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DLC Coatings in High Temperature Hydrogen Sulfide Environment

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ABSTRACT

Surface protection in high temperature hydrogen sulfide environment remains a significant challenge with limited number of materials providing adequate protection. Diamond-like carbon (DLC) thin films are recognized across different sectors as a promising way of controlling wear and the corrosion performance of components. The aim of this paper is to test the hypothesis that thin DLC coatings may act as an efficient corrosion barrier for steel components in high temperature hydrogen sulfide environment. The DLC coating was deposited in this work using Plasma-Enhanced Chemical Vapor Deposition (PECVD) process and the coating was characterized in terms of the structure morphology and mechanical properties. Coated test coupons were exposed to high pressure high temperature tests simulating sour production environments for the period of 28 days. The performance of DLC coating was compared with data obtained from a large tank lining joint industry project focusing on tank lining study previously completed by one of the authors.

Key words: Diamond-like carbon, DLC, hydrogen sulfide, sour corrosion, high temperature, high pressure, tank lining.

INTRODUCTION

Coatings used for corrosion protection of the internal of vessels, tank linings and flow devices frequently have to perform under severely corrosive environments. There are many commercially available coatings that claim to be effective under a wide range of operating conditions. However, field experience indicates that problems such as blistering, cracking, and delamination are not uncommon.[1,2]

Hydrogen sulfide (H_2S) occurs naturally in crude oils or it can be formed during the refining process. Moreover, the average sulfur content in crude oils across the world's petroleum refineries continues to increase,[3] contributing to greater emphasis on the safety, environmental and operational concerns associated with hydrocarbon management. Hydrogen sulfide as a highly corrosive compound puts a

strain on processing and storage equipment and increases the difficulty and cost of integrity management programs.

Metallic materials suffer corrosion in hydrogen sulfide environment which might lead to hydrogen generation and resulting hydrogen embrittlement and cracking problems.[4] It has been shown that sulphide stress corrosion cracking (SSC) of carbon and low alloy steels is dependent on the partial pressure of H_2S.[5] Integrity management program measures against SSC include corrosion monitoring plans, preventive maintenance, corrosion inhibitors and a variety of coatings and linings. Typical coating solutions to prevent SSC are relatively thick (above 100µm) organic coatings, however an increased interest in more effective solutions and novel materials including diamond-like carbon (DLC) coatings has been observed recently.

DLC is a generic term used to describe a range of amorphous carbon films which include hydrogen free DLC (a-C), hydrogenated DLC (a-C:H), tetrahedral amorphous carbon (ta-C), hydrogenated tetrahedral amorphous carbon (ta-C:H), and those containing silicon or metal dopants, such as Si DLC and Me DLC.[6] The first report of successful deposition of DLC coating dates back to 1971, when Aisenberg and Chabot processed hydrogen free diamond-like carbon films using carbon ions.[7] DLC coatings are recognized in many sectors as a promising way of controlling wear and the corrosion performance of components. DLC coatings are well established in the automotive industry where they are applied to the moving parts of direct injection fuel systems operating under frictional conditions at high pressures and in the aggressive environment of the combustion chamber. Over the last few years, there have also been an increasing number of reports of DLC coating applications in oil and gas production contexts, including pipes, shut-off gates and various types of valves.[8]

DLC coatings are metastable materials and deposition methods of DLC films are non-equilibrium processes where energetic ions interact with the surface. Such films are deposited by Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD) techniques. A wide range of available amorphous carbon DLC coating architectures and a number of possible deposition methods allow tailoring of the coating functionality to certain applications. As such, apart from corrosion protection they can be designed to provide other benefits like e.g. low friction or anti-fouling properties. Typical applications for DLC coatings in energy sector would include high-value/high-risk components like valves and other flow assurance components.

