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Letter to the Editors

The effect of UV light irradiation on the removal of tritium from the codeposited carbon–tritium layer in fusion reactors

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Abstract

A series of experiments have been performed at the Karlsruhe Tritium Laboratory to examine the effects of UV light on tritium removal from the codeposited layers on carbon fiber composite tiles removed from the JET fusion device. Codeposited layers were exposed to UV light from a mercury lamp (254 nm) for various temperatures using air and argon atmospheres. Samples were also heated externally with no UV light to compare tritium release with and without UV exposure © 2002 Published by Elsevier Science B.V.

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1. Introduction

Detritiation of codeposited layers in graphite-containing fusion devices is an important issue for fusion today. Codeposited layers form predominantly in shadowed areas close to erosion zones where the rate of carbon deposition exceeds the rate of erosion. These layers, which can grow to several tens of microns thick, are amorphous and can be characterized as a hydrogenated, diamond-like film (a:C–H). The tritium content in the codeposited layer accounts for a large percentage of the in-vessel tritium inventory [1]. It has been shown [2] that heating the codeposited films on graphite tiles removed from TFTR in air at temperatures greater than 600 K will remove much of the tritium from the films. This technique is not desirable for in situ decontamination of tritium in a tokamak due to the collateral damage to metals in the vacuum vessel by oxidation and due to problems caused by leaving oxygen in the vessel to contaminate future plasmas. New methods of tritium removal from codeposited layers are therefore desired. The goal is a low temperature treatment that removes tritium from the layer or simply erodes the layers formed during plasma operation.

The dissociation energies at room temperature for several bonds between C, H, and O are shown in Table 1 [3]. The energy of most of these bonds is of the order of UV photons. Also, in the presence of air, UV light creates ozone and atomic oxygen. The experiments performed here were based on the possibility that UV photons would break hydrogen–carbon bonds in the codeposited layer and incorporate ozone and atomic oxygen into the material to oxidize the carbon, releasing the tritium in the process.

Zhang and Nakayama [4] studied the effects of UV irradiation on amorphous carbon and carbon nitride films. The film without the nitrogen showed a decrease of hydrogen and an increase in the oxygen incorporation after 130 h of irradiation. The film was seen to decrease in thickness from 0.7 to 0.5 μm. Ishikawa et al. [5] used UV light to selectively etch graphite from diamond-like

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Table 1
Dissociation energies at 298 K for selected bonds between C, H and O [3]

Bond	Dissociation energy	
	kJ/mol	eV
C–C		
Diamond	354	3.7
Graphite	630	6.5
HC–HC	960	9.9
$H_2C{=}H_2C$	718	7.4
$H_3C–H_3C$	368	3.8
C–O		
C–O	1075	11.1
OC=O	532	5.5
$CH_2{=}O$	742	7.7
$CH_3{=}OH$	383	4.0
C–H		
C–H	399	4.1
HC–H	427	4.4
$H_2C–H$	461	4.8
$H_3C–H$	434	4.5
$CH_2{=}CH–H$	455	4.7
CH–C–H	500	5.2

thin films. It was determined that the temperature required to etch the non-diamond carbon was reduced from 873 K down to 623 K. By the selective placement of masks, the researchers were able to show that the effect was due to the production of ozone and atomic oxygen, not the direct interaction of the photons. This is a concern for any UV detritiation technique used in the presence of oxygen. Creation of these highly reactive species could cause more collateral damage in a tokamak than a high-temperature oxygen exposure.

2. Experimental

Samples with relatively high tritium concentrations (codeposited areas) were taken from the edges of a carbon fiber composite (CFC) JET tile. Each sample was approximately 2 cm by 1 cm with a thickness of 1 mm. The experimental setup is shown in Fig. 1. The sample with attached thermocouple and mercury UV lamp were placed in the fixed volume chamber. Gas (air or argon) was flowed through the chamber, and subsequently through a bubbler for removal of the released tritiated water. The gas then continued through a catalyst bed for oxidation of any remaining tritium, and finally into two more bubblers in series for complete collection of all tritium. When argon was used as the sweep gas, oxygen was added to the gas as it entered the catalyst bed. Sample heating was provided directly by the UV lamp, and varying the distance from the sample to the lamp controlled the temperature. This of course resulted in the hottest sample having the greatest UV intensity. Because heat alone is known to cause the release of tritium from the codeposited layer [2], one sample was heated to 593 K (same as the hottest sample exposed to UV) without UV present. In this case, the sample was heated by attaching it to a heated copper block.

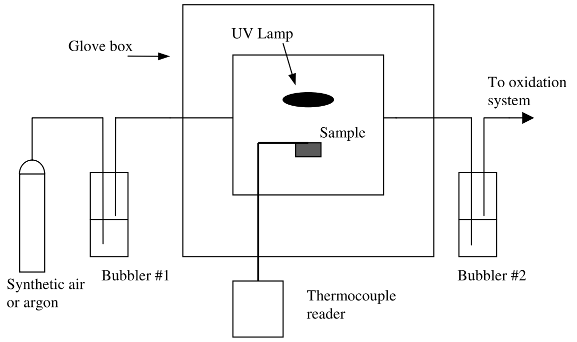

Fig. 1. UV exposure apparatus. Sweep gas directs released tritium through water bubbler #2 to capture oxidized component. Molecular hydrogen (DT, T_2, etc.) is sent to oxidation system for capture. Bubbler #1 filled with water after UV exposure to sweep released tritiated water that may have condensed on the walls of the exposure chamber.

