Consequences of Deuterium Retention and Release from Be-containing Mixed Materials for ITER Tritium Inventory Control

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Abstract. In order to assess the tritium removal procedure currently suggested for ITER (wall baking at 513 K (240°C) for the main chamber, and 623 K (350°C) for the divertor), deuterium (D) retention and release behaviour of beryllium (Be) containing materials are investigated. In pure Be, D is predominantly released around 470 K with a relatively sharp desorption peak. Mixing of tungsten (W) or carbon (C) into Be changes the D desorption behaviour causing less efficient D removal by the baking procedure. Especially, high C concentrations in Be affect the D release behaviour significantly and prevents removal of the retained D by baking at 623 K. As a consequence, the baking operation in ITER would work for tritium removal from the first wall and Be-rich deposited layers formed at low temperature areas, while it does not work for C-rich co-deposited layers and/or plasma-facing surfaces heated above 623 K during a discharge.

1. Introduction

Since the current design of ITER plasma-facing components consists of different armour materials depending on the operational requirements - i.e. beryllium (Be) for the first wall material, tungsten (W) as divertor armour and carbon fibre composite for the area around the strike points [1] -, interaction of those wall materials with the plasma obviously leads to the formation of mixed material layers as seen in some of current machines - for example, in JET [2,3]. Material mixing can change fuel retention properties of the plasma-facing wall as well as its thermo-mechanical properties, which influences the hydrogen recycling on the plasma-facing surface and the tritium inventory in the vacuum vessel. In ITER, for safety reasons, periodic tritium removal will be required before the in-vessel tritium inventory reaches its administrative limit [4], meaning that control of tritium inventory strongly affects the ITER operation program after the launch of Deuterium-Tritium burning phase.

We need, therefore, to develop some reasonable tritium removal methodologies in parallel with reliable estimation of in-vessel tritium inventory build-up. 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 as a tritium removal operation in ITER [5]. In order to assess the efficiency of tritium removal by such wall baking, it is necessary to know the hydrogen release behaviour from not only the pure materials but also mixed materials, especially, Be-related mixed materials because Be forms the majority of the ITER plasma-facing material (~ 690 m^2, i.e. ~ 80 % of plasma-facing area). In this study, from these viewpoints, the thermal deuterium release behaviour from Be-containing mixed materials was investigated under controlled laboratory conditions, and the efficiency of the baking procedure is discussed for the conditions in ITER.

2. Experimental procedure

2.1. Sample preparation

Be-containing mixed samples with two different concepts were prepared. The first concept is the compound layers of Be with W or C, the second is preparation of mixed layer by means of simultaneous deposition of Be with W or C.

Compound layers were fabricated by thermally treating the different material combinations of film-substrate samples. The detailed procedure is as follows: The surface of polycrystalline Be with 99.4 % purity (provided by Goodfellow Co. Ltd.) was covered by C or W film produced by magnetron sputter deposition with the thickness of 200-300 nm. After film deposition, samples were annealed at a certain temperature and duration (773K / 3hrs for C on Be sample, 1073 K / 10 hrs for W on Be sample) under a pressure of ~10-8 mbar based on previous studies [6,7]. The resulting samples stoichiometrically showed the formation of Be_2C with ~ 900 nm thickness in the case of C on Be system and $Be_{12}W$ with ~ 2 μm in the case of W on Be system, which was confirmed by Rutherford Backscattering Spectroscopy (RBS). The details of these procedures are summarized in ref. [8].

Beryllium-related depositions were done by means of Thermionic Vacuum Arc (TVA) deposition method [9] in MEdC. TVA setup has been upgraded recently allowing simultaneous Be-W or Be-C deposition using different target anodes, and succeeded in fabricating Be-W or Be-C layers with varying the Be/W or Be/C ratios [10,11]. Note that no thermal treatment was done for those Be/W or Be/C simultaneous deposited layers. Each prepared layer was also subsequently analyzed by RBS to check its thickness and composition.

