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Comparison of the Thermal Stability of the Codeposited Carbon/Hydrogen Layer to that of the Saturated Implant Layer in Graphite*

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This paper presents the results of an experimental study of the thermal stability in air and vacuum of the codeposited carbon/hydrogen layer formed in a carbon-lined fusion reactor. Results are also presented for the stability of the saturated layer formed by the implantation of energetic hydrogen ions into a graphite surface. For both films, the hydrogen isotope release occurs at a much lower temperature in air than it does in a vacuum. At temperatures above 600 K, the hydrogen isotope release in air is very rapid and is emitted in a condensible form. It is speculated that isotopic exchange with the water present in air is responsible for this release. In vacuum, temperatures in excess of 1000 K are required to produce a rapid release from either film. The implications of these results to the safety of tritium in carbon-lined fusion reactors are discussed.

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I. Introduction

Graphite is presently used in almost every fusion device as the plasma-facing material. This use stems from graphite being a low-Z material with excellent high temperature properties. As a plasma-facing component, the hydrogen isotope recycling of graphite plays an important role in the operation and performance of the reactor. Also, with the possibility that tritium may be used in the next generation machines, there are serious concerns about the retention of tritium in and on graphite.

When graphite was first being considered for use in fusion reactors, saturation of the near-surface region by energetic particles was thought to be the principal means of hydrogen isotope retention in graphite. This process was studied extensively[1-6]. While the saturated surface area contributes very strongly to recycling, it is the codeposition of the hydrogen isotopes along with sputtered carbon into a thick layer that will contribute most strongly to the hydrogen isotope inventory in a fusion reactor[7,8]. It is this higher retention that makes the codeposited layer the dominant concern for tritium release during air venting and accidents.

The purpose of this paper is to examine the thermal stability of the codeposited films produced in the Tokamak Fusion Test Reactor (TFTR) and to compare these findings with those measured for the saturated layer. Results are presented here for the release of deuterium and tritium as a function of temperature both in vacuum and in air. The implications of these results to the safety of the tritium in carbon-lined fusion reactors is discussed.

II. Experimental Procedures

The experiments on the release of hydrogen isotopes from the codeposited layer were performed with samples obtained from the sides of graphite tiles removed from the TFTR fusion reactor. These layers varied in thickness from several micrometers up to as high as 50 micrometers. These layers have been described in detail by Mills et al.[9] and by Wampler et al.[10]. The hydrogen isotope content (principally deuterium) of these layers was approximately 0.4 atomic fraction. Part of the hydrogen isotope content was composed of tritium produced in TFTR by the D-D reactions. The layers used in this study had tritium levels in the range of 10^{12} to 10^{13} T/cm^2 depending on location.

Hydrogen isotope release measurements were performed for the codeposited layer both in vacuum and air. A long 2 mm thick sample was removed from the side of a TFTR tile. This was then cut into smaller samples, some of which served as controls. In these experiments, the fraction of the original hydrogen isotope remaining after isochronal anneals was determined by liquid scintillation counting of distilled acid solutions used to dissolve the samples. Samples retained as controls were used to determine the tritium content prior to the anneal. The vacuum anneals were performed in the Tritium Plasma Experiment (TPX) located in the Tritium Research Laboratory at Sandia National Laboratories in Livermore by flowing an electrical current through the samples. A thermocouple was rigidly attached to the samples to determine the temperature. After the one hour anneals at 200°C, 500°C, or 800°C, the samples were removed for dissolution counting. For the air anneals, the samples were placed on a hot plate with the codeposited layer up. A thermocouple was pressed against the front surface. These anneals were performed for 30 minutes with dissolution counting also used to determine the amount of remaining tritium.

Because there was no data available in the literature on the stability of the saturated layer in air, these measurements were also conducted as part of this study. These experiments were performed using the 3 keV Colutron ion source at Sandia National Laboratories in Albuquerque. The samples were saturated using 3 keV D_2 ions to a fluence of 8.7×10^{17} D/cm^2. Each sample was then mounted on a small resistance heater with the temperature monitored using an attached thermocouple. The deuterium content was determined by nuclear reaction analysis using 750 keV He-3 ions from the in-air external beam apparatus of the 4.5 MV EN Tandem Van de Graaff accelerator also located at Sandia, Albuquerque. Two samples were examined using this technique. For the first sample, the deuterium analysis was performed after 30 minutes at 150°C, 30 minutes at 250°C, and 30 minutes at 350°C. For the second sample, deuterium analysis was performed after each 5 minute anneal with 20°C increments.

