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A Novel Corrosion Resistant Internal Coating Method Using Hollow Cathode PECVD Technology with Improved Hardness

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Abstract

A novel technology developed for coating the internal surfaces of parts from small components to production pipe will be described. The coating is appropriate for use in many environments for corrosion, erosion and wear reduction. The process technology that enables the coating of interior surfaces with a hard, wear and corrosion resistant DLC layer will be described. Additionally the development of improved hardness of the DLC will be decribed, based on the selection of precursor and process parameters hardness of > 25GPa has been achived while maintaining a high deposition rate.

Introduction

The new process technology uses a Plasma Enhanced Chemical Vapor Deposition (PECVD) process that has been modified to use a high density, hollow cathode plasma that enables a high depositon rate that is generated based on the diameter of the pipe and the pressure, this in conjunction with DC plasma pulsing enables very high deposition rates of >0.3 micron/min. Coating properties down the length of a steel pipe are controlled by adjusting process parameters. Ion bombardment is used to improve film quality by biasing the part negative. The process doesn't require a traditional vacuum chamber, but uses the pipe or part itself as the vacuum chamber. In addition to improving corrosion resistance the films are hard, pure, amorphous, dense and wear resistant.

Environmentally friendly precursors such as acetylene or other hydrocarbons are used to deposit inert corrosion resistant DLC based films with the potential to replace environmentally damaging precursors such as hexavalent chromium. Adhesion is improved by adding silicon to the DLC layer at the steel interface, and wear resistance and corrosion is improved with a pure DLC cap layer.

This paper reports the results of a study evaluating the use of a range of hydrocarbon precursors with respect to hardness, adhesion and deposition rate. With the optimization of process parameters the hardness was improved from an average of 15GPa using acetylene to 25 GPa using butene, while maintaining a high deposition rate. Several authors have reported the effect of ion energy per carbon atom on the hardness of DLC coatings. Optimum ion energy per carbon atom of approximately 70eV is reported for high hardness and high sp3 content with softer films reported at lower or higher energy per carbon atom. *(Roberston, 2002)* The size of the hydrocarbon precursor molecule will effect this energy as the molecule will break apart on impact with the substrate, for example as an acetylene molecule ion is accelerated across the plasma sheath with an energy of 1000 eV compared to a butene molecule with the same bias, and assuming a collisionless sheath, the acetylene will have an energy of 500eV per carbon atom and the butane will have an energy of 250eV per atom. Higher hydrogen content has also been reported to reduce hardness of DLC coatings. Since the process used in this report operates at a higher pressure of ~70mtorr, there are some collisions in the plasma sheath so the correlation to precursor size is not straightforward; additionally there is significant radical based chemical film growth at these pressures that will also be affected by the precursor used.

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 inside a one foot long SS304 pipe with 1.375 inch diameter (aspect ratio of 8.72). This method takes advantage of plasma ion immersion and high density hollow cathode plasma generated within the pipe itself allowing decomposition of precursor 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.

