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(54) **SELECTIVE HYDRAULIC FRACTURING TOOL AND METHOD THEREOF**

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See application file for complete search history.

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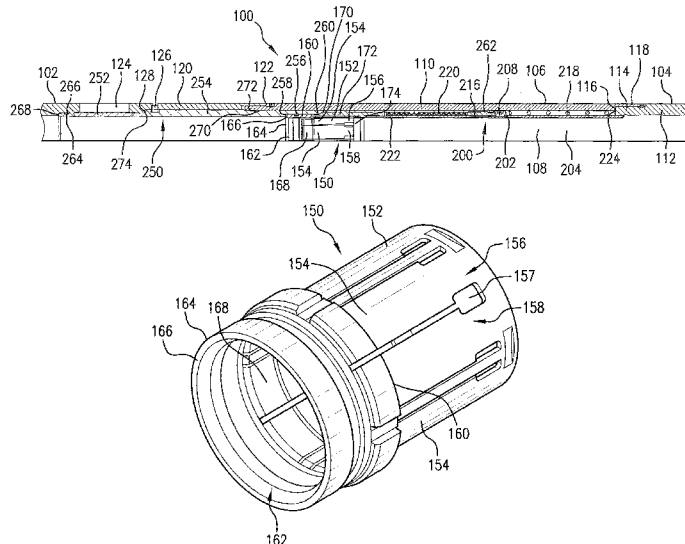
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(57) **ABSTRACT**

A selective downhole tool including a tubular having a longitudinal bore enabling passage of fluids there through. Having a valve opening in a wall of the tubular. An expandable ball seat selectively movable between a first size sized to trap a ball to block flow through the tubular. A larger second size sized to release the ball through the tubular. A valve cover longitudinally movable within the tubular, the valve cover including a dissolvable insert. Also included is a method of operating a downhole tool.

19 Claims, 10 Drawing Sheets



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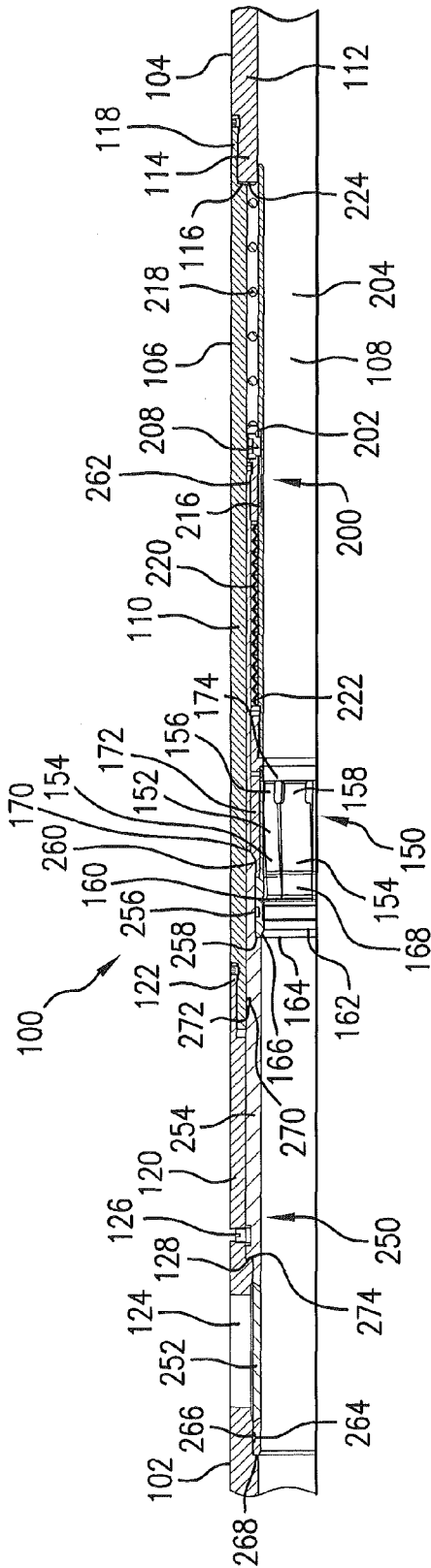


