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## Mixed-material coating formation on plasma-facing components

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### Abstract

When any plasma confinement device is fabricated from more than a single material which can come into contact with either particle or heat flux, there is the potential for migration of one of these materials to the locations of other materials. This combination of materials, or mixed materials, can have substantially different properties than either of the original materials. The PISCES-B linear plasma device is examining the formation conditions and properties of mixed-material surface layers which can form on plasma-facing components. The PISCES-B device has been modified to incorporate an impurity gas (CD<sub>4</sub>, CO, O<sub>2</sub>, etc.) puffing system in the target interaction region. It is, therefore, possible to control the fraction of impurities in the incident plasma and to perform systematic tests on the conditions necessary to form mixed-materials surface layers. The concentration of the species in the plasma column is measured spectroscopically, as well as by a residual gas monitor on the vacuum chamber. Measurements of the rate of growth of the thickness of the mixed material layer are performed. A simple erosion model can adequately describe the growth rate of the mixed-material layer and may allow for growth rate predictions in other plasma environments. It is also important to investigate the role of redeposition of metallic impurities in the formation of mixed material layers. A beryllium evaporator has been independently installed upstream of the target-interaction region to allow seeding of the incident plasma with beryllium. The presence of beryllium on the sample surface is observed to reduce the chemical erosion of the graphite by more than the reduction of the surface carbon concentration. And finally, the hydrogen isotope retention properties of carbon-containing layers on beryllium could have serious implications for tritium accumulation in ITER. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* PISCES-B; Film growth rate; Erosion/redeposition

### 1. Introduction

The trend in plasma confinement devices has been toward using a single material for all plasma-facing components, or of providing a uniform coating, such as carbonization [1], over a variety of plasma-facing materials. For the ITER device, this approach is unacceptable because of the extreme design criteria [2]. To meet the challenge the ITER design has settled on employing different materials on different plasma-facing

components. Beryllium will exist as the largest area plasma-facing material because of its use on the first wall. Carbon will exist on the highest power load components in the divertor. And tungsten will exist in other areas of the divertor and in the transition region, the lower baffle, to the first wall.

Each of these materials: beryllium, carbon and tungsten, are chosen in certain regions for specific material properties. However, it is unrealistic to imagine that these plasma-facing materials will remain only where they are originally placed. Erosion during normal operation, as well as off-normal events (such as disruptions), will tend to distribute each of the materials to areas which were perhaps originally designed for other

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materials. This combination of materials, or mixed-materials, can have substantially different properties than the originally designed for material.

The PISCES-B linear plasma device [3] is examining the formation conditions and properties of mixed-material surface layers which can form on plasma-facing components. The formation of the layers is a complicated process governed not only by the material's properties of the surfaces (such as temperature, particle reflection coefficients and sputtering yield), but also on the conditions in the adjacent plasma (redeposition probability, impinging particle energy and impurity content). This paper will focus on the C/Be mixed-material system, whereas the C/W system is presented by Sze [4]. After a description of the experimental setup, the formation conditions for a carbon-containing mixed-material layer on a beryllium substrate will be discussed. The implications for erosion of both carbon on beryllium and beryllium on carbon will then be examined. Finally, the hydrogen isotope retention properties of a carbon-containing mixed-material layers will be presented.

### 1.1. Experimental arrangement

The PISCES machines [5] are reflex-arc linear plasma simulator devices which are used to study plasma material interactions at the University of California, San Diego. The PISCES-B device has been modified to investigate mixed-materials in several ways. An impurity gas puffing system has been installed in the target interaction region. To date experiments have focused on puffing deuterated methane ( $\text{CD}_4$ ) into the plasma, but future plans involve the use of other impurity gasses, such as CO and  $\text{O}_2$ . In addition, a beryllium evaporation ball can be inserted upstream in the plasma column to seed the plasma with beryllium as it flows toward the target. This evaporator is necessary because sputtered beryllium atoms leave the surface with an energy of 1–2 eV, leading to an ionization mean-free-path which is longer than the plasma column radius for sputtered beryllium in the PISCES-B plasma geometry. The evaporator is used to introduce beryllium atoms with thermal energies into the plasma column, so that the ionization mean-free-path is short compared to the plasma diameter. A schematic diagram of the PISCES-B mixed-material experimental setup is shown in Fig. 1.

