



Response of beryllium to deuterium plasma bombardment

R.P. Doerner^{*}, A. Grossman, S. Luckhardt, R. Seraydarian, F.C. Sze,
D.G. Whyte, R.W. Conn

Fusion Energy Research Program, University of California, San Diego, EBU-II, Room 460, La Jolla, CA 92093-0417, USA

Received 27 October 1997; accepted 1 May 1998

Abstract

Experiments have been conducted in the PISCES-B device to investigate the erosion and deuterium retention characteristics of beryllium. The impurity fractions of both carbon and oxygen in a deuterium plasma have been reduced to 0.2% for carbon and 0.2% or less for oxygen. Under these conditions, the measured sputtering yield of the beryllium samples agrees with beryllium-oxide sputtering. The clean plasma conditions allow for investigation of the surface morphology of the samples under various exposure conditions. During high-temperature exposure the surface develops a porous structure, unlike the smooth surface resulting from low-temperature exposures. The hydrogen isotope retention characteristics of beryllium are measured under conditions which simulate the ITER first wall and baffle plasma interaction regions. The beryllium samples develop a saturated surface layer under these high-flux bombardment conditions. Thermal desorption spectroscopy (TDS) is used to measure the release temperature of the retained deuterium. The TMAP4 code is used to model the deuterium release from the beryllium. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The response of beryllium materials, when exposed to ITER-like plasma heat and particle flux, has been investigated in the PISCES-B [1] linear plasma simulation device. Both the material erosion and hydrogen isotope retention characteristics of beryllium have been measured under conditions which simulate the ITER [2] first wall (surface temperature = 200°C, ion flux = $1 \times 10^{21} \text{ m}^{-2} \text{ s}^{-1}$, ion bombardment energy = 100 eV) and divertor baffle (surface temperature = 500°C, ion flux = $1 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$, ion bombardment energy = 100 eV) plasma interaction regions. Plasma exposures have been varied from 30 min up to 8 h to study any fluence dependent effects which may occur during the operation of ITER.

The PISCES devices [3] operate on the principle of a reflex arc plasma source. Electrons emitted from a hot LaB₆ cathode ionize a prefill neutral gas (10^{-3} – 10^{-4}

Torr) which is leaked into the vacuum chamber. In these experiments, the fill gas used is deuterium in order to differentiate retained plasma ions from any background hydrogen present in the samples. The background vacuum pressure, with the LaB₆ source hot, is around 10^{-7} Torr and is predominantly CO originating from the hot source. The deuterium prefill pressure is adjusted to control the plasma ion flux to the sample. For all measurements discussed here, the plasma density is in the range between 10^{17} and 10^{18} m^{-3} . The electron temperatures vary between 20 and 35 eV and are adjusted to obtain the desired ion flux to each sample. The sample exposure temperature can be controlled, within certain limits determined by the ion flux, by adjusting the cooling flow rate to the sample. The ion bombarding energy is set to 100 eV by applying a negative bias to the sample.

2. Sputtering yield

The sputtering yield of beryllium measured in an ion beam device is observed to be temperature dependent

^{*} Corresponding author.

[4]. The measured sputtering yield increased at elevated temperatures and was explained as resulting from beryllium diffusion through a surface beryllium-oxide layer. In previous work on PISCES-B, the sputtering yield of beryllium was also observed to be temperature dependent [5], however the dependence was the opposite. At low sample exposure temperature ($<250^{\circ}\text{C}$), the sputtering yield was measured to be close to that of beryllium-oxide. At higher exposure temperatures, the sputtering yield was affected by intrinsic impurities within the plasma. The trace ($\approx 1\%$ carbon and $\approx 1\%$ oxygen) impurities in the plasma were believed to deposit on the samples surface. Because of the elevated surface temperature, the impurities diffuse into the bulk material to form a mixed material surface layer. This mixed material layer reduced the sputtering yield of beryllium, both because it diluted the concentration of beryllium at the surface and because molecules with higher binding energy at the surface (i.e. beryllium-oxide and beryllium-carbide) could form.

