A hollow cathode high density plasma process for internally coating cylindrical substrates

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ABSTRACT

A new and exciting technique for performing material deposition on the inside of cylindrical substrates, in particular pipes, will be described. Using the hollow cathode effect (HCE), a high density plasma can be generated within such cylindrical substrates by using Plasma Enhanced Chemical Vapor Deposition (PECVD). As the pipe itself is the vacuum chamber, such high density plasmas can be maintained by using asymmetric bipolar direct current (DC) pulsed power. Very high deposition rates can thus be achieved of the order of 1micron/min. A vast number of applications can greatly benefit from this novel process, on both a large and small scale. Examples of such applications would be industrial piping, offshore drilling, chemical delivery systems, gun barrels and medical devices. A future application of this process would be in drug delivery systems. The films generated from this vacuum deposition technique can be optimized for whatever a specific application requires. In general these films have high corrosion, erosion and wear resistant properties but changing the process parameters can improve any of these properties. Details of the actual process and deposition system will be described in detail as well as how the technology works and how such high density plasmas can be maintained for various lengths and diameters of pipe. Results of the testing of these films by various techniques will be shown with the main properties of interest being hardness, adhesion, layer thickness, wear and corrosion resistance.

1. INTRODUCTION

Numerous deposition techniques for applying a corrosion and/or wear resistant coating to the inside of cylindrical substrates, such as pipes, have been extensively studied previously. Most common techniques such as electroplating, painting or spraying (thermal, arc and high velocity Oxy-Fuel) are considered for this application. Typically these involve specialised materials such as tungsten carbide and most require further finishing of the coating surface to obtain a useful smoothness and finish. These traditional coating methods were primarily developed to coat exterior or exposed surfaces and often have limited effectiveness when applied to coating internal surfaces outside of a limited size range. In addition, many of the raw materials or process by products can be toxic or environmentally unfriendly.

This paper will present a new and exciting technique for depositing extremely hard, smooth, corrosion and erosion resistant films on the interior surface of metallic components such as pipes and tunes through a hollow cathode plasma immersion ion processing (HCPIIP) method. This technique utilises the hollow cathode effect (HCE) to generate and maintain an extremely high density plasma inside the part which can be used to form coatings and films through a plasma enhanced chemical vapour deposition (PECVD) process in the presence of certain precursor gases.

By using carbon containing precursors, such as acetylene, extremely hard diamond-like carbon (DLC) films can be formed on the inside of the component. As has been extensively reported elsewhere [1], DLC films have high hardness, low friction, electrical insulation, chemical inertness, biological compatibility, smoothness and resistance to wear. The unique properties of these films have attracted great interest in a large number of industries including oil and gas, automotive, aerospace, medical, military and paper. Most of the deposition techniques for producing DLC films are slow, $\ll$ 1 µm/hr, have limited capability or effectiveness in coating internal or unexposed surfaces, and produce high residual stresses in the film so limiting the practical coating thickness to a few µm. In the case of piping and tubing, which typically are transmitting a potentially corrosive chemical or exhaust the attractive properties of DLC coatings could be envisioned to reduce corrosion, wear and abrasion on the inside of the part to increase useful lifetimes. In addition, the inherent smoothness and low coefficient of friction properties of DLC films could be of benefit to reduced lines losses as liquids and slurries flow through a coated tube.

Another advantage of the described PECVD process is the ability to change the film composition or introduce multiple layer films through the addition of other precursors. This allows formation of adhesion layers at the coating interface to promote strong bonding of the film, or multiple layer structures to enhance specific properties of the film

This article will give an overview of the vacuum deposition system and the technology which goes behind the deposition of these films. Some general information about the characterization and testing of the resulting DLC films will be described to give an overview of the range of properties that can be achieved.. Finally some detailed information on potential applications will be reviewed to describe potential commercial benefits of the coating applied to interior.

2. EXPERIMENTAL

A novel hollow cathode plasma immersion ion processing (HCPIIP) deposition method has been developed with the intention of depositing hard thick films on the inside of metallic substrates. This method uses the hollow cathode effect (HCE) to generate an extremely high density plasma within the pipe itself. Figure 1 shows a schematic of the deposition system.

