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ABSTRACT

Infrared astronomical instruments require absorptive coatings on internal surfaces to trap scattered and stray photons. This is typically accomplished with any one of a number of black paints. Although inexpensive and simple to apply, paint has several disadvantages. Painted surfaces can be fragile, prone to shedding particles, and difficult to clean. Most importantly, the vacuum performance is poor. Recently a plasma enhanced chemical vapor deposition (PECVD) process was developed to apply thick (30 μm) diamond-like carbon (DLC) based protective coatings to the interior of oil pipelines. These DLC coatings show much promise as an infrared black for an ultra high vacuum environment. The coatings are very robust with excellent cryogenic adhesion. Their total infrared reflectivity of < 10% at normal incidence approaches that of black paints. We measured outgas rates of $<10^{-12}$ Torr liter/sec cm^2, comparable to bare stainless steel.

Keywords: black coatings, infrared black, diamond like carbon, outgassing, vacuum

1. INTRODUCTION

Adequate suppression of stray and scattered light is essential to achieving the design performance of an optical instrument. Baffles and light traps are often added to an optical layout to block unwanted beams so that only the desired signal photons reach the detector. Black coatings on these baffle surfaces ensure that a high percentage of incident photons are absorbed and have no further effect.

In the infrared, black body radiation from components near ambient temperature is another source of unwanted photons. Cold shields are often used to restrict the field of view of detector elements so that they only view cold surfaces with minimal thermal emission. These surfaces must be blackened so that photons originating from warm objects are not reflected or scattered into the detector. The difficulties become more severe in low flux applications such as the imaging of weak sources or in high-resolution spectroscopy. One may need a cold enclosure around the detector and optics that is completely blackened on the inside surface.

Many materials and processes have been used to blacken optical surfaces. Descriptions of their properties and performance may be found in the literature. Two good reviews include a chapter in the Handbook of Optics written by Pompea and Breault[1] as well as a paper on blacks for space-borne infrared systems by Persky[2]. For many applications, especially in the visible region, a number of black paints are adequate. They are cheap, effective and easy to apply. Other types of black coatings have also gained popularity, including textured and anodized surfaces. However, where good vacuum is required, as in most infrared applications, the blackened surfaces must have low outgassing.

We required an infrared black coating with good cryogenic adhesion for use in a hermetically sealed vacuum dewar. This dewar has only a small getter pump and must maintain adequate vacuum for several years. The allowable outgas rate is comparable to that found in an ultra-high vacuum (UHV) system. Very few black surfaces in current use can meet this requirement. This was the starting point for this study.

In Section 2 we will compare our requirements and the performance of existing black coatings. Section 3 reviews previous use of DLC as a black coating at 1.06 μm for an interferometric gravity wave detector. The performance of a thin single layer DLC coating in the mid- and long wave infrared is discussed in Section 4. Section 5 presents outgassing

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and infrared reflectivity measurements on thick multilayer DLC coatings. Section 6 presents a summary and conclusions as well as future directions for this technology.

2. COATING REQUIREMENTS

We have two major requirements on our infrared black coating: having a sufficiently low outgas rate to maintain a gettered vacuum for several years and providing sufficiently low reflectivity to block unwanted infrared photons. We will first examine the vacuum requirement.

2.1 Vacuum requirements

Consider a dewar with 1 liter internal volume and 2000 cm^2 internal surface area of which 200 cm^2 must be blackened. The capture pump (metal appendage pump, SAS Getters) contains 20 grams of St707 nonevaporable getter material. It traps residual gases either on the surface or in the bulk of the getter. The pumping speed is 1 to 2 liter/sec. Getter capacity depends on the gas: 400 Torr liter for H_2, which is absorbed in the bulk; 0.1-1.0 Torr liter for other active gases, which absorb on the surface. To achieve a 2 year lifetime, the allowable initial outgas rates are 6.3×10^{-6} Torr liter/sec for H_2, 1.6×10^{-8} Torr liter/sec for H_2O and 1.6×10^{-9} Torr liter/sec for CO. These are conservative estimates since the amount of residual gas bound to surfaces in a sealed dewar is fixed (unless a leak is present) and therefore the outgas rate will decrease with time.

In a cryogenic dewar, a vacuum of order 10^{-5} Torr is sufficient to reduce the heat conduction by residual gas to a negligible value[3]. However the pressure requirement set by getter life is lower by three orders of magnitude (10^{-8} Torr) for gases other than hydrogen.

Quantitative outgassing data on black coatings are difficult to find in the literature. NASA Goddard has compiled a comprehensive database[4] "Outgassing Data for Selected Spacecraft Materials," that lists total mass loss and condensable (on a 25ºC surface) volatiles during a 24 hour vacuum bake at 125ºC. NASA considers a material low outgassing if the total mass loss is <1.0% and the condensable volatiles comprise < 0.1%. But this database has no information on the residual gas composition nor on quantitative outgas rates.

Martin Black, an anodized surface treatment for aluminum, has outstanding optical properties and meets the NASA criteria. However, measurements after a 60 hour vacuum bake at 120ºC gave an outgas rate of 9.0×10^{-7} Torr liter/sec cm^2 with water vapor as the dominant species[5]. The reason for this high rate is the highly textured surface, which has an effective area for water absorption that is much, much greater than its geometric area. Only 0.017 cm2 of Martin Black in the dewar would saturate the SAES getter pump in 2 years.

Ames 24E2 is a black paint[6] developed for baffles on far infrared space telescopes (e.g. SIRTF). We obtained a sample, brushed it onto both sides of a 12 cm x 12 cm aluminum sheet and then heat cured it. The painted surface is quite rough due the quantity of SiC grit mixed in to reduce specular reflectivity. The sample was then placed in a vacuum chamber and baked for 90 hours at 135ºC. Upon cooldown to room temperature an outgas rate of 1.3×10^{-9} Torr liter/sec cm^2 was measured. The outgassed species comprised 50% CO, 25% hydrogen and about 25% methane. A surface blackened with 2.5 cm^2 of Ames 24E2 would saturate the getter with CO in 2 years.

