Temperature influence on deuterium retention for Be-W mixed thin films prepared by Thermionic Vacuum Arc method exposed to PISCES B plasma

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Abstract

Beryllium-tungsten thin films with well controlled elemental composition were prepared using Thermionic Vacuum Arc (TVA) technique and subsequently exposed to steady state, high ion flux ($5.5 - 9.8 \times 10^{22}$ ions $\text{m}^{-2}\text{s}^{-1}$) deuterium (D) plasma in the PISCES-B facility to consistent fluences of 2.3×10^{26} m^{-2} . Six types of layers were studied, ranging from pure Be, composite Be-W, having the atomic ratios of 9:1; 7:3; 1:1; 3:7; to pure W with a total deposited layer thickness of 2 μm . The sample exposure temperatures, namely 300K, 473K, 573K and 773K, respectively, were measured in situ with a thermocouple placed on the back of the sample. Morphological and structural examinations were undertaken before and after plasma exposure. Results show an influence of temperature on the subsequent morphology of the surface. Thermal Desorption Spectrometry (TDS) spectra showed a change in the D release behavior for different Be-W ratio for a certain exposure temperature.

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1. Introduction

Beryllium (Be) and tungsten (W) are the preferred candidate materials to be used for next generation fusion reactors. The present ITER design [1] employs beryllium tiles as the first wall plasma facing material, and tungsten in the divertor. Due to the high density plasma conditions in a fusion reactor, material migration is likely to generate Be-W mixed surfaces. These mixed surfaces can influence fuel retention and desorption from the initial plasma-facing components, which in turn will affect the hydrogen recycling and in-vessel tritium inventory [2-3]. Examining the morphological and structural changes of the plasma facing materials, as well as fuel retention and release from such mixed material surfaces, as a function of exposing temperature was one of the aims of this work.

Be-W mixed material layers, with well controlled elemental composition were prepared using Thermionic Vacuum Arc technique [4]. Six types of layers were studied, ranging from pure Be, composite Be-W, having the atomic ratios of 9:1; 7:3; 1:1; 3:7; to pure W with a total deposited layer thickness of 2 μm . Each type of samples was exposed to deuterium (D) plasma in the PISCES B facility [5]. The sample exposure temperatures were 300K, 473K, 573K and 773K, respectively. The present work reports the surface temperature influence on the morphological and structural changes as well as on deuterium retention and release mechanism from the different Be-W mixed layers.

2. Experiment - sample preparation and PISCES B deuterium plasma exposure

Be-W mixed material layers were produced using TVA method. This technique is well described elsewhere [6-7]. The set-up is schematically presented in figure 1 and consists in two individually anode-cathode systems. The cathode was of a tungsten filament wire with 0.8 mm in diameter, which was heated by a DC high current supply. For the Be cathode it was used a current value between 36A to 43A, and 43-83A in the case of the tungsten cathode. The emitted electrons from the cathode were focused through a wehnelt cylinder, placed around the tungsten filament on the anode, by applying a high voltage on it, between 0.9-1.3 kV for the Be anode and 1.5-2kV for the tungsten one. Polished stainless steel disks with a 25 mm in diameter served as substrates. In order to obtain good adherence and good compactness of the films, the substrates were negatively biased at -750V [8]. In this way energetic ions from both Be and W plasmas were accelerated towards the substrate. Prior to the coating process, the substrates were heated up by an oven placed above the substrate holders, to a maximum temperature of 673K which was kept constant for the whole deposition process. In situ independent deposition rate and thickness were recorded for each material using two quartz microbalance systems (QMB). The main purpose was to obtain different Be-W mixtures with controlled relative elemental concentration. The characteristic of each set of samples is presented in table 1.

The PISCES-B facility, which is a linear plasma simulator specially designed for plasma and materials interaction experiments [9-11] was used to provide a steady-state, high ion flux ($5.5 - 9.8 \times 10^{22} \text{ ions m}^{-2}\text{s}^{-1}$) deuterium plasma. Be-W samples were exposed to consistent fluences of $2.3 \times 10^{26} \text{ m}^{-2}$. For all the studied samples the deuterium plasma condition were kept constant ($T_e \sim 3.5 \text{ eV}$, $n_e \sim 8.7 \times 10^{12} \text{ cm}^{-3}$) the incident ion energy was assured by a negative bias potential of -60V applied on the exposed sample. The temperature was measured in situ with a thermocouple pressed against the back of the sample and was varied 300-773K being controlled throughout the discharge duration.