The resultant materials surface can be analyzed in situ in the attached surface analysis chamber equipped with Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS). The analysis chamber is also equipped with an ion gun for depth profiling measurements. Ex situ analysis includes a scanning electron microscope (SEM) with energy dispersive X-ray analysis

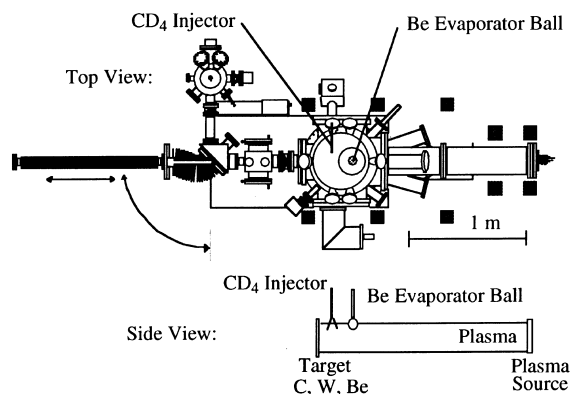


Fig. 1. Experimental configuration for mixed-material experiments on PISCES-B.

(EDX). Thermal desorption spectroscopy (TDS) is used to measure the amount of deuterium retained in a sample after removing it from the PISCES-B vacuum chamber.

Two important quantities to determine for these mixed-material studies are the impurity concentration in the plasma and the temperature of the exposed sample. The sample temperature is monitored with an IR pyrometer, but because of difficulties with the changing emissivity of the sample surface as a mixed-material layer forms, a thermocouple is also pressed against the back surface of the sample to record the temperature. The samples used in these measurements are thin,  $\approx 1.5$  mm, and the heat removal from the back surface fairly poor, so the temperature gradient across the thickness of the sample should be small. The plasma impurity concentration is also measured in two ways. 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. The RGA is calibrated against both an ion pressure gauge that functions accurately only in the absence of magnetic fields, as well as with impurity puffing into vacuum with a calibrated mass flow rate controller. Since the RGA measures only volatile neutrals reaching the analyzer, the validity of the RGA impurity measurement was checked by using a visible spectrometer to measure the impurity ion line radiation (e.g. CII) [6] emitted from the plasma 2–3 cm in front of the sample during operation. Comparing this intensity with the neutral line emission of deuterium and using the calculated excitation rates [7] allows the impurity concentration to be calculated to within 25%. The two techniques agree to within this accuracy. Background impurity concentrations of both carbon and oxygen in the PISCES-B plasma are 0.2% or less.

## 2. Results and discussion

### 2.1. Mixed-material layer formation conditions

The formation of any surface layer is a competition between deposition and removal processes. Deposition from a plasma will be influenced by such factors as the impurity concentration of the plasma, the sticking coefficient of the impurity (and hence the type of impurity – molecular, atomic, ionic) on the surface, the incident energy of the impurity and probably many others. Removal will be influenced by chemical bonding on the surface, the plasma ion energy, neutral bombardment onto the surface, the probability of redeposition and again probably many other factors. Influential in both the removal and deposition processes is the temperature of the surface. The temperature will influence the chemical structure of the surface as well as the inter-diffusion of impurities and the bulk material. At elevated temperatures ( $>400^{\circ}\text{C}$ ), molecules such as carbides are more likely to form and impurities deposited in the implantation zone can more easily diffuse into the bulk material and become less likely to remove. Therefore, it is more likely to form a surface layer at higher temperatures, all other variables being constant. In principle, a study of the formation of mixed-material surface layers should include variations of all of these quantities. In practice, this work will focus on variations of the temperature of the surface and the concentration of impurities in the incident plasma.

During earlier work on PISCES-B, thin films composed of light impurities from the plasma were observed to form on the surface of beryllium samples exposed to deuterium plasma bombardment [8] and showed the importance of the surface temperature on the formation process. Subsequent work improved the vacuum conditions such that the impurity concentration was low enough to avoid the formation of mixed-material layers over the range of temperature up to  $550^{\circ}\text{C}$  [9]. This work has systematically approached variations of both surface temperature and impurity concentration to develop a two dimensional map to determine if the formation of mixed-material layers are likely in ITER.