MH-2200 (formerly ECP-2200 from 3M) is a solar absorbing black paint. It has a matte finish but is not rough like the prior materials. Erikson et al.[7] measured an outgas rate of 8.6×10^{-11} Torr liter/sec cm^2 after a 24 hour vacuum bake at 100ºC. The residual gas was 45% hydrogen, 30% CO and 15% water vapor. A surface coated with 60 cm^2 of this paint would saturate the getter with CO in 2 years. This material is clearly better than the previous options but still does not meet our requirements.

In a real system, one cannot allocate all the getter capacity to the gas load produced solely by the blackened surfaces. One must allow some margin for outgassing from other surfaces and materials within the dewar. Metallic surfaces if properly cleaned contribute minimally to the total outgas rate. By contrast organic materials like plastics for thermal and electrical insulation and adhesives contribute significantly to the gas load. So our vacuum requirement is for a black coating with an outgas rate of $\leq 10^{-11}$ Torr liter/sec cm^2 for species other than hydrogen.

2.2 Reflectivity requirements

A lesson from the vacuum analysis is that very rough surfaces, although minimizing specular reflection, generally have high outgas rates. One must then consider using smooth, specularly reflecting surfaces as light traps and baffles. Given a specific value of reflectivity one can use ray tracing to design a configuration such that all rays of stray light encounter a sufficient number of surfaces to provide the desired level of attenuation. For example, 3 bounces from 5% reflective surfaces or 4 bounces from 10% reflective surfaces can achieve 10^{-4} attenuation. Stray light analysis codes (e.g. FRED from Photon Engineering LLC) can be helpful in testing such designs.

Total reflectivity (specular plus diffuse) is a good way to compare different black coatings. These measurements are best made using an integrating sphere to collect photons scattered in all directions. Values for commonly used blacks may be found in the literature. Mean hemispherical reflectivity measurements at near normal incidence over the 5 to 25 µm range were reported by Persky[2]. He recorded values of 5% for the Martin Black anodized coating and 9% for the black paints Chemglaze Z306 and 3M Nextel. At LLNL we used a diffuse gold integrating sphere, a CO2 laser, and a thermal power meter to measure hemispherical reflectance at 10.6 µm. The angle of incidence was near normal. We obtained reflectivity values of 12% for MH-2200, 9% for Ames 24E2 and 11% for Cat-a-Lac black, an epoxy-based black paint.

In summary, a very smooth black surface with mainly specular reflectivity can be acceptable with proper optical design. A total hemispherical reflectivity of order 10% would be comparable to commonly used black paints.

2.3 Other considerations

It is important that the coating adhere well at cryogenic temperatures and maintain that adhesion through numerous cycles from room temperature to cryogenic and back to room temperature. Shedding of particles is not allowed as they could find their way to an image plane. Other considerations include cost, compatibility with a wide range of substrates and ease of application. Since coated parts may undergo some handling during assembly, ruggedness and the ability to clean the blackened surface are beneficial.

3. USE OF DLC AS AN OPTICAL BLACK AT 1.06 µm

As is often the case, we were not the first ones in need of a very low outgassing black coating. A survey of the literature showed there to be an analogous requirement in design of interferometric gravity wave detectors. These are long arm, laser fed interferometers designed to measure the extremely small $\Delta L/L$ (of order 1 part in 10^{21}) produced by the passage of gravity waves generated by nearby astronomical events. The extreme sensitivity is a result of long path lengths (several hundred meters to several kilometers) a very high Q interferometer cavity, high laser power and painstaking attention to a myriad of noise sources[8].

Interferometric gravity wave detectors require black coatings on baffle plates, beam dumps and the inner surfaces of the beam tubes to suppress scattered light that contributes noise. There are very strict requirements on the outgassing of organics as any deposition on the mirrors can reduce the very high Q of the cavity. Pressure fluctuations in the residual gas between the mirrors, even at very small levels, produce changes in signal levels that can mimic those produced by gravity waves. So a vacuum of better than $1.0\text{x}10^{-8}$ Torr is necessary in the beam tubes. This places a very tight limit on allowable outgas rates and excludes most optical blacks.

In Japan a study was conducted to determine the best coating considering both optical and vacuum requirements for the TAMA300, a 300 meter interferometric detector near Tokyo[9,10]. Several materials were tested including an etched and smooth nickel-phosphorous plating, a chrome oxide coating, an aluminum oxide coating and a 1 µm thick DLC coating, all on stainless steel substrates. The DLC, deposited by direct current plasma chemical vapor deposition, had by far the lowest outgassing, with a rate two orders of magnitude lower than any of the other black coatings. It was an order of magnitude lower than electropolished stainless steel, which is considered to be a very low outgassing material. It has been hypothesized that DLC has such low rate because the surface is very smooth and the effective surface area is the geometric surface area. It also helps that diamond has a very high surface energy such that few things can adhere to it. DLC also provides a barrier to hydrogen diffusion from the bulk of the stainless. Takahashi[8] measured outgas rates from an unbaked DLC coating of 1.5×10^{-10} Torr liter/sec cm^2 after 1 hour of pumping, 1.9×10^{-11} Torr liter/sec cm^2 after 10 hours and 3.0×10^{-12} Torr liter/sec cm^2 after 50 hours.

