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Cutter Elements for Drill Bits and Methods for Fabricating Same

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(54) **CUTTER ELEMENTS FOR DRILL BITS AND METHODS FOR FABRICATING SAME**

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C23C 16/455	(2006.01)
E21B 10/567	(2006.01)

(52) **U.S. Cl.**
CPC ***C23C 16/4417*** (2013.01); ***C23C 16/45555*** (2013.01); ***E21B 10/567*** (2013.01)

(58) **Field of Classification Search**
None
See application file for complete search history.

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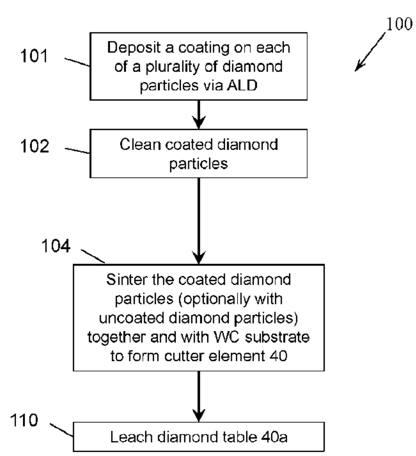
(74) *Attorney, Agent, or Firm* — Conley Rose, P.C.

(57) **ABSTRACT**

A method of fabricating a PCD cutter element including a diamond table including a plurality of coated diamond particles fabricated using an atomic layer deposition (ALD) process.

19 Claims, 13 Drawing Sheets



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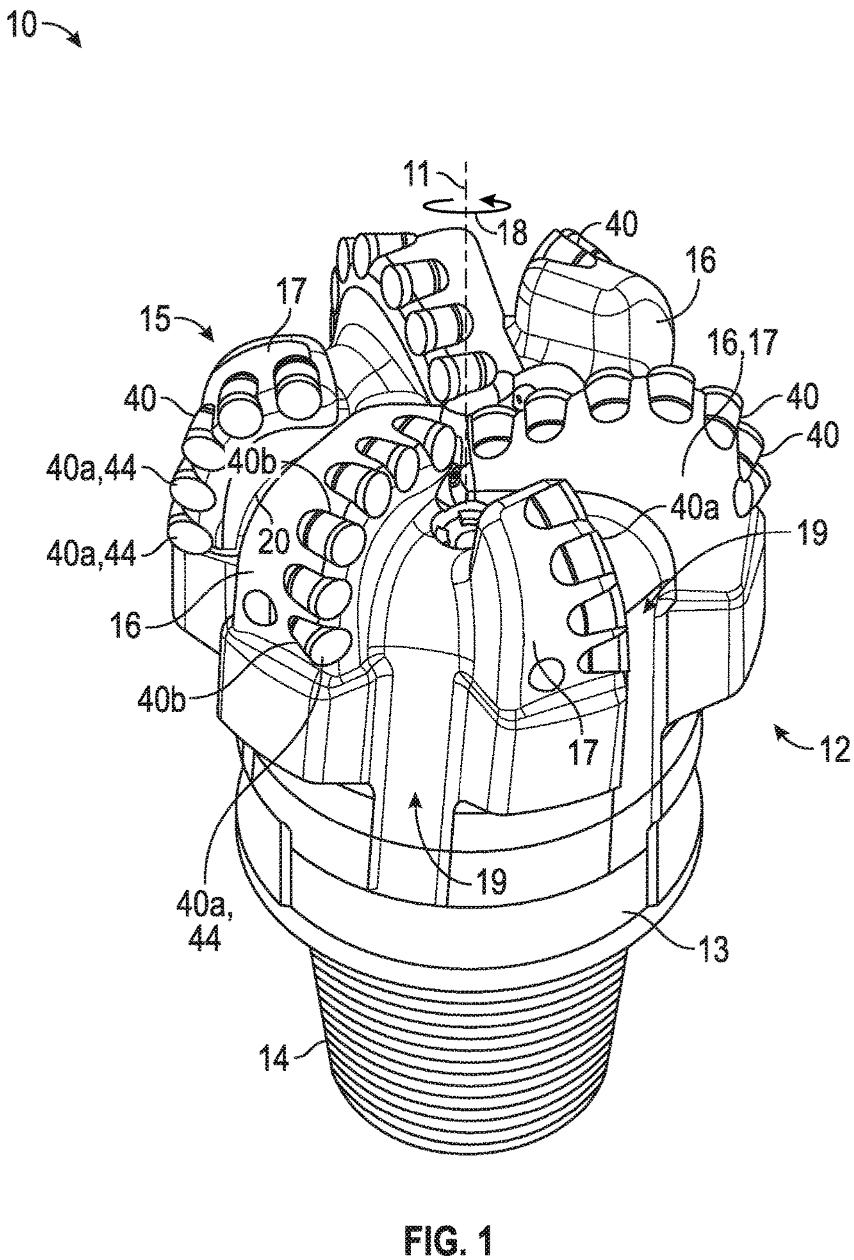

10
11
18
40
16
16,17
40
40
15
17
40
40a,44
40b
40a,44
20
16
40a
19
40b
17
12
19
40a,
44
13
14

FIG. 1

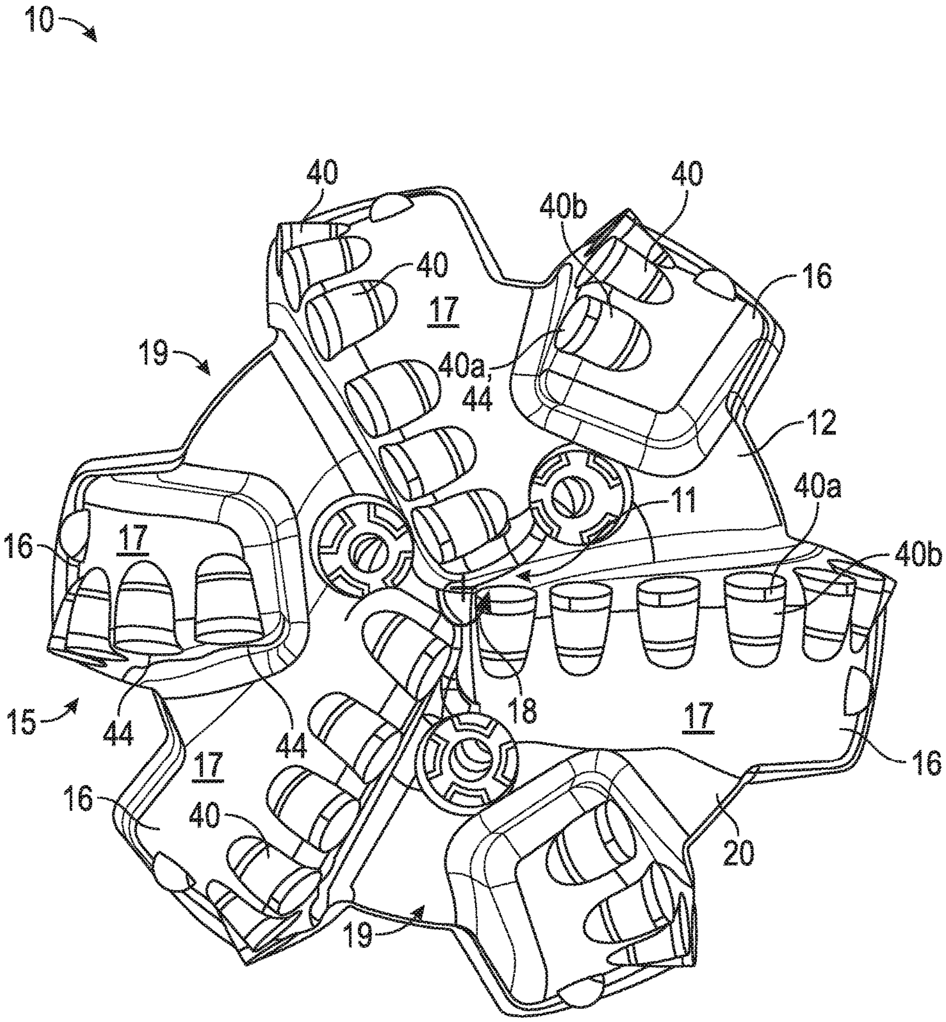

10
40
40b
40
40
16
17
19
40a,
44
12
11
40a
16
17
40b
18
17
15
44
44
16
17
16
40
20
19