DLC coatings are typically deposited with functional interlayers providing enhanced adhesion to substrate material, low permeability etc. Corrosion performance of DLC coatings with various interlayers was investigated by Azzi et al. in the context of biomedical applications.[9] It was found that a-SiNx interlayer significantly improved the corrosion resistance of the DLC system since it was highly impervious to the liquid. The effects of Si incorporation on the electrochemical and nanomechanical properties of DLC thin films was studied by Papakonstantinou et al.[10] It was observed that introduction of Si in the DLC led to significant improvements in the corrosion resistance of DLC, as revealed by increase in the charge transfer resistance and reduction in the anodic current of the polarisation curves. Relatively thick (above 30µm) DLC coating was tested in high temperature hydrogen sulfide environments by Boardman et al.[11-13] The coating was deposited using a proprietary equipment where plasma was generated within the pipe itself and a gaseous precursor was introduced and ionized causing a coating to be deposited on the internal wall of the pipe. The coating showed resistance to attack by gas mixture containing H_2S at 90°C and 190°C. Moreover, the coating demonstrated high ASTM [(1)] G65 [14] dry abrasion resistance when compared to tool steel sample.

In this study, the following hypothesis will be tested: thin DLC coatings with adhesive Cr interlayer may act as an efficient corrosion barrier for steel components in high temperature hydrogen sulfide environment.

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[1] ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959, USA.

EXPERIMENTAL PROCEDURE

Coating Deposition

Steel substrates (UNS G52986 chrome steel) were prepared for the DLC coatings. The discs were mechanically polished to 0.05 µm Ra. They were washed with acetone in an ultrasonic bath and stored to dry. A customized Hauzer Flexi Coat 850† machine was used in this study to produce the carbon films. Acetylene was used as the gas precursor. In the coating step of DLC layer, a high pulsed bias voltage (~700V) was applied in order to assist the plasma deposition. Substrates were mounted on the bias table with the rotation speed of 1 rpm. The deposition time for DLC layer step was set to 150 min, although it is noted that the whole process time for the coating is about 5 hours.

Coating Characterization Methods

The hardness was measured by nanoindentation platform (Micromaterials†) and the indentation load was set to 2 mN. The resulted depth was about 120 nm. Normal force and normal displacement were measured during nano-indentation tests. The thickness of the coating was measured by the ball craterer (calo tester) from Tribotechnic†. 25 mm diameter ball was used to create the crater. The adhesion of the carbon coating was determined using a scratch-tester Millennium 200†. An ISO [(2)] standard, 20502, Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of adhesion of ceramic coatings by scratch testing was followed for the adhesion measurement.

High Temperature Hydrogen Sulfide Environment Testing

The pressure vessel used in this study for high temperature and high pressure experiment is shown in Figure 1. It was designed to simulate conditions in pressurized pipelines, theaters, and vessels. The product that demonstrates the least amount of reaction is considered the most reliable for use in that particular service. Tests can utilize supplied fluids and gases but generally standard mixtures are used including H_2S to simulate sour service.

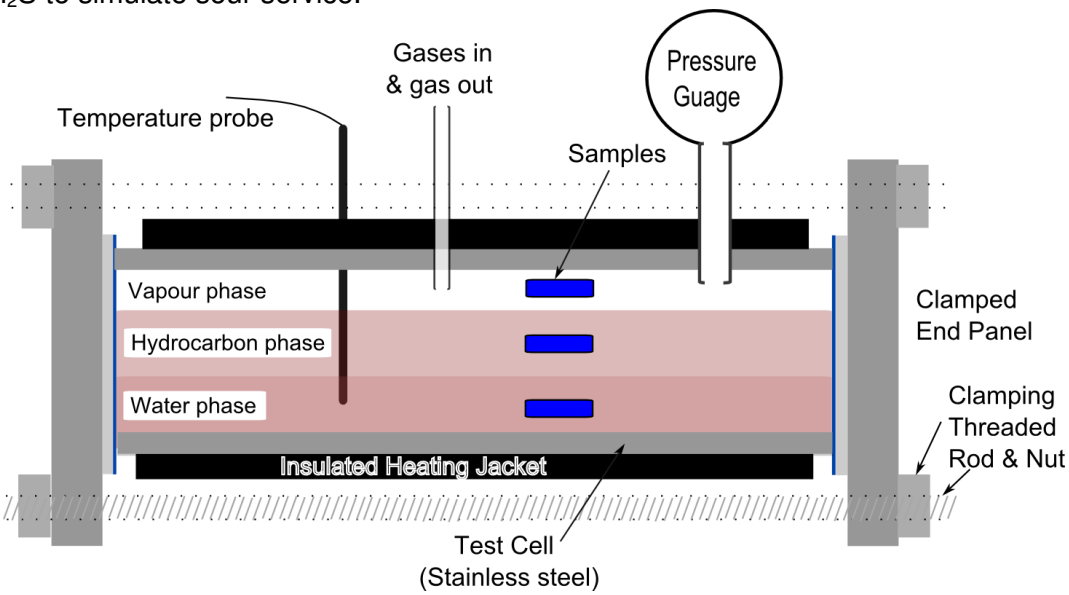

Figure 1: Pressure Vessel Used for High Temperature Hydrogen Sulfide Environment Testing

