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Corrosion and Wear Properties of Diamond-like Carbon Films Deposited Using a Novel PACVD Interior Coating Method

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ABSTRACT

A new enabling technology for coating the interior surfaces of cylinders, pipes, and various parts with a hard, corrosion and wear resistant diamond-like carbon (DLC) coating is described. The coating method utilizes plasma assisted chemical vapor deposition (PACVD) technology augmented by the generation of a hollow cathode discharge plasma within the pipe. Asymmetric direct current (DC) pulsing applies a large negative bias to the pipe generating the intense high density plasma providing a very small plasma sheath enabling the coating of complex geometries such as pipe threads while also adding the benefit of very high deposition rates.

Improving component lifetime under exposure to corrosive and abrasive environments is a high priority for many military and aerospace applications. Properties of this coating are discussed for different environments including exposure to hot and room temperature hydrochloric acid (HCl), NaCl brine solution, and hydrogen sulfide (H_2S) gas. Mechanical properties include high hardness, high adhesion, and excellent wear resistance in dry, wet and sand slurry environments.

INTRODUCTION

Military applications for internal metal components require protection from exposure to harsh environments from the hot sands of the desert to the ice of the artic and the corrosive salts of the sea to the high temperatures and stresses inside gun barrels. The DoD has many applications which battle corrosion, wear, abrasion and erosion on a daily basis. Many types of coatings are available for external applications but very exist few for internal surfaces.[1]

This paper will describe a new process for coating interior surfaces using a hollow cathode plasma immersion ion processing (HCPIIP) method.[2] This technique uses the hollow cathode effect (HCE) to generate a high density plasma within the part, which can then be used to form coatings within the part by introducing precursor gases which are ionized and coat the interior of the part.

Diamond-Like Carbon DLC films are known to produce extremely hard coatings with very low wear rates and low coefficient of friction (COF).[3-5] Most of the techniques for depositing DLC were slow << 1µm/hr and limited in thickness to <10µm due to high compressive stress in the film. This limits the use of DLC's for applications that require greater thickness such as corrosion or high velocity erosion.

An important advantage of the new internal coating method is the ability to use the high density HCE plasma to produce a high deposition rate coating (~1µm/min) and with the use of various precursors to tailor adhesion layers for specific substrates and to engineer blend layers to reduce film stress and enable thicker coatings needed for corrosion and abrasion resistance.

This study demonstrates the ability of this new PECVD technology to deposit DLC based coatings on the internal surfaces of pipes and other components to provide excellent wear and corrosion protection properties.

EXPERIMENTAL

A new hollow cathode plasma immersion ion processing (HCPIIP) method has been developed and used to deposit thick, hard wear resistant DLC films on a variety of metal substrates, including rough (~110µin Ra) carbon steel substrates. Figure 1 shows a diagram of the experimental set-up, here the part to be coated is biased as the cathode and anodes are placed at the openings of the pipe or tube. A DC pulse power supply is used so that high peak power pulses can be delivered to the plasma, this in conjunction with the hollow cathode effect (HCE) results in a high ion density, high deposition rate plasma. The HCE is produced by adjusting the pressure inside the tube in relation to the diameter of the tube such that high energy electrons will oscillate between opposing cathode walls causing multiple ionizing collisions.