In a plasma without impurities, a mixed-material layer will not form regardless of the sample temperature. When the impurity concentration is high, deposits will grow at any temperature. These two conditions can be seen in Fig. 2 showing film formation conditions in PISCES-B. At low impurity concentrations, 0.2% carbon, no films form at any temperature. At impurity concentrations of 3% carbon, films form during room temperature exposures. Deuterium plasmas with 100 eV ion energy bombardment of the surface are used to generate the data in this graph. The ion flux varies from a low of  $1 \times 10^{21} \text{ m}^{-2}\text{s}^{-1}$  up to  $2 \times 10^{22} \text{ m}^{-2}\text{s}^{-1}$  and is related to the temperature of the surface (because the ions are

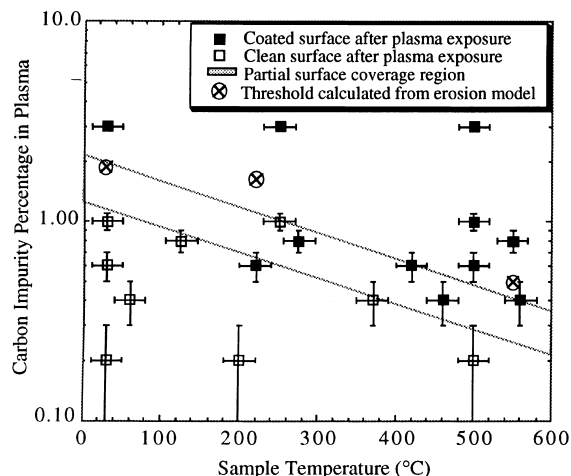


Fig. 2. Carbon-containing mixed-material layer formation conditions for beryllium exposed to 100 eV deuterium ion plasma bombardment. A transition region is observed between the region where clean and coated surfaces result. A simple erosion model seems to adequately predict the impurity concentration threshold necessary for film growth.

accelerated through the sample bias potential). Exposure times range from 1000–7200 s. (2 h). The difficulty of the definition of what constitutes film formation arises for the region between the two extremes.

For lack of a better definition, a surface concentration of at least 50% carbon (measured by AES) is used in Fig. 2 to define when a mixed-material surface layer formed on a sample. It should be noted that some of the 'clean' data points in Fig. 2 had a carbon surface concentration of up to 30%. Also, several of the high-temperature 'coated' surfaces were measured to consist entirely of carbon and oxygen, without any evidence of the underlying beryllium substrate. The surface concentration may be somewhat misleading, however, because many of the films that were formed in a transition region were observed to crack and flake off. A region indicative of this transition from clean to coated surfaces is sketched onto Fig. 2.

The growth rate of the film was measured under the condition of 0.8% carbon impurity concentration at a sample temperature of  $550^{\circ}\text{C}$ . The layer thickness is measured using a profilometer at a location on the sample where the surface film had exfoliated from the substrate revealing the beryllium surface below. Fig. 3 shows a SEM picture of a region of the sample where such an exfoliation occurred. The predominantly carbon (with small amounts of oxygen) containing film is clearly seen partially covering an apparently clean beryllium surface below.

If the growth rate of the film is determined by the diffusion rate of the underlying substrate through the

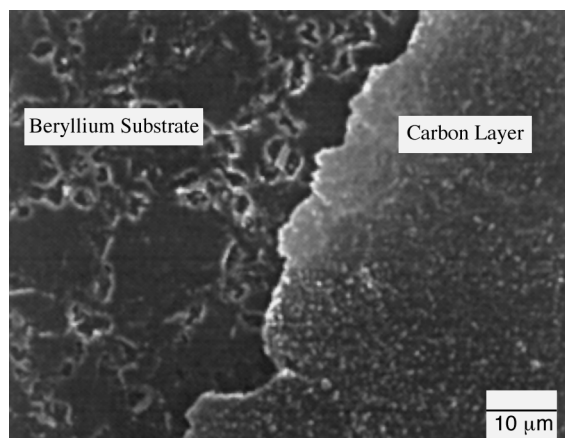


Fig. 3. SEM photograph showing the edge region of a carbon-containing film which has cracked and fallen off the beryllium substrate. The substrate is seen to have the appearance of a 'clean' beryllium surface.

impurity layer, the thickness will have a time to the one half dependence [10]. If the growth rate is determined by the arrival rate of the impurity atoms at the surface, a constant growth rate in time is expected. Fig. 4 compares these two growth rate models (normalized at the measured data point of 3 μm) with the measured film thickness obtained from some of the samples exposed in PISCES-B. The linear growth rate model more closely matches the experimental results, meaning that the impurity arrival rate at the surface governs the growth rate of the film.