2.2. Deuterium ion implantation and post mortem 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 fluences were up to $\sim 4 \times 10^{23}$ D/m^2 with a flux of $\sim 3 \times 10^{19}$ D/m^{2}s (note that the particle fluence to the ITER first wall is expected to be order of 10^{23} /m^2 after only single 400 s discharge). The incident angle was normal to the target surface, and the implantation temperature was varied from room temperature to 570 K.

After the implantation, the D release behaviour of each sample was measured by thermal desorption spectroscopy (TDS) in the Thermal Effusion Spectroscopy Setup (TESS) [12] in IPP-Garching except for samples using bulk Be substrates which were analyzed in the PISCES facility in the University of California at San Diego. The temperature ramp rates were very similar for both cases, i.e. ≈ 0.25 K/s in TESS and ≈ 0.29 K/s in PISCES. For some of these samples, TDS was done with a specific temperature ramp program, i.e. the temperature was ramped up to 623 K, and held 20 min. at 623 K, and then further ramped up to the final temperature, in order to simulate and assess the D release during the ITER wall baking scenario. The amount of D retained in the sample was also cross-checked by nuclear reaction analysis using the D(^{3}He, p)^{4}He nuclear reaction before TDS.

3. Results

Figure 1 shows D_2 desorption spectra from pure Be and Be-containing mixed layers after the implantation with a fluence of 10^{23} D/m^2 at room temperature. In the case of pure Be, the dominant fraction of retained D is released around 430-470 K in a rather sharp desorption peak which has been commonly observed as the predominant D desorption stage also in Be-D co-deposited layers [13] and D-implanted single/polycrystalline bulk Be with the fluences above 10^{21} D/m^2 [14-16]. Although the trapping states of D released at this low-temperature stage are not yet completely understood, a possible explanation is that D is trapped as in an unstable amorphous Be:D state in the structurally-modified region due to the supersaturation of the matrix and cavities formed by defect aggregation in the supersaturated region [15-17]. There is also a small desorption shoulder at 500-600 K, which agrees well with the decomposition temperature of Beryllium deuteride [18]. In the case of Be_2C, the TDS spectrum shows a similar desorption peak around 420-470 K, but its intensity is lower than that of pure Be. In addition, a broad desorption feature appears in the range from 650 to 900 K. Such a D desorption pattern in the high-temperature range is always observed in D ion implanted carbon materials. Spectroscopic studies have suggested that hydrogen release in the range from 600 to 1000 K is due to the decomposition of the *sp*^{3}-CH group [19,20]. This result implies that D implanted into Be_2C was eventually retained with either Be-related trapping (mostly released below 500 K) or C-D bond formation (released above 600 K). The D desorption pattern of $Be_{12}W$ has also the primary peak starting from around 430K. However, it shows a qualitative change, i.e. its intensity is much lower and the peak itself becomes broader compared to the case of pure Be. The discontinuous profile at 623 K seen in Be and Be_2C samples is due to the 20 min. hold at this temperature.