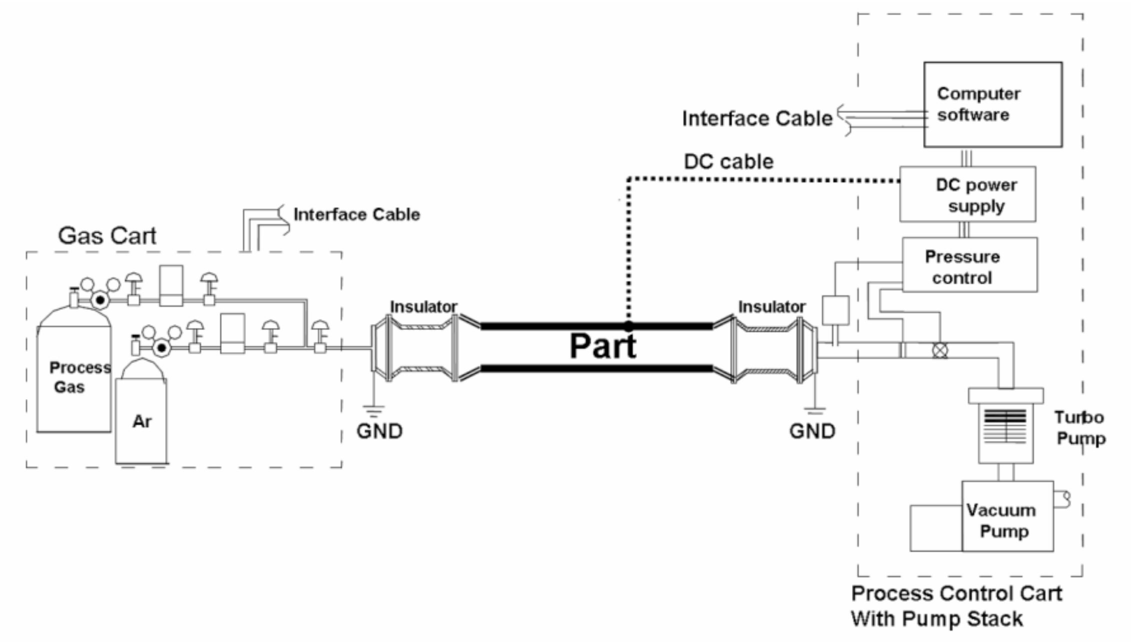

Figure 1 : Diagram of process set-up [4]

From the main gas source system, process and precursor gases are introduced into the entrance head. It then travels down the pipe where it is ionized quickly and deposition then takes place. At the exit head, a high vacuum pump is used to pump away any by-products. The pipe itself acts as the cathode which is initially negatively biased with anodes, initially positively biased, located at the entrance and exit heads. The anodes are separated from the conductive tubing by isolative spacers. . The negative pulse bias plays an important role in improving the stress, density and adhesion of the films by ion bombardment energy. Under suitable vacuum conditions, a bipolar asymmetric DC pulse is used to maintain a high density plasma inside the component. Energetic positive ion bombardment is controlled by the magnitude of the applied voltage and by the pressure. Gas flow and pumping speed are varied such that the pressure inside the component provides a hollow cathode when a voltage is applied to the component. This pressure is such that the electron mean free path is fractionally less than the pipe diameter, which cause electrons to oscillate across the tube resulting in multiple collisions and a high density plasma being maintained [4]. As DLC films are insulative, short pulses (< 30µsecs) are used to dissipate any positive charge build up on the coating surface. This charge is compensated when the plasma sheath collapses during the off cycle. Adjusting the duty cycle of the DC waveform can allow good control of the film uniformity and thus allows the gas to replenish during the off cycle. A high density plasma promotes high deposition rates and also allows some influence over the residual stress state and bonding state of the applied film. Using a high bias voltage can result in ion implantation of ions which deposit below the surface of the film and such ions help to promote adhesion of the film to the substrate. Before process gas is introduced into the chamber, an Ar preclean takes place to remove contaminants from the internal surface. Also, a nitrogen preheat can be used to reach an initial temperature within the pipe, which eliminates any external heating requirement.

This technique can be used to investigate a number of different aspect ratios. High aspect ratio pipes can be coated with higher flows and low duty cycles [4]. Currently an aspect ratio of 24/1 is possible. Being able to coat different size pipes means that knowledge of the main scaling properties of the deposition process is necessary. It has previously been shown that the hollow cathode scales with a constant ~ pressure x diameter, hence small diameter = high pressure. Current scales with surface area of the cathode with high current used for large pipes. Duty cycle of the bipolar pulse is also adjusted for pipe length and temperature control. More details about the deposition process can be found in reference [4].

