

# Investigation of deuterium retention in/desorption from beryllium-containing mixed layers



K. Sugiyama<sup>a,\*</sup>, C. Porosnicu<sup>b</sup>, W. Jacob<sup>a</sup>, I. Jecu<sup>b</sup>, C.P. Lungu<sup>b</sup>

<sup>a</sup> Max-Planck-Institut für Plasmaphysik, D-85748 Garching, Germany

<sup>b</sup> National Institute for Laser, Plasma and Radiation Physics, 077125 Bucharest, Romania

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## ABSTRACT

This article reports experimental results regarding the deuterium (D) retention and release characteristics of beryllium-containing mixed material layers. The main aim is an assessment of the efficiency of the tritium removal procedure currently suggested for ITER, i.e., wall baking at 513 K (240 °C) for the main chamber walls and 623 K (350 °C) for the divertor.

It is observed that the tritium retention as well as the removal efficiency by a following baking procedure will strongly depend on the composition of the deposited layer and the wall temperature during plasma operation. In the case that D is implanted at moderate temperatures (300 to 400 K), which would correspond to the “cool divertor” scenario in ITER, a large fraction of retained D is trapped in states having a low D binding energy and correspondingly low release temperature. Therefore, in this case baking can release a significant amount of retained D. On the other hand, if D is implanted at temperatures above 520 K, which would correspond to the “hot divertor” scenario in ITER, the amount of retained D will be significantly lower, but the retained D is predominantly trapped in high-energy binding states. In such a case, even baking at 623 K might not efficiently remove the retained tritium.

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## 1. Introduction

ITER plasma-facing components consist of different armour materials: the first wall of the main chamber will be covered with beryllium (Be), and a full tungsten (W) divertor is presently foreseen [1]. The interaction of these wall materials with the plasma can result in the formation of Be-W mixed material layer. Furthermore, typical impurities in vacuum, e.g. carbon (C), oxygen (O) etc., can be also incorporated in redeposited layers. Fuel retention properties of the plasma-facing surfaces can be modified by such material mixing and finally affecting the in-vessel tritium inventory. The safety regulation of ITER defines that the amount of tritium in the vacuum vessel is to be kept below the regulatory limit of 1 kg [2], which requires proper removal procedures before the in-vessel tritium inventory reaches the regulatory limit value. In ITER a wall baking procedure with technically accessible temperatures of 513 K (240 °C) for the main chamber and 623 K (350 °C) for the divertor is considered as a baseline procedure for tritium removal [2,3]. In order to be able to assess the tritium inventory in wall materials as well as the efficiency of tritium removal by the foreseen wall baking procedures it is necessary to

know the hydrogen retention/release behaviour not only of the pure materials, but also of mixed materials.

Fuel retention/release characteristics in W-/C-related mixed materials have been studied in various laboratories [4–7], whereas studies with Be-containing materials are still rather limited mainly due to the difficulties to handle Be as a toxic material. However, since Be covers the majority of ITER's plasma-facing surface, Be and Be-containing mixed materials will most probably play an important role for the fuel retention in ITER as recently seen in JET with the ITER-Like Wall configuration [8–10]. From this viewpoint, we have investigated deuterium (D) retention in and release from Be-containing mixed material layers under controlled laboratory conditions [11,12]. This article summarizes our experimental results regarding deuterium retention in and release from Be-containing mixed material layers, and discusses possible scenarios regarding tritium retention and removal in ITER.

## 2. Experimental procedures

### 2.1. Sample preparation and characterization

Be-containing layers were prepared by the Thermionic Vacuum Arc (TVA) deposition method [13]. The TVA setup is equipped with

\* Corresponding author. Tel.: +49 089 3299 1492; fax: +49 089 3299 1212.