3. Results and discussion

3.1 Morphological analysis

Morphological and structural examinations were undertaken before and after plasma exposure in order to investigate the behavior of the plasma material interaction with respect to different exposure temperatures. Scanning Electron Microscopy (SEM), using a JEOL JSM 6360 system was used to study surface morphology. As an example figure 2 shows SEM image for the W(30) structure which presents no particular shapes before exposure, the surface being mostly smooth with some defects due to the coating process. Signs of the stainless steel substrate roughness influence on the morphology of the coated Be-W structure can be seen. For the sample W(30)_07 (figure 3), exposed to a 473 K signs of blistering effect were observed, which is typical of pure W exposed at this temperature [12]. The exfoliation and blister appearance was observed for all studied samples exposed to this temperature. Despite that, higher magnification images ($\times 10000$) showed no significant modification of the surface morphology on films compositionally rich in W. One possible reason could be the higher W elemental concentration in the Be-W mixed thin films, which is known to have a rather lower sputtering yield than Be under D exposure. Moreover, this change in the morphology can be also attributed to the design of each individual Be-W mixture, taking into consideration that each set of samples is a multilayer combinatorial mixture. On the other hand, SEM images showed considerable changes in morphology for pure Be samples. As can be seen in figure 4, SEM images for the pure beryllium Be(100) sample before D plasma exposure show the specific hexagonal shape structures grown on the stainless steel substrates. The pre-exposed surfaces are identical, and roughness is apparent. After the plasma interaction, the surface of pure Be samples suffers an obvious change of the morphology (figure 5)

For the 300K exposed sample, Be(100)_02, a strong influence on the surface morphology was found and the sputter yield determined to be 6.8×10^{-4} per ion at 50eV, calculated assuming

single ionized D^+ ions and $E_{ion} \approx V_{bias} - 2k_B T_e$ [13]. In addition D^+ is assumed as being the dominant ion species [14] for the pure deuterium plasma. For the Be(100)_05 sample exposed at 473K, a change of the sample surface is also noted. The hexagonal shape structures are no longer obvious. Weight measurements after the plasma exposure showed a mass loss for Be(100)_05 consistent with a calculated sputter yield of 4.2×10^{-4} per ion. For 573K exposure at the same condition, SEM images (Be(100)_04) show a more effective influence on the surface morphology and the calculated sputter yield was 5.8×10^{-4} per ion. While there is slight difference between the mass loss during higher temperatures up to 573K and room temperature, it can be considered that the net mass loss from this pure Be samples after deuterium plasma exposure is constant, regardless of the exposing temperature up till 573K, as previously found by Doerner et al. [10]. The SEM image for the Be(100)_01 sample, exposed at 773K, shows a strong influence on the surface morphology after the plasma exposure as well. As it can be seen from SEM images, the samples exposed to lower temperature show a less prominent structure shape surface, while the 773K exposed sample shows a different surface morphology. Weight loss measurement after the plasma treatment, revealed a calculated sputter yield of 4.54×10^{-4} per ion.

As previous studied [15-16] showed the surface morphology of the Be targets exposed at low temperature are characterized by the “grass-like” structures as also seen for the 300K exposed sample here. Yet as the exposing temperature is increased, the surface morphology reveals reduced morphology. In comparison with low temperature exposures (300K-600K) the higher mobility of Be atoms on the hot surface at 773K likely affects surface morphology development [17] as in figure 5.

3.2 Compositional analysis

Using a surface analysis suite (PHI System) connected to PISCES B facility, Be-W thin films were subjected to Auger Electron Spectroscopy (AES) before and after the exposure,

without any outside air contamination risk. Figure 6 shows PHI surface evolution of each individual element with respect with the original Be-W ratio. It was seen that after the plasma exposure, regardless of the exposing temperature, the Be signal drops significantly and relative atomic concentration being 0% for samples W(90) and W(70). For the W(50) and W(30) sets, the relative atomic concentration was found to be around 3%. The only sample, for which, the relative atomic concentration of beryllium was higher than 3%, was recorded for the W(10) sample exposed to 773K. This lower value in the atomic concentration of beryllium after the plasma exposure is complemented by an increase of the tungsten AES signal.