FIG. 1

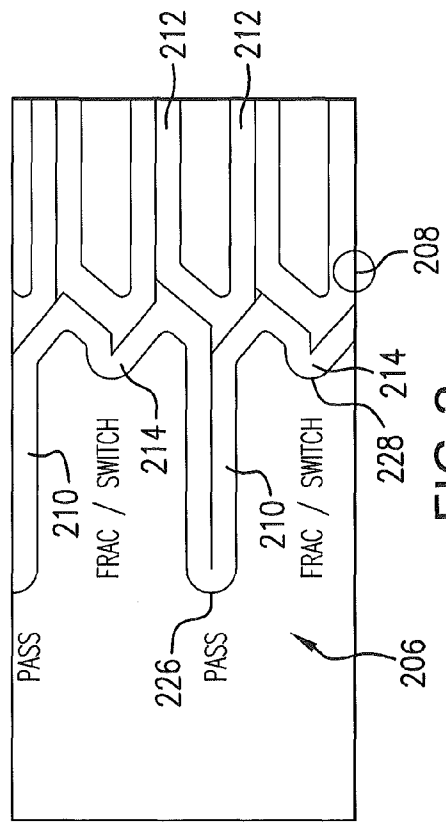


FIG. 3

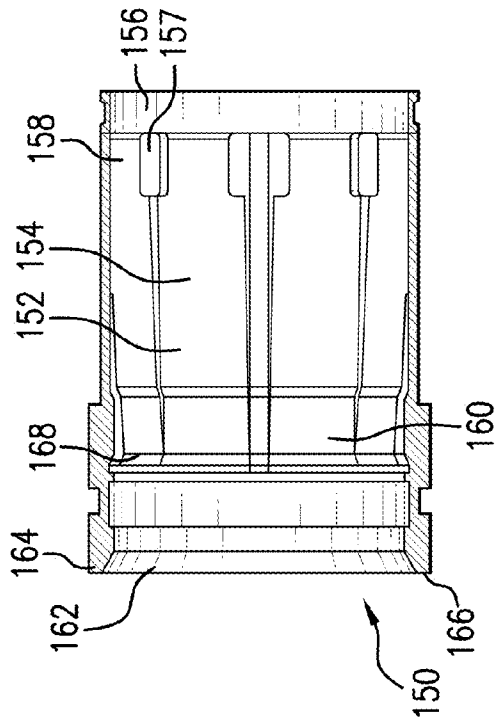


FIG. 2B

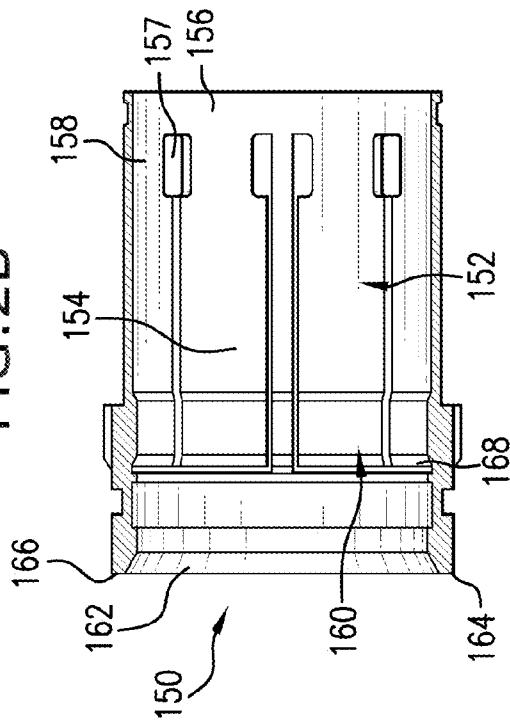


FIG. 2C

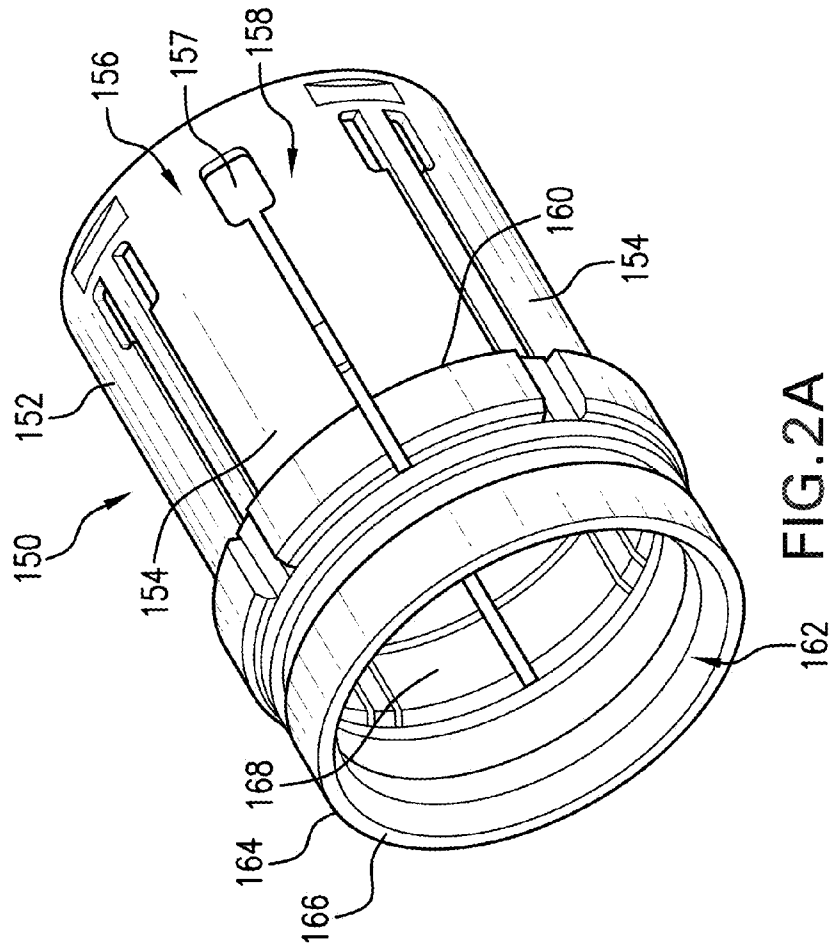


FIG. 2A

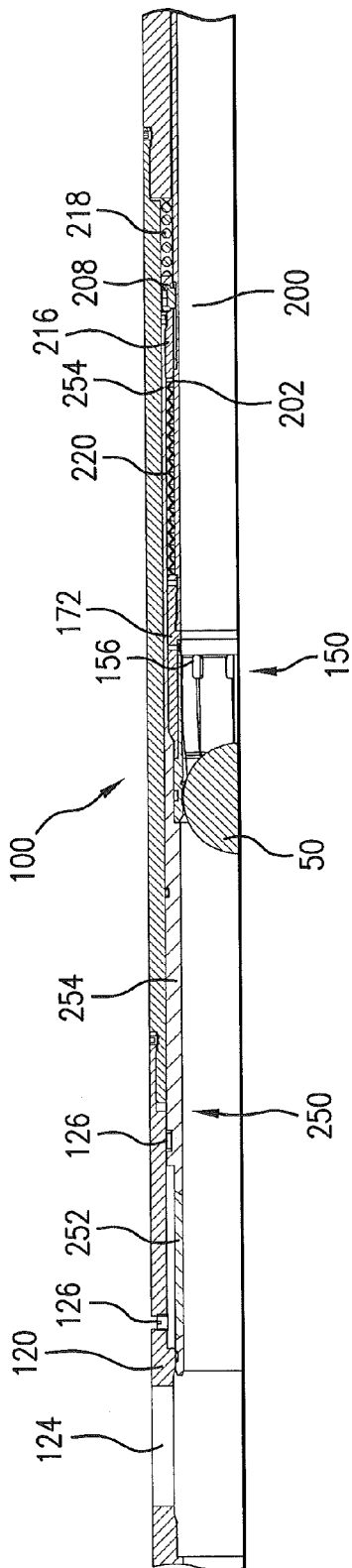


FIG. 4

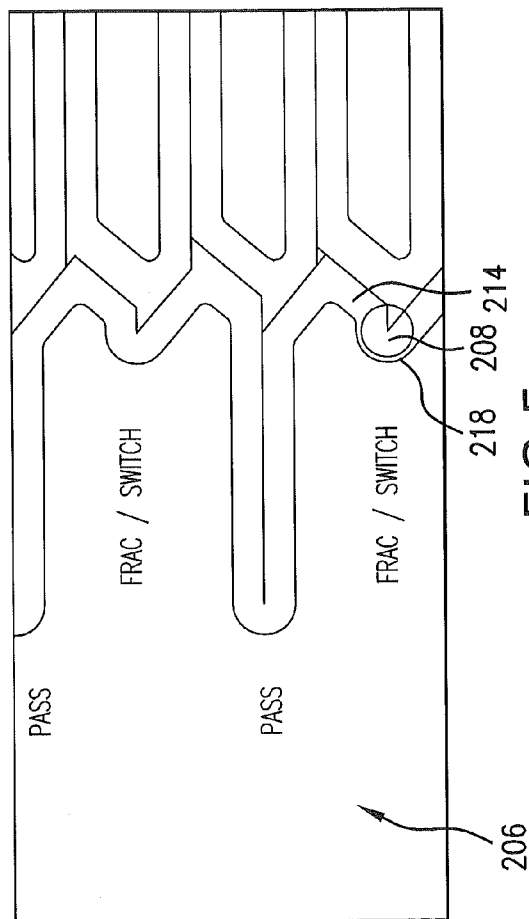


FIG. 5

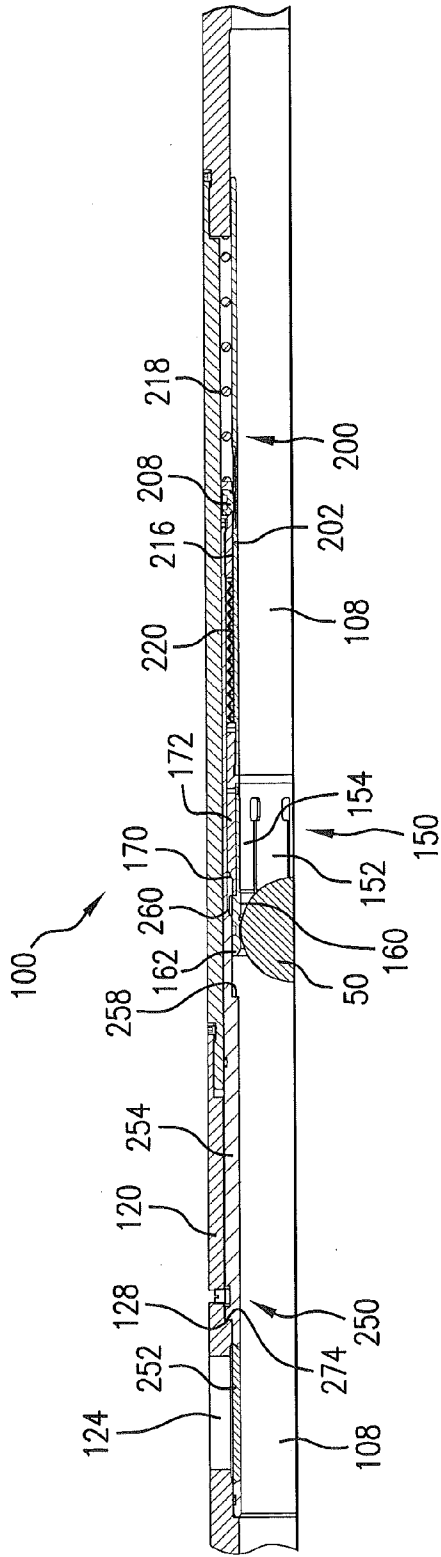


FIG. 6

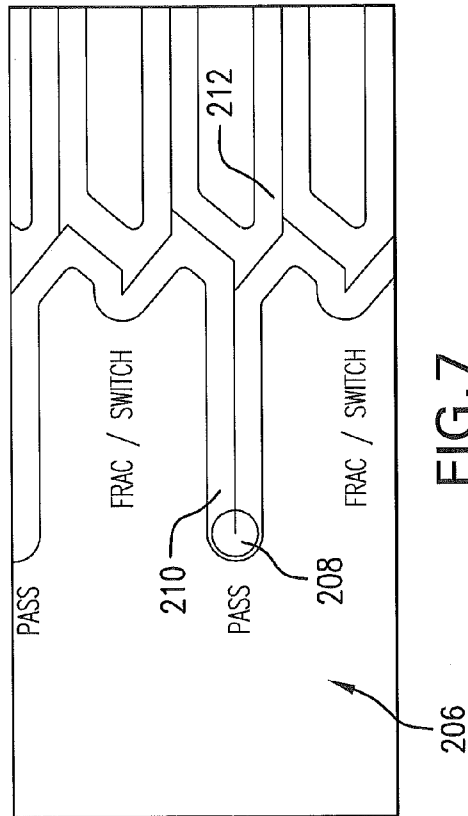
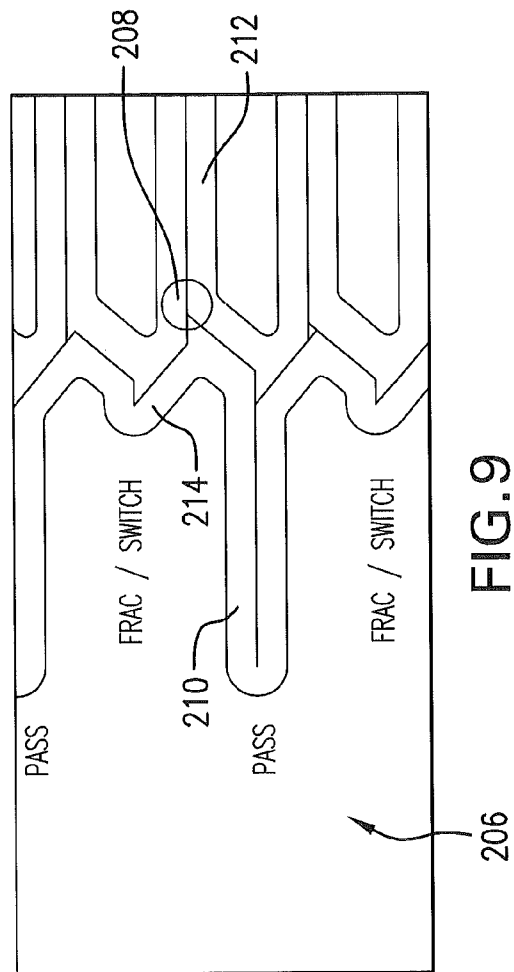
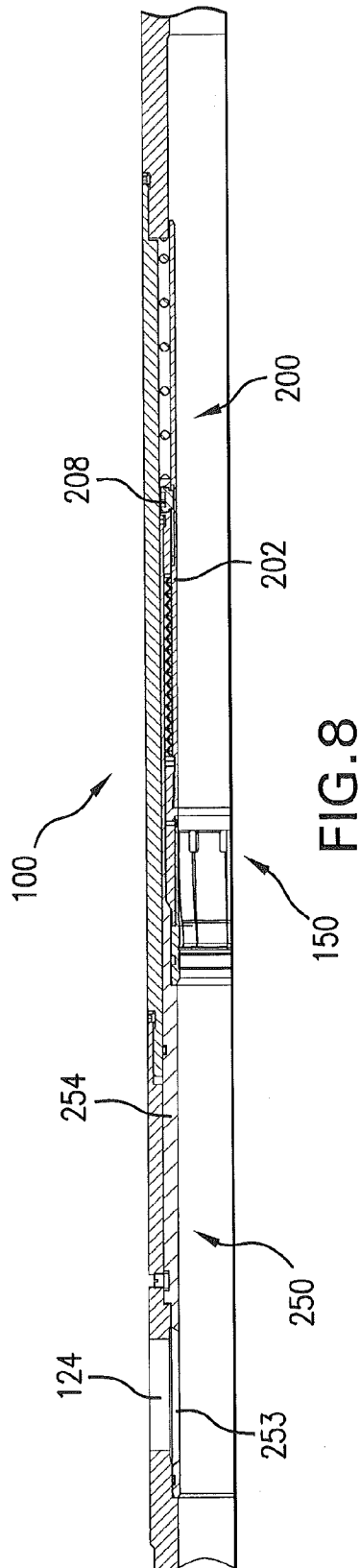