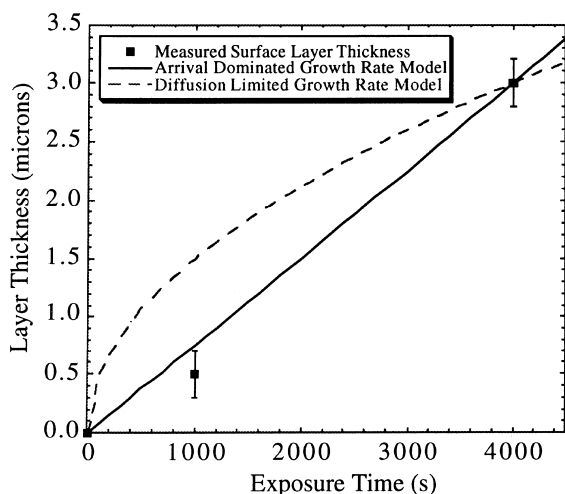


Fig. 4. The measured mixed-material layer thickness in PISCES-B is governed by the arrival rate of carbon ions at the surface (constant growth in time), rather than by the diffusion of bulk atoms through the surface layer (thickness proportional to  $t^{1/2}$ ).

Since the arrival rate is determining the layer growth rate, it should be possible to quantify the growth rate model. The film growth rate will be equal to the arrival rate of the impurity minus the erosion rate of the impurity layer. The arrival rate,  $g$ , of carbon ions at the surface is the carbon impurity fraction, 0.008, times the deuterium ion flux, or in this case  $1.6 \times 10^{20}$  carbon ions/ $m^2s$ . The erosion rate is determined from the sputtering yield and the fraction of redeposited material. The ionization mean-free path for physically sputtered carbon atoms under these plasma conditions ( $T_e = 30$  eV,  $n_e = 8 \times 10^{17} m^{-3}$ ) is 0.035 m. The plasma column radius is 0.025 m. Integrating over the typical cosine distribution for physically sputtered particles gives a redeposited fraction,  $f$ , of 70% for the conditions listed above. The ionization mean-free path for chemically sputtered molecules is shorter than the plasma column radius, so 100% redeposition is assumed for chemically eroded carbon material. The growth rate,  $G$ , of the surface film can then be calculated as

$$\begin{aligned}
 G &= g - (1 - f)Y\Gamma \\
 &= 1.6 \times 10^{20} - (1 - 0.7)(0.016)(2.0 \times 10^{22}) \\
 &= 6.4 \times 10^{19} \text{ atoms}/m^2s,
 \end{aligned}$$

where  $Y$  is the physical sputtering yield for 100 eV  $D^+$  on carbon, 0.016 [11], and  $\Gamma$  is the measured flux of  $D^+$  ions. For comparison, the measured growth rate of the 3 μm thick film is  $8.2 \times 10^{19}$  atoms/ $m^2 s$ , assuming the density of graphite ( $1.1 \times 10^{29}$  atoms/ $m^3$ ) in the coating. This simple model seems to adequately reproduce the experimentally measured quantities given the realization that the layer which forms will certainly have a more porous structure than fully dense graphite.

The threshold concentration for film formation can be calculated from this model by setting the growth rate,  $G$ , equal to zero. For the plasma conditions specified above the threshold impurity concentration is calculated to be 0.005, very similar to the observed value. To reduce the sample exposure temperature, the plasma ion flux (and thereby the redeposited fraction) is reduced. The erosion model has been applied for the plasma conditions at a few additional representative exposure temperatures and the resultant threshold concentrations for film formation are also plotted in Fig. 2.

But, can such a simplistic model, neglecting surface chemistry and film properties, actually represent the complicated interactions occurring at the surface? A few other observations can further corroborate the validity of this simple model. The diffusion rate of beryllium through a carbon layer has been measured [12] at 500°C to be around 0.02 nm/s. This value is quite a bit smaller than the film growth rate of 0.75 nm/s measured here at 550°C, so one would not expect to see much carbide in the surface layer. Perhaps the most striking indication that chemical interactions are playing a minor role in the

film growth is the fact that the measured film formation threshold concentration is approximately the same for the tungsten–carbon system [4] as for this beryllium–carbon system. Material interdiffusion and the formation of carbide layers will have a dominant effect at slower film growth rates, or higher surface temperatures, when the diffusion and formation rates are comparable to the film growth rate.