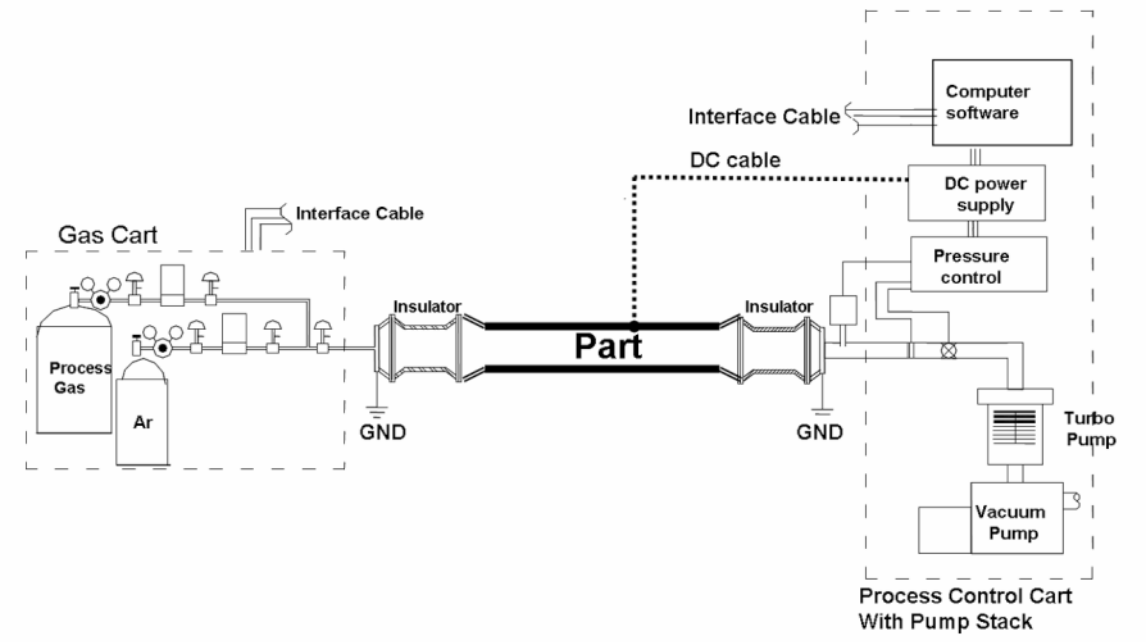


Figure 1 - Diagram of Process Set-up

This technology is being used to deposit amorphous hydrogenated DLC-Si based coating on internal surface of pipes with a variety of aspect ratio ranging 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 *(Boardman, 2006).*

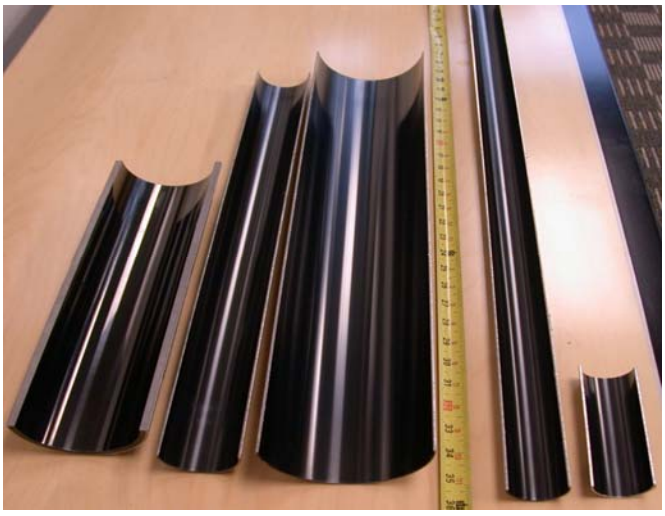


Figure 2 – DLC-Si based coating deposited on internal surface of pipes with a variety of aspect ratio. *(Casserly, 2007)*

A layered coating structure was deposited onto the internal surface of a SS304 pipe. The layers consist of five layers: (1) Silicon carbon adhesion layer (2) silicon doped DLC layer (3) DLC 'cap' layer (4) silicon doped DLC layer (5) DLC 'cap' layer.

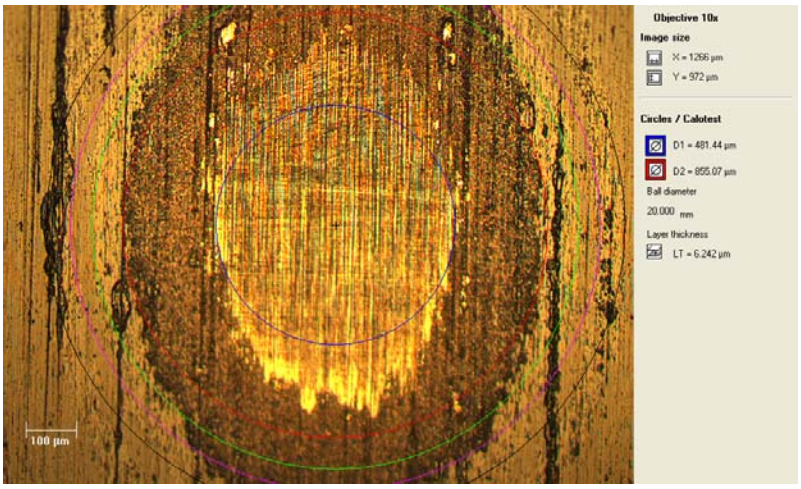


Figure 3: Optical micrograph of a Calotest crater showing structure of a C_2H_2 film.

A total coating thickness of 23.9um was measured in middle of the pipe using a standard calo-test method, see Figure 3. Approximately the layers consist of 6.2um of silicon carbon adhesion layer, 2.9um of silicon doped DLC layer, 2.2um of DLC 'cap' layer, 2.8um of silicon doped DLC layer, 9.8um of DLC 'cap' 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 175C.

