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Corrosion and Abrasion Resistant PECVD Coatings for the Internal Coating of Pipes

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ABSTRACT

A new method for coating internal surfaces using Plasma Enhanced Chemical Vapor Deposition (PECVD) is described which makes use of the Hollow Cathode Effect (HCE) to achieve a high deposition and ion bombardment rate. The method produces a dense, void free, hard, wear and corrosion resistant diamond-like carbon (DLC) coating. It uses the pipe itself as the plasma deposition chamber, with DC pulse biasing of the pipe as the cathode to attract ionized gaseous precursor (e.g., acetylene) to the interior of the pipe, forming the coating. Lab testing data is presented to demonstrate the corrosion and abrasion resistant properties for these internal coatings.

1. INTRODUCTION

This paper describes a well adhered diamond-like carbon (DLC) coating which has excellent corrosion and abrasion resistant properties. This coating also has advantages of high density and hardness, void free, scaling and fouling resistance, and chemical inertness. It can reduce corrosion effects in oil and gas applications, particularly wells and pipelines, where highly corrosive media like carbon dioxide (CO_2), hydrogen sulfide (H_2S) and free water are present. In wells and pipelines, internal corrosion is influenced by temperature, CO_2 and H_2S content, water chemistry, flow velocity and surface condition of the steel substrate. The coating can be applied on the internal surfaces of low grade alloy steels which eliminate the need to use expensive exotic alloys. The coating technology is not limited to DLC. Other precursors, including metal bearing gases, can be introduced into the plasma to further modify the properties for various applications. The described DLC coating is multilayer in nature, where various environmentally safe precursors, such as acetylene, are used to deposit the multilayer structure. A silicon-based adhesion layer is initially deposited on the substrate to provide a superior bond for subsequent layers. Multiple layers of Si-DLC are then grown on top of each preceeding layer to make up the intermediate layers of the film stack. A pure DLC surface layer provides an inert, corrosion resistant surface with high hardness and low friction. It has been reported that having Si-DLC layers in the center of the film stack acts as a stress reliever [1]. Recent studies have also suggested that using a multilayer stack in this way can provide improved corrosion resistance [2-3].

Several techniques including chemical vapor deposition (CVD), physical vapor deposition (PVD), electroplating, polymer linings and sol-gel have previously been considered to coat components requiring corrosion resistance. In particular, sol-gel and polymer linings have been used to protect the internal surfaces of pipe type components. However, these coating processes do not provide dense, hard, low friction coatings which are sufficient to be a barrier to corrosion and wear. These coatings can also be very thick and restrict flow. For CVD and PVD coatings, the component must be contained within a vacuum chamber which is problematic for the lengths and diameters required for oilfield pipe components. Subsequent sections of this paper provide details behind the Plasma Enhanced Chemical Vapor Deposition (PECVD) technique used to deposit these novel internal DLC coatings along with test results demonstrating the corrosive and abrasive characteristics of these unique DLC coatings.

The described coating can increase component life in applications where internal surfaces are exposed to corrosive and abrasive media. Such applications of interest are oil and gas exploration and production tubulars, industrial piping, automotive, military and aerospace.

2. EXPERIMENTAL

A PECVD technique in conjunction with Hollow Cathode Plasma Immersion Ion Processing (HCPIIP) is the deposition method developed to create thick hard DLC based films on the interior surfaces of metallic components, including carbon steel pipes. This method uses the Hollow Cathode Effect (HCE) to generate extremely high density plasma within the pipe itself. Maintaining a hollow cathode discharge within the component is important for rapid growth (high deposition rates ~0.5μm/min) of thick DLC based films with very low residual stress. The critical parameters for maintaining such a discharge are the internal diameter of the pipe and the operating pressure [4]. This new method is significant because it enables both thick, high-quality internal coatings and high deposition rates for the first time using the described combination of PECVD and HCE techniques. Figure 1 demonstrates a schematic of the deposition system.

Gas is continually fed from one side of the system and fills up the volume inside the pipe while simultaneous vacuum pumping from the opposite end controls the desired vacuum pressure. As the component itself is effectively a vacuum chamber containing a low pressure gas, applying an electrical bias to the part generates a plasma in the gas. Negatively biasing the part allows deposition to take place inside of the component, and the cathode bias helps improve the stress, adhesion and density of the films through ion bombardment energy. The pipe or component is an active element of the plasma electrical circuit, serving as the negatively biased cathode with respect to positively biased anodes, located at the entrance and exit heads. The anodes are electrically isolated from the cathode by insulating spacers.

Asymmetric, bipolar pulsing is used to control the temperature of the part as the coating is growing through variation in the duty cycle. When the pulse is in a positive polarity state this allows any positive charge build up on the coating surface to be dissipated and this quick removal of charge helps to maintain a high deposition rate. It also helps to eliminate any arcing effects from the coating due to its insulative nature.

Film adhesion is promoted through application of a high bias voltage to the pipe which results in ion implantation below the surface of the film, along with suitable precursors introduced at the start of the deposition cycle. Also, sputtering of the internal surface of the component with argon or a reducing agent such as hydrogen is used to clean up the metallic surface and remove any thin oxide layers that have grown on surface. This enables the first layer of the coating to bond directly onto the metallic component and give greater adhesion strength. The advantage of using the component itself as the vacuum chamber allows for very thick conformal coatings to be deposited where a uniform plasma sheath is generated on all internal surfaces of the component. Extensive details of the coating process and technology used has been reported elsewhere [4-5].

