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Deposition of thick and adherent Teflon-like coating on industrial scale stainless steel shell using pulsed dc and RF PECVD

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ABSTRACT

A unique combination of pulsed dc and radio frequency (RF) discharge deposition was used to deposit thick (~5 μm) and adherent (2–4 MPa) Teflon-like coatings on a stainless steel (SS) shell of 2 m diameter size, through plasma enhanced chemical vapor deposition (PECVD). The details of deposition on such a big industrial scale component are reported for the first time. In this method, highly adherent thin interface layers were grown on SS shell that was electrically grounded, using pulsed dc discharge, followed by RF discharge deposition to build up the required coating thickness. The fluorocarbon precursor molecules, required for the deposition of Teflon-like coating, are generated indigenously by pyrolyzing the Teflon powder. The deposited coating was studied for its chemical bond state, surface roughness (Ra), morphology, thickness, and adhesive strength. These studies were carried out by using XPS, AFM, SEM, etc. The adhesive strength of the coating was measured by pin-pull test as per ASTM D4541 standard test. The coatings deposited with pulsed dc discharge were observed to have higher adhesive strength when compared with those deposited with RF discharge.

1. Introduction

Teflon or poly tetrafluoroethylene (PTFE) is a polymer, known for its unique properties such as low coefficient of friction, low refractive index, low dielectric constant, superhydrophobicity, and a combination of good corrosion resistance, biological compatibility, chemical stability, and good plasticity. Teflon is a fluorocarbon compound and has a simple linear chain molecular structure. It has found applications in various fields like MEMS, biomaterials, non-stick coatings, anti-adhesive coatings [1], super hydrophobic coatings [2], etc. Thin films of Teflon-like coatings have been deposited by various methods viz. RF sputtering [1,3,4], ion beam sputtering [5], plasma polymerization using RF discharge [6], pulsed laser deposition [7–10]. Further, in order to deposit thicker Teflon-like coatings at very high deposition rates, spray technique is resorted to. In spray technique, PTFE coatings are obtained by thermal spraying of the Teflon powder, and the coating needs to be followed up by high temperature curing (~150 to ~250 °C) [11].

In general, deposition of any type of coating on an industrial scale object is a challenge. Though, in the case of PTFE deposition, spray coating method would be more suitable to obtain thick and adherent coatings on industrial sized components; the requirement of high curing temperature does not go down well with the process. The industrial components of considerable weight and of complicated shapes will tend to distort due to this high temperatures. In the present paper, we report about a method to deposit thick (~5 μm) and adherent (2–4 MPa) Teflon-like coatings on a stainless steel shell of 2 m diameter size. The primary requirement of the deposited coating, in the current application, is to offer an adherent and lubricious surface.

In the present study, we have deposited Teflon-like coating on the inner surface of the 2 m diameter stainless steel shell, using PECVD technique. The deposition was carried out as a batch process and a special box coater was designed for this purpose. The box coater houses the curved live electrode and is also provided with a mechanism to supply the feed gases. In a given batch, an area of 800 mm × 120 mm has been uniformly deposited with Teflon-like coating. The precursors were generated by pyrolyzing the Teflon tailings/powder at 450 °C. These precursor gases were fragmented in the plasma that was excited by pulsed dc and RF power sources. In the present work, we have also studied the effect of the type of plasma excitation (i.e. pulsed dc and RF) on the adhesion strength of the deposited coatings. The shell was always kept at the ground potential. During optimization of the process, silicon wafers were positioned on the inner surface of the shell and these wafers deposited with Teflon-like coatings were analyzed using XPS, SEM, and AFM. The adhesion strength was measured – directly on the shell – with an elcometer (Aeroquip, model 108).