Layers	Precursor	Pressure (mTorr)	Power (W)	Thickness (um)	Deposition rate (um/min)
Adhesion	Silicon precursor	70	240	6.2	0.5
SiC	Silicon and Acetylene precursor	90	160	5.7	
DLC	Acetylene precursor	110	160	12.0	

Table 1: Table summarizing coating deposition process conditions

Coating analysis

For microstructure and composition analysis, a combination of techniques were used including scanning electron microscope (SEM) transmission electron microscope (TEM), electron dispersive X-rays (EDX). Tribology property characterization includes wear rate, coefficient of friction, coating-substrate adhesion, hardness and modulus measurement. The method to perform wear testing is in accordance to ASTM G133-02 using a tungsten carbide ball with 5mm diameter. A normal load of 5N with a sliding distance of 200 meters and stroke length of 10mm was used.

The method of measuring adhesion is by ASTM C 1624 Single Point Scratch Test, where a 200µm diamond stylus is moved across the coating with progressively increasing load and the critical load (Lc3) is recorded upon film delamination from the substrate, the maximum load achievable with our tool is 30N.

Coating hardness and elastic modulus is tested using a micro-indenter as per reference.*(CSM)* In this test, an indenter tip, normal to the sample surface, is driven into the sample by applying an increasing load up to a predefined value. The load is then decreased until partial or complete relaxation of the material occurs. The resultant load-depth curve is then used to

calculate mechanical properties such as hardness and elastic modulus. 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. Values obtained from the test are hardness and modulus (in GPa).
Corrosion resistance analysis was performed using exposure to 15% HCl at room temperature and 10% NaCl at 70C. Figure 6 shows the sample coupons of the coating exposed to 15% HCL and 10% NaCl for a duration of 24 hours. Visual and optical observations were performed for any failure mechanisms that may occur during this time and reported.

RESULTS AND DISCUSSIONS

The interfaces between DLC–Si coatings and steel substrate were investigated, 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. Figure 4a shows high magnification bright field cross-sectional TEM micrograph of the interfaces (region 2 in Fig. 4b) between the substrate and the coating. The XRD pattern shows some crystalline structure is present within amorphous matrix at the interface while graded DLC-Si films are amorphous (region 9). Figure 4b shows bright field TEM and associated EDX analysis which shows that the interface between substrate and the layered adhesion layer contains mixing of substrate constituents with adhesion layer constituents. The copper is an artifact as the sample grid is made of copper. This layered adhesion structure with mixing of substrate and adhesion layer constituents provides excellent adhesion preventing corrosive undercut in acid or NaCl exposure test even on rough (~110μin Ra) carbon steel substrates.