E-mail address: [kazuyoshi.sugiyama@ipp.mpg.de](mailto:kazuyoshi.sugiyama@ipp.mpg.de) (K. Sugiyama).

multiple (up to 3) independent deposition target sources allowing the simultaneous deposition of Be and other admixed elements [14]. For preparation of the films used for this study, one deposition source was operated with Be and the other source with either W or C. The TVA plasma produces metallic ions as well as neutral atoms. The generated ions are deposited on the negatively-biased substrates on the substrate stage located at a distance of about 30 cm from the targets. There is also a minor contribution of neutral atoms which reach the substrate in direct line of sight. Overall the typical deposition rate is several nanometer/minutes. The layer composition is controlled by adjusting the electrical operation parameters for each target. The substrate holder was not actively cooled, resulting in a temperature rise of the substrates during deposition to the range of 340–425 K due to the ion bombardment and radiation from the heated targets. We have also prepared some Be/O mixed layers by depositing Be layers under controlled oxygen atmosphere. One of those Be/O layer with higher O concentration, which consists of ~ 50 at.% of O coinciding with stoichiometric composition of Be-oxide, was not very stable at elevated temperatures (the layer partially cracked). Therefore, this layer was only used for low-temperature experiments.

Silicon was mainly used as substrate (with the dimension of 15 mm × 12 mm) because of the ease of preparation and compatibility with experiments at elevated temperatures. For each deposition batch in the TVA setup several graphite substrates were coated together with the silicon substrates. These layers on the carbon substrates were only used for the subsequent layer characterization by ion beam analyses because they allow a better quantification of the layer stoichiometry compared with the silicon substrates.

After deposition, the prepared sample sets were characterized by Rutherford backscattering spectrometry (RBS) which provides quantitative information about the layer areal density and composition. For the RBS measurement,  $^4\text{He}^+$  with 2.0 MeV was used as the probe beam, and the backscattered particles were detected by a detector located at a laboratory angle of 165°. Each obtained RBS spectrum was then analyzed using the SIMNRA program [15] to determine the areal density and composition. The obtained layer compositions are summarized in Table 1. Although no direct thickness measurement was performed due to the limited Be handling capability, the thickness was estimated to be in the range of 300–600 nm by taking theoretical densities of Be and Be-related compounds into account.

## 2.2. Deuterium loading

Mixed-material layers were irradiated by a D ion beam in the High Current Ion Source [16] setup HSQ at IPP-Garching.  $\text{D}_3^+$  ions were extracted with 3600 eV from the ion source and decelerated with 3000 eV in front of the sample resulting in an ion energy of 600 eV. This corresponds to energy of 200 eV per impinging D. The typical D flux in HSQ is about  $10^{19}$  D m $^{-2}$ s $^{-1}$  and the applied implantation fluence was  $1 \times 10^{23}$  Dm $^{-2}$  for all samples. The incident angle was normal to the target surface. We focus here on the retention/release of samples D-loaded at elevated temperatures because the tempera-

ture on the ITER wall is expected to be higher than room temperature. Therefore, the sample was heated during D irradiation by radiation from a heater located behind the sample. The irradiation temperatures chosen for this study were 398 K (125 °C), 523 K (250 °C) and 623 K (350 °C). For comparison samples were also loaded at 320 K which is the lowest accessible temperature in HSQ. The sample temperature was monitored by a K-type thermocouple that was in contact with the sample surface. Since the irradiation chamber was kept in ultra-high vacuum condition with the background pressure being in the range of  $10^{-7}$ – $10^{-6}$  Pa, significant oxidation of the layer during heating or irradiation would be not expected.

## 2.3. Post-irradiation analyses

After D irradiation, the amount of retained D was measured by nuclear reaction analysis (NRA) using the  $\text{D}(^3\text{He}, \text{p})^4\text{He}$  reaction. The energy of the perpendicularly impinging  $^3\text{He}^+$  beam was set to 800 keV. With this  $^3\text{He}^+$  energy the measurable information depth for D in Be is roughly 2  $\mu\text{m}$ , meaning that it is sufficient to measure the total D amount in submicron thick layers used in this study. The high energy protons produced from the  $\text{D}(^3\text{He}, \text{p})^4\text{He}$  nuclear reaction were counted using a thick, large angle surface barrier detector at a scattering angle of 135° with the solid angle of 29.9 msr. The D concentration profile (at depths < 300 nm) was determined by measuring the energy of the alpha particles generated from the nuclear reaction. The emitted alphas were detected by a detector located at the laboratory scattering angle of 102° with the solid angle of 9.16 msr. The alpha spectra were transformed into D depth profiles using the SIMNRA program [15]. The depth resolution for determination of the D depth profile was calculated using RESOLNRA [17]. For our experimental conditions the depth resolution at the surface is  $3 \times 10^{21}$  at./m $^2$  corresponding to about 25 nm in Be. The D amount in the sample was quantified using the cross section published by Alimov et al. [18].