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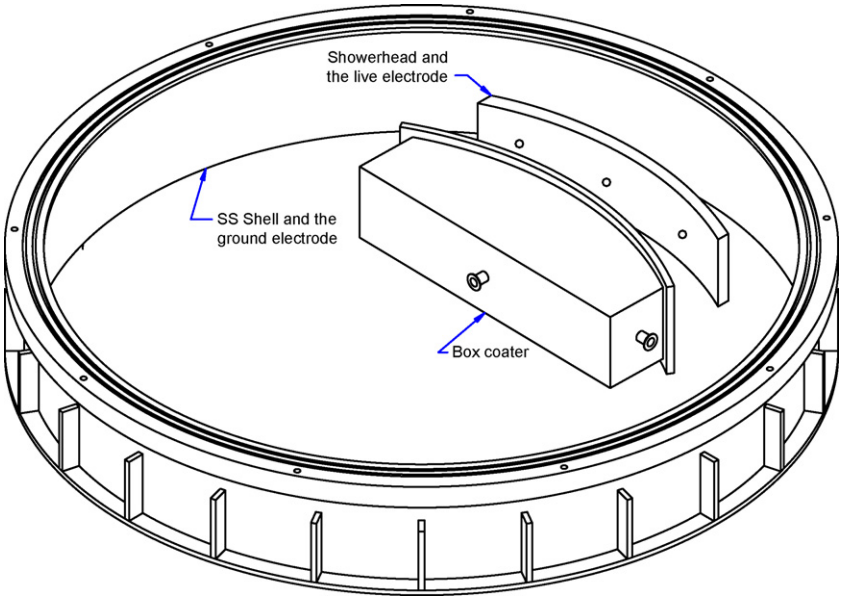

Fig. 1. Schematic of the experimental setup.

2. Experimental procedure

The schematic of the experimental set-up used in the present study is shown in Fig. 1. The cylindrical SS shell that is to be coated with Teflon-like coating, acted as the grounded electrode, where as the live electrode was housed inside the box coater. The box coater is basically a vacuum compatible enclosure made up of stainless steel, and has provisions for inserting the feed gas and for the electrical connections. The live electrode was a double walled stainless steel construction/structure which also acts as a feed gas shower-head. This structure was made up of two curved SS plates, whose radius of curvature was equal to that of the SS shell. The entire surface area of the shower-head, except the area which was facing the grounded shell, was covered with a proper electrical insulation. This un-insulated area was pierced with a number of holes of each 2 mm in diameter, and the holes were spaced 15 mm apart in both *x* and *y* directions, to make up the shower-head. The other side of the curved structure was provided with three gas inlets to have uniform gas distribution through the shower-head. The box coater was provided with a groove where a vacuum sealing O-ring sits and the box coater could be fixed with the SS shell, face to face, and was clamped mechanically. The live electrode was fixed inside the box coater in such a way that it was electrically isolated from the body of the box coater and an inter electrode gap of 30 mm was maintained between the SS shell and the live electrode. A rotary pump with a pumping capacity of 2000 lpm was used to create the necessary low pressure inside the box coater. The base vacuum obtained was 1×10^{-3} mbar. An indigenously developed pyrolyzer was used to pyrolyze Teflon powder to generate the required precursors. The pyrolyzer was heated, using an ordinary industrial heater, to a temperature of 450 °C so that the Teflon powder gets decomposed into tetrafluoroethylene (CF_2=CF_2) and hexafluoropropene (CF_3–CF=CF_2) [12]. Nitrogen gas of 99.99% purity was used as plasmagen gas and as well as the carrier gas. Nitrogen and the precursor gases were mixed in a particular ratio (during deposition), and the mixture was introduced in to the inter electrode gap through the shower-head.

Literature suggests that the coatings deposited on the live electrode have better adhesion properties compared with those deposited on the grounded electrode [13]. In the present case, since the object to be deposited with the coating being very large, it could not be made a live electrode and hence it was a challenging task to deposit adherent coatings on the grounded shell.

Before the box coater was fixed on to the SS shell, the region to be coated on the shell and the live electrode, were cleaned thoroughly using acetone and/or petroleum ether. Those sections which need not be coated were properly masked. Then the box coater was clamped with the shell and the pumping system was activated. After attaining the base vacuum, the required operating pressure was obtained by admitting the concerned gases. The exposed shell area was initially plasma cleaned for 30 min, by exciting the plasma with pulsed dc power. A 10 kHz pulsed dc power source (−1000 V, 1 A) and 50% duty cycle were used. Subsequently the deposition process followed. The initial interface layers were deposited with pulsed dc discharge for half an hour which was followed by RF (13.56 MHz) deposition for developing thicker coatings. The deposition process was repeated for several batches and the inner surface of the entire shell was deposited with the required coating. The operating parameters are given in Table 1. During the optimization process, single crystal silicon wafers were affixed on the shell, so that the deposited coatings could be analyzed for their thickness measurement. The deposited films, on small SS samples, were analyzed using Leo's Scanning Electron Microscope (SEM) for the morphology and X-ray Photoelectron Spectroscope (XPS) for the chemical bond state and Atomic Force Microscopy (AFM) for surface roughness. SEM was also used for measuring the coating thickness by studying the cross-section of the coated silicon crystal. An elcometer was used to measure the adhesion strength of the deposited coating, directly on the shell.