The TAMA300 uses a Nd:YAG laser as a light source so coatings for this application are tested at 1.06 µm. The lowest reflectivity coatings (<1%) are those with rough etched surfaces. Unfortunately they also have the largest effective surface areas and perform poorly in vacuum. The 1 µm thick DLC on stainless steel had a normal incidence reflectivity of about 35%. This is a mediocre result. However, baffles can be designed to make optimal use of the reflectivity characteristics of the surface and the fact that the source of stray light is a polarized laser. At 40º incidence the DLC on stainless reflects only 5% of the p-polarization. By making proper use of the polarization properties of the YAG laser, good baffle performance can be achieved. The study concluded that for large area coverage, where outgassing was the primary consideration, DLC was the coating of choice.

4. SINGLE LAYER DLC AS AN IR BLACK

The extremely low outgas rates reported by Takahashi for his DLC coatings were encouraging. Despite the mediocre reflectivity at 1 µm we decided to acquire a sample and test its performance in the MWIR and LWIR. An internet search showed many vendors supplying DLC coating services[11]. There is a substantial market for DLC coatings on a variety of products ranging from razor blades to hard discs to high performance automotive parts. They are also used as a protective coating on optics in severe environments.

A survey of the literature[12-14] shows that DLC is not a single material but rather a family of materials that can be produced by a number of different processes. Robertson defines DLC as a form of amorphous carbon with a significant fraction of sp^3 (tetrahedral or diamond-like) carbon-carbon bonds. There can be substantial hydrogen content (20-40% by atom) depending on the deposition process. The sp^3 bonds are a result of the impact of 100 eV carbon or hydrocarbon ions onto the growing film. It is important to specify the material and the deposition process when comparing properties. Commercial vendors mostly use ion beam deposition which coats in a line-of-sight and plasma enhanced chemical vapor deposition (PECVD) that will coat any conductive surface exposed to the plasma.

One company supplied a 3 µm thick coating of DLC on a polished aluminum substrate for our initial tests. The sample was one inch wide by two inches long with the DLC covering half of the surface. Our first test was for cryogenic adhesion, as we needed a coating that would survive temperature from ambient to below 50 K without flaking, cracking or peeling. The large mismatch in thermal expansion between aluminum and DLC was of concern. DLC films in general have a high intrinsic compressive stress that limits the maximum thickness to ~ 5 µm.

The sample was clamped to the cold tip of a Stirling cryocooler (Sunpower CryoTel CT) with an intervening layer of indium. It was cooled to 40 K in about 20 minutes. After warming to ambient temperature the DLC film showed no evidence of damage or loss of adhesion.

An unpolarized CO_2 laser at 10.6 µm wavelength was used to measure the reflectivity of the single layer DLC over a range of incidence angles from 20º to 70º. The results were encouraging with values ranging from 6.5% near 20º, to 12% at 40º, and 30% at 70º (see Table 1). Next we measured the spectral reflectance of the DLC from 2.5 to 25 µm using a Perkin Elmer Fourier transform infrared (FTIR) spectrometer. It came with an accessory that allows the measurement of specular reflectivity at a 45º angle of incidence. The results are shown in figure 1. The periodicity indicates interference between reflections from the air-DLC interface and the DLC-aluminum interface. The high peak values of reflection show that the absorption in the DLC is low. Unfortunately the encouraging CO_2 laser measurements were near a minimum in spectral reflectivity and not indicative of the broadband behavior. To achieve low reflectivity over a broad band in the infrared does not seem possible with a thin single layer of DLC. Increasing the coating thickness, were that even possible given the high intrinsic stress in DLC, may still not achieve the desired result, as the infrared absorption of the DLC is low.

While the spectral reflectance was being measured we had the vendor coat some parts by their PECVD process. Good coating uniformity was achieved on flat plates. The spectral reflectance was similar to the polished sample. However on internal surfaces like the inside of cylinders, the coating was visibly thinner than on flat surfaces with unrestricted exposure to the plasma.

Our conclusions on thin single layer DLC were that the cryogenic adhesion was very good and that the outgas rate though not tested was likely superb. However there were issues with coating coverage in complex shaped parts. More importantly the coating only had low reflectivity over narrow ranges of wavelength. Its utility as an infrared black except for some unique situations is therefore limited.

5. PROPERTIES OF MULTILAYER DLC COATINGS

About the time we were discovering the limitations of single layer thin DLC as an infrared black coating we became aware another process for depositing DLC-based coatings. A hollow cathode plasma immersion ion processing (HCPIIP) method had been developed to deposit hard, corrosion resistant coatings on the internal surfaces of metal tubes, specifically oil and gas pipelines[15]. This technique uses the hollow cathode effect to generate and maintain an extremely high-density plasma inside the part, which can be used to form coatings and films through a PECVD process in the presence of certain precursor gases.

These proprietary coatings with a DLC outer layer and underlying adhesion layers were intriguing for several reasons. First they are available in much greater thicknesses (up to 60 µm) than single layer DLC. Greater thickness offers the possibility of greater IR absorption. Secondly, the hollow cathode discharge produces a very uniform coating on internal features. This raises the possibility of coating an entire optical assembly, consisting of multiple shields, baffles and structural elements at one time with much savings of time and labor over painting individual parts by hand. Furthermore plasma coated parts are inherently clean and ready for vacuum use, while painted parts require cleaning and prolonged vacuum baking to drive off solvents and other volatiles. Finally the HCPIIP method is not limited to DLC. One can deposit a wide variety of materials by changing the precursor gases. This opens up the possibility of designing and depositing a custom multilayer DLC-based coating specifically optimized for infrared absorption and good vacuum properties as opposed to abrasion or corrosion resistance.

