

Diamond Like Carbon Coatings for Rhenium Wires and Foils

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Abstract

Diamond like carbon has been deposited as a protective layer for coronary stenting applications. Taking advantage of DLC's resistance to chemical attack, its flexibility, and other properties, our current technical objective is to develop DLC as a coating for radioactive rhenium stents. Radioactive rhenium stents are being investigated to limit smooth muscle cell growth following coronary surgery. The DLC coating is being investigated to reduce the release of radioactive rhenium (released activity) into the blood following the stenting procedure. An inductively coupled RF plasma system was used to deposit the DLC onto rhenium substrates. Foils, wires, and coils were coated and tested for adhesion, cytotoxicity, and release of radioactive rhenium. Our initial results indicate up to a three-fold decrease in released activity relative to uncoated rhenium.

Introduction

Diamond like carbon (DLC) films are known to be smooth, hard, chemically stable, impermeable, and highly lubricating.^{1,2,3,4} Biocompatibility of DLC films has been established in non-blood-contacting applications in which a wear resistant material is required. Evans *et al.* investigated the biocompatibility of DLC films *in vitro* using mouse peritoneal macrophages.³ Their results show no degradation of cell integrity following exposure to the DLC material. Dowling *et al.* investigated DLC as a wear resistant coating of hip implants;⁵ no mutagenic response was observed in either *in vitro* or *in vivo* tests.⁵

Most DLC films that have been studied for biomedical applications were deposited using a saddle field source without independent control of substrate bias.^{3,4,5} Substrate bias, or the voltage difference between the plasma and the substrate, is critical to the resulting film properties.^{1,2} The DLC films used in this work were deposited by RF inductively coupled plasma (RFICP). RFICP deposition will allow for independent control of discharge power and substrate bias.^{6,7} Christiansen *et al.* have reported good mechanical, chemical, and biocompatible properties for DLC films deposited by RF plasma.⁴ McLaughlin *et al.* have also reported good adhesion of DLC, deposited by RF plasma, on medical guidewires.⁸ DLC was used in this application for its good flexibility, low surface roughness, and high chemical resistance.

We are investigating the ability of DLC coatings to prevent the release of radioactive rhenium from a radioactive rhenium source without attenuating the dose. Radioactive materials are used not only to reduce or eliminate tumor cells, but also to minimize extensive scar formation. Scar formation occurs not only in the skin, but also inside of blood vessels after mechanical damage. In the U.S., about 500,000 people undergo percutaneous transluminal coronary angioplasty (PTCA) each year. PTCA is a process in which an atherosclerotic vessel is widened by blowing up a small balloon inside the artery. Unfortunately, between 30 to 40% of these patients will develop a re-narrowing of the same vessel (restenosis) within 6 months. Radioactive stents have been used successfully to reduce the rate of restenosis in animals^{9,10} and they are currently undergoing clinical patient trials.^{11,12} Because both total radiation dose and dose-rate seem to be important for the treatment outcome, it has been suggested that

endovascular brachytherapy with stents of shorter half-lives than ^{32}P ($T_{1/2}$ of 14 days) might be beneficial.¹³ One class of beta-emitting isotopes with shorter half-lives are the rhenium isotopes ^{186}Re and ^{188}Re ($T_{1/2}$ of 90.6 and 17 hours, respectively)¹⁴.

One limitation of rhenium stents, however, is the tendency to slowly oxidize and then release radioactive rhenium in the form of the highly water soluble perrhenate anion ReO_4^- (released activity). Released activity can be reduced by coating the stents with a thin, radiation hard material. DLC is one such coating with potentially good biocompatibility, good adhesion, and radiation hardness¹⁵. As shown below, coating radioactive rhenium with DLC is effective in reducing the released activity.