The D release behaviour from each sample was measured by temperature-programmed desorption spectroscopy (TPD) in the quartz tube of the TESS device. A basic description of TESS is given in [19]. The temperature response of the samples to the linear oven temperature ramp was calibrated in independent experiments by a thermocouple fixed to an uncoated silicon substrate of identical size. D-containing gases, such as HD, D $_2$ , heavy water, and hydrocarbons, released during heating were analyzed by a quadrupole mass spectrometer (QMS). For the quantitative analysis the QMS signals for H $_2$  and D $_2$  were calibrated using a calibrated leak, and the calibration factor for HD was assumed to be intermediate between those of H $_2$  and D $_2$ . D desorption determined by TPD provides information about D trapping and the corresponding release temperatures. For each sample type and applied irradiation temperature, a “normal” TPD run was performed as a reference. For this normal TPD run the sample was heated up to 1000 K with a temperature ramp rate of about 0.25 K/s.

Other samples were analyzed by TPD with a specific temperature program, i.e., the temperature was ramped up to either 513 or 623 K, which are the suggested baking temperatures for the first wall and the divertor in ITER, respectively, and held at these temperatures for durations of 2 and 20 hours, in order to assess the D release during the long term baking foreseen in ITER. These temperature-holding experiments were performed mostly for samples D implanted at 523 K, and for some samples implanted at 623 K.

## 3. Result and discussion

### 3.1. Deuterium retention characteristics

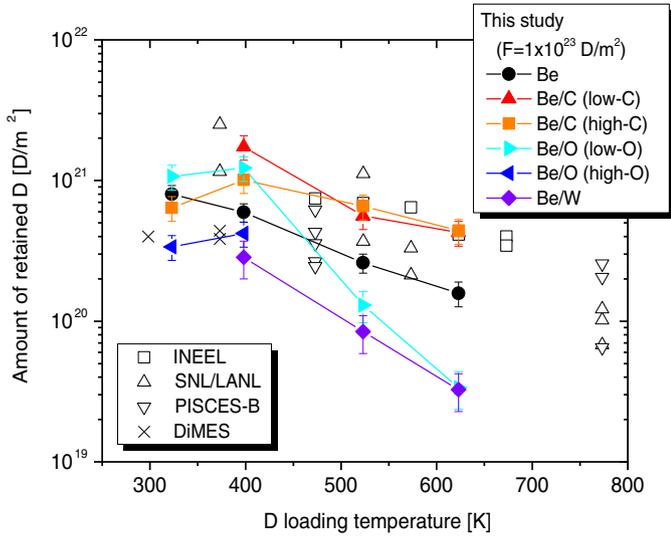
Fig. 1 shows the total retained D amount in the different investigated layers after a D loading fluence of  $1 \times 10^{23}$  D/m $^2$  as a

**Table 1**

List of prepared layers and summary of the layer characterization results. The stoichiometry and areal density were determined by RBS.

Layer type	Layer areal density	Layer stoichiometry
Be	$6.9 \times 10^{18}$ at./cm $^2$	(O impurity $\leq 1$ at.%)
Be/W	$4.3 \times 10^{18}$ at./cm $^2$	W: $6 \pm 2$ at.% (O: $\sim 10$ at.%)
Be/C (low C)	$6.2 \times 10^{18}$ at./cm $^2$	C: $13 \pm 1$ at.% (O: $\sim 7$ at.%)
Be/C (high C)	$4.6 \times 10^{18}$ at./cm $^2$	C: $50 \pm 1$ at.% (O: $\sim$ at.%)
Be/O (low O)	$4.1 \times 10^{18}$ at./cm $^2$	O: $\sim 6 \pm 1$ at.%
Be/O (high O) <sup>a</sup>	$2.6 \times 10^{18}$ at./cm $^2$	O: $\sim 50 \pm 1$ at.%

<sup>a</sup> The Be/O layer with high O concentration was used only for low-temperature experiments since the layer delaminated at higher temperatures (see text).