FIG. 7



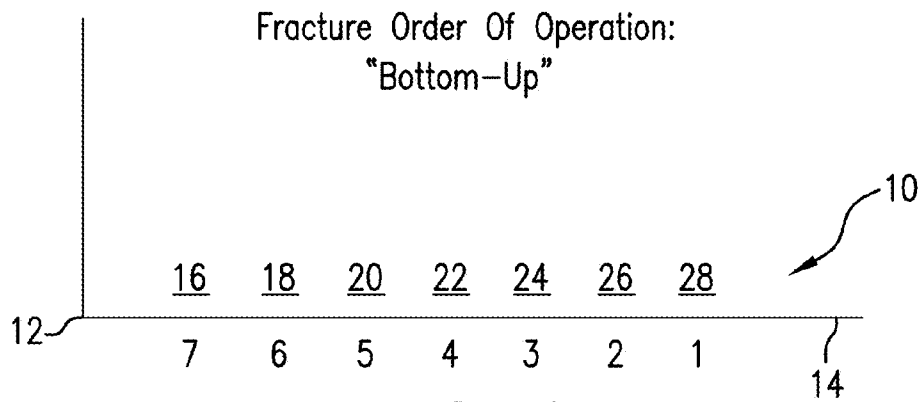


FIG. 10

PRIOR ART

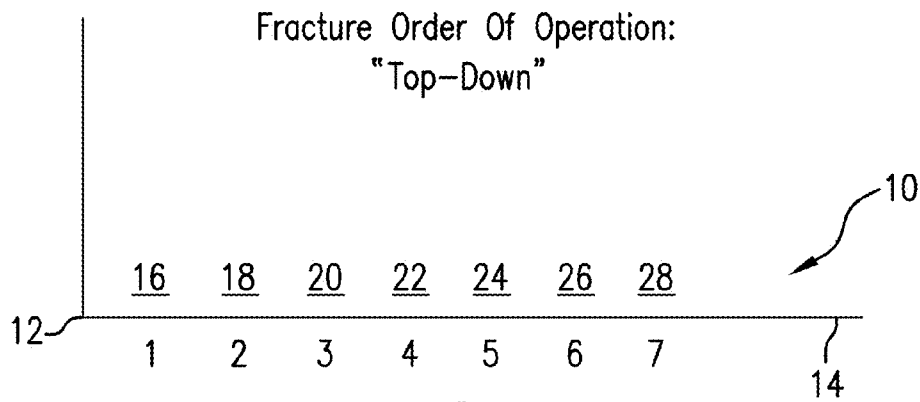


FIG. 11

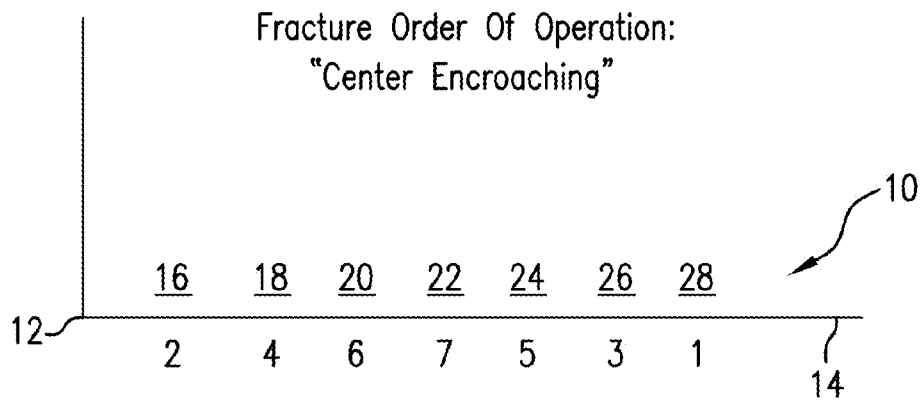


FIG. 12

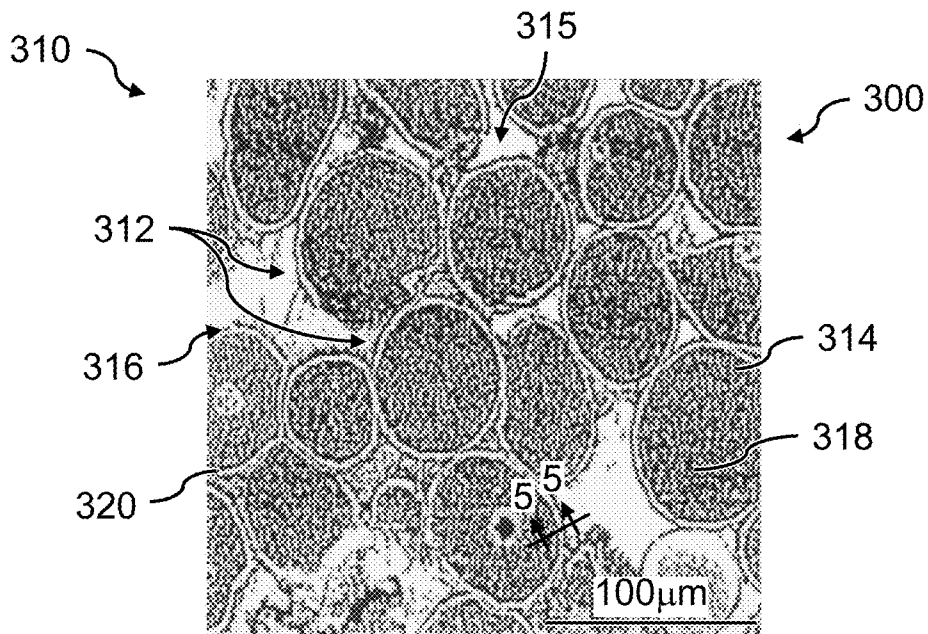


FIG. 13

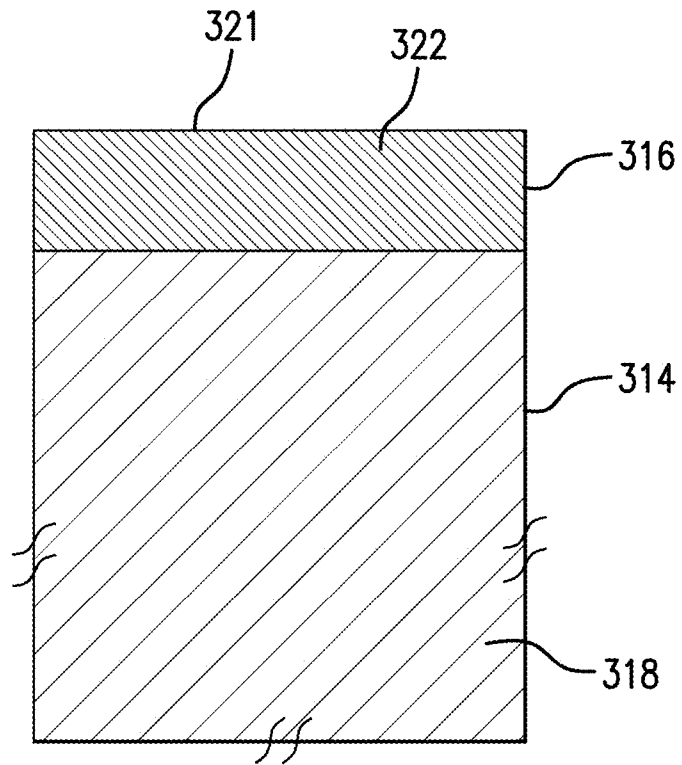


FIG. 14

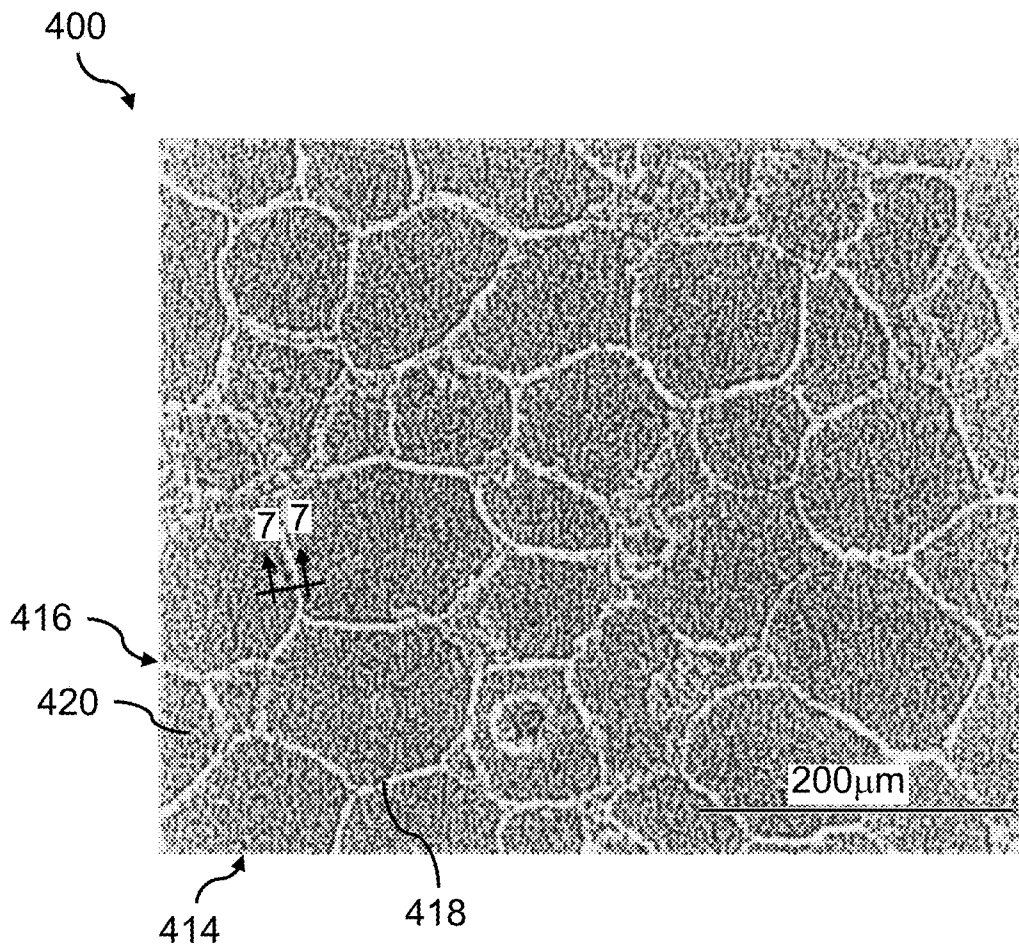


FIG. 15

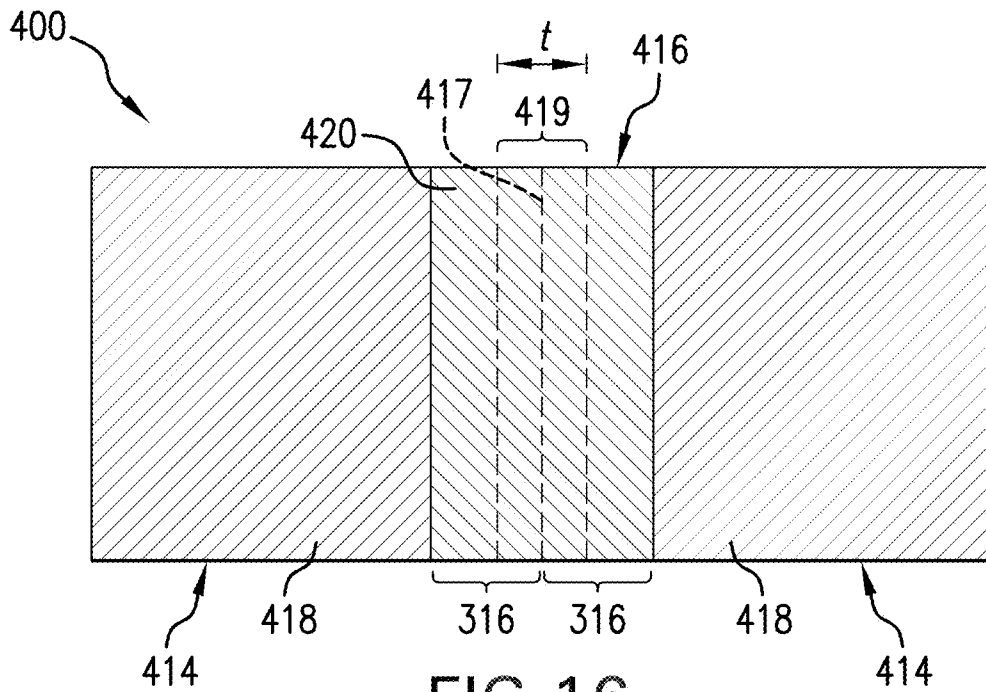


FIG. 16

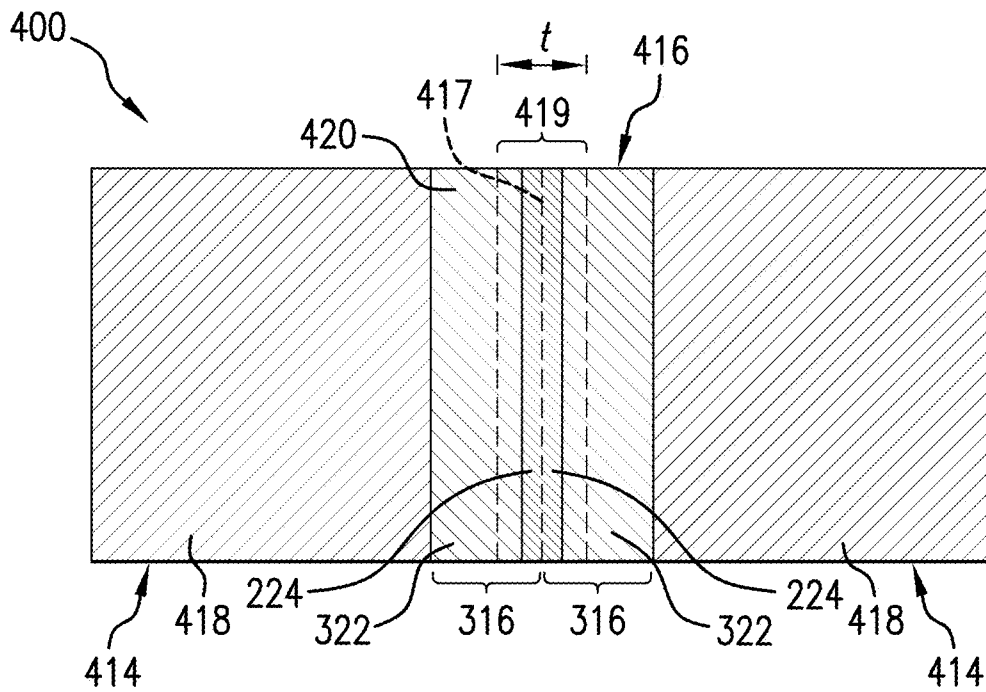


FIG. 17

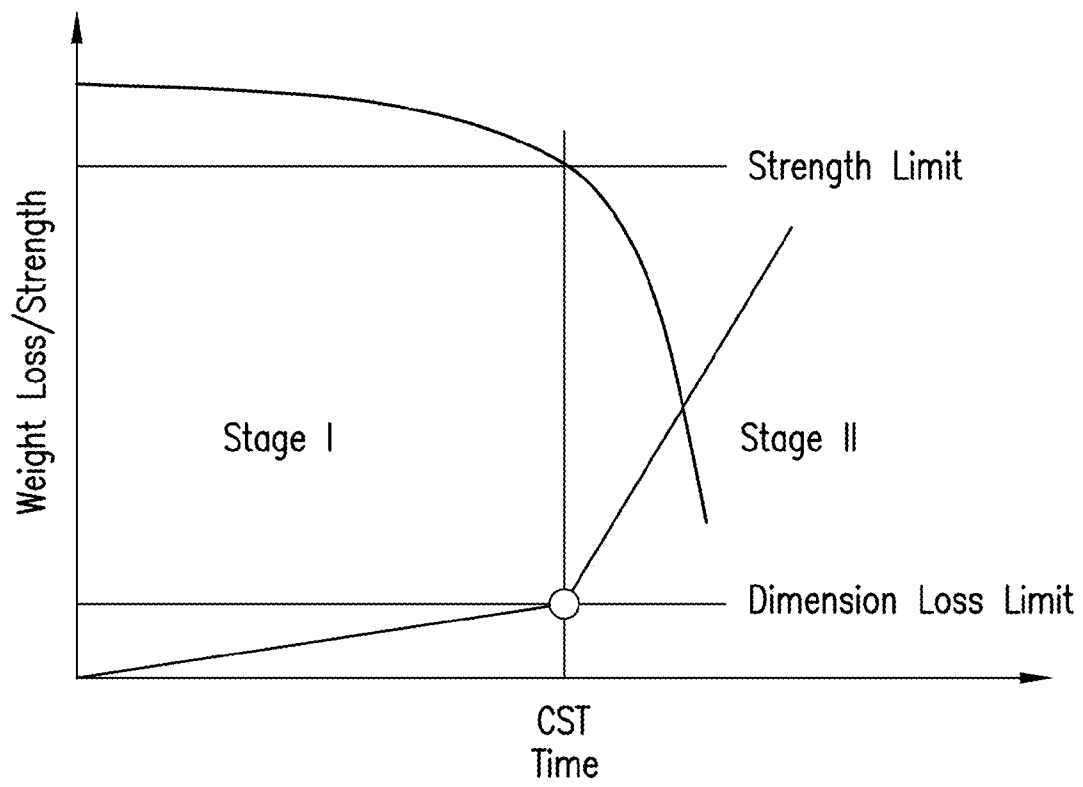


FIG. 18

SELECTIVE HYDRAULIC FRACTURING TOOL AND METHOD THEREOF

BACKGROUND

In the drilling and completion industry, the formation of boreholes for the purpose of production or injection of fluids is common. The boreholes are used for exploration or extraction of natural resources such as hydrocarbons, oil, gas, water, and CO₂ sequestration. For enhancing production and increasing extraction rates from a subterranean borehole, the formation walls of the borehole may be fractured using a pressurized slurry, proppant containing fracturing fluid, or other treating fluids. The fractures in the formation wall may be held open with the particulates once the injection of fracturing fluids has ceased.

A conventional fracturing system passes pressurized fracturing fluid through a tubular string that extends downhole through the borehole that traverses the zones to be fractured. The string may include valves that are opened to allow for the fracturing fluid to be directed towards a targeted zone. To remotely open the valves from the surface, a ball is dropped into the string and lands on a ball seat associated with a particular valve to block fluid flow through the string and consequently build up pressure uphole of the ball which forces a sleeve downhole thus opening a port in the wall of the string. When multiple zones are involved, the ball seats are of varying sizes with a downhole most seat being the smallest and an uphole most seat being the largest, such that balls of increasing diameter are sequentially dropped into the string to sequentially open the valves from the downhole end to an uphole end. Thus, the zones of the borehole are fractured in a “bottom-up” approach by starting with fracturing a downhole-most zone and working upwards towards an uphole-most zone.

