors permit adjacent particles to be directly adhered to one another.

Referring to FIG. 8, a cross-sectional view of the coated core particle 100 of FIG. 5 after coating the second plurality of nanoparticles 106' with a third coating material 104'' is shown. Though the third coating material 104'' is shown as a coating of uniform thickness covering the entire exposed outer surface 110 of the second plurality of nanoparticles 106' and the underlying second coating material 104', the third coating material 104'' may be of non-uniform thickness and may cover only a portion of the exposed outer surfaces of components (*e.g.*, the underlying second coating material 104' and the second plurality of

- 13 -

nanoparticles 106') of the coated core particle 100 in practice. The third coating material 104'' may carry a net charge opposite the net charge of the outer surface 110 of the second plurality of nanoparticles 106', which may facilitate adhesion of the third coating material 104'' to the outer surface 110 of the second plurality of nanoparticles 106', for example, by adsorption. The third coating material 104'' may comprise an amine terminated group, such as, for example, any of the amine terminated group materials described previously in connection with the first coating material 104. The third coating material 104'' may comprise the same material as the first coating material 104 and the second coating material 104' in some embodiments. In other embodiments, the third coating material 104'' may comprise a different material from at least one of the first coating material 104 and the second coating material 104'.

The third coating material 104'' may be disposed on the coated core particle 100 by any of several well-known processes. For example, the third coating material 104'' may be disposed on the coated core particle 100 by any of the processes described previously in connection with the first coating material 104. As a specific example, a plurality of coated core particles 100 having adhered thereto an outer second plurality of nanoparticles 106' that have been surface treated using a corona treatment to impart a net negative charge to the outer surface 110 of the second plurality of nanoparticles 106' may be disposed in an aqueous solution of polyallylamine, which carries a net positive charge, and the polyallylamine may thereby be disposed on and adhered to the outer surface 110 of the second plurality of nanoparticles 106'.

Referring to FIG. 9, a cross-sectional view of the coated core particle 100 of FIG. 8 is shown after a third plurality of nanoparticles 106'' has been disposed on the third coating material 104''. Though the third plurality of nanoparticles 106'' is depicted as having a circular cross-section for the sake of simplicity, the third plurality of nanoparticles 106'' may comprise any shape, and specifically may have irregular shapes, in practice. In addition, though the third plurality of nanoparticles 106'' is depicted as being disposed on the third coating material 104'' at fairly regular intervals over the entire third coating material 104'', the third plurality of nanoparticles 106'' may be disposed on the third coating material 104'' at

irregular intervals over only a portion of the third coating material 104". The third plurality of nanoparticles 106" may comprise any of the materials described previously in connection with the first plurality of nanoparticles 106. Thus, the material of the third plurality of nanoparticles 106" may be the same as the material of the core particle 100, the material of the first plurality of nanoparticles 106, and the material of the second plurality of nanoparticles 106' in some embodiments. In other embodiments, the third plurality of nanoparticles 106" may comprise a different material from one, some, or all of the materials of the core particle 100, the first plurality of nanoparticles 106, and the second plurality of nanoparticles 106'. In some embodiments, the third plurality of nanoparticles 106" may comprise at least some nanoparticles 106" of one material (*e.g.*, graphite), and at least some other nanoparticles 106" of another material (*e.g.*, a Group VIIIA element catalyst material). As a specific non-limiting example, the core particle 100 shown in FIG. 9 may comprise a diamond crystal, the first plurality of nanoparticles 106 may comprise nanographite, the second plurality of nanoparticles 106' may comprise nanographene, and the third plurality of particles 106" may comprise carbon nanotubes.