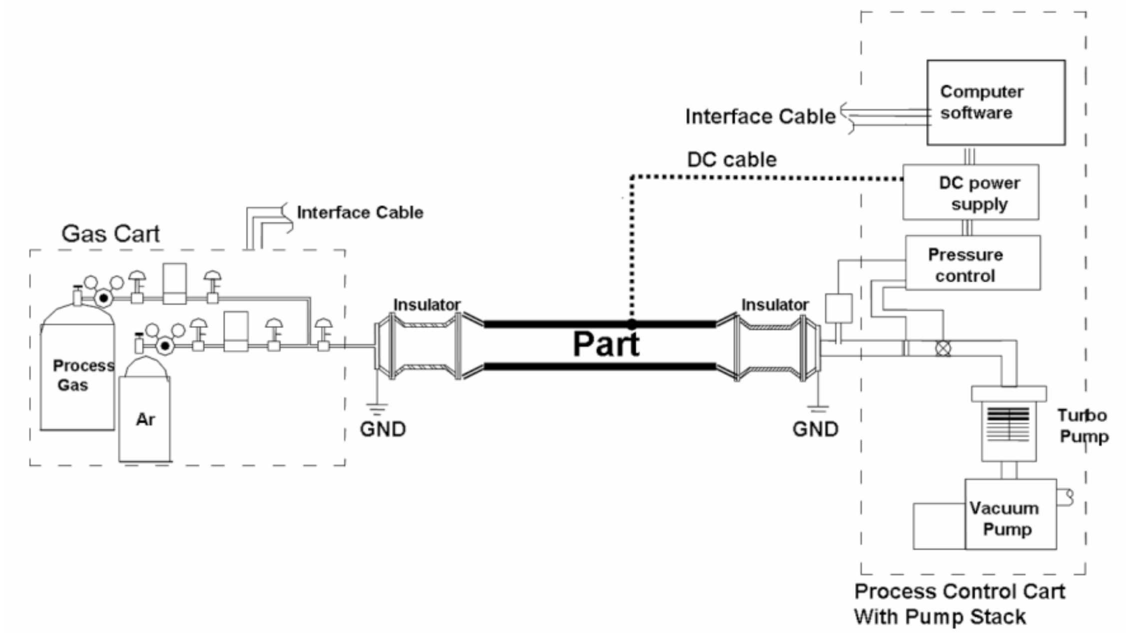

Figure 1. Schematic of hollow cathode immerion ion processing method developed for the coating of internal surfaces.[2]

This technology is being used to deposit amorphous hydrogenated DLC based coatings with a variety of dopants such as silicon, and germanium on internal surfaces of pipes and other components with a variety of aspects ratios as seen in Figure 2.

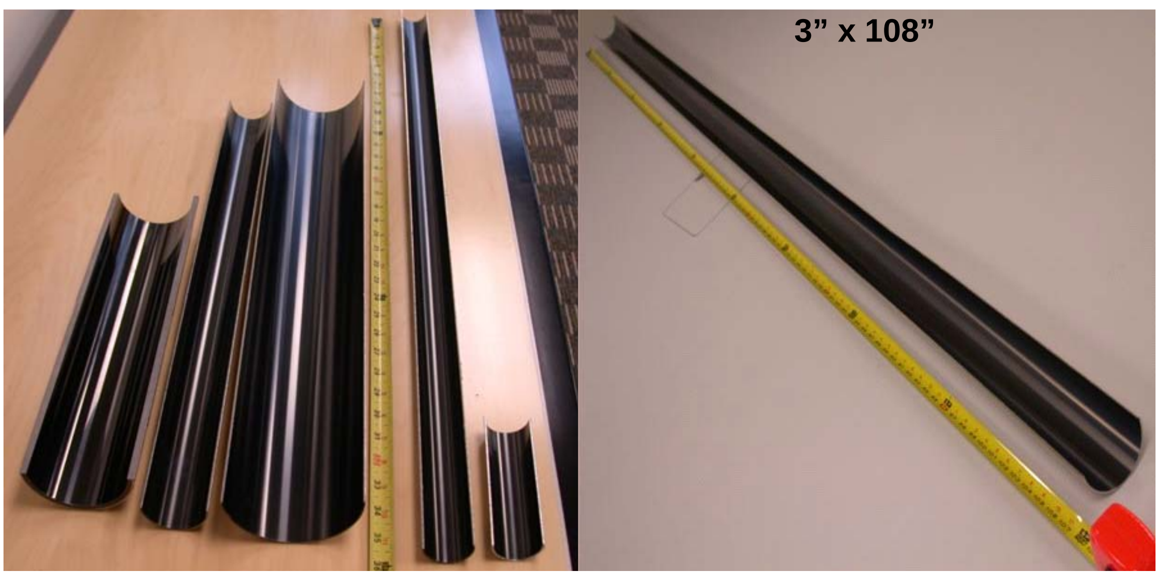

Figure 2. Variety of substrate types and aspect ratios coated with a DLC based hard, wear and corrosion resistant coating utilizing this novel PACVD method.[6]

Adhesion is promoted by several techniques. Surface oxides and other contaminates are removed either chemically via reduction reactions using a hydrogen plasma, physically by sputtering with argon, or a combination of both. Proper selection of adhesion layer chemistry promotes a strong bond between the substrate and the adhesion layer (typically, group IVb elements or metallic elements are used). High peak power bursts of Argon are optionally utilized to promote mixing of the adhesion layer and the substrate itself. A wide variety of conductive substrates have been coated with this technology including various high chrome and mild carbon steels, stainless steel, Inconel, Hastelloy, titanium, and aluminum. The data presented within are results from experiments performed using 2” diameter x 12” long 1020 carbon steel substrates with an approximate inner diameter (ID) of 1.75” and 1.5” (1.375” ID) x 12” long type 304L or 316L stainless steel pipes.

