Investigation of DLC-Si Film Deposited Inside a 304SS Pipe Using a Novel Hollow Cathode Plasma Immersion Ion Processing Method

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ABSTRACT

A novel hollow cathode plasma immersion ion processing method is developed and used to deposit silicon containing diamond like carbon (DLC-Si) coatings inside a one foot long 304 stainless steel (304SS) pipe with 1.5 inch diameter and 0.065 inch wall thickness. A multilayer DLC-Si coating structure was deposited using a combination of carbon and silicon precursors starting with silicon-rich adhesion layer. Result shows that the interface between the substrate and adhesion layer contains silicon as well as substrate constituents. Within this interface, isolated crystalline structure embedded within amorphous matrix was present while deposited DLC-Si coating is amorphous. Data show that the layered DLC-Si coating structure not only improves the friction and wear performance of the internal surface of 304SS pipe but also improves the corrosion resistance. The hardness and modulus of the coating was measured at 19GPa and 138GPa, respectively. It is suggested that this new technology enables wide spread use of DLC based coatings to increase component life in applications where the internal surface of pipes are exposed to corrosive and abrasive environments especially in oil and gas industry.

INTRODUCTION

Diamond-like carbon (DLC) coatings have excellent properties such as high wear resistance, very low friction coefficient and high corrosion resistance [1-3]. Because of these excellent properties, DLC coatings have attracted great attention for use in various applications in industries such as oil and gas, semiconductor, medical and automotive. In the oil and gas industry, DLC coatings are especially expected to improve the tribological and corrosion performance of components that experience extreme environments. For piping or tubing that delivers corrosive material, obviously the interior surface that is in contact with the corrosive material is the surface that must be coated. There are several methods available to deposit DLC based protective coatings at the outer surface of component such as chemical vapor deposition (CVD), physical vapor deposition (PVD), electroplating, flame spray and sol-gel. However, coating internal surfaces remains a challenge especially for large aspect ratio (length to diameter ratio) components and very limited information is available in literature.

Various methods of coating the interior surfaces of tubes have been attempted whereby the source material to be coated is inserted into the tube and then sputtered or arced off onto the tube [4,5]. It is reported that a chamber based plasma assisted chemical vapor deposition (PACVD) can be used to deposit coating on small aspect ratio components such as small hollow pins (15mm x 100mm) with a thin layer of DLC-Si [6,7]. In contrast to the work presented here where, these processes use a separate chamber and have a much lower deposition rates, so that much thicker films, needed for corrosion and abrasion resistance, can not be deposited.

This article demonstrates the potential of a new technology to deposit multilayer DLC-Si based film on internal surfaces of pipes and presents microstructural, corrosion and mechanical performance data.

EXPERIMENTAL

Coating Deposition

A novel hollow cathode plasma immersion ion processing method is developed and used to deposit silicon containing diamond like carbon (DLC-Si) films onto the internal surface of a 304SS pipe. This method takes advantage of plasma ion immersion and hollow cathode plasma generated within the pipe itself allowing decomposition of precursor gases and subsequent deposition of DLC-Si based films. As seen in Figure 1, this is done by negatively pulse biasing the pipe, which acts as the cathode, with anodes attached at the ends. A gaseous precursor is introduced and ionized causing a coating to be deposited on the pipe, with by-products pumped out [8].

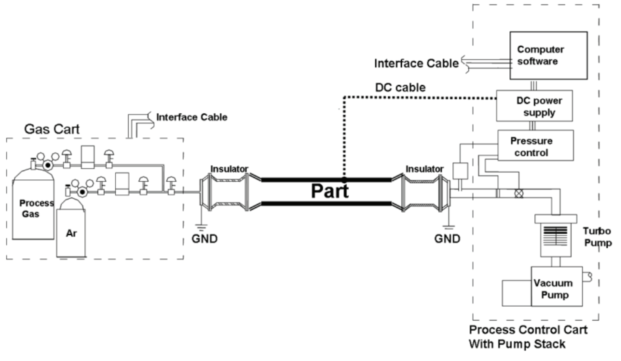

Figure 1: Diagram of Process Set-up [8].

