Study of deuterium retention in / release from ITER-relevant Be-containing mixed material layers implanted at elevated temperatures

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Abstract

D implantation into Be-containing mixed material layers: Be, Be-W (W: ~6 at.%) and Be-C (C: ~50 at.%), was performed at elevated temperatures. The temperature dependence of D retention varied depending on the admixed element. D retention in Be and Be-W layers decreases with increasing implantation temperature, while the Be-C layers maintained rather high D retention in the present investigated temperature range (up to 623 K). D desorption behaviour from Be-C suggests the contribution of C-D bonds to D retention. W admixture into Be can significantly suppress D retention in Be. Long-term isothermal annealing at 513 and 623 K for D removal was also performed to simulate the ITER-wall-baking scenario. Even extended annealing at temperatures comparable to or lower than the implantation temperature does not lead to a significant release of retained D.

PSI-20 Keywords: Deuterium inventory, Beryllium, Carbon-based materials, Tungsten, Thermal desorption

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1. Introduction

Current design of ITER plasma-facing components consists of different armour materials, i.e. beryllium (Be) for the first wall material, tungsten (W) as divertor armour and carbon fibre composite for the strike point areas [1]. The interaction of these wall materials with the plasma obviously results in the formation of mixed material layers. Such material mixing can change fuel retention properties of the plasma-facing surfaces, which affects the hydrogen recycling and in-vessel tritium inventory. Because of safety regulations in ITER, tritium removal will be required before the in-vessel inventory reaches its administrative limit [2]. In ITER, a wall baking procedure with technically accessible temperatures, at 513 K (240°C) for the main chamber and 623 K (350°C) for the divertor, is currently accepted as baseline for a tritium removal operation [3]. In order to assess the efficiency of tritium removal by such wall baking, it is necessary to know the hydrogen retention/release behaviour of not only the pure materials but also mixed materials. Fuel retention in W-Carbon (C) mixed material has been studied in various laboratories [4-7]. But also, the investigation with Be-containing mixed materials is a critical issue because Be covers the majority of the ITER plasma-facing surface (~ 690 m^2, i.e. ~ 80 % of plasma-facing area).

In this sense, we have previously investigated deuterium (D) retention in and release from Be-containing mixed material layers [8]. In these studies, D loading to the layers was mostly performed at 300 ~ 350 K. However, it is obviously necessary to perform retention studies also under D loading at elevated temperatures, because the temperature on the ITER wall is expected to be higher than 300 K. In the present study, therefore, D implantation to Be-containing mixed material layers are performed at elevated temperatures. This article reports the influence of the implantation temperature on the retention/release behaviour of prototypical mixed material layers.

2. Experimental procedure

2.1 Be-containing mixed layer preparation and characterization

All sample layers were deposited by the Thermionic Vacuum Arc (TVA) deposition method [9]. The TVA setup is equipped with two independent deposition sources, allowing the simultaneous deposition of Be and C or W [10]. The layer composition can be controlled by adjusting the input power for each deposition target. Since erosion yields of Be and C due to low-energy hydrogen ion bombardment are much higher than those of W, Be and C are expected to be the dominant deposition species in ITER. In this sense, the layers of pure Be, Be-C with 50 at.% C and Be-W with 6 at.% W were prepared for this investigation. Layers for implantation experiments were deposited on silicon substrates and layers for the compositional analysis were deposited onto polished isotropic graphite substrates.

After deposition, the stoichiometry of the layers was characterized by Rutherford backscattering spectroscopy (RBS) using $^{4}He^{+}$ with 2.0 MeV as the probe beam. The obtained RBS spectra were analyzed using the SIMNRA program [12] to determine the layer thickness and composition. The obtained layer thicknesses and compositions are summarized in table 1.

2.2. Deuterium ion implantation and analysis

Deuterium (D) implantation into the prepared samples was performed in the High Current Ion Source at IPP-Garching. The energy of the D ion beam was 600 eV D_3^+ (= 200 eV/D), which is a characteristic value derived from typical boundary plasma temperatures including sheath acceleration. The implantation fluence was 1.0×10^{23} D/m^2 with a flux of ~ 10^{19} D/m^{2}s. A particle fluence to the ITER first wall accumulated during one single 400 s discharge is expected to be order of 10^{23} /m^2. The incident angle was normal to the target surface. As mentioned above, the implantations in this study were performed at elevated temperatures: 398, 523 and 623 K. Sample were heated by radiation from a filament heater located behind the

sample, and the sample temperature was measured by a thermocouple attached to the sample surface.

