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# Removal of the Codeposited Carbon Layer using He-O Glow Discharge

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## Abstract

In this study we examine the combination of a He-O glow discharge with heating as a possible technique to remove deuterium from TFTR tiles. Samples were cut from a relatively large area containing a uniform codeposited layer of deuterium and carbon. Auger/SEM was used to generate micrographs of each of the samples. The samples were also examined using Rutherford Back-Scattering to determine the near surface composition. Individual samples were then exposed to a He-O glow discharge while being heated. After the exposure, the samples were returned for Auger/SEM and RBS of the same areas examined prior to the exposure. Comparing the samples before and after exposure revealed that the amount of the codeposited layer removed was significantly less than 1 μm. Removal rates this low would suggest that He-O glow discharge with heating is insufficient to remove the thick layers predicted for ITER in a timely fashion.

## Introduction

The problem of tritium codeposition with carbon to yield excessive tritium inventories presents the ITER fusion reactor with one of its greatest challenges. Unless disruptions can be controlled, graphite or carbon composites must be placed in the bottom of the tokamak divertor to allow the vacuum vessel to survive the tremendous energy deposition during a disruption. With carbon present, nearby surfaces where the rate of deposition is greater than the erosion rate will have codeposited layers of carbon and hydrogen isotopes growing indefinitely. Since ITER will be operating with a mixture of tritium and deuterium, the codeposited layer has a high potential for generating an excessive tritium inventory. If we combine the high tritium inventory with the fact that the a-C:H codeposited layer is not stable at elevated temperatures in the presence of air [1], we have a potential environmental hazard in the event of an accidental vacuum loss when the tokamak vessel is hot.

Several techniques have been examined as ways of removing the codeposited layer. These techniques include heating in air or oxygen [1-5], laser ablation [6,7], flash lamps [8], and He-O glow discharge [9]. While each of these techniques has shown some success in reducing the quantity of tritium in the codeposited layer, no technique has been identified as the solution to the problem. As an example, heating in air will completely remove the codeposited layer if the temperature is sufficiently high. Unfortunately, ITER will be limited to an upper bake out temperature of approximately 500 K. At this temperature, only about 30% to 50% of the film can be removed during a several hour bake in air or oxygen.

He-O glow discharge at room temperature has been tried in the past as a removal technique for the codeposited layer. Hsu [9] compared the glow discharge removal rate of a codeposited layer using several different types of gases. Of nitrogen, hydrogen, helium, and oxygen, only oxygen (in the form of He-O) was found to have a measurable removal rate. He determined an effective removal rate of approximately 5 atoms of carbon for each oxygen ion striking the layer. While the film was produced by the plasma decomposition of methane, and was therefore a "soft film" with a significant fraction of weakly bound atoms, this result certainly suggested that He-O might present a reasonable removal process for the codeposited layer. In unpublished experiments [10], Cowgill used a He-O discharge to remove a codeposited layer from a tile taken from the TFTR reactor. These experiments demonstrated a removal rate of ~1.2 µm/r (about 2.5 carbon atom/O ion) during the initial stage of the experiment, but noted that the removal rate decreased with time. The decrease was attributed to surface texturing. He-O glow discharge was also used directly in the TFTR reactor. Nagy et al. [11] reported that the technique performed well initially, but decreased with time. For the same experiments, Skinner [12] reported the process to release 50 Ci/hr and to be constant with time. This value should be compared to an initial removal rate of 170 Ci/hr for deuterium glow discharge, but a steady state release rate of only 10 Ci/hr. In a somewhat related series of experiments, Jacob et al. [13] performed a systematic study of the removal of a-C:H layers using electron cyclotron resonance discharges (ECR). Several different species were used for the ECR low-pressure discharges ($O_2$, $D_2$, $H_2$, $H_2O$, and $O_2/H_2$), but oxygen always showed the highest removal rates. They noted a codeposited removal rate as high as 1.7 µm/hr at 300 K. The authors noted increased yield with increased voltage or temperature, but found the two were not additive.

The essential difference between most the earlier studies and that reported here is that heating during the discharge has been added. An area of net deposition on a graphite tile removed from TFTR prior to the DT campaign was used to provide a codeposited layer similar to that expected for ITER. Small samples cut from these tiles were examined prior to and after exposure to a He-O at temperatures from 373 K up to 513 K for one to four hours. Changes in the layer thickness and near surface deuterium content were measured.

## Experimental Procedures

Samples used in this experimental program were obtained from a graphite tile removed from the TFTR reactor. The tile had remained in the reactor for several months of deuterium operation, and was covered with a relatively thick codeposited layer. A description of similar tiles removed at the same time and their codeposited layers can be found in [14]. Analysis performed on the tile showed a uniform codeposited layer with a D/C ratio of approximately 0.2. The samples were obtained by slicing approximately a 2 mm thick layer off of the top of the graphite tile. The area of the tile from which the samples were obtained was selected only after microscopy of the entire tile had shown this area to have a relatively uniform codeposited layer.