In this work, the impurity concentration in the deuterium plasma has been reduced to about 0.2%, or less, for carbon and oxygen. The impurity concentration is measured both before and during the plasma discharge by way of a specially designed, high-pressure quadrupole residual gas analyzer (RGA). The RGA is shielded from the influence of the plasma confining magnetic fields by a mu-metal housing. As a check of the accuracy of the RGA measurement, a spectroscopic diagnostic was used to measure the intensity of the impurity line radiation emitted from the plasma during operation. By also spectroscopically measuring the deuterium atom line emission from the plasma, the plasma impurity ion concentration could be calculated [6]. The two techniques agree within the accuracy of the measurements. These measurements indicate that carbon is the dominant impurity in the PISCES-B deuterium plasma at 0.2% and the level of oxygen impurity is below the 0.2% limit of detection for oxygen of the spectroscopic system. This purity is better than that typically found in the edges of existing tokamaks [7,8].

The sputtering yield of the beryllium is measured by a weight loss method. Each sample is weighed before and after plasma exposure on a microbalance which has an accuracy of ± 0.05 mg. Typical weight losses from these plasma exposures range from 0.5 to 10 mg. Any error introduced by the formation of an oxide layer on the samples during the weighing process in atmosphere would be less than 0.01 mg. Since there is no evidence of impurity deposition on the surface of the samples at these levels of plasma purity (surface diagnostics detect beryllium and beryllium-oxide) and since the ionization mean-free path [9,10] for sputtered beryllium atoms ($>10\text{cm}$) is calculated to be much longer than the plasma column radius (3 cm), this method can be used to directly measure the sputtering yield. The plasma ion flux

to the sample is established to closely replicate conditions expected at the first wall ($\Gamma = 1-2 \times 10^{21} \text{ m}^{-2} \text{ s}^{-1}$) and at the divertor baffle ($\Gamma = 1-2 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$) of ITER. The flux to the sample is measured by a reciprocating Langmuir probe located approximately 2 cm in front of the sample surface. The probe measurements also ensure that the plasma conditions across the entire face of the sample are uniform.

The ion flux to the sample consists of both atomic (D^+) and molecular (D_2^+ and D_3^+) ions. Previous measurements [3] under similar plasma conditions indicate an ion species mix ($\text{D}^+:\text{D}_2^+:\text{D}_3^+$) of (80:15:5). Sputtering by a molecular ion, such as D_2^+ , can be treated as equivalent to bombardment by two atomic ions, each of which has half the energy of the incident molecular ion [11]. Using this approach, the effect of bombardment by molecular ions in the PISCES plasma is calculated to be such that the measured sputtering yield underestimates the actual sputtering yield by only 10%.

The material used in these investigations was S-65C press-sintered beryllium supplied by Brush Wellman. All samples were annealed to 650°C prior to plasma exposure. Samples were exposed at temperatures ranging from room temperature up to 650°C . Additionally, at surface temperatures of both 200°C and 500°C , a series of samples were exposed for varying times (between 0.5 and 8 h) to determine if any time dependent effects were occurring (such as a change in sputtering after the removal of the native oxide layer present on all beryllium samples before plasma exposure). Finally, several plasma sprayed beryllium samples ($>95\%$ density, supplied by Los Alamos National Laboratory) were included in the study to determine if surfaces repaired in ITER using this technique might exhibit different lifetimes from the original beryllium tiles.

The results of all these erosion measurements are presented in Fig. 1. Also included in the figure are TRIM-95 [12] sputtering calculations (assuming 100% D^+ ion bombardment) for both pure beryllium (surface binding energy = 3.38 eV) and beryllium oxide (surface binding energy = 6.1 eV) [13]. All the data are observed to agree with the expected sputtering yield of beryllium oxide to within the error of the measurements. The cluster of data points at both 200°C and 500°C contain fluence variations of over an order of magnitude with no appreciable change in the erosion rate. Certainly, at higher plasma impurity concentrations the sputtering yield measured in this manner would be expected to decrease [5].