3. Results and discussion

In the present work we had converted the Teflon powder into precursor gases such as tetrafluoroethylene (CF_2=CF_2) and hexafluoropropene (CF_3–CF=CF_2), using an indigenously developed pyrolyzer. The details of the mechanism are provided elsewhere [2]. The precursor gases – along with the carrier gas – were introduced in to the inter electrode region, through the shower-head, and the required operating pressure was obtained. Then the electrodes were powered with the appropriate power supply and the plasma was generated. The precursor gases were interacted with

Table 1
Operating parameters.

Parameter	Pulsed dc (−ve) plasma cleaning	Pulsed dc (−ve) coating	RF coating
Gases used	Nitrogen	Nitrogen, and Teflon precursor	Nitrogen, and Teflon precursor
N_2 to precursor ratio	–	3:1	3:1
Operating pressure	0.1 mbar	0.1 mbar	0.1 mbar
Frequency	10 kHz	10 kHz	13.56 MHz
Duty cycle	50%	50%	–
Power density	0.04 W/cm^2	0.04 W/cm^2	0.05 W/cm^2
Duration	30 min	30 min	10 h

the plasma and get fragmented. This interaction results in to the formation of radicals. Later these fragmented species reach on to the surface of the substrate and polymerize on the surface.

The photograph of the 2 m diameter SS shell, deposited with the Teflon-like coating along with the box coater, is shown in Fig. 2.

3.1. SEM results

The thickness and morphology of the deposited coatings were studied using SEM. A small piece of single crystal silicon wafer was placed on the inner surface of the shell and was deposited with the Teflon-like coating and it was used for the SEM study. The thickness of the coating was measured by studying the cross-section of the cut silicon wafer. As the deposited coating is non-conductive in nature, before the wafer was subjected to SEM study, it was deposited with a very thin layer of gold to avoid the charging effects. The cross-sectional SEM pictures of the coatings deposited by pulsed dc (for 35 min) and RF PECVD (for 10 h) are shown in Figs. 3 and 4, respectively. These pictures give an indication about the uniformity of the deposited coatings, in both the methods.

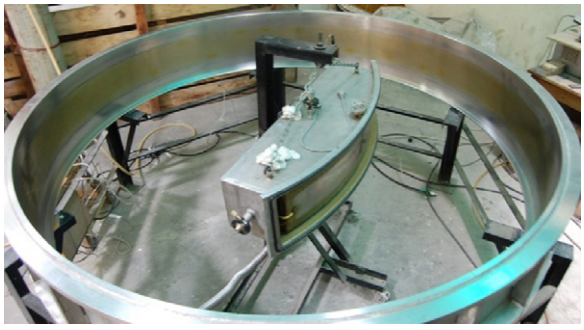

Fig. 2. Photograph of the SS shell deposited with Teflon-like coating, and the box coater.

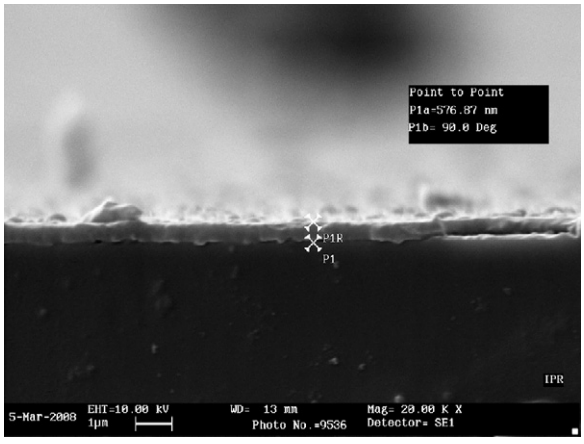

Fig. 3. SEM pictures of Teflon-like coating deposited by pulsed dc PECVD.

