Sampling device with diamond-like carbon coating

Inventors: Bradley Martin, ST FARDEAU PONTHIERRY (FR); Rashmi Bhavsar, Houston, TX (US); Dave MacWilliam, Aberdeenshire (GB)

Correspondence Address:
SCHLUMBERGER OILFIELD SERVICES
200 GILLINGHAM LANE, MD 200-9
SUGAR LAND, TX 77478 (US)

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Abstract
A diamond-like carbon coating is provided on a metal interior surface of a sample chamber of a well fluid sampling apparatus to render the sample chamber substantially impervious to the absorption of at least H₂S, mercury, and/or mercaptans. The coating is a dense, amorphous, diamond-like carbon with an sp³ content greater than about 65% and is composed of about 70 percent (% carbon, 30 percent (% hydrogen. The coating may be applied over the surface in one or more layers by a suitable method, e.g., plasma assisted chemical vapor deposition or a PAVCD process, and is between about 10 and about 20 microns thick. One or more of the layers of the coating includes a small percentage of silicon to increase both the adherence to the metal interior surface of the sample chamber and the absorption resistance of the coating. The resulting sample chamber provides H₂S, mercaptan, and mercury retention of greater than about 95% of the original concentration in samples stored up to 14 days.
FIG. 1
SAMPLING DEVICE WITH DIAMOND-LIKE CARBON COATING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is related to and claims the benefit of U.S. Provisional Patent Application 61/104,116, filed on Oct. 9, 2008, the entire contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention generally relates to sampling devices for oilfield reservoir fluids that allow sampling and measurement of trace amounts of H₂S, and is specifically concerned with a diamond-like carbon coating applied over the internal surfaces of the sampling chamber of such devices that renders the chamber substantially impermeable (or non absorbent) to H₂S and able to withstand acid and alkaline fluids.

[0004] 2. Discussion of the Background

[0005] Existing sampling technology preserves samples above reservoir pressure ensuring representative pressure/volume/temperature (PVT) analysis. However, for chemical or trace element analysis some components of the samples are lost due to physical or chemical processes, most of which are time dependent. Samples are collected downhole or at surface and shipped to the laboratory for further analysis, which is typically weeks or months after capture. Many of the components will react with the walls of sampling tools/sample bottles and/or decompose with time. The accurate measurement of trace elements is required for rigorous process and completion equipment design, as these results can be used to determine metalurgy of downhole and topside process equipment. The degradation of the trace element initial concentration can have serious implications. For example, a completion or gas processing facility may be designed for zero H₂S, but may be producing 100 ppm H₂S concentration, in reality, during production.

[0006] During a well test, it takes time for the mercury or H₂S level to stabilize, as the drill-stem-test (DST) string tubing and process equipment must be saturated before getting an accurate measurement. Therefore, it is essential that bottomhole samples can be taken that are truly representative of the composition of the fluid at reservoir conditions.

[0007] Existing sampling devices used in the oilfield employ a plurality of coatings. One example of a sampling tool is disclosed in U.S. Pat. No. 5,609,205 issued on Mar. 11, 1997, to Massie et al., the entire contents of which are hereby expressly incorporated by reference. The Massie patent describes a well fluid sampling tool and method for retrieving chemically accurate hydrocarbon samples from new wells wherein the tool is coated with one of sapphire, ceramic, and glass. However, all such coatings are generally deficient as a barrier to H₂S, mercaptans, and mercury and may crack due to elastic deformation of the sampler.

[0008] Another example of a known coating used for covering the interior surface of sampling cylinders includes SULFINERT, which is commercially available from RESTEK Corporation, a U.S. company. This is generally satisfactory in terms of H₂S barrier, but is deficient in terms of mechanical resistance and chemical resistance to alkaline environments.