## 2.2. Mixed-material erosion behavior

The effect of a carbon-containing mixed-material layer on the erosion of beryllium has been described in Ref. [8], where the layer appears close to the diffusion limited growth regime described above, but where lack of an impurity concentration measurement hampered the interpretation of the results. The reduction of the erosion of beryllium was attributed to two factors. First, as carbon covers parts of the plasma bombarded surface, the amount of beryllium exposed to the plasma is reduced, but this does not account for the entire reduction. A fraction (26%) of the carbon was measured to be bound up in beryllium carbide bonds which act to inhibit the loss of beryllium because of the increased binding energy of the carbide. The combination of these two effects resulted in a factor of 3–4 reduction in the erosion yield of beryllium in a mixed-material layer [8]. The formation of mixed-material layers on the ITER first wall can, therefore, have beneficial consequences for the lifetime of the wall.

The other question is to what extent beryllium eroded from the first wall and upper baffle will be transported into the divertor and influence the erosion of the graphite divertor dump plate. Calculations have estimated the amount of beryllium which will be deposited on the ITER dump plates [13]. One would expect to observe at least a reduction in carbon erosion proportional to the amount of beryllium surface coverage on the divertor plate. However, it might also be possible for the beryllium to act much like a dopant in the graphite [14,15] and to further reduce the chemical erosion from the dump plate.

This effect has been investigated by lowering the beryllium getter into the PISCES-B deuterium plasma column. As the temperature of the getter increases, beryllium begins to evaporate from the surface and is ionized in the adjacent plasma. The ionized beryllium will then flow along with the plasma to a graphite sample inserted into the target region. The CD band intensity emitted from the plasma can be used as a relative measure of the change in the chemical erosion of the graphite as the concentration of beryllium on the surface changes.

The experimental conditions during the measurements were: ion flux =  $1 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$ , ion bombarding energy = 60 eV, electron temperature = 20 eV and car-

bon surface temperature = 400°C. The CD band emission is insensitive to small changes in the electron temperature in this range [16], so the CD band emission is a reliable indication of the chemical erosion of the graphite. The discharge was periodically terminated and the sample analyzed in situ with AES to determine the surface concentrations of beryllium and carbon. A small amount of oxygen, about 10%, was also usually detected on the surface. The discharge was then reinitiated for a period of time and then the CD band intensity remeasured, followed by additional surface analysis. The background CD band intensity in the device was measured, and subtracted from the signals, by using a pure beryllium sample. The resultant graph is shown in Fig. 5. Also plotted in Fig. 5 is the expected chemical erosion based purely on the fractional carbon surface coverage. As can be seen, the beryllium which will be eroded from the first wall and transported to the ITER divertor will act to inhibit the formation of hydrocarbons. By reducing the chemical erosion of the ITER graphite dump plates, one can expect a reduction in the total tritium inventory [2] within the device. The fact that this reduction should occur somewhat naturally during ITER operation is an added benefit.

## 2.3. Hydrogen isotope retention in mixed-material layers

The hydrogen isotope retention in the beryllium first wall has been shown to reach a saturated value and then to have only a small dependence on increasing fluence [9,17,18]. However, an impurity layer could easily be expected to form on the ITER first wall as was shown in Section 2.1. As the mixed-material layer forms it is possible that the retention in the surface layer may

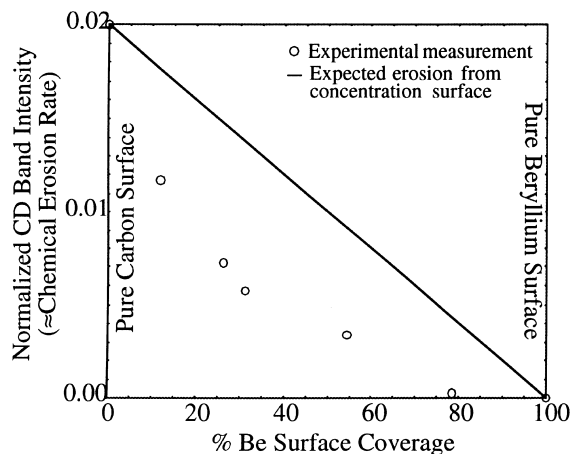


Fig. 5. Beryllium deposits on a graphite substrate act to inhibit the chemical erosion of carbon. The line is the expected reduction in chemical erosion from the depletion of the carbon surface concentration.

dominate the retention in the underlying, or bulk, beryllium.