The measured sputtering yield agreeing with that of BeO is somewhat surprising. Each beryllium sample is initially inserted into the plasma with the beryllium-oxide surface because of its prior exposure to atmosphere. TRIM-95 calculations indicate that both the beryllium and the oxygen sputter from a beryllium-oxide surface with a yield of about 0.007 from 100 eV incident deu-

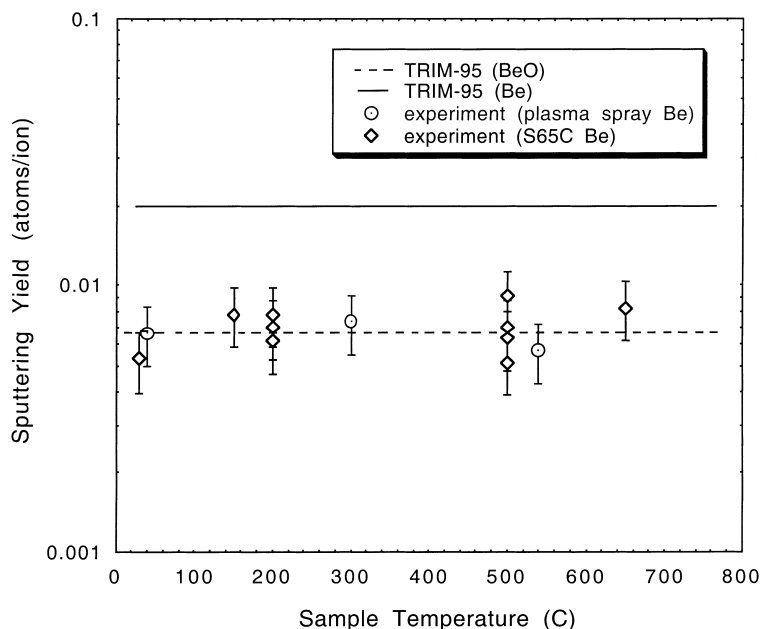


Fig. 1. Sputtering yield measurements of beryllium show no temperature dependence and agree with the computed sputtering yield of beryllium oxide. The data points at 200°C and 500°C contain fluence variations of over an order of magnitude with little change of the erosion rate.

terium ions. The arrival rate of oxygen at the sample surface is $\approx 0.002\Gamma$ (the plasma oxygen impurity concentration) for these experiments. It would, therefore, be expected to remove the oxide layer after a short time (<30 s) under these plasma bombardment conditions and then to measure the sputtering yield of a pure beryllium surface.

It should be noted that ion beam data [14] have shown good agreement between the sputtering yield of both beryllium and beryllium-oxide materials with theoretical calculations. On the other hand, recent sputtering yields inferred from beryllium codeposition measurements [15] were found to be 0.006, under plasma bombardment conditions which should have produced interactions with a pure beryllium surface. Similarly, interpretation of results from JET [16,17] have also had to assume BeO sputtering yields instead of those of pure Be in regions of intense plasma bombardment.

3. Surface characterization

An important aspect of plasma-surface interactions is the alteration of the surface morphology due to plasma bombardment. These experiments began with polished beryllium surfaces exposed to the plasma. Morphology changes under various exposure conditions were, therefore, easily discernible. Fig. 2 shows scanning electron microscope (SEM) pictures of the surface of a sample

which was exposed to plasma under first low surface temperature conditions and then again exposed under high surface temperature conditions. By changing the sample holder cap between exposures it was possible to obtain regions of the sample which were unexposed to plasma (Area 3), exposed to plasma only at low temperature (Area 2) and exposed to plasma at low and subsequently high temperatures (Area 1). Little difference is seen between the unexposed surface and the surface exposed at low temperature. Both surfaces remain smooth and remain clean of any contamination. The surface exposed at low temperature (fluence = $5.2 \times 10^{25} \text{ m}^{-2}$) shows little impact of plasma exposure, beyond the smooth surface typical of an eroded surface. Surface sputtering during the high flux plasma ion bombardment may be responsible for the absence of surface blistering which has been observed in previous ion beam bombardment experiments [18]. At low temperature the surfaces are similar to those observed in earlier experiments on PISCES-B [5]. The surface exposed at high temperature shows a much different structure.