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This technology can be used to deposit DLC-Si based coatings on internal surfaces of pipes with a variety of aspect ratio as seen in Figure 2. Data reported in this article is for 1 foot long pipe with 1.375 inch internal diameter. A detailed description of the technology is provided in reference [8].

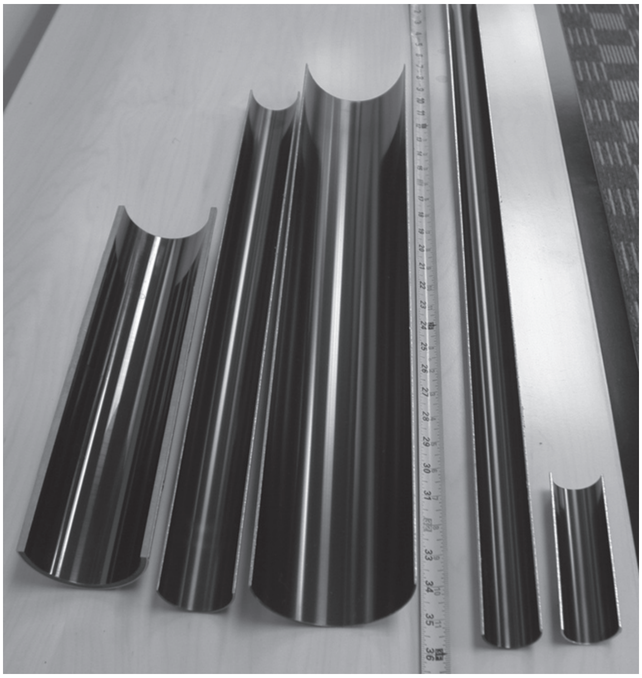

Figure 2: DLC-Si based coating deposited on internal surface of pipes with a variety of aspect ratios.

A multilayer coating structure was deposited and the coating consists of five layers: (1) SiC adhesion layer, (2) high silicon doped DLC layer (Si_xC), (3) first DLC layer, (4) low silicon doped DLC layer (Si_yC, x>y), and (5) final DLC layer as seen in Figure 3. A detailed description of the deposition method and process conditions is provided in reference [9].

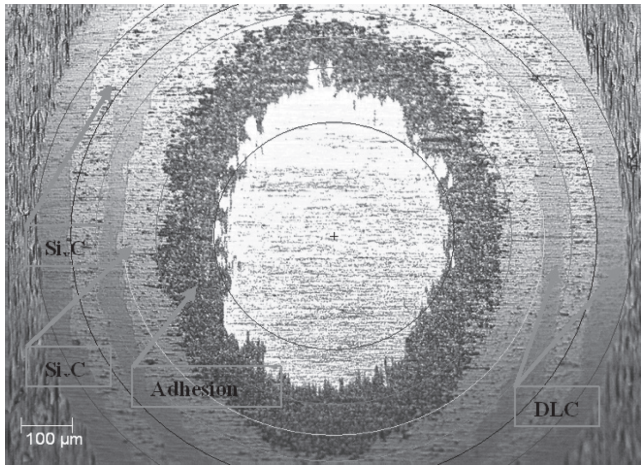

Figure 3: Optical micrograph of a Calotest crater showing multilayer coating structure.

A total coating thickness of 19.8μm was measured using a standard calotest method, see Figure 3. The layers consist of 4.5μm of SiC adhesion layer, 3.6μm of SixC, 3.2μm of first DLC, 3.2μm of SiyC and 5.2μm second surface DLC layer. Process conditions for each layer are summarized in Table 1. No external heating of the substrate was employed and the maximum temperature during the deposition (due to plasma heating) was 175°C.