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† Trade name
[2] ISO, 1, ch. de la Voie-Creuse, CP 56, CH-1211 Geneva 20, Switzerland.

The pressure vessel was selected to measure the ability of the coating to protect the metal substrate from corrosion in a multiphase environment (water, hydrocarbon, hydrogen sulphide, carbon dioxide and methane) under high pressure and temperature.

Prior to test, coated samples were assessed for pre-test surface damage under the optical microscope. The test method consisted of putting three coated discs into a cylindrical cell in a way that each sample is exposed to different phase: vapour, hydrocarbon and water. The cell was filled with 500ml of 1% NaCl in distilled water and 800ml of hydrocarbons mixture (toluene and kerosene). The remaining volume of the cell (about 20%) was pressurized to 1000psi (6.89 MPa) with H_2S, CO_2 and CH_4 mixture. The heating jacket was turned on and the pressure was monitored until full temperature was reached. The test conditions are presented in Table 1.

Temperature	100°C/212°F
Pressure	1000 psi/6.89 MPa
Gas	5% H_2S, 5% CO_2, 90% CH_4
Water	1% NaCl in distilled water
Hydrocarbon	Toluene:Kerosene (1:1 volume)
Duration	28 days

Table 1. High Temperature Hydrogen Sulfide Environment Test Conditions

After 28 days of exposure, the heating system was stopped and the test vessel was allowed to cool to 25°C/77°F. The pressure was slowly released at the rate of 100psi (0.69 MPa) per minute. The samples were removed and rated for blistering (ASTM D714 [15]), cracking, delamination, as well as changes in coating colour.

After evaluation, all three samples were installed back in the pressure vessel the same way as previously and the test media loading procedure was repeated as described above. The test unit was pressurized and heated to the test temperature and the samples were maintained at the test conditions for 24 hours. After this time, the rapid decompression procedure, simulating a blow-down event during service was carried out and the pressure was rapidly released at the rate of 500psi (3.45 MPa) per second. The samples were removed and again rated for blistering (ASTM D714 [15]), cracking, delamination, as well as changes in coating colour.

RESULTS AND DISCUSSION

Coating Characterization

The outcome of the calo test coating thickness measurement is a “crater” worn through the coating exposing the substrate. Coating thickness is calculated after measuring diameters of the circles representing exposed substrate and coating shown in Figure 2a. It is worth noting that the DLC coating system thickness (1.43 µm) is of an order of magnitude smaller that typically used organic coatings for high temperature hydrogen sulfide applications. Figure 2a shows also DLC coating surface morphology, which is smooth and free from surface cracks and porosity. Figure 2b shows a schematic diagram of the coating architecture with Cr interlayer and DLC top layer deposited on steel substrate.

Table 2 summarizes DLC coating mechanical properties including coating thickness, adhesion and hardness.