3.3 D retention and release evaluation

Deuterium retention and release of the samples were evaluated using programmed Thermal Desorption Spectroscopy (TDS) in an infrared heated quartz tube oven with a 0.3 K s^{-1} linear temperature ramp, up to 1273K and a hold time of 10 minutes at the maximum temperature. Partial pressure during desorption were recorded with a high resolution MKS Microvision 6u RGA and a Stanford Research System RGA100. After each deuterium plasma exposure, the samples were taken out from the high vacuum PISCES B facility and exposed to air, in order for the SEM measurements to be performed. The time between each plasma exposure and the TDS measurements was of two weeks, time for which the samples were air exposed. In figure 7 it is shown the TDS spectra for the structure W(50), which is composed of 50 at% of tungsten and 50 at% of beryllium. The recorded TDS spectra traces of D_2 mass are shown in the figure. For the sample exposed at room temperature, namely 300K, the desorbed deuterium spectra shows a major wide peak at around 600K and two minor peaks around 850K and 1100K. As the exposing temperature of the studied samples increased to 473K, it was observed one major obvious peak, at around 820K, and two minor peaks, one at a lower temperature, namely 600K and the third one was noticed at 1100K. The desorbed deuterium spectra of the 573K exposing sample temperature, showed one major peak at around 650K. The

second major peak was not that obvious, but was found around 1080K. It was noticed that all samples exposed to 300K, 473K and 573K presented a common peak at around 600-650K. For the sample exposed to 773K, the lower temperature peak was not present. The TDS spectrum in this case is characterized by a single wide peak, in the range 900-1273K. Deuterium desorption process starts around the exposing temperature, for each studied samples. As the exposing temperature has a greater value, it was noticed a decrease of the integrated desorption, as well as a shift in the primary peaks.

In figure 8 it can be seen the mass traces spectra of D_2 for the pure beryllium samples. For the sample exposed at room temperature characteristic desorption peaks with a major one around 575K and a minor one at around 640K were observed. These two temperatures correspond to reported trapping states in Be, i.e. as BeD_2 , BeO-related trapping and defects respectively [18]. As the exposing temperature was increased to 473K, it was observed the primary peak at around 640K, and the other one at a higher temperature 740K, which is not that obvious. The TDS spectra of the sample exposed at 573K shows two major peaks, the first at around 660K, and the second one at about 800K. In comparison with the sample exposed at lower temperature, it was observed a slight shift of the two major peaks. The sample exposed to the 573K, present also a minor peak at a much higher temperature, namely 1050K. For the highest exposing temperature, 773K the TDS spectrum shows a single major peak at around 850K. Its signal it's less detectable then in the case of the previous samples exposed at lower temperatures, which may suggest that at elevated temperatures the amount of the retained and desorbed deuterium has a lower value than in the case of lower exposing temperatures.

Figure 9 shows the evolution of the deuterium desorption spectra, function of the elemental Be-W ratio present in each sample, and also function of the exposing temperature. For all of the studied samples, the low temperature desorption peak was found in the range of 500K-600K, and the second major peak, corresponding to a higher temperature was found in

the range of 1000K-1200K. As the relative concentration of tungsten decreases and beryllium increases, it can be seen that the high temperature desorption peak disappears, and a lower temperature desorption peak emerges. Moreover, as the concentration of beryllium is increased, the first major peak, corresponding to the lower temperature value is more prominent. This can be attributed to low temperature peak of saturated deuterated beryllium [18].

In figure 10 calculated D_2 retention value are shown as obtained by integrating the TDS spectra. It is found that a dual dependence for desorbed deuterium as a function of the elemental concentration in each sample as follows: starting with pure W samples and moving towards 50% W a decreasing slope is observed for retention values at 473K and 573K exposures. As the Be concentration in the samples is increased toward pure Be samples, it is found that retention values increase. One reason for this high values of the calculated retentions for the rich W containing samples might be the multilayer combinatorial Be-W thin film obtained by TVA technology. Because the 2 μm thin film is made out of several layers of Be-W mixtures, it might be affected deuterium retention and desorption from the samples. After each individual Be-W layer was obtained (hundreds of nm), the film was exposed to air, and the coating process continued in this way till the 2 μm thickness was reached. Another possible explanation for the behavior at high W concentration would be the presence of blisters and exfoliation which occurred during plasma exposure. The surface exposed to D plasma increases, consisting in the exfoliated layer (on top and underneath) and the new surface that is on the stable film and exposed due to blistering. In this way, deuterium plasma affected also the layers underneath. The resulted retention might be a sum of all affected layers, knowing that deuterium is trapped in pure beryllium in the first 300 nm and 2-3 μm for tungsten. The calculated retention values ranged from $1.4 \times 10^{16} \text{ D}_2/\text{cm}^2$ specific to the high temperature exposure of pure W samples to $4 \times 10^{17} \text{ D}_2/\text{cm}^2$ for the pure Be samples exposed at room temperature and are consistent with previous experiments [19-20]. It was observed also a temperature influence on the desorbed

quantity of deuterium out of the studied samples. For the highest exposing temperature, namely 773K, the calculated retention had a lower value than in the case of lower temperature exposures. The highest calculated retention values were obtained for the 473K temperature exposure.