The surface exposed at high temperature (fluence = $2.7 \times 10^{25} \text{ m}^{-2}$) has a three-dimensional structure. Large, up to micron-sized, voids can be seen in the surface of the beryllium. Similar surface morphology is seen on samples exposed only at high temperatures, so the prior bombardment at low temperature is not important in the formation of this surface. In earlier ex-

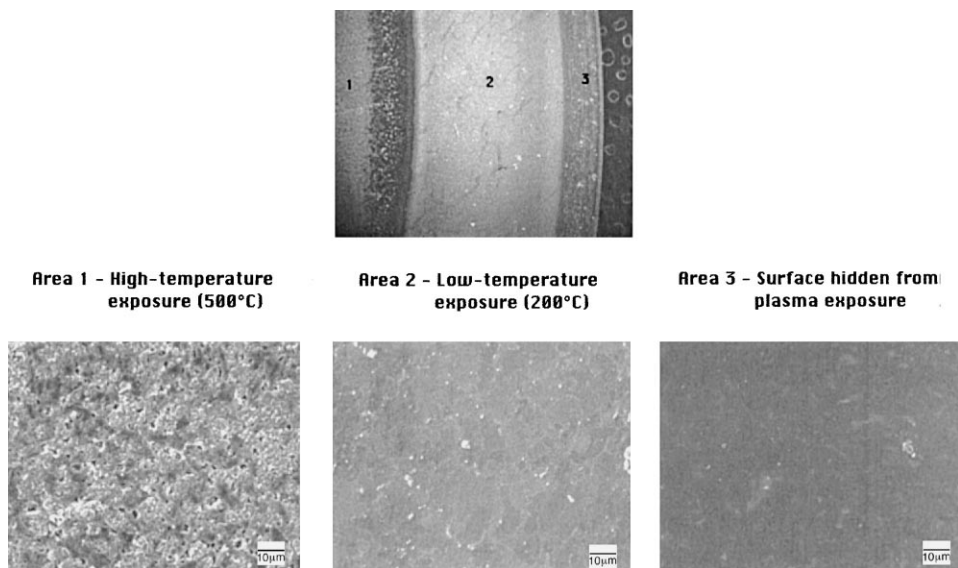


Fig. 2. A single sample was exposed to different plasma conditions (Area 1 – high-temperature exposure, Area 2 – low-temperature exposure, Area 3 – no plasma exposure) to highlight changes in surface morphology. High temperature sample exposure leads to a porous structure with the formation of damage well beyond the implantation zone.

periments [5], at high temperature and higher plasma impurity content, the formation of a three-dimensional surface resulting from impurity deposition on the sample was seen. The impurity deposition tended to cover any other effects caused by plasma bombardment. Now, with cleaner plasma conditions the impact of plasma bombardment can be more clearly observed.

The high-temperature exposed surfaces appear similar to measurements of surfaces exposed to deuterium ion bombardment in ion beam devices [19–21]. The explanation for the formation of ‘interconnected channels forming extended labyrinths’ [21] is the larger vacancy mobility at higher surface temperatures. Depth profiles of the damage created in the ion beam devices showed a damage profile much deeper than the implantation zone of the ions during bombardment at elevated (450°C)

temperature and showed damage profiles peaking at the implantation depth for low (room) temperature exposures [22].