5.1 Details of DLC deposition

Some details of the Sub-One DLC deposition method have appeared in the literature[16,17]. Reference 17 describes its application to deposition of silicon containing diamond-like carbon (DLC-Si) films onto the inside surface of a 304SS pipe 12 inches long and 1.375 inches inside diameter. 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 2, 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. This technology can be used to deposit amorphous hydrogenated DLC-Si based coating on internal surface of pipes with a variety of aspect ratios. A more detailed description of the technology is provided in the patent literature[18].

In one demonstration[17] a multilayer coating structure was deposited onto the internal surface of a 304SS pipe. The coating consisted of five layers: (1) a 4.5 µm silicon carbide adhesion layer, (2) 3.6 µm of high silicon doped DLC layer (Si_xC), (3) 3.2 µm first DLC layer, (4) 3.2 µm of low silicon doped DLC layer (Si_yC), and (5) 5.2 µm top DLC layer. A total coating thickness of 19.8 µm was measured at entry of the pipe. The average deposition rate was 0.3 µm/minute. No external heating of the substrate was employed and the maximum temperature during the deposition (due to plasma heating) was 175ºC.

Although originally developed for internal surfaces, this technology has recently been extended to coat external surfaces (curved and flat) as well. See figure 3 for an illustration. Samples of the multilayer DLC coating in thicknesses ranging from 15 to 50 microns were prepared on aluminum and stainless steel substrates for evaluation and testing.

5.2 Cryogenic adhesion

Samples were initially obtained of Sub-One DLC deposited on the inside surfaces of 1.5 inch diameter aluminum and stainless steel tubing. The surfaces were very smooth. As before the first test was to verify cryogenic adhesion. We opted for a very severe test, thermally shocking the coating by plunging the tubing directly into liquid nitrogen. No cracking, flaking, peeling or other damage was seen after several cycles.

5.2 Infrared reflectivity

Reflectivity was measured in a similar manner to the thin DLC sample, but was complicated by the cylindrical substrate. The tubes were first cut axially into 5 or 6 strips to expose the inner surface. Cylindrical sections 0.5 inch wide were then sliced from the strips. The specular reflectivity attachment to the FTIR spectrometer is designed for flat samples. So one must normalize the reflectivity of a coated sample to an uncoated reference substrate of the same curvature to obtain a correct result. Additionally we had to machine all samples and references to the same size so that the reflecting surfaces were in exactly the same position relative to the collection optics. A shift in position of 0.004 inches along the beam path produces a 15% difference in signal level.

Samples #992 (coating thickness 50 µm) and #922 (coating thickness 39 µm), both on 316 stainless substrates, had the lowest broadband reflectivity. Spectral traces are shown in figures 4 and 5. Compared to the thin DLC we still see interference effects between reflections from the air and substrate interfaces of the coating but with much higher periodicity due to the increased thickness. There is little evidence of interference from reflections within the coating. Some spectral regions show no interference. These are believed to be wavelengths where the coating has high absorption and very little energy is reflected from the substrate. To verify the FTIR data we used a CO_2 laser and a power meter to measure the 45º incidence reflectivity at 10.6 µm. Both samples #992 and #922 registered a reflectivity of ~8 % in agreement with the FTIR data at that wavelength.

Sub-One later coated some flat substrates. The spectral reflectivity of one of the better samples, #1697, is shown in figure 6. There was some concern that the mill finish (average roughness of 0.6 µm) on the aluminum substrate was not sufficiently smooth. This could result, especially at shorter wavelengths, in scattered incident light producing an erroneously low reflectivity. We used a CO2 laser and a diffuse gold integrating sphere to independently measure the total reflectivity at 10.6 µm. The value obtained was about 15%, slightly higher then the FTIR measurement (14%) but within the margin of experimental error.

5.3 Outgassing measurements

The LLNL Vacuum Sciences & Engineering Lab has a facility for measuring outgas rates[19]. An orifice of known conductance separates the sample chamber, a stainless steel cube 6 inches on a side, from an actively pumped chamber (see figure 7). Each chamber has a high accuracy, calibrated ion gauge (Granville Phillips Stabil-ion) monitoring its pressure. The difference in pressures across the orifice multiplied by its conductance (0.518 liter/sec) gives the outgas rate. An Inficon Transpector II residual gas analyzer (RGA) is mounted on the actively pumped chamber to monitor the outgassed species and their partial pressures.

Three type 304 stainless steel tubes 12 inches in length, 1.50 inches ID and 1.37 inches OD were coated both inside (20 µm thick) and outside (10 µm thick) by the Sub-One plasma process. Each tube was then cut into two pieces approximately 5.8 inches long, sized to fit into the sample chamber (see figure 8). In addition a 13.12 inch length of 6 inch diameter 304SS pipe (5.76 inch ID) was coated internally with DLC (20 µm thick). This pipe, with 8 inch conflat flanges on each end, was bolted to the chamber with a copper gasket and blanked off with a conflat flange. The total area of DLC coating in the test chamber was 3555 cm^2 compared 1394 cm^2 of chamber surface.

Prior to the measurement the chamber was baked for several days at 200ºC to remove all contamination from previous tests. The RGA and ion gauges were degassed as well. After cooling to ambient temperature both ion gauges read approximately the same value when the both chambers were pumped at the same speed. Before introducing the samples the chamber was vented to atmospheric pressure with dry nitrogen. This coats the chamber walls with a few monolayers of nitrogen molecules and serves two functions. The nitrogen serves as an impediment to atmospheric water molecules attaching to the walls while the samples are being loaded. Water desorbs very slowly and greatly prolongs pump down. This also brings the chamber walls to a consistent and uniform state before the start of each experiment.