FIG. 2

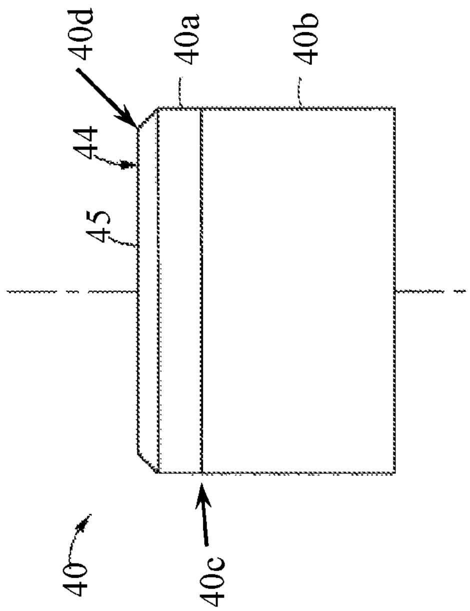


FIG. 3B

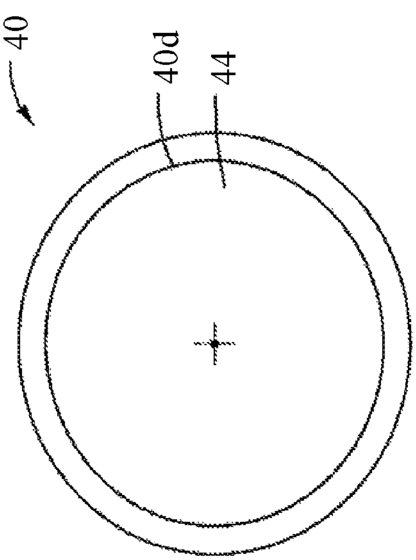


FIG. 3A

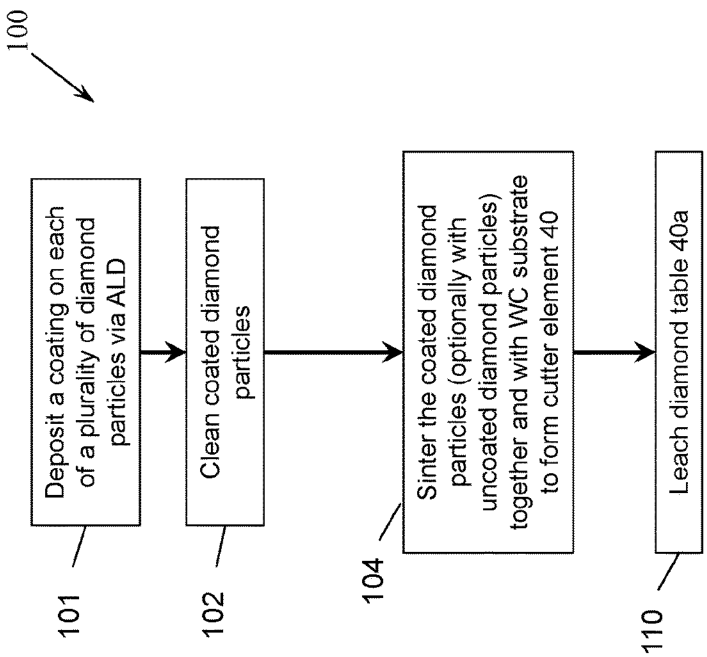

100
Deposit a coating on each of a plurality of diamond particles via ALD
101
Clean coated diamond particles
102
Sinter the coated diamond particles (optionally with uncoated diamond particles) together and with WC substrate to form cutter element 40
104
Leach diamond table 40a
110

FIGURE 4

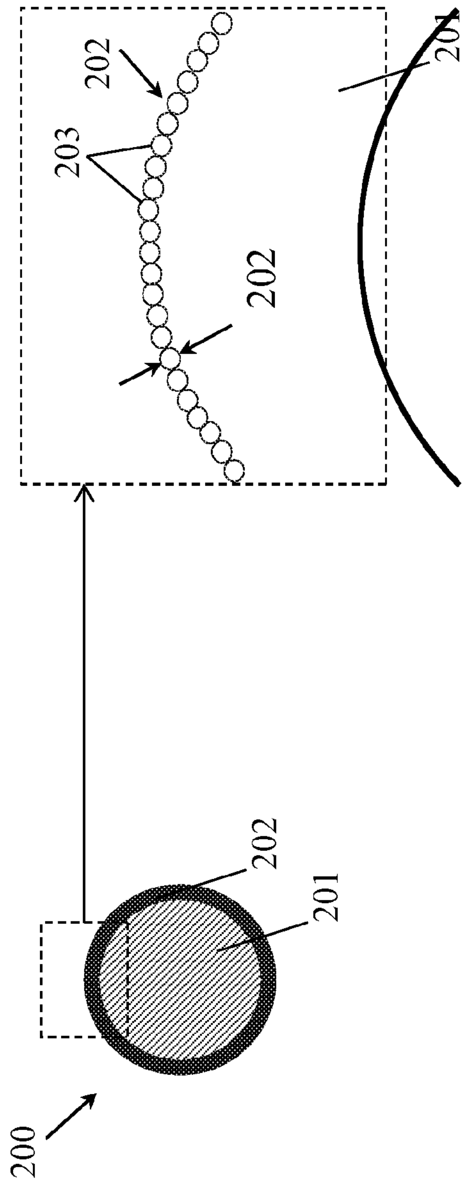
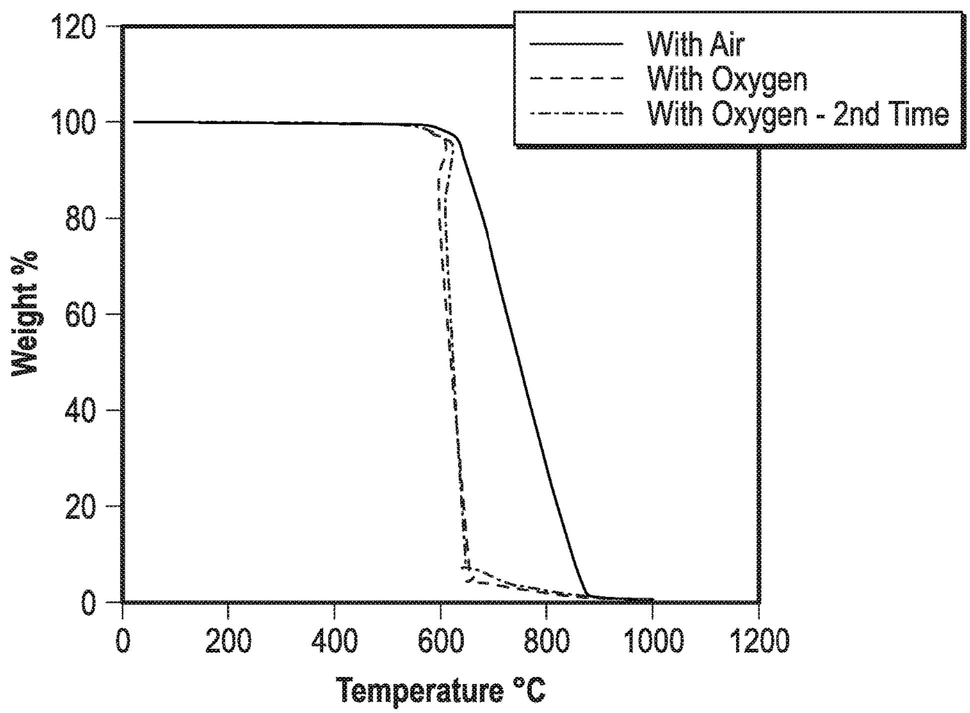


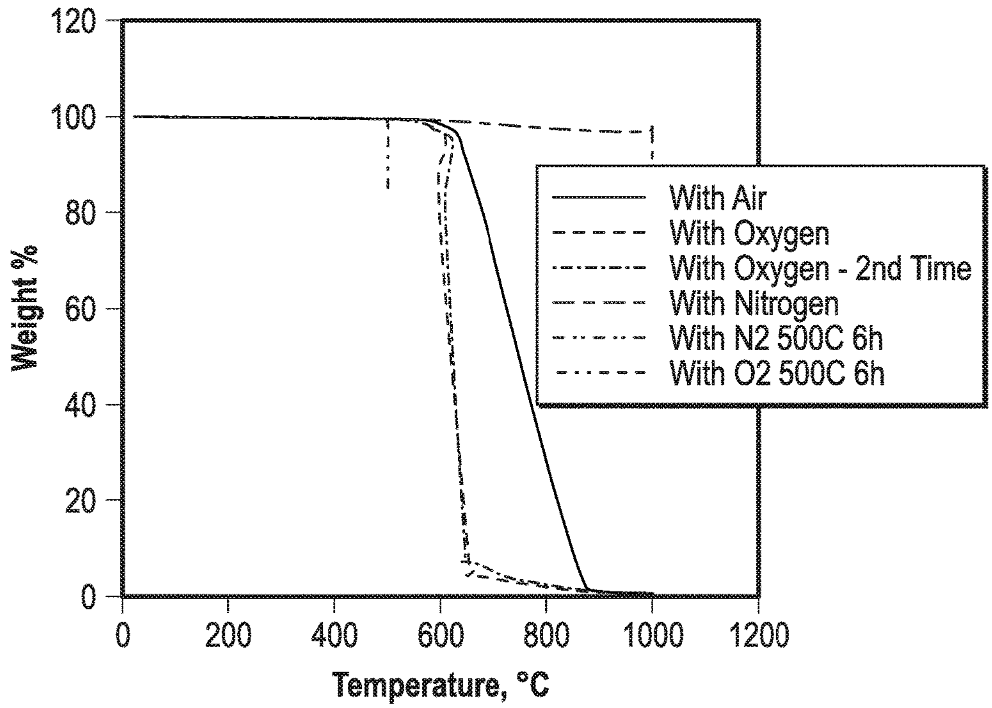
FIG. 5B

FIG. 5A



120
100
80
60
40
20
0
Weight %
0
200
400
600
800
1000
1200
Temperature °C
With Air
With Oxygen
With Oxygen - 2nd Time

FIG. 6



120
100
80
60
40
20
0
Weight %
0
200
400
600
800
1000
1200
Temperature, °C
With Air
With Oxygen
With Oxygen - 2nd Time
With Nitrogen
With N2 500C 6h
With O2 500C 6h