After implantation, the amount of D retained in the sample was measured by nuclear reaction analysis (NRA) using an 800 keV $^3He^+$ beam. The D release behaviour of each sample was then measured by thermal desorption spectroscopy (TDS) in the Thermal Effusion Spectroscopy Setup (TESS) [13]. The sample was heated up to 1000 K with the temperature ramp rate of ≈ 0.25 K/s. Desorbed gasses were analyzed by a quadrupole mass spectrometer.

In reality, ITER wall baking will be performed on a time scale of hours/days of operation. This motivated us to investigate the D release behaviour during long-term isothermal annealing. For this, some sets of layer samples were annealed at 513 or 623 K for durations of 2 or 20 hours.

3. Result and Discussion

3.1. Dependence of D retention on the implantation temperature

NRA with $^3He^+$ can determine the near-surface D depth profile by analyzing the energy spectrum of alpha particles emitted from the D(^{3}He, α)H reaction. Fig. 1 shows alpha spectra obtained from various samples after D implantation. Fitting the simulated profile to the experimental alpha spectrum using the SIMNRA programme [12] yields the D depth profile. Previous studies have shown that the D retention in Be reaches a quasi-saturation in the D fluence range of > 10^{22} D/m^2. Since the fluence applied in this study (10^{23} D/m^2) was about a factor of 10 higher, it can be assumed that the maximum D concentration in the depth profile corresponds to D saturation concentration (D_{sat}). At least, these values can be considered as a lower limit for D_{sat}. Such obtained D_{sat} values are summarized as D/X (X = fraction of other materials) in Fig. 2, together with an experimentally-obtained database on D concentration in "co-deposition" with ITER-relevant materials compiled by Doerner et al. [13]. Since D

incorporation in co-deposition layers depends on the deposition conditions, the D/X varies in some range. The results presented here are obtained not by co-deposition, as the data in [13], but by D ion implantation. Nevertheless, D/X values in Be layers show relatively reasonable agreement with the Be data obtained from co-depositions. Similar to Be, D/X values in Be-W decrease with implantation temperature ($T_{implant}$), but they are lower than for pure Be, suggesting that even a small fraction of W impurity can reduce the D saturation concentration in Be. On the other hand, the Be-C layer maintains rather high D/X values even at high $T_{implant}$. This can be attributed to the strong chemical bonding of hydrogen to carbon, which is generally quite stable in this temperature range.

3.2. D desorption from mixed material layers

Fig. 3 shows D_2 desorption spectra. The desorption spectra vary strongly depending on the material mixture, which reflects the D trapping natures and the densities. For instance, the following trapping states for D in Be have been suggested in previous studies: (1) supersaturated a-Be:D state in the implanted region and/or cavities formed by defect aggregation in the supersaturated region with the release temperature ($T_{release}$) of 450-500 K [14,15], (2) Beryllium-hydride (BeD_2) which decomposes at around 550 K [16,17], (3) Be-O related trap, likely as Beryllium-hydroxide, with $T_{release} \approx$ 670-700 K [15] and (4) implantation-induced defects with $T_{release}$ in the range of 750-900 K [15] (each $T_{release}$ somewhat varies depending on the experimental conditions, such as the temperature ramp rate). The D release profiles of pure Be measured in this study can be well reproduced by combination of these release peaks. It is generally observed [8,15] that the amount of D desorption from states (2) and (3) increases under D implantation at moderately elevated temperatures (up to ~500 K), compared to 320 K implantation (shown in Fig. 3 (a) as reference). This indicates that the formation of Be-hydride/-hydroxide can be enhanced at slightly elevated temperatures. For

implantation at 523 K, both the 550-570 K and 670-700 K desorption features became quite small, meaning that D trapping in states (2) (hydride formation) and (3) (hydroxide formation) is significantly reduced at this temperature.

D in Be-C layer can, in addition to the Be-related traps, also be retained by forming C-H chemical bonds.. C-H bonds are quite stable with the binding energy range of 3 to 4 eV, requiring high temperature, generally above 600 K, for the desorption as hydrogen molecule [18-20]. The Be-C layers show a broad desorption feature in the temperature range from 600 to 1000 K, which are attributed to the contribution of C-D chemical bonds.