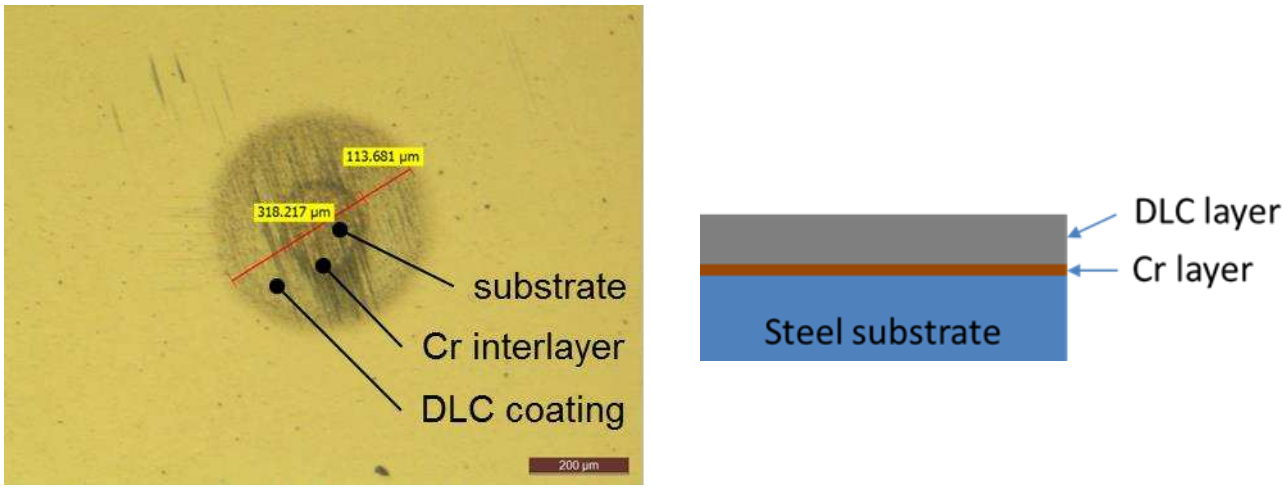

Figure 2: DLC Coating: a) Coating Thickness Measurement; b) Coating Architecture

Coating thickness (including Cr interlayer)	1.43 µm
Adhesion (critical load)	19N
Hardness	HV=2153, HVpl = 2614

Table 2: DLC Coating Mechanical Properties

High Temperature Hydrogen Sulfide Environment Test

After 28 days of exposure to gas, hydrocarbon and water phases samples were removed from a pressure vessel, cleaned with soft brush and laboratory detergent and inspected for changes in coating appearance and any surface damage. No visible evidence of corrosion war observed either in gas, hydrocarbon or water phase (Figure 3). There was no indication of coating undercutting from the sample edges.