Typical process parameters are shown in Table 1 for a process using a silicon carbon based adhesion layer. This recipe was used to deposit a layered coating structure inside a stainless steel pipe.

Table 1. Typical process steps for deposition of a silicon based adhesion layer and layered DLC inside a 1.5" x 12" SS316 pipe.

Process Step	Chemistry	Pressure (mTorr)	Power (W)	Thickness (μm)
Clean	Argon / Hydrogen	70	200	N/A
Adhesion	Silicon precursor	70	240	5
Blend	Silicon and hydrocarbon precursor	70-100	160	15
DLC	Hydrocarbon precursor	120	160	10

Coating Analysis

The coatings are evaluated for adhesion, hardness, modulus, coefficient of friction (COF) and wear factor (both dry and in wet media with abrasive particles using bentonite mud). Adhesion is measured using the single point scratch test technique per ASTM C1624, in which a 200μm diamond stylus is moved across the coating with a progressively increasing load and the critical load (Lc3) is recorded upon film delamination from the substrate. The maximum load achievable with using a CSM Micro-Combi is 30N. A tribometer is utilized for linear reciprocating wear measurements per ASTM G133-02 using a 5mm tungsten carbide ball. Coating hardness and modulus are measured using a micro-indenter with a Vickers tip and an applied force to achieve a penetration depth of less then 10% of the coating thickness.[7] Anti-erosion performance of the coating is characterized utilizing ASTM G76. Corrosion properties are measured by exposure to 15% HCl and 10% NaCl and also by exposure to NACE specification #TM0185 sour autoclave test. TEM and SEM analysis of the coating is also performed.

RESULTS

Hard, conformal, corrosion resistant coatings with an extremely low wear factor have been deposited on the internal surfaces of a variety of substrate materials with a wide range of geometries including very small, 3/8” ID, and large 8.5” ID pipes, as well as threaded couplers, “tees,” and “dead-end” bottle geometries. This paper will discuss results on two different standard coupons, 1.5” x 12” SS316, and 2” x 12” 1020 carbon steel. Hardness values can be tailored from 10 to 28 GPa by varying process conditions and precursor gases independent of substrate material. Table 2 shows hardness, adhesion and wear properties for two different types of multi-layer DLC coatings with a pure DLC cap on two different substrates, 1020 carbon steel and type 316SS pipe. High hardness provides improved wear and abrasion protection with some tradeoff due to increased stress in the film, which is alleviated with the use of a strong adhesion layer and stress reducing blend layers.

Table 2. Mechanical properties of layered DLC on stainless and carbon steel pipes.

Film thickness (μm)	Scratch Adhesion (Lc3 - N)	Young's Modulus (GPa)		Hardness (GPa)		COF		Wear Coefficient ($mm^3/N \cdot m$)	
		Film	Substrate	Film	Substrate	Film	Substrate	Film	Substrate
41 μm on 1020CS	>30	100	171	14.6	2.7	0.05 (dry), 0.04 (bentonite)	0.12 (dry), 0.15 (bentonite)	1.56E-06 (dry), 1.97E-06 (bentonite)	3.40E-05 (dry), 3.80E-05 (bentonite)
25 μm on 316SS	22	184	193	22.7	2	0.01 (dry)	0.05 (dry)	4.72E-07 (dry)	3.4E-04 (dry)

Linear reciprocating wear data includes COF and wear coefficient k. Where k is defined as; k ($mm^3/N \cdot m$) = (volume of material removed (mm^3) / (Load in Newtons) x (length of wear track in meters). Wear data for a variety of substrate types and coatings under a 25N load are shown in Figure 3 for dry conditions and in Figure 4 for wet abrasive conditions using bentonite mud, a viscous clay containing silica particles, as the lubricating fluid.