Since the W concentration in the investigated Be-W mixed layer is very low, Be-related traps are expected to play a dominant role for D retention in the layer rather than W-related traps. Nevertheless, the desorption spectrum is much different from Be. At 398 K implantation, D_2 release in the temperature range 400 ~ 700 K is quite small compared to Be, indicating that even a small amount of W admixture can significantly suppress the trapping by states (2) and (3), i.e. hydride/hydroxide formation. Overall, W admixture into Be reduces the retention compared to pure Be, which might be a positive message for ITER envisaging Be first wall and full-W divertor configuration in the D-T burning phase.

3.3. D release during the long-term isothermal annealing

Long-term isothermal annealing was performed for layers implanted at 523 and 623 K. The TDS results show that D release below $T_{implant}$ is very small or negligible. However, it is still worth to confirm whether the “long-term” annealing can remove some of the retained D or not.

According to the D release profiles (not shown here), the desorption rate during the isothermal annealing was very low if the annealing temperature (T_{anneal}) is comparable to $T_{implant}$. In fact, it was in this case close to the detection limit of our experimental setup. At

moderately higher T_{anneal} than $T_{implant}$, the desorption rate is still low, but clearly measurable. The amount of D retained in the sample after the isothermal annealing was measured by NRA and summarized in Fig. 4. The removal efficiency is generally not high under "($T_{implant} \geq T_{anneal}$" conditions, as seen in both "$T_{implant}$ = 523 K / T_{anneal} = 513 K" and "$T_{implant}$ = 623 K / T_{anneal} = 623 K" cases. Only for the "$T_{implant}$ = 523 K / T_{anneal} = 623 K" case, we found a reasonable reduction of the retained D amount by the long-term annealing. This reduction is in agreement with what we can anticipate from the TDS spectra, i.e., the remaining D amount after annealing at 623 K is comparable to that after D implantation at 623 K. The result confirms that it is quite difficult to remove tritium from plasma-facing surfaces if the baking temperature is not significantly higher than the operation temperature. On the other hand, initial retention decreases with the surface temperature rise as shown in Fig. 1.

4. Concluding remarks

In this study, D implantation into Be-containing mixed materials was performed at elevated temperatures, and the influence of the implantation temperature on the retention/release behaviours was investigated. D retention in Be and Be-W (W: ~ 6 at.%) layers decreased with increasing the implantation temperature, while D retention in Be-C (C: ~ 50 at.%) layer maintained an approximately constant up to 623 K. This is attributed to the strong chemical bonding of hydrogen to carbon which is quite stable and does not lead to significant desorption in this temperature range. D desorption behaviour of Be-W layer showed that the W admixture into Be can significantly suppress some of trapping states in Be, likely hydride and hydroxide formation, and therefore D retention is reduced compared to pure Be. Long-term isothermal annealing (up to 20 hours) at 513 and 623 K results indicate that ITER wall baking will reduce tritium from layers deposited on surfaces which have during loading a lower temperature than the baking temperature., However, baking will not efficiently remove tritium

from codeposited layers grown at comparable or higher temperature than baking temperature.

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Table 1:

Stoichiometry of mixed material layers prepared by TVA deposition. Concentrations were determined by RBS analysis using a 2.0 MeV $^{4}He^{+}$ beam. Layers for composition analysis were deposited on silicon substrates.

Layer type	Layer Thickness	Concentration of admixed element in Be layer
Be	570 nm	
Be-C	360 nm	C: 50 ±1 at.%
Be-W	380 nm	W: 6 ±2 at.%

Figure captions

Figure 1:

NRA results: α-particle energy spectra obtained from (a) Be, (b) Be-C (C: ~ 50 at.%) and (c) Be-W (W: ~ 6 at.%) after D implantation at 398, 523 and 623 K, together with each SIMNRA fitting result. The profile corresponds to the near surface deuterium depth profile.