Prior to being deposited onto the third coating material 104", the third plurality of nanoparticles 106" may be modified by a surface treatment in some embodiments. For example, the outer surface 112 of the third plurality of nanoparticles 106" may be derivatized to exhibit a net charge opposite a net charge of the third coating material 104", which may be a net negative charge or a net positive charge. Surface treatment may be accomplished using, for example, any of the surface treatments described previously in connection with the core particle 100 and other surface treatments known in the art. By alternating the net charge carried by the successive components of the coated core particle 100, each successive component (*e.g.*, the core particle 100, the first coating material 104, the first plurality of nanoparticles 106, the second coating material 104', the second plurality of nanoparticles 106', the third coating material 104", and the third plurality of particles 106") may be adhered to its adjacent components.

The third plurality of nanoparticles 106" may be disposed on the third coating material 104" by, for example, dispersing the third plurality of

nanoparticles 106'' in a continuous phase material to form a dispersion. The resulting dispersion may be, for example, a suspension, a colloid, or a solution, depending on the type of continuous phase material used and the material of the third plurality of nanoparticles 106''. As a specific example, the third plurality of nanoparticles 106'' may comprise nanoscale particles of BeO suspended in water. The third plurality of nanoparticles 106'' shown disposed on the third coating material 104'' in FIG. 9 may represent only a small proportion of an overall third plurality of nanoparticles 106'' in the dispersion to ensure that a sufficient quantity of nanoparticles 106'' is present for adhering to the third coating material 104''. A plurality of coated core particles 100, such as coated core particle 100 shown in FIG. 8, may then be exposed to the dispersed third plurality of nanoparticles 106'' by disposing the plurality of coated core particles 100 in the dispersion. In some embodiments, the dispersion may then be agitated to circulate the plurality of coated core particles 100 and the third plurality of nanoparticles 106'' and increase the likelihood that at least some of the third plurality of nanoparticles 106'' may adhere to the third coating material 104'' disposed on the plurality of coated core particles 100. As a result, at least some of the third plurality of nanoparticles 106'' may be disposed on and adhered to the third coating material 104''.

Referring to FIG. 10, a cross-sectional view of the coated core particle 100 of FIG. 9 after coating the third plurality of nanoparticles 106'' with a fourth coating material 104''' is shown. Though the fourth coating material 104''' is shown as a coating of uniform thickness covering the entire exposed outer surface 112 of the third plurality of nanoparticles 106'' and the underlying third coating material 104'', the fourth coating material 104''' may be of non-uniform thickness and may cover only a portion of the exposed outer surfaces of components (*e.g.*, the underlying third coating material 104'' and the third plurality of nanoparticles 106'') of the coated core particle 100 in practice. The fourth coating material 104''' may carry a net charge opposite the net charge of the outer surface 112 of the third plurality of nanoparticles 106'', which may facilitate adhesion of the fourth coating material 104''' to the outer surface 112 of the third plurality of nanoparticles 106'', for example, by adsorption. The fourth coating material 104''' may comprise an amine terminated group, such as, for example, any of the amine terminated group

- 16 -

materials described previously in connection with the first coating material 104. The fourth coating material 104''' may comprise the same material as the first coating material 104, the second coating material 104', and the third coating material 104'' in some embodiments. In other embodiments, the third coating material 104'' may
5 comprise a different material from at least one of the first coating material 104, the second coating material 104', and the third coating material 104''.

The fourth coating material 104''' may be disposed on the coated core particle 100 by any of several well-known processes. For example, the fourth coating material 104''' may be disposed on the coated core particle 100 by any of the
10 processes described previously in connection with the first coating material 104. As a specific example, a plurality of coated core particles 100 having adhered thereto an outer third plurality of nanoparticles 106'' that has been surface treated using a corona treatment to impart a net negative charge to the outer surface 112 of the third plurality of nanoparticles 106'' may be disposed in an aqueous solution of
15 polyallylamine, which carries a net positive charge, and the polyallylamine may thereby be disposed on and adhered to the outer surface 112 of the third plurality of nanoparticles 106''.