The sputtering threshold energy for deuterium ion bombardment of a beryllium surface is estimated to be about 15 eV. These experiments on PISCES-B indicate that during low ion energy (100 eV) bombardment, significant damage occurs, and at elevated temperature, can agglomerate and extend well past the implantation zone into the surface of the material. TRIM calculates the implantation depth of 100 eV deuterium ions in beryllium to be only 1–2 nm. The amount of surface damage continues to increase as the total fluence to the sample increases. Fig. 3 compares the same high-temperature exposed surface shown in Fig. 2 to a surface which was exposed at the same surface temperature and

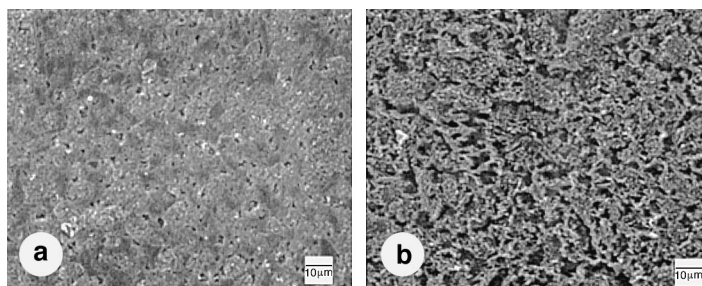


Fig. 3. Surface damage increase with increasing fluence during high temperature sample exposure to plasma (a) ion flux = $1.5 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$, ion energy = 100 eV, exposure duration = 30 min (b) ion flux = $1.5 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$, ion energy = 100 eV, exposure duration = 6 h.

plasma bombarding flux, but for a factor of 12 longer time. As can be seen, all evidence of the original flat surface has disappeared as many of the damage sites appear to merge and interconnect. The voids in the surface appear to be increasing in depth as well (although it is not really possible to measure the depth of these features using these SEM pictures). Several of the high-temperatures exposed samples are being sectioned to allow for edge viewing to get a quantitative measure of the depth of the damage as a function of the fluence, or the duration of the bombardment.

It is interesting to recall Fig. 1 which showed no dependence of the sputtering yield as a function of temperature. Apparently, the increased roughness and porosity of the surface, which develops during high sample temperature exposure to plasma does not significantly alter the global erosion properties of the surface.

4. Deuterium retention

The deuterium retention characteristics of beryllium have also been investigated under ITER relevant conditions during this work. A series of exposures (1/2, 1.7, 2 and 8 h) were conducted under 200°C conditions and another series (1/2, 2 and 6 h) under 500°C conditions. After exposure the samples were transported through atmosphere to a thermal desorption apparatus. The temperature of the samples was ramped up to 650°C

while recording the partial pressures of all the deuterium containing molecules (D_2 , HD, D_2O , HDO) which were released. The released deuterium was recorded primarily in the mass = 3 ($\approx 66\%$ of the total) and mass = 4 ($\approx 33\%$ of the total) peaks following the 500°C exposures and roughly 50% as mass 3 and 50% as mass 4 following the 200°C exposures. The hydrogen (in the HD peaks) is suspected to come primarily from within the outgassing chamber rather than directly from the beryllium samples. The mass 19 and 20 peaks were less than 1% of mass 3 and 4 peaks and were, therefore, ignored. The system was calibrated with a deuterium standard leak. The HD peak was assumed to have the same calibration as the calibrated D_2 peak. Previous measurements have shown that 650°C is sufficient to desorb all the retained deuterium within beryllium [23].

The total deuterium retention in each case is plotted in Fig. 4. Under both exposure conditions, the retention appears to have only a small dependence on increasing exposure time, consistent with measurements from other ion beam and plasma bombardment facilities [24–26]. The retention properties of beryllium are reduced under high-temperature bombardment conditions. Modeling of the plasma interaction behavior of beryllium [27] confirm the formation of high porosity surfaces resulting in a ready release of implanted ions back to the plasma. This high-porosity surface has been shown in Fig. 2.

In addition to the total quantity of deuterium released from the sample [28], the temperature dependence