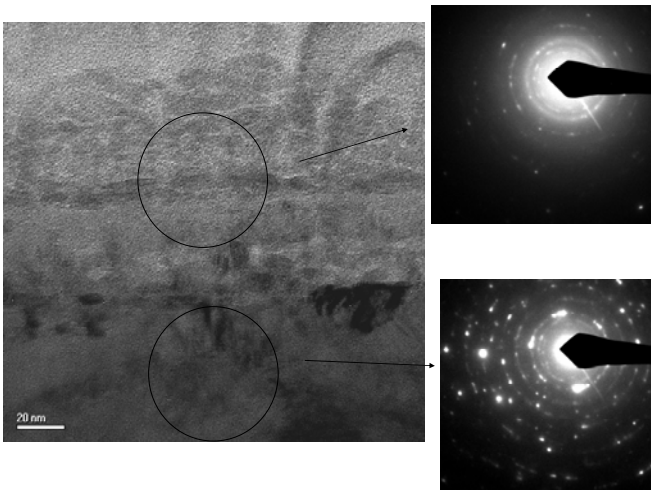


Figure 4a: High Mag. TEM micrographs and XRD pattern

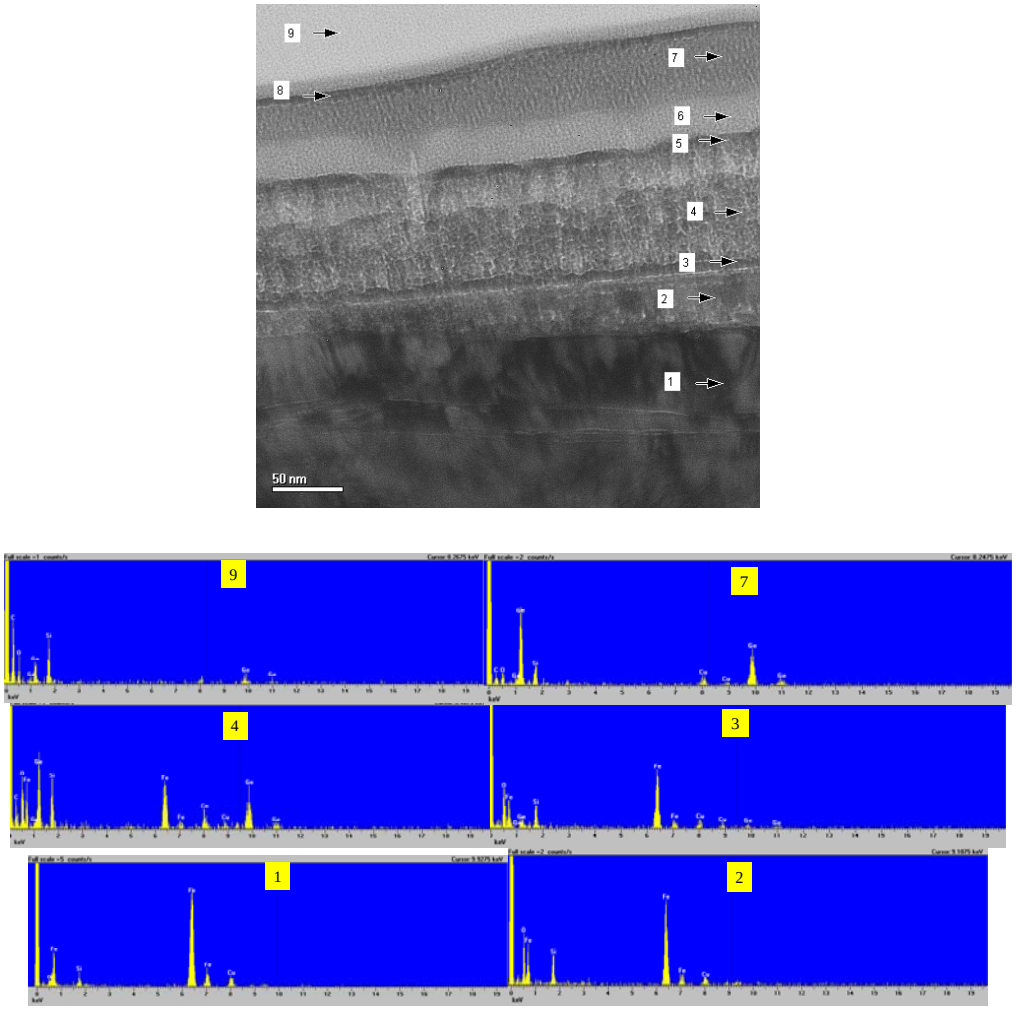


Figure 4b: Bright field TEM micrographs and associated EDX spectra showing substrate-coating interface.

Figure 5 shows a SEM cross-section of a similar multilayer coating deposited by the same technique. In the SEM cameo image, the color is related to the atomic number, with brighter or warmer areas having higher average atomic number compositions. Thus the brightest area is the steel substrate followed by the regions deposited with silicon precursor and the darkest regions being deposited with hydrocarbon precursor, while the intermediate brightness areas are deposited with blended silicon and hydrocarbon precursors. This SEM also shows the lack of any voids and the excellent coverage that is obtained over substrate defects by this coating technique.

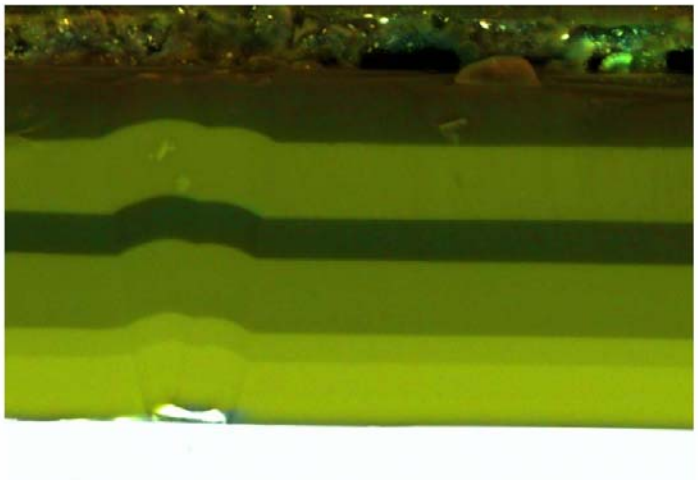


Figure 5: SEM cross-section of ~40 micron film on steel substrate.