FIG. 7

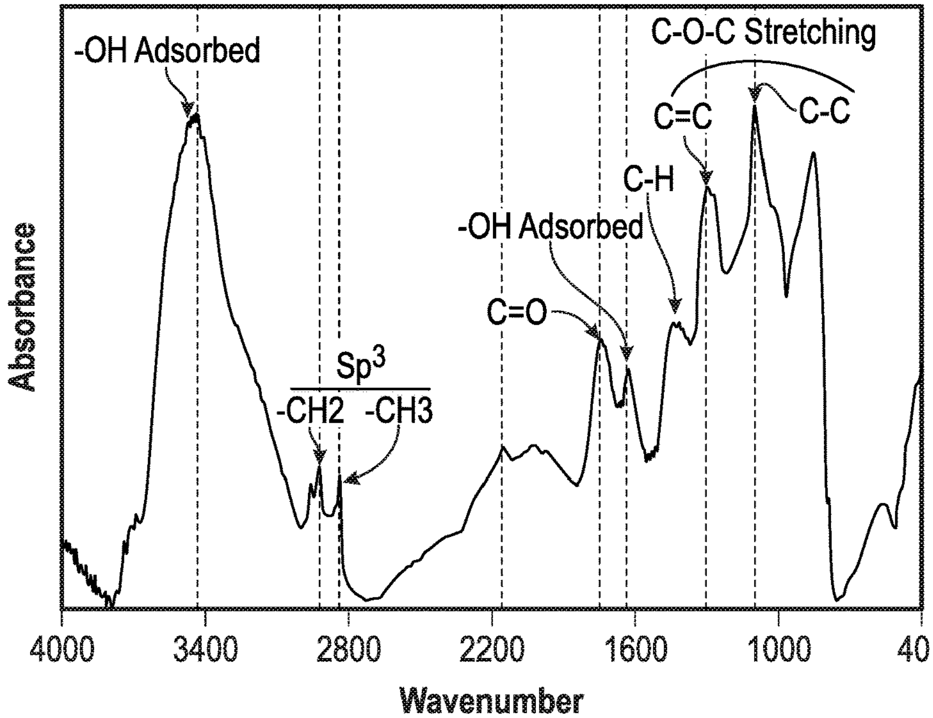

-OH Adsorbed
Sp3
-CH2
-CH3
C=O
-OH Adsorbed
C-H
C=C
C-O-C Stretching
C-C
Absorbance
4000
3400
2800
2200
1600
1000
40
Wavenumber

FIG. 8

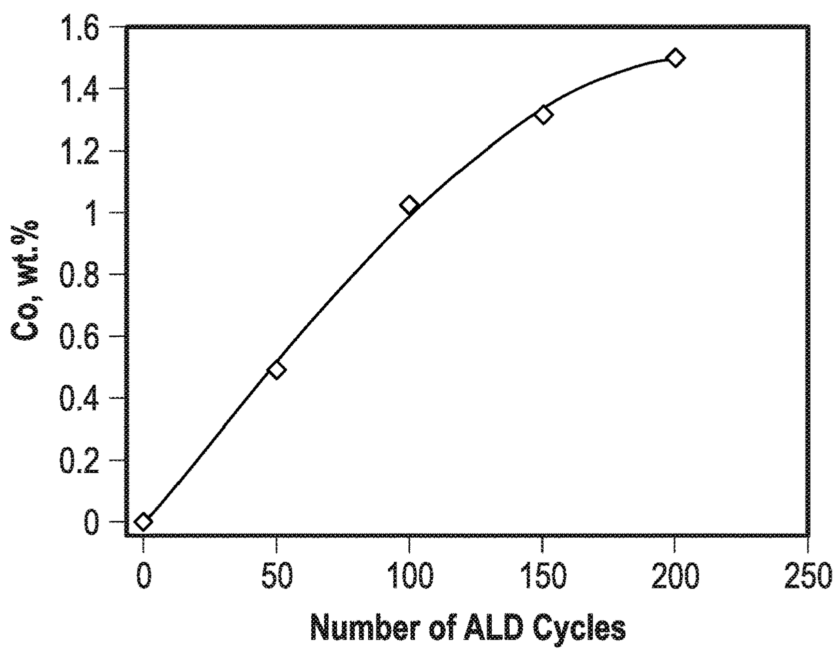

1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Co, wt.%
0
50
100
150
200
250
Number of ALD Cycles

FIG. 9

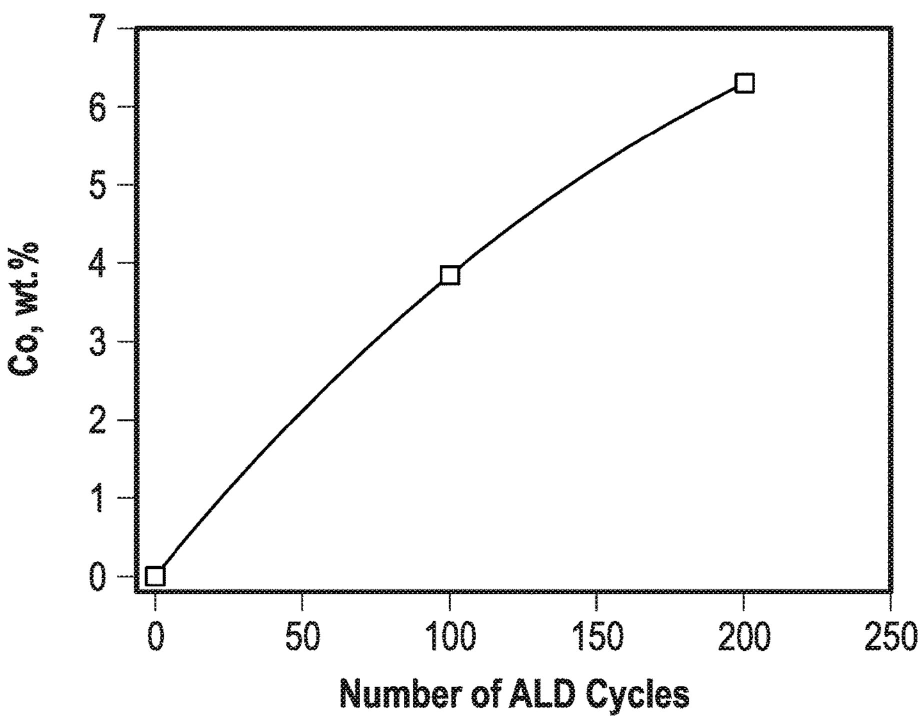


FIG. 10

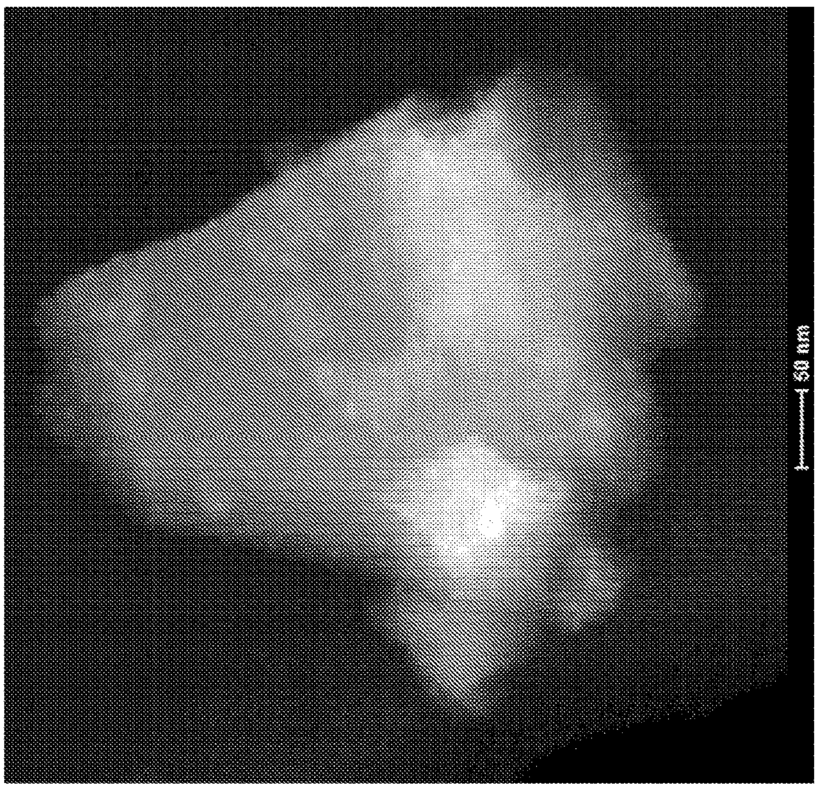


FIG. 11

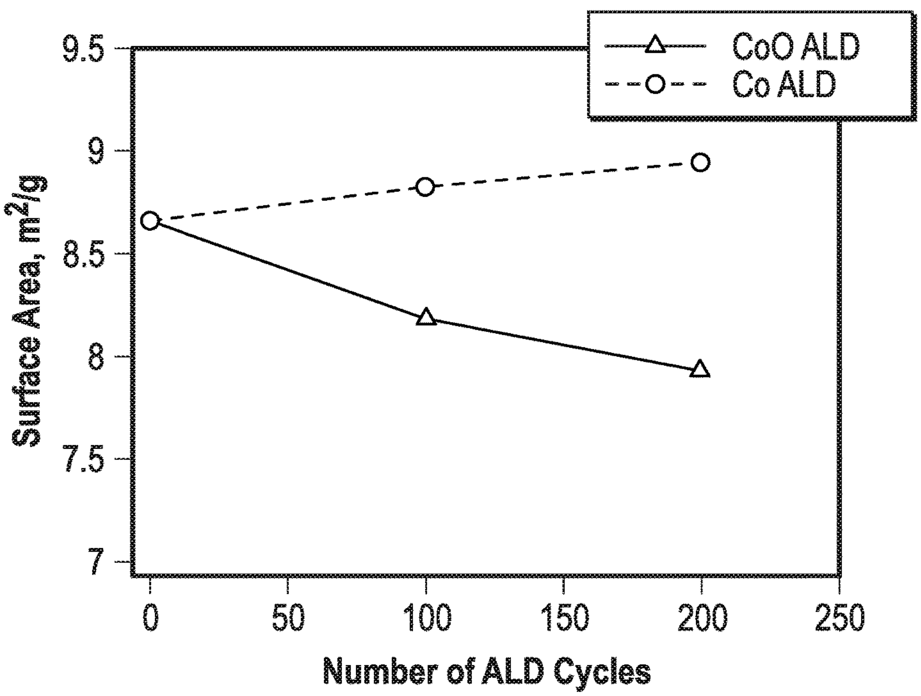

CoO ALD
Co ALD
Surface Area, m2/g
9.5
9
8.5
8
7.5
7
0
50
100
150
200
250
Number of ALD Cycles