The samples were first examined microscopically using Auger scanning electron microscopy. They were then analyzed using $He^3$ Nuclear Reaction Analysis (NRA) to determine the deuterium concentration versus depth to a depth of about 1.2 mg/cm$^2$. If the film is assumed to have a density of 1.5 g/cm$^3$, typical of tokamak codeposited layers, the 1.2 mg/cm$^2$ would correspond to a thickness of 8 µm's. Additionally, 2.5 MeV proton RBS was used to determine the total thickness of the film. The samples were then exposed to a He-O glow discharge at temperatures varying from 373 K to 513 K (the latter being the highest obtainable temperature in the ITER reactor). The gas consisted of 80% helium and 20% oxygen, and was held at a pressure of 13.2 Pa during the discharge. Slowly pumping on the vacuum vessel at the same time fresh gas was supplied, retained the purity of the gas. A voltage of 470 volts was required to generate the discharge, and an incident flux of approximately $10^{19}$ ions/m$^2$-s was obtained. After exposure to the discharge, the samples were then analyzed again using the Auger scanning electron microscopy technique and ion beam analyses.

## Experimental Results and Discussion

The amount of codeposited layer removed was determined using two different techniques. The first technique involved direct observation of the sample before and after He-O glow discharge using scanning electron microscopy. The second technique was 2.5 MeV RBS. Additionally, the amount of deuterium removed from the codeposited layer was determined using nuclear reaction profiling. The exposure conditions for the four different samples are shown in Table I.

The scanning electron microscopy results for sample 4 are shown as Figure 1; all other samples show less erosion. Even in the more extreme cases of the 443 K exposure for 4 hours and the 513 K exposure for 1 hour, by overlaying the figures the images suggest, qualitatively, that the amount removed was less than 1 µm. Similar results were seen with the Rutherford Backscattering. Figure 2 shows the RBS results for sample 4; the other three samples show similar behavior.

It is interesting to examine the upper limit of removal as determined by the RBS technique. Sample 4 with the 4 hour exposure at 443 K is considered here. For this sample the upper limit of removal is 5% of 13.3 µm, or 0.667 µm, this limit was found by fitting the RBS data using SIMNRA [15] with uniform and non-uniform assumptions. Based on a density of 1.5 g/cm$^3$, this distance represents $5x10^{18}$ carbon atoms removed per cm$^2$. During the 4 hour exposure, the total fluence was $1.44x10^{19}$ ions/cm$^2$. This result would suggest a removal rate of approximately 0.35 carbon atoms/ion. This amount should be compared to the approximately 5 carbon atoms/ion reported by Hsu [9]. There are two possible explanations for this difference in apparent removal rates. One possibility is that the film examined by Hsu was different. That film was produced by the plasma decomposition of methane. Depending upon the deposition conditions, films produced by this technique may have higher hydrogen content and lower density [5]. While it is probable that the two different film types do in fact have different removal rates, another possibility is that the removal rate may start out at a very high rate, but decrease with time. This is exactly what was seen by Cowgill [10] in his unpublished study on He-O removal of codeposited layers. Monitoring of the CO and $CO_2$ levels in the chamber using a differentially pumped mass spectrometer showed the apparent etch rate of the codeposited layer to substantially decrease with time. Microscopic examination of his samples after exposure revealed a “grass-like” or “hair-like” structure**.** Glow discharge produces an ion flux that is normal to the sample surface. It is quite likely that this normal angle of incidence creates the special structure that is resistant to further removal. Part of the justification for the present study using increased temperature was to examine whether the oxygen would react with the individual strands of the structure to result in a continuous, high removal rate. The apparent answer is that this does not occur. The initial versus long-term removal rate may also explain the difference between results seen in the present study and that performed by Jacob et al. [13]. Their maximum removal rate was 1.7 µm/hr while the present results were limited to only 0.17 µm/hr (0.667 µm/4 hours). Due to there being no reference to time or thickness in their report, it is not possible to conclude that this is the explanation. It would only be necessary for their films to have a thickness less than the length of the "grass-like" structure for this explanation to hold.

While the above results show He-O glow discharge cleaning with heating to be an ineffective removal technique for a thick codeposited layer, the results do not show the technique to also fail at removal of the hydrogen isotopes from the layer. Due to similarities of the results for the different samples, the Nuclear Reaction Analysis (NRA) results for only one of the four samples is shown (Figure 3). While the results would appear to suggest some loses of deuterium throughout the first micron or so, it is more likely that the loss of deuterium is restricted to only that very near the surface. Removal of either 5 nm or 500 nm would appear almost identical due to both being less than the depth resolution of the technique. The energetic oxygen ions from the He-O glow should only penetrate about 5 nm into the deposited layer.

## Conclusion

Experimental results using scanning electron microscopy, Rutherford Backscattering, and nuclear reaction analysis of sample exposed to He-O glow discharge during heating all confirm the combination of removal techniques is not an effective way of removing the codeposited carbon/tritium layer produced in fusion reactors. Surface roughening along with near surface removal of hydrogen isotopes does occur, but the etch rate of the layer is too slow for use on the thick films anticipated for ITER and other future fusion devices.

