ABSTRACT
Downhole apparatus and methods of using the apparatus are described, the apparatus comprising at least one metallic component having a DLC coating thereon, the coating present at least on one or more internal passageways of the base metal or alloy to be exposed to downhole environments. Methods of using an apparatus in downhole oilfield operations are also described. This abstract allows a searcher or other reader to quickly ascertain the subject matter of the disclosure. It will not be used to interpret or limit the scope or meaning of the claims.
DOWNHOLE OILFIELD APPARATUS
COMPRIING A DIAMOND-LIKE CARBON
COATING AND METHODS OF USE

CROSS REFERENCE TO RELATED
APPLICATION


BACKGROUND OF THE INVENTION

[0002] 1. Field of Invention
[0003] The present invention relates generally to the field of coating materials useful for applications where corrosion and wear are important to overcome, as found in oilfield exploration, production, and testing, and more specifically to downhole oilfield apparatus comprising one or more internal surfaces or passageways with a diamond-like coating (DLC) finish.

[0004] 2. Related Art
[0005] Diamond-like coatings are known for various purposes. U.S. Pat. Nos. 7,052,736 and 6,764,714 (Wei, et al.) disclose methods for coating an interior surface of ferromagnetic and non-ferromagnetic tubular structures with such coatings using gaseous bonding precursors. Suitable silicon-containing gaseous bonding precursors include silanes, trimethyl silanes, and the like. Other suitable gaseous bonding precursors disclosed include CH₄, C₂H₆, N₂, or Cr(CO)₆. The patents note that when combinations of SiH₄, C₂H₂, C₂H₆, N₂, or Cr(CO)₆ are introduced, a coating containing silicon, silicon nitrides, silicon carbides, diamond-like carbon (DLC) and carbon nitrides can be obtained. If a hydrocarbon gas is used, such as CH₄ or C₂H₂, an amorphous carbon film forms. If an organometallic gas is used (such as Cr₂, Al₂, Ti-containing precursors), a metallic or ceramic coating is deposited. The term “amorphous carbon” is accepted in the art and refers to a carbonaceous coating composed of a mixture of sp² and sp³ hybridized carbon. sp² carbon refers to double bonded carbon commonly associated with graphite. sp³ hybridized carbon refers to single bonded carbon.

[0006] U.S. Pat. No. 6,450,271 (Tibbitts, et al.) discloses a rotary-type drill bit for drilling subterranean formations having areas or components having surfaces exhibiting a relatively low adhesion, preferably non-water-wettable (non-wettable by water), over at least a portion thereof. Superabrasive materials such as diamond, polycrystalline diamond, diamond-like carbon (DLC), nanocrystalline carbon, amorphous carbon and related vapor-deposited (e.g. plasma vapor deposition or chemical vapor deposition) carbon-based coatings such as carbon nitride and boron nitride can be applied to large surface areas at temperatures (as low as less than 300°F) below that which would affect the metallurgical integrity of the bit material being coated. The vapor-deposited, carbon-based coatings preferably achieve a hardness of at least 3000 Vickers, provide a sliding coefficient of friction of 0.2 or less, and are not wetted by water.

[0007] U.S. Pat. No. 5,831,743 (Ramos, et al.) discloses optical probes for use downhole. After an oil well has been drilled, lined and cased, and is producing, it may be desirable in situ (either at the wellhead or downhole) to measure, and log record, the rate at which fluid, and its several distinct components, is flowing out of the geological formations through which the bore has been drilled and is passing into and up the casing. A useful type of detector system for this purpose is an optical probe, and the patent describes a design of probe which has a doubly-angled tip, there being measured the light totally internally reflected at the interface, which depends on the ratio of the refractive indices of the probe tip and fluid component in which it is immersed. The exposed tip of each probe is protected from the fluid under test by providing a hard, protective layer or coating on the tip, which must not upset the optics of the probe—it should preferably be: amorphous, so facilitating the formation of an optically flat coating; adequately transparent at the probe’s operating wavelength; such that it may be deposited with controllable thickness, and of a refractive index greater than that of the probe’s fiber optic (and that of any likely fluid component), so as not itself to cause total internal reflection of probe light. Suitable materials are diamond (as polycrystalline diamond) and a number of diamond-like substances, such as DLC, which is also known as Amorphous Partially Hydrogenated Carbon (or a-C:H). DLC is transparent in the infra-red region, has a refractive index around 2.2, and provides a smooth amorphous hydrophobic coating finish.

[0008] U.S. Pat. No. 6,881,475 (Ohtani, et al.) discloses cutting tools comprising a tungsten carbide (WC) base formed of a hard phase with WC as the main component, and a bonded phase with a transition metal such as cobalt as the main component. An amorphous carbon film is applied to the base, and may include films such as a hard carbon film, diamond-like carbon film, DLC film, or a-C:H, i-carbon film. The tools are described as suitable for working on aluminium and alloys thereof, and other non-ferrous materials such as titanium, magnesium or copper. The tools are described as effective for cutting a variety of materials and may be used for ferrous alloys such as stainless steels in addition to non-ferrous materials by virtue of the high hardness of the amorphous carbon film.