After the samples were loaded and the chamber sealed off the pump down began. A bypass valve was opened so that the sample chamber was pumped at the same speed as the actively pumped chamber, about 25 liter/sec. The pressure dropped to the 10^{-5} Torr range 5 minutes after the start of pumping and reached the 10^{-7} Torr range in one hour. Water was the dominant species detected by the RGA with N_2 next. After 16 hours the bypass valve was closed so that the sample chamber was only pumped through the orifice in order to measure the outgassing. The total outgas rate was $5.1x10^{-7}$ Torr liter/sec with the main components H_2: 55%, CO: 16%, CO_2: 7%, H_2O: 11%, N_2: 5%, CH_4: 3%, O_2: 2%. The bypass was reopened for another 30 hours of pumping then heaters were turned on to increase the chamber temperature to 100 ºC. After 80 hours at 100ºC the total outgas rate was measured to be $1.8x10^{-7}$ Torr liter/sec, with the gas composition H_2: 77%, CO: 14%, CO_2: 3%, N_2: 2%, CH_4: 2%. The heaters were then shut and the chamber cooled to room temperature. After 16 more hours of pumping the total outgas rate was measured to be $3.2x10^{-9}$ Torr liter/sec at 20ºC, with the residual gas consisting of H_2: 90%, CO: 8%, H_2O: 2%.

After completion of the test the chamber was vented up on dry nitrogen and opened to remove the DLC coated parts. The chamber was then sealed and pumped for 7 days to determine the background level. At the end of this period both ion gauges read $<2x10^{-9}$ Torr and the net outgas rate was $<1.5x10^{-10}$ Torr liter/ sec. What this means is that the sample chamber background is negligible or more correctly balanced by the outgassing of the RGA in the actively pumped chamber. So no background corrections are needed to the measured rates. Dividing by the coated area the outgassing of the Sub-One DLC was $1.4x10^{-10}$ Torr liter/sec cm^2 after 16 hours of room temperature pumping. This is roughly an order of magnitude higher then Takahashi's DLC. After 140 hours of pumping including an 80 hour bake at 100ºC, the outgas rate was $9.0x10^{-13}$ Torr liter/sec cm^2. This is an extremely low rate, comparable to that of stainless steel, and a factor of 100 lower than that of MH-2200 black paint.

6. SUMMARY AND CONCLUSIONS

The infrared reflectivity and outgas rate measurements made on Sub-One DLC coatings demonstrate much promise for their application as an infrared black in an ultra high vacuum environment. The coatings are very rugged and have excellent adhesion at cryogenic temperatures. Plasma deposition offers several advantages over paint application, including the lack of volatile organics and the ability to uniformly coat complex shapes and complete assemblies relatively easily.

Some mention should be made of interesting recent developments in carbon nanotube-based black coatings. A low-density vertically aligned array of nanotubes demonstrated a record low integrated total reflectivity of 0.045%[20]. The nanotube array is deposited by a 750ºC process[21] not suitable for many substrates but will certainly have its applications. A lower tech approach involves brushing or spraying a mixture of nanotubes and solvent onto a surface and letting the solvent evaporate[22]. It also yields good results. One potential concern is the very high specific surface area of nanotubes, of order 300 square meters per gram[23]. A high effective surface area provides many absorption sites to trap molecules. For this reason nanotubes have been proposed as a hydrogen storage medium[24]. As seen earlier high effective area is usually associated with high outgas rates. But the vacuum properties of nanotubes have yet to be quantified.

There are several logical extensions of this present work. The measurements reported in this paper used standard Sub-One DLC coatings that were designed to provide high abrasion and corrosion resistance not necessarily low infrared reflectivity. The optical properties of DLC can be modified by the addition of nitrogen and fluorine atoms during the deposition[25,26]. The resonant frequencies of C-N and C-F bonds differ from C-H and can provide enhanced absorption in other spectral regions.

One can view the multilayer DLC as an interference coating. If the optical constants of the layers are accurately known and can be well controlled during deposition then it should be possible to use optical design codes to tailor reflectivity and absorptivity to produce desired results. Work has been done in the visible and near infrared on so-called dark mirrors. These are interference coatings on metal surfaces that have very low reflectivity over a broad spectral region, up to a 2:1 range of wavelengths[27,28].

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DLC reflectivity measurements vs. incidence angle with a CO_2 laser

Angle of Incidence	Reflectivity (specular)
20º	6.5%
30º	9%
40º	12%
50º	21%
60º	26%
70º	30%

Table 1 Reflectivity measurements on 3 µm thick single layer DLC at 10.6 µm wavelength