To avoid the inevitable complications associated with employing differently sized ball seats, the smallest of which may overly restrict the flow through the string, and correspondingly different sized balls, the use of deformable balls and ball seats has been proposed, however the rate at which the balls are forced through the ball seats introduces additional complexities including dealing with different rates of deformation of the selected material since it may not function as desired in downhole environments. Also, despite providing certain advantages over using differently sized balls, the order of fracturing operations is still limited to the “bottom-up” approach.

BRIEF DESCRIPTION

A selective downhole tool includes a tubular having a longitudinal bore enabling passage of fluids there through and having a valve opening in a wall of the tubular; an expandable ball seat selectively movable between a first size sized to trap a ball to block flow through the tubular and a larger second size sized to release the ball through the tubular; and a valve cover longitudinally movable within the tubular, the valve cover including a dissolvable insert.

A method of operating a downhole tool, the method includes running the downhole tool in a bore hole, the tool including a tubular having a valve opening covered by a valve cover; moving the valve cover longitudinally to expose the valve opening; recovering the valve opening with the valve cover subsequent an operation through the valve opening; and dissolving a portion of the valve cover to re-expose the valve opening.

BRIEF DESCRIPTION OF THE DRAWINGS

The following descriptions should not be considered limiting in any way. With reference to the accompanying drawings, like elements are numbered alike:

FIG. 1 depicts a cross-sectional view of an exemplary embodiment of a selective hydraulic fracturing tool in a run-in position;

FIGS. 2A-2C depict perspective and cross-sectional views of an exemplary embodiment of a ball seat for use within the selective hydraulic fracturing tool of FIG. 1;

FIG. 3 depicts a schematic view of an exemplary embodiment of a portion of an indexing path and indexing pin for the position of the selective hydraulic fracturing tool of FIG. 1;

FIG. 4 depicts a cross-sectional view of the selective hydraulic fracturing tool of FIG. 1 with a ball dropped and pressure built therein;

FIG. 5 depicts a schematic view of the portion of the indexing path and indexing pin for the position of the selective hydraulic fracturing tool of FIG. 4;

FIG. 6 depicts a cross-sectional view of the selective hydraulic fracturing tool of FIG. 1 with a ball seat expanded;

FIG. 7 depicts a schematic view of the portion of the indexing path and indexing pin for the position of the selective hydraulic fracturing tool of FIG. 6;

FIG. 8 depicts a cross-sectional view of the selective hydraulic fracturing tool of FIG. 1 with the ball seat retracted;

FIG. 9 depicts a schematic view of the portion of the indexing path and indexing pin for the position of the selective hydraulic fracturing tool of FIG. 8;

FIG. 10 depicts a schematic view of a fracture order of operation according to the prior art and achievable with the selective hydraulic fracturing tool;

FIG. 11 depicts a schematic view of an exemplary embodiment of another fracture order of operation achievable with the selective hydraulic fracturing tool;

FIG. 12 depicts a schematic view of an exemplary embodiment of still another fracture order of operation achievable with the selective hydraulic fracturing tool;

FIG. 13 is a photomicrograph of a powder 310 as disclosed herein that has been embedded in a potting material and sectioned;

FIG. 14 is a schematic illustration of an exemplary embodiment of a powder particle 312 as it would appear in an exemplary section view represented by section 5-5 of FIG. 13;

FIG. 15 is a photomicrograph of an exemplary embodiment of a powder compact as disclosed herein;

FIG. 16 is a schematic of illustration of an exemplary embodiment of the powder compact of FIG. 15 made using a powder having single-layer powder particles as it would appear taken along section 7-7;

FIG. 17 is a schematic of illustration of another exemplary embodiment of the powder compact of FIG. 15 made using a powder having multilayer powder particles as it would appear taken along section 7-7; and

FIG. 18 is a schematic illustration of a change in a property of a powder compact as disclosed herein as a function of time and a change in condition of the powder compact environment.

DETAILED DESCRIPTION

A detailed description of one or more embodiments of the disclosed apparatus and method are presented herein by way of exemplification and not limitation with reference to the Figures.

A selective hydraulic fracturing tool **100**, shown in FIGS. **1**, **4**, **6**, and **8** and method is disclosed herein to fracture a borehole **10**, schematically shown in FIGS. **10-12**, in multiple configurations including “top-down”, “bottom-up”, and “center-encroaching”. While previous tools and methods have been limited to the “bottom-up” approach to fracturing a borehole as shown in FIG. **10** by starting with small diameter balls and working uphole with consecutively larger balls, the selective hydraulic fracturing tool **100** provides a monobore solution enabling a variety of fracturing orders to be accomplished therewith.

An exemplary embodiment of the selective hydraulic fracturing tool **100** is shown in FIG. **1** in a “run-in” position for running the tool **100** into a borehole. While the tool **100** is described as a fracturing tool, the tool **100** may be employed for performing alternative operations and tasks in a borehole. For the purposes of description, the tool **100** includes an uphole end **102** and a downhole end **104**, although it should be understood that the uphole end **102** may not necessarily be the uphole-most end of the tool **100** and the downhole end **104** may not necessarily be the downhole-most end of the tool **100**, as the downhole end **104** and/or the uphole end **102** may be connected to another section of the tool **100** that includes additional repetitive features as those shown in FIG. **1** for fracturing additional zones, or may be connected to tubing joints, tubing extensions, or other downhole tool portions not shown. The tool includes a tubular body **106** having a bore **108** centrally located therein and running axially there through for the flow of materials such as, but not limited to, fracturing fluids, production fluids, etc.

The tool includes an expandable ball seat **150** that allows an operator to use a single sized ball for all zones, and thus provides for a mono-bore operation that allows both improved simplicity in manufacturing the tool **100** as well as improved simplicity in operation. While a spherical ball is typically employed in such an operation, the term ball includes any shaped object which can be dropped into the bore **108** and be trapped and subsequently released from the ball seat **150**. A j-mechanism indexing apparatus **200** provides alternate positions for the ball seat **150** to be located in and allows balls to pass through the ball seat **150** without shearing/activating the tool **100**. A valve cover **250** includes dissolvable material that allows an insert **252** to close off a fractured zone and then dissolve, without intervention, to allow production from the zone after the borehole **10** is completed.

In an exemplary embodiment of the expandable ball seat **150**, a collet **152** including a plurality of fingers **154** is engaged with the indexing apparatus **200**. The ball seat **150** is shown by itself in FIGS. **2A-2C**. The fingers **154** extend longitudinally from a base **156** which may be integrally attached to a fixed end **158** of the fingers **154**. Openings **157** are provided near the fixed ends **158** of the fingers **154** to provide flexibility to the fingers **154**. The free ends **160** of the fingers **154** are radially movable relative to the base **156** from a first condition in which the free ends **160** of the fingers **154** collapse slightly inward to provide a reduced first diameter as shown in FIG. **1** and FIG. **2B** to a second condition in which the free ends **160** of the fingers **154** are biased back to an uncompressed condition to provide an increased second diameter as shown in FIG. **6** and FIG. **2C**. As can be understood, in operation of the tool **100**, a ball **50** having a diameter that becomes trapped in the ball seat **150** when the collet **152** is in the first condition, and passable through the ball seat **150** when the collet **152** is in the second condition is used in conjunction with the tool **100**. The ball seat **150** further includes a funnel shaped portion **162** for guiding the ball **50**

into the ball seat **150** and towards the free ends **160** of the fingers **154**. The funnel shaped portion **162** may be sealed relative to a valve sleeve **254** of the valve cover **250** using a seal **256** such as an O-ring. An uphole end **164** of the funnel shaped portion **162** includes a shoulder **166** that abuts with a ledge **258** of the valve sleeve **254**. Downhole of the funnel shaped portion **162**, the free ends **160** of the fingers **154** may also include inclined surfaces **168** that flare outwardly towards the uphole end **102** of the tool **100** for accepting the ball **50** within the collet **152**. When compressed together, the inclined surfaces **168** of the fingers **154** form a funnel shape that receives the ball **50** therein. The free ends **160** of the fingers **154** may be compressed together in the first condition by the ramped surface **260** of the valve sleeve **254**.

While a collet **152** has been described for forming the expandable ball seat **150**, an alternative exemplary embodiment of an expandable ball seat may include a split ring or “C” ring where movement of the indexing apparatus **200**, or a feature connected to the indexing apparatus **200**, between the body **106** and the ring will force the ring to be compressed to thereby reduce an inner diameter of the ring thus preventing a ball **50** from passing there through until movement of the indexing apparatus **200** away from the ring opens the ring to increase the aperture size of the ring allowing for passage of the ball **50**.

In an exemplary embodiment of the j-mechanism indexing apparatus **200**, the apparatus **200** includes an indexing sleeve **202** having a central longitudinal aperture **204** for fluid flow, where the aperture **204** passes through the bore **108** of the tubular body **106**. The sleeve **202** also includes an indexing path **206**, such as a groove, that is formed about a diameter of the sleeve **202**. A portion of the indexing path **206** is shown in FIGS. **3**, **5**, **7**, and **9**, although it should be understood that the path **206** may be formed non-stop about the perimeter of the sleeve **202** for an indexing pin **208** to pass. The path **206** includes first sections **210** that are extended longitudinal uphole portions, second sections **212** that are extended longitudinal downhole portions, two for every first section **210**, and third sections **214** that are slightly protruding longitudinal uphole portions interposed between the first sections **210**, where the third sections **214** connect two adjacent second sections **212**. The uphole ends **226**, **228** of the first and third sections **210**, **214** are stopping points which bias the indexing pin **208** to remain therein until purposely removed therefrom. The indexing pin **208** passes through the first, second, and third sections **210**, **212**, **214** while attached to a movable tubular section **216** trapped between the indexing sleeve **202** and an outer middle body portion **110** of the tool **100**. Multiple indexing pins **208** may be employed to distribute the load about the body **106**, in which case each indexing pin **208** would be located in either a first, second, or third section **210**, **212**, **214** at relatively the same time as the other pins **208** depending on the stage of the tool **100**. A compression spring **218** surrounds the indexing sleeve **202** and is located downhole of the indexing pin **208** to bias the indexing pin **208** relative to the indexing sleeve **202**, and a spring member **220** uphole of the indexing pin **208** and the movable tubular section **216** also surrounds the indexing sleeve **202**. The uphole end **222** of the spring member **220** abuts with the inner tubular **172** that includes the ramped surface **170**. The spring member **220** and compression spring **218** may include a series of alternately stacked spring washers. Also, although depicted differently, the compression spring **218** and the spring member **220** may be any form of spring that works in compression.

The outer middle body portion **110** of the tool **100** is connected to a downhole body portion **112** of the tool **100**. The downhole body portion **112** of the tool **100** includes an

indented section 114 that includes an uphole surface 116 that contacts a downhole end 224 of the compression spring 218. The indented section 114 of the downhole body portion 112 is attached to a downhole end 118 of the middle body portion 110, where the middle body portion is indented to match and overlap the indented section 114 of the downhole body portion 112. A downhole end 262 of the valve sleeve 254 is fixedly attached to the movable tubular section 216 and therefore surrounds the spring member 220, ball seat 150, and inner tubular 172. An uphole body portion 120 of the tool 100 surrounds an uphole portion of the valve sleeve 254. The downhole end 122 of the uphole body portion 120 is connected to the outer middle body portion 110. The uphole body portion 120 includes a valve opening 124 for allowing a fracturing operation to occur by allowing the passage of fracturing fluids there through. The valve opening 124 may also be used for the passage of production fluids or other downhole operations. The uphole body portion 120 is connected to the valve sleeve 254 by a shear pin 126.

In an exemplary embodiment of the valve cover 250, the valve cover 250 includes the valve sleeve 254 as previously described as connected via a shear pin 126 to the uphole body portion 120 and connected to the movable tubular section 216 at the downhole end 262 of the valve sleeve 254. An indent 264 for a seal 266 is provided at an uphole end 268 of the valve sleeve 254, and an indent 270 for a seal 272 is provided at a central area of the valve sleeve 254. The valve cover 250 also includes the dissolvable insert 252 made of a dissolvable material, and the insert 252 is located downhole of the seal 266 provided at the uphole end 268 of the valve sleeve 254. In a run-in position, as shown in FIG. 1, the insert 252 is aligned with the valve opening 124 to prevent access to any zones. The seals 266, 272 further insure that any fluids pumped through the bore 108 do not exit the tool 100 until intended. An outer perimeter of the dissolvable insert 252 is larger than an outer perimeter of the valve opening 124, and may have an oval or rectangular slotted shape, circular, rectangular, or oval shape, or any other shape deemed necessary for a fracturing operation or other downhole operation. The dissolvable insert 252 and/or the valve cover 250 may include engagement features to retain the dissolvable insert 252 in place within the valve cover 250 until it is dissolved. Such engagement features may include, but are not limited to, any number of lips, tongue and grooves, ledges, meshing teeth perimeters, etc. Additional features such as pins and bonding materials may also be employed. Alternatively, or additionally, the material of the dissolvable insert 252 may be directly molded within the opening of the valve cover 250 such that the dissolvable insert 252 is bonded to the valve cover 250 until the dissolvable inert 252 is dissolved.