3. RESULTS & DISCUSSION

Within this section details of a multilayer DLC coating which has been deposited by this technique and information on various characterisation techniques which have been used to find out information about the hardness, scratch adhesion, corrosion, thickness and pinhole investigation will be shown.

3.1 Thickness

The technique used for determining the thickness of such a film is the Calotest system which is manufactured by CSM Instruments [5]. Typically a tungsten carbide ball of diameter (~20mm) is used with a diamond slurry to wear through the film surface until the substrate has been reached by the ball. The film is then removed and put under an optical microscope where geometry is used to measure the coating thickness. Figure 2 shows the Calotest technique.

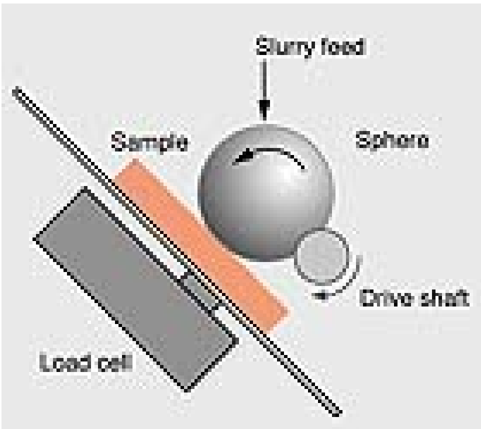

Figure 2 : Principle of the calotest technique [6]

The coating shown in Figure 3 shows an optical microscope image of the layer structure used. Using a silicon and hydrocarbon precursor, an initial layer of SiC is deposited upon the bare stainless steel (SS)304 substrate, acting as an adhesive layer. By using this layer it is possible to deposit a thick stack of DLC dominant films for the required application due to increased bonding of the layers to the adhesion layer. In this case, on top of the adhesion layer is a high silicon doped DLC layer, DLC cap layer, low Si doped DLC layer and a final DLC cap layer as the surface later [7].

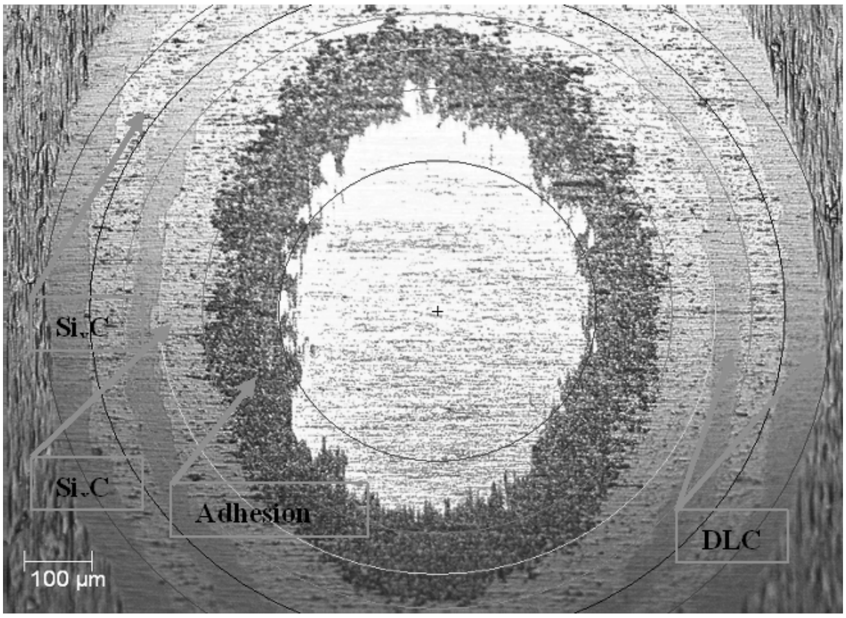

Figure 3 : Image from optical microscope of film after calotest [7]

Figure 4 shows a cross-section of another typical coating deposited by the described technique.