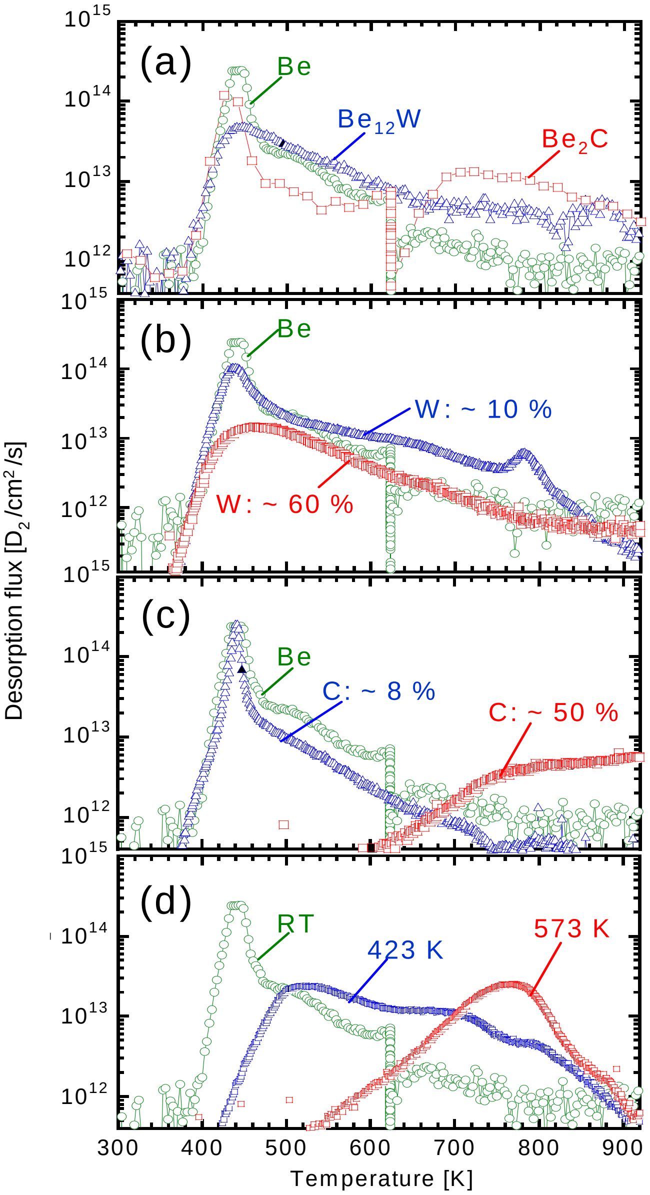

FIG. 1. Thermal desorption spectra of D from: (a) Be and compounds ($Be_{12}W$ and Be_2C), (b) Be and Be-W mixed deposited layers (W concentrations of ~10 % and ~60 %), (c) Be and Be-C mixed deposited layers (C concentrations of ~ 8 % and ~ 50 %), and (d) Be implanted at different temperatures (RT, 423 K and 573K). For pure Be and Be_2C samples the temperature was hold 20 min. at 623 K (see text and Fig. 2). D implantation to samples in (a), (b) and (c) was done at room temperature.

Figure 2 shows the TD spectra of these samples as a function of operational time. The desorption flux exponentially drops down (with a time constant of roughly 125 s) after the stop of the temperature ramp, and it reaches the background level within about 400 s. The amount of released D during the 20 min. hold is only 5-10 % of initially retained.

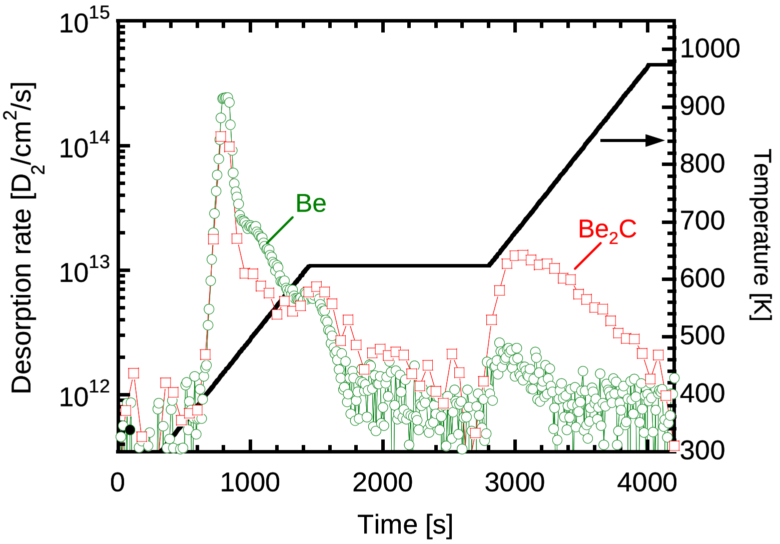

FIG. 2. Thermal desorption spectra of D from Be and Be2C samples under the temperature programmed heating with 20 min. hold at 623 K (350 C). D implantation to those samples was done at room temperature.