III. Results and Discussion

The results for the hydrogen isotope retention in the in-vacuum annealed codeposited layer are shown in Figure 1 where they are compared to the earlier results for saturated layers produced using 8 keV particles by Langley et al.[1], using 1.5 keV particles by Doyle et al.[3], and using 20 keV particles by Braun et al.[6]. It can be seen that the measured retentions in the two types of films as a function of temperature are almost identical. This agreement is interesting from two points of view. First of all, the agreement is important in recognizing the similarity of the two films. Next, it is interesting because agreement was seen even though all of the anneals were performed for significantly different times. Langley used 30 minutes anneals, Doyle used 5 minutes anneals, and Braun used 10 minute anneals.

Figure 2 shows a comparison of the in-air release results for the codeposited layer to that for the saturated layer. As described in the Experimental Procedures section, the codeposited layer and one of the saturated layers were heated for 30 minutes at each of the different temperatures. The other saturated layer was annealed at more temperature increments, but only for 5 minutes each. Again, agreement was seen between the fractional releases from the two different types of films even though different anneal times were used. The temperatures required to get substantial release from the two layers in air were significantly lower than those required for the vacuum anneals.

The first point of discussion is whether the two different films are sufficiently similar in structure and chemical bonding to have expected them to have the same hydrogen release characteristics. To answer this question, a general discussion of the characteristics of the two materials is necessary. Because of the interest in carbon films by the electronics industry, research in the area of codeposited films (a-C:H) has increased significantly in the last several years. In their study of the codeposited film, Dischler et al.[11] found the hydrogen bonding to be predominantly monohydride with sp^3, sp^2, and sp^1 bonding in decreasing probability. For a similar type of film, Nyaiesh and Nowak[12] found 25 at.% hydrogen with about 1/3 of it chemisorbed. Angus et al.[13] reported films with 50 at.% hydrogen with part of the hydrogen unbonded. Nuclear reaction profiling of films one year after their production showed only very near surface release of the hydrogen. This showed the unbonded hydrogen to be strongly chemisorbed. Fink et al.[14] varied the bias voltage during his codeposited film production and found the hydrogen to decrease from 60 at.% at 200 V down to 25 at.% at 1200 V. The bonding was reported to be 2/3 sp^3 and 1/3 sp^2. Nadler et al.[15] in their study of amorphous carbon films produced by ion beam processes found the sp^3 bonds to lose hydrogen and convert to sp^2 at around 500°C. The remaining hydrogen was released at approximately 700°C. These release temperatures agree quite well with those reported here for the vacuum anneals. While the information presented here is varied, the principal findings are that the codeposited film is amorphous, has a large amount of hydrogen, has hydrogen bonded at several types of sites, and has hydrogen that is chemisorbed on the carbon.

For research on the saturated layer produced by hydrogen isotope bombardment of carbon surfaces, Niwase et al.[16] used transmission electron microscopy to examine the change in crystal structure. Results showed the crystallinity of the surface region of the implant area to decrease with increasing particle fluence. At high fluences, the surface became completely amorphous. Wright et al.[17] used Ramam spectroscopy to examine the effect of 15 keV hydrogen ions on graphite surfaces. They noted a changeover to amorphous structure with the formation of conjugated acetylenic bonds. Kitijimi et al.[18] also used Raman to look at graphite surfaces exposed to deuterium glow discharge. While the surface was significantly changed by the discharge, it was not possible to completely change the surface to being amorphous. In their work using transmission electron microscopy and xray photoelectron spectroscopy of the saturated layer formed by the bombardment of graphite with hydrogen and deuterium, Gotoh et al.[19,20] saw the crystallite size decrease from 100 nm down to only 0.5 nm during the irradiation. A positive shift in the C1s line was seen with deuterium but not with helium bombardment. The shift along with an increase in the interlayer spacing was given as proof of hydrogen-carbon bonding. Ashida et al.[21] used xray photoelectron spectrometry and SIMS to examine the saturated layer formed by deuterium bombardment. Results were given to show proof of C-D and C_2-D (bridge type) bonds. From these references it can be concluded that, similar to the codeposited layer, the saturated layer is amourphous, contains substantial hydrogen, and contains this hydrogen at a variety of different bonding sites.