A series of measurements has been made by injecting controlled amounts ( $\approx 2\%$ ) of  $CD_4$  into a deuterium plasma column. The exposure in each case lasted for two hours. Although the thicknesses of the resultant films were not measured, they are assumed to be similar since exposure conditions were similar. After the conclusion of each exposure the sample was removed from vacuum and inserted in a separate vacuum chamber where TDS was performed. The sample temperature was then ramped up to a maximum of  $900^\circ C$  while recording the partial pressures of all the deuterium containing molecules ( $D_2$ , HD,  $D_2O$ , HDO) which were released. The amount of deuterium released in the HDO and  $D_2O$  peaks was measured to be negligible ( $<1\%$ ) compared to the HD and  $D_2$  peaks. The results of the TDS measurements are compared in Fig. 6 to the retention measured in uncoated ('clean') beryllium samples, both plasma-sprayed and press-sintered, exposed to plasma containing the 0.2% background carbon impurity concentration. Regardless of the substrate material the formation of a carbon-containing mixed-material layer is measured to increase the amount of deuterium retained.

At least an order of magnitude more deuterium is retained in the samples containing the mixed-material layers formed during room temperature exposures. As the temperature of the layer formation increases the amount of additional deuterium retained decreases until at  $500^\circ C$  there is no detectable difference in the retention between coated and clean samples. Although it is evident that the retention in mixed-material layers should be a

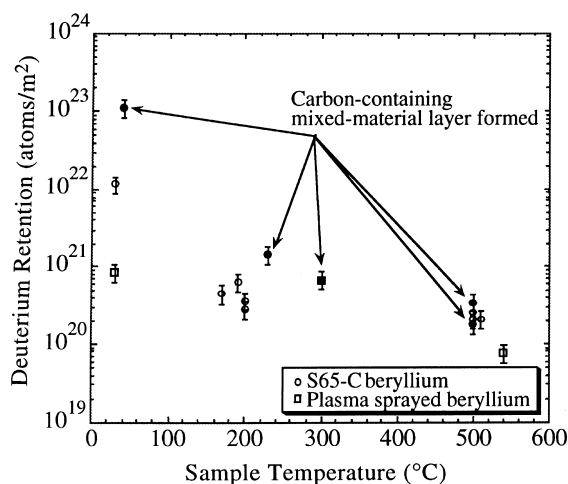


Fig. 6. Deuterium retention in beryllium samples can increase when mixed-material layers form. The temperature dependence of the retention in the mixed-material layer is similar to that expected from a pure carbon sample.

concern for ITER, is also apparent that the proper design of the heat removal from the wall can minimize these concerns.

There are two possible explanations for the reduced retention in the mixed-material layers at elevated temperatures. The first involves the temperature dependence of the retention in carbon films formed at different temperatures [19], as carbon films themselves form at higher temperature they tend to retain less hydrogen isotopes. It is also possible that at elevated temperatures there begins to be interdiffusion of the depositing carbon and the substrate beryllium. At temperatures above  $490^\circ C$ , beryllium carbide is expected to form and reduced retention is expected in beryllium carbide [20].

### 3. Conclusions

Mixed-material effects have begun being investigated in PISCES-B. A simple model, which ignores surface chemistry effects, has been used to determine the growth rate of the surface layer. Under these PISCES-B operating conditions, which mimic the first wall and baffle conditions of ITER, carbon rich surface layers form and grow rather quickly. These surface layers are also observed to be poorly adherent to the substrate material. These results can be used to guide future research toward the regime where surface chemistry effects will become important.

The influence of beryllium on the chemical erosion properties of a graphite substrate have shown that the beryllium which will inherently flow from the ITER first wall to the divertor will lead to a beneficial reduction in the erosion properties of the divertor dump plate. Finally, the hydrogen-isotope retention properties of carbon-containing mixed-material layers on beryllium is shown to be temperature dependent. The retention is larger than that of a clean beryllium surface, the surface layer appears to have retention properties of a pure carbon sample.

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