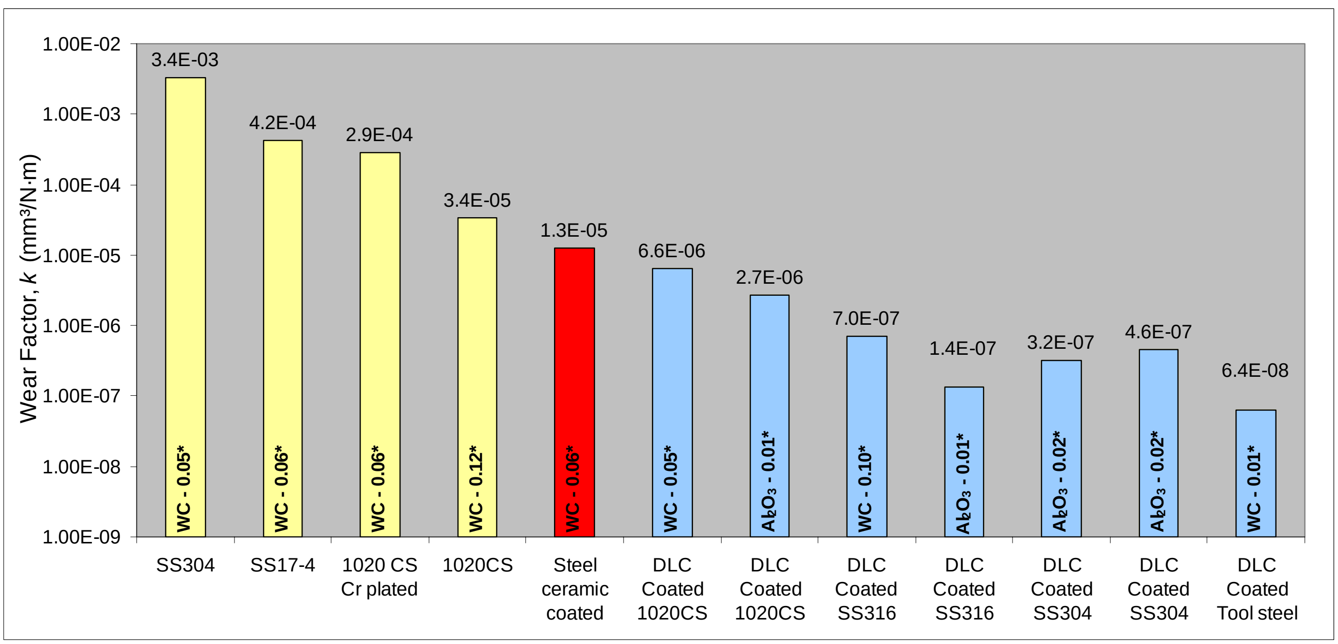

Figure 3. Wear factors and (*) COF, along with ball type, for coated and uncoated steels under dry conditions with a 25N load per ASTM standard G133-02.