[0009] The disclosures of all documents referred to herein are expressly incorporated by reference herein in their entirety. As may be seen, oilfield prior art has been restricted to uses of DLC and similar carbon coatings in drill bits, specialty optical sensors, and fluid-conveying-only tubes. There has not been disclosure of their use in any sort of downhole tool used to control, change, isolate, restrict, and/or monitor flow of a fluid, solids, or transfer heat and/or momentum to fluids and/or solids. Many downhole oilfield tools, such as safety valves, flow control valves, packers, connectors, submersible pump components (for example pump housings, shafts, impellers, and diffusers), mandrels and components thereof, sand controls (screens), non-optical sensors, blow out preventer components, bottom hole assemblies (BHA) or components thereof, sucker rods, O-rings, T-rings, gaskets, tube seals, valves and valve components, power cables, communication wires and cables, bulkheads such as those used in fiber optic connections and other downhole tools, pressure sealing elements for fluids (gas, liquid, or combinations thereof), and the like may be exposed during use to wide ranges of temperatures, pressures, and environments; e.g. sour, brine, or seawater environments for citing only a few examples. Many are also exposed to very corrosive fluids comprising any number of abrasive elements in a variety of sizes, for instance sand particles and metallic debris from other downhole components. Therefore it would be of con-
siderable advantage to have available downhole oilfield tools of this nature having DLC or other amorphous carbon-based coatings, especially on their surfaces exposed to such aggressive environments (these surfaces are typically internal surfaces and passageways), so that they may have a high corrosion resistance (including resistance to stress-corrosion and sulfide-stress cracking, microbiological corrosion, etc.), a high bond strength (adhesion), high mechanical properties (e.g., static and dynamic strength, resistance toward compressive loads, high fatigue strength, etc.) along with an ultra-low friction coefficient, as needed in particular in the presence of sealing apparatus (e.g., a piston moving in an internally coated borehole).

SUMMARY OF THE INVENTION

[0010] In accordance with the present invention, apparatus and downhole methods of use thereof are described, the apparatus comprising a base metal or alloy having a diamond-like carbon (DLC) coating thereon comprising amorphous and/or crystalline carbon produced by a process such as physical vapor deposition (PVD), and CVD-like processes, including a process known as the hollow cathode plasma ion immersion process and disclosed by SubOne Technology (www.subone.com), the coating presents at least on some of internal surfaces of the base metal or alloy to be exposed to downhole environments, the apparatus selected from downhole equipment having one or more of the following functions: control, change, isolate, restrict, and/or monitor flow of, or transfer heat and/or momentum to or from, a fluid, solids, or combinations of fluid and solids. Apparatus of the invention typically operate in aggressive environments, in which many metallic materials suffer from corrosion and wear damages.

[0011] Exemplary apparatus of the invention may be termed “completion accessories”, “completion tools”, or more generally “well completions.” The terms are used interchangeably herein. As used in the industry, “completion accessory” product lines may be further characterized as comprising tubing-mounted equipment and flow control equipment, both of which may be used to customize well completions. A general list might include, but is not limited to: nipples, plugs, pressure settings tools, locks, standing valves, shock absorbers, packoffs, protectors, joints (expansion, slip, and safety), polished bore receptacles, unions, subs, sleeves, and on-off attachments. A more specific list of tubing-mounted equipment might include, but is not limited to: standpipe, expansion joints, pumpout sub, and other specialized items that are included in most tubing strings for production or injection operations in the oil and gas industry. Flow-control equipment comprises equipment that is deployed inside the tubing string with standard slickline methods. A list might include, but is not limited to locks, blanking plugs, equalizing standing valves, circulating plugs, and other specialized equipment. These tools are used to control flow into or from the reservoir.

[0012] The base metal or alloy in apparatus of the invention may be selected from ferrous and non-ferrous metals and alloys, and may be non-magnetic, partially magnetic, or fully magnetic. Suitable ferrous materials include the known and foreseeable various carbon steels and stainless steels. Suitable non-ferrous metals include nickel and titanium as examples and alloys thereof. Apparatus of the invention may include coated ferrous components and coated non-ferrous components, as well as non-coated metallic and non-coated non-metallic components.

[0013] DLC coatings are typically inert carbon films with various ratios of amorphous to crystalline carbon or carbon phases that give them attractive properties for downhole applications such as high resistance against contact loads and impacts (wear, abrasion), high chemical resistance (inertness), good cohesion and adhesion to materials frequently used in downhole tools (e.g. carbon steels, stainless steels, nickel alloys), as well as low friction coefficients (anti-stick properties) due to an extremely slick surface finish. DLC coatings may be deposited through a variety of techniques. Prior art includes many methods for the deposition of DLC coatings from a variety of carbonaceous precursor materials through a variety of processes, including: direct ion beam deposition, pulsed laser ablation, filtered cathodic arc deposition, ion beam conversion of condensed precursor, magnetron sputtering, RF plasma-activated chemical vapor deposition, plasma source ion implantation and deposition, and all sort of hybrid and plasma enhanced CVD processes, including the plasma ion immersion process for SubOne Technology (www.sub-one.com). Using the hollow cathode plasma ion immersion process, they may be grown onto “cold” metallic materials (at temperatures less than about 300°C (570°F)) at reasonably fast rates and potentially over long distances and areas (e.g. for well completions). The family of DLC films covers a wide range of structures and compositions, thus properties. These properties of DLC are controlled by sp²/sp³ ratios (i.e. diamond/graphite structure ratios), process gases (hydrogen, methane, ethane, siloxane, etc.), hydrogen content, interface design (layering), and deposition process.

[0014] Certain apparatus embodiments of the invention comprise one or more intermediate metal layers between the base metal and the DLC coating. One or more of these intermediate layers may be selected from carbide-forming elements such as silicon, chromium, tantalum, or other transition-metals.

[0015] In addition to the completion tools cited earlier, apparatus within the invention include, but are not limited to packers, connectors, submersile pump components (for example pump housings, shafts, impellers, diffusers), mandrels and components thereof, sensors, blow out preventer components, bottom hole assemblies (BHA) or components thereof, sucker rods, drill string components, tube seals, valve components, power cables, communication wires and cables, bulkheads such as those used in fiber optic connections and other tools, pressure sealing elements for fluids (gas, liquid, or combinations thereof), sand controls (screens), sampling bottles, HPHT dynamic seals, mud motor stators (e.g., of helical form and metallic), SCAR family tools, pressure compensating sleeves, and the like. Apparatus within the invention include those having one or more of the follow features coated with a diamond-like coating: components defining internal passageways of valves (for example safety valves, formation isolation valves, check valves, circulation valves, gas lift valves, frac valves, and the like); walls defining hydraulic chamber bores, hydraulic piston bores, flow tube internal surfaces; components defining internal passageways of completion tools (e.g. tubing-mounted equipment and flow control equipment); seal bore assemblies; joints (expansion, slip, and safety joints, for example); components defining internal passageways and surfaces of low accessibility of pumps (housings, impellers, diffusers, stages, and the like), for example as found in submersible pumps, frac pumps, and the like; bearings in power drive tools, drilling tools; control
line sections; threads and seal surfaces; external surfaces of internal tubing, collets and like components (the surface will then be considered internal, and a sub-element of a combination element; typically the surface is then part of a component defining an internal passageway).