FIG. 12

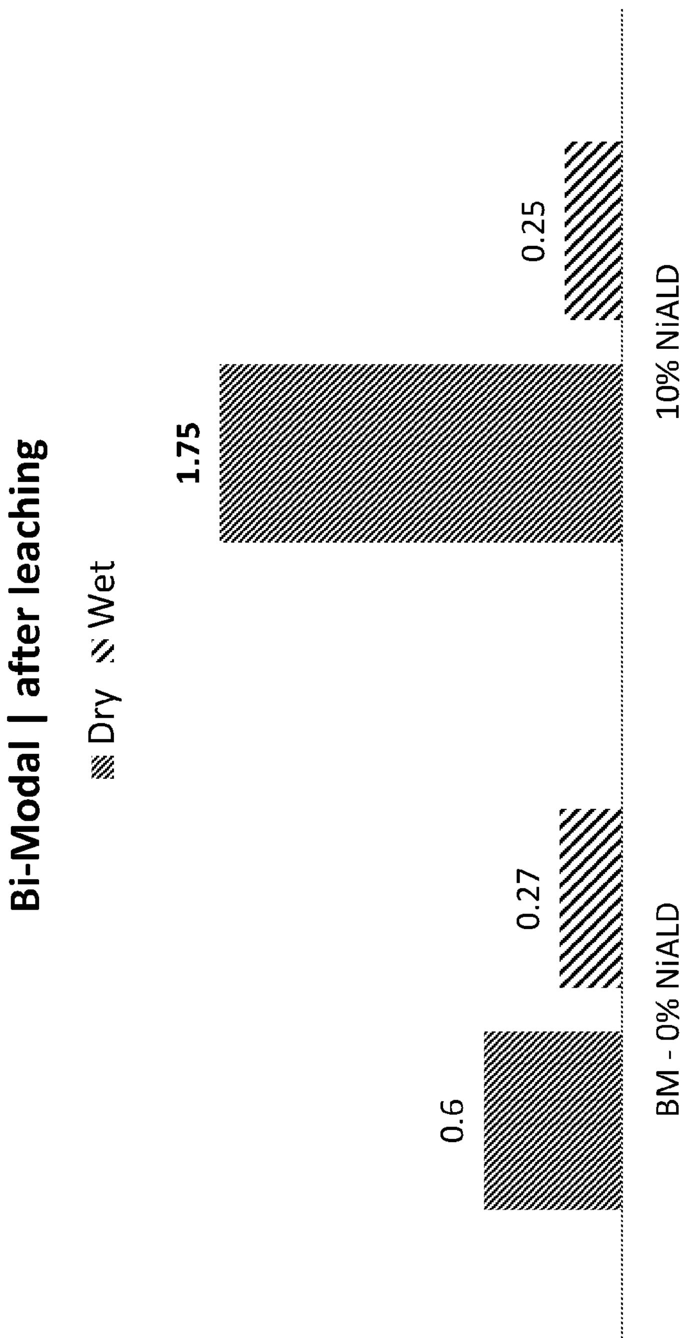

Bi-Modal | after leaching
Dry
Wet
0.6
0.27
1.75
0.25
BM - 0% NiALD
10% NiALD

FIG. 13A

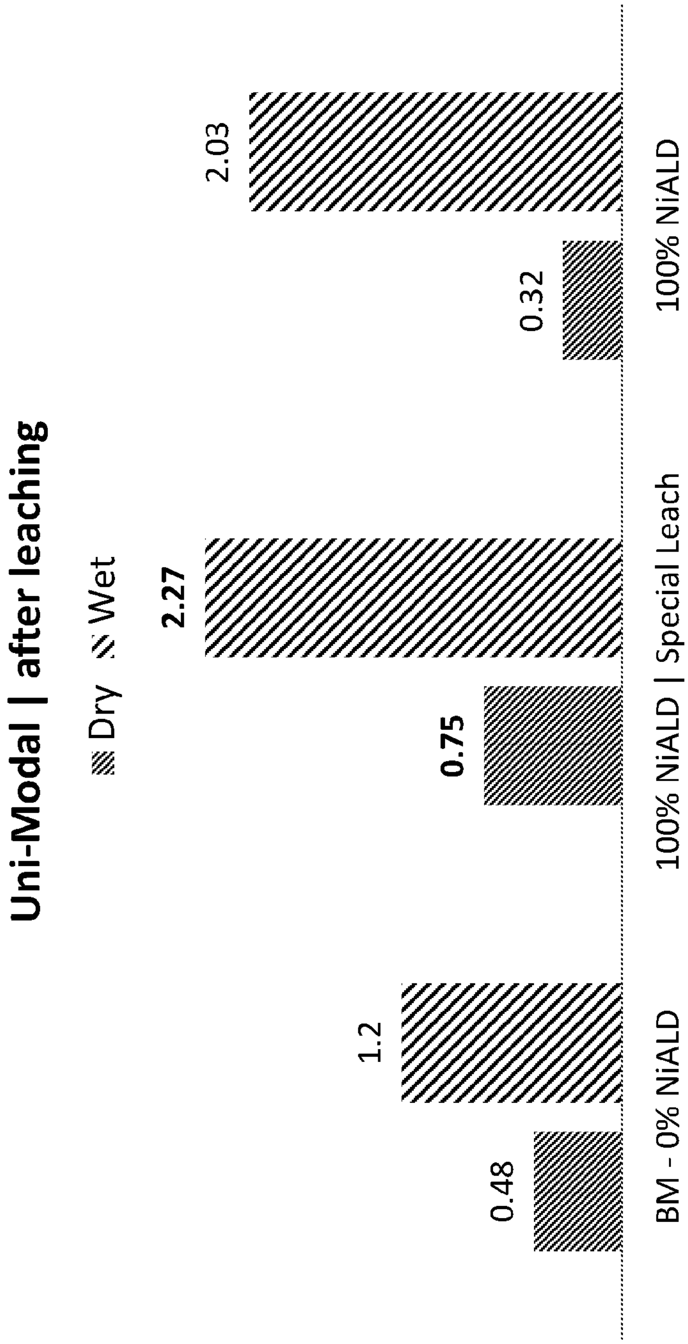

Uni-Modal | after leaching
Dry
Wet
0.48
1.2
0.75
2.27
0.32
2.03
BM - 0% NiALD
100% NiALD | Special Leach
100% NiALD

FIG. 13B

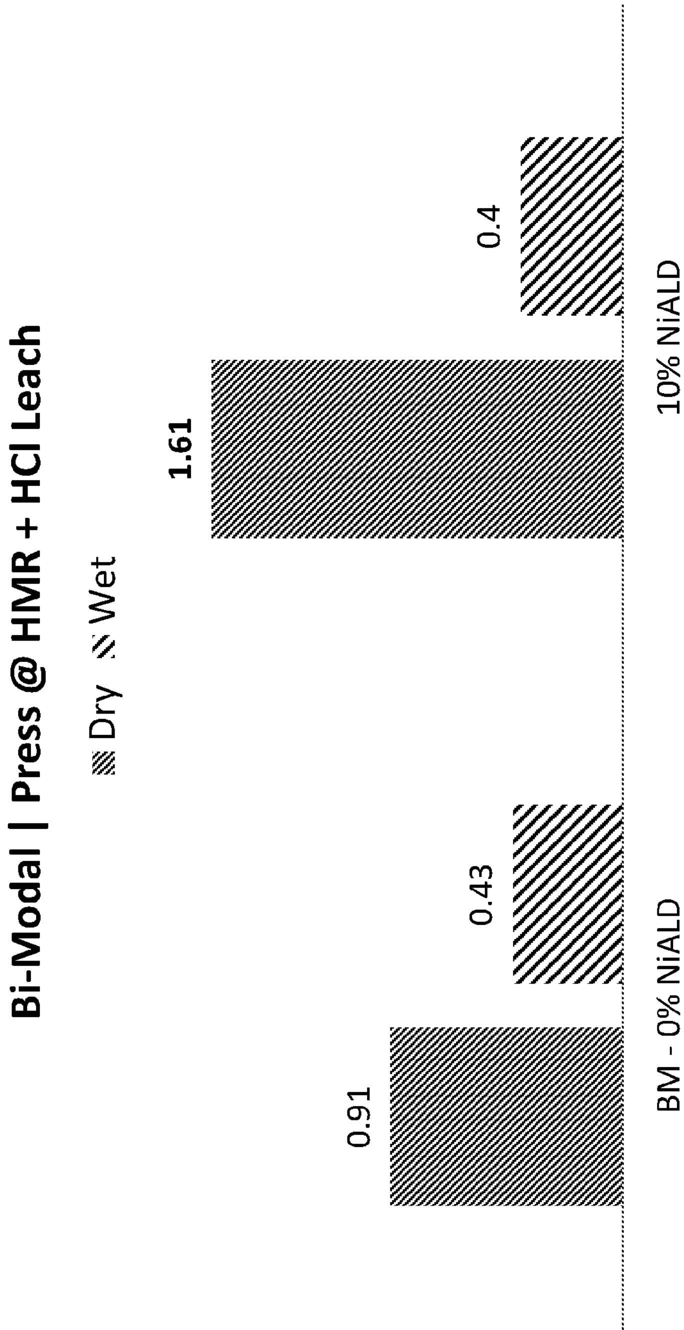

Bi-Modal | Press @ HMR + HCl Leach
Dry
Wet
0.91
0.43
1.61
0.4
BM - 0% NiALD
10% NiALD

FIG. 13C

CUTTER ELEMENTS FOR DRILL BITS AND METHODS FOR FABRICATING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a 35 U.S.C. § 371 national stage application of PCT/US2016/032343 filed May 13, 2016, and entitled "Cutter Elements for Drill Bits and Methods for Fabricating Same," which claims benefit of U.S. provisional patent application Ser. No. 62/160,793 filed May 13, 2015, and entitled "Cutter Elements for Drill Bits and Methods for Fabricating Same," each of which is hereby incorporated herein by reference in their entirety for all purposes.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not applicable.