Figure 2:

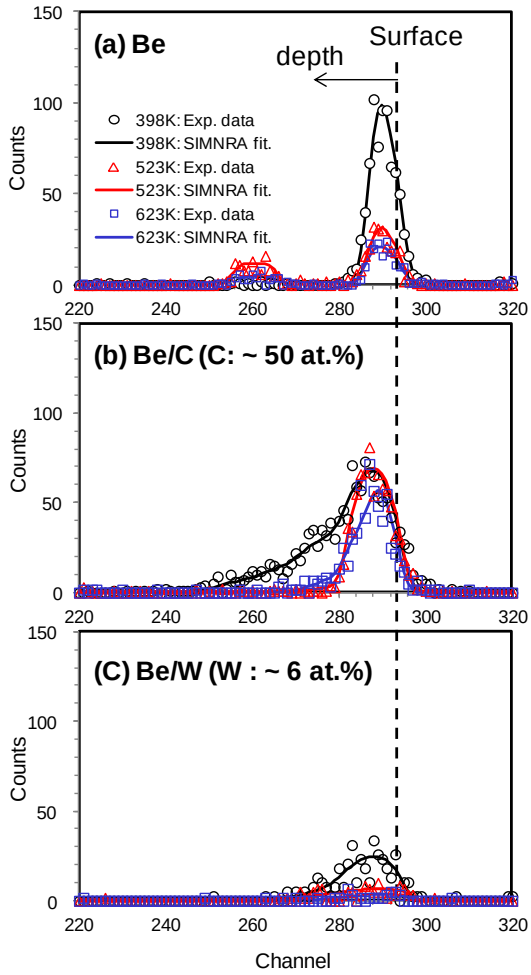
Maximum D concentration (D/X) in different Be-containing mixed material layers as a function of implantation temperature. The areas labeled as Be, C or W indicate results from a data compilation of experimentally-obtained D/X values for the D concentration in "codeposition layers" [13].

Figure 3:

D_2 desorption spectra obtained from different mixed material layers D-implanted at (a) 398 K, (b) 523 K and (c) 623 K. D_2 desorption from Be implanted at 320 K is also shown as reference in (a). Lines labeled as "513 K" and "623 K" indicate the ITER baking temperatures for the main chamber and the divertor, respectively.

Figure 4:

D retention in mixed layers implanted 523 and 623 K as a function of annealing duration at 513 and 623 K. In the figure, "$T_{implant}$" and "T_{anneal}" indicate the D implantation and annealing temperatures, respectively.



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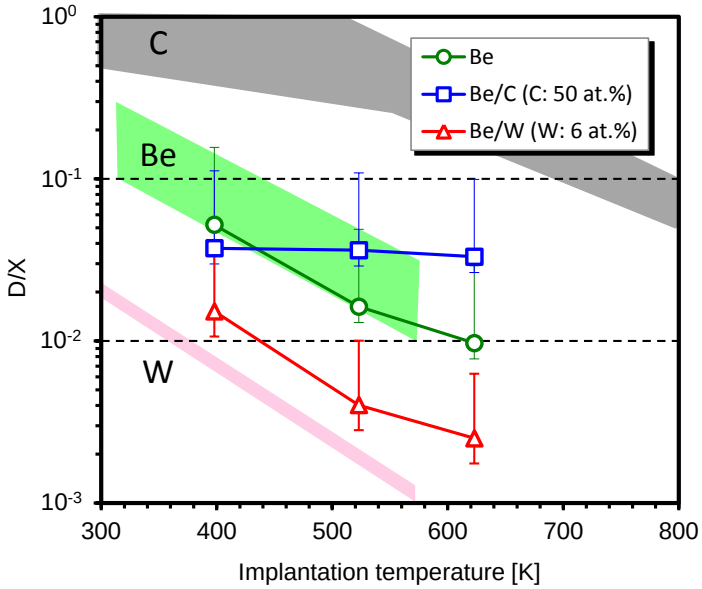