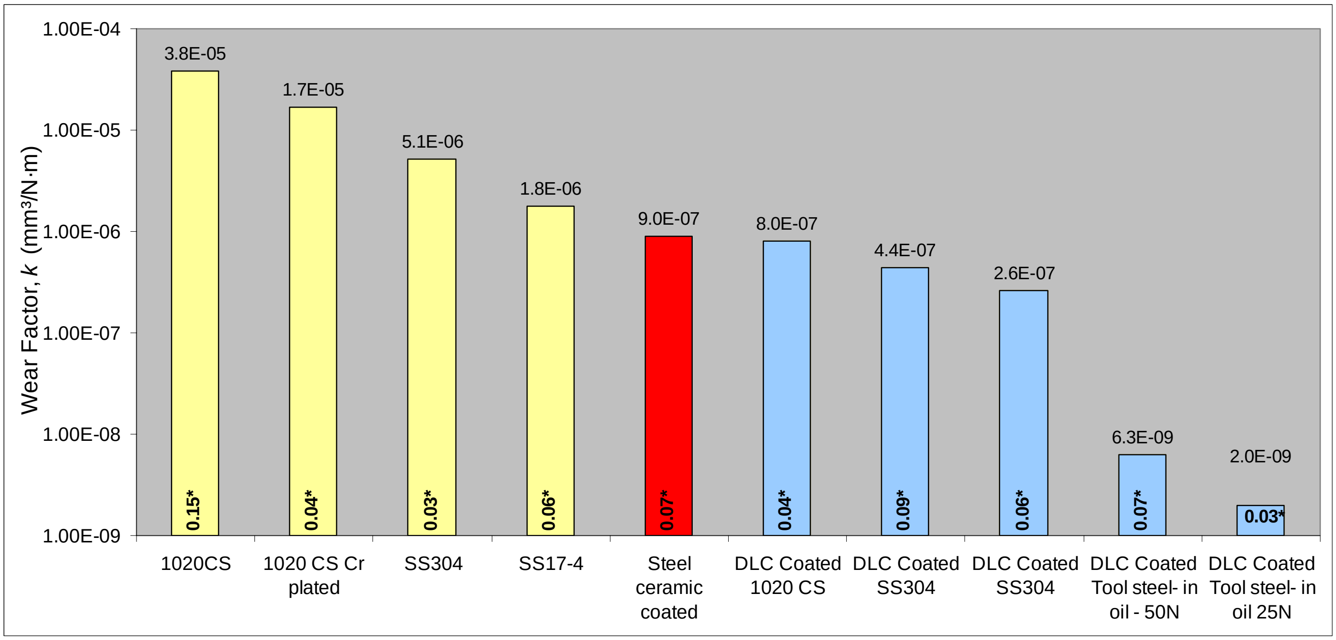

Figure 4. Wear factors and (*) COF for coated and uncoated steels under lubricated conditions using bentonite, a viscous mud containing silica particles, under a 25N load unless otherwise stated.

In addition to excellent wear resistance, the deposition method can "heal" minor surface defects and provide a barrier to corrosion and chemical attack. Figure 5 shows an SEM cameo image of a cross section of the coating indicating the multi-layer structure and the good coverage over surface defects. In a SEM cameo image, the color is related to the atomic number, with brighter or warmer areas having higher average atomic number compositions. The brightest area at the bottom of the image is the steel substrate. The adhesion layer deposited from a silicon containing precursor is next followed by layers of silicon doped DLC layers, with the darkest layers deposited from a hydrocarbon source only. Notice the continuous nature of the film, no cracks or dislocations are present in the coating around or above surface defects as a result of the high plasma density and thin plasma sheath associated with the deposition mechanism.

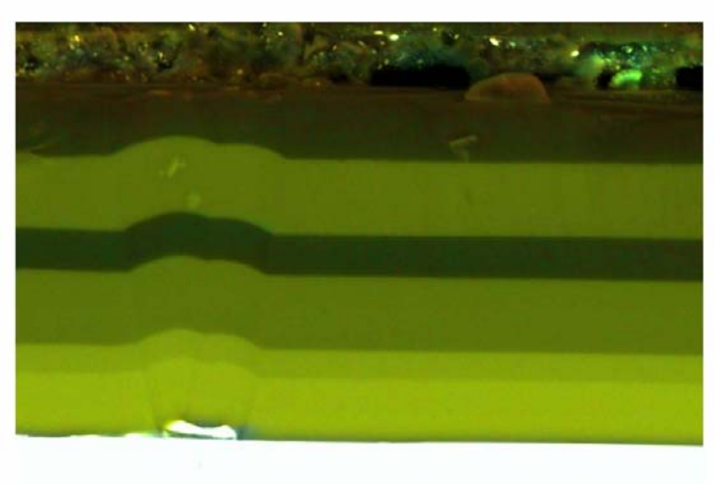

Figure 5. SEM Cameo image of cross section of ~40µm film showing excellent coverage and continuous film even over surface defects.

Corrosion resistance is measured against many environments. Figures 6a and 6b show optical micrographs of a coated 1020 carbon steel sample after exposure to 10% NaCl brine solution at 160°F and 15% HCl solution at room temperature for 24 hours. The DLC is chemically inert and serves as a barrier between the corrosive agent and the substrate. Also of note is the lack of undercut attack from the site of a Rockwell C indent which intentionally breached the coating, or from the exposed edges of the saw cut section, indicating the good adhesion and chemical inertness of the coating layer, at the interface with the substrate, as suggested by the TEM images.