United States Patent Publication No. 2011/0135953 (Xu, et al.) is hereby incorporated by reference in its entirety. The dissolvable material of the insert 252 may include a controlled electrolytic metallic material 300, as shown in FIG. 13, such as CEM™ material available from Baker Hughes Inc. The material 300 is used as the dissolvable inserts 252 to close off a zone after fracturing and allow other zones to be fracked without leaking into previous zones. After all of the zones have been fracked, the material 300 can be dissolved away with exposure to certain chemicals, leaving an aperture in the valve sleeve 254, and thus allow production from all of the previously fracked zones. The dissolvable inserts 252 incorporate the degradable material 300 in the form of a barrier, block, or layer at least partially blocking or obstructing the aperture in the valve sleeve 254. Material 300 is initially at least partially blocking/obstructing the aperture. The material 300 will then corrode, dissolve, degrade, or

otherwise be removed based upon exposure to a fluid in contact therewith. Generally, as used herein, the term “degradable” shall be used to mean able to corrode, dissolve, degrade, disperse, or otherwise be removed or eliminated, while “degrading” or “degrade” will likewise describe that the material is corroding, dissolving, dispersing, or otherwise being removed or eliminated. Any other form of “degrade” shall incorporate this meaning. The fluid may be a natural borehole fluid such as water, oil, etc. or may be a fluid added to the borehole for the specific purpose of degrading the material 300. Material 300 may be constructed of a number of materials that are degradable as noted above, but one embodiment in particular utilizes a high degradable magnesium based material having a selectively tailorable degradation rate and or yield strength. The material itself is discussed in detail later in this disclosure. This material exhibits exceptional strength while intact and yet easily degrades in a controlled manner and selectively short time frame. The material is degradable in water, water-based mud, downhole brines or acid, for example, at a selected rate as desired (as noted above). In addition, surface irregularities to increase a surface area of the material 300 that is exposed to the degradation fluid such as grooves, corrugations, depressions, etc. may be used. During degradation of the material 300, the aperture in the valve sleeve 254 may be opened, unblocked, created, and/or enlarged. Because the material 300 disclosed above can be tailored to completely degrade the material in about 4 to 10 minutes, the apertures can be opened, unblocked, created, and/or enlarged virtually immediately as necessary. Even if initially completely blocked by degradable material 300, the apertures in the valve sleeve 254 are still considered and referred to as apertures because the degradable material 300 of the dissolvable inserts 252 is intended to be removed.

The materials 300 in the dissolvable inserts 252 as described herein are lightweight, high-strength metallic materials. These lightweight, high-strength and selectably and controllably degradable materials 300 include fully-dense, sintered powder compacts formed from coated powder materials that include various lightweight particle cores and core materials having various single layer and multilayer nanoscale coatings. These powder compacts are made from coated metallic powders that include various electrochemically-active (e.g., having relatively higher standard oxidation potentials) lightweight, high-strength particle cores and core materials, such as electrochemically active metals, that are dispersed within a cellular nanomatrix formed from the various nanoscale metallic coating layers of metallic coating materials, and are particularly useful in borehole applications. These powder compacts provide a unique and advantageous combination of mechanical strength properties, such as compression and shear strength, low density and selectably and controllable corrosion properties, particularly rapid and controlled dissolution in various borehole fluids. For example, the particle core and coating layers of these powders may be selected to provide sintered powder compacts suitable for use as high strength engineered materials having a compressive strength and shear strength comparable to various other engineered materials, including carbon, stainless and alloy steels, but which also have a low density comparable to various polymers, elastomers, low-density porous ceramics and composite materials. As yet another example, these powders and powder compact materials may be configured to provide a selectably and controllable degradation or disposal in response to a change in an environmental condition, such as a transition from a very low dissolution rate to a very rapid dissolution rate in response to a change in a property or condition of a borehole proximate the dissolvable inserts 252

formed from the compact, including a property change in a borehole fluid that is in contact with the powder compact. The selectable and controllable degradation or disposal characteristics described also allow the dimensional stability and strength of the dissolvable inserts **252** made from these materials to be maintained until they are no longer needed, at which time a predetermined environmental condition, such as a borehole condition, including borehole fluid temperature, pressure or pH value, may be changed to promote their removal by rapid dissolution. These coated powder materials and powder compacts and engineered materials formed from them, as well as methods of making them, are described further below.

Referring to FIGS. **13-18**, further specifics regarding material **300** can be gleaned. In FIG. **13**, a metallic powder **310** includes a plurality of metallic, coated powder particles **312**. Powder particles **312** may be formed to provide a powder **310**, including free-flowing powder, that may be poured or otherwise disposed in all manner of forms or molds (not shown) having all manner of shapes and sizes and that may be used to fashion precursor powder compacts and powder compacts **400** (FIGS. **15** and **16**), as described herein, that may be used as, or for use in manufacturing, various articles of manufacture, including the dissolvable inserts **252**.

Each of the metallic, coated powder particles **312** of powder **310** includes a particle core **314** and a metallic coating layer **316** disposed on the particle core **314**. The particle core **314** includes a core material **318**. The core material **318** may include any suitable material for forming the particle core **314** that provides powder particle **312** that can be sintered to form a lightweight, high-strength powder compact **400** having selectable and controllable dissolution characteristics. Suitable core materials include electrochemically active metals having a standard oxidation potential greater than or equal to that of Zn, including as Mg, Al, Mn or Zn or a combination thereof. These electrochemically active metals are very reactive with a number of common borehole fluids, including any number of ionic fluids or highly polar fluids, such as those that contain various chlorides. Examples include fluids comprising potassium chloride (KCl), hydrochloric acid (HCl), calcium chloride (CaCl₂), calcium bromide (CaBr₂) or zinc bromide (ZnBr₂). Core material **318** may also include other metals that are less electrochemically active than Zn or non-metallic materials, or a combination thereof. Suitable non-metallic materials include ceramics, composites, glasses or carbon, or a combination thereof. Core material **318** may be selected to provide a high dissolution rate in a predetermined borehole fluid, but may also be selected to provide a relatively low dissolution rate, including zero dissolution, where dissolution of the nanomatrix material causes the particle core **314** to be rapidly undermined and liberated from the particle compact at the interface with the borehole fluid, such that the effective rate of dissolution of particle compacts made using particle cores **314** of these core materials **318** is high, even though core material **318** itself may have a low dissolution rate, including core materials **318** that may be substantially insoluble in the borehole fluid.

With regard to the electrochemically active metals as core materials **318**, including Mg, Al, Mn or Zn, these metals may be used as pure metals or in any combination with one another, including various alloy combinations of these materials, including binary, tertiary, or quaternary alloys of these materials. These combinations may also include composites of these materials. Further, in addition to combinations with one another, the Mg, Al, Mn or Zn core materials **318** may also include other constituents, including various alloying additions, to alter one or more properties of the particle cores

314, such as by improving the strength, lowering the density or altering the dissolution characteristics of the core material **318**.

Among the electrochemically active metals, Mg, either as a pure metal or an alloy or a composite material, is particularly useful, because of its low density and ability to form high-strength alloys, as well as its high degree of electrochemical activity, since it has a standard oxidation potential higher than Al, Mn or Zn. Mg alloys include all alloys that have Mg as an alloy constituent. Mg alloys that combine other electrochemically active metals, as described herein, as alloy constituents are particularly useful, including binary Mg—Zn, Mg—Al and Mg—Mn alloys, as well as tertiary Mg—Zn—Y and Mg—Al—X alloys, where X includes Zn, Mn, Si, Ca or Y, or a combination thereof. These Mg—Al—X alloys may include, by weight, up to about 85% Mg, up to about 15% Al and up to about 5% X. Particle core **314** and core material **318**, and particularly electrochemically active metals including Mg, Al, Mn or Zn, or combinations thereof, may also include a rare earth element or combination of rare earth elements. As used herein, rare earth elements include Sc, Y, La, Ce, Pr, Nd or Er, or a combination of rare earth elements. Where present, a rare earth element or combinations of rare earth elements may be present, by weight, in an amount of about 5% or less.

Particle core **314** and core material **318** have a melting temperature (T_p). As used herein, T_p includes the lowest temperature at which incipient melting or liquation or other forms of partial melting occur within core material **318**, regardless of whether core material **318** comprises a pure metal, an alloy with multiple phases having different melting temperatures or a composite of materials having different melting temperatures.

Particle cores **314** may have any suitable particle size or range of particle sizes or distribution of particle sizes. For example, the particle cores **314** may be selected to provide an average particle size that is represented by a normal or Gaussian type unimodal distribution around an average or mean, as illustrated generally in FIG. **13**. In another example, particle cores **314** may be selected or mixed to provide a multimodal distribution of particle sizes, including a plurality of average particle core sizes, such as, for example, a homogeneous bimodal distribution of average particle sizes. The selection of the distribution of particle core size may be used to determine, for example, the particle size and interparticle spacing **315** of the particles **312** of powder **310**. In an exemplary embodiment, the particle cores **314** may have a unimodal distribution and an average particle diameter of about 5 μm to about 300 μm , more particularly about 80 μm to about 120 μm , and even more particularly about 100 μm .

Particle cores **314** may have any suitable particle shape, including any regular or irregular geometric shape, or combination thereof. In an exemplary embodiment, particle cores **314** are substantially spheroidal electrochemically active metal particles. In another exemplary embodiment, particle cores **314** are substantially irregularly shaped ceramic particles. In yet another exemplary embodiment, particle cores **314** are carbon or other nanotube structures or hollow glass microspheres.

Each of the metallic, coated powder particles **312** of powder **310** also includes a metallic coating layer **316** that is disposed on particle core **314**. Metallic coating layer **316** includes a metallic coating material **320**. Metallic coating material **320** gives the powder particles **312** and powder **310** its metallic nature. Metallic coating layer **316** is a nanoscale coating layer. In an exemplary embodiment, metallic coating layer **316** may have a thickness of about 25 nm to about 2500

nm. The thickness of metallic coating layer **316** may vary over the surface of particle core **314**, but will preferably have a substantially uniform thickness over the surface of particle core **314**. Metallic coating layer **316** may include a single layer, as illustrated in FIG. **14**, or a plurality of layers as a multilayer coating structure. In a single layer coating, or in each of the layers of a multilayer coating, the metallic coating layer **316** may include a single constituent chemical element or compound, or may include a plurality of chemical elements or compounds. Where a layer includes a plurality of chemical constituents or compounds, they may have all manner of homogeneous or heterogeneous distributions, including a homogeneous or heterogeneous distribution of metallurgical phases. This may include a graded distribution where the relative amounts of the chemical constituents or compounds vary according to respective constituent profiles across the thickness of the layer. In both single layer and multilayer coatings **316**, each of the respective layers, or combinations of them, may be used to provide a predetermined property to the powder particle **312** or a sintered powder compact formed therefrom. For example, the predetermined property may include the bond strength of the metallurgical bond between the particle core **314** and the coating material **320**; the interdiffusion characteristics between the particle core **314** and metallic coating layer **316**, including any interdiffusion between the layers of a multilayer coating layer **316**; the interdiffusion characteristics between the various layers of a multilayer coating layer **316**; the interdiffusion characteristics between the metallic coating layer **316** of one powder particle and that of an adjacent powder particle **312**; the bond strength of the metallurgical bond between the metallic coating layers of adjacent sintered powder particles **312**, including the outermost layers of multilayer coating layers; and the electrochemical activity of the coating layer **316**.

Metallic coating layer **316** and coating material **320** have a melting temperature (T_C). As used herein, T_C includes the lowest temperature at which incipient melting or liquation or other forms of partial melting occur within coating material **320**, regardless of whether coating material **320** comprises a pure metal, an alloy with multiple phases each having different melting temperatures or a composite, including a composite comprising a plurality of coating material layers having different melting temperatures.

Metallic coating material **320** may include any suitable metallic coating material **320** that provides a sinterable outer surface **321** that is configured to be sintered to an adjacent powder particle **312** that also has a metallic coating layer **316** and sinterable outer surface **321**. In powders **310** that also include second or additional (coated or uncoated) particles, as described herein, the sinterable outer surface **321** of metallic coating layer **316** is also configured to be sintered to a sinterable outer surface **321** of second particles. In an exemplary embodiment, the powder particles **312** are sinterable at a predetermined sintering temperature (T_S) that is a function of the core material **318** and coating material **320**, such that sintering of powder compact **400** is accomplished entirely in the solid state and where T_S is less than T_P and T_C . Sintering in the solid state limits particle core **314**/metallic coating layer **316** interactions to solid state diffusion processes and metallurgical transport phenomena and limits growth of and provides control over the resultant interface between them. In contrast, for example, the introduction of liquid phase sintering would provide for rapid interdiffusion of the particle core **314**/metallic coating layer **316** materials and make it difficult to limit the growth of and provide control over the resultant

interface between them, and thus interfere with the formation of the desirable microstructure of particle compact **400** as described herein.