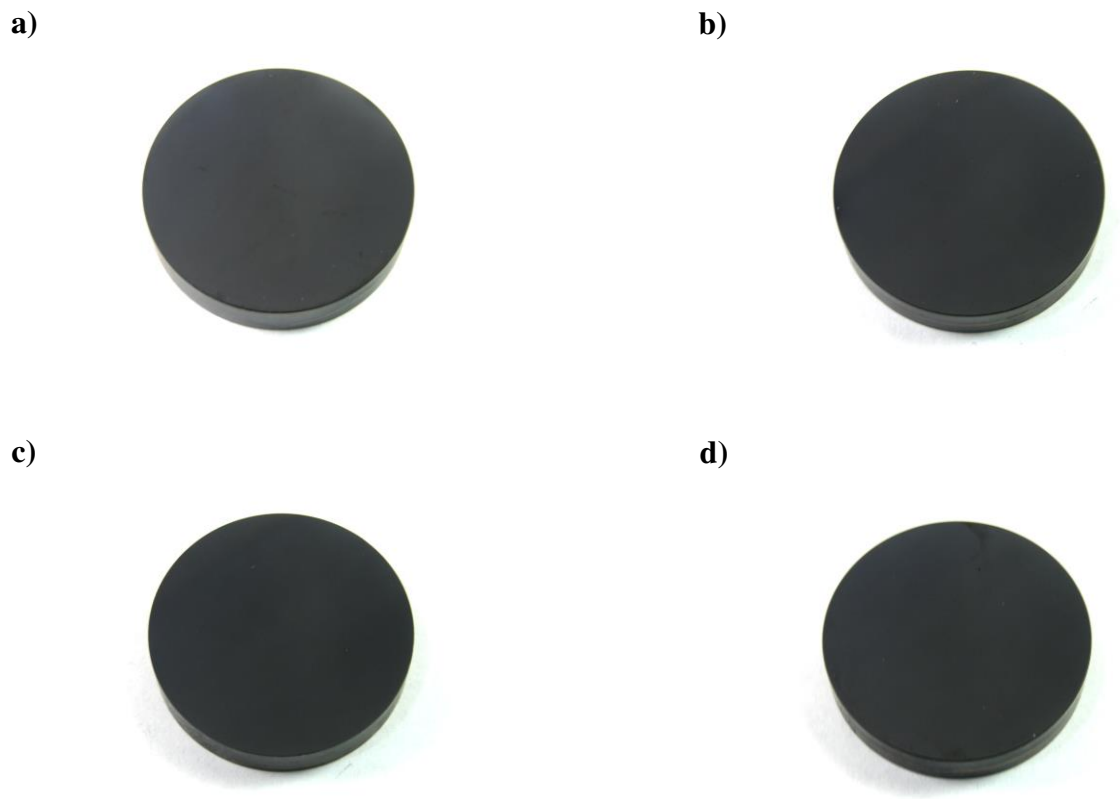

Figure 3: DLC Coating Before and After 28 Days High Temperature Hydrogen Sulfide Test: a) Sample Before Immersion; b) Sample After 28 Days Immersion Test in Gas Phase; c) Sample After 28 Days Immersion Test in Hydrocarbon Phase; d) Sample After 28 Days Immersion Test in Water Phase (diameter of coated coupons: 30mm).

Rapid Decompression

Rapid depressurization of lined pipelines and vessels can cause catastrophic failure to the coating systems. This problem is most evident in systems with CO_2 in the vapor space, which permeates the coating and when a rapid depressurization event occurs, vapor expands inside the coating and typically causes cohesive failure in the form of blisters. Rapid depressurization was also linked to various cavitation processes causing additional coating damage.[16]

No coating damage was observed after exposing DLC coated samples to high temperature hydrogen sulfide environment and performing rapid decompression procedure. Coating appearance was the same as after 28 days high temperature hydrogen sulfide test as shown in Figure 3. Due to its relatively low volume and high density (comparing to organic coatings), DLC coating shown complete resistance to rapid depressurization event.

Comparison of DLC Coating Performance with Tank Lining Protective Coatings

In 2004, a tank lining joint industry project was initiated by one of the authors focusing on comparative performance of tank lining coating systems.[17] The purpose of the study was to provide information on the performance of a range of the coatings under various operating conditions and the performance of thirty-one (31) coating systems were compared using a series of tests designed to simulate potential service conditions. The obtained data was used to assist in the selection of appropriate coating systems for any given environment in the oilfield. In this study, data obtained from the tank lining joint industry project [17] is compared with performance of DLC coating in relation to high temperature hydrogen sulfide environment.

Protective coatings selected for the tank lining joint industry project can be divided into several classes according to the basic chemical reactions involved in the film forming process.[17] Figure 4 shows the coating types used in this study and the generic resin materials in each coating as reported in the supplier's data sheet and the volume solids. Note that for simplicity's sake, no differentiation of products is made according to hardener, though this has a very real effect on the coating characteristics. Similarly, the inclusion of abrasive resistant particles or other specialized additives has not been used in the characterization.

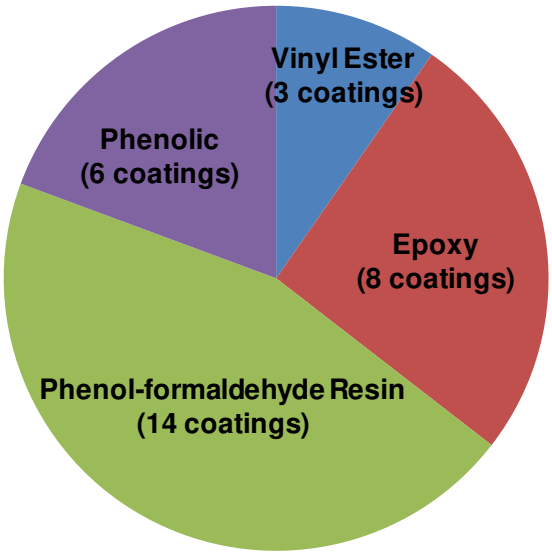

Figure 4: Coating Types Included in the Comparative Study [17]

One of the tests performed in the tank lining joint industry project was the Autoclave Test conducted according to NACE [(3)] TM0185-2000.[18] All the coatings were tested under the same conditions as the high temperature hydrogen sulfide environment test used in this study for DLC coatings (Table 1), including slow rate and rapid rate decompression. The only difference was in test duration which was set at 7 days for all 31 tank lining protective coatings.