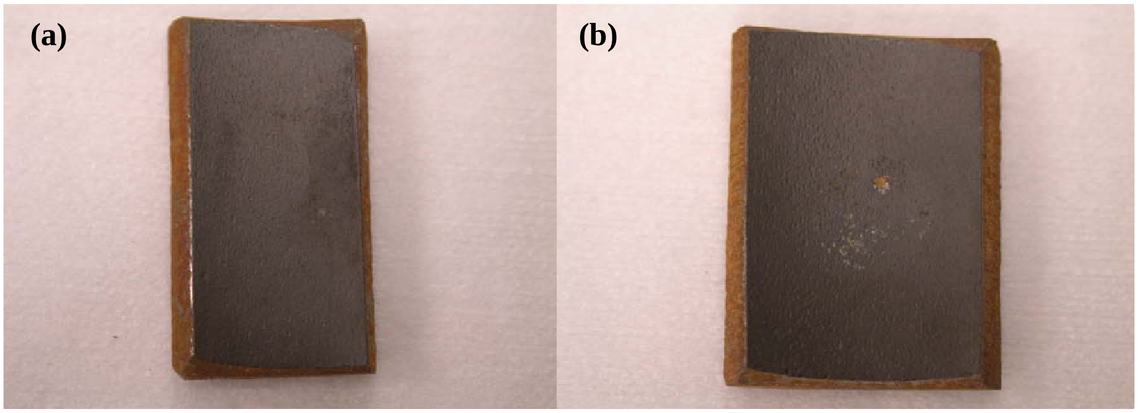

Figure 6. Optical micrograph of coated 1020 carbon steel sample afer exposure to (a) 10% NaCl brine solution at 160°F and (b) 15% HCl at room temperature for 24 hours.

Sour autoclave as per NACE TM0185 Results are shown for a 2” diameter by 12” long carbon steel pipe that has been cut into 4” long sections and exposed to sour autoclave conditions according to NACE TM0185 standard. The pipe sections are exposed to three phases: an aqueous phase of deionized water, and organic phase of xylene, and a gaseous phase consisting of 1% hydrogen sulfide (H_2S) of 14% methane (CH4) and 85% carbon dioxide (CO_2). The autoclave was run at a pressure of 1000 psig and 90°C for thirty days. Figure 7 shows the images of the film prior to exposure (labeled Figures 1, 3, and 5 inset corresponding to the middle 4”, entry 4”, and exit 4” with respect to gas flow during the coating process) and after the sour autoclave test (labeled Figures 2, 4, and 6). All sections of the coating passed the NACE standard test with no damage or blistering of the coating and additionally passed a 67.5V holiday (pinhole) test both before and after autoclave exposure.

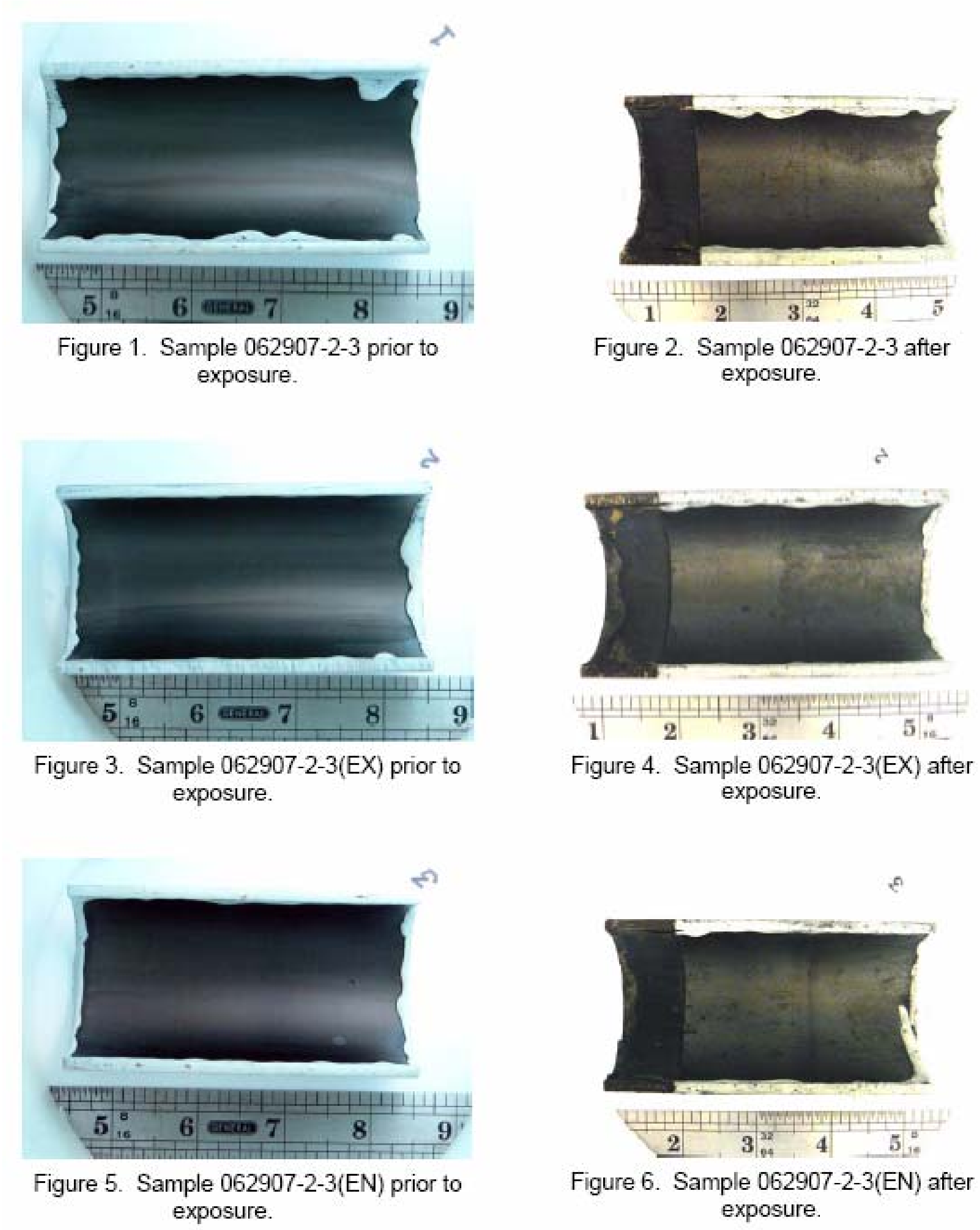

Figure 1. Sample 062907-2-3 prior to exposure.

Figure 2. Sample 062907-2-3 after exposure.

Figure 3. Sample 062907-2-3(EX) prior to exposure.

Figure 4. Sample 062907-2-3(EX) after exposure.

Figure 5. Sample 062907-2-3(EN) prior to exposure.

Figure 6. Sample 062907-2-3(EN) after exposure.

Figure 7. Photographs of a coated 1020 carbon steel pipe before (Figs. 1, 3, & 5) and after (Figs. 2, 4, & 6) a 30 day sour autoclave test at 1000 psig and 90°C with three phases (1) DI water, (2) Xylene, & (3) Gas composed of 1% H_2S, 14% CH_4, and 85% CO_2.

Recently work has been done using hydrogen to further improve the interface properties between the metal substrate and the adhesion layer of the coating, as this interface is critical for preventing both delamination of the film under high load conditions such as abrasion and erosion and also to prevent corrosive undercut of the film in the event the film is damaged or penetrated. The interface between the

DLC-Si coatings and the steel substrate was investigated using TEM microscopy for hydrogen pretreatment and argon pretreatment. Figure 8a shows an argon pretreatment which produces a 16nm amorphous film which contains FeO. By comparison, Figures 8b and 8c show the steel silicon interface layer following a hydrogen treatment. Figure 8c shows a close up with the interatomic spacing of approximately two angstroms which is the same as (110) Fe, indicating that the interface is chemically etched of any FeO. This oxide free interface layer produces higher thickness normalized scratch adhesion critical loads on type 316L stainless steel pipe substrates. Average normalized scratch adhesion for Argon pretreatments is approximately 80% while a process utilizing the new hydrogen plasma pretreatment is just over 100% yielding a 25% increase in normalized scratch adhesion performance by engineering the surface. Here scratch adhesion is normalized to thickness due to the effect of a soft substrate supporting a hard coating, this effect results in an increase in the load that can be applied as the coating thickness increases due to reduced deformation of the substrate.[6]

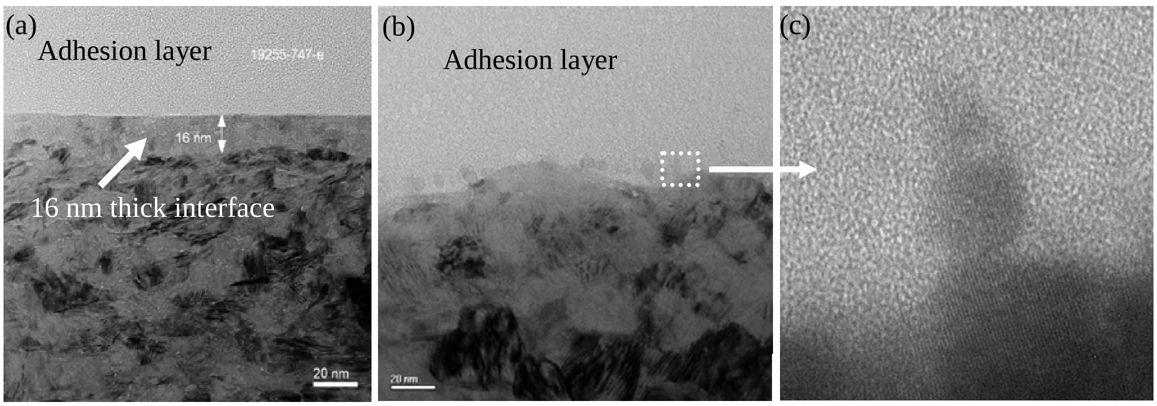

Figure 8. TEM images of SS316/adhesion layer interface after (a) Argon plasma pretreatment, (b) Hydrogen plasma pretreatment, (c) close up of figure 8b showing an interatomic of ~2Å equivalent to that of (110) Fe indicating complete etch of the FeO found in 8a.

CONCLUSIONS

A novel hollow cathode plasma immersion ion processing method is developed and used to deposit thick multi-layered diamond-like carbon films on the internal surfaces of pipes and other parts. A layered coating structure was developed including a chemical etch of surface oxides with a hydrogen plasma pretreatment to improve adhesion of the coating while a DLC top layer provides excellent wear resistance and low coefficient friction for sliding wear. Data showed that such a coating provides excellent corrosion protection to internal surfaces of pipes against aggressive and varied environments including hydrochloric acid, brine, and sour autoclave conditions. Application of this coating technology in industries such as oil and gas is expected to yield tremendous benefits in performance and lifetime of various components such as pump barrels, downhole pipes, drilling fixtures, and drilling bores, etc. The benefits of this coating technology for application in the harsh environments faced by the armed services may include reduced wear and longer lifetime of critical components such as large and small bore gun barrels among others.

REFERENCES

1. H. Wesemeyer, H. Veltrop, US patent 5026466, “Method and device for coating cavities of objects,” June 25, 1991

2. Boardman et. al., “Method and System for Coating Internal Surfaces of Prefabricated Process Piping in the Field,” US Patent Application, Pub. No. US 2006/0011468 A1

3. J. Robertson, “Diamond-Like Amorphous carbon”, *Materials Science and Engineering*, R 37, pp. 129-281, 2002

4. H. Mori and H. Tachikawa, “Increased adhesion of diamond-like carbon–Si coatings and its tribological properties”, *Surface and Coatings Technology*, 149, pp. 225–230, 2002

5. A. Varma, V. Palshin and E. I. Meletis, “Structure-property relationship of Si-DLC films”, *Surface and Coatings Technology*, 148, pp. 305–314, 2001

6. T. Casserly, K. Boinapally, M. Oppus, D. Upadhyaya, B.Boardman, A. Tudhope, “Investigation of DLC-Si film deposited inside a 304SS pipe using a novel hollow cathode plasma immersion ion processing method”, Proceedings of the Society of Vacuum Coaters Annual Technical Conference, 2007

7. CSM Instruments SA ,Rue de la Gare 4,Galileo Center,CH-2034 Peseux, Switzerland