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**Table 1 Exposure conditions for the for samples.**

| | Temperature (K) | Time |
|---|---|---|
| **Sample 1** | 373 | 1 hour |
| **Sample 2** | 443 | 1 hour |
| **Sample 3** | 513 | 1 hour |
| **Sample 4** | 443 | 4 hours |

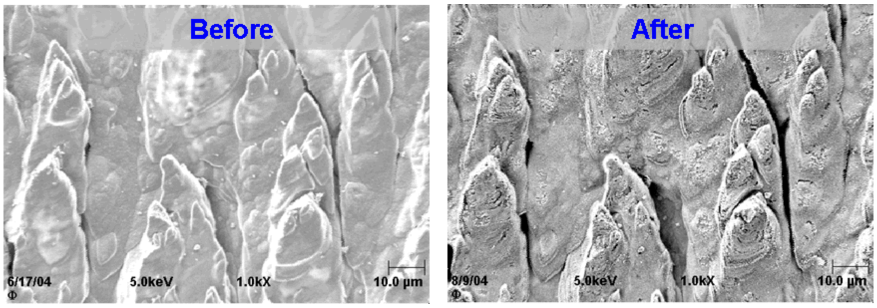

**Figure 1 SEM for sample 4 before and after exposure at 443 K for 4 hours.**

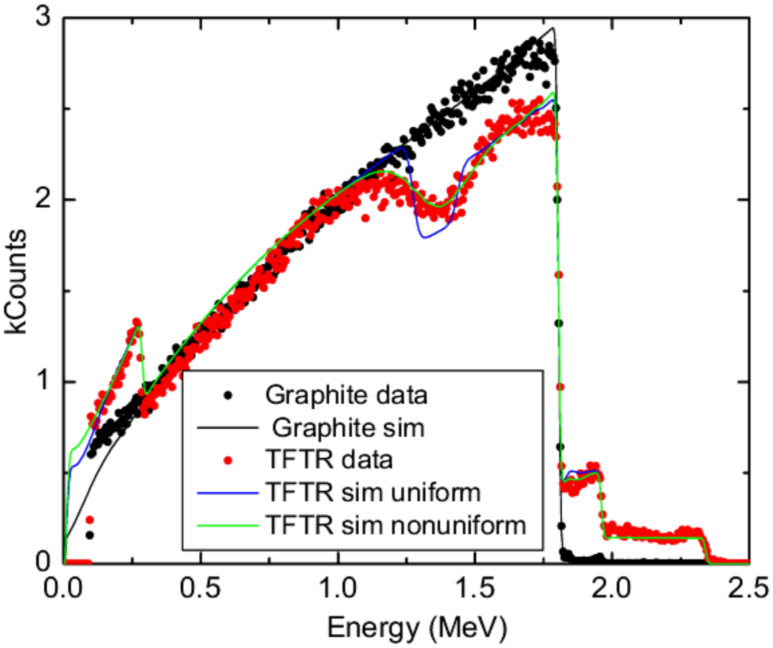

**Figure 2 Rutherford Backscattering results for sample 4 after exposure at 443 K for 4 hours. The plot shows the fit to the data from SIMNRA using a uniform and non-uniform thickness assumption.**

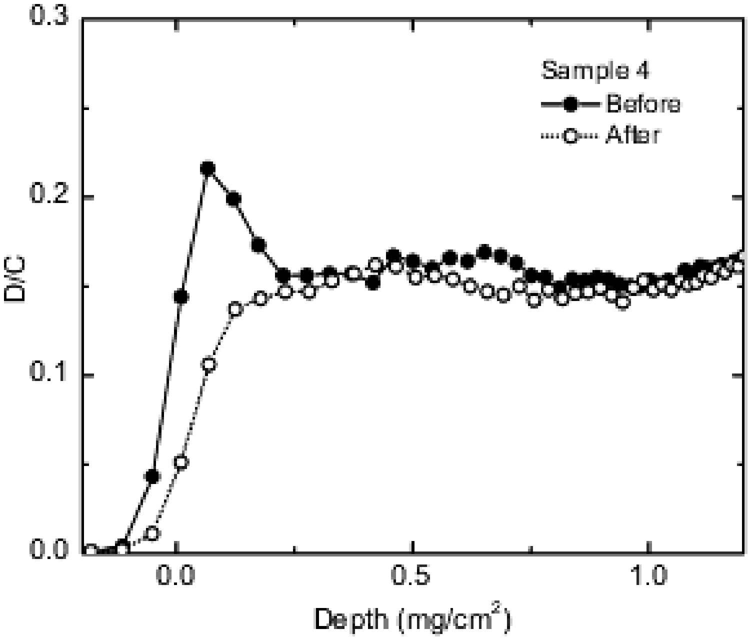

**Figure 3  Nuclear Reaction Analysis of sample 4 before and after exposure.**