3. RESULTS AND DISCUSSION

Various analysis of the DLC multilayered coatings will be discussed. Characterizations of the coating microstructure, as well as corrosion and abrasion tests were performed to determine various properties of the deposited films for potential service in environments of high corrosion and/or abrasion.

3.1. Coating Structure and General

As described in the previous section, the DLC based films are multilayer in formation. Figure 2a shows a scanning electron microscopy (SEM) image of a typical coating. In this case, the bare metallic substrate has been overcoated by a Cr plated layer, thus the DLC based film has been deposited onto a Cr surface. A thin adhesion layer is initially deposited, and then a number of doped DLC layers are deposited dependent upon the coating application. Finally, a pure DLC film is deposited on as the surface layer. One interesting note is that the Cr plating has produced an imperfection in the substrate before coating. Due to the fact that the component is acting as the cathode, the ions attracted to the cathode will fill in resulting holes or cracks in the coating or substrate, effectively areas where higher current exists. This can be seen on Figure 2a where the crack is filled in by the coating. Biasing the pipe as a cathode, promotes formation of very dense, low defect density films. Figure 2b shows a DLC based coating on a carbon steel pipe which is representative of the samples examined in this paper and widely used in the oil and gas industry. Coating thickness of such a structure is calculated by using the Calotest system [6], where typically a tungsten carbide ball is used with diamond slurry to wear through the film until the substrate is reached. The film is then put under an optical microscope and simple geometry is used to calculate the coating thickness.

Table 1 shows the typical range of properties of the described coatings, showing a combination of high hardness and adhesion, good corrosion resistance and very low wear and Coefficient of Friction (COF).

Table 1 – Summary of DLC Film Properties from this Novel Process

Hardness (GPa)	20
Modulus (GPa)	150
Wear (mm^3/Nm)	1E-7
COF	< 0.15
Scratch Adhesion (N)	> 15
Thickness (µm)	1 – 60
Corrosion resistance (15% HCL – 19hrs)	No damage to substrate
Corrosion resistance (10% NaCl – 19hrs)	No damage to substrate

3.2. Corrosion Resistance

Corrosion resistance was investigated using two aggressive sour autoclave conditions to simulate corrosion behavior in sour well environments. The sour autoclave testing follows the procedure outlined in the NACE TMO 185 standard [7]. The high temperature, high pressure, three phase autoclave test (liquid, hydrocarbon and gas) has been extensively used as an accelerated corrosion test to characterize performance of coatings in simulated oilfield environments. Samples from the interior of 3” internal diameter carbon steel pipes were used. The samples had a coating thickness of 40µm and a hardness of 11 GPa.

Figure 3 describes the conditions and shows the tested sample after 30 days of exposure for the first autoclave test. The gas phase contained both H_2S and CO_2 which are the common contaminants associated with corrosion in oilfield tubular components. The hydrocarbon phase is 100% Xylene and the main liquid phase uses distilled (DI) water. Prior to the test, three mechanical indents were made through the coating surface to expose a bare steel surface to each phase in order to assess the ability of the film to protect the underlying steel pipe in the presence of voids and/or mechanical damage to the surface layer. Also, an epoxy masking agent was used to coat the back and edges of the specimens so that they would not be exposed to the test. As is evident in Figure 3 there is no bulk attack of the sample surface after exposure to the autoclave conditions and more importantly there is no undercutting or accelerated corrosion observed at the mechanical indents. This clearly demonstrates the damage tolerance of the film as well as the resistance to undercutting in the presence of any type of film defect.

The second autoclave test, again for 30 days of exposure, involved high concentrations of H_2S and CO_2 as well as a much higher temperature of 190°C in order to simulate some very aggressive down well conditions. Figure 4 describes the test conditions and shows some images of the sample after test. The first autoclave test involved having a significantly higher ratio of CO_2 to H_2S. In this second test, the ratio is reversed whereby the H_2S content is higher than CO_2 which it generally understood to be more aggressive. Conducting tests over a broad range of concentrations demonstrates a large window of H_2S environments where the described DLC based coating will protect the underlying steel pipe. Figure 4(a) shows an image of the coating surface after test and Figure 4(b) shows the uncoated side of the sample after test. Looking at these figures it is clear that the bare metal outer diameter has corroded significantly in the autoclave which confirms is the aggressive nature of this procedure. It is also demonstrates how the described internal coating could protect the internal surface against corrosion in oilfield tubulars and other pipe applications. Comparison of the corroded outer diameter surface to the internal diameter surface shown in Figures 4(a) and 4(c) shows there is no evidence of attack and that the DLC coating is providing an excellent, well adhered barrier to prevent corrosion. Figure 4(c) is an image of the coating sample after it has been cleaned with DI water and acetone. This figure further demonstrates the excellent corrosion resistant properties of this film and any marks that are on the coating surface are due to water-acetone stains which occurred during the cleaning process.

These high pressure/temperature autoclave tests simulate the challenging corrosion environments encountered in some common down well environments and the results demonstrate the ability of DLC coatings to protect against varying concentrations of H_2S and CO_2. The coating has performed well under these conditions indicating that it could a viable solution for these oil and gas applications. These DLC based coatings have also been tested in various other corrosive environments, such as hydrochloric acid submersion and salt water spray. Results from these tests have been previously reported [7] and support the excellent corrosion resistance of these barrier type DLC surface layers.