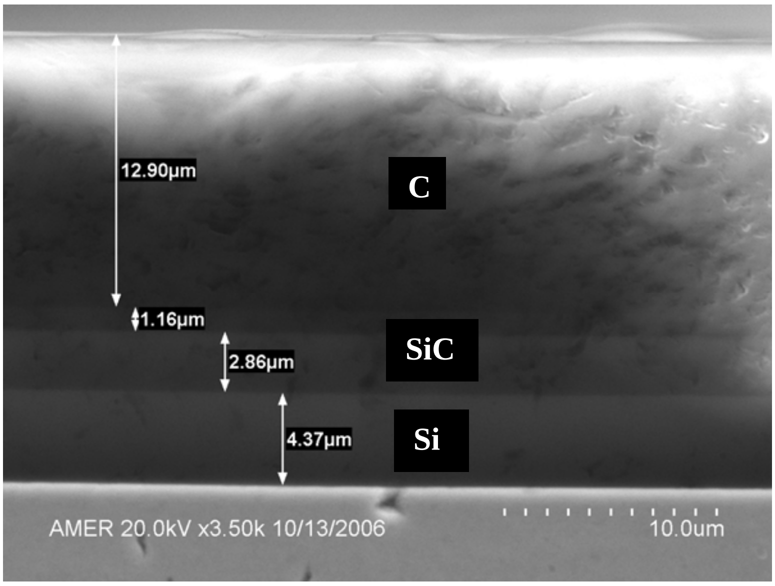

Figure 4 : Cross-section of 20µm from SEM [8]

This cross-section shows a 20µm stack of a similar layer structure as shown in Figure 3. This coating is deposited at a temperature of ~200˚C and when the coating relaxes back to room temperature, there is no sign of any cracking or breaking up of the film. For a single layer of DLC thick film of 20µm on SS304 substrate, as the coating cools back down to room temperature, the coating starts to break up and come away from the substrate. For most well-known deposition techniques, to get DLC to adhere to a metallic substrate, a film of a few µm thick is the limitation before degradation appears. DLC films of 20µm and above are extremely difficult to deposit but this technique can easily do this and also, a coating up to 70 µm has been deposited using this technique and with various hydrocarbon precursor combinations.

3.2 Scratch Adhesion

To understand how the multilayer DLC film is adhering to the metallic substrate, scratch testing of the sample is done. A Vickers pyramid diamond tip with a radius of 200µm is used. At constant speed, the tip is pulled along the surface of the film and as the sample is scanned, the tip is subjected to an increasing load up to a maximum of 30N. Figure 5 shows an image of a scratch test. This sample is a multilayer DLC film deposited on SS 304 substrate.

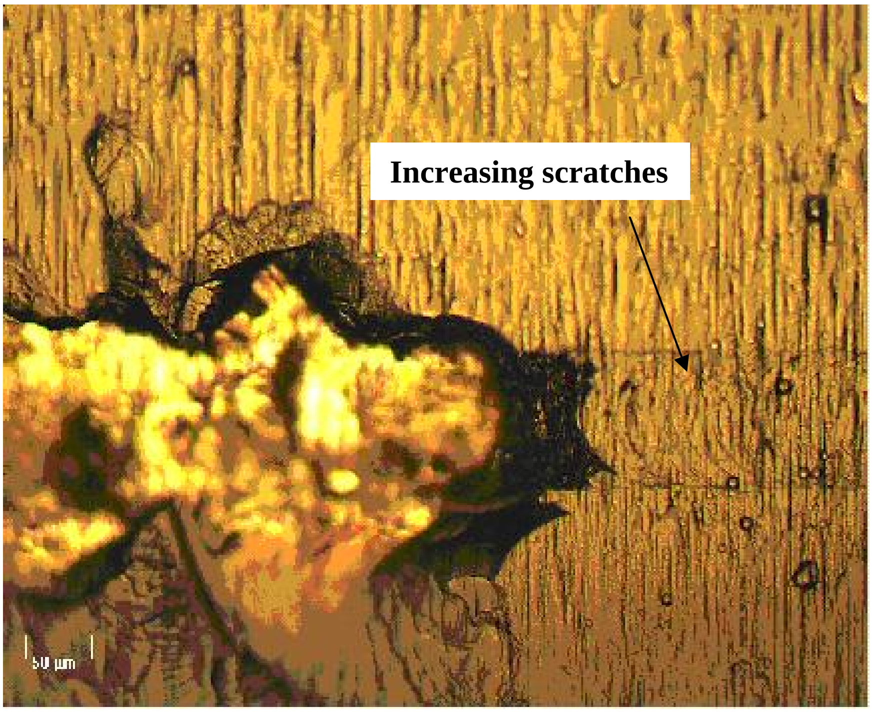

Figure 5 : Scratch adhesion test

Coming along from the right hand side of the figure you can see the scratch marks on the surface of the film. An increasing load then leads to increasing scratches until de-lamination occurs. The vertical lines are substrate crack marks. Table 1 shows typical load parameters used for scratch testing.