In an exemplary embodiment, core material **318** will be selected to provide a core chemical composition and the coating material **320** will be selected to provide a coating chemical composition and these chemical compositions will also be selected to differ from one another. In another exemplary embodiment, the core material **318** will be selected to provide a core chemical composition and the coating material **320** will be selected to provide a coating chemical composition and these chemical compositions will also be selected to differ from one another at their interface. Differences in the chemical compositions of coating material **320** and core material **318** may be selected to provide different dissolution rates and selectable and controllable dissolution of powder compacts **400** that incorporate them making them selectable and controllably dissolvable. This includes dissolution rates that differ in response to a changed condition in the borehole, including an indirect or direct change in a borehole fluid. In an exemplary embodiment, a powder compact **400** formed from powder **310** having chemical compositions of core material **318** and coating material **320** that make compact **400** is selectively dissolvable in a borehole fluid in response to a changed borehole condition that includes a change in temperature, change in pressure, change in flow rate, change in pH or change in chemical composition of the borehole fluid, or a combination thereof. The selectable dissolution response to the changed condition may result from actual chemical reactions or processes that promote different rates of dissolution, but also encompass changes in the dissolution response that are associated with physical reactions or processes, such as changes in borehole fluid pressure or flow rate.

As illustrated in FIGS. **13** and **14**, particle core **314** and core material **318** and metallic coating layer **316** and coating material **320** may be selected to provide powder particles **312** and a powder **310** that is configured for compaction and sintering to provide a powder compact **400**, shown in FIGS. **15-17**, that is lightweight (i.e., having a relatively low density), high-strength and is selectable and controllably removable from a borehole in response to a change in a borehole property, including being selectable and controllably dissolvable in an appropriate borehole fluid, including various borehole fluids as disclosed herein. Powder compact **400** includes a substantially-continuous, cellular nanomatrix **416** of a nanomatrix material **420** having a plurality of dispersed particles **414** dispersed throughout the cellular nanomatrix **416**. The substantially-continuous cellular nanomatrix **416** and nanomatrix material **420** formed of sintered metallic coating layers **316** is formed by the compaction and sintering of the plurality of metallic coating layers **316** of the plurality of powder particles **312**. The chemical composition of nanomatrix material **420** may be different than that of coating material **320** due to diffusion effects associated with the sintering as described herein. Powder metal compact **400** also includes a plurality of dispersed particles **414** that comprise particle core material **418**. Dispersed particle cores **414** and core material **418** correspond to and are formed from the plurality of particle cores **314** and core material **318** of the plurality of powder particles **312** as the metallic coating layers **316** are sintered together to form nanomatrix **416**. The chemical composition of core material **418** may be different than that of core material **318** due to diffusion effects associated with sintering as described herein.

As used herein, the use of the term substantially-continuous cellular nanomatrix **416** does not connote the major constituent of the powder compact, but rather refers to the minor-

ity constituent or constituents, whether by weight or by volume. This is distinguished from most matrix composite materials where the matrix comprises the majority constituent by weight or volume. The use of the term substantially-continuous, cellular nanomatrix is intended to describe the extensive, regular, continuous and interconnected nature of the distribution of nanomatrix material **420** within powder compact **400**. As used herein, "substantially-continuous" describes the extension of the nanomatrix material throughout powder compact **400** such that it extends between and envelopes substantially all of the dispersed particles **414**. Substantially-continuous is used to indicate that complete continuity and regular order of the nanomatrix around each dispersed particle **414** is not required. For example, defects in the coating layer **316** over particle core **314** on some powder particles **312** may cause bridging of the particle cores **214** during sintering of the powder compact **400**, thereby causing localized discontinuities to result within the cellular nanomatrix **416**, even though in the other portions of the powder compact the nanomatrix is substantially continuous and exhibits the structure described herein. As used herein, "cellular" is used to indicate that the nanomatrix defines a network of generally repeating, interconnected, compartments or cells of nanomatrix material **420** that encompass and also interconnect the dispersed particles **414**. As used herein, "nanomatrix" is used to describe the size or scale of the matrix, particularly the thickness of the matrix between adjacent dispersed particles **414**. The metallic coating layers that are sintered together to form the nanomatrix are themselves nanoscale thickness coating layers. Since the nanomatrix at most locations, other than the intersection of more than two dispersed particles **414**, generally comprises the interdiffusion and bonding of two coating layers **316** from adjacent powder particles **312** having nanoscale thicknesses, the matrix formed also has a nanoscale thickness (e.g., approximately two times the coating layer thickness as described herein) and is thus described as a nanomatrix. Further, the use of the term dispersed particles **414** does not connote the minor constituent of powder compact **400**, but rather refers to the majority constituent or constituents, whether by weight or by volume. The use of the term dispersed particle is intended to convey the discontinuous and discrete distribution of particle core material **418** within powder compact **400**.

Powder compact **400** may have any desired shape or size, including that of a cylindrical billet or bar that may be machined or otherwise used to form useful articles of manufacture, including the dissolvable inserts **252**. The pressing used to form precursor powder compact and sintering and pressing processes used to form powder compact **400** and deform the powder particles **312**, including particle cores **314** and coating layers **316**, to provide the full density and desired macroscopic shape and size of powder compact **400** as well as its microstructure. The microstructure of powder compact **400** includes an equiaxed configuration of dispersed particles **414** that are dispersed throughout and embedded within the substantially-continuous, cellular nanomatrix **416** of sintered coating layers. This microstructure is somewhat analogous to an equiaxed grain microstructure with a continuous grain boundary phase, except that it does not require the use of alloy constituents having thermodynamic phase equilibria properties that are capable of producing such a structure. Rather, this equiaxed dispersed particle structure and cellular nanomatrix **416** of sintered metallic coating layers **316** may be produced using constituents where thermodynamic phase equilibrium conditions would not produce an equiaxed structure. The equiaxed morphology of the dispersed particles **414** and cellular network **416** of particle layers results from sintering and

deformation of the powder particles **312** as they are compacted and interdiffuse and deform to fill the interparticle spaces **315** (FIG. 13). The sintering temperatures and pressures may be selected to ensure that the density of powder compact **400** achieves substantially full theoretical density.

In an exemplary embodiment as illustrated in FIGS. 16 and 17, dispersed particles **414** are formed from particle cores **314** dispersed in the cellular nanomatrix **416** of sintered metallic coating layers **316**, and the nanomatrix **416** includes a solid-state metallurgical bond **417** or bond layer **419**, extending between the dispersed particles **414** throughout the cellular nanomatrix **416** that is formed at a sintering temperature (T_S), where T_S is less than T_C and T_P . As indicated, solid-state metallurgical bond **417** is formed in the solid state by solid-state interdiffusion between the coating layers **316** of adjacent powder particles **312** that are compressed into touching contact during the compaction and sintering processes used to form powder compact **400**, as described herein. As such, sintered coating layers **316** of cellular nanomatrix **416** include a solid-state bond layer **419** that has a thickness (t) defined by the extent of the interdiffusion of the coating materials **320** of the coating layers **316**, which will in turn be defined by the nature of the coating layers **316**, including whether they are single or multilayer coating layers, whether they have been selected to promote or limit such interdiffusion, and other factors, as described herein, as well as the sintering and compaction conditions, including the sintering time, temperature and pressure used to form powder compact **400**.

As nanomatrix **416** is formed, including bond **417** and bond layer **419**, the chemical composition or phase distribution, or both, of metallic coating layers **316** may change. Nanomatrix **416** also has a melting temperature (T_M). As used herein, T_M includes the lowest temperature at which incipient melting or liquation or other forms of partial melting will occur within nanomatrix **416**, regardless of whether nanomatrix material **420** comprises a pure metal, an alloy with multiple phases each having different melting temperatures or a composite, including a composite comprising a plurality of layers of various coating materials having different melting temperatures, or a combination thereof, or otherwise. As dispersed particles **414** and particle core materials **418** are formed in conjunction with nanomatrix **416**, diffusion of constituents of metallic coating layers **316** into the particle cores **314** is also possible, which may result in changes in the chemical composition or phase distribution, or both, of particle cores **314**. As a result, dispersed particles **414** and particle core materials **418** may have a melting temperature (T_{DP}) that is different than T_P . As used herein, T_{DP} includes the lowest temperature at which incipient melting or liquation or other forms of partial melting will occur within dispersed particles **414**, regardless of whether particle core material **418** comprise a pure metal, an alloy with multiple phases each having different melting temperatures or a composite, or otherwise. Powder compact **400** is formed at a sintering temperature (T_S), where T_S is less than T_C , T_P , T_M and T_{DP} .

Dispersed particles **414** may comprise any of the materials described herein for particle cores **314**, even though the chemical composition of dispersed particles **414** may be different due to diffusion effects as described herein. In an exemplary embodiment, dispersed particles **414** are formed from particle cores **314** comprising materials having a standard oxidation potential greater than or equal to Zn, including Mg, Al, Zn or Mn, or a combination thereof, may include various binary, tertiary and quaternary alloys or other combinations of these constituents as disclosed herein in conjunction with particle cores **314**. Of these materials, those having

dispersed particles **414** comprising Mg and the nanomatrix **416** formed from the metallic coating materials **316** described herein are particularly useful. Dispersed particles **414** and particle core material **418** of Mg, Al, Zn or Mn, or a combination thereof, may also include a rare earth element, or a combination of rare earth elements as disclosed herein in conjunction with particle cores **314**.

In another exemplary embodiment, dispersed particles **414** are formed from particle cores **314** comprising metals that are less electrochemically active than Zn or non-metallic materials. Suitable non-metallic materials include ceramics, glasses (e.g., hollow glass microspheres) or carbon, or a combination thereof, as described herein.

Dispersed particles **414** of powder compact **400** may have any suitable particle size, including the average particle sizes described herein for particle cores **414**.

Dispersed particles **314** may have any suitable shape depending on the shape selected for particle cores **314** and powder particles **312**, as well as the method used to sinter and compact powder **310**. In an exemplary embodiment, powder particles **312** may be spheroidal or substantially spheroidal and dispersed particles **414** may include an equiaxed particle configuration as described herein.

The nature of the dispersion of dispersed particles **414** may be affected by the selection of the powder **310** or powders **310** used to make particle compact **400**. In one exemplary embodiment, a powder **310** having a unimodal distribution of powder particle **312** sizes may be selected to form powder compact **400** and will produce a substantially homogeneous unimodal dispersion of particle sizes of dispersed particles **414** within cellular nanomatrix **416**, as illustrated generally in FIG. **15**. In another exemplary embodiment, a plurality of powders **310** having a plurality of powder particles with particle cores **314** that have the same core materials **318** and different core sizes and the same coating material **320** may be selected and uniformly mixed as described herein to provide a powder **310** having a homogenous, multimodal distribution of powder particle **312** sizes, and may be used to form powder compact **400** having a homogeneous, multimodal dispersion of particle sizes of dispersed particles **414** within cellular nanomatrix **416**. Similarly, in yet another exemplary embodiment, a plurality of powders **310** having a plurality of particle cores **314** that may have the same core materials **318** and different core sizes and the same coating material **320** may be selected and distributed in a non-uniform manner to provide a non-homogenous, multimodal distribution of powder particle sizes, and may be used to form powder compact **400** having a non-homogeneous, multimodal dispersion of particle sizes of dispersed particles **414** within cellular nanomatrix **416**. The selection of the distribution of particle core size may be used to determine, for example, the particle size and interparticle spacing of the dispersed particles **414** within the cellular nanomatrix **416** of powder compacts **400** made from powder **310**.

Nanomatrix **416** is a substantially-continuous, cellular network of metallic coating layers **316** that are sintered to one another. The thickness of nanomatrix **416** will depend on the nature of the powder **310** or powders **310** used to form powder compact **400**, as well as the incorporation of any second powder, particularly the thicknesses of the coating layers associated with these particles. In an exemplary embodiment, the thickness of nanomatrix **416** is substantially uniform throughout the microstructure of powder compact **400** and comprises about two times the thickness of the coating layers **316** of powder particles **312**. In another exemplary embodi-

ment, the cellular network **416** has a substantially uniform average thickness between dispersed particles **414** of about 50 nm to about 5000 nm.

Nanomatrix **416** is formed by sintering metallic coating layers **316** of adjacent particles to one another by interdiffusion and creation of bond layer **419** as described herein. Metallic coating layers **316** may be single layer or multilayer structures, and they may be selected to promote or inhibit diffusion, or both, within the layer or between the layers of metallic coating layer **316**, or between the metallic coating layer **316** and particle core **314**, or between the metallic coating layer **316** and the metallic coating layer **316** of an adjacent powder particle, the extent of interdiffusion of metallic coating layers **316** during sintering may be limited or extensive depending on the coating thicknesses, coating material or materials selected, the sintering conditions and other factors. Given the potential complexity of the interdiffusion and interaction of the constituents, description of the resulting chemical composition of nanomatrix **416** and nanomatrix material **420** may be simply understood to be a combination of the constituents of coating layers **316** that may also include one or more constituents of dispersed particles **414**, depending on the extent of interdiffusion, if any, that occurs between the dispersed particles **414** and the nanomatrix **416**. Similarly, the chemical composition of dispersed particles **414** and particle core material **418** may be simply understood to be a combination of the constituents of particle core **314** that may also include one or more constituents of nanomatrix **416** and nanomatrix material **420**, depending on the extent of interdiffusion, if any, that occurs between the dispersed particles **414** and the nanomatrix **416**.