Measurements of the surface activity of each sample were taken before and after testing using a PIN diode surface monitor [6] developed by Sandia National Laboratories. As the primary betas were detected by this system, changes in the tritium concentration to a depth of approximately 1 μm were measured. Fractional changes in the tritium content for the entire sample were determined by comparing the amount of tritium collected during the UV exposure or heating cycle and comparing it with the tritium remaining in the sample after the exposure. The amount remaining in the sample was determined by combusting the entire sample and collecting all tritiated water released during the combustion in a bubbler system.

The mercury UV lamp used in these experiments was a 500 W medium pressure mercury lamp. The irradiance of this lamp was not measured, but was calculated at a distance of 5 cm (shortest distance used in these experiments) to be 42 mW/cm^2. The photons produced by this lamp had a mean wavelength of 254 nm (4.882 eV). These photons have sufficient energy to break many of the C–H bonds listed in Table 1. Higher energy photons would be required to break most of the C–C and C–O bonds.

An experiment was also performed using a deuterium lamp. The UV radiation from a deuterium lamp of 147 nm (8.437 eV) cannot only break C–H bonds but also split water molecules into a so-called geminate radical pair (H + OH) and this with high quantum yield. There are therefore good reasons to expect significant release of tritium from the codeposited layer when a deuterium

Table 2
PIN diode and combustion results from the exposure experiments performed in this work

Experiment no.	Distance (cm)	Sweep gas	Temperature (K)	Time (min)	PIN before (dpm)	PIN after (dpm)	Released (Bq)	Remaining (Bq)
1	15	Argon	453	60	21,844	20,065	–	–
2	15	Air	433	50	20,065	19,014	–	–
3	5	Air	593	50	51,268	29,723	52,409	152,000
4	n/a	Air	593	60	41,304	33,275	65,065	164,800

lamp is used as light source unless the kinetics is very slow or some shadowing effect plays a role.

3. Results and discussion

The experimental results using the mercury lamps are shown in Table 2. The experiments performed at 433 and 453 K were designed to examine the effect of UV exposure with mild heating in air and argon. For both of these experiments, no tritium was released into the bubbler system and only small changes, 8% for the experiment in argon and 5% for the experiment in air, were seen in the PIN diode detector readings. These results immediately showed that direct interaction of the UV with the carbon–tritium bonds was not effective at releasing the tritium. Due to the negative results, the samples were not combusted after the exposures.

The negative results for the removal of the tritium from the codeposited layer was not unexpected. According to Windt and Cirelli [7], UV light penetrates only a few tens of nanometers into amorphous carbon. Tritium distributed through layer microns thick could not be substantially affected by such a surface specific process. The two remaining experiments were performed at 593 K in air with and without UV exposure to examine the possibility that the UV would produce atomic oxygen and ozone that might enhance the tritium removal at higher temperatures. While the total tritium release from both of these samples agreed fairly well (25.6% in the UV exposed sample and 28.3% in the non-exposed sample), a more significant difference was seen the surface sensitive PIN diode measurements. The UV exposure in addition to the heating resulted in approximately 42.0% release of the tritium in the near surface while the heating only resulted in a decrease of only 19.4% of the initial tritium. The smaller decrease in the near surface tritium (in comparison to the total tritium release) for the heat-only sample is not immediately understood. It is possible that tritium atoms in this area are more tightly bound than those at lower layers perhaps due to their connection to impurities. More significant for this report is the 42.0% release of the near surface tritium when UV light from the mercury lamp was added to the heating.

It is not surprising that the UV in the presence of air was able to enhance the tritium release in the near surface. As mentioned in the introduction, UV of the frequency used in this study is able to produce atomic oxygen and ozone. This enhanced removal of the tritium agrees with the report by Ishikawa et al. [5] where heating a diamond thin film to 623 K with UV present resulted in the erosion of graphite contained in the film. For fusion applications, it is unfortunate that the release fraction was not higher. It was hoped that all of the tritium in the near surface might be removed by heating to this temperature with air and UV present. Future fusion devices will have long burn cycles of 1000 s and beyond where codeposited layers of several microns per burn cycle will be produced [1]. A treatment involving heating to 593 K with air and UV for 1 h to remove only a fraction of the tritium in the top 1 μm is not useful.

PIN diode readings were taken on a sample exposed to light from the deuterium lamp. The temperature of the sample during exposure from this lamp increase 5° from the ambient temperature. No significant change in count rate was observed after exposure to this lamp.

4. Conclusion

UV light in the 254 nm band is not useful for the removal of the codeposited tritium–carbon layer. Even in air, the UV does not result in removal of tritium from this layer at temperatures in the 450 K range. An enhancement of the tritium release at 593 K in air was noted in these experiments, but the increase was not sufficient to justify its use in a tokamak.

References

[1] G. Federici, D. Holland, G. Janeschitz, C.H. Wu, J. Nucl. Mater. 241–243 (1997) 260.

[2] R.A. Causey, W.R. Wampler, D. Walsh, J. Nucl. Mater. 176&177 (1990) 987.

[3] JANAF Thermochemical Tables and NBS Technical Notes. Data and reference found in A. Miyahara, T. Tanabe, J. Nucl. Mater. 155–157 (1988) 49.

[4] M. Zhang, Y. Nakayama, J. Appl. Phys. 82 (10) (1997) 4912.

[5] Y. Ishikawa, J. Yoshimi, Y. Hirose, Jpn. J. Appl. Phys. 34 (1995) L1609.

[6] W.R. Wampler, B.L. Doyle, Nucl. Instrum. and Meth. A 349 (1994) 473.

[7] D.L. Windt, R.A. Cirelli, J. Vac. Sci. Technol. B 17 (3) (1999) 930.