BACKGROUND

The disclosure relates generally to cutter elements for drill bits used to drill boreholes in a subterranean formation. More particularly, the disclosure relates to methods for fabricating polycrystalline diamond (PCD) cutter elements for drill bits.

An earth-boring drill bit is typically mounted on the lower end of a drill string and is rotated by rotating the drill string at the surface or by actuation of downhole motors or turbines, or by both methods. With weight applied to the drill string, the rotating drill bit engages the earthen formation and proceeds to form a borehole along a predetermined path toward a target zone.

Earth boring bits used in oilfield drilling operations are frequently one of two types: fixed cutter bits or rolling cutter bits. Fixed cutter drill bits have multiple cutting surfaces that are pressed into and dragged through a formation. This type of bit primarily cuts the formation by shearing and scraping. Rolling cutter bits include one or more rotatable cutters that perform their cutting function due to the rolling movement of the cutters acting against the formation material. The cutters roll and slide upon the bottom of the borehole as the bit is rotated, the cutters thereby engaging and disintegrating the formation material in its path. The rotatable cutters may be described as generally conical in shape and are therefore sometimes referred to as rolling cones or rolling cone cutters. The earth disintegrating action of rolling cutter bits is enhanced by providing a plurality of cutters or cutting elements that extend from each of the rolling cones. Applying weight to the drill bit while rotating forces the cutting elements into engagement with the earth and rotates the cones. A rolling cutter drill bit primarily cuts the formation by compression, crushing, gouging, chipping and scraping. Two common classifications of rolling cutter drill bits include "insert" bits and "tooth" bits. In insert bits, the cutting elements extending from the cones comprise inserts that are press fit into undersized apertures in the cone surface prior to drilling with the bit. In tooth bits, the cutting elements comprise teeth that are milled, cast or otherwise integrally formed with the rolling cone.

While the bit is rotated, drilling fluid is pumped through the drill string and directed out of the face of the drill bit. The fixed cutter bit typically includes nozzles or fixed ports spaced about the bit face that serve to inject drilling fluid into the flow passageways between the several blades. The flowing fluid performs several important functions. The fluid removes formation cuttings from the bit's cutting structure. Otherwise, accumulation of formation materials on the cutting structure may reduce or prevent the penetration of the cutting structure into the formation. In addition, the fluid removes cut formation materials from the bottom of the hole. Failure to remove formation materials from the bottom of the hole may result in subsequent passes by cutting structure to re-cut the same materials, thereby reducing the effective cutting rate and potentially increasing wear on the cutting surfaces. The drilling fluid and cuttings removed from the bit face and from the bottom of the hole are forced from the bottom of the borehole to the surface through the annulus that exists between the drill string and the borehole sidewall. Further, the fluid removes heat, caused by contact with the formation, from the cutter elements in order to prolong cutter element life. Thus, the number and placement of drilling fluid nozzles, and the resulting flow of drilling fluid, may significantly impact the performance of the drill bit.

The cutter elements disposed on the several blades of a fixed cutter bit are typically formed of extremely hard materials and include a layer of polycrystalline diamond ("PCD") material. In the typical fixed cutter bit, each cutter element or assembly comprises an elongate and generally cylindrical support member which is received and secured in a pocket formed in the surface of one of the several blades. In addition, each cutter element typically has a hard cutting layer of polycrystalline diamond or other superabrasive material such as cubic boron nitride, thermally stable diamond, polycrystalline cubic boron nitride, or ultrahard tungsten carbide (meaning a tungsten carbide material having a wear-resistance that is greater than the wear-resistance of the material forming the substrate) as well as mixtures or combinations of these materials. The cutting layer is exposed on one end of its support member, which is typically formed of tungsten carbide.

BRIEF SUMMARY OF THE DISCLOSURE

In an embodiment disclosed herein, a method for fabricating a PCD cutter element, comprising: (a) coating a plurality of diamond particles by directly depositing the coating on an outer surface of each diamond particle of the plurality of diamond particles by atomic layer deposition (ALD); cleaning the coated diamond particles after (a) to remove oxides from coating; using the coated diamond particles after (b) to form the PCD cutter element.

In an alternate embodiment disclosed herein, a method of fabricating a PCD cutter element, comprising: (a) providing a plurality of diamond particles; (b) directly depositing a nickel oxide or cobalt oxide coating on an outer surface of each diamond particle of the plurality of diamond particles by atomic layer deposition (ALD), wherein the nickel oxide coating directly contacts the outer surface of the corresponding diamond particle; (c) removing oxides from the nickel oxide coating after (b) to convert the nickel oxide coating on each diamond particle to a nickel coating on each diamond particle; (d) sintering the coated diamond particles after (c) to form a diamond table; and (e) mounting the diamond table to a tungsten-carbide substrate to form the PCD cutter element.

Embodiments described herein comprise a combination of features and advantages intended to address various shortcomings associated with certain prior devices, systems, and methods. The foregoing has outlined rather broadly the features and technical advantages disclosed herein in order that the detailed description of the invention that follows may be better understood. The various characteristics described above, as well as other features, will be readily apparent to those skilled in the art upon reading the following detailed description, and by referring to the accompanying drawings. It should be appreciated by those skilled in the art that the conception and the specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes as disclosed herein. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

For a detailed description of the preferred embodiments of the invention, reference will now be made to the accompanying drawings in which:

FIG. **1** is a perspective view of an embodiment of a drill bit made in accordance with principles described herein;

FIG. **2** is an end view of the bit of FIG. **1**;

FIGS. **3**A and **3**B are end and side views, respectively, of one of the PCD cutter elements of the bit of FIG. **1**;

FIG. **4** is a flow chart illustrating an embodiment of a method for making the PCD cutting element of FIGS. **3**A and **3**B;

FIGS. **5**A and **5**B are schematic cross-sectional views of one coated diamond particle fabricated according to the method shown in FIG. **4**;

FIG. **6** is a graph illustrating thermogravimetricanalysis (TGA) of samples of uncoated diamond particles fabricated according to embodiments described herein;

FIG. **7** is a graph illustrating thermogravimetricanalysis (TGA) of samples of uncoated diamond particles fabricated according to embodiments described herein;

FIG. **8** is a graph of the Fourier Transform Infrared Spectrometer (FTIR) analysis of uncoated diamond particles fabricated according to embodiments described herein;

FIG. **9** is a graph of the inductively coupled plasma-atomic emission spectroscopy (ICP) analysis of cobalt ALD coated diamond particles;

FIG. **10** is a graph of ICP results indicating that the content of Co on 500 nm diamond particles increased with the increase of the number of CoO ALD coating cycles using bis(cyclopentadienyl)cobalt(II) and oxygen as precursors;

FIG. **11** is a transmission electron microscopy (TEM) image of Co nanoparticles with a uniform particle size distribution that were deposited on diamond particle surfaces using ALD; and

FIG. **12** is a graph of the Brunauer-Emmet-Teller (BET) surface area of the 500 nm diamond particles coated with various cycles of Co or CoO ALD.

FIGS. **13**A-**13**C illustrate abrasion results for PCD cutter elements fabricated according to embodiments of the present disclosure.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following discussion is directed to various exemplary embodiments. However, one skilled in the art will understand that the examples disclosed herein have broad application, and that the discussion of any embodiment is meant only to be exemplary of that embodiment, and not intended to suggest that the scope of the disclosure, including the claims, is limited to that embodiment.

Certain terms are used throughout the following description and claims to refer to particular features or components. As one skilled in the art will appreciate, different persons may refer to the same feature or component by different names. This document does not intend to distinguish between components or features that differ in name but not function. The drawing figures are not necessarily to scale. Certain features and components herein may be shown exaggerated in scale or in somewhat schematic form and some details of conventional elements may not be shown in interest of clarity and conciseness.

In the following discussion and in the claims, the terms "including" and "comprising" are used in an open-ended fashion, and thus should be interpreted to mean "including, but not limited to . . . ." Also, the term "couple" or "couples" is intended to mean either an indirect or direct connection. Thus, if a first device couples to a second device, that connection may be through a direct connection, or through an indirect connection via other devices, components, and connections. In addition, as used herein, the terms "axial" and "axially" generally mean along or parallel to a central axis (e.g., central axis of a body or a port), while the terms "radial" and "radially" generally mean perpendicular to the central axis. For instance, an axial distance refers to a distance measured along or parallel to the central axis, and a radial distance means a distance measured perpendicular to the central axis. Any reference to up or down in the description and the claims is made for purposes of clarity, with "up", "upper", "upwardly", "uphole", or "upstream" meaning toward the surface of the borehole and with "down", "lower", "downwardly", "downhole", or "downstream" meaning toward the terminal end of the borehole, regardless of the borehole orientation.