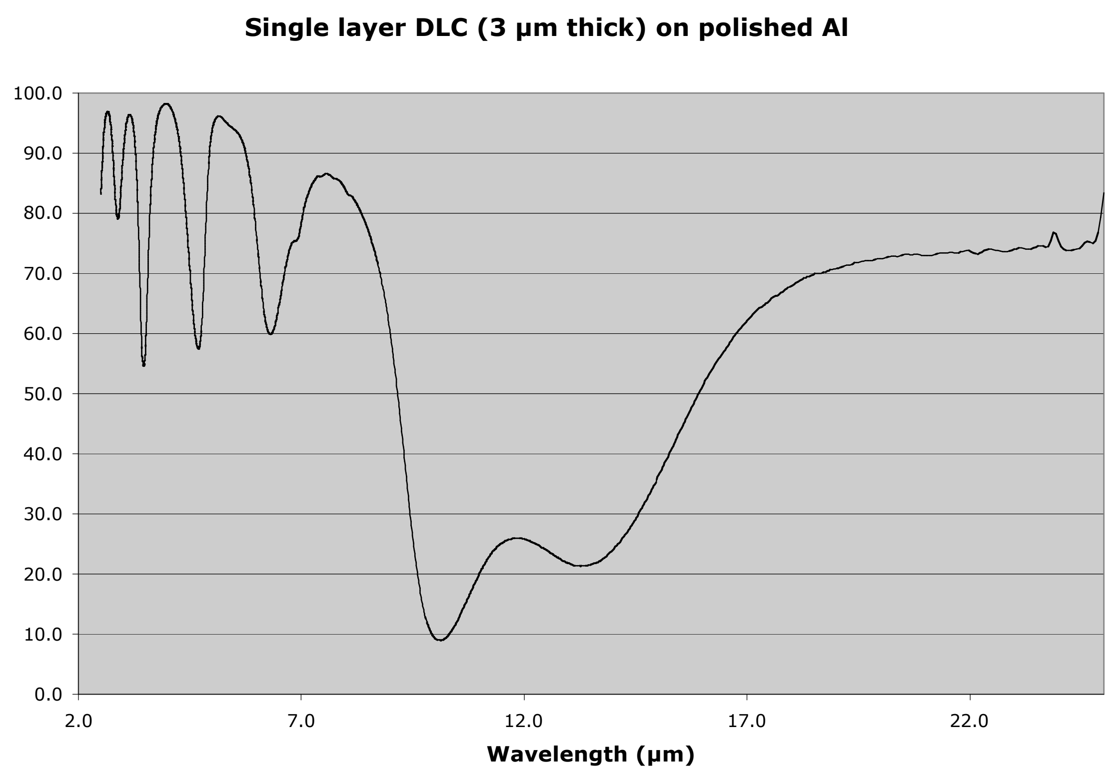

Figure 1 Specular reflectivity of 3 µm thick DLC vs. wavelength at 45º incidence

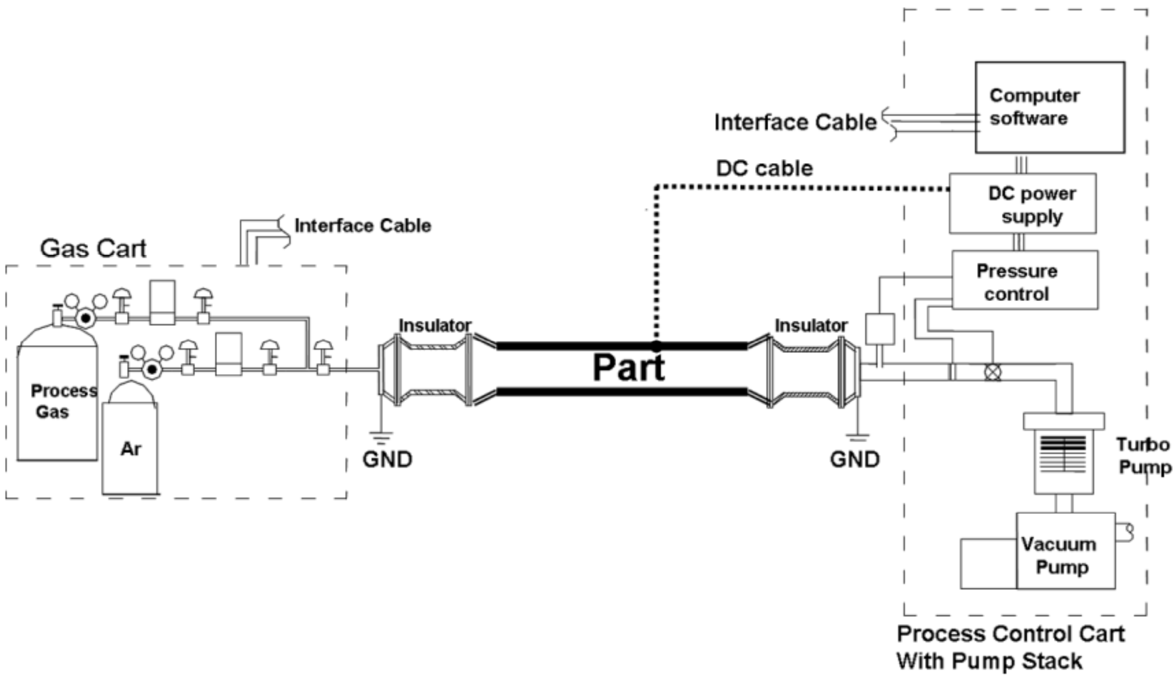

Figure 2 - Diagram of Process Set-up

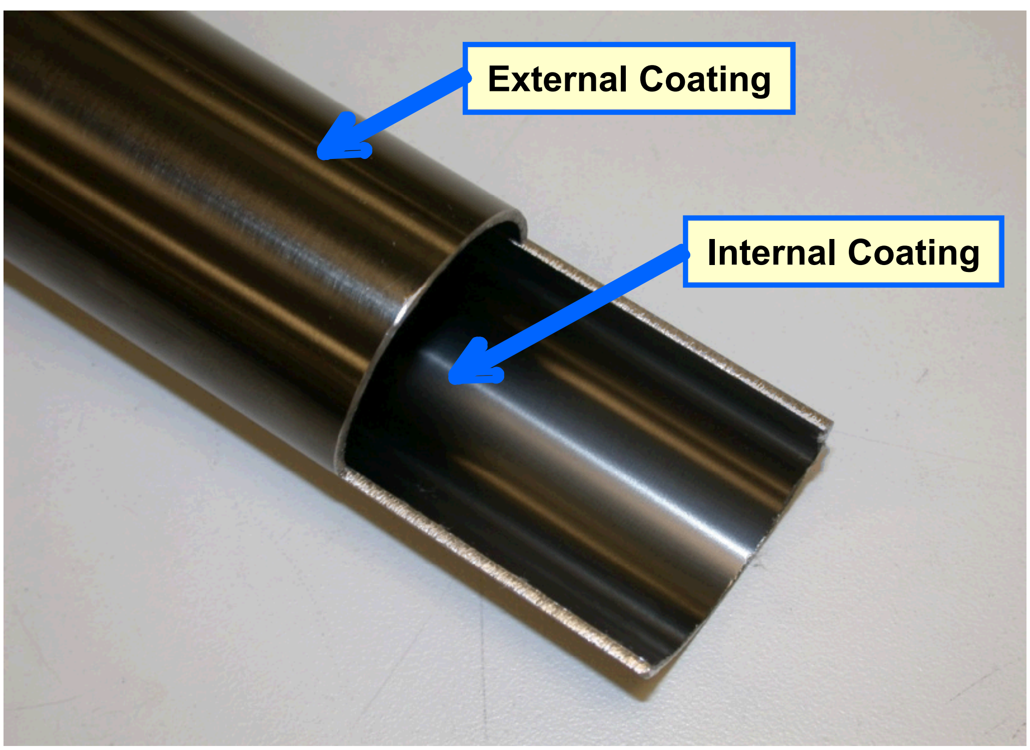