Coating properties including hardness, modules, adhesion by scratch test and coefficient of friction and wear rate (abrasive bentonite mud environments) is shown in Table 2. It is clear that top DLC coating provides excellent hardness, COF as well as wear rate in comparison to an uncoated stainless steel substrate. Typically high sp^3 content DLC films have higher compressive stress in addition to higher hardness, which can limit the thickness of these films. However, we are able to deposit coatings with high hardness with thicknesses up to 80μm indicating lower stress in the coating due to addition of dopants as well as layered structured. *(Casserly, 2006)*

Film thickness (um)	Adhesion (N)	Young's Modulus (GPa)		Hardness (GPa)		COF
		DLC-Si	Substrate	DLC-Si	Substrate	DLC-Si
23.9	18	100	190	14	1.0	0.26(Bentonite)

Material	Wear Rate Bentonite (mm^3/Nm)
DLC-Si	8.8E-07
304 SS	5.1E-06

Table2: Young's modulus and Hardness of coating of C2H2 film on 304 stainless steel substrate. Modulus and hardness is average of five measurements along the length of 12 inch long pipe. Wear rate and coefficient of friction (COF) is also presented.

Corrosion resistance is measured by exposure for 24 hours to 10% NaCl solution at 150F and 15% HCl at room temperature. Figure 6 (a and b) shows optical micrograph of a coated 304SS sample after exposure to HCl and brine solutions showing that DLC-Si coating provide excellent corrosion protection for the substrate. It is because DLC is chemically inert and acts as a physical barrier between the substrate and corrosion environment provided coating defects are minimized. It can also be noted that there is no corrosive undercut from the Rockwell C indent that was intentionally done to breach 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.