3.2. XPS results

X-ray Photoelectron Spectroscope was used to study the chemical bond state of the deposited coatings, using Al Kα source. The X-ray flux of 150 W was used. The deconvoluted C1s spectrum of the coatings deposited by pulsed dc and RF are shown in Figs. 5 and 6, respectively. The spectrum were corrected for the charging effects

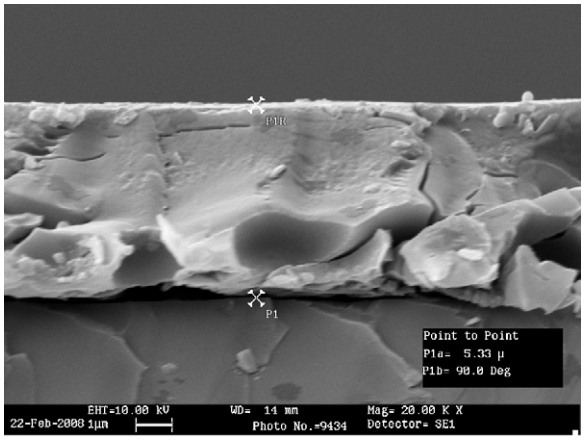

Fig. 4. SEM picture of Teflon-like coating deposited by RF PECVD.

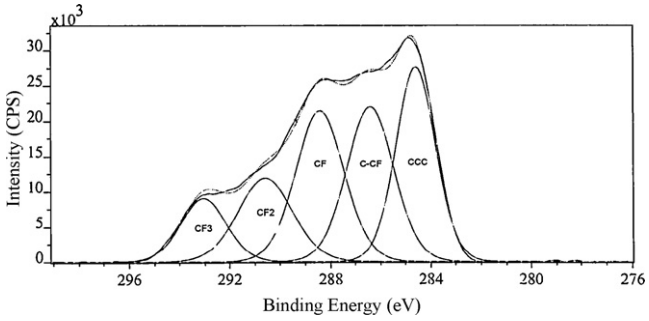

Fig. 5. XPS spectrum of the Teflon-like coating deposited with pulsed dc discharge.

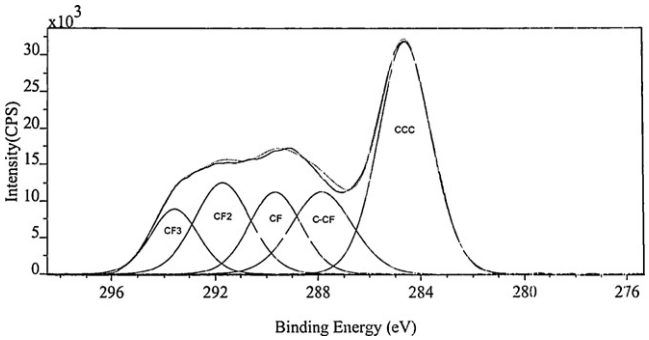

Fig. 6. XPS spectrum of the Teflon-like coating deposited with RF discharge.

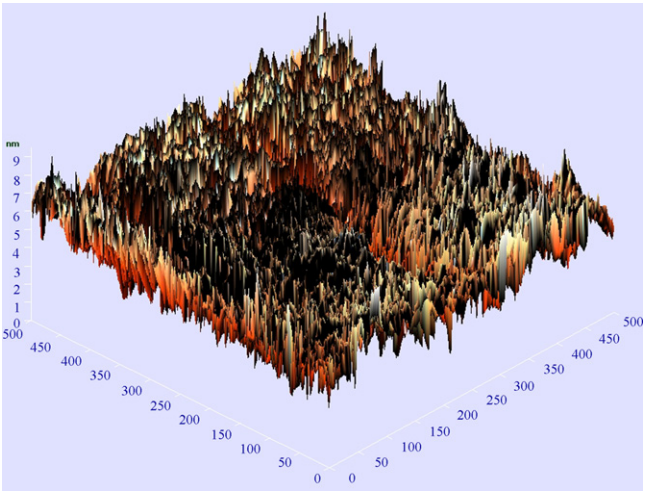

Fig. 7. AFM micrograph of the coating deposited by pulsed dc discharge.

by referencing them to F1s (688.8 eV) as an internal standard, present in the sample [14]. Carbon and fluorine are the main constituents of the XPS survey spectrum with traces of oxygen and nitrogen. From the figure it is clear that deposited coatings are dominated by various fluorocarbon moieties indicating that the coatings are Teflon like. However, the concentration of CF, and C-CF moieties is found to be more in the case of the coatings deposited with pulsed dc, when compared with those deposited by RF discharge, that could give rise to more cross-linking.

3.3. AFM results

Atomic Force Microscope (NT-MDT, model no. SOLVER-PRO 47) was used to study the surface morphology and roughness of the deposited coatings. The AFM micrographs of the coatings deposited with pulsed dc and RF discharges are shown in Figs. 7 and 8, respectively. Roughness analysis of the coatings deposited with pulsed dc discharge indicates the peak to peak (S_y) and average (S_a) roughness are 52.5 nm and 11.99 nm, respectively. Similarly in the case of coatings deposited with RF discharge, S_y and S_a are measured to be 96.6 nm and 20.54 nm, respectively. The higher roughness values observed in the case of RF discharge deposited coatings is attributed to the ion bombardment on the surface of the substrate.

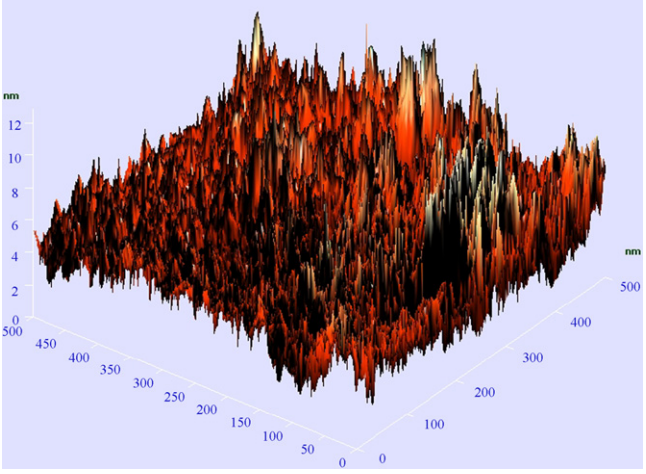

Fig. 8. AFM micrograph of the coating deposited by RF discharge.

Table 2
The comparison of the adhesive strengths of Teflon-like coating deposited by various discharges on flat samples of 2 inch diameter.

No.	Pulsed DC (MPa)	RF (MPa)	Pulsed DC + RF (MPa)
1	7.5	2.5	4
2	9.5	3.5	4
3	14	3.5	4.5
4	11	3	5
5	8.5	3	4
6	6.5	2.5	4
Average	9.5	3.0	4.25

3.4. Adhesion

The adhesive strength of the deposited coatings was measured, using an elcometer. The tests were performed as per ASTM D4541, a standard pin-pull test. The adhesive strength values of various samples, deposited with Teflon-like coatings using pulsed dc, RF and their combination are shown in Table 2. The samples were placed at the same position and the above data was collected from different deposition runs. For this particular study, the deposition was carried out on flat samples (of 2 inch diameter) for only half an hour, independently by pulsed dc and RF discharge PECVD methods. In the case of the deposition in which both the methods were sequentially used, the total deposition time was 1 h. It is very clear from the table that the adhesive strength of the coatings, deposited using pulsed dc discharge is higher as compared to that of the coatings deposited using RF discharge. A detailed study is in progress to understand the reasons for the observed higher adhesion strength values in the case of pulsed dc deposition. However it is not possible to deposit thicker Teflon-like coatings – which are insulating in nature – with pulsed dc discharge alone, as it would lead to the initiation of a DBD like discharge and the associated streamers, as the thickness of the coating increases. These streamers would result in puncturing of the coating and the film damage. Hence RF discharge was used to deposit thicker coatings.

The above observation (from the sample level experiments), that the adhesive strength of the pulsed dc deposited coating was high, has been used effectively on 2 m diameter shell by depositing thin adherent interface layers with pulsed dc, followed by RF discharge deposition for developing thicker coatings. However, when the RF deposition was carried out for longer durations (i.e. 10 h to produce films thicker than 5 μm), the adhesion strength of the coatings deposited with the sequential combination of pulsed dc and RF discharge were observed to be lower (2–4 MPa) than the values shown in Table 2. This might be because of the internal stresses developed in the film due to larger thickness.

4. Conclusion

Thick and adherent Teflon-like coatings have been successfully deposited using the combination of pulsed dc and RF PECVD discharges on the internal surface of an industrial scale object of 2 m diameter SS shell that acted as a grounded electrode. The coatings deposited with pulsed dc discharge, used for growing the interface layer, were observed to have higher adhesion strength, while the RF discharge could produce thicker coatings. The sequential combination of pulsed dc and RF discharge were used innovatively to deposit thicker and adherent Teflon-like coatings.

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