In an exemplary embodiment, the nanomatrix material **420** has a chemical composition and the particle core material **418** has a chemical composition that is different from that of nanomatrix material **420**, and the differences in the chemical compositions may be configured to provide a selectable and controllable dissolution rate, including a selectable transition from a very low dissolution rate to a very rapid dissolution rate, in response to a controlled change in a property or condition of the borehole proximate the compact **400**, including a property change in a borehole fluid that is in contact with the powder compact **400**, as described herein. Nanomatrix **416** may be formed from powder particles **312** having single layer and multilayer coating layers **316**. This design flexibility provides a large number of material combinations, particularly in the case of multilayer coating layers **316**, that can be utilized to tailor the cellular nanomatrix **416** and composition of nanomatrix material **420** by controlling the interaction of the coating layer constituents, both within a given layer, as well as between a coating layer **316** and the particle core **314** with which it is associated or a coating layer **316** of an adjacent powder particle **312**. Several exemplary embodiments that demonstrate this flexibility are provided below.

As illustrated in FIG. **16**, in an exemplary embodiment, powder compact **400** is formed from powder particles **312** where the coating layer **316** comprises a single layer, and the resulting nanomatrix **416** between adjacent ones of the plurality of dispersed particles **414** comprises the single metallic coating layer **316** of one powder particle **312**, a bond layer **419** and the single coating layer **316** of another one of the adjacent powder particles **312**. The thickness (t) of bond layer **419** is determined by the extent of the interdiffusion between the single metallic coating layers **316**, and may encompass the entire thickness of nanomatrix **416** or only a portion thereof. In one exemplary embodiment of powder compact **400** formed using a single layer powder **310**, powder compact **400** may include dispersed particles **414** comprising Mg, Al,

Zn or Mn, or a combination thereof, as described herein, and nanomatrix **316** may include Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni, or an oxide, carbide or nitride thereof, or a combination of any of the aforementioned materials, including combinations where the nanomatrix material **420** of cellular nanomatrix **416**, including bond layer **419**, has a chemical composition and the core material **418** of dispersed particles **414** has a chemical composition that is different than the chemical composition of nanomatrix material **416**. The difference in the chemical composition of the nanomatrix material **420** and the core material **418** may be used to provide selectable and controllable dissolution in response to a change in a property of a borehole, including a borehole fluid, as described herein. In a further exemplary embodiment of a powder compact **400** formed from a powder **310** having a single coating layer configuration, dispersed particles **414** include Mg, Al, Zn or Mn, or a combination thereof, and the cellular nanomatrix **416** includes Al or Ni, or a combination thereof.

In another exemplary embodiment, powder compact **400** is formed from powder particles **312** where the coating layer **316** comprises a multilayer coating layer **316** having a plurality of coating layers, and the resulting nanomatrix **416** between adjacent ones of the plurality of dispersed particles **414** comprises the plurality of layers (t) comprising the coating layer **316** of one particle **312**, a bond layer **419**, and the plurality of layers comprising the coating layer **316** of another one of powder particles **312**. In FIG. 16, this is illustrated with a two-layer metallic coating layer **316**, but it will be understood that the plurality of layers of multi-layer metallic coating layer **316** may include any desired number of layers. The thickness (t) of the bond layer **419** is again determined by the extent of the interdiffusion between the plurality of layers of the respective coating layers **316**, and may encompass the entire thickness of nanomatrix **416** or only a portion thereof. In this embodiment, the plurality of layers comprising each coating layer **316** may be used to control interdiffusion and formation of bond layer **419** and thickness (t).

Sintered and forged powder compacts **400** that include dispersed particles **414** comprising Mg and nanomatrix **416** comprising various nanomatrix materials as described herein have demonstrated an excellent combination of mechanical strength and low density that exemplify the lightweight, high-strength materials disclosed herein. Examples of powder compacts **400** that have pure Mg dispersed particles **414** and various nanomatrices **416** formed from powders **310** having pure Mg particle cores **314** and various single and multilayer metallic coating layers **316** that include Al, Ni, W or Al_2O_3 , or a combination thereof. These powder compacts **400** have been subjected to various mechanical and other testing, including density testing, and their dissolution and mechanical property degradation behavior has also been characterized as disclosed herein. The results indicate that these materials may be configured to provide a wide range of selectable and controllable corrosion or dissolution behavior from very low corrosion rates to extremely high corrosion rates, particularly corrosion rates that are both lower and higher than those of powder compacts that do not incorporate the cellular nanomatrix, such as a compact formed from pure Mg powder through the same compaction and sintering processes in comparison to those that include pure Mg dispersed particles in the various cellular nanomatrices described herein. These powder compacts **400** may also be configured to provide substantially enhanced properties as compared to powder compacts formed from pure Mg particles that do not include the nanoscale coatings described herein. Powder compacts **400** that include dispersed particles **414** comprising Mg and nanoma-

trix **416** comprising various nanomatrix materials **420** described herein have demonstrated room temperature compressive strengths of at least about 37 ksi, and have further demonstrated room temperature compressive strengths in excess of about 50 ksi, both dry and immersed in a solution of 3% KCl at 200° F. In contrast, powder compacts formed from pure Mg powders have a compressive strength of about 20 ksi or less. Strength of the nanomatrix powder metal compact **400** can be further improved by optimizing powder **310**, particularly the weight percentage of the nanoscale metallic coating layers **316** that are used to form cellular nanomatrix **416**. Strength of the nanomatrix powder metal compact **400** can be further improved by optimizing powder **310**, particularly the weight percentage of the nanoscale metallic coating layers **316** that are used to form cellular nanomatrix **416**. For example, varying the weight percentage (wt. %), i.e., thickness, of an alumina coating within a cellular nanomatrix **416** formed from coated powder particles **312** that include a multilayer (Al/ Al_2O_3 /Al) metallic coating layer **316** on pure Mg particle cores **314** provides an increase of 21% as compared to that of 0 wt % alumina.

Powder compacts **400** comprising dispersed particles **414** that include Mg and nanomatrix **416** that includes various nanomatrix materials as described herein have also demonstrated a room temperature shear strength of at least about 20 ksi. This is in contrast with powder compacts formed from pure Mg powders, which have room temperature shear strengths of about 8 ksi.

Powder compacts **400** of the types disclosed herein are able to achieve an actual density that is substantially equal to the predetermined theoretical density of a compact material based on the composition of powder **310**, including relative amounts of constituents of particle cores **314** and metallic coating layer **316**, and are also described herein as being fully-dense powder compacts. Powder compacts **400** comprising dispersed particles that include Mg and nanomatrix **416** that includes various nanomatrix materials as described herein have demonstrated actual densities of about 1.738 g/cm³ to about 2.50 g/cm³, which are substantially equal to the predetermined theoretical densities, differing by at most 4% from the predetermined theoretical densities.

Powder compacts **400** as disclosed herein may be configured to be selectively and controllably dissolvable in a borehole fluid in response to a changed condition in a borehole. Examples of the changed condition that may be exploited to provide selectable and controllable dissolvability include a change in temperature, change in pressure, change in flow rate, change in pH or change in chemical composition of the borehole fluid, or a combination thereof. An example of a changed condition comprising a change in temperature includes a change in borehole fluid temperature. For example, powder compacts **400** comprising dispersed particles **414** that include Mg and cellular nanomatrix **416** that includes various nanomatrix materials as described herein have relatively low rates of corrosion in a 3% KCl solution at room temperature that range from about 0 to about 11 mg/cm²/hr as compared to relatively high rates of corrosion at 200° F. that range from about 1 to about 246 mg/cm²/hr depending on different nanoscale coating layers **216**. An example of a changed condition comprising a change in chemical composition includes a change in a chloride ion concentration or pH value, or both, of the borehole fluid. For example, powder compacts **400** comprising dispersed particles **414** that include Mg and nanomatrix **416** that includes various nanoscale coatings described herein demonstrate corrosion rates in 15% HCl that range from about 4750 mg/cm²/hr to about 7432 mg/cm²/hr. Thus, selectable and controllable dissolvability in response to

a changed condition in the borehole, namely the change in the borehole fluid chemical composition from KCl to HCl, may be used to achieve a characteristic response as illustrated graphically in FIG. 18, which illustrates that at a selected predetermined critical service time (CST) a changed condition may be imposed upon powder compact 400 as it is applied in a given application, such as a borehole environment, that causes a controllable change in a property of powder compact 400 in response to a changed condition in the environment in which it is applied. For example, at a predetermined CST changing a borehole fluid that is in contact with powder contact 400 from a first fluid (e.g. KCl) that provides a first corrosion rate and an associated weight loss or strength as a function of time to a second borehole fluid (e.g., HCl) that provides a second corrosion rate and associated weight loss and strength as a function of time, wherein the corrosion rate associated with the first fluid is much less than the corrosion rate associated with the second fluid. This characteristic response to a change in borehole fluid conditions may be used, for example, to associate the critical service time with a dimension loss limit or a minimum strength needed for a particular application, such that when a borehole tool or component formed from powder compact 400 as disclosed herein is no longer needed in service in the borehole (e.g., the CST) the condition in the borehole (e.g., the chloride ion concentration of the borehole fluid) may be changed to cause the rapid dissolution of powder compact 400 and its removal from the borehole. In the example described above, powder compact 400 is selectively dissolvable at a rate that ranges from about 0 to about 7000 mg/cm²/hr. This range of response provides, for example the ability to remove a 3-inch diameter ball formed from this material from a borehole by altering the borehole fluid in less than one hour. The selectable and controllable dissolvability behavior described above, coupled with the excellent strength and low density properties described herein, define a new engineered dispersed particle-nanomatrix material that is configured for contact with a fluid and configured to provide a selectable and controllable transition from one of a first strength condition to a second strength condition that is lower than a functional strength threshold, or a first weight loss amount to a second weight loss amount that is greater than a weight loss limit, as a function of time in contact with the fluid. The dispersed particle-nanomatrix composite is characteristic of the powder compacts 400 described herein and includes a cellular nanomatrix 416 of nanomatrix material 420, a plurality of dispersed particles 414 including particle core material 418 that is dispersed within the matrix. Nanomatrix 416 is characterized by a solid-state bond layer 419, which extends throughout the nanomatrix. The time in contact with the fluid described above may include the CST as described above. The CST may include a predetermined time that is desired or required to dissolve a predetermined portion of the powder compact 400 that is in contact with the fluid. The CST may also include a time corresponding to a change in the property of the engineered material or the fluid, or a combination thereof. In the case of a change of property of the engineered material, the change may include a change of a temperature of the engineered material. In the case where there is a change in the property of the fluid, the change may include the change in a fluid temperature, pressure, flow rate, chemical composition or pH or a combination thereof. Both the engineered material and the change in the property of the engineered material or the fluid, or a combination thereof, may be tailored to provide the desired CST response characteristic, including the rate of change of the particular property (e.g., weight loss,

loss of strength) both prior to the CST (e.g., Stage 1) and after the CST (e.g., Stage 2), as illustrated in FIG. 18.

Without being limited by theory, powder compacts 400 are formed from coated powder particles 312 that include a particle core 314 and associated core material 318 as well as a metallic coating layer 316 and an associated metallic coating material 320 to form a substantially-continuous, three-dimensional, cellular nanomatrix 416 that includes a nanomatrix material 420 formed by sintering and the associated diffusion bonding of the respective coating layers 316 that includes a plurality of dispersed particles 414 of the particle core materials 418. This unique structure may include metastable combinations of materials that would be very difficult or impossible to form by solidification from a melt having the same relative amounts of the constituent materials. The coating layers and associated coating materials may be selected to provide selectable and controllable dissolution in a predetermined fluid environment, such as a borehole environment, where the predetermined fluid may be a commonly used borehole fluid that is either injected into the borehole or extracted from the borehole. As will be further understood from the description herein, controlled dissolution of the nanomatrix exposes the dispersed particles of the core materials. The particle core materials may also be selected to also provide selectable and controllable dissolution in the borehole fluid. Alternately, they may also be selected to provide a particular mechanical property, such as compressive strength or sheer strength, to the powder compact 400, without necessarily providing selectable and controlled dissolution of the core materials themselves, since selectable and controlled dissolution of the nanomatrix material surrounding these particles will necessarily release them so that they are carried away by the borehole fluid. The microstructural morphology of the substantially-continuous, cellular nanomatrix 416, which may be selected to provide a strengthening phase material, with dispersed particles 414, which may be selected to provide equiaxed dispersed particles 414, provides these powder compacts with enhanced mechanical properties, including compressive strength and sheer strength, since the resulting morphology of the nanomatrix/dispersed particles can be manipulated to provide strengthening through the processes that are akin to traditional strengthening mechanisms, such as grain size reduction, solution hardening through the use of impurity atoms, precipitation or age hardening and strength/work hardening mechanisms. The nanomatrix/dispersed particle structure tends to limit dislocation movement by virtue of the numerous particle nanomatrix interfaces, as well as interfaces between discrete layers within the nanomatrix material as described herein. This is exemplified in the fracture behavior of these materials. A powder compact 400 made using uncoated pure Mg powder and subjected to a shear stress sufficient to induce failure demonstrated intergranular fracture. In contrast, a powder compact 400 made using powder particles 312 having pure Mg powder particle cores 314 to form dispersed particles 414 and metallic coating layers 316 that includes Al to form nanomatrix 416 and subjected to a shear stress sufficient to induce failure demonstrated transgranular fracture and a substantially higher fracture stress as described herein. Because these materials have high-strength characteristics, the core material and coating material may be selected to utilize low density materials or other low density materials, such as low-density metals, ceramics, glasses or carbon, that otherwise would not provide the necessary strength characteristics for use in the desired applications, including borehole tools and components.