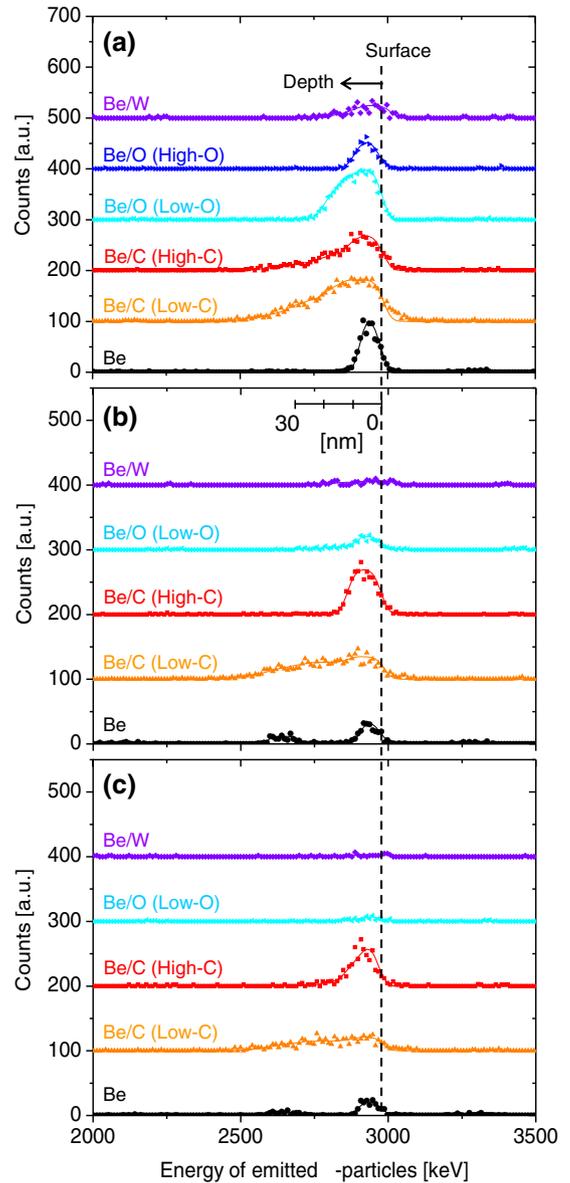


**Fig. 1.** Amount of retained D in different Be-containing mixed material layers after a D fluence of  $1 \times 10^{23} \text{ D/m}^2$  as a function of D loading temperature. Literature data of pure Be after plasma exposure obtained at INEEL [20], SNL/LANL-TPE [22], PISCES-B [23] and DiMES [24] are additionally shown for comparison.

function of D loading temperature. For pure Be, it is commonly observed that D retention saturates at fluences above about  $10^{22} \text{ D/m}^2$  [20,21], which is well below the present fluence. For the other mixed materials the fluence dependence are presently not known. The measured D amounts in the different investigated materials do not change significantly between 320 and 400 K. At 400 K the material with the highest retained D amount is Be/C with  $2 \times 10^{21} \text{ D/m}^2$ , the lowest is found for Be/W with about  $3 \times 10^{20} \text{ D/m}^2$ . Be/O with low O concentration shows slightly higher D retention than pure Be, indicating that some fraction of O impurity can enhance the fuel retention in this temperature range. For higher implantation temperatures the retained D amounts decrease monotonically with increasing irradiation temperature. Compared with the other samples the temperature dependence of D retention in Be/C mixed layers is very weak. In Fig. 1, some literature data [20,22–24] on D retention in pure Be are plotted together with the present result. The data scatter somewhat likely due to the difference of experimental conditions. Nevertheless, the total D retention in Be is, in general, consistent with the present result.