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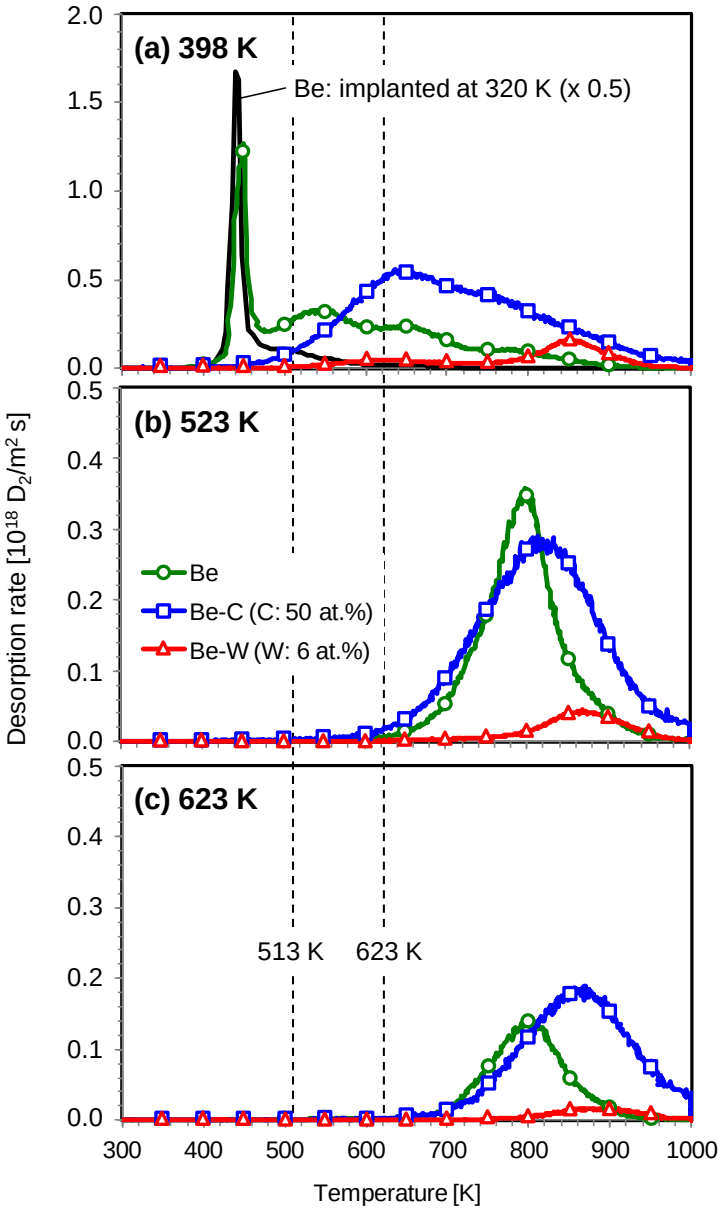

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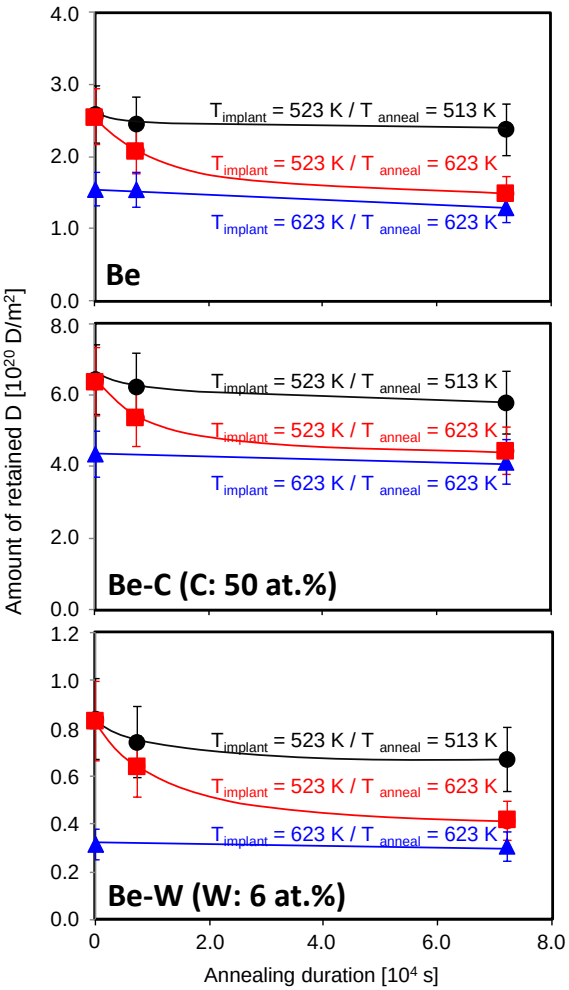

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