During the formation of both types of films, there is substantial deposition of kinetic energy directly into the films. It is this energy deposition that makes the two films similar in chemical and physical properties through constant stirring and bond breaking. In certain cases (low energy plasma deposition), the codeposited film contains more hydrogen than the saturated layer[13,14,22,23]. It is suggested here that the increased hydrogen concentration in the codeposited layer (H/C as high as 1) is due to the limited amount of surface agitation during the formation of those films. During the production of the saturated layer (as well as higher energy deposition of codeposited films), much of the weaker hydrogen-carbon bonds such as that for multiple hydrogens per carbon are destroyed by this constant bombardment.

It is the multiple bonding sites that also explains how agreement can be obtained in fractional release measurements even when different anneal times are used. Doyle et al.[3] in their discussion of the saturated layer proposed that a series of trap energies exist. These trap energies correspond to different bond and chemisorption sites. Doyle proposed the trap energies to be continuous, but modelled the release results seen in their experiments by assuming ten distinct energies. With these assumptions, the retention is calculated to drop when there is an increase in temperature, but the decrease is a function of time for only a short time. The lowest energy traps dump quickly, and the higher ones are not affected. The process is repeated each time the temperature is increased as more of the trap sites become affected.

The next point of discussion is the difference between the temperatures where the hydrogen isotopes are released for both films depending on whether they are in air or vacuum. For vacuum anneals, temperatures in excess of 800°C are required to release all of the hydrogen. For the air anneals, 350°C is sufficient to release all of the hydrogen. It is believed that isotopic exchange with the water vapor in the air was the cause of this difference. Causey et al.[24] in a related study, found the release rate of tritium from a thin codeposited layer in air was reduced by flowing the air through a liquid nitrogen cold trap prior to flowing it across the sample. This simple liquid nitrogen cold trap should not have been sufficient to remove all of the oxygen in the air, but was capable of removing all water vapor. Also, it was determined in that study that the tritium was released in a form easily removed by a cold trap, presumably water.

The implications of the stability of the different types of films for fusion power are simple. Graphite surfaces in direct contact with the D-T plasma will have the surface become saturated with the hydrogen isotopes as long as the temperature does not exceed approximately 500 to 800°C. Surfaces near the graphite (including the plasma protected sides of the graphite tiles) will become coated with a layer of codeposited carbon and hydrogen isotopes if the same temperature constraint is maintained. Unless these surfaces are heated to high temperatures (>800°C), little of the deuterium and tritium will be released as long as the vacuum is maintained. If, on the other hand, there is a loss of vacuum when the surfaces are at temperatures on the order of 300°C or higher, all of the deuterium and tritium will be released almost instantaneously. While it may be possible to take advantage of this as a tritium removal technique when the inventory reaches a critical point, it should be viewed more as a safety problem, capable of dumping gram quantities of tritium into the environment during accidents involving the loss of vacuum in the torus.

IV. Conclusions

Graphite surfaces saturated with hydrogen isotopes during energetic bombardment have almost identical release characteristics for those isotopes during air and vaccum anneals as that for the films produced by the codeposition of carbon and hydrogen isotopes. Both types of films required temperatures on the order of 800°C to release most of the deuterium and tritium when the anneals were performed in vacuum. In air, the same release could be obtained for temperatures as low as 300°C. A review of the literature reveals the fact that the two films may differ in the way they are produced, but differ only slightly in chemical and physical properties. The hydrogen isotopes in these films are located at many different types of bonding sites, and the activation energies for them are almost continuous. The in-air release results for both films suggest that loss of vacuum for a graphite-lined fusion reactor could result in a significant release of tritium.