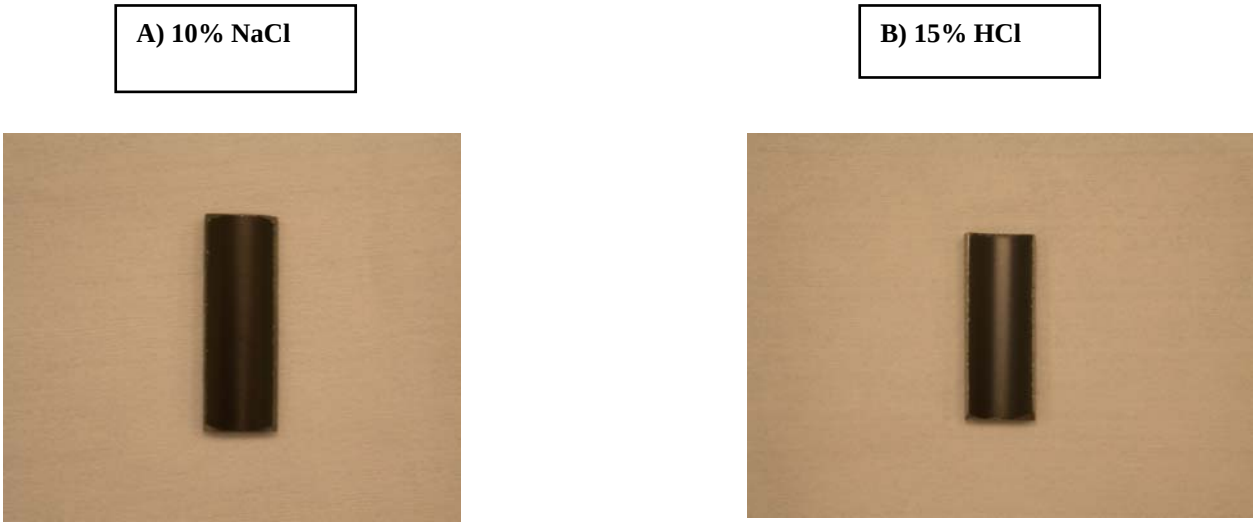
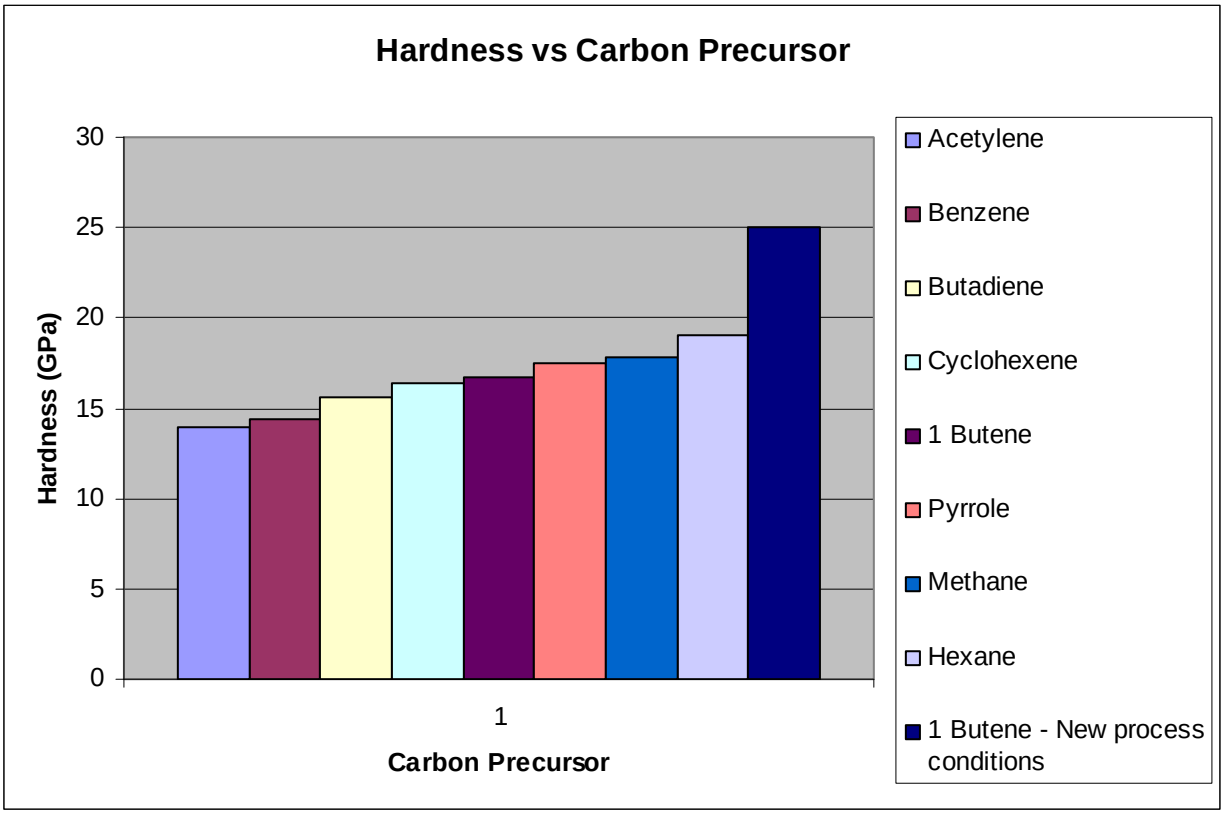


Figure 6: Optical micrograph of a coated 304SS sample after exposure to a) 10% NaCl b) 15% HCl solutions for 24 hours.