To manufacture PCD tables for cutter elements and bond the tables to the substrate, diamond powder is placed at the bottom of a first mold or can along with a catalyst. The substrate is then placed on top of the diamond powder within the first mold, a second mold or can is placed on top of the substrate, and a seal is formed between the first and second cans. This entire assembly is then subjected to high pressure and temperature conditions to form a PCD cutter element. In general, any Group VIII element (e.g., cobalt, nickel, or iron) can be used as the catalyst, however, in most cases, cobalt (Co) is employed. The catalyst is driven into the interstitial spaces between the diamond grains and promotes intergrowth therein, to form a solid PCD diamond table suitable for use in a cutter element. However, conventional powder mixing techniques do not always result in uniform distribution of the diamond and catalyst powders. Consequently, non-homogenous microstructures may result, potentially reducing the PCD table durability.

The catalyst in the PCD diamond table typically has a coefficient of thermal expansion different than that of the diamond, and thus, thermal stresses experience during drilling operations can undesirably cause cracks to form within the PCD diamond table. A common approach for removing the catalyst from a PCD table is to leach the PCD table to remove some or substantially all of the interstitial catalyst from the PCD lattice structure, thereby transforming the PCD material into thermally stable polycrystalline diamond. Leaching typically involves placing the cutter element in a strong acid bath at an elevated temperature to expose the PCD table to the acid. Suitable acids for leaching include nitric acid, sulfuric acid, hydrofluoric acid, hydrochloric acid, and combinations thereof. Although such leaching acids can aid in removing the catalyst from the PCD table, they can also damage the underlying substrate to which the

PCD table is secured. In addition, conventional leaching via acid bath is a relatively time-consuming as it may take days or even weeks to remove a sufficient quantity of the binding agent from the PCD table. This increases the overall time, and associated costs, to manufacture cutter elements and fixed cutter drill bits.

As will be described in more detail below, embodiments described herein offer the potential for more uniform distribution of diamond and catalyst materials, resulting in improved diamond-to-diamond bonding and PCD table durability. In addition, embodiments described herein off the potential for improved PCD table thermal stability, thereby decreasing the need for leaching and/or reducing the time necessary for sufficient leaching.

Referring now to FIGS. **1** and **2**, an embodiment of a drill bit **10** for drilling a borehole in a subterranean earthen formation is a fixed cutter bit, sometimes referred to as a drag bit. Bit **10** includes a body **12**, a shank **13** and a threaded connection or pin **14** for connecting bit **10** to a drill string (not shown), which is employed to rotate the bit in order to drill the metal structure. Body **12** includes a bit face **20**, which supports a cutting structure **15** generally disposed on the end of the bit **10** that is opposite pin **14**. Bit **10** has a central axis **11** about which bit **10** rotates in the cutting direction represented by arrow **18**. Body **12** may be formed in a conventional manner using powdered metal tungsten carbide particles in a binder material to form a hard metal cast matrix. Alternatively, the body can be machined from a metal block, such as steel, rather than being formed from a matrix.

Body **12** may include bores and/or passages that permitting fluid (e.g., lubricating fluid, drilling fluid, etc.) to flow from the drill string into bit **10**, and out of drill bit **10** through ports or nozzles disposed in bit face **20**. Such bores and passages may serve to distribute fluid around cutting structure **15** to flush away formation cuttings during drilling through the formation and to remove heat from bit **10**.

Referring still to FIGS. **1** and **2**, cutting structure **15** is provided on face **20** of bit **10** and includes a plurality of blades **16** extending along bit face **20**. In this embodiment, the plurality of blades **16** are uniformly circumferentially-spaced about the bit face **20**. Blades **16** are integrally formed as part of, and extend perpendicularly outwardly from body **12** and bit face **20**. In addition, blades **16** extend generally radially across bit face **20** and longitudinally along a portion of the periphery of bit **10**. Each blade **16** has a radially inner end at or proximal axis **11** and a radially outer end proximal shank **13**. Blades **16** are separated by fluid flow courses **19**. Each blade **16** on bit face **20** provides a cutter-supporting surface **17** to which a plurality of cutter elements **40** are mounted.

Each cutter element **40** includes a layer or table **40***a* of polycrystalline diamond (PCD) mounted to an elongated and generally cylindrical support member or substrate **40***b* made of tungsten carbide. Substrate **40***b* is received and secured in a pocket formed in the surface of the blade **16** to which it is fixed, and table **40***a* defines a forward facing cutting face **44** positioned and oriented to engage and shear the formation as bit **10** is rotated in the cutting direction **18**.

Referring now to FIGS. **3**A and **3**B, one cutter element **40** is shown, it being understood that each cutter element **40** of bit **10** is the same. As previously described, cutter element **40** includes a PCD table **40***a* mounted to a cylindrical tungsten carbide (WC) substrate **40***b*. In general, the interface **40***c* between PCD table **40***a* and substrate **40***b* can be planar or non-planar. The central portion **45** of cutting face **44** is planar in this embodiment, although concave, convex, or ridged surfaces can be employed. In this embodiment, the outer periphery of cutting face **44** comprises a beveled edge **40**.

Referring now to FIG. **4**, an embodiment of a method **100** for manufacturing one cutter element **40** is shown. Starting in block **101**, a plurality of diamond particles are coated with a layer, which may also be referred to as a coating, comprising a diamond crystallization catalyst such as Co, CoO, Ni, NiO, or Group VIII element or Group VIII element oxide via atomic layer deposition (ALD). In some embodiment, the coating is deposited in a single step, whereas in other embodiments, the coating comprises a plurality of layers deposited one after the other. In an embodiment of the method **100**, at block **101**, the coating of the plurality of diamond particles with a crystallization catalyst in block **101** is performed via ALD techniques known in the art. For example, for a Co coating, bis(cyclopentadienyl)cobalt(II) and hydrogen precusors can be used in the ALD process; for CoO, bis(cyclopentadienyl)cobalt(II) and oxygen precursors can be used in the ALD process. One or more additives may optionally be included with the catalyst in the coating. Examples of suitable additives included, without limitation, refractory metals such as tungsten (W), tantalum (Ta), vanadium (V), and combinations thereof.

Referring briefly to FIGS. **5**A and **5**B, one coated diamond particle **200** made according to block **101** is shown, it being understood that each coated diamond particle made according to block **101** is the same. Coated diamond particle **200** includes a diamond particle **201** having an outer surface that is completely and entirely coated with a layer or coating **202** comprising a diamond crystallization catalyst (optionally including an additive) as previously described. Thus, there are no gaps or voids in coating **202**. As best shown in FIG. **5**B, the catalyst coating **202** comprises a plurality of discrete catalyst particles **203** disposed directly on the outer surface of diamond particle **201**. In other words, there is no intermediate layer or coating of material between diamond particle **201** and the coating **202** since particles **203** are in direct contact with the particle **201**. In addition, in this embodiment, the coating **202** includes only a single layer of particles **203**, with each particle **203** having substantially the same size (e.g., diameter). Consequently, in this embodiment, the coating **202** has a radial thickness T_{202} that is equal to the width or diameter of one particle **203**. In other embodiments, the catalyst coating (e.g., coating **202**) includes multiple layers of catalyst particles (e.g., particles **203**). In some embodiments, the catalyst particles have different sizes, which may fall within a predetermined range or ratio of catalyst particle sizes to the particle **201** size (diameter). Thus, in embodiments, the radial thickness of the catalyst coating (e.g., thickness T_{202}) can be greater than the width or diameter of one catalyst particle (e.g., greater than the width or diameter of one catalyst particle **203**).

In general, each of the diamond particles **201** employed at block **101** can have any suitable size or diameter. In embodiments described herein, the diamond particles **201** employed in block **101** may have an average size or diameter between about 1.0 micron to 10.0 microns, and in some embodiments about 4.0 microns to 8.0 microns. In general, each catalyst particle **203** employed in block **101** can have any suitable size or diameter, and the range of variation between sizes within a plurality of catalyst particles **203** may be between about +/−1.0 micron to about +/−5.0 microns. In certain embodiments described herein, the plurality of diamond particles **201** employed in block **101** have an average size or diameter between about 1.0 nm to 5.0 nm, and more preferably an average size or diameter between about 1.0 nm to 3.0 nm. Due to the size of the diamond particles **201** and the catalyst particles **203**, and resulting thickness T_{202} of coating **202**, the coated diamond particles **200** formed in block **101** are generally in the form of a diamond powder. Depending upon the embodiment, different ranges of particle sizes may be employed, for example, 1-8 microns, 2-8 microns 6-18 microns, and 16-36 microns. These particle sizes and the ranges of particle sizes may be used in combinations of different wt % in diamond mixes for PDC cutter synthesis fabricated according to embodiments of the present disclosure.

As previously described, a coating **202** is applied to each diamond particle **201** in block **101** via particle ALD as opposed to other techniques for coating materials such as chemical vapor deposition (CVD). In an embodiment, the coating **202** may be about 1 angstrom in thickness. As is known in the art, CVD is a coating process in which gaseous reagents are used to create a film on particles or other material. However, with CVD, there is no inherent control of the thickness of the film as its growth on the underlying particle or material is dependent on a variety of factors including, without limitation, reaction time, flux of reactants, and reaction temperature. In addition, competing gas phase reactions can produce nanoparticles that are scavenged, often resulting in granular films, and further, precursor feed rates are limited by particle mixing times. Still further, CVD is typically limited to use on particles larger than about 10 μm because van der Waals forces cause smaller particles to fluidize as aggregates, which are "glued" together by the CVD processing.