Figure 3 Sample of Sub-One DLC internal and external coating on a stainless tube

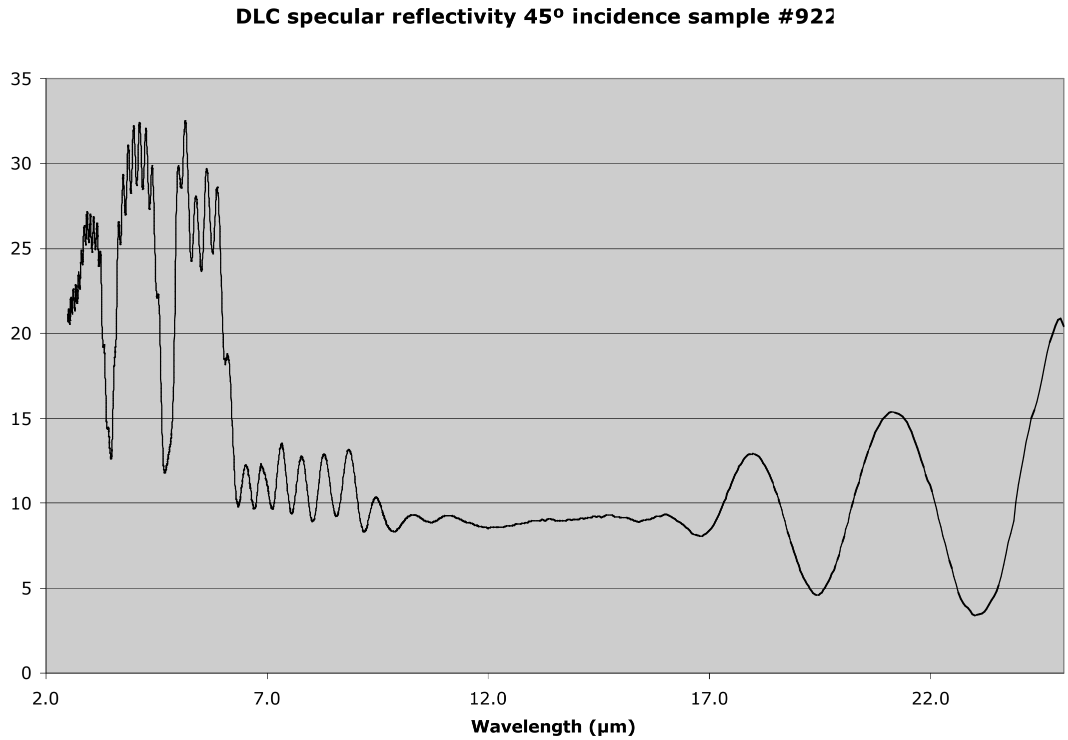

Figure 4 Specular reflectivity vs. wavelength at 45º incidence angle for 39 μm thick DLC inside stainless tube