Figure 1 (b) and (c) show D desorption behaviour from Be-W and Be-C layers deposited simultaneously. One can discern that the D desorption behaviour obviously changes due to the mixing of W or C into Be. Already a 10 at.% fraction of W in Be broadens substantially the primary release peak. With an increase of the W concentration up to ≈ 60 at.%, this peak broadens further, while the retained amount becomes much less. The influence of C in Be on D release behaviour is even more significant. While ≈ 8 at.% of C still does not bring considerable change, in the case of C concentration of 50 at.%, the desorption peak in the low temperature stage totally disappears, and the desorption above 550 K becomes dominant. This result indicates that D in C-rich Be-C mixed layer is predominantly trapped in C-related trapping sites. More detail about D retention in Be-W and Be-C simultaneous deposited layers is available elsewhere [10,11].

D release behaviour from Be layers after the implantation at different temperatures is summarized in Fig.1 (d). By increasing the implantation temperature up to 423 K, the primary peak in the low temperature stage decreases significantly while the minor peak at 500-600K slightly increases. At the implantation temperature of 573 K, D release up to 520 K is suppressed while it shows pronounced D desorption around 700-800K. It can be assumed that an increase of the implantation temperature sets off chemical surface modifications, which can enhance the D trapping as the hydride or hydroxide phase.

4. Discussion

Fig. 3 shows the remaining fraction of initially retained D in each sample as a function of desorption temperature, which is derived from TDS results. Because of the dominant desorption peak observed at low temperatures, the remaining fractions start dropping at temperatures around 420 K. Roughly 90 % of initially retained D is released at 623 K in the case of pure Be whereas the desorption efficiency decreases by mixing of W or C into Be. Especially, as mentioned in the previous section, almost no D is released from C-rich Be-C deposited layer (C/Be ≈ 1) until temperatures of 650 K. For implantation temperatures higher than desorption temperatures no retention of D can be expected. Therefore, D retained during implantation at 573 K starts being released only at 623 K as shown in Fig. 3 (c).