In contrast, particle ALD allows finer/smaller particles to be coated than does CVD. In addition, ALD techniques use self-limiting surface chemistry that enables control over the coating thickness and produces conformal, non-granular, pinhole-free coatings on primary particle surfaces. In particular, the ALD reaction is split into two sequential surface half reactions, which means the surface reacts with each reagent only until it is completely coated with a new atomic layer. Once this occurs, no further reactions will take place, making the reaction, and the resultant thickness are self-limiting. Consequently, coatings applied by ALD can be as thin as 1 Å. New functional groups are then in place to react with the second reagent. The steps can be repeated until the desired film thickness is achieved. In other words, in the method **100**, the block **101** can be repeated to apply the multiple layers or coatings **202** one each diamond particle **201**. In addition, ALD is independent of line-of-sight, no competing gas phase reaction occurs, and nearly 100% of the precursor is used, greatly reducing waste.

Referring again to FIG. **4**, moving now to block **102**, the coated diamond particles (e.g., particles **200**) formed in block **101** via ALD are "cleaned" to remove undesirable contaminants from coating **202**. In this embodiment, the coated diamond particles are cleaned in the block **102** to remove oxides from coating **202** as oxides may not be desirable in a coating especially if the component comprising that coating is used for high temperature and high pressure applications. In particular, the coated diamond particles are placed in an atmosphere of pure hydrogen (i.e., 100% hydrogen) for a period of time at an elevated temperature preferably between 800° C. and 1200° C. In one embodiment, the coated diamond particles are placed in pure hydrogen at about 950° C. for about 5 minutes, and then the temperature is increased to about 1000° C. and maintained at 1000° C. for about 3 hours. At the end of that process, the temperature is slowly lowered (as opposed to a quench). One or more cycles of cleaning via block **102** can be performed to sufficiently remove contaminants from coating **202**.

After cleaning the coated diamond particles in block **102**, a cutter element **40** is formed in block **104**. In general, the cutter element **40** is formed by simultaneously sintering the cleaned, coated diamond particles to each other and to WC substrate **40***b*, thereby forming table **40***a* and bonding table **40***a* to substrate **40***b* to form the cutter element **40**. More specifically, the cleaned, coated diamond particles, in the form of a diamond powder, are placed at the bottom of a first mold or can, and substrate **40***b* is then placed on top of the cleaned, coated diamond particles in the first mold. Next, a second mold or can is placed on top of the substrate **40***b*, and a seal is formed between the first and second cans.

This entire assembly is then subjected to high pressure and temperature conditions to form a PCD cutter element **40** via sintering of the cleaned, coated diamond particles to form table **40***a* simultaneous with sintering of the cleaned, coated diamond particles with substrate **40***b*. During the sintering process in block **104**, the catalyst particles **203** in the coatings **202** promote intergrowth therein, to form a solid PCD diamond table **40***a*. The high pressure and temperature conditions also facilitate bonding between the newly formed PCD table **40***a* and the substrate **40***b*, thereby resulting in a fully formed PCD cutter element **40**. Since each individual diamond particle **201** includes a catalyst coating **202**, the catalyst particles **203** are inherently uniformly distributed throughout the diamond powder during block **104**. Such uniform distribution of catalyst particles **203** enhances the uniformity and homogeneity of the bonding and crystallization within the table **40***a*, thereby offering the potential for a more robust, durable diamond table **40***a* as compared to a conventional diamond table formed by simply mixing catalyst powder with diamond powder prior to sintering.

Although the diamond powder used to form diamond table **40***a* in block **104** is described as comprising only cleaned, coated diamond particles from block **102**, in this embodiment, it should be appreciated that the cleaned, coated diamond particles from block **102** can be mixed with a plurality of uncoated diamond particles and/or with a plurality of cleaned, coated diamond particles having a different coating **202** prior to forming cutter element **40** in block **104**. In other words, the diamond table **40***a* formed in block **104** can be formed from a diamond powder comprising cleaned, coated diamond particles from block **102** and uncoated diamond particles, diamond powder comprising cleaned, coated diamond particles from block **102** cleaned, coated diamond particles having a different coating **202**, or combinations thereof. In such embodiments, selected sizes for the diamond particles mixed together may be preferred; this may be based on a percentage of particles with a particular measurement, or may be a ratio of particle sizes. For example, in one embodiment, a first plurality of cleaned, coated diamond particles having an average size or diameter of about 1.0 to 3.0 microns are mixed with a second plurality of cleaned, coated diamond particles having an average size or diameter of about 4.0 to 8.0 microns. In some embodiments, the weight of the first and the second pluralities of diamond coated particles may be equal, and in alternate embodiments the weight of one plurality may be greater than the other. For most applications, the cleaned, coated diamond powders that are mixed together to form the diamond table preferably have average sizes or diameters that are within 1.0 to 2.0 microns of each other. In one embodiment where cleaned, coated diamond particles from block **102** are mixed with uncoated diamond particles prior to forming the cutter element **40** in block **104**, the mixture used to form the table **40***a* in block **104** preferably comprises about 10 wt. % cleaned, coated diamond particles from block **102** and about 90 wt. % uncoated diamond particles that have an average size or diameter ranging from about 20.0 to 40.0 microns.

Moving now to block **110**, the diamond table **40***a* is leached (e.g., acid leached) to remove at least some of the catalyst particles **203** from the diamond table **40***a*. Since each individual diamond particle **201** includes a relatively thin catalyst coating **202**, the volume and concentration of the catalyst particles **203** in the diamond table **40***a* formed in block **104** are generally less as compared to a conventional diamond table formed by mixing diamond powder and catalyst powder. Consequently, in embodiments described herein, the need for leaching the diamond table **40***a* in block **110** is generally less than for a similarly sized conventional diamond table. Accordingly, in some embodiments, the quantity and concentration of the catalyst particles **203** in diamond table **40***a* is sufficiently low such that the length of time for leaching can be decreased and/or leaching can be completely eliminated (i.e., block **110** can be eliminated). This offers the potential to decrease the overall time to manufacture cutter element **40** as compared to a conventional PCD cutter element, as well as reduce the likelihood of inadvertently damaging the underlying WC substrate **40***b*.

In one example, the coated diamond particles **1302** may be referred to as the inner coated polycrystalline diamond particles, and the uncoated nanocrystalline diamond particles may be referred to as the outer polycrystalline diamond particles. The "outer" term refers to the presence of these particles which may be on the outermost surface of the coated diamond particles **1302**. The outer polycrystalline diamond particles are generally smaller, nanocrystalline diamond particles, and the inner coated polycrystalline diamond particle is a generally larger micron polycrystalline diamond particle. The outer nanocrystalline diamond particles may also be referred to herein as "nanoparticles" or "nano-satellited diamond particles." When sintered under high pressure and high temperature (HPHT) conditions, such outer nanocrystalline diamond coated diamond particles exhibit enhanced bonding between diamond grains within the table **40***a*, by generating a greater number of grain boundaries and diamond-to-diamond bonds per unit of surface area as compared to some conventional PCD materials and cutter elements. Consequently, tables **40***a* offers the potential for increased density and thermal stability.

To further illustrate various illustrative embodiments of the present invention, the following examples are provided.

Example I

A plurality of diamond particles were analyzed to assess thermal stability in an ALD environment. The diamond particles had an average diameter of about 500 nm. First, the specific surface area of the diamond particles was calculated by the Brunauer-Emmett-Teller (BET) method from the N_2 adsorption isotherms obtained at −196° C. Before starting the adsorption measurements, each sample was outgassed by heating under vacuum at 200° C. for 5 hours. The surface area of the diamond particles was calculated to be 8.6 m^2/g.

The thermal stability of the diamond particles in the ALD environment was assessed via thermos gravimetric analysis (TGA). FIGS. **6** and **7** are graphs illustrating the thermos gravimetric analysis (TGA) analysis of the diamond particles. As shown in FIGS. **6** and **7**, the 500 nm diamond particles began to decompose at about 600° C. in air, and the decomposition was faster in the atmosphere of oxygen as compared to the nitrogen. As shown in FIG. **7**, the 500 nm diamond particles were stable in oxygen at temperature less than 500° C. for up to 3 hr. Accordingly, the results of TGA indicated it would be acceptable to use oxygen as precursor when the reaction temperature is lower than 500° C.

Example II

Diamond particles were coated with CoO via ALD and then analyzed. The ALD process was carried out in a fluidized bed reactor with bis(cyclopentadienyl)cobalt(II) and oxygen used as precursors to apply the CoO coating to the diamond particles. The ALD reaction was conducted at a temperature as high as 450° C. In a typical ALD run, 2 grams of diamond particles were loaded into the reactor. Various coating cycles were carried out using different dimensions of diamond particle size and density, concentrations of diamond volume, diamond weight, coating volume, and coating weight and weight percent. The ALD coated samples were characterized by X-ray photoelectron spectroscopy (XPS) for the composition of cobalt, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was employed to determine cobalt content, and TEM was used for the morphology of the particles after coating.

FIG. **8** is an FTIR graph illustrating the functional groups present on the diamond particles, which is necessary to initiate CoO ALD coating process. As shown in FIG. **8**, the functional groups on the 500 nm diamond particle surface included C═C, C—C, C—H, C—O, CH2, and CH3.