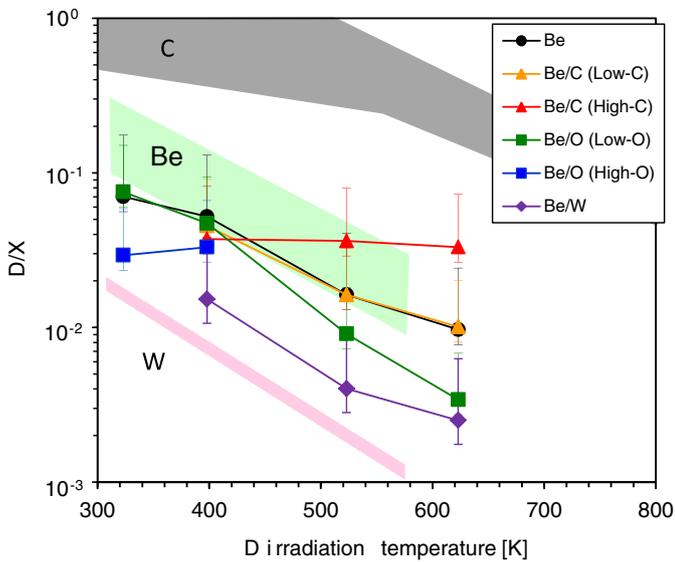
At elevated temperatures, D retention in the bulk due to diffusion might be an additional issue to be considered. Fig. 2 shows energy spectra of the alpha particles produced in the nuclear reaction for each layer after D irradiation. The alpha energy spectra correspond roughly to the depth profiles of the D concentration in the near surface layer. For most cases, D is retained in the near surface region (up to  $1.5 \times 10^{22} \text{ at./m}^2 \approx 120 \text{ nm}$  in Be). This is true even for elevated temperatures, except for Be/C with low-C concentration layer which shows relatively deep diffusion tails. The reason is not very clear, but it might be due to the structure of this Be/C layer.

Fitting the simulated profile to the experimental  $\alpha$ -spectrum using the SIMNRA program [15], as indicated with solid lines in Fig. 2, yields the quantitative near-surface D depth profile. From the depth profiles, we can also determine the maximum D concentration in each layer. As mentioned, D retention in Be tends to saturate for D fluences larger than  $10^{22} \text{ D/m}^2$ , and a similar saturation behaviour has been also observed for C (graphite) [25]. In this respect, although the fluence dependences for the mixed materials are presently not known, it is fair to assume that the D surface concentration in the present layers reaches saturation after  $10^{23} \text{ D/m}^2$ . Assuming that the measured maximum D concentration corresponds to the D saturation concentration at the used irradiation temperature we can plot the



**Fig. 2.** Energy spectra of the alpha particles from NRA after D irradiation at (a) 398 K, (b) 523 K and (c) 623 K. The high energy edge at about 3000 keV corresponds to alpha particles created at the surface as indicated by the dashed line in the figure. Alpha particles generated in larger depth appear at lower energies. In first approximation the peak shape corresponds to the D depth profile in the near surface region. The data points are the experimental data and the solid lines are the SIMNRA fitting results which yield the quantitative D depth profiles (not shown).

temperature dependence of the saturation concentration as shown in Fig. 3. In the figure such obtained maximum D concentrations are summarized as  $D/X$  ( $X$  = fraction of other materials). The data has relatively large error margin because of experimental uncertainties and the limited depth resolution of our NRA measurement. The calculated ion range of 200 eV D in Be is roughly 9 nm including straggling. This corresponds to only about 1/3 of the NRA depth resolution. If we assume that D does not diffuse substantially under the conditions of our experiment and remains where it was implanted then the real D concentration in this much thinner layer would be higher by roughly a factor of 3. The D concentration determined by NRA has, therefore, to be considered as a lower limit of the real concentration. The upper error margin of the error bars in Fig. 3 is derived taking the D ion range and NRA depth resolution into consideration.  $D/X$  values in both Be/O and Be/W layers are lower than those in pure Be,