SUMMARY OF THE INVENTION

[0009] Therefore, there is a need to develop sampling devices that can be used to sample oilfield fluids that have traces of H₂S and are able to measure the H₂S. There is further a need to develop a sampling device having an internal coating that can withstand alkaline chemical environment and that also has superior mechanical wear resistance. To these ends, the present invention provides a well fluid sampling device (or tool) including a sample chamber for receiving and holding a sample well fluid that has been coated with a diamond-like coating (DLC). The coating employed in the inventive sampling device substantially prevents absorption of H₂S as well as of other components such as mercury and mercaptan into the walls of the sampling device. The same coating can also be used likewise in any type of sampling and analysis devices, such as sampling bottles, flow lines and associated equipment, gas chromatographs, mercury analyzers, etc. The coating is also chemically resistant to both acid and alkaline environments, provides scratch resistance, and allows for representative compositional analysis of the samples taken even of very small trace amounts of components, even after many long days of storage.

[0010] One embodiment of the invention is directed to a well fluid sampling apparatus, which comprises a sample chamber for receiving and holding a sample well fluid, and a diamond-like carbon coating (DLC) provided on an interior of the sample chamber that is preferably between about 10 and about 20 microns in thickness. The coating substantially prevents absorption of at least one of H₂S, mercury, and a mercaptan through it.

[0011] The DLC coating is preferably dense, amorphous, diamond-like carbon with an sp³ content greater than about 65% and has a composition comprising about 70 percent (%) carbon and about 30 percent (%) hydrogen. The coating substantially prevents absorption of at least one of H₂S, mercury, and a mercaptan through it.

[0012] The well fluid sampling apparatus is provided with a substantially chemically inert sample chamber which is achieved by applying the DLC coating of the invention to the material of the sample chamber (usually a non-corrosive metal such as stainless steel or a nickel alloy steel). The apparatus may also be referred to herein as a “tool” or “sampling device”. The apparatus may be lowered to the required depth in the well where a well fluid sample is admitted to the sample chamber, which is subsequently sealed. The tool is preferably arranged so that pressures inside and outside the sample chamber remain substantially equal during and after sample taking. The sample may be subjected to post-sampling pressurization to keep the sample in its original single-phase state. The substantial chemical inertness of the sample chamber avoids removal of reactive components of the well fluid from the sample by chemical reaction with the material forming the sample chamber (conventionally a metal). This enables accurate assessment of new wells without the need for extended flow testing. Equalization of pressures inside and outside the sample chamber enables the material of the sample chamber to be selected for its chemical inertness rather than for mechanical strength to resist forces otherwise arising from pressure imbalances.
Another embodiment is directed to a method of rendering an interior surface of a sample chamber of a well fluid sampling apparatus substantially impervious to absorption of at least one of H2S, mercury, and a mercaptan, comprising applying a diamond-like carbon coating over the interior surface of the sample chamber.

Still other aspects, features, and advantages of the present invention are readily apparent from the entire description thereof, including the figures, which illustrate a number of exemplary embodiments and implementations. The present invention is also capable of other and different embodiments, and its several details can be modified in various respects, all without departing from the spirit and scope of the present invention. Accordingly, the figures and descriptions are to be regarded as illustrative in nature, and not as restrictive.

BRIEF DESCRIPTION OF THE FIGURES

The embodiments of the present invention are illustrated by way of example, and not by way of limitation, in the figures of the accompanying figures and in which like reference numerals refer to similar elements and in which:

FIG. 1 shows H2S concentration testing for the exemplary sampling device, according to an exemplary embodiment of the present invention.

DETAILED DESCRIPTION

Various embodiments and aspects of the invention will now be described in detail with reference to the accompanying figures. The terminology and phraseology used herein is solely used for descriptive purposes and should not be construed as limiting in scope. Language such as “including,” “comprising,” “having,” “containing,” or “involving,” and variations thereof, is intended to be broad and encompass the subject matter listed thereafter, equivalents, and additional subject matter not recited.

The terms “sample apparatus,” “sample chamber,” “sampler,” and variations thereof are used herein to include all elements required for sampling, such as bottles, flowlines, pistons, valves and the like.