Successive deposition of pluralities of nanoparticles and coating materials, a process known in the art as layer-by-layer or "LbL" deposition, may continue for as
20 many times as desired or practicable. For example, fourth, fifth, sixth, seventh, *etc.*, pluralities of nanoparticles may be disposed on fourth, fifth, sixth, seventh, *etc.*, coating materials. Such subsequent deposition of pluralities of nanoparticles and coating materials may comprise materials and may be accomplished using processes such as those described previously in connection with the first plurality of
25 nanoparticles 106 and the first coating material 104 (FIG. 3).

After a desired number of iterations of deposition of coating materials and pluralities of nanoparticles has occurred, the coating materials may be cross-linked. Cross-linking the coating materials may enhance the mechanical strength and stability of the coating materials. Cross-linking may be accomplished using, for
30 example, addition of a cross-linking reagent, ultraviolet radiation, electron beam radiation, heat, or other processes for cross-linking known in the art.

- 17 -

FIG. 11 depicts a cross-sectional view of a mold 114 that may be used to form a cutting element. The mold 114 may include one or more generally cup-shaped members, such as the cup-shaped member 114a, the cup-shaped member 114b, and the cup-shaped member 114c, which may be assembled and swaged and/or welded together to form the mold 114. A plurality of particles 116 comprising a superhard material may be disposed within the inner cup-shaped member 114c, as shown in FIG. 11, which has a circular end wall and a generally cylindrical lateral side wall extending perpendicularly from the circular end wall, such that the inner cup-shaped member 114c is generally cylindrical and includes a first closed end and a second, opposite open end.

The plurality of particles 116 may comprise at least one coated particle, such as any of those shown in FIGS. 3 through 10. In some embodiments, each particle of the plurality of particles 116 may comprise a coated particle similar to the other coated particles of the plurality of coated particles. In other embodiments, at least some of the particles may comprise coated particles with a different number of coatings and/or a different combination of materials than others of the particles of the plurality of particles 116. In still other embodiments, coated particles, such as any of those shown in FIGS. 3 through 10, may be intermixed with or interlayered with uncoated particles, such as that shown in FIG. 1, within the plurality of particles 116. In some embodiments, an optional catalyst material 118 in the form of a powder may be interspersed among the plurality of particles 116 comprising a superhard material. The plurality of particles 116 may comprise a mono-modal or a multi-modal grain size distribution.

A substrate 120 comprising a hard material suitable for use in earth-boring applications may be disposed adjacent the plurality of particles 116 in the mold 114. The hard material of the substrate 120 may comprise, for example, a ceramic-metal composite material (*i.e.*, a “cermet” material) comprising a plurality of hard ceramic particles dispersed throughout a metal matrix material. The hard ceramic particles may comprise carbides, nitrides, oxides, and borides (including boron carbide (B_4C)). More specifically, the hard ceramic particles may comprise carbides and borides made from elements such as W, Ti, Mo, Nb, V, Hf, Ta, Cr, Zr, Al, and Si. By way of example and not limitation, materials that may be used to form hard

- 18 -

ceramic particles include tungsten carbide, titanium carbide (TiC), tantalum carbide (TaC), titanium diboride (TiB₂), chromium carbides, titanium nitride (TiN), aluminum oxide (Al₂O₃), aluminum nitride (AlN), and silicon carbide (SiC). The metal matrix material of the ceramic-metal composite material may include, for example, cobalt-based, iron-based, nickel-based, iron- and nickel-based, cobalt- and nickel-based, and iron- and cobalt-based alloys. The matrix material may also be selected from commercially pure elements such as cobalt, iron, and nickel. As a specific, non-limiting example, the hard material may comprise a plurality of tungsten carbide particles in a cobalt matrix, known in the art as cobalt-cemented tungsten carbide.

The plurality of particles 116, the optional catalyst material 118, and the substrate 120 may then be subjected to a high temperature/high pressure (HTHP) process. Although the exact operating parameters of HTHP processes will vary depending on the particular compositions and quantities of the various materials being sintered, the pressures in the heated press may be greater than about 5.0 GPa and the temperatures may be greater than about 1,400 °C. The pressures in the heated press may be greater than about 6.5 GPa (*e.g.*, about 6.7 GPa), and may even exceed 8.0 GPa in some embodiments. Furthermore, the materials being sintered may be held at such temperatures and pressures for a time period between about 30 seconds and about 20 minutes. If necessary or desirable, the temperature may be reduced to about 1,000 °C and held for up to about one hour, or more to assist in the *in situ* nucleation of grains of superhard material. Additionally, the temperature may be reduced and maintained at a temperature between about 400 °C and about 800 °C for at least about 30 minutes (*e.g.*, up to about 24 hours or more) in a process similar to those known in the art of metallurgy as “re-crystallization annealing” process.

Referring to FIG. 12, a partial cutaway perspective view of a cutting element 122 formed by an HTHP process is shown. The cutting element 122 includes a polycrystalline table 124 attached to an end of a substrate 120. The polycrystalline table 124 comprises a polycrystalline superhard material, such as, for example, polycrystalline diamond. Though the cutting element 122 is depicted as having a cylindrical shape, coated core particles, such as any of those shown in FIGS. 3 through 10, may be used to form polycrystalline tables 124 having any

- 19 -

shape, such as, for example, dome-shaped, conic, tombstone, and other shapes for superhard polycrystalline materials known in the art.

Referring to FIG. 13, a perspective view of an earth-boring tool 126 to which cutting elements 122 may be attached is shown. The earth-boring tool 126 includes a bit body 128 having blades 130 extending from the bit body 128. The cutting elements 122 may be secured within pockets 132 formed in the blades 130. However, cutting elements 122 and polycrystalline tables 124 as described herein may be bonded to and used on other types of earth-boring tools, including, for example, roller cone drill bits, percussion bits, impregnated bits, core bits, eccentric bits, bicenter bits, reamers, expandable reamers, mills, hybrid bits, and other drilling bits and tools known in the art.

While the present invention has been described herein with respect to certain 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 embodiments described herein may be made without departing from the scope of the invention as hereinafter claimed, including legal equivalents. 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 inventor.

20

CONCLUSION

In some embodiments, coated particles comprise a core particle comprising a superhard material and having an average diameter of between 1 μm and 500 μm . A coating material is adhered to and covers at least a portion of an outer surface of the core particle, the coating material comprising an amine terminated group. A plurality of nanoparticles selected from the group consisting of carbon nanotubes, nanographite, nanographene, non-diamond carbon allotropes, surface modified nanodiamond, nanoscale particles of BeO, and nanoscale particles comprising a Group VIIIA element is adhered to the coating material.

In other embodiments, methods of coating a particle comprise at least partially coating a core particle comprising a superhard material and having an average diameter of between 1 μm and 500 μm with a coating material comprising

- 20 -

an amine terminated group. The coating material adheres to an outer surface of the core particle. The at least partially coated core particle is disposed in a dispersion comprising a plurality of nanoparticles comprising a material selected from the group consisting of graphite, graphene, a non-diamond allotrope of carbon, surface modified diamond, BeO, and a Group VIIIA element dispersed in a continuous phase material. At least some nanoparticles of the plurality of nanoparticles adhere to the coating material.

In additional embodiments, methods of forming a polycrystalline compact comprise at least partially coating a plurality of core particles comprising a superhard material and having an average particle size of between 1 μm and 500 μm with a coating material comprising an amine terminated group. The coating material adheres to an outer surface of the plurality of core particles. The at least partially coated plurality of core particles is disposed in a dispersion comprising a plurality of nanoparticles comprising a material selected from the group consisting of graphite, graphene, a non-diamond allotrope of carbon, surface modified diamond, BeO, and a Group VIIIA element dispersed in a continuous phase material. At least some nanoparticles of the plurality of nanoparticles adhere to the coating material. At least some of the at least partially coated plurality of core particles are interbonded by subjecting them to a high temperature/high pressure process to form a polycrystalline material.

CLAIMS

What is claimed is:

- 5 1. A coated particle, comprising:
a core particle comprising a superhard material and having an average diameter of
between 1 μm and 500 μm ;
a coating material adhered to and covering at least a portion of an outer surface of the
core particle, the coating material comprising an amine terminated group; and
10 a plurality of nanoparticles selected from the group consisting of carbon nanotubes,
nanographite, nanographene, non-diamond carbon allotropes, surface modified
nanodiamond, nanoscale particles of BeO, and nanoscale particles comprising a
Group VIIIA element adhered to the coating material.
- 15 2. The coated particle of claim 1, wherein the outer surface of the core
particle comprises a first net charge, the coating material comprises a second net charge
opposite the first net charge, and an outer surface at least some nanoparticles of the
plurality of nanoparticles comprises a third net charge opposite the second net charge.
- 20 3. The coated particle of claim 1, further comprising at least a second
coating material adhered to and covering at least a portion of the plurality of
nanoparticles.
4. The coated particle of claim 3, further comprising at least a second
25 plurality of nanoparticles selected from the group consisting of carbon nanotubes,
nanographite, nanographene, non-diamond carbon allotropes, surface modified
nanodiamond, nanoscale particles of BeO, and nanoscale particles comprising a Group
VIIIA element adhered to the at least a second coating material.
- 30 5. The coated particle of claim 4, wherein the plurality of nanoparticles
comprises a material different from the material of the at least a second plurality of
nanoparticles.

- 22 -

6. The coated particle of claim 4 or claim 5, wherein the core particle, the coating material, the plurality of nanoparticles, the at least a second coating material, and the at least a second plurality of nanoparticles comprise a net charge opposite a net charge of their adjacent components.

7. The coated particle of claim 4 or claim 5, further comprising a plurality of other coating materials and other pluralities of nanoparticles successively disposed on and adhered to one another.

10

8. The coated particle of claim 1, wherein the coating material comprises at least one of polyallylamine and branched polyethylenimine.

9. A method of coating a particle, comprising:
15 at least partially coating a core particle comprising a superhard material and having an average diameter of between 1 μm and 500 μm with a coating material comprising an amine terminated group;
adhering the coating material to an outer surface of the core particle;
disposing the at least partially coated core particle in a dispersion comprising a
20 plurality of nanoparticles comprising a material selected from the group consisting of graphite, graphene, a non-diamond allotrope of carbon, surface modified diamond, BeO, and a Group VIIIA element dispersed in a continuous phase material; and
adhering at least some nanoparticles of the plurality of nanoparticles to the coating
25 material.

10. The method of claim 9, further comprising:
imparting a first net charge opposite a second net charge of the coating material to the outer surface of the core particle; and imparting a third net charge opposite the
30 second net charge to an outer surface of at least some nanoparticles of the plurality of nanoparticles.

- 23 -

11. The method of claim 9, further comprising:
at least partially coating the at least some nanoparticles of the plurality of nanoparticles
with a coating material comprising an amine terminated group; and
adhering the coating material to the at least some nanoparticles of the plurality of
5 nanoparticles.

12. The method of claim 11, further comprising:
disposing the core particle, the coating material, and the at least some nanoparticles of
the plurality of nanoparticles in a dispersion comprising another plurality of
10 nanoparticles comprising a material selected from the group consisting of
graphite, graphene, a non-diamond allotrope of carbon, surface modified
diamond, BeO, and a Group VIIIA element dispersed in a continuous phase
material; and
adhering at least some nanoparticles of the another plurality of nanoparticles to the
15 coating material.

13. The method of claim 12, wherein disposing the core particle, the
coating material, and the at least some nanoparticles of the plurality of nanoparticles in
a dispersion comprising another plurality of nanoparticles comprising a material
20 selected from the group consisting of graphite, graphene, a non-diamond allotrope of
carbon, surface modified diamond, BeO, and a Group VIIIA element dispersed in a
continuous phase material comprises disposing the core particle, the coating material,
and the at least some nanoparticles of the plurality of nanoparticles in a dispersion
comprising another plurality of nanoparticles comprising a material different from the
25 material of the at least some nanoparticles of the plurality of nanoparticles.