[0016] Certain apparatus embodiments may include low accessibility portions. As used herein the term “low accessibility” means internal surfaces of partially hollow or fully hollow downhole tool components, as well as surface pits or crevices, or the roots of threads.

[0017] Another major aspect of the invention includes methods of using an apparatus of the invention in performing a defined task downhole, one method comprising:

(a) selecting an apparatus of the invention according to a downhole operation to be performed; and

(b) deploying the apparatus during the downhole operation.

[0020] Methods of the invention may include, but are not limited to, those wherein the downhole operation is selected from various completion operations, such as circulation, cleanout, pumpout, and the like; acidizing, fracturing, flow diverting and other operations. The environmental conditions of the wellbore during running and retrieving of the apparatus may be the same or different from the environmental conditions during use of the apparatus downhole. Methods of the invention include those comprising using a first apparatus of the invention to perform a first task downhole, and a second apparatus of the invention to perform a second task downhole. For example, a first packer apparatus of the invention may be employed to block the wellbore below a wellbore zone to be treated, followed by a second packer apparatus of the invention positioned above the wellbore zone to be treated.

[0021] The various aspects of the invention will become more apparent upon review of the brief description of the drawings, the detailed description of the invention, and the claims that follow.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] The manner in which the objectives of the invention and other desirable characteristics can be obtained is explained in the following description and attached drawings in which:

[0023] FIGS. 1-8 are schematic cross-sectional views of apparatus embodiments of the invention; and

[0024] FIGS. 9-11 are test samples of coated base materials.

[0025] It is to be noted, however, that the appended drawings are highly schematic, not necessarily to scale, and illustrate only typical embodiments of this invention, and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

DETAILED DESCRIPTION

[0026] In the following description, numerous details are set forth to provide an understanding of the present invention. However, it will be understood by those skilled in the art that the present invention may be practiced without these details and that numerous variations or modifications from the described embodiments may be possible.

[0027] All phrases, derivations, collocations and multi-word expressions used herein, in particular in the claims that follow, are expressly not limited to nouns and verbs. It is apparent that meanings are not just expressed by nouns and verbs or single words. Languages use a variety of ways to express content. The existence of inventive concepts and the ways in which these are expressed varies in language-cultures. For example, many lexicalized compounds in Germanic languages are often expressed as adjective-noun combinations, noun-preposition-noun combinations or derivations in Romance languages. The possibility to include phrases, derivations and collocations in the claims is essential for high-quality patents, making it possible to reduce expressions to their conceptual content, and all possible conceptual combinations of words that are compatible with such content (either within a language or across languages) are intended to be included in the used phrases.

[0028] The invention describes shaped articles of manufacture (apparatus) employing a base metal or alloy having a DLC coating thereon comprising amorphous carbon, and methods of using the apparatus in a downhole operation.

[0029] A “downhole apparatus” as used herein is an apparatus that is utilized downhole in a downhole operation in a downhole environment. A “well completion” apparatus is any apparatus used to enable safe and efficient production from an oil or gas well. An example is a subsurface safety valve (SSSV), a safety device installed in the upper wellbore to provide emergency closure of the producing conduits in the event of an emergency. Two types of subsurface safety valve are available: surface-controlled and subsurface controlled. In each case, the safety-valve system is designed to be fail-safe, so that the wellbore is isolated in the event of any system failure or damage to the surface production-control facilities. A surface-controlled subsurface safety valve (SCSSV), is a downhole safety valve that is operated from surface facilities through a control line strapped to the external surface of the production tubing. Two basic types of SCSSV are common: wireline retrievable, whereby the principal safety-valve components can be run and retrieved on slickline, and tubing retrievable, in which the entire safety-valve assembly is installed with the tubing string. The control system operates in a fail-safe mode, with hydraulic control pressure used to hold open a ball or flapper assembly that will close if the control pressure is lost. A subsurface surface-controlled safety valve (SCSSV) is also a downhole safety valve designed to close automatically in an emergency situation. There are two basic operating mechanisms: valves operated by an increase in fluid flow and valves operated by a decrease in ambient pressure. Given the difficulties in testing or confirming the efficiency of these valves, surface-controlled safety valves are much more common.

[0030] As mentioned in the Summary of the Invention, exemplary apparatus of the invention are completion accessories, including tubing-mounted equipment and flow control equipment, both of which may be used to customize well completions. Tubing-mounted equipment includes, but is not limited to, sliding sleeves, landing nipples, expansion joints, pumpout subs, and other specialized items that are included in most tubing strings for production or injection operations in the oil and gas industry. Flow-control comprises equipment that is deployed inside the tubing string with standard slickline methods. This includes locks, blanking plugs, equalizing standing valves, circulating plugs, gas lift valves, and other specialized equipment. These tools are used to control flow into or from the reservoir. A non-exhaustive list of completion accessories which may have a surface or surfaces exposed to downhole conditions during their use, and which surfaces may have an amorphous carbon coating, such as a DLC
coating, may also include flow control equipment (locks, blanking plugs and standing valves), tubing mounted completion accessories (protectors, nipples, expansion joints, adjustable unions, temporary tubing plugs, sliding sleeves, safety joints, chemical injection nipples, On-Off attachments, tubular accessories).