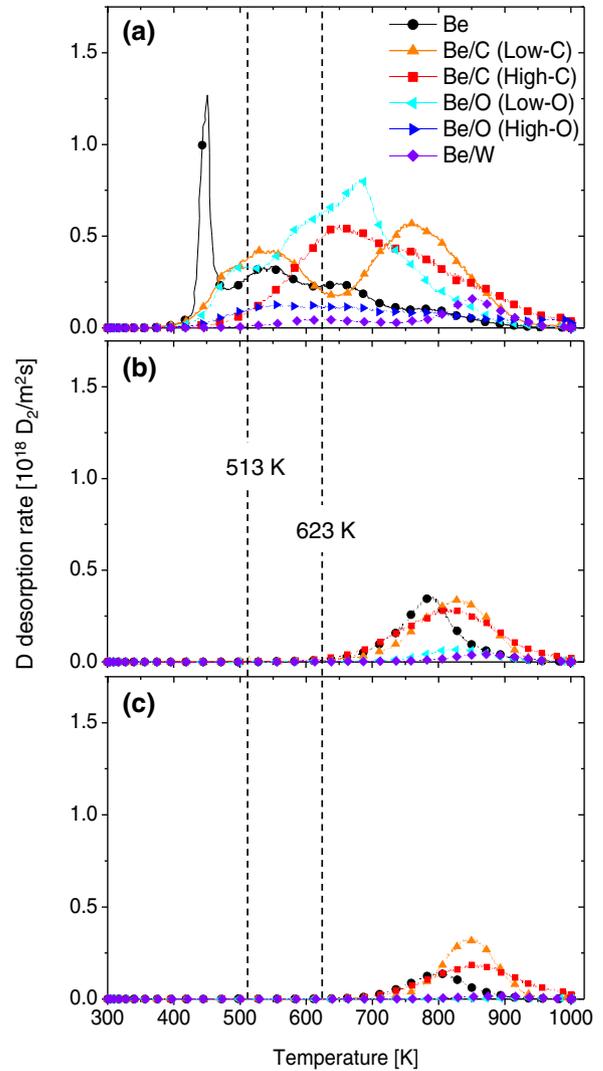


**Fig. 3.** Maximum D concentration ( $D/X$ ) in various Be-containing mixed material layers determined from the NRA  $\alpha$ -spectra as a function of D implantation temperature. The areas labelled as C, Be or W indicate results from a data compilation of experimentally-obtained  $D/X$  values for the D concentration in co-deposited layers [26].

indicating that a small fraction of those impurities can reduce the D saturation concentration in Be. The Be/C with low-C concentration layer shows quite similar result to pure Be although apparent D retention is relatively large due to the deep diffusion, while the Be/C with high-C concentration layer has rather high  $D/X$  even at high temperatures. This can be attributed to the strong chemical bonding of hydrogen to carbon. C-H chemical bonds, which are the reason for the high co-deposition with carbon, are quite stable in this temperature range [26]. Fig. 3 shows additionally an experimentally-obtained database on D concentration in “co-deposition” with ITER-relevant materials compiled by Doerner et al. [27]. Since D incorporation in co-deposition layers strongly depends on the deposition conditions, the  $D/X$  varies in some range, e.g., the D/C ratio in the so-called “hard a-C:D layer” is normally around 0.4, while that in “soft a-C:D layer” exceeds 1. The present results are obtained not by co-deposition but by D ion implantation, nevertheless, they show a relatively reasonable agreement with the data obtained for co-deposited layers.