3.3. Abrasion Resistance

Two tests of the described DLC coatings have also been performed to analyze the resistance to wear and abrasion under different conditions. In the first test, a wet slurry abrasive media is used which follows the ASTM G75 procedure and in the second a dry abrasive media is used following the ASTM G65 test procedure. The samples used were 1” x 0.5” flat carbon steel substrates.

Table 2 – Wet Slurry Abrasion Test Conditions using a Falex Miller Machine

ASTM G75 Wet Slurry Abrasion Test Conditions	
Stroke speed (spm)	48
Stroke length (in)	8
Duration (cycles)	5760
Duration (min)	120
Test Load (lbf)	5
Temperature (°C)	Ambient

In the wet slurry abrasive test (ASTM G75), samples are analyzed on a Falex Miller machine with the general testing conditions described in Table 2. This system measures the mass loss of the sample over time to determine how much abrasion has taken place in the coating. The sample is loaded inside the wet slurry with a 5 lb weight. A rotating crank is used to set up a reciprocating motion to move the sample back and forth inside the slurry. For this test, the slurry was a mixed concentration of 50% sand by weight in a solution of 30% NaCl and 70% DI water. The sand type used is AFS 50/70 grit silica test sand. Further details on the test procedure can be found in the ASTM standard [9].

A comparison was made between a DLC coated carbon steel substrate and a bare carbon steel substrate to determine the relative mass loss under the described test conditions. The DLC based sample had a thickness of 77 µm and a hardness of 17 GPa. Figure 5 shows the mass loss for each sample measured after 6 hrs. As the figure shows, the DLC based coating has reduced the mass loss by over 80% as compared to the uncoated substrate. This G75 test, and the high sand content slurry that was utilized, demonstrates the ability of DLC based coatings to protect steel pipes under conditions of abrasive fluids commonly encountered in oil and gas wells. Examples of these conditions include mud slurry during drilling or reciprocating wear under rod lift conditions. Even under conditions with high solids content such as sand, the coating protects the pipe.

The second abrasion test uses the procedure detailed in ASTM G65 where a rotating rubber wheel and dry sand is used to abrade the surface over time. The volume loss is calculated to determine the resistance of the coating to direct abrasion. The same sand was used as the G75 test. Table 3 details the test conditions that were used. Additional information on the procedure and method of calculation for the volume loss can be found in the ASTM standard [10].

Table 3 – Dry Rubber Wheel Abrasion Test Conditions

ASTM G65 Dry Rubber Wheel Test Abrasion Test Conditions	
Wheel speed (rpm)	200
Duration (cycles)	1000
Duration (min)	5
Test Load (lbf)	30
Sand Flow (g/min)	300-400
Wheel Diameter (inch)	9

A comparison between coated and uncoated samples was carried out to measure the ability of DLC coatings to protect the metal surface from sand type abrasive wear. The bare metallic samples analyzed were a tool steel sample (TS) with a hardness of 6.5 GPa and a super duplex stainless steel sample (SSDS) with a hardness 2.4 GPa. For comparison, both the hardened tool steel and the super duplex were coated with a 33 µm DLC coating with a hardness of 19 GPa.

The volume loss results are shown in Figure 6 for the four samples. The coated sample greatly reduces the amount of material being removed under dry sand erosion conditions even when compared to a common abrasion resistant material such as hardened tool steel. The improvement is due to the high intrinsic hardness of the DLC coating as well as the low coefficient of friction [1]. The high hardness and slippery nature of the DLC surface [8] facilitate the sand particles sliding over the surface with minimal interaction with the bulk coating. Previous wear testing in the presence of different lubricants as well as dry media confirm DLC coatings improve the wear rate and reduce the COF under a broad range of conditions [8]. This result confirms that in sliding wear applications, such as rod pumps and sucker rods, protecting the internal diameters with DLC would be expected to promote longer component life.

4. CONCLUSIONS

A novel hollow cathode plasma enhanced chemical vapor deposition technique can deposit thick, multilayer DLC films on the internal diameter of metal pipes. The DLC coatings impart excellent corrosion, abrasion and wear resistance to the bare metal surfaces. The deposition technique is well suited to treating enclosed internal surfaces, such as the tubing and piping used in the oil and gas industry and these same benefits apply to other industries such as automotive, military and aerospace. The excellent corrosion resistance of the coatings was demonstrated through accelerated autoclave tests which have shown the ability of DLC films to provide both protection and surface damage tolerance in the presence of a range of very aggressive temperature, H_2S and CO_2 conditions. The ability of DLC to provide protection under both wet and dry highly abrasive conditions was described and showed significant improvement over bare metal even when compared to traditional wear prevention solutions such as hardened steel. The unique coating technology facilitates the formation of thick, well adhered, highly protective layers of DLC on internal tubing surfaces and provides a new solution to protect these critical components from the increasingly aggressive environments seen in many exploration and production activities today.