Figure 11 shows a different plot of D₂ retention in Be-W mixed layers as a function of exposing temperature in respect with pure Be (black solid line) [21] and pure W (dashed black line) [12-and refs. there in]. For comparison purpose the two dashed lines in the figure are the polynomial fit to pure D₂ exposure data for pure W where the upper dashed line represents the plot of the largest retention values obtained and the lower dashed line is the plot of the lowest retention values obtained for pure W in reference 12 and all references there in. As it can be seen deuterium retention for pure W(100) and rich W samples (W(70)) obtained by TVA technology are relatively consistent with the data found in the literature for high fluence exposure $\Phi_D^+ > 10^{25} \text{m}^{-2}$ and temperature range 473K-773K.

D₂ retention for pure Be samples are as well consistent with data found in the literature. The retention in the case of Be-W mixed layers, in particular the ones with high Be atomic concentration (W(50);W(30);W(10)) is influenced by the presence of Be. The obtained trend for deuterium retention for Be-W thin films is more consistent with the D₂ retention results for pure crystallographic Be.

4. Conclusions

Results show an influence of temperature on the subsequent morphology of the Be-W samples surface. Layers exposed at 473K, showed blister formation as well as layer exfoliations. This effect was noticed for each rich W-containing samples. Blister formation was reduced for the 573K exposure and not apparent at 773 K. Nevertheless, high magnification SEM images showed considerable changes in morphology only for pure Be samples. AES measurements indicated a preferential sputtering effect of Be at the surface, following plasma exposure, regardless of temperature. Only 27 at% residual Be after the exposure was noticed for the Be-W

(9:1 original composition) sample, for the 773K exposure, in comparison to residual Be values of 0-3 at % for other compositions explored. TDS spectra showed a significant shift of the desorption peaks for each type of layer depending on the exposure temperature, as well as a change in the D release behavior for different Be-W ratio for a certain exposure temperature. An increase of the exposure temperature leads to a lower calculated retention by integrating the TDS spectra. This behavior was observed for all studied samples. Calculated retention values for pure Be and pure W samples were consistent with the data found in literature. For the case of low W concentration samples, deuterium retention in Be-W mixed layers is influenced by the presence of Be.

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Table 1:

Be-W prepared samples

Be-W ratio (at%)	Thickness (μm)	Sample code
Pure Be	3	Be(100)
9:1	2	W(10)
7:3	1.5	W(30)
1:1	2	W(50)
3:7	2	W(70)
Pure W	2	W(100)

Figure captions

Figure 1:

Schematic representation of the deposition system and the electrical connections used to obtain the Be-W mixture

Figure 2:

SEM image for the W(30)_08 structure before the exposure

Figure 3:

SEM images for the W(30) structure after the exposure

Figure 4:

SEM image for the Be(100) structure before the exposure

Figure 5:

SEM images for the Be(100) structure after the exposure

Figure 6:

AES elemental evolution in respect with the Be:W ratio

Figure 7:

Thermal desorption spectra of D₂ signal for the W(50) structure

Figure 8:

Thermal desorption spectra of D₂ signal for pure Be samples

Figure 9:

Evolution of the thermal desorption spectra function of Be-W elemental ratio and exposing temperature

Figure 10:

D₂ desorption values function of the Be-W elemental ratio, for four different exposing temperatures

Figure 11:

D₂ retention in Be-W mixed layers as a function of exposing temperature in respect with pure Be (black solid line) and pure W (dashed black line) found in the literature

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Evolution of the thermal desorption spectra function of Be-W elemental ratio and exposing temperature

Figure 10:

D_2 desorption values function of the Be-W elemental ratio, for four different exposing temperatures

Figure 11:

D_2 retention in Be-W mixed layers as a function of exposing temperature in respect with pure Be (black solid line) and pure W (dashed black line) found in the literature