Example III

Diamond particles were coated with Co and CoO via ALD and then analyzed. Both Co or CoO ALD coatings were employed by adjusting the precursor dose time for each type of coating. Bis(cyclopentadienyl)cobalt(II) and hydrogen were used as precursors for the Co coating. Bis(cyclopentadienyl)cobalt(II) and oxygen were used as precursors for the CoO coating. The reaction temperature range was 400-450° C. for both the Co and CoO coatings.

FIG. **9** is a graph of an ICP analysis of the ALD fabricated Co coated diamond particles. The ICP results in FIG. **9** indicated that the content of Co on 500 nm diamond particles increased with the increase of the number of Co ALD coating cycles using bis(cyclopentadienyl)cobalt(II) and hydrogen as precursors. FIG. **10** is a graph of an ICP analysis of the ALD fabricated CoO coated diamond particles. The ICP results in FIG. **10** indicated that the content of Co on 500 nm diamond particles increased with the increase of the number of CoO ALD coating cycles using bis(cyclopentadienyl)cobalt(II) and oxygen as precursors.

FIGS. **9** and **10** indicated that both Co and CoO coatings can be deposited directly on the outer surface of the diamond particles without an intermediate seed layer. For Co ALD, the loading of cobalt was about 1.5 wt. % after 200 cycles of ALD coating. For CoO ALD, the growth rate is much higher; the loading of Co was about 6 wt. % after 200 cycles of ALD coating.

FIG. **11** is a TEM image of the Co nanoparticles deposited on a diamond particle via ALD. FIG. **11** illustrates Co nanoparticles with a uniform particle size distribution were deposited on 500 nm diamond particle surfaces after 200 cycles of Co ALD. In this embodiment, the particle size of Co nanoparticles is about 2 nm.

FIG. **12** is a graph using the Brunauer-Emmett-Teller (BET) method of the surface area of the 500 nm diamond particles coated with various cycles of Co or CoO ALD. The surface area of the particles with various cycles of Co or

CoO ALD coating was estimated by the BET method from the N_2 adsorption isotherms obtained at −196° C. As shown in FIG. **11**, the surface area of the CoO ALD coated diamond particles decreased slightly with the increase in the number of ALD coating cycles. In an embodiment, this may be due to the presence of larger coated diamond particles due to the ALD film coating and slight particle aggregation, and the CoO ALD film has a higher density than the diamond particle substrate. All these factors will contribute to a lower surface area. For the Co ALD coated diamond particles, however, the surface area increased with the increase in the number of Co ALD coating cycles. The above-mentioned similar effects existed during the Co ALD coating process, and they could result in a lower surface area of the coated particles. However, the main difference between Co ALD and CoO ALD is that Co nanoparticles were formed in the Co ALD process, instead of a continuous layer of film. From the TEM imaging, it was observed that the Co was loaded as −2 nm particles, which contributed to a higher surface area of the samples. In an alternate embodiment, for NiO ALD, the NiO coating was deposited on a plurality of 1-3 micron diamond particles. Up to about 2 wt. % Ni on 1-3 microns diamond particles can be achieved. As used herein, the weight percent of a coating may be defined as the percentage of the coating weight as compared to the total weight of the particle, this may also be referred to as an average weight percent, measured across the plurality of coated diamond particles.

FIGS. **13**A-**13**C illustrate abrasion results for PCD cutter elements fabricated according to embodiments of the present disclosure. Samples of various compositions, as shown in Table 1, underwent abrasion testing under both wet and dry conditions. FIG. **13**A illustrates the abrasion results for bi-modal samples, FIG. **13**B illustrates abrasion results for uni-modal samples, and FIG. **13**C illustrates abrasion results for bi-modal samples with a HCl leach, the compositions are as noted below. A bi-modal sample comprises 10% wt. % as indicated below, "UC" indicates uncoated diamond particles, NiALD is Nickel Oxide ALD in a hydrogen-reduced process, and the "BM" samples are those that were processed without any ALD coated diamond feedstock.

TABLE 1

Sample	Type	Composition	Process	Dry	Wet
10% ALD	BiModal	10% 4-8 u NiALD + 90% 22-36 u UC	Pressed @STN + HCl Leach (HL)	1.75	0.25
BM- 0% ALD	BiModal	10% 4-8 u UC + 90% 22-36 u UC	Pressed @STN + HCl Leach (HL)	0.60	0.27
100% ALD	UniModal	100% 4-8 u NiALD	Pressed @ HMR special leaching	0.75	2.27
			Pressed @ HMR + HCl Leach (HL)	0.32	2.03
BM- 0% ALD	UniModal	100% 4-8 u UC	Pressed @ HMR + HCl Leach (HL)	0.48	1.20
10% ALD	BiModal	10% 4-8 u NiALD + 90% 22-36 u UC	Pressed @ HMR + HCl Leach (HL)	1.61	0.40
BM- 0% ALD	BiModal	10% 4-8 u UC + 90% 22-36 u UC	Pressed @ HMR + HCl Leach (HL)	0.91	0.43

In the manner described, an angstrom-thick layer or coating of in-situ catalyst is applied to submicron or nanocrystalline diamond particles via atomic layer deposition (ALD). The coated diamond particles are then cleaned and used to form a diamond table for a cutter element. Although the cleaned, coated diamond particles are described as being used for forming diamond tables for cutter elements used in PDC drill bits, it should be appreciated that embodiments of

cleaned, coated diamond particles described herein can be sintered or otherwise used to form other devices or products (e.g., other types of downhole tools, drill bits, etc.), particularly devices and products that experience high-temperature and/or high-pressure environments.

While preferred embodiments have been shown and described, modifications thereof can be made by one skilled in the art without departing from the scope or teachings herein. The embodiments described herein are exemplary only and are not limiting. Many variations and modifications of the systems, apparatus, and processes described herein are possible and are within the scope of the invention. For example, the relative dimensions of various parts, the materials from which the various parts are made, and other parameters can be varied. Accordingly, the scope of protection is not limited to the embodiments described herein, but is only limited by the claims that follow, the scope of which shall include all equivalents of the subject matter of the claims. Unless expressly stated otherwise, the steps in a method claim may be performed in any order. The recitation of identifiers such as (a), (b), (c) or (1), (2), (3) before steps in a method claim are not intended to and do not specify a particular order to the steps, but rather are used to simplify subsequent reference to such steps.

The invention claimed is:

1. A method for fabricating a PCD cutter element, comprising:

(a) coating, by atomic layer deposition (ALD), a plurality of diamond particles by directly depositing the coating on an outer surface of each diamond particle of the plurality of diamond particles to form a plurality of coated diamond particles;

(b) removing oxides from the plurality of coated diamond particles after (a);

(c) forming a PCD cutter element using the coated diamond particles after (b) by sintering the coated diamond particles together to form a diamond table and leaching the diamond table after sintering the coated diamond particles to remove one or more metals from the diamond table.

2. The method of claim **1**, wherein (c) comprises leaching the diamond table to remove cobalt from the diamond table.

3. The method of claim **1**, wherein the coating deposited in (a) comprises nickel (Ni) or nickel oxide (NiO).

4. The method of claim **1**, wherein the plurality of diamond particles have an average size less than about 500 microns.

5. The method of claim **1**, wherein (b) comprises exposing the coated diamond particles to pure hydrogen at an elevated temperature.

6. The method of claim **5**, wherein the elevated temperature is between about 800° C. and about 1200° C.

7. The method of claim **6**, wherein the elevated temperature is about 1000° C.

8. The method of claim **1**, wherein the ALD is performed using a precursor comprising bis(cyclopentadienyl)cobalt (II) and hydrogen.

9. The method of claim **1**, wherein the ALD is performed using a precursor comprising bis(cyclopentadienyl)cobalt (II) and oxygen.

10. The method of claim **1**, wherein the ALD is performed using a precursor comprising bis(cyclopentadienyl)nickel (II) and hydrogen.

11. The method of claim **1**, wherein the ALD is performed using a precursor comprising bis(cyclopentadienyl)nickel (II) and oxygen.

12. The method of claim **1**, wherein the coating comprises a plurality of particles, wherein the particles of the coating have an average diameter of about 2.0 nm.

13. A method of fabricating a PCD cutter element, comprising:

(a) providing a plurality of diamond particles;

(b) directly depositing a nickel oxide coating on an outer surface of each diamond particle of the plurality of diamond particles by atomic layer deposition (ALD), wherein the nickel oxide coating directly contacts the outer surface of the corresponding diamond particle;

(c) removing oxides from the nickel oxide coating after (b) by exposing the coated diamond particles to pure hydrogen at an elevated temperature between about 800 and about 1200° C. to convert the nickel oxide coating on each diamond particle to a nickel coating on each diamond particle;

(d) sintering the coated diamond particles after (c) to form a diamond table; and

(e) mounting the diamond table to a tungsten-carbide substrate to form the PCD cutter element.

14. The method of claim **13**, further comprising (f) leaching the diamond table after (e) to remove one or more metals.

15. The method of claim **14**, wherein the plurality of diamond particles have an average diameter from about 1 micron to about 3 microns.

16. The method of claim **14**, wherein the plurality of diamond particles have an average diameter from about 4 microns to about 8 microns.

17. The method of claim **14**, wherein the elevated temperature is about 1000° C.

18. The method of claim **14**, wherein (f) comprises leaching the diamond table after (e) to remove one or more metals that infiltrate into the diamond table from the tungsten carbide substrate.

19. The method of claim **13**, wherein (c) further comprises:

(c1) exposing the exposing the coated diamond particles to pure hydrogen at an elevated temperature between about 800 and about 1200° C.;

(c2) lowering the temperature after (c1); and then

(c3) repeating steps (c1) and (c2) at least once.

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