14. The method of claim 12 or claim 13, further comprising repeating the
acts of at least partially coating, adhering, disposing in a dispersion, and adhering a
predetermined number of times.
30

15. The method of claim 9, further comprising derivatizing the outer
surface of the core particle before at least partially coating the core particle.

16. The method of claim 9, further comprising derivatizing an outer surface of the plurality of nanoparticles before disposing the at least partially coated core particle in the dispersion comprising the plurality of nanoparticles.

5

17. The method of claim 9 or claim 16, further comprising:
disposing the core particle, the coating material, and the at least some nanoparticles of the plurality of nanoparticles in a dispersion comprising a plurality of nanoparticles comprising a material selected from the group consisting of
10 graphite, graphene, a non-diamond allotrope of carbon, surface modified diamond, BeO, and a Group VIIIA element dispersed in a continuous phase material, wherein the plurality of nanoparticles comprises a charge opposite a charge of the at least some of the nanoparticles; and
adhering at least some other nanoparticles of the plurality of nanoparticles to the at
15 least some nanoparticles of the nanoparticles.

18. The method of claim 9 or claim 16, further comprising cross-linking the coating material.

20 19. The method of claim 9 or claim 16, wherein at least partially coating a core particle comprising a superhard material and having an average diameter of between 1 μm and 500 μm with a coating material comprising an amine terminated group comprises at least partially coating the core particle with at least one of polyallylamine and branched polyethylenimine.

25

- 25 -

20. A method of forming a polycrystalline compact, comprising:
at least partially coating a plurality of core particles comprising a superhard material
and having an average particle size of between 1 μm and 500 μm with a
coating material comprising an amine terminated group;
5 adhering the coating material to an outer surface of the plurality of core particles;
disposing the at least partially coated plurality of core particles in a dispersion
comprising a plurality of nanoparticles comprising a material selected from the
group consisting of graphite, graphene, a non-diamond allotrope of carbon,
surface modified diamond, BeO, and a Group VIIIA element dispersed in a
10 continuous phase material;
adhering at least some nanoparticles of the plurality of nanoparticles to the coating
material; and
interbonding at least some at least partially coated core particles of the at least partially
coated plurality of core particles by subjecting them to a high temperature/high
15 pressure process to form a polycrystalline material.

21. The method of claim 20, further comprising:
imparting a first net charge opposite a second net charge of the coating material to the
outer surface of the plurality of core particles; and
20 imparting a third net charge opposite the second net charge to an outer surface of at
least some nanoparticles of the plurality of nanoparticles.

22. The method of claim 20, further comprising at least partially coating the
at least some nanoparticles of the plurality of nanoparticles with a coating material
25 comprising an amine terminated group.

- 26 -

23. The method of claim 22, further comprising:
disposing the plurality of core particles, the coating material, and the at least some
nanoparticles of the plurality of nanoparticles in a dispersion comprising
another plurality of nanoparticles comprising a material selected from the group
consisting of graphite, graphene, a non-diamond allotrope of carbon, surface
modified diamond, BeO, and a Group VIIIA element dispersed in a continuous
phase material; and
adhering at least some nanoparticles of the another plurality of nanoparticles to the
coating material.
24. The method of claim 23, wherein disposing the plurality of core
particles, the coating material, and the at least some nanoparticles of the plurality of
nanoparticles in a dispersion comprising another plurality of nanoparticles comprising
a material selected from the group consisting of graphite, graphene, a non-diamond
allotrope of carbon, surface modified diamond, BeO, and a Group VIIIA element
dispersed in a continuous phase material comprises disposing the plurality of core
particles, the coating material, and the at least some nanoparticles of the plurality of
nanoparticles in a dispersion comprising another plurality of nanoparticles comprising
a material different from the material of the at least some nanoparticles of the plurality
of nanoparticles.