In order to identify coatings that are particularly well suited for a given service environment, one needs to identify criteria to indicate "good performance". In case of the autoclave test, "good performance" was defined by a coating that does not blister or crack in any phase of testing and that maintains an acceptable adhesion (rating A: coating may shear within itself but does not release from substrate after test in all three phases – gas, hydrocarbon and aqueous) when measured by parallel scribe method. Figure 5 summarizes data obtained from autoclave test showing that out of the 31 coatings studied in

[3] NACE International, 15835 Park Ten Place, Houston, Texas 77084, USA.

the project only 13 showed good performance in slow decompression test and 2 in rapid decompression test.

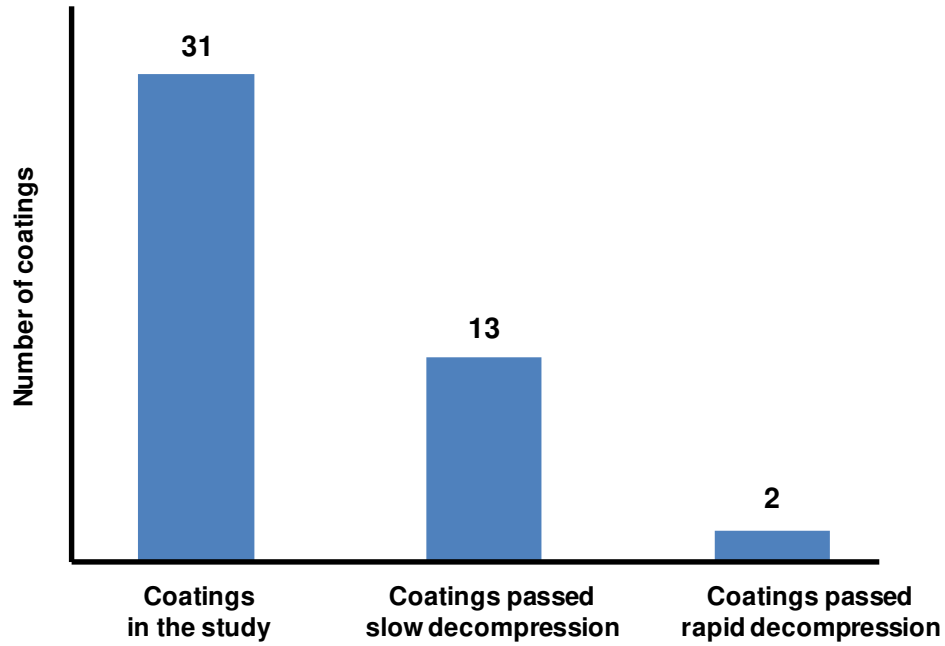

Figure 5: Tank Lining Protective Coatings: Summary of Autoclave Test

It was shown that in the presence of acid gases and a pressure of 1000psi (6.89 MPa), many coatings did not perform well, showing that coatings that are resistant to higher temperatures may degrade when exposed to high temperature hydrogen sulfide environment. Coatings tended to blister and/or suffer severe adhesion loss when subjected to rapid depressurization. A number of coatings reacted by forming small surface blisters, some of which recovered after test, indicating that most of the coatings would be damaged in the case of a rapid pressure loss.

CONCLUSIONS

In this study, DLC coating with Cr interlayer was deposited using Plasma-Enhanced Chemical Vapor Deposition process. Coated test coupons were exposed to high pressure high temperature test simulating sour production environments for the period of 28 days. The performance of DLC coating was compared with data obtained from a large tank lining joint industry project focusing on tank lining study. The following conclusions can be drawn:

- The hypothesis that DLC coatings may act as an efficient corrosion barrier for steel components in high temperature hydrogen sulfide environment has been validated (up to 100°C/212°F, 5% H_2S – limits in this study).
- Very thin DLC coating system (1.43 µm) showed superior performance to most of the thick organic coatings when tested in the same high temperature hydrogen sulfide environment.
- DLC coating shown complete resistance to rapid depressurization event.

Having other beneficial properties, like low friction and wear resistance, DLC coatings might be an attractive alternative for organic coatings. Typical applications for DLC coatings would include high value-high risk components like valves and flow assurance components. DLC coating is a general term which relates to a wide range of carbon based coatings and further work is necessary in order to tailor DLC coatings to certain component geometry and operational conditions.

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