Table 1 : Scratch adhesion load parameters

Loading Range	**0 – 30N**
Loading Rate	**30N/min**
Scratch Length	**10mm**
Scratching Speed	**10mm/min**

3.3 Hardness

When depositing films with the aim of them having high corrosion and erosion resistant properties then hardness testing of these films is of importance. This is done by using a Vickers diamond 100µm diamond tip, where a number of indents are taken along the sample at a constant load typically 150mN. Each indent is taken at 20µm intervals. The hardness and modulus is then taken from the average of these indents. For the multilayer DLC film shown in Figure 2, hardness = 15GPa and modulus = 110GPa. Table 2 shows the typical test settings

Table 2 : Hardness load parameters

Force	**100mN**
Loading Rate	**0.3N/min**
Unloading Rate	**0.3N/min**
Pause	**15s**

3.4 Wear

An even better technique for measuring the erosion of the film is wear testing where information on the coefficient of friction (COF) of the film can be found. Using the pin and disc method in a linear motion, a tungsten carbide ball is reciprocated back and forth along the sample surface. A load of 10 – 20N is used but this load is based upon what results from earlier scratch tests. Figure 6 shows a graph of COF versus time. A COF of < 0.15 is a typical value for our films.

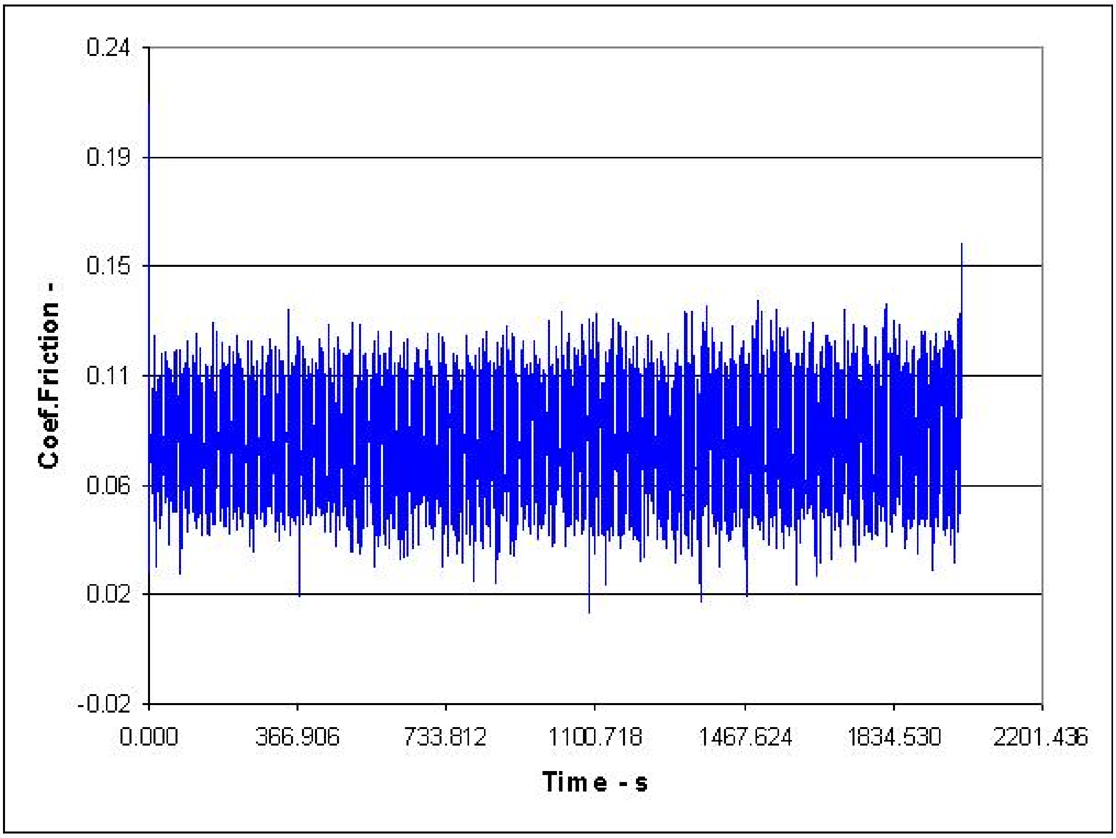

Figure 6 : COF measurement using tribometer

The wear track is then analysed using a surface profiler where the wear rate can be found. An altitude profile is measured which is then converted into a line profile, where the depth of the wear area can be measured. From this measurement and by then using a certain equation, the wear rate can be obtained

3.5 Other techniques