V. References

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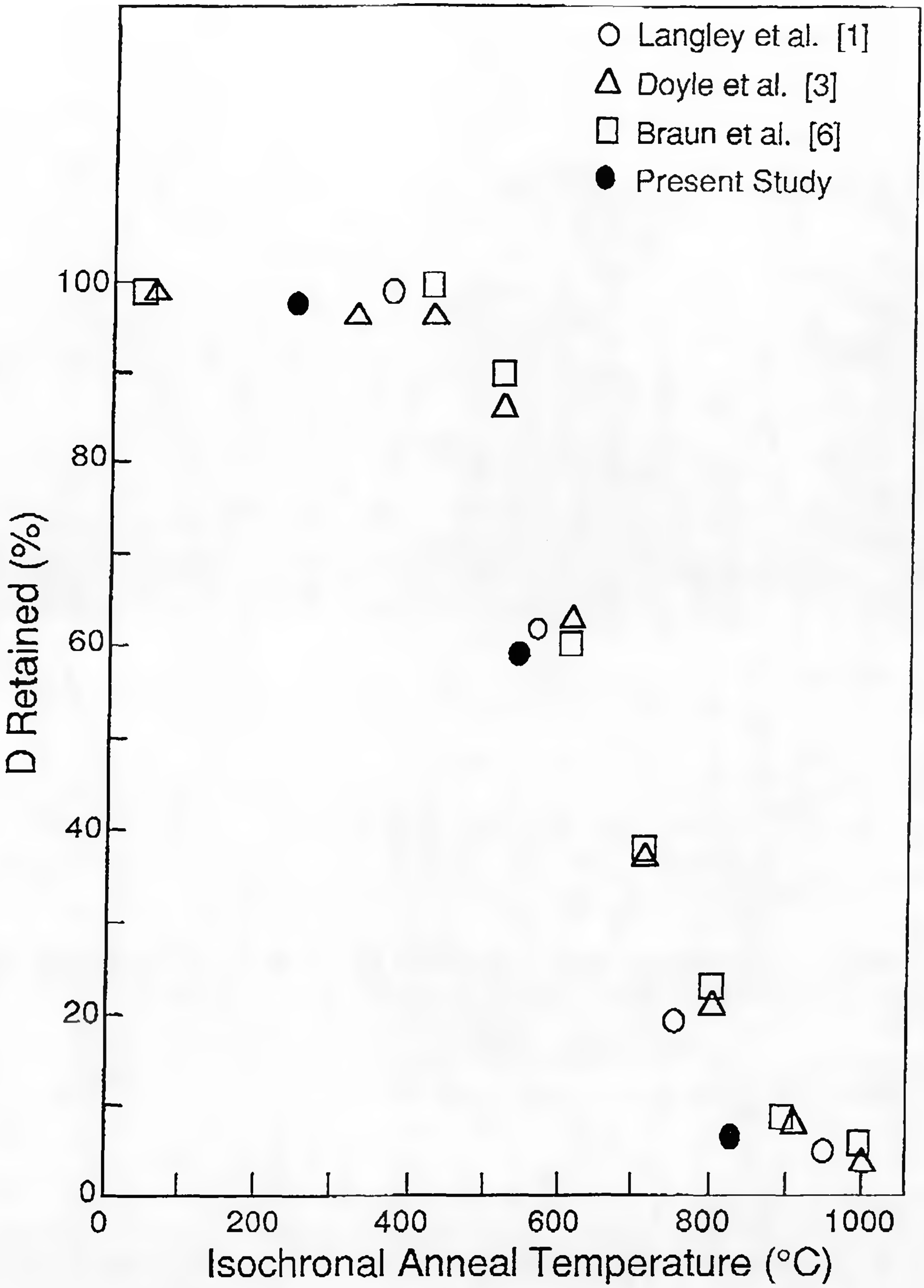
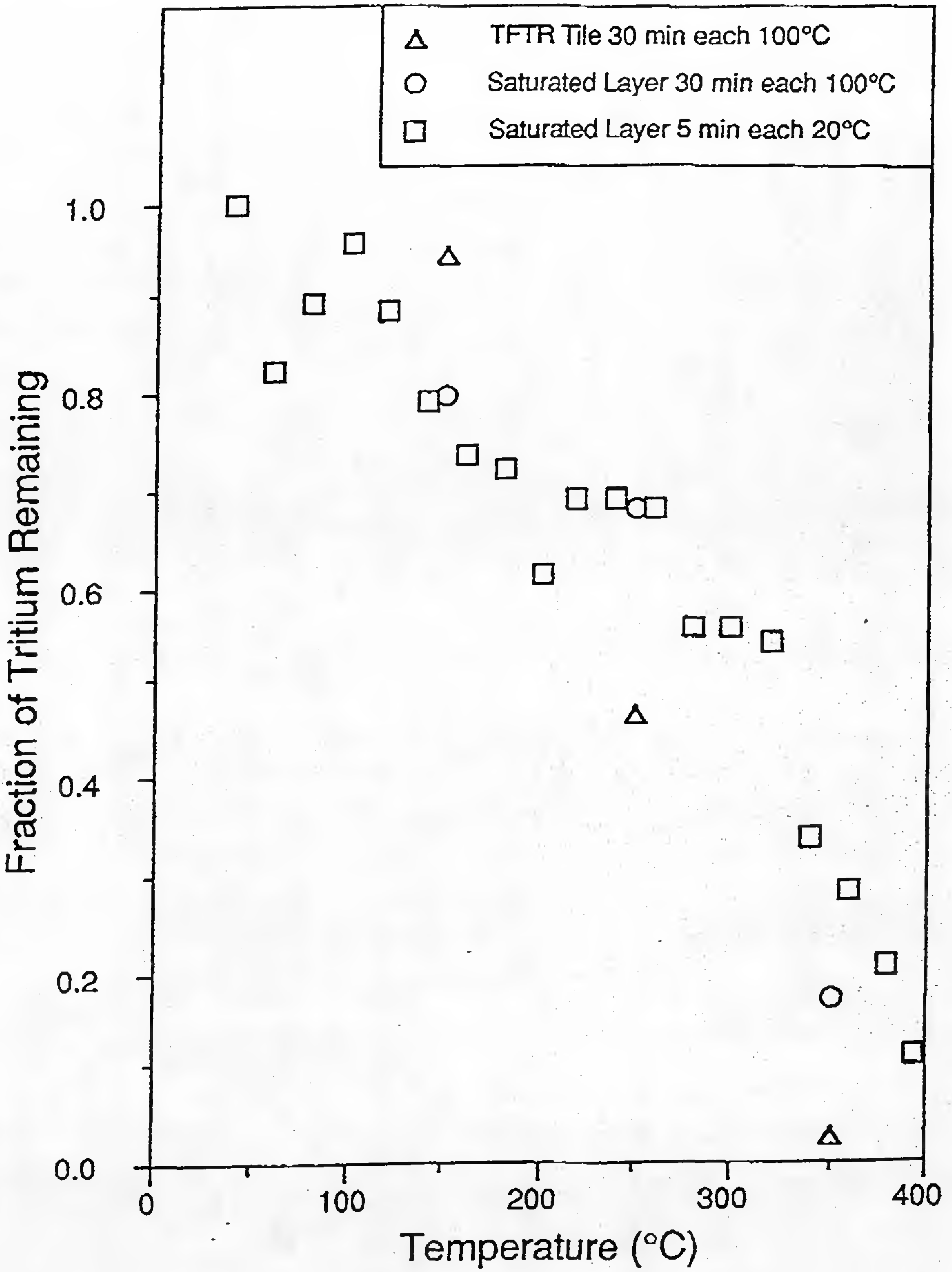
Figure List

Figure 1. Comparison of the in vacuum hydrogen isotope retention in a codeposited film to that for a saturated layer.

Figure 2. Comparison of the in air hydrogen isotope retention in a codeposited film to that for a saturated layer.


○ Langley et al. [1]
△ Doyle et al. [3]
□ Braun et al. [6]
● Present Study
D Retained (%)
100
80
60
40
20
0
0
200
400
600
800
1000
Isochronal Anneal Temperature (°C)

51090A



△ TFTR Tile 30 min each 100°C
○ Saturated Layer 30 min each 100°C
□ Saturated Layer 5 min each 20°C
Fraction of Tritium Remaining
0.0
0.2
0.4
0.6
0.8
1.0
0
100
200
300
400
Temperature (°C)

62089A