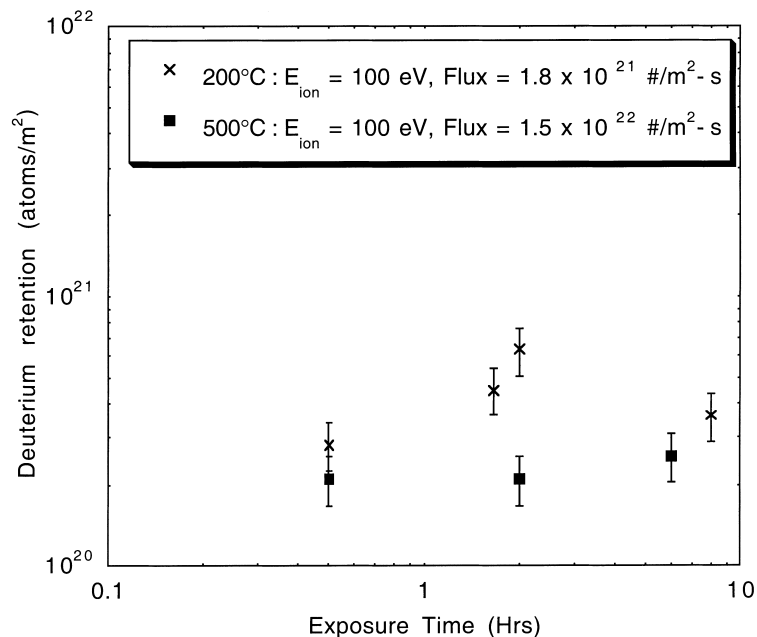


Fig. 4. Deuterium retention in beryllium exhibits only a weak dependence on increasing fluence.

of the experimental desorption spectra has been modeled. TMAP4 [29] is used to model the release of deuterium from the exposed beryllium samples. Fig. 5 shows a comparison of a TMAP4 calculation to the amount of deuterium desorbed from a beryllium sample which was outgassed in the TDS system. The sample which is modeled here was exposed, at 250°C for 20 min, to a flux of 5×10^{21} ions $\text{m}^{-2} \text{s}^{-1}$ [30].

The transport of deuterium in the beryllium sample, during both the implantation and desorption phases of the experiment, was modeled using TMAP4. The implantation calculation used a sample temperature of 250°C and a source term of 5×10^{20} $\text{m}^{-2} \text{s}^{-1}$ for 1200 s which is significantly less than the flux of incident deuterium during the experiment. The reduction of the source term is justified as an attempt to model a saturated surface layer [28]. The source peaking factor was supplied by the TRIM code. After 1200 s, the source term was turned off, and the sample allowed to cool to room temperature. Diffusion and solubility during this part of the calculation were taken to be standard Arrhenius expressions for beryllium determined by Abramov [31] and Swansiger [32].

There are several ways to impose a saturated surface layer in the calculations. The above method reduces the incident flux such that the concentration at the end of the implantation time (1200 s in this case) is equivalent to the reported saturated surface layer concentration of D/Be = 0.39 [33]. This method was chosen to allow diffusion to act for the duration of the exposure. However, the results were similar when the incident flux was kept at the experimentally measured value, but the exposure

duration terminated once the concentration reached the saturated level. Because of the imposition of the saturation effect on the implantation phase of the calculation, the results were found to be insensitive to the actual values of the diffusion coefficient used during the implantation calculations.

The desorption calculation was then performed as a TMAP4 restart run with linear temperature ramp from room temperature to 650°C in 2000 s to correspond to the experimental thermal desorption ramp. The resulting TMAP4 surface fluxes were then compared with the calibrated experimentally determined desorption fluxes. The best fit to this data was obtained with a diffusion coefficient given by

$$D (\text{m}^2 \text{s}^{-1}) = 8.0\text{e}^{-7} \times \exp(-9000/(T(^{\circ}\text{C}) + 273)) \quad (1)$$

which has a prefactor that is two orders of magnitude larger than the Abramov value, and an activation energy which is a factor of 2.1 larger than that used by Abramov. Including this saturation effect and varying the diffusivity away from the Abramov value during the desorption calculation allowed good agreement in both the shape of the desorption curve and its absolute magnitude. The necessity of increasing the diffusion coefficient during the desorption calculation is consistent with enhanced diffusion resulting from surface damage induced by the plasma ion bombardment.