Another important part of the testing procedure is in detecting pinholes on the surface of the film. Any pinhole in the film that penetrates to the substrate can pave a way for any localised or pitting corrosion to take place. Testing for pinholes can be done by a method known as the "holiday test". By grounding the uncoated side of the pipe, water is applied to the surface of the coating . By applying a voltage to the water by means of a probe electrode, any pinhole which may be present in the film will cause bubbles to appear which can be easily viewed on an optical microscope. The structure of the film can also enhance the possibility of pinholes. A columnar structure may do this due to diffusion through grain boundaries.

Corrosion testing is also of great importance to these films. This has been done by using 2 different solutions of 15% HCL and 10% NaCl at 70˚C for an exposure time of 19hours [7]. Figure 7 shows photographs of a coated SS304 sample after exposure to the described solutions.

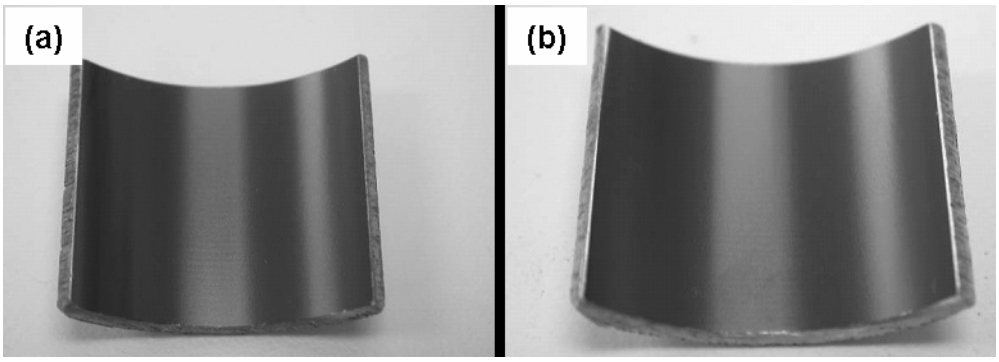

Figure 7 : DLC coatings on SS304 substrate after exposure to (a) 15% HCL and (b) 10% NaCl at 70˚C [7]

Photograph (a) is the HCL exposed sample and (b) is the NaCl exposed sample. Inspection by optical microscopy shows no damage to the substrate indicating that good adhesion is evident for these samples. The chemically inert DLC is acting as an excellent barrier to the corrosive solutions.

Another important property of DLC films can be found from Raman spectroscopy. As is well-known from previous literature, there is a dependence on the quality of DLC films from the C ion energy. By performing Raman analysis, an idea of the sp3 content of the DLC films can be found, which can tell us how graphitic or diamond-like the films are. Figure 8 shows how the ion energy can tell this [1].