[0031] Downhole operations include, but are not limited to, well pressure control, completion operations (which may range from nothing but a packer on tubing above an openhole completion ("barefoot" completion), to a system of mechanical filtering elements outside of perforated pipe, to a fully automated measurement and control system that optimizes reservoir economics without human intervention (an "intelligent" completion), well stimulation operations, such as hydraulic fracturing, acidizing, acid fracturing, fracture acidizing, fluid diversion or any other downhole well activity, whether or not performed to restore or enhance the productivity of a well.

[0032] Coatings suitable for use in the invention include DLC coatings and other amorphous coatings comprising carbon. Though "diamond-like", DLC coatings do not resemble crystalline diamond; DLC coatings have a graphitic-like color (black), they are not as hard as diamond and they are mainly amorphous. Hydrogen, like other additives such as nitrogen, silicon, sulfur, tungsten, titanium, silver, and the like, are frequently used to control the mechanical and tribological behavior of DLC coatings. Like diamond, DLC coatings are chemically inert and are unmatched to protect engineering materials against environmental degradations (e.g. corrosion, wear, galling, etc.). Engineering materials to receive DLC coatings that are primary interests include carbon and low alloy steels, stainless steels, nickel-based alloys, titanium alloys, and the like. DLC coatings of particular interest for use as coatings for downhole apparatus (apparatus) of the invention may have the following properties:

[0033] Hardness (Vickers)>1000 (in certain embodiments up to 3000);
[0034] Extreme smoothness and lubricity (i.e. a surface of low friction coefficient with practically no cracks);
[0035] Thickness>5 μm, in certain embodiments 25 μm or more;
[0036] High adhesion to metals typically used in oilfield applications (to increase adhesion the coating may be applied with a pre-coating of an interlayer or/and a chemical or mechanical surface pretreatment (peening for instance); the interlayer may be a functionally graded material, i.e. a material that itself is made of layers of various chemical compositions and structures, for instance to provide a high adhesion of the DLC coating on its substrate and accommodate the difference in physical properties between DLC and substrate.
[0037] Chemical resistance in oilfield environments (for example comprising pH ranging from 0 to 14);
[0038] High resistance to thermal and mechanical loads (shocks, vibrations);
[0039] Deposition temperatures such the base metal materials have their bulk properties (i.e. away from surfaces) substantially unaffected by the DLC coating process (i.e. no tempering, softening, and the like); and
[0040] Inexpensive in Raw Materials (e.g. Carbon)

[0041] The previous characteristics may be achieved using a variety of techniques. The prior art includes many methods for the deposition of DLC coatings from a variety of carbonaceous precursor materials through a variety of processes, including: direct ion beam deposition, pulsed laser ablation, filtered cathodic arc deposition, ion beam conversion of condensed precursor, magnetron sputtering, RF plasma-activated chemical vapor deposition, plasma source ion implantation and deposition, and all sort of hybrid plasma-enhanced CVD processes. All of these processes are well-known in the art and require little explanation here. U.S. Pat. Nos. 7,052,736 and 6,764,714 (Wei, et al.), previously incorporated herein by reference, disclose methods for coating an interior surface of ferromagnetic and non-ferromagnetic tubular structures with an amorphous carbon film when a hydrocarbon gas is used, such as CH4 or C2H6. Suitable silicon-containing gaseous bonding precursors include silanes, trimethyl silane, and the like, and other suitable gaseous bonding precursors such as N2 or Cr(CO)6 may be used. The patents note that when combinations of SiH4, CH4, C2H6, N2 or Cr(CO)6 are introduced, a coating containing silicon, silicon nitrides, silicon carbides, diamond-like carbon (DLC) and carbonitrides may be obtained. By limiting SiH4, N2 and Cr(CO)6, a coating comprising a major amount of DLC may be formed.

[0042] The previous characteristics may also be achieved using the hollow cathode plasma ion immersion process (HCPiIP), as described and marketed under the trade designation "Sub-One" by Sub-One Technology, Pleasanton, Calif. (www.Sub-one.com). This process is capable of applying high-performance coatings extremely smooth, hard, pure films on the interior surfaces of parts exposed to downhole conditions. DLC coatings are especially for internal surfaces of downhole apparatus (but not exclusively) to prevent all forms of corrosion (including stress-corrosion cracking, sulfide stress cracking) and damages from external forces (wear, erosion, etc) at oilfield temperatures and pressures. A critical part of this invention is therefore the application of DLC coatings to downhole apparatus with no restrictions on the internal diameters and lengths; therefore, all parts, components, and the like that define passageways of downhole apparatus may benefit from an amorphous carbon coating, such as DLC coatings, and are therefore considered within the invention. The processes and means to achieve these coatings are not part of this invention, the HCPiIP process and variants thereof being useful to produce the coatings. Downhole apparatus or components thereof covered by this invention include, but are not limited to:

[0043] Components defining internal passageways of downhole valves (standing valves, safety valves, formation isolation valves, check valves, circulation valves, gas lift valves, frac valves, completion accessories, and the like);
[0044] Walls defining hydraulic chamber bores, hydraulic piston bores, flow tube internal surfaces, and the like;
[0045] Components defining internal passageways of well completions;
[0046] Seal bore assemblies;
[0047] Joints (including expansion, slip, and safety joints);
[0048] Components defining internal passageways of pumps (housing, impellers, diffusers, stages, and the like e.g. found in electrical submersible pumps, frac pumps, and the like);
[0049] Bearings in powerdrive tools, drilling tools;
[0050] Control line sections used downhole;
[0051] All threads and seal surfaces used downhole;
[0052] External surfaces of internal tubing, collets and like components (the surface will then be considered internal, and a sub-element of a combination element; typically the surface is then part of an internal passageway).
In addition to protecting surfaces from corrosive and damaging environments, the use of amorphous carbon coatings such as DLC non-stick surfaces may minimize scale problems in well completions, for example in safety valves, thus providing a safer work environment.

Base materials may be either ferrous or non-ferrous metals. Of particular interest to well completions are carbon steels (e.g. 4130, 4140), stainless steels (e.g. 410, 420, 9 Cr-1 Mo), titanium alloys (e.g. Ti-6Al-4V), nickel alloys (e.g. 825, 925, 718, 725), and cobalt alloys (e.g. MP35N).

FIGS. 1-8 illustrate examples of downhole apparatus of the invention that may comprise several components, any or all of which may comprise a DLC-coated surface. FIG. 1 illustrates a subsurface safety valve 10 having a DLC coating 12 on a flow tube inner surface. A threaded portion 14 is also coated with a DLC coating, near a flap 16. A fail safe spring 18 is illustrated, as well as a hydraulic piston bore 20 having a DLC coating 22 thereon. Also illustrated is a bore of a hydraulic chamber housing 24, which may also have a DLC coating.

FIGS. 2 A, 2B, and 2C are schematic cross-sectional views of a flow reversing valve of the invention in different modes of operation. Any and all of the parts of the reversing valve may have a DLC coating thereon, and may have one or more intermediate layers, such as chrome, between the base metal and the DLC coating. Illustrated are coiled tubing wall 32, an engineered section 32a of coiled tubing wall 32, and a hydraulic system installed in engineered section 32a. Engineered section 32a may either be formed in the coiled tubing wall itself during fabrication of the coiled tubing, or comprise a piece retrofitted into coiled tubing 32. An opening 36 in CT wall 32 allows fluid communication with the annulus formed between wall 32 and the inside diameter of a well bore or well casing (not shown). FIG. 2A depicts the normal flow mode, where fluid traverses through CT opening at 30, in the direction of the arrow, through an opening 38 and channel in an upper dart valve member 41, past dart 40, through a sleeve 54, and finally past a flapper 76 of a flapper-style check valve.

Because of the nature of dart valve 40, a minimum pressure differential is necessary in order to flow across the valve. This pressure differential charges the hydraulic system by creating a high pressure zone 42 above the valve and a low pressure zone below. Note that the differential pressure that charges the hydraulic system need not be limited to that created by flowing across the dart valve and can be increased, for example, by adding a flow restriction (such as an orifice) below the dart valve. The pressure differential begins to move compression piston 50 to allow oil to flow above and shift dart valve 40 and flapper check valve. Also, the differential begins to move pressure lock piston 62 to its locked position. As the flow rate increases, as shown in FIG. 2B, pressure lock piston 62 continues to move down until the piston lands on a seat that prevents further movement. Just before pressure lock piston 62 seats, a seal takes place that prevents flow of oil around the piston. Additional oil flow due to added flow rate and greater pressure drop will now occur across the hydraulic check valve.

If flow stops after pressure lock piston 62 seats, pressure lock piston 62 will stay seated and hydraulic check valve 46/48 will prevent the charged oil from returning to compensation chamber 52. Consequently, the closed volume of oil in high pressure chamber 42, a passage 45, and annular chamber 47 above the dart valve will force it in the down position, which also forces the flapper check valve 76 open with a push sleeve 54. Once the system is charged and the pressure locked, flow can take place in both directions (as indicated by the double-headed arrow in FIG. 2C) across the flapper check valve and dart valve. When reverse circulation is completed, solenoid 44 is actuated to move ball 46 of the hydraulic check valve off its seat. In doing so, stored pressure in high pressure chamber 42 is released. The system returns to its original position, and flapper check valve 76 and dart 40 are returned to their normal position that prevents uphole flow.

FIG. 3 is a schematic side elevation view, partially in cross-section, and not necessarily to scale, of a downhole submersible pump 300 in accordance with the invention. Any and all of the parts of downhole submersible pump 300 may have a DLC coating thereon, and may have one or more intermediate layers, such as chrome, between the base metal or alloy and the DLC coating. Pump 300 includes two different pump stages indicated by dashed line boxes 301 and 302 and connected through a connector 303. Also illustrated is a pump housing 304 which houses pump stages 301 and 302. Pump intake 305 allows well or reservoir fluids to enter pump 300. A first set of impellers 306 and diffusers 307 move fluid through stage 302 as depicted by curved line 308 (upwards in FIG. 3), although the invention is not so limited toward second stage 301, having a different set of impellers 306' and diffusers 307', eventually forcing fluid out through a discharge 309. Impellers 306 and 306' are all removably fastened to a pump shaft 310, which is powered by one or more motors (not illustrated). In certain embodiments, the stage producing the higher flow rate may be positioned on the "bottom", in this case stage 302, although the invention is not so limited. Sealing rings (not illustrated) may be installed in stages directly below connector 303. Bearing housings may be placed at the first stage below the top or last diffuser in stage 302. The bearing housing location may increase one stage for each housing length required. The top-most diffuser (nearest the pump discharge) may have its male nest removed.

FIG. 4 is a schematic side elevation view, partially in cross-section, of an embodiment of an oilfield tool component that may comprise one or more DLC-coated components in accordance with the invention. FIG. 4 illustrates an oilfield tool component 190 known under the trade designation A-2 Equalizing Standing Valve, available from Schlumberger, modified in accordance with the invention to include at least one amorphous carbon coated surface, for example surfaces 191, 193, and 195. These valves include a stickline-retrievable connection 192, a bull-and-sent-type check valve 194 with integral running 196 and pulling 198 necks, and are designed to hold pressure only from above. The equalizing standing valve 190 may be used in intermittent gas lift wells to contain fluid in the tubing string during an injection cycle. They may also be used to set packers and test a tubing string. An appropriate pulling tool and attached standing valve may be lowered into the tubing until the assembly shoulders against the packing bore of the nipple. The valve packing seals in the polished section. Downward jarring releases the pulling tool for retrieval to the surface. When removing the equalizing standing valve, upward jarring with the appropriate pulling tool equalizes and removes the assembly, and when the valve 190 approaches the well pressure control components at the surface, magnets (not illustrated) may allow one or more magnetic field sensors (not illustrated) to sense the location of the magnets, and lessen the risk that the
valve will hit the inside top of the lubricator. This may reduce the risk that the valve will be disconnected and possibly drop back into the well bore.

[0060] FIG. 5 is a schematic side elevation view, partially in cross-section, illustrating a sliding sleeve packoff assembly 500, components of which incorporate a DLC coating in accordance with the teachings of the invention. Sliding sleeve packoffs are designed to be attached to a lock type that matches the integral landing nipple in the sliding sleeve. When production from an upper zone is not desired and the sliding sleeve leaks fluid between the tubing and casing annulus when closed, a packoff is used to isolate this zone. Packoff assemblies are used to isolate the sliding sleeve ports and prevent migration of fluids between the tubing and casing annulus, as well as to provide a path for flow of production fluids to the surface. In operation, a running tool and pulling tool appropriate for the attached lock 502 are used to install and retrieve the sliding sleeve packoff assembly. Lock 502 is attached to the packoff anchors and seals in a tubing mounted sliding sleeve 504. The lock packing seals in an upper nipple bore 506 of sleeve 504, and packing 508 located on the lower end of the packoff seals in the bottom polished bore 510 in the sliding sleeve. The simplicity of the packoff design assures ease of setting and unsetting of lock 502 and packoff assembly by standard slickline methods. Downward jarring sets lock 502, and upward jarring releases lock 502 from sliding sleeve 504 to allow retrieval of the packoff assembly. The packoff is run into position on the appropriate running tool by standard slickline methods and is locked into upper nipple 506 integral to sliding sleeve 504. The packoff allows restricted flow up the production tubing and completely seals off the ported area in sliding sleeve 504. Lock 502 is released by upward jarring using the appropriate pulling tool. Continued upward pulling removes the packoff assembly from the bore of sliding sleeve 504, allowing it to be removed from the well.

[0061] FIG. 6 is a schematic side elevation view, partially in cross-section, illustrating a sliding sleeve 600 known under the trade designation “CS-1-Series”, available from Schlumberger, modified in accordance with the invention to incorporate a DLC coating on one or more components thereof. Sliding sleeves are used to establish communication between the tubing string and the casing annulus for single- or multiple-tubing string completions. Other applications include equalizing pressure between an isolated formation and the tubing string, spot acidizing and fracturing, killing a well, and directing the flow from the casing to the tubing in alternate or selective completions. As an option, sizeable chokes can be installed on the sliding sleeve to adjust the flow rate through the openings 602 and 602’ (FIGS. 6A and 6B, respectively) to the tubing annulus. The sliding sleeve components may be manufactured from stainless steel or nickel alloys, modified to comprise an amorphous carbon coating in accordance with the invention. These sliding sleeves feature primary and secondary seals (603 and 604) to reduce the possibility of total seal failure, and equalizing slots 606 in the inner sleeve permit gradual equalization between the tubing and casing annulus. Sliding sleeves may be opened or closed using a shifting tool and standard wireline and coiled tubing methods. The sliding sleeve known under the trade designation CS-1U shifts up to open and down to close, and the sliding sleeve known under the trade designation CS-1D shifts down to open and up to close. The sliding sleeves may be assembled to, and form part of, the tubing string, and generally are available with separation tools and packoffs. Equalizing pressure between the tubing and casing annulus is normally accomplished by applying pressure or filling the tubing or casing with fluid. Sliding sleeve 600 can also be opened even if facilities for equalizing pressures beforehand are not available. This requires careful monitoring of tubing and annulus pressures while slowly opening the sleeve until equalization.

[0062] FIG. 7 is a schematic side elevation view, partially in cross-section, illustrating an A-slip lock, 700, modified to include a DLC coating in accordance with the invention. The A-slip lock includes a slickline-retrievable anchor 702 with cup-type seals 703. 704 used to lock and seal subsurface controls in tubing strings that were installed without landing nipples. These slip locks can be set at any depth in the tubing. The A-slip lock comprises a fishing neck 705 that is attached to hardened slips 706 and mounted on a tapered body 707. A lower portion of tapered body 707 has cup-type seals 703, 704, energized by a pressure differential from below the lock, to seal against the tubing wall. The outer threads 706 on the lower end of slips 706 provide an attachment point for subsurface control devices. During installation, the A-slip lock and attached flow control device (not illustrated) are made up to the appropriate A running tool and lowered into the tubing using standard slickline methods. When the desired depth is reached, a rapid upward pull on the slickline moves tapered body 707 under slips 706. Upward jarring secures the slip lock firmly against the tubing wall (not illustrated). Flowing the well will energize cup-type seals 703, 704 against the tubing wall. Before removing the A-slip lock, pressure must be equalized across the lock assembly. Downward jarring with the appropriate pulling tool drives tapered body 707 from beneath the slips. The A-slip lock can then be slowly pulled from the well.

[0063] FIG. 8 is a schematic side elevation view, partially in cross-section, illustrating a gravel pack 800 installed in a cased well. Illustrated are production tubing 801, production casing 802, a gravel pack packer 803, and a sump packer 806. A gravel pack comprises sized particles 804 placed in between the sand face a centralized screen, 805, which may have a DLC coating thereon in accordance with the teachings of the invention. Gravel packs can be used in both open holes, which may be underreamed, and cased holes and prevent sand from being produced through the pores between the gravel particles. Gravel packing is the most widely used method of controlling sand production. When properly designed and executed, this method is highly effective for controlling sand, especially in initial completions. In order to achieve long-term production in a cased hole gravel pack, the gravel must be tightly packed in the perforation tunnels and screen-casing annulus. However, the gravel is erosive. Because of its low coefficient of friction, an a DLC coating, will not only protect the tool surface but also enable the sand to flow with less frictional resistance from the bore internal surfaces.

[0064] Specific oilfield applications of the inventive apparatus include well stimulation treatments. Stimulation treatments fall into two main groups, hydraulic fracturing treatments and matrix treatments. Fracturing treatments are performed above the fracture pressure of the reservoir formation and create a highly conductive flow path between the reservoir and the wellbore. Matrix treatments are performed below the reservoir fracture pressure and generally are designed to restore the natural permeability of the reservoir following damage to the near-wellbore area.
Hydraulic fracturing, in the context of well workover and intervention operations, is a stimulation treatment routinely performed on oil and gas wells in low-permeability reservoirs. Specially engineered fluids are pumped at high pressure and rate into the reservoir interval to be treated, causing a vertical fracture to open. The wings of the fracture extend away from the wellbore in opposing directions according to the natural stresses within the formation. Propellant, such as grains of sand of a particular size, is mixed with the treatment fluid kept the fracture open when the treatment is complete. Hydraulic fracturing creates high-conductivity communication with a large area of formation and bypasses any damage that may exist in the near-wellbore area. Compositions of the invention may be used as supplemental propellant materials.

In the context of well testing, hydraulic fracturing means the process of injecting one or more fluids into a closed wellbore with powerful hydraulic pumps to create enough downhole pressure to crack or fracture the formation. The hydraulic pumps may include components comprising one or more compositions of the invention. This allows injection of propellant into the formation, thereby creating a plane of high-permeability sand through which fluids can flow. The propellant remains in place once the hydraulic pressure is removed and therefore props open the fracture and enhances flow into the wellbore.

Acidizing means the pumping of acid into the wellbore to remove near-well formation damage and other damaging substances. Acidizing commonly enhances production by increasing the effective well radius. When performed at pressures above the pressure required to fracture the formation, the procedure is often referred to as acid fracturing. Fracture acidizing is another procedure for production enhancement, in which acid, usually hydrochloric (HCl), is injected into a carbonate formation at a pressure above the formation-fracturing pressure. Flowing acid tends to etch the fracture faces in a nonuniform pattern, forming conductive channels that remain open without a propping agent after the fracture closes. The length of the etched fracture limits the effectiveness of an acid-fracture treatment. The fracture length depends on acid leakoff and acid spending. If acid fluid-loss characteristics are poor, excessive leakoff will terminate fracture extension. Similarly, if the acid spends too rapidly, the etched portion of the fracture will be too short. The major problem in fracture acidizing is the development of wormholes in the fracture face; these wormholes increase the reactive surface area and cause excessive leakoff and rapid spending of the acid. To some extent, this problem can be overcome by using inert fluid-loss additives to bridge wormholes or by using viscousified acids. Fracture acidizing is also called acid fracturing or acid-fracture treatment. Apparatus of the invention may be used in these applications.

In the oilfield context, a “wellbore” may be any type of well, including but not limited to, a producing well, a non-producing well, an injection well, a fluid disposal well, an experimental well, an exploratory well, and the like. Wellbores may be vertical, horizontal, deviated some angle between vertical and horizontal, and combinations thereof, for example a vertical well with a non-vertical component.

Examples

Diamond-like coatings were tested in aqueous environments with various hydronium ion concentrations, or pH, with temperatures ranging from room temperature to water boiling. The DLC coatings were applied on the internal surface of a 410 stainless steel (13 Cr-type) cylindrical piece (see FIGS. 9, 10A and 10B). Table 1 lists the visible results of the DLC coating after exposure for 24 hours. DLC coatings were produced using the “Sub-One” process (Sub-One Technology, Pleasanton, Calif.) hollow cathode plasma immersion ion processing (HCPIIP).

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water pH = 9 24 hrs</td>
<td>No effect on DLC</td>
</tr>
<tr>
<td>Water pH = 7 24 hrs</td>
<td>No effect on DLC</td>
</tr>
<tr>
<td>Water pH = 3 24 hrs</td>
<td>No effect on DLC</td>
</tr>
<tr>
<td>Pure HCl (10 min)</td>
<td>No effect on DLC</td>
</tr>
<tr>
<td>Water pH = 0; 10% NaCl</td>
<td>Heavily concentrated</td>
</tr>
<tr>
<td>NaOH in water</td>
<td>No effect on DLC</td>
</tr>
</tbody>
</table>

FIG. 11 shows a drawing of a seal testing device, wherein an internal cylindrical surface is coated with a DLC coating and a piston is moved cyclically from one side to the other by controlling pressure on either side of this piston. FIG. 11, though representing a test apparatus rather than a downhole oilfield product, exemplifies the type of applications in which a DLC coating, on internal surface of a borehole or other passageway, may be used. In this example, testing has shown that the extreme smoothness of the DLC coating improved the lifetime of the elastomer seals. Furthermore, the absence of pitting or corrosion damages on the internal surfaces of the borehole, as guaranteed by the slick DLC coating, promote extended lifetime to the sealing component. Preliminary tests under downhole typical temperatures (e.g. 250°F) have shown that such active seals will have unique advantages for the great diversity of downhole equipments listed in this patent. Such active seals are covered in applications listed in claims of this patent.

Although only a few exemplary embodiments of this invention have been described in detail, those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this invention as defined in the following claims. In the claims, no clauses are intended to be in the means-plus-function format allowed by 35 U.S.C. § 112, paragraph 6 unless “means for” is explicitly recited together with an associated function. “Means for” clauses are intended to cover the structures described herein as performing the recited function and not only structural equivalents, but also equivalent structures.

What is claimed is:

1. A downhole oilfield apparatus of base metal or alloy having a coating thereon comprising diamond-like carbon (DLC), the coating present at least on one or more internal passageways of the base metal or alloy to be exposed to downhole environments such as completion and produced fluids, the apparatus selected from downhole tools having one or more of the following functions: control, change, isolate, restrict, and/or monitor flow of, or transfer heat and/or momentum to or from, a fluid, solids, or combinations of fluid and solids.
2. The downhole apparatus of claim 1 wherein the DLC coating is deposited by a process selected from PVD, CVD, or any enhanced-plasma CVD process such as the hollow cathode plasma ion immersion process to provide anti-wear, ultra-low friction, and environmentally resistant surfaces.