These modeling results did not appear to be sensitive to the solubility or pressure. Use of the Abramov diffusion during the desorption phase of the calculation persistently yielded a desorption flux that peaked at a temperature considerably lower than that observed ex-

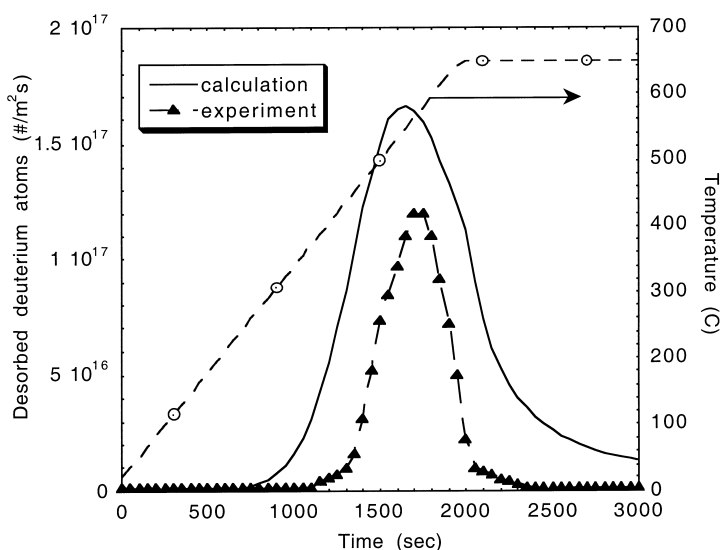


Fig. 5. Comparison of the deuterium desorption spectra during thermal desorption spectroscopy from a beryllium sample exposed in PISCES-B to calculations using the TMAP4 computer code.

perimentally. The inclusion of trapping in the calculation at various concentrations was explored, but found to be responsible for additional peaks in the desorbed flux were not observed experimentally, and was taken out to obtain the best fit to the experimental data. The modeling we report suggests that the diffusivity is much more important than the solubility for understanding these experiments.

5. Conclusions

The interactions of a relatively clean (0.2% carbon and <0.2% oxygen impurity concentrations) deuterium plasma with beryllium surfaces has been studied in PISCES-B. The sputtering yield is equal to the value expected from sputtering of a beryllium-oxide surface and is independent of sample exposure temperature. The magnitude of the sputtering yield is rather surprising. Sputtering yields of clean beryllium surfaces, measured in ion beam devices, are typically larger, but other plasma devices record similar reductions. It is possible that surface conditions are acting to reduce the sputtering yields, but it is also possible that the atomic physics that goes into the calculations of mean-free paths may need to be reexamined.

The change in the surface morphology of the exposed beryllium samples is strongly dependent on the exposure temperature. During high-temperature exposures (500°C), the surface develops porosity well beyond the implantation depth of the bombarding ions. This surface porosity may play a role in enhancing the transport of implanted deuterium atoms to the surface for subsequent recombination and desorption. The deuterium retention properties of the beryllium samples, under ITER conditions, appears to quickly saturate at a level that decreases with increasing exposure temperature. The agreement between the experimental results and the modeling of the deuterium desorption spectra from the implanted beryllium samples improves when the diffusion coefficient is increased, which is consistent with the effects of the surface damage.

Acknowledgements

The unselfish interactions by members of the ITER PFC community during discussions of these and other data are gratefully appreciated. In addition, special thanks are given for the efforts of each of the members of the PISCES team who spent numerous hours in the ‘box’ to make this research possible. This work was supported by the US Department of Energy, DOE grant # DE-FG03-95ER-54301.