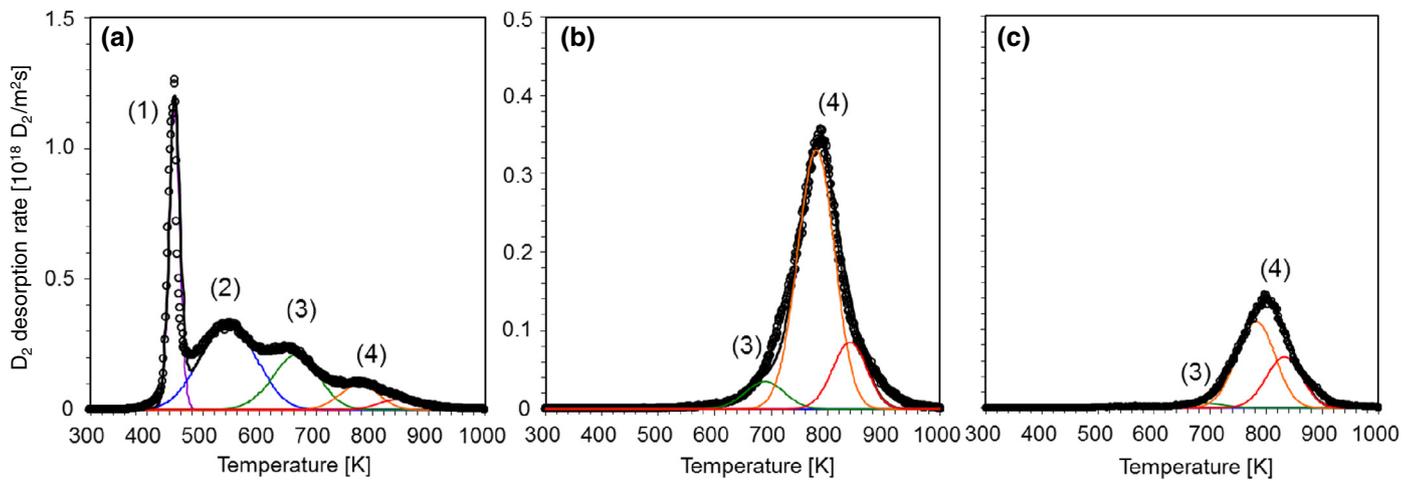
### 3.2. Deuterium desorption characteristics

D in the layers can be thermally released as hydrogen molecules (HD and  $D_2$ ) or possibly as other species such as heavy water ( $D_2O$  or HDO) or hydrocarbons. In the present study, it was observed that D was mostly released as HD or  $D_2$  and signals of heavy water or hydrocarbons were very small for Be-rich layers (pure Be, Be/W, Be/O with low O and Be/C with low C). On the other hand, signals of heavy water or hydrocarbons increased for Be/O with high O or Be/C with high C layers, respectively (quantification of those species is difficult due to their sticking to the chamber walls). In any case, the desorbed D amounts determined by summing up the HD and  $D_2$  TPD release peaks generally showed good agreement with those determined by NRA measurements before and after TPD (cf. Section 3.3 and Fig. 9). Therefore, it is reasonable to assume that the dominant fraction of retained D is released as HD or  $D_2$  even for Be/O with high O or Be/C with high C fraction. Fig. 4 shows the  $D_2$  desorption spectra obtained from the normal TPD procedure. In general, D desorption below the implantation temperature is quite low or negligible. In the case of the pure Be layer, the desorption profile consists of 5–6 different desorption peaks. In previous studies, the following trapping states for D in