The coating is made of a dense, amorphous, diamond-like carbon with an sp3 content greater than about 65% by weight (wt.) and is comprised of about 70 wt. % carbon, and about 30 wt % hydrogen, with a small amount of silicon. The coating is applied using a plasma assisted chemical vapor deposition process or a plasma assisted vapor phase coat deposition (PAVCD) process. The coating can be applied in one or more layers (such as two layers) having an overall thickness of from about a few microns all the way up to about 50 microns, although coatings having a thickness of between about 10 and about 20 microns are preferred. Thicknesses greater than about 50 microns start causing problems with the piston of the sampling device. At least one layer, and usually each of the layers of the coating includes a small percentage of silicon to increase both the adherence to the metal interior surface of the sample chamber and the absorption resistance of the coating. The present invention includes recognition that generally coatings of smaller thicknesses (i.e., less than about 20 microns and more preferably about 15 microns) are more effective as H2S barrier and also offer satisfactory mechanical and chemical resistance.

Preferably, the coating should be applied in a thickness of from about 10 microns to about 30 microns and more preferably from about 10 to about 20 microns. In one embodiment, the coating is no more than about 15 microns thick. Also, if the coating is applied in more than one layer, the composition of the layers may slightly differ from one another. For example, in one embodiment, the coating includes a first layer adjacent to (i.e., covering) the metal of the sampling device (or tool) that is specifically designed for increased adhesion to the metal of the sampling tool. The coating further includes an outer layer or top layer that is specially treated and is deposited on top of the first layer to make it inert to the well fluid. The outer layer is made adherent to the first layer by any suitable means.

The novel sampling tool provides H2S, mercaptan and mercury retention of greater than about 95% of the original concentration in the samples stored up to 14 days. It should be noted that in a preferred embodiment, the sampling tool of the present invention may be used both downhole and at surface.

Optionally the coating can include at least one intermediate layer for providing increased adhesion between the first and top layers.

The exemplary sampling device provides a spectrum of improved features and benefits, including chemical inertness, especially to alkaline fluids. The sampling device includes a diamond-like carbon based coating that provides an improved barrier and substantially prevents H2S, mercaptan and mercury absorption into the walls of the sampling device.

The apparatus to which the coating of the invention is applied may be any apparatus known in the art for well fluid sampling, such as (without limitations) the well fluid sampling tool of Massie et al., U.S. Pat. No. 5,609,205, or any of the oilfield devices described in US Published Patent Application 2008/0236842, owned by the same assignee as the present application, the entire contents of which are hereby expressly incorporated into this disclosure by reference thereto.

EXAMPLES

Several tests are carried out using samplers having diamond-like carbon coatings covering all internal surfaces in contact with the sample and using two different formulations. A first formulation F1 includes a diamond-like carbon top layer, and a first layer with graded, silicon containing diamond-like carbon, for optimized adhesion to the metal. A second formulation F2 is used including a top layer and a first layer, with both layers made of silicon-containing diamond-like carbon. The overall thickness of each coating formulation is adjusted by controlling the number of intermediate layers.

Both formulations F1 and F2 include a dense, amorphous, diamond-like carbon, with high carbon diamond bonding (sp3 content greater than about 65%, as shown by RAMAN). Total composition of each formulation is about 70 percent (%), silicon and about 30 percent (%), hydrogen. Silicon is added to the first layer of formulation F1 to promote adhesion to the metal of the sampler. The coatings are applied using a plasma assisted chemical vapor deposition or PAVCD process.

The results are compared against existing uncoated samplers and against coated commercial samplers that employ SULFINERT coating from RESTEK Corporation.

Various stainless steel cylinders having a volume of 500 cc were coated with different thicknesses of the diamond-like carbon coating. The coatings were tested at the laboratory
with 50 ppm H2S concentrated samples maintained at temperatures as high as up to 70°C and pressures up to 1300 psi. The tests results are shown in FIG. 1. As seen from FIG. 1, a 15 micron (nm) thickness of Formulation 1 and Formulation 2 have improved performance and are able to provide greater than 95% H2S retention within the sample. Without wishing to be bound by any openness theory, it is believed that the non-intuitive result of a thinner (i.e., 15 micron thick) coatings having better H2S retention than thicker (i.e., >20 micron thick) coatings may be obtained because the application process creates voids in the thicker layers which compromises the integrity of the coating.

Successful tests are carried out to verify the inaccessibility of the coating for H2S retention, mechanical and chemical testing to confirm that the application of coating will not alter the physical or chemical properties of the metal or affect strength, hardness, life span, and the like. Test results show that the coating is not affected by well fluids, acid/alkalis and other chemical additives. The tests also show excellent mechanical resistance to scratching.

While the present invention(s) have been described in connection with a number of exemplary embodiments, and implementations, the present invention(s) are not so limited, but rather cover various modifications, and equivalent arrangements, which fall within the purview of the appended claims.

What is claimed is:

1. A well fluid sampling apparatus, the apparatus comprising:
   a sample chamber for receiving and holding a sample well fluid; and
   a diamond-like carbon coating provided on an interior of the sample chamber, that substantially prevents absorption of at least one of H2S, mercury, and a mercaptan therethrough.

2. The well fluid sampling apparatus of claim 1, wherein the coating is a dense, amorphous, diamond-like carbon, with an sp3 content greater than about 65%.

3. The well fluid sampling apparatus of claim 1, wherein the coating composition comprises about 70 percent (%) carbon and about 30 percent (%) hydrogen.

4. The well fluid sampling apparatus of claim 1, wherein the thickness of the coating is no more than about 20 microns.

5. The well fluid sampling apparatus of claim 1, wherein the thickness of the coating is between about 10 and about 15 microns.

6. The well fluid sampling apparatus of claim 1, wherein the diamond-like coating includes a first layer that overlies a surface of the sample chamber, and a second layer that overlies the first layer and defines an interior surface of the sample chamber.

7. The well fluid sampling apparatus of claim 6, wherein the coating further includes a third layer between said first and second layers of diamond-like coating to increase adhesion between the first and second layers.

8. The well fluid sampling apparatus of claim 6, wherein the first layer of diamond-like coating includes silicon to promote adhesion to a metal surface of the sampler.

9. The well fluid sampling apparatus of claim 6, wherein the second layer of diamond-like coating includes silicon to render it more inert to absorption of at least one of H2S, mercury, and a mercaptan therethrough.

10. A well fluid sampling apparatus, the apparatus comprising:
    a sample chamber for receiving and holding a sample well fluid; and
    a diamond-like carbon coating provided on an interior of the sample chamber and that substantially prevents absorption of at least one of H2S, mercury, and a mercaptan therethrough.

11. The well fluid sampling apparatus of claim 10, wherein the thickness of the coating is no more than about 20 microns.

12. The well fluid sampling apparatus of claim 10, wherein the thickness of the coating is no more than about 15 microns.

13. The well fluid sampling apparatus of claim 10, wherein the diamond-like coating includes a first layer that overlies a metal surface of the sample chamber, and a second layer that overlies the first layer and defines an interior surface of the sample chamber, and wherein said first layer includes silicon to increase adherence between the metal surface of the sample chamber and the coating.

14. The well fluid sampling apparatus of claim 13, wherein the second layer of diamond-like coating also includes silicon to render it more inert to absorption of at least one of H2S, mercury, and a mercaptan therethrough.

15. The well fluid sampling apparatus of claim 13, wherein the coating further includes a third layer between said first and second layers of diamond-like coating to increase adherence between the first and second layers.

16. A method of rendering an interior surface of a sample chamber of a well fluid sampling apparatus substantially impervious to absorption of at least one of H2S, mercury, and a mercaptan, comprising:
    applying a diamond-like carbon coating over said interior surface of the sample chamber.

17. The method of claim 16, wherein the diamond-like carbon coating is applied over said surface by one of a plasma assisted chemical vapor deposition process or a PVD process.

18. The method of claim 16, wherein the coating is a dense, amorphous, diamond-like carbon with an sp3 content greater than about 65% and having a composition comprising about 70 percent (%) carbon, about 30 percent (%) hydrogen.

19. The method of claim 16, wherein said application step includes applying a first layer of diamond-like carbon coating over the interior surface of the vessel, and then applying a second layer of diamond-like carbon coating over the first layer.

20. The method of claim 19, further including the step of applying an intermediate layer of diamond-like carbon coating between said first and second layers to increase adherence therebetween.

21. The method of claim 17, wherein said coating is applied to a thickness of between about 10 and about 20 microns.

22. The method of claim 17, wherein said coating is applied to a thickness of between about 10 and about 15 microns.