3. The downhole apparatus of claim 1 wherein the base metal or alloy is ferrous or non-ferrous and includes oilfield metallic materials such as carbon steels, stainless steels, nickel alloys, and titanium alloys.

4. The downhole apparatus of claim 1 with at its surfaces one or more intermediate metallic or semi-metallic layers between the base metal or alloy of claim 3 and the DLC coating to produce a functionally graded material that permit the formation of an adherent and slick DLC coating.

5. The downhole apparatus of claim 4 wherein the intermediate layer comprises a metal, in particular selected from transition-metals and/or carbide-forming elements; for instance silicon, chromium, tantalum, titanium, and combinations thereof.

6. The downhole apparatus of claim 1 selected from subsurface safety valves, packers, connectors, submersible pump components, mandrels and components thereof, sensors, blow out preventer components, bottom hole assemblies (BHA) or components thereof, sucker rods, drill string components, valve components, power cables, fiber optic connections and other tools, pressure sealing elements for fluids, and sand-control equipments.

7. The downhole apparatus of claim 1 selected from: valves with internal passageways, wherein the valve is selected from safety valves, formation isolation valves, check valves, circulation valves, gas lift valves, and frac valves; hydraulic chamber bores and hydraulic piston bores; flow tube internal surfaces; internal passageways of completion tools; seal bore assemblies; joints; internal surfaces of pumps; bearings in powerdrive tools and drilling tools; control line sections; threads and seal surfaces; external surfaces of internal tubing, collets and like components; nipples; plugs; pressure setting tools; locks; standing valves; shock absorbers; pack-offs; control-line protectors; polished bore receptacles; unions; subs; sleeves; and on-off attachments.

8. A downhole apparatus comprising at least one component comprising an internal surface comprising a base metal or alloy having a DLC coating thereon, the DLC coating present at least on some of the internal surface of the base metal or alloy to be exposed to an downhole environment, the DLC coating derived from PVD, CVD, or an enhanced-plasma CVD process such as the hollow cathode plasma ion immersion process, the apparatus selected from subsurface safety valves, packers, connectors, submersible pump components, mandrels and components thereof, sensors, blow out preventer components, bottom hole assemblies (BHA) or components thereof, sucker rods, drill string components, power cables, fiber optic connections and other tools, pressure sealing elements for fluids, screens, valves having components defining internal passageways, wherein the valve is selected from safety valves, formation isolation valves, check valves, circulation valves, gas lift valves, and frac valves; hydraulic chamber bores and hydraulic piston bores; flow tube internal surfaces; internal passageways of completion tools; seal bore assemblies; joints; internal surfaces of pumps; bearings in powerdrive tools and drilling tools; control line sections; threads and seal surfaces; external surfaces of internal tubing, collets and like components; nipples; plugs; pressure setting tools; locks; standing valves; shock absorbers; pack-offs; control-line protectors; polished bore receptacles; unions; subs; sleeves; and on-off attachments.

9. The downhole apparatus of claim 8 comprising one or more intermediate metallic layers between the base metal or alloy and the DLC coating, wherein the intermediate layer comprises in particular selected from transition-metals and/or carbide-forming elements; for instance silicon, chromium, tantalum, titanium, and combinations thereof.

10. A downhole apparatus comprising a hydraulic chamber, the hydraulic chamber having an internal surface defined by a base metal or alloy, at least some of the internal surface having a DLC coating thereon, the DLC coating derived from PVD, CVD, or an enhanced-plasma CVD process such as the hollow cathode plasma ion immersion process.

11. A downhole flow control apparatus comprising at least one internal passageway, this internal passageway having an internal surface defined by a base metal or alloy, at least some of the internal surface having a DLC coating thereon, the DLC coating derived from PVD, CVD, or an enhanced-plasma CVD process such as the hollow cathode plasma ion immersion process.

12. A downhole pump apparatus comprising at least one component having an internal passageway having an internal surface defined by a base metal or alloy, at least some of the internal surface having a DLC coating thereon, the DLC coating derived from PVD, CVD, or an enhanced-plasma CVD process such as the hollow cathode plasma ion immersion process.

13. A method comprising:
(a) selecting a downhole apparatus comprising a base metal or alloy having a DLC coating thereon produced from PVD, CVD, or an enhanced-plasma CVD process such as the hollow cathode plasma ion immersion process, the DLC coating present at least on one or more internal passageways of the base metal or alloy to be exposed to downhole environments, the apparatus selected from downhole tools having one or more of the following functions: control, change, isolate, restrict, and/or monitor flow of, or transfer heat and/or momentum to or from, a fluid, solids, or combinations of fluid and solids; and
(b) deploying and using the downhole apparatus downhole during a downhole operation.

14. The method of claim 13 wherein the downhole operation is selected from completion operations, pumping, circulating, acidizing, fracturing, flow diverting and combinations thereof.

15. The method of claim 14 wherein the downhole operation is a completion operation, and the downhole apparatus is selected from one or more of packers, connectors, submersible pump components, mandrels and components thereof, sensors, blow out preventer components, bottom hole assemblies (BHA) or components thereof, sucker rods, drill string components, power cables, communication wires and cables, bulkheads such as those used in fiber optic connections and other tools, pressure sealing elements for fluids, screens, valves having components defining internal passageways, wherein the valve is selected from safety valves, formation isolation valves, check valves, circulation valves, gas lift valves, and frac valves; hydraulic chamber bores and hydraulic piston bores; flow tube internal surfaces; internal passageways.
ways of completion tools; seal bore assemblies; joints; internal surfaces of pumps; bearings in powerdrive tools and drilling tools; control line sections; threads and seal surfaces; external surfaces of internal tubing, collets and like components; nipples; plugs; pressure setting tools; locks; standing valves; shock absorbers; packoffs; control-line protectors; polished bore receptacles; unions; subs; sleeves; and on-off attachments.

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