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FIG. 1 shows the tool 100 in a run-in position with the valve cover 250 in a position such that the dissolvable insert 252 is aligned with the valve opening 124 of the uphole body portion 120 to prevent any fluids from flowing into or out of the bore 108 through the valve opening 124. The valve sleeve 254 of the valve cover 250 is attached to the uphole body portion 120 by shear pin 126 adjacent the valve opening 124. In the run-in position, a ledge 128 on the uphole body portion 120 between the shear pin 126 and the valve opening 124 abuts with a shoulder 274 on the valve sleeve 254. Also in the run-in position, the ramped surface 260 of the valve sleeve 254 compresses the fingers 154 of the collet 152 of the ball seat 150 inwardly to provide the ball seat 150 in a ball catching position, ready for receipt of a ball 50. The indexing pin 208 is positioned as shown in FIG. 3 within a second section 212 of the indexing path 206.

FIG. 4 shows the tool 100 upon receipt of a ball 50 within the ball seat 150. With the ball 50 completely or at least substantially blocking fluid through the bore 108, pressure can be built uphole of the ball 50 which forces the ball 50 and the accompanying ball seat 150 in a downhole direction. Due to the attachment of the base 156 of the ball seat 150 to the inner tubular 172 which abuts with the indexing apparatus 200, the indexing apparatus 200 also moves in a downhole direction which positions the indexing pin 208 as shown in FIG. 5 within a third section 214 of the indexing path 206 which is a frac/switch position. Because the valve sleeve 254 is fixedly attached to the uphole body portion 120 via the shear pin 126 the ball seat 150 and indexing apparatus 200 cannot move further in the downhole direction until the shear pin 126 is sheared. If pressure is bled off prior to reaching the shear value, the ball seat 150 will return to the run in position and the indexing pin 208 will be positioned in the second position 212 of the indexing path 206. If the pressure is increased past the shear value, the shear pin 126 will shear and the valve cover 250, ball seat 150, and indexing apparatus 200 will move in the downhole direction and compress the compression spring 218 and thus expose the valve opening 124 in the uphole body portion 120. The zone may then be fracked, or other downhole operation may be performed through the valve opening 124. At this stage, the ball seat 150 is locked into position due to the indexing apparatus 200 which, as shown in FIG. 5, is retaining the indexing pin 208 at an uphole end 228 of the third section 214 and will not move from there until pressure is released. The collet 152 of the ball seat 150 is still in the restricted diameter condition to retain the ball 50 therein. As long as the collet 152 is uphole of the ramped surface 260, the collet 152 will remain in the restricted diameter condition.

FIG. 6 shows the tool 100 in a position, such as after a tracking operation on the particular zone is complete, where the pump pressure is bled from the bore 108 of the tool 100 so that the pressure is relieved from the ball seat 150. As the ball 50 and ball seat 150 are allowed to move back towards an uphole position, the valve sleeve 254 returns to the position as shown in FIG. 1 where the insert 252 again blocks the valve opening 124. The valve sleeve 254 is brought back to this position via the spring force of the compression spring 218 which pushes on the movable tubular portion 216 to which the valve sleeve 254 is connected. The shoulder 274 of the valve sleeve 254 abuts with the ledge 128 of the uphole body portion 120 so that the insert 252 aligns appropriately with the valve opening 124. The indexing pin 208 indexes to the second section 212 between the positions shown in FIGS. 4 and 6. When pressure is reapplied with the ball 50 on ball seat 150 the indexing sleeve 202 indexes such that the indexing pin 208 is aligned with the first section 210 corresponding to a

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“pass” section. With the indexing pin 208 all the way in the extended longitudinal portion of the first section 210, the spring member 220 becomes compressed and the inner tubular 172 is pulled downhole such that the connected collet 152 is pulled downhole. Thus, the funnel shaped portion 162 of the ball seat 150 does not abut with the ledge 258 on the valve sleeve 254, and the ramped surface 170 of the inner tubular 172 does not abut with the ramped surface 260 of the valve sleeve 254 such that the free end 160 of the fingers 154 are no longer compressed together, and thus they assume a condition such that an inner diameter of the collect 152 is large enough to allow the ball 50 to pass there through to a lower, or more downhole, zone.

With respect to FIGS. 8 and 9, after the ball 50 passes, the spring member 220 moves the indexing sleeve 202 back to the second section 212 of the path 206, and the ball seat 150 returns to a reduced diameter condition as shown in FIG. 1 during the run-in position. Different from FIG. 1, however, the dissolvable insert 252 of FIG. 1 is shown in FIG. 8 with the material dissolved at the selected time deemed appropriate by the operator, generally after all zones have been fracked. Once the dissolvable insert 252 is dissolved, aperture 253 in the valve cover 250 is provided and may be selectively aligned with the valve opening 124 in the tubular body 106.

As shown in FIG. 10, the fracture order of operation currently enabled by conventional equipment, as well as enabled by the selective hydraulic fracturing tool, is the “bottom-up” approach. A schematic view of a borehole 10 includes an uphole end 12 closest to a surface location, and a downhole end 14, furthest from the surface location, where the surface location is the point of entry for a bottomhole tool. The borehole 10 is shown with seven zones targeted for fracturing operations, including zones 16, 18, 20, 22, 24, 26, and 28, although a different number of zones may be targeted. In the “bottom-up” approach, the first fracturing operation 1 is conducted at zone 28, the second fracturing operation 2 is conducted at zone 26, the third fracturing operation 3 is conducted at zone 24, the fourth fracturing operation 4 is conducted at zone 22, the fifth fracturing operation 5 is conducted at zone 20, the sixth fracturing operation 6 is conducted at zone 18, and the seventh fracturing operation 7 is conducted at zone 16. Thus, in the “bottom-up” order, the lowest/farthest zone 28 is fractured first, and then fracturing operations are completed up the borehole by fracturing each successive zone. In the conventional fracturing tool, the initial fracture would be enabled by dropping a small diameter ball in the tool, and then consecutively larger sized balls would be dropped while working up the borehole. After all the zones are fracked, the balls would flow back to the surface with production.

FIGS. 11 and 12 respectively show two alternative fracture order of operations that are enabled by the selective hydraulic fracturing tool described herein, but not by conventional downhole tools. FIG. 11 shows a “top-down” approach which is a reversal of the “bottom-up” approach shown in FIG. 10. In other words, the first fracturing operation 1 is conducted at zone 16, the second fracturing operation 2 is conducted at zone 18, the third fracturing operation 3 is conducted at zone 20, the fourth fracturing operation 4 is conducted at zone 22, the fifth fracturing operation 5 is conducted at zone 24, the sixth fracturing operation 6 is conducted at zone 26, and the seventh fracturing operation 7 is conducted at zone 28. In this “top-down” order, the highest zone 16 is fracked first, and then fractures are completed working down the borehole by fracturing each successive zone. This order was not possible with a conventional fracturing tool because the ball on seat would prevent an operator from producing lower zones, and

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even if the ball on seat was capable of being removed, the zone that was just fracked would be left open and therefore when a frac is attempted at a lower zone, all of the pumping would be lost to the upper zone. However, in the selective fracturing tool, after fracturing an upper zone, the ball must be passed through the expandable ball seat to frac any lower zones, and a single ball could be used to frac all zones.

FIG. 12 shows a "center encroaching" fracture order of operation, where the first fracturing operation 1 is conducted at zone 28, the second fracturing operation 2 is conducted at zone 16, the third fracturing operation 3 is conducted at zone 26, the fourth fracturing operation 4 is conducted at zone 18, the fifth fracturing operation 5 is conducted at zone 24, the sixth fracturing operation 6 is conducted at zone 20, and the seventh fracturing operation 7 is conducted at zone 22. Thus, the "center encroaching" frac operation is where the zones are fractured in an alternating fashion from the lowest to highest zone until the center zone is reached. After fracturing an upper zone, the ball must be passed through the expandable ball seat to frac any lower zones. After fracturing an upper zone, the ball would be used to frac the corresponding lower zone. In the illustrated embodiment, the zone 16 ball would then pass to zone 26 and frac that zone.

While two additional fracture order of operations have been described, it should be understood that the selective hydraulic fracturing tool may be utilized to fracture zones of the borehole in any order deemed appropriate by the operator or borehole conditions.

While the invention has been described with reference to an exemplary embodiment or embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the claims. Also, in the drawings and the description, there have been disclosed exemplary embodiments of the invention and, although specific terms may have been employed, they are unless otherwise stated used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention therefore not being so limited. Moreover, the use of the terms first, second, etc. do not denote any order or importance, but rather the terms first, second, etc. are used to distinguish one element from another. Furthermore, the use of the terms a, an, etc. do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item.

What is claimed:

1. A selective downhole tool comprising:

a tubular having a longitudinal bore enabling passage of fluids there through and having a valve opening in a wall of the tubular;

an expandable ball seat selectively movable between a first size sized to trap a ball to block flow through the tubular and a larger second size sized to release the ball through the tubular; and

a valve cover longitudinally movable within the tubular, the valve cover including a dissolvable insert;

wherein the insert covers the valve opening in a first condition and is longitudinally movable within the tubular to expose the valve opening in a second condition, and the insert re-covers the valve opening in a third condition.

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2. The selective downhole tool of claim 1 wherein the valve cover cooperates with the ball seat and is longitudinally movable with the ball seat in response to a pressure change within the tubular.

3. The selective downhole tool of claim 1 wherein the ball seat has the first size in the first and second conditions, and the second size in the third condition.

4. The selective downhole tool of claim 3, wherein the insert is dissolved in the fourth condition.

5. The selective downhole tool of claim 1, wherein the expandable ball seat includes a collet having a plurality of fingers, the free end of the fingers moving from the first size to the second size, a base connecting a fixed end of the fingers.

6. The selective downhole tool of claim 1, further comprising a shear pin fixedly connecting the valve cover to the tubular in a run-in condition of the tool.

7. The selective downhole tool of claim 1, wherein the dissolvable insert includes a selectively degradable material including a sintered powder compact formed from electrochemically active metals.

8. A selective downhole tool comprising:

a tubular having a longitudinal bore enabling passage of fluids there through and having a valve opening in a wall of the tubular;

an expandable ball seat selectively movable between a first size sized to trap a ball to block flow through the tubular and a larger second size sized to release the ball through the tubular;

a valve cover longitudinally movable within the tubular, the valve cover including a dissolvable insert disposed in an aperture in the valve cover, and the aperture is selectively alignable with the valve opening; and

an indexing apparatus engageable with the expandable ball seat, the expandable ball seat lockable in one of the first size and the second size by the indexing apparatus.

9. The selective downhole tool of claim 8, wherein the indexing apparatus includes an indexing sleeve having an indexing path, an indexing pin movable with respect to the indexing sleeve, and at least one spring biasing member acting on the indexing pin.

10. The selective downhole tool of claim 9, wherein the at least one spring biasing member includes a compression spring on one side of the indexing pin and a compression spring on an opposite side of the indexing pin.

11. The selective downhole tool of claim 9, wherein the indexing path includes a uphole extending first section to lock the ball seat in the second size, a downhole extending second section allowing movement of the indexing pin, and an uphole extending third section shorter than the first section to lock the ball seat in the first size.

12. The selective downhole tool of claim 11, wherein the indexing path is a continuous path around a diameter of the indexing sleeve and includes a second section interposed between every first section and third section.

13. A method of operating a downhole tool, the method comprising:

running the downhole tool in a bore hole, the tool including a tubular having a valve opening covered by a valve cover;

moving the valve cover longitudinally to expose the valve opening;

re-covering the valve opening with the valve cover subsequent an operation through the valve opening; and dissolving a portion of the valve cover to re-expose the valve opening.

14. The method of claim 13, further comprising repeating exposing the valve opening, performing an operation through

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the valve opening, and re-covering the valve opening for a plurality of valve openings and corresponding valve covers, and subsequently dissolving a portion on the valve covers to expose the valve openings.

15 15. The method of claim 14, wherein the operation is a fracturing operation performed on a plurality of zones of the borehole, and further comprising allowing entry of production fluids through the valve openings after dissolving a portion on the valve covers.

10 16. The method of claim 14, wherein an order of operations performed through the valve openings is a top-down order where a first operation is performed through an upholemost valve opening and a last operation is performed through a downholemost valve opening.

15 17. The method of claim 14, wherein an order of operations performed through the valve openings is a center encroaching order where successive operations are performed alternately through downhole and uphole valve openings closing in on a center valve opening.

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18. The method of claim 13 further comprising:

dropping a ball in the tubular into an expandable ball seat; catching the ball within the ball seat;

building pressure within the tubular and forcing the ball and ball seat in a downhole direction; and,

bleeding pumping pressure;

wherein moving the valve cover longitudinally occurs with the building of pressure within the tubular and re-covering the valve opening with the valve cover occurs with the bleeding of pumping pressure.

15 19. The method of claim 13, wherein the valve cover is fixedly attached to the tubular via a shear screw while running the downhole tool in the bore hole, and further comprising shearing the screw after the valve opening is aligned with a target zone in the bore hole.

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