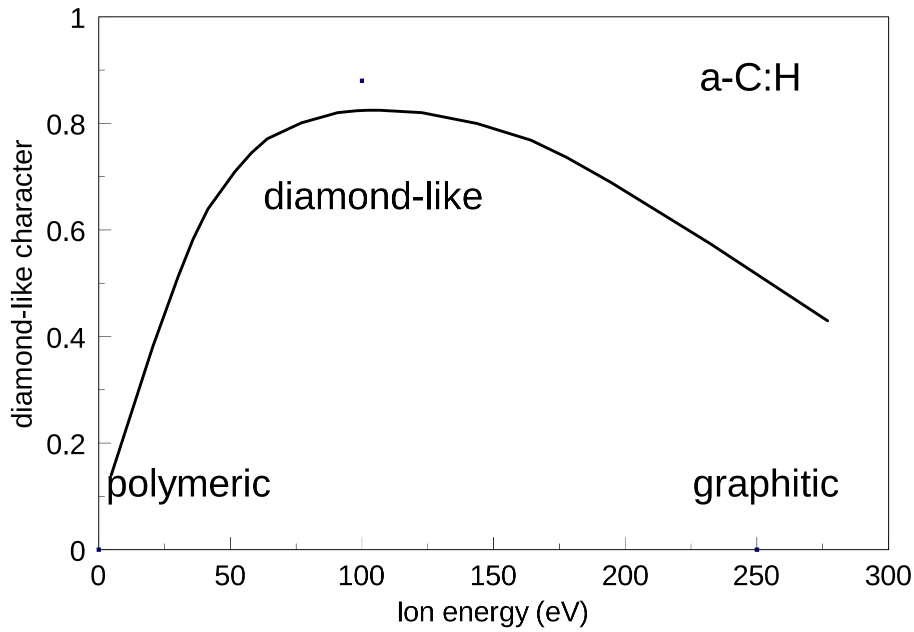

Figure 8 : Importance of ion energy on the DLC film quality [1]

Knowing the sp3 content of these films can then give information about the density and hardness. Raman analysis is ongoing at present with a certain emphasis on the residual stresses present within the layers being explored. A more detailed analysis on what the important properties of DLC films from Raman spectroscopy are can be found in reference [1]. Plasma processing is also taking place using a Langmuir probe and optical emission spectrometer (OES) to try and find out information about the ion density and the ion energy of the process which we can then correlate with the Raman spectrometer data. Table 3 below shows a summary table of the main properties of the DLC films deposited by this novel technique.

Table 3 : Summary of DLC film properties from this novel process

Hardness (GPa)	**20**
Modulus (GPa)	**150**
Wear (mm^3/Nm)	**1E-7**
COF	**< 0.15**
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**

4. APPLICATIONS

As overviewed in Table 3, the potential film properties achievable through the described PECVD process are quite unique, particularly on internal surfaces, and many applications can be envisioned where these properties could improve the useful life or enhance the performance of industrial components. Potential applications include automotive, military, medical, aerospace, oil and gas and pulp and paper and many of these have been examined to various levels. Some examples of applications are for the military, the most obvious application is in gun barrels, in both a small and large scale. For the small scale, especially in sandy environments, there is a need to use arms without oils to stop jamming of guns. On the larger scale there is a need to replace Cr plating for large calibre guns used on ships, tanks and in the artillery [9].

For the medical industry there is a need for corrosion resistance on the inside of valves and tubes where good adhesion and smoothness is required. Also, implants for internal joints would need coated since these can corrode inside the human body and as DLC is chemically inert this would be advantageous for that [9].

For the pulp and paper industry, there is a need to replace expensive alloys which are used for corrosion resistance, with cheaper coated alloy steels. In the pulp mill, there are a large number of pipes and valves which carry corrosive material where a coating on the inside of these parts would increase the lifetime of the parts and be cost effective [9].

In geothermal systems, pipes are used to bring hot water from the ground and heat exchangers. Lower frictional losses means higher transfer rates and obviously in oil and gas you have offshore drilling and gas delivery systems which would benefit from this technology [9].

Further advancing the technology for extended geometry applications, such as transmission pipelines, will involve both further scaling of the process to accommodate the greater lengths and diameters associated with these applications as well as configuring the process to allow for on-site coating of seams, joints and repairs. Experiments and modelling to allow further scale-up are in progress and prototype in-situ coating concepts are being explored.

5. CONCLUSIONS

A novel hollow cathode processing method has been described which can deposit multilayer coatings on the internal surfaces of cylindrical substrates, including layers with a diamond-like carbon nature. Details of the deposition system and technology have been shown with the actual part itself acting as the vacuum chamber and the cathode. A description of a multilayer DLC coating which has been deposited using the coating and the testing procedures have been shown which demonstrate the unique combinations of high hardness, corrosion resistance and wear resistance, all with very good adhesion to the metallic substrate. Well adhered surface layers of this type offer a new way to protect internal surfaces and cavities including the inside of pipes. An extensive list of applications has been shown where corrosion and erosion problems have existed and it has been shown that such industries can benefit greatly from this process.

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