References

- [1] Y. Hirooka, R.W. Conn, T. Sketchley et al., *J. Vac. Technol.* A8 (1990) 1790.
- [2] R. Parker, G. Janeschitz, H.D. Pacher et al., *J. Nucl. Mater.* 241–243 (1997) 1.
- [3] D.M. Goebel, J. Bohdanský, R.W. Conn et al., *Nucl. Fusion* 28 (1998) 1041.
- [4] J. Bohdanský, J. Roth, *J. Nucl. Mater.* 122&123 (1984) 1417.
- [5] J. Won, F.E. Spada, R. Boivin et al., *J. Nucl. Mater.* 241–243 (1997) 1110.
- [6] D.G. Whyte, R. Seraydarian, R. Doerner, Characterization of intrinsic impurities in PISCES-B using visible spectroscopy, U.C. San Diego report # UCSD-ENG-052 (1997).
- [7] The JET Team, *J. Nucl. Mater.* 176&177 (1990) 3.
- [8] D.G. Whyte, M.R. Wade, D.F. Finkenthal et al., Measurement and verification of Zeff radial profiles using charge exchange recombination spectroscopy on DIII-D, *Nucl. Fus.*, Sept. (1997), in press.
- [9] K.L. Bell, H.B. Gilbody et al., *J. of Phys. and Chem. Ref. Data*, 12 (1983) 891.
- [10] M.A. Lennon, K.L. Bell et al., *J. Phys. Chem. Ref. Data* 17 (1988) 1285.
- [11] P. Sigmund, in *Topics in Applied Physics*, Vol. 47, *Sputtering by Particle Bombardment I*, Ed. R. Behrish, Springer, Berlin, 1981, p. 9.
- [12] J.P. Biersack, W. Eckstein, *Appl. Phys. A* 34 (1984) 73.
- [13] R. Kelly, N.Q. Lam, *Radiat. Eff.* 19 (1973) 39.
- [14] J. Roth, W. Eckstein, M. Guseva, *Fus. Eng. Design* 37 (1997) 465.
- [15] R. Causey, D. Walsh, *J. Nucl. Mater.* (1998), in press.
- [16] R.D. Monk, A. Loarte, A. Chankin et al., *J. Nucl. Mater.* 241–243 (1997) 396.
- [17] H.Y. Guo, J.P. Coad, S.J. Davies et al., *J. Nucl. Mater.* 241–243 (1997) 385.
- [18] K. Touhouche, B. Terreault, *Mater. Res. Soc. Symp. Proc.* 316 (1994) 987.
- [19] R.A. Anderl, M.R. Hankins, G.R. Longhurst et al., *J. Nucl. Mater.* 196–198 (1992) 986.
- [20] V.Kh. Alimov, V.N. Chernikov, A.P. Zakharov, *J. Nucl. Mater.* 241–243 (1997) 1047.
- [21] V.N. Chernikov, V.Kh. Alimov, A.V. Markin, A.P. Zakharov, *J. Nucl. Mater.* 228 (1006) 47.
- [22] R.A. Anderl, A.B. Denison, S. Szpala et al., in *Hydrogen Effects in Materials*, Eds. A.W. Thompson, N.R. Moody, The Minerals, Metals & Materials Society, 1996, p. 105.
- [23] W.R. Wampler, *J. Nucl. Mater.* 196–198 (1992) 981.
- [24] A.A. Haasz, J.W. Davis, *J. Nucl. Mater.* 241–243 (1997) 1076.
- [25] R.A. Causey, G.R. Longhurst, W. Harbin, *J. Nucl. Mater.* 241–243 (1997) 1041.
- [26] G. Federici, R. Anderl, J.N. Brooks et al., *Proc. ISFNT-4*, Tokyo, 1997, to be published in *Fus. Eng. Design*.
- [27] G.R. Longhurst, Modeling of hydrogen plasma interactions with beryllium surfaces, ITER Engineering Design File # ITER/US/97/TE/SA-1.
- [28] G.R. Longhurst, R.A. Anderl, R.A. Causey et al., *Proc. ICFRM-8*, Sendai, Japan, *J. Nucl. Mater.* (1998) in press.

- [29] G.R. Longhurst et al., TMAP4 user's Idaho National Engineering Laboratory Report # EGG-FSP-10315,(12 June, 1992).
- [30] J. Won, PhD thesis, UCLA, 1996.
- [31] E. Abramov, M.P. Riehm, D.A. Thomson, W.W. Smeltzer, J. Nucl. Mater. 175 (1990) 90.
- [32] W.A. Swansiger, J. Vac. Sci. Technol. A 4 (1986) 1216.
- [33] A.A. Haasz, J.W. Davis, J. Nucl. Mater. 241–243 (1997) 1076.