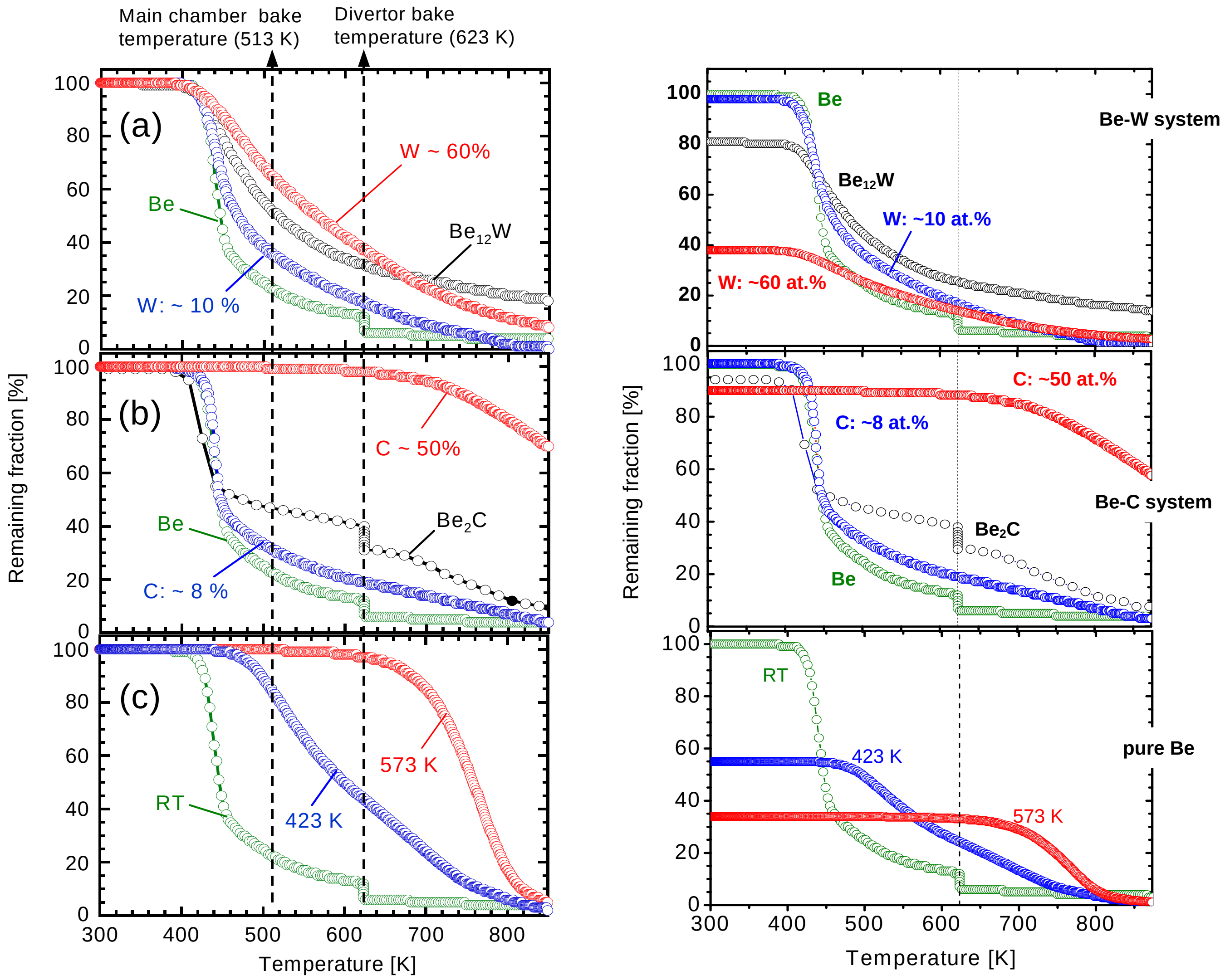

FIG. 3. Left panel: Remaining fraction of D normalized to the content after implantation in each sample as function of desorption temperature of (a) Be-W system, (b) Be-C system and (c) Be implanted at different temperatures (RT, 423 K and 573 K).
Right panel: the same data normalized to the D content after implantation in pure Be

For the appraisement of the success of thermal outgassing the normalization of the D content to the case of pure Be at room temperature is more important. For Be mixtures and compounds, already at room temperature the retained D can be reduced and implantation at elevated temperatures also tend to reduce the retention. Therefore, in the right panel of Fig. 3 the same data are shown after normalization to the content in pure Be implanted at room temperature. Now it becomes clear that increasing the amount of intermixed W into Be at room temperature decreases the retention of D. After outgassing to 623 K the remaining content is very similar for Be and W, while most D is retained in $Be_{12}W$. For implantation of D in pure Be the best results are actually obtained after room temperature implantation, while implantation at elevated temperatures increases the remaining fraction at outgassing temperatures above 450 K.

Based on the results given above, the performance expected for the ITER wall baking scenario can be discussed as follows:

- Best performance of the wall baking would be expected for tritium removal from high purity Be layers deposited on the main chamber wall -under the assumption that the temperature of main chamber wall surface is not so high (expected to be ~ 430 K)-.