20.67

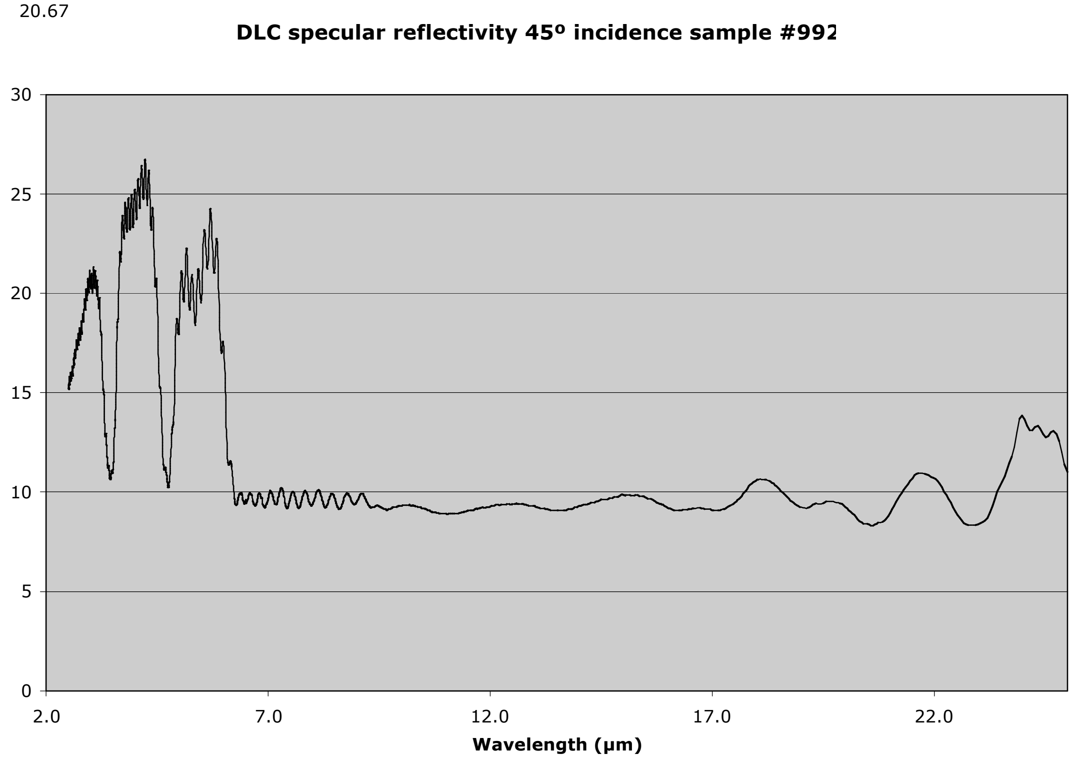

Figure 5 Specular reflectivity vs. wavelength at 45º incidence angle for 50 μm thick DLC inside stainless tube

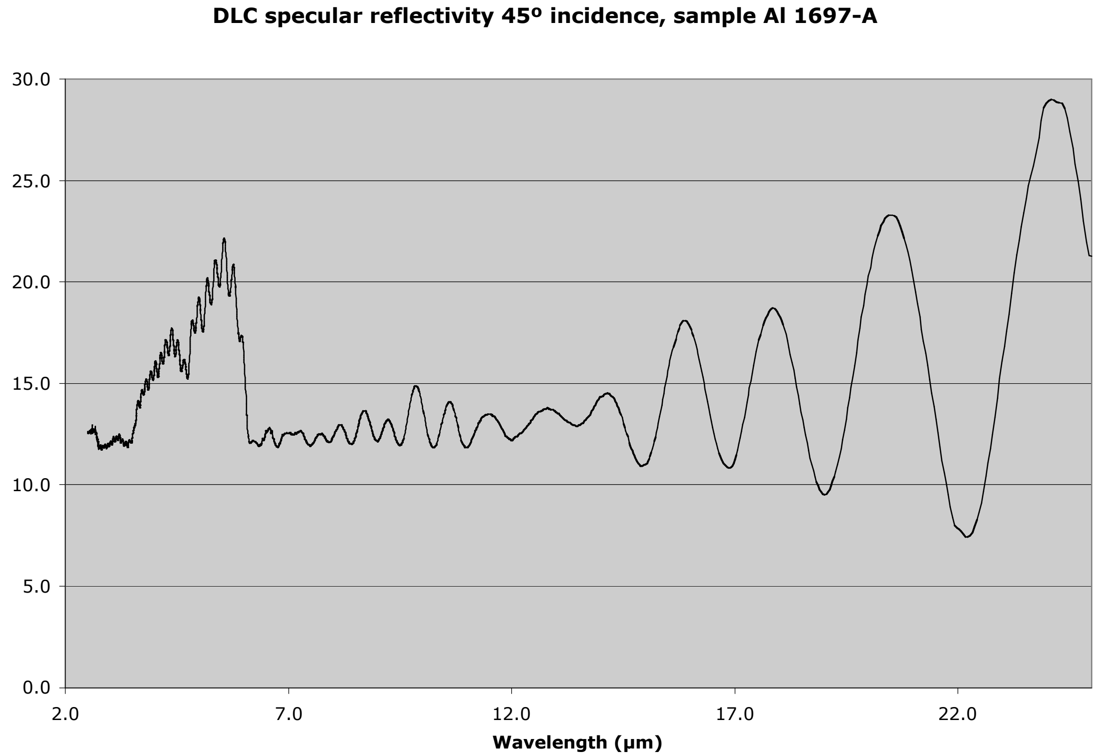

Figure 6 Specular reflectivity vs. wavelength at 45º incidence angle for 48 µm thick DLC on flat aluminum substrate

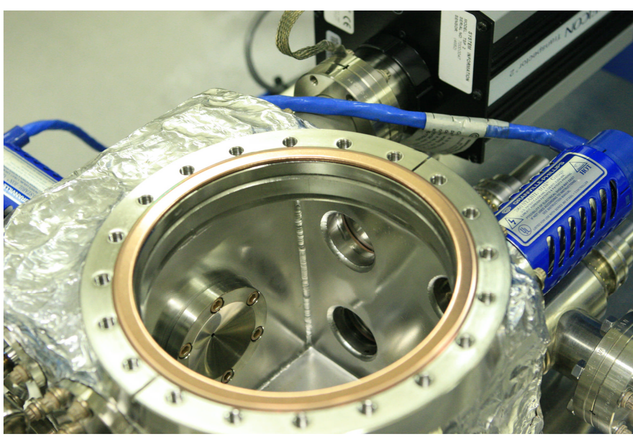

Figure 7 Outgas test setup showing sample chamber, orifice, ion gauges and RGA

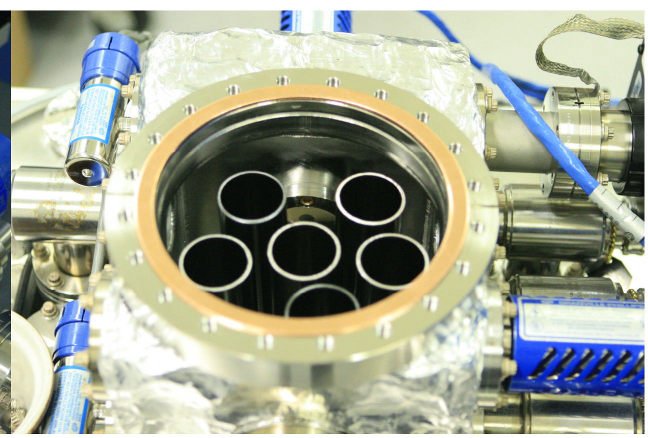

Figure 8 DLC coated tubes in sample chamber