Experimental Methods

Carbon films were grown from a methane/argon mixture by plasma enhanced chemical vapor deposition. An inductively coupled RF plasma system was used to deposit the films; the design of this RF plasma system was proposed and first tested by Hopwood and co-workers.^{6,7} The dual RF inductively coupled plasma (ICP) provides high ion densities and uniform deposition over large areas. The substrates to be coated are placed on top of the substrate electrode, which is mounted within the vacuum chamber parallel to the planar coil electrode. The bias voltage, which is provided by the substrate electrode, is varied to control the ion bombardment energy. The substrate electrode temperature is normally maintained at 25°C.

Films were deposited on rhenium foils, wires, and coils, and on glass microscope slides. Multiple foils were coated at each set of conditions. The foils were used for measuring released activity. The wires and coils were used to assess the film adhesion and the ability to deposit films onto complex shapes. Films were deposited onto glass substrates for identification and characterization by FTIR spectroscopy. Deposition conditions were varied to determine the main effects on the resulting free release of radioactive rhenium. The deposition pressure was varied between 20 and 55 millitorr, the induction power was varied between 0 and 100 watts, and the bias voltage was varied between 400 and 500 volts. The source gas was kept constant at a methane to argon ratio of 9:1.

Following deposition of the DLC film, the rhenium foils were made radioactive using a nuclear reactor. The foils were first cleaned by immersing in 95% and 100% ethanol and acetone. The foils were then neutron-activated at a neutron flux of $5 \times 10^{12} \text{ n/cm}^2\text{sec}^{-1}$ for 5 to 30 minutes to yield between 0.4 and 2.6 MBq ^{186}Re and 2.5 and 15.1 MBq ^{188}Re . The neutron activation was carried out at Ohio State University in Columbus, Ohio. The radioactive foils were then incubated in 3 ml of 0.9% saline at 37° C for up to 1 month. The released activity, or the amount of radioactive rhenium which escaped from the rhenium sample into the liquid (supernatant), was measured together with the activity of the foil at each time point. The released activity was then divided by the total activity (supernatant plus foil) and graphed as a percent. For both the foil and the supernatant, the activity measurements include the decay from both radioisotopes (^{186}Re and ^{188}Re). Comparisons to uncoated control samples were made and the relative free release determined.

Results and Discussion

The films were evaluated using adhesion tests, scanning electron microscopy (SEM), electron energy loss spectroscopy (EELS), and FTIR spectroscopy. The films were evaluated for adhesion using tape tests and bend tests. In general, films adhered to the substrates following these tests. SEM analysis indicated that the films were smooth and pinhole free. The films were confluent on the wires and coils that were coated. Figure 1 shows a scanning electron

micrograph of a rhenium wire that has been coated with DLC using the RFICP system. Preliminary tests show that the DLC films adhere well to the wire and do not delaminate following bending tests. The micrograph in Figure 1 was taken following a 90° bend test. These results are in agreement with the preliminary work done by McLaughlin *et. al.*, who showed good adhesion of DLC on stainless steel medical guidewires.⁸



Figure 1: SEM micrograph of a DLC coated rhenium wire following a 90° bend test. The wire is 0.5 mm in diameter.

EELS spectra were taken for the films to determine the energy loss of reflected electrons from the sample surface; the primary or incident beam energy was 1 KeV.¹⁶ An EELS spectrum for a film deposited at 55 mtorr, 400 volts bias, and an induction power of 100 watts is shown in Figure 2. The position of the primary energy loss peak (-3.6eV) is in good agreement with the work of Wang *et al.* for hydrogenated diamond like carbon. Based on the work of Wang *et al.*, the EELS spectra can be used to determine the relative amount of hydrogen within the films. In turn, the hydrogen content is related to the relative amount of sp^3/sp^2 bonded carbon. The hydrogen content in our films varied from 38-47%. The ratio of sp^3/sp^2 bonded carbon varied from 0.42 to 0.96.

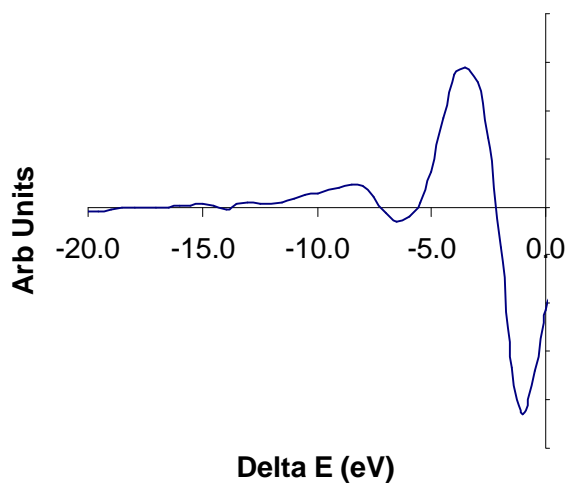


Figure 2: Second derivative of EELS data ($d^2(N(E))/dE^2$) taken from a DLC coating on rhenium foil.

FTIR absorption spectra were taken for the films deposited on glass slides. All films exhibited a peak centered at 2920 cm^{-1} ; the broad peak centered on 2920 cm^{-1} is characteristic of a:C-H films.¹⁷

Our preliminary results are consistent with previous research that demonstrated the biocompatibility of DLC films.⁵ Figure 3 shows a DLC coated wire that has been incubated in 9L-glioblastoma tumor cells. Within 7 days, the cells became confluent and encircled the wire (top left) without showing any growth inhibition. The attachment to the wire and avid growth on it means that DLC coated wires are a good substrate, *e.g.* for the re-endothelialization of intravascular metal wires.

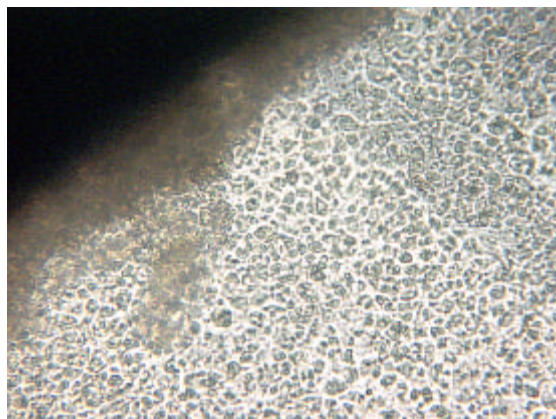


Figure 3: SEM micrograph of 9L-glioblastoma tumor cells attached to a DLC coated rhenium wire. The wire is in the upper left hand corner.

The objective of this work was to determine if DLC or a:C-H films could provide a suitable protective layer for radioactive rhenium to be used *in vivo*. The DLC films must prevent the release of radioactive rhenium into the surrounding fluid. To determine the relative free release from different DLC films, rhenium foils were used. Measures of free release were taken over a two week period for each sample. The free release from the coated samples was compared to the free release of an uncoated, control sample. Figures 4 and 5 show the free release from samples coated under different conditions; the initial activity was higher for samples in runs 17 and 27 (Figure 5) (the initial radioactivity varied as a result of the different neutron activation conditions). The released activity was lowest from samples deposited at the highest bias voltages and the highest induction powers. More data is required to make correlations between process conditions and the resulting film properties.

The DLC coating of rhenium wires produces wires with excellent biocompatibility and non-toxicity to the tested monolayer cells. The DLC coated samples also have good oxidation resistance, reducing the release of perrhenate from the radioactive wire. The currently used metal coatings, titanium or titanium nitride, might enclose a radioactive source to the same degree, however, they are not as inert towards tissue as DLC. Furthermore, using the method of inductive plasma coating, DLC could also be easily applied to highly irregular metallic structures such as stents, coils and inner surfaces of devices. DLC can be deposited as a very thin, protective layer, much thinner than other candidate materials (teflon, TiN, etc.). A thin film coating for radiolabeled implants minimizes interference with the radiation (*e.g.* bremsstrahlung production), thus allowing even the use of low energy beta-emitters or alpha-emitters without radiation dose attenuation.

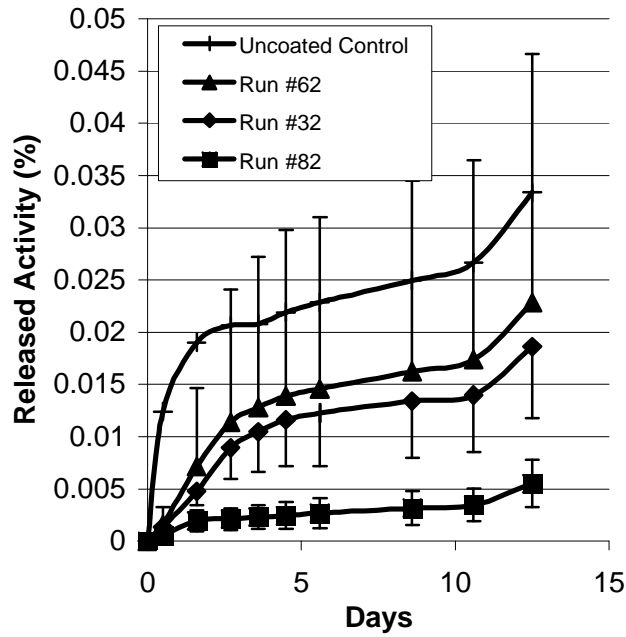


Figure 4: Percentage of released activity from DLC coated radioactive rhenium foils.

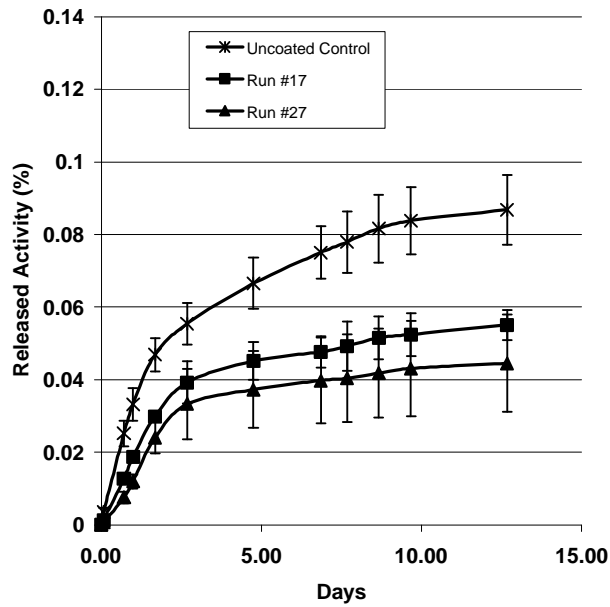


Figure 5: Percentage of released activity from DLC coated radioactive rhenium foils. The initial activity of the foils was higher than in those reported in Figure 5.

The trends observed in our initial data suggest that the oxidation resistance can be improved. We have shown up to a three fold decrease in the released activity by coating the samples with DLC. Furthermore, there are differences in the released activity based on differences in the plasma conditions. The samples with the lowest released activity were

deposited at higher bias voltages and induction powers. As bias voltage increases the energy of the ions hitting the sample increases; as induction power is increased the ion density and the overall plasma volume increase. The sp^3 bonded carbon content of the film is controlled by the ion energy of the species hitting the growth surface. As the sp^3 content of the film increases the film density increases. The EELS data indicated that the sp^3/sp^2 ratio had a maximum value of 0.96. Future work, therefore, will focus on improving the release behavior of the films by going to higher bias voltages and higher induction powers to increase the sp^3/sp^2 ratio.

Conclusions

DLC carbon films have been deposited by RFICP onto rhenium substrates. The DLC films showed no toxic effects to cells. The DLC films were effective in reducing the released activity from radioactive rhenium substrates. The released activity was decreased by up to a factor of three relative to the control samples. Further improvement in the release behavior can be achieved by increasing the density of the films.

Acknowledgements

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