Coating Analysis

For fracture, microstructure and composition analysis, a combination of techniques were used including scanning electron microscope (SEM) transmission electron microscope (TEM), electron dispersive X-rays (EDX), Raman spectroscopy techniques (Raman). A Dual beam focused ion beam (FIB) technique was used to prepare in-situ sample cross-sections for SEM as well as TEM samples.

Table 1: Summary of coating deposition process conditions.

Layers	Precursor	Pressure (mTorr)	Power (W)	Thickness (μm)	Avg. Deposition rate (μm /min)
Adhesion	Silicon precursor	70	240	4.5	0.3
SixC	Silicon and Hydrocarbon precursor	70	100	3.6	
DLC	Hydrocarbon precursor	70	100	3.2	
SiyC	Silicon and Hydrocarbon precursor	70	100	3.2	
DLC	Hydrocarbon precursor	70	100	5.2	

Tribological property characterization includes wear rate, coefficient of friction (COF), coating-substrate adhesion, hardness and modulus measurement. The method to perform wear testing is in accordance with ASTM G133-02 using a tungsten carbide ball with 5mm diameter, 10N load, sliding distance of 200 meters and stroke length of 10mm. Coating hardness and elastic modulus was tested using a micro-indenter as per reference [10]. Data reported in this article is based on a Vickers type indenter with an applied force to achieve a penetration of less than 10% of coating thickness and values obtained from the test are hardness and modulus reported in GPa.

Corrosion resistance analysis was performed by exposing sample coupons to 15% hydrochloric acid (HCl) and 10% sodium chloride (NaCl) solution at 70°C for 19 hours. Testing was performed at ambient pressure, temperature and humidity (unless otherwise stated). Visual and optical microscopy observations were performed for any failure mechanisms that may occur during this time and reported.

RESULTS AND DISCUSSIONS

The interface between DLC–Si coatings and steel substrate was investigated to understand the adhesion mechanism. Figure 4 shows bright field cross-sectional TEM micrograph of the interface (region 2) between the substrate and the first silicon-rich coating layer. A higher magnification dark field TEM micrograph of the same region is also presented. EDX analysis of region S1 to S4 shows that the interface between substrate and the adhesion layer contains substrate constituents as well as oxygen arising possibly from FIB sample preparation. Isolated crystalline structure is present within amorphous interface matrix while the silicon based adhesion layer is amorphous. Copper in the EDX is an artifact as the TEM sample grid is made of copper.

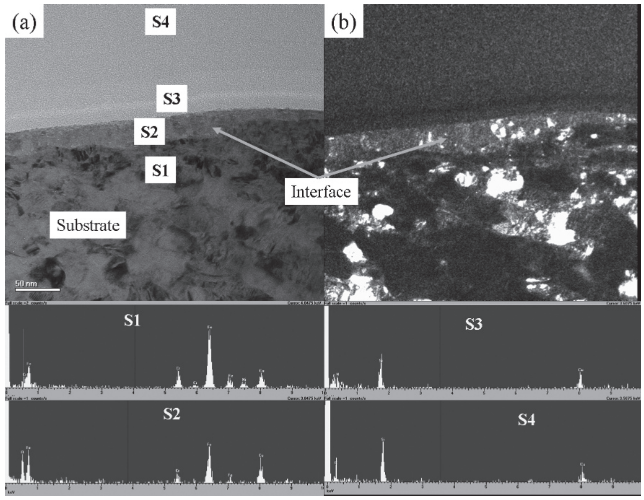

Figure 4: (a) Bright field and (b) dark filed TEM micrographs and associated EDX spectra showing substrate-coating interface.

Coating properties including hardness, modules, coefficient of friction and wear rate is presented in Table 2. It is clear that top DLC coating provides excellent COF as well as wear rate. Typically high sp^3 films have higher compressive stress in addition to higher hardness, which can limit the thickness of these films. However, we are able to deposit coating with high hardness with thicknesses up to 45μm indicating lower stress in the coating due to the presence of silicon dopant as well as layered structured [9].

The coating fracture behavior under Vickers indenter loading is presented in Figure 5. Figure 5a shows the top SEM view of indent area and Figure 5b shows the FIB cross-section of indented area. The sequence of events leading to coating fracture is: (1) plastic deformation in the substrate during loading, (2) crack formation in the coating, (3) growth of cracks (peak load), (4) propagation of cracks on unloading

Table 2: Young's modulus and Hardness of coating and 304SS substrate. Reported modulus and hardness is the average of five measurements along the length of 12 inch long pipe. Wear rate and coefficient of friction (COF) is also presented.

Film thickness (um)	Young's Modulus (GPa)		Hardness (GPa)		COF	Wear Rate mm^3/Nm
	DLC-Si	Substrate	DLC-Si	Substrate	DLC-Si	DLC-Si
19.3 micron	138	193	19.1	2	0.02	7.60E-07

at stress concentration point at sharp indenter edges and (5) delamination within layered structure. It is interesting to note that cracks propagate along the indenter edges likely due to stress concentration created by the sharp indenter edges during loading cycle. The benefit of a layered coating structure is evident as various layers present deflection points for a propagating crack.

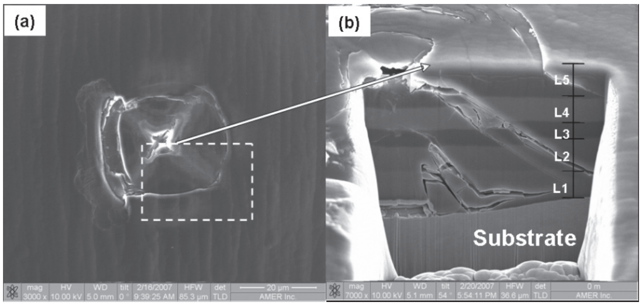

Figure 5: (a) Top view SEM of 5N Vickers indent, (b) Cross-section SEM of indented area after FIB.

Corrosion resistance was measured by exposing the sample coupons to 10% NaCl solution at 70°C and 15% HCl for 19 hours, see Figure 6. Figures 6a and 6b show photographs of a coated 304SS sample after exposure to HCl and 10% NaCl solutions. Optical inspection shows no damage to the substrate indicating that the DLC-Si coating provides excellent corrosion protection. DLC is a chemically inert material and acts as a physical barrier between the substrate and corrosive environment provided coating defects are minimized.

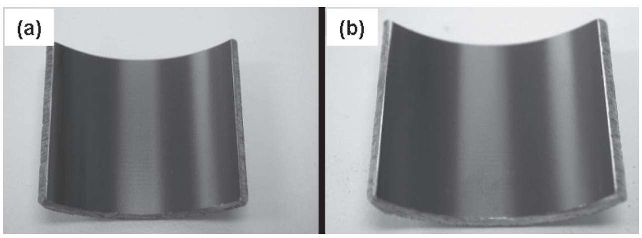

Figure 6: (a) DLC-Si coated internal surface of 304SS tube after 19hrs exposure to a 15% hydrochloric acid solution, (b) DLC-Si coated internal surface of 304SS tube after 19 hours exposure in 10% sodium chloride solution at 70°C.

CONCLUSIONS

A novel hollow cathode plasma immersion ion processing method is developed and used to deposit DLC-Si coating inside a one foot long 304SS pipe with 1.375 inch internal diameter. A layered coating structure was developed to improve fracture behavior of the coating while top DLC layer provided excellent wear and friction characteristics. Data showed that such coating provides excellent corrosion protection to the internal surface of pipes. Application of this coating technology is in industries such as oil and gas where tribological and corrosion performance improvement is expected for components such as pump barrels, down-hole pipes, drilling fixtures, drilling bores, and other down-hole tools.

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