- The efficiency of tritium removal will be limited for compounds and Be-W / Be-C simultaneously deposited layers as summarized in Fig 4. Especially, mixing of C into Be results in a significant change of hydrogen desorption behaviour. In the case of C-rich Be-C deposition, hydrogen is difficult to remove by a baking at 623 K even though the deposition is formed under low temperature conditions. For such cases, we have to consider the application of other removal methods like laser / flash heating, oxygen discharge etc.
- It is clear that tritium cannot be removed from plasma-facing surfaces where the temperature rises above 623 K during a discharge. Even for an implantation temperature of 423 K, only about 50 % is released at 623 K. On the other hand, it can be expected that the amount of primary tritium retention decreases with the surface temperature rise as shown in ref. [21]

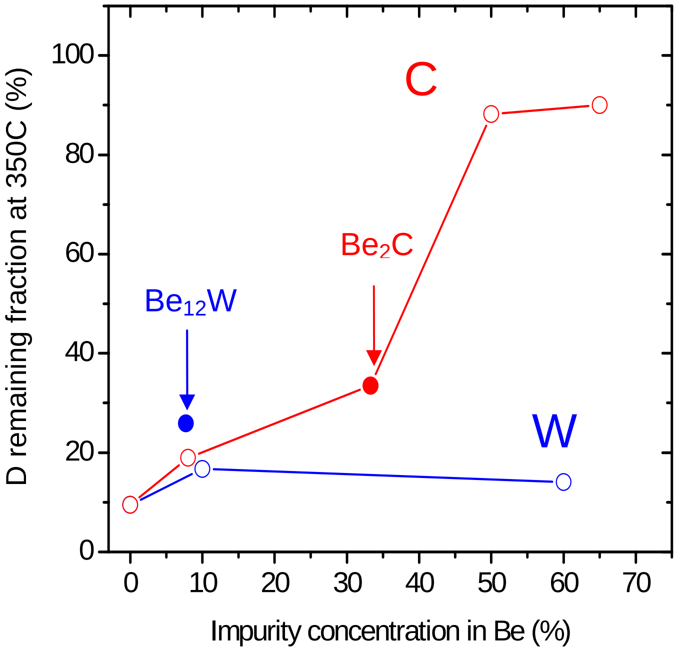

FIG. 4. D remaining fraction after outgassing at 623 K for 20 mins in Be-containing samples as a function of each impurity (W or C) concentration in Be. The data are normalised to the retention in pure Be

5. Conclusion

In order to assess the tritium removal operation currently suggested for ITER, (wall baking at 513 K (240 °C) for the main chamber, and 623 K (350 °C) for the divertor), deuterium (D) retention and release behaviour of Beryllium (Be)-containing materials are investigated.

In pure Be, D is predominantly released around 420-470 K within a relatively sharp desorption peak. Operation at elevated temperatures reduces the retained D, but the remaining D is less efficiently outgassed at 623 K. Mixing of tungsten (W) or carbon (C) in Be changes the D release behaviour resulting in less efficient D removal by the baking procedure. Especially, C concentration in Be affects D release behaviour significantly causing it to become difficult to remove by baking at 623 K.

As a consequence, the baking operation in ITER would work well for tritium removal from the first wall where Be-rich deposited layers are expected to form in low temperature areas (< 423 K). Low operation temperatures are preferable and require the lowest outgassing temperatures. Under these conditions outgassing temperatures of 500 K may be sufficient. Mixed material deposition is expected to occur mainly in the divertor. Be-W mixtures release about 70% of the retained hydrogen at 623 K related to pure Be co-deposits. Outgassing does not work efficiently for C-rich co-deposited layers or plasma-facing surfaces heated above

623 K during a discharge. An exchange of the divertor cassettes as foreseen several times during ITER operation may alleviate this problem.

Further measurements should extend the present investigations to thicker deposited layer (μm rather than nm), which requires a proper simulation of D co-deposition during film deposition. More temperature steps and longer temperature holding times (hours rather than mins) will make the extrapolation to ITER more reliable.

7. Acknowledgement

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