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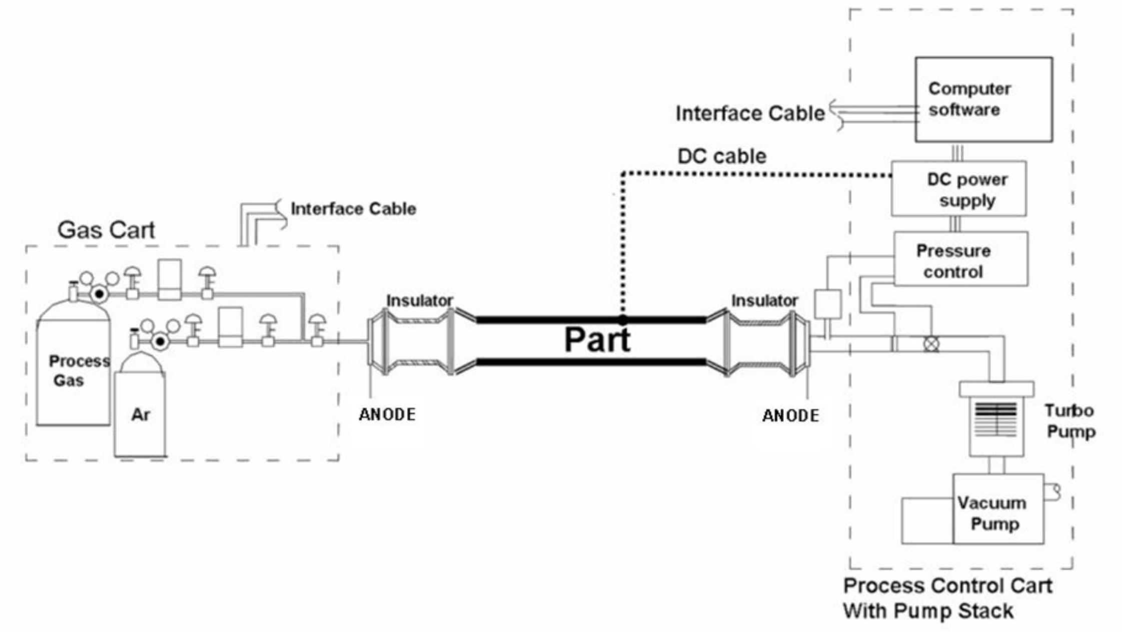


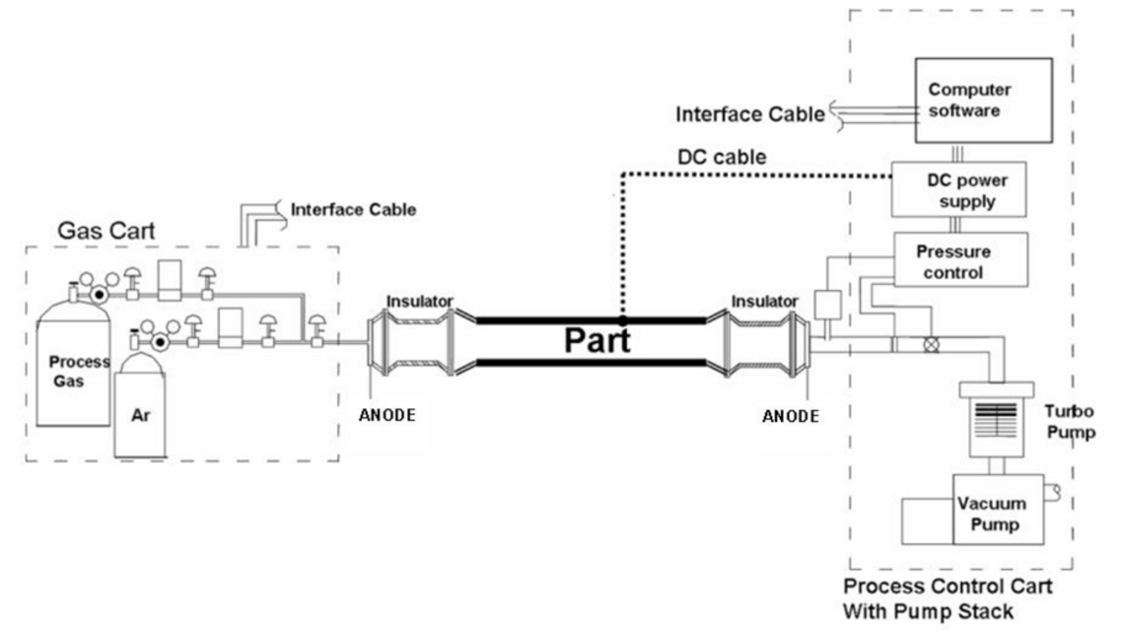
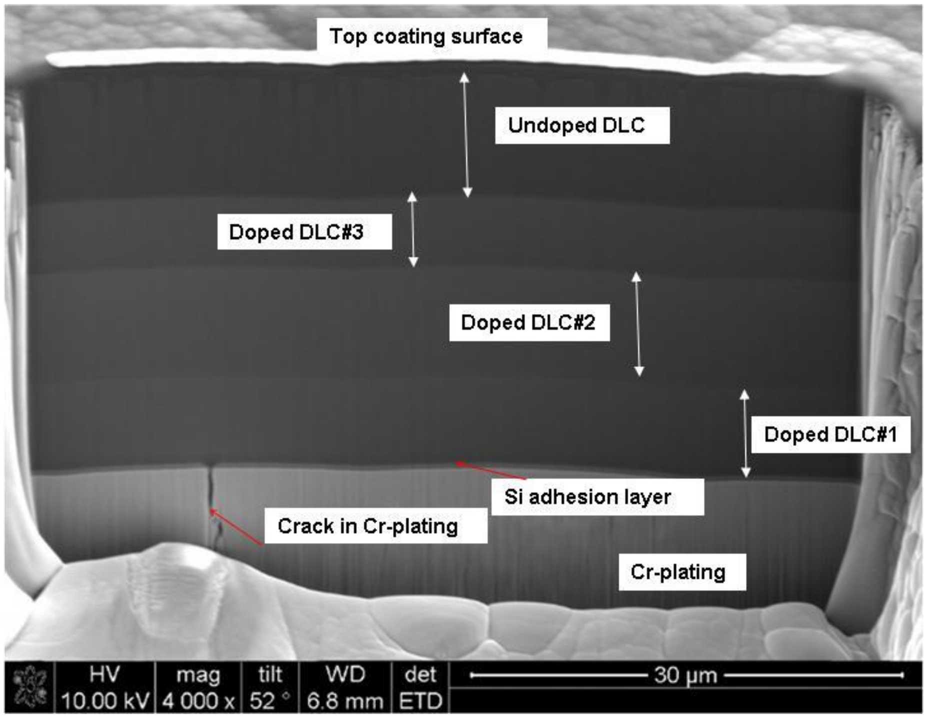


Figure 1 – Schematic of PECVD Deposition System [5]



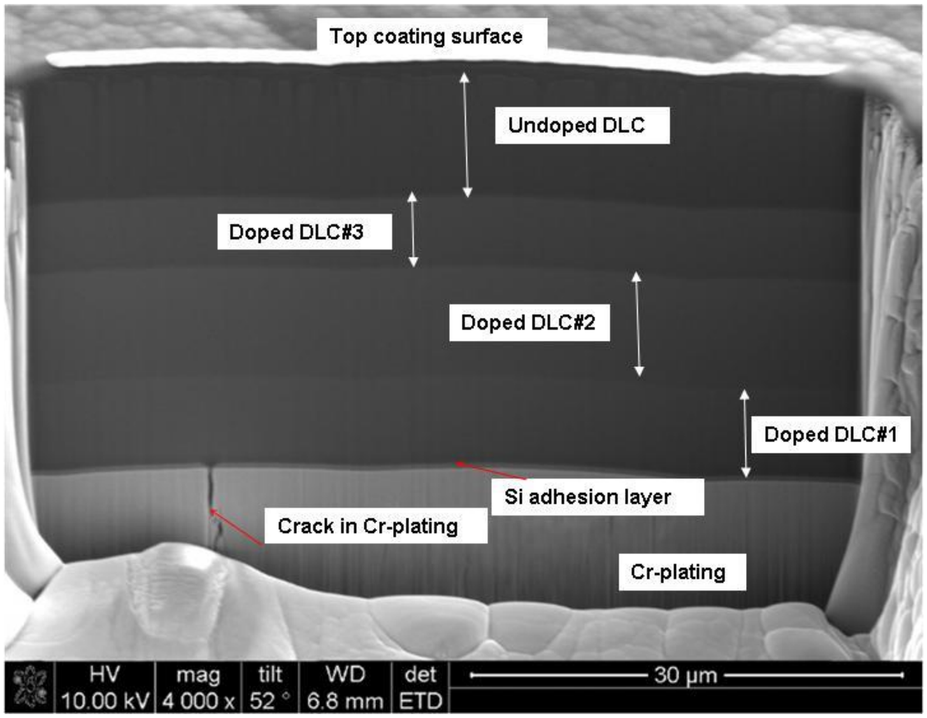
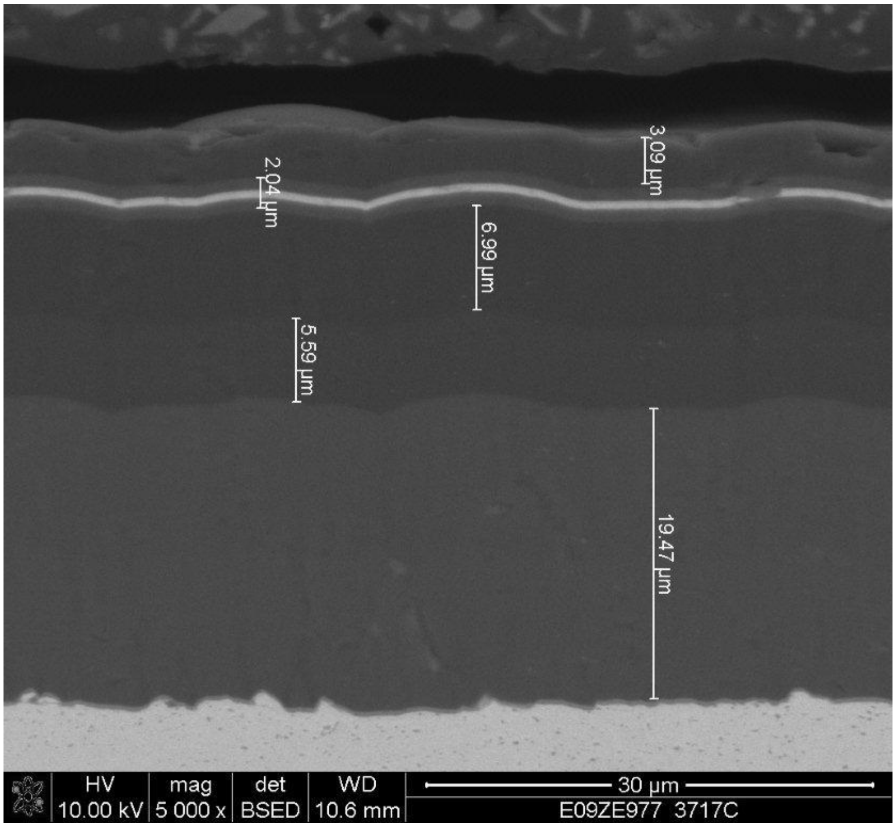


Figure 2a – SEM Image of Typical DLC Multilayer Stack of Roughly 30 µm Total Thickness Used for Protection of Internal Pipe Diameters



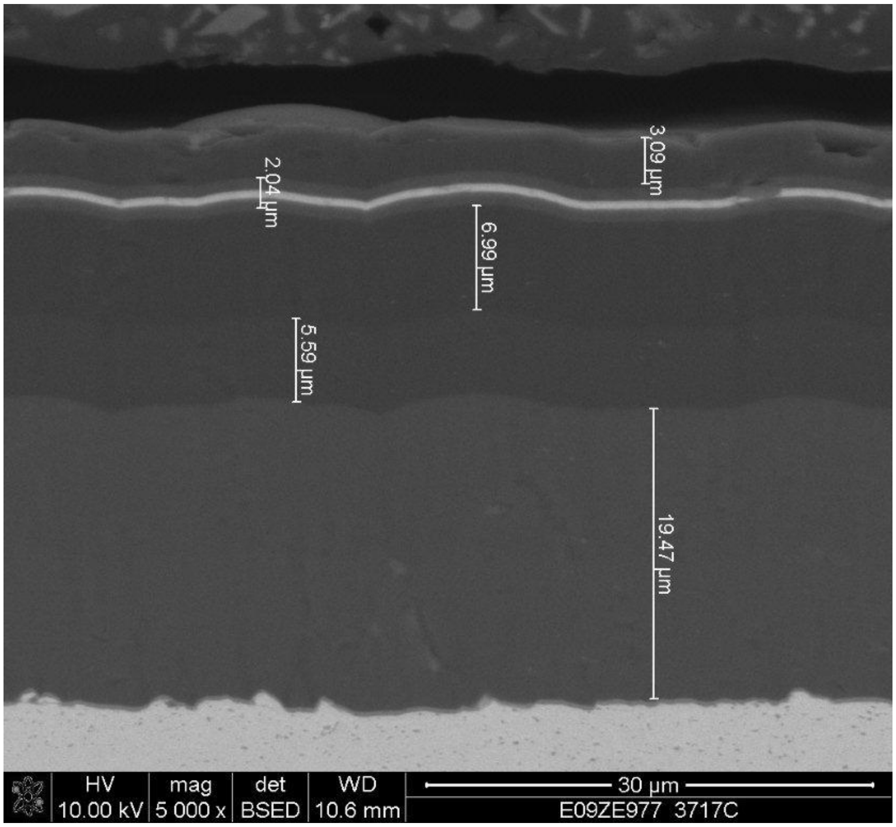
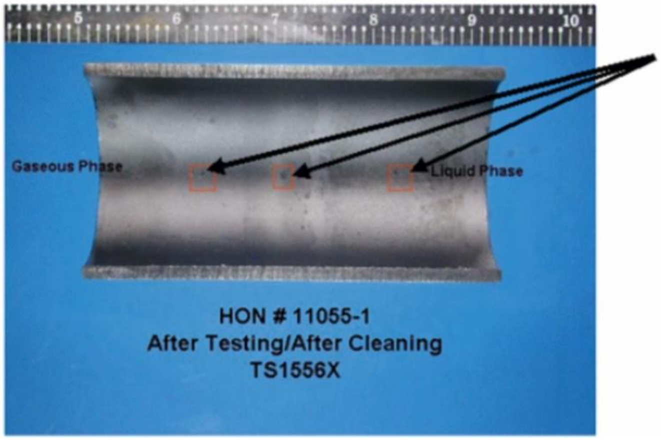


Figure 2b – SEM Image of Typical DLC Multilayer Stack of Roughly 37µm Total Thickness Used for Protection of Internal Pipe Diameters

The conditions of the autoclave for the duration of the test are as follows:

Temperature	90° C
Pressure	1000 psig
Gas Composition	1% H_2S, 85% Carbon Dioxide CO_2, 14% Methane CH_4
Organic Liquid Phase	Xylene
Aqueous Phase	DI Water
Exposure Time	30 days



3 indents prior to test. No undercutting shown after test

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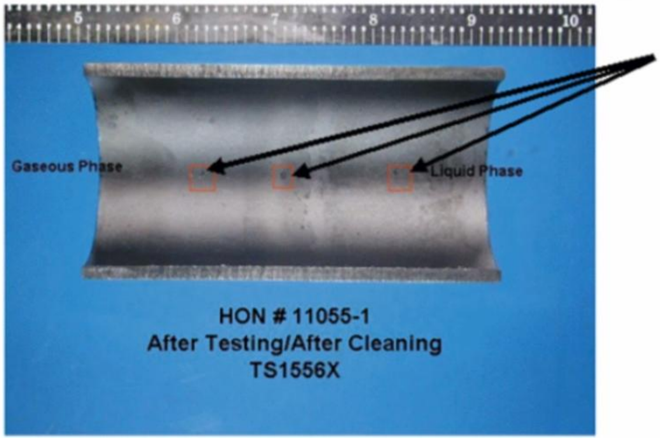
Pressure	1000 psig
Gas Composition	1% H_2S, 85% Carbon Dioxide CO_2, 14% Methane CH_4
Organic Liquid Phase	Xylene
Aqueous Phase	DI Water
Exposure Time	30 days



3 indents prior to test. No undercutting shown after test

Figure 3 – 30 Day Sour Autoclave Test Conditions and As-Tested Sample

Temperature	190°C
NaCl brine (Aqueous Phase)	40,000 mg/kg chloride ions
H_2S partial pressure at temperature	350 psia
CO_2 partial pressure at temperature	250 psia
Exposure time	30 days

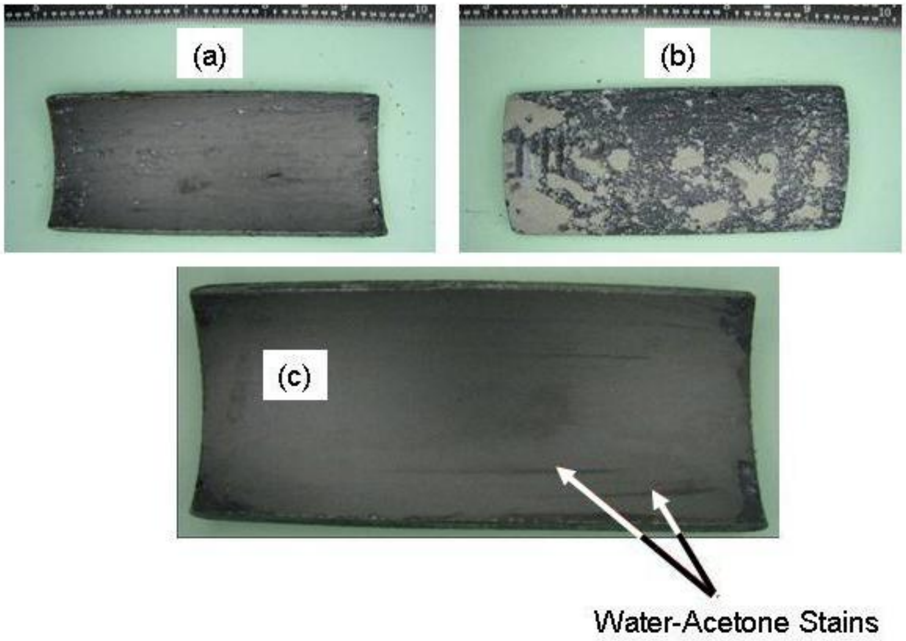
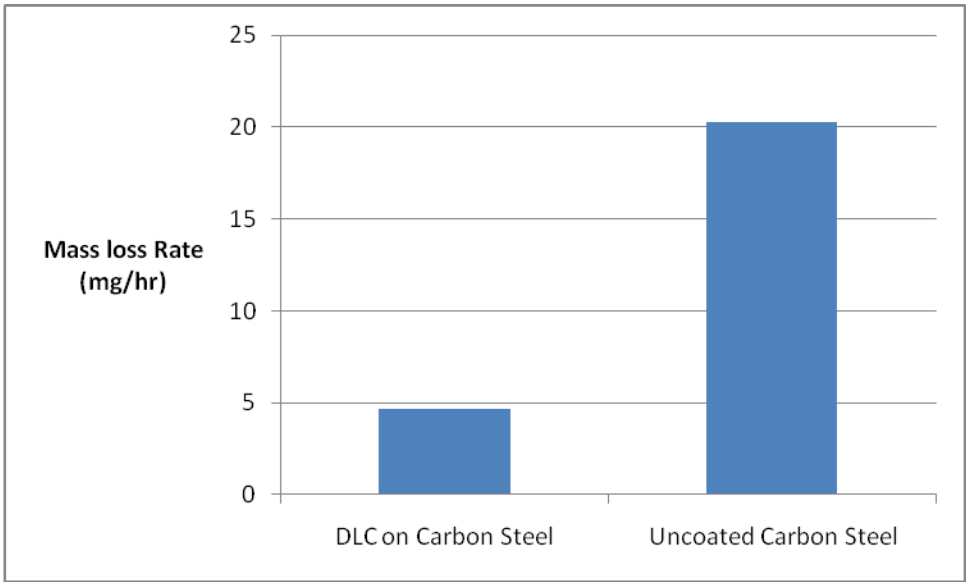


Figure 4 – 30 Day Sour Autoclave Conditions and As-Tested Sample with Higher Temperature and H_2S Conditions



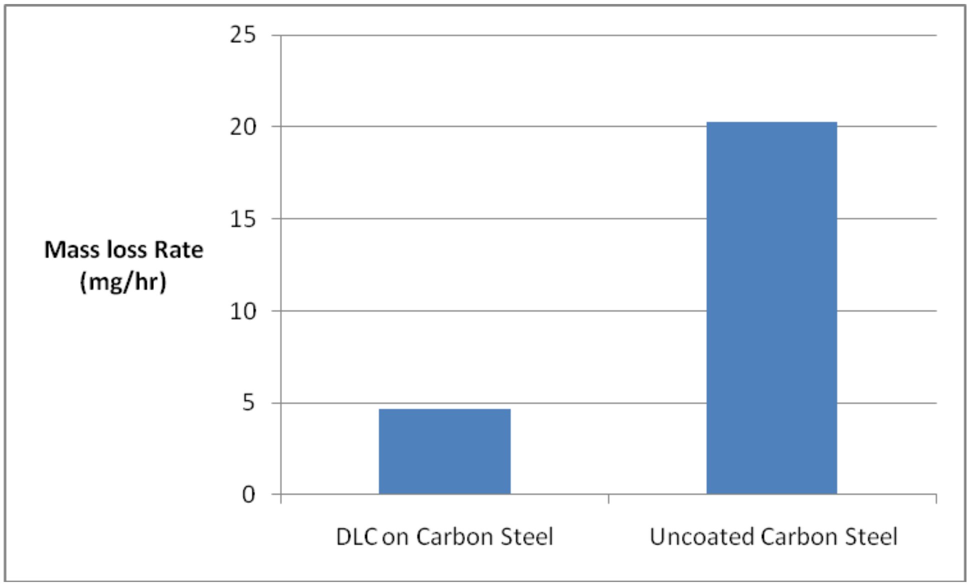
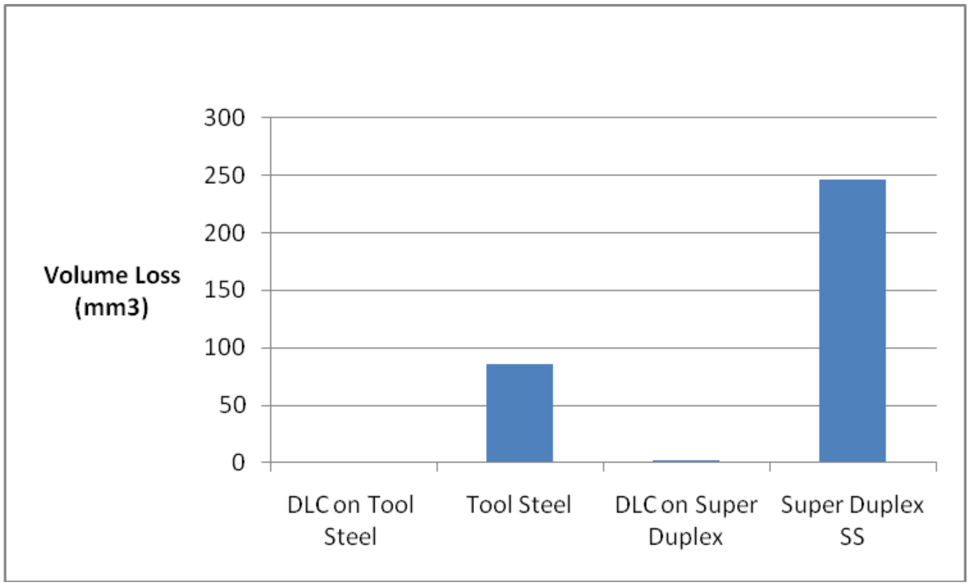


Figure 5 – Mass Loss Comparison for DLC Coated Carbon Steel and Uncoated Carbon Steel Using an ASTM G75 Wet Slurry Abrasion Test. A DLC coating of 77 µm and a hardness of 17 GPa was used.



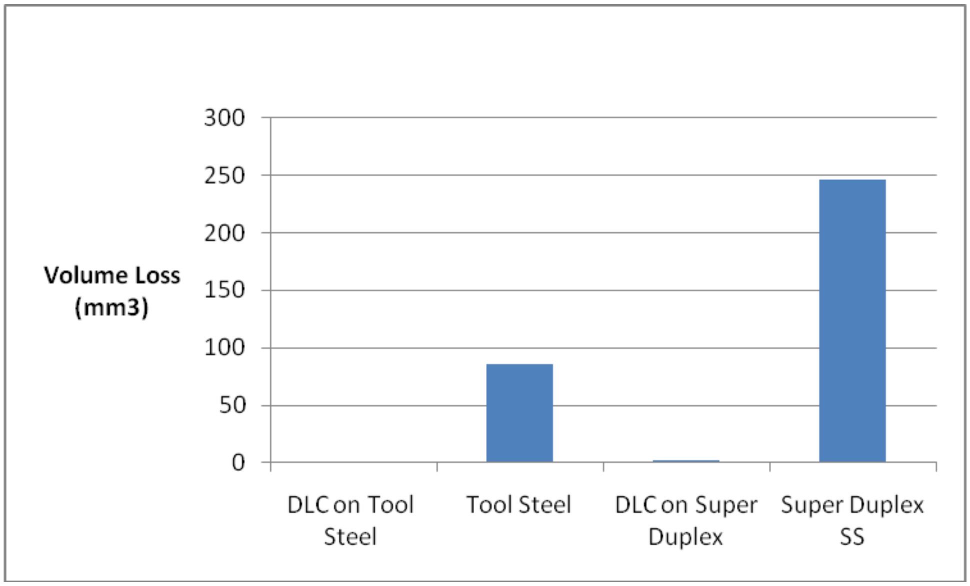


Figure 6 – Volume Loss Comparison for Coated and Uncoated Samples under ASTM G65 Dry Sand Abrasion Test for a Super Duplex Stainless Steel and a Hardened Tool Steel. A DLC coating of 33µm with a hardness of 19GPa was used to protect the super duplex and tool steel base materials.