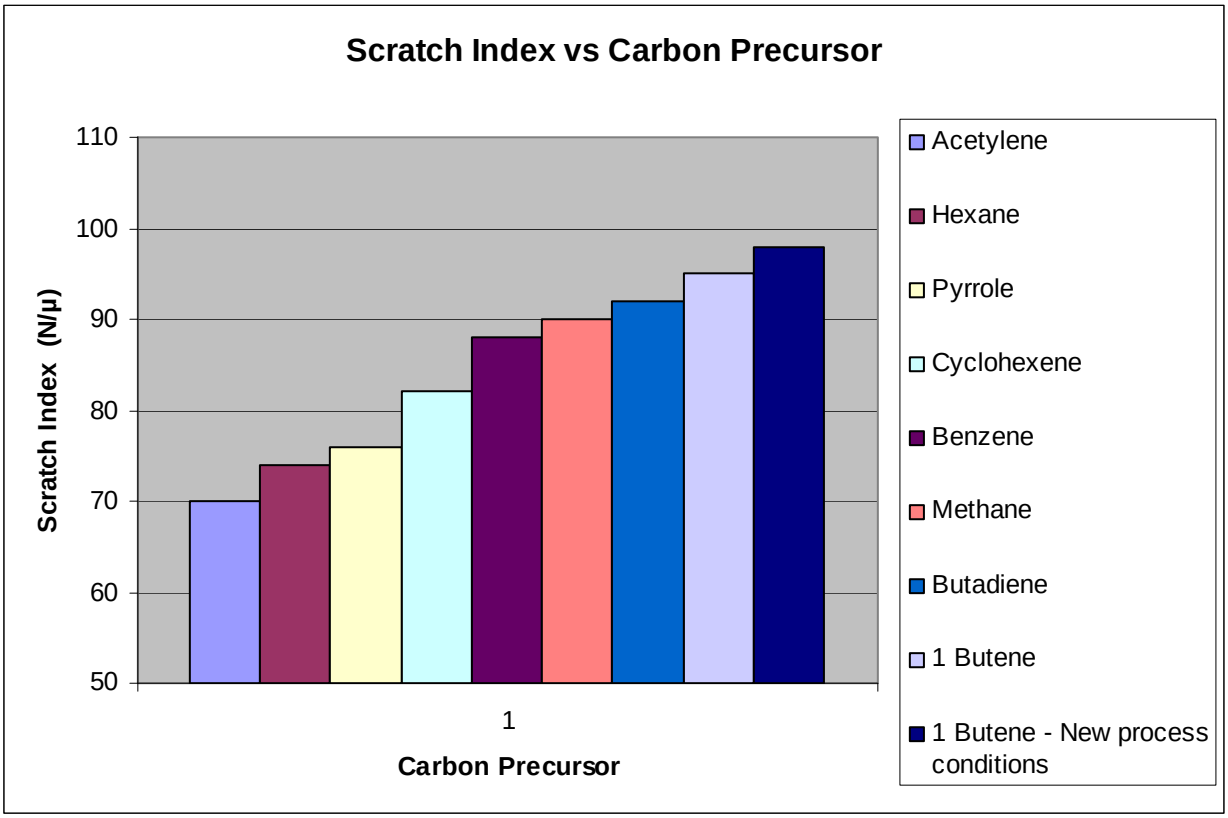
Different carbon precursors & hardness improvement:

Eight different gaseous hydrocarbon precursors were evaluated and characterized based on optimization of high hardness, deposition rate and adhesion. The hydrocarbons were selected to contain both single, double and triple bonded carbon and various ratios of hydrogen / carbon within the precursor molecule. All of the precursors were evaluated using the same process conditions. As can be seen from Plot 1, 2 and 3 and from Table 3, butene produced the best combination of adhesion scratch index, hardness and deposition rate. Sp3 content was determined using Raman spectroscopy and hydrogen content using Hydrogen Forward Scattering (HFS). The process conditions were then optimized to dramatically further increase the hardness by nearly 50%, with only a slight decrease in deposition rate, this was done by removing argon from the process, increasing the pressure and slightly increasing the power.

A trend is observed in the data for hardness based on the degree of saturation of the molecule. Fully saturated molecules (methane and hexane) have higher hardness while less saturated molecules have lower hardness, e.g. the triple bonded acetylene has the lowest hardness and benzene with multiple double bonds also has low hardness. This trend is also observed for deposition rate with fully saturated methane and hexane having the lowest deposition rate while acetylene and benzene have the fastest deposition rate. The high deposition rate for the unsaturated hydrocarbons can be explained by the more reactive nature of the pi bonds and the probable greater formation of reactive radicals in the plasma. It is probable that these same pi bonds within the precursor would cause the formation of a more sp2 rich coating, thus explaining the reduced hardness. A similar trend is shown for sp3 content and precursor saturation, with sp3 content measured by Raman spectroscopy increasing with precursor saturation. There is not a trend indicated for increasing hardness with decreasing hydrogen concentration, indicating that the hardness is dominated by the precursor saturation. The results indicate that for the pressure regime used for this high deposition rate process, that the hardness is dominated by the hydrocarbon precursor saturation rather then the ion energy or hydrogen concentration, indicating a more radial based film formation mechanism.



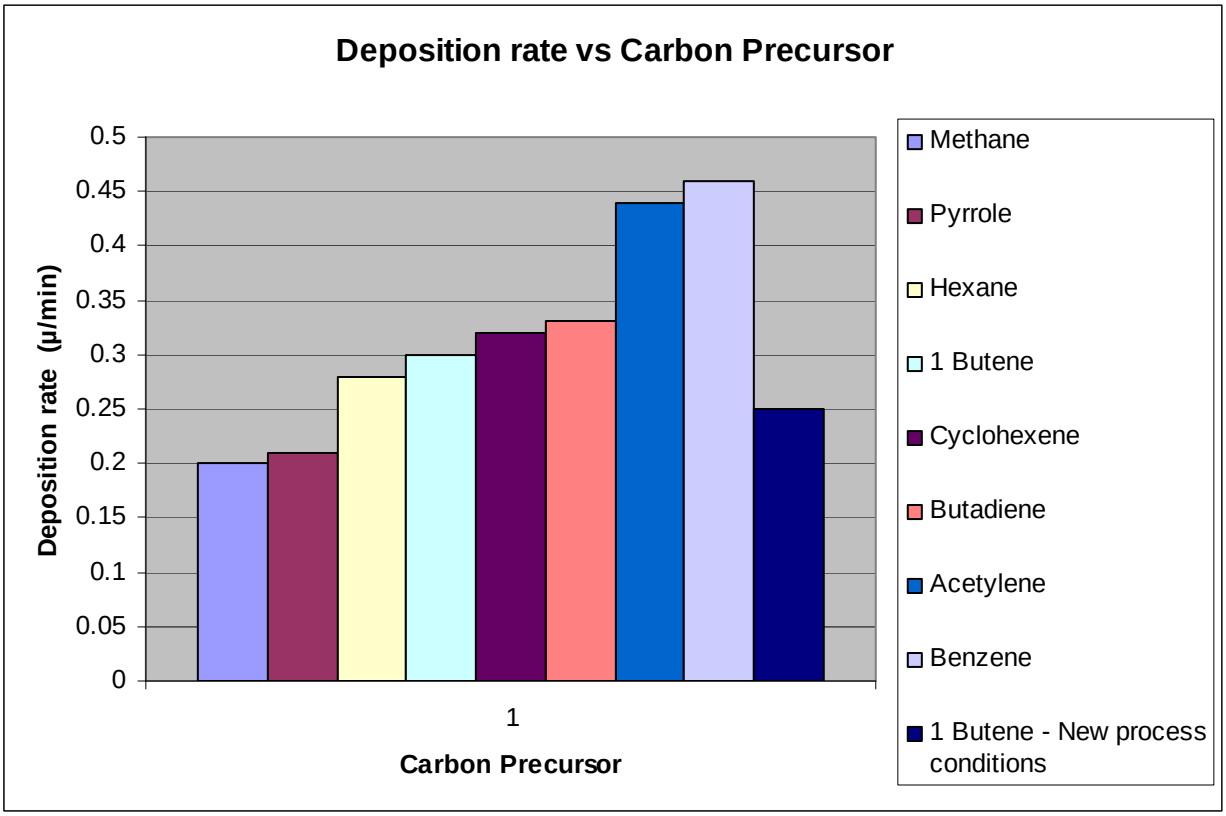
Plot 1: Plot comparing the Hardness with different carbon precursors.



Plot 2: Plot comparing the scratch Index with different carbon precursors.

Precursor	Hardness (Gpa)	% Sp3	% Hydrogen	Deposition rate (µ/min)	Scrath Index (N/ µ)
Acetylene C2H2	14.0	52	26	0.44	70
Benzene C6H6	14.4			0.46	88
Butadiene C4H6	15.6	58		0.33	92
Cyclohexene C6H12	16.4			0.32	82
Butene C4H8	16.7	62	28	0.3	95
Methane CH4	17.8	57	30.5	0.2	90
Pyrrole C4H5N	17.5	45	20	0.21	76
Hexane C6H14	19.0	64	27	0.28	74
Butene – New process Conditions	25.0			0.25	98

Table 3: Table comparing the film properties with different carbon precursors.



Plot 3: Plot comparing the Depostion rate of the film with different carbon precursors.

Conclusions

A novel hollow cathode plasma immersion ion processing method is developed and used to deposit silicon containing diamond like carbon (DLC-Si) films inside a one foot long 1020CS pipe with 1.75 inch diameter. A layered coating structure was developed, including an improved adhesion layer with good mixing of substrate and coating constituents, to improve adhesion of the coating while a DLC top layer provided excellent wear and friction characteristics. Data showed that such a coating provides excellent corrosion and wear protection to internal surfaces of pipes. Application of this coating technology is in industries such as oil and gas, tribological and corrosion performance improvement is expected for components such as pump barrels, downhole pipes, drilling fixtures, and drilling bores, etc.

Hardness, deposition rate and adhesion can be controlled based on the selection of hydrocarbon precursor. Trends are observed based on the degree of saturation of the hydrocarbon precursor with saturated molecules producing a harder coating with a slower deposition rate while unsaturated precursors producing a softer coating with a faster deposition rate.

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