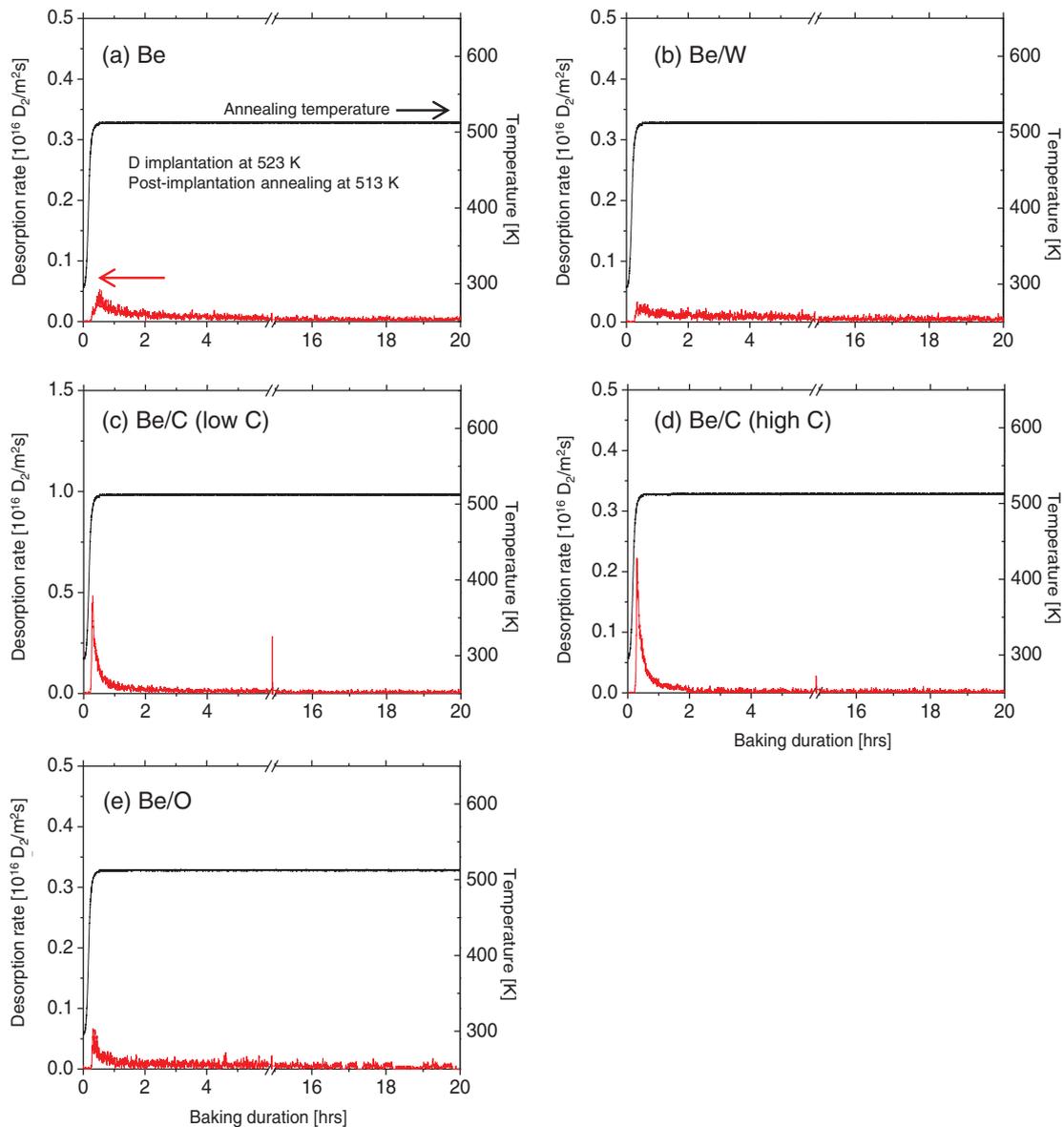


**Fig. 4.**  $D_2$  desorption spectra from various mixed layers after D irradiation at (a) 398 K, (b) 523 K and (c) 623 K. The temperature ramp rate was 0.25 K/s. Dashed lines labelled as “513 K” and “623 K” indicate the ITER wall baking temperatures for the main chamber and the divertor, respectively.

Be have been suggested: (1) supersaturated a-Be:D state in the implanted region with the release temperature of 450–500 K [28,29], (2) Beryllium-hydride ( $BeD_2$ ) which decomposes at around 550 K [30,31], (3) Be-O related trap, likely as Beryllium-hydroxide, with the release temperature of 670–700 K [21] and (4) implantation-induced defects (there are at least 2 types of defects) with the release temperature range of 750–900 K [29] (individual release temperatures vary somewhat depending on the experimental conditions for the TPD analysis, e.g., 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 as shown in Fig. 5. It is generally observed [12,29] that the amount of D desorption from states (2) and (3) increases, compared to implantation at about 300 K, for D implantation at moderate temperatures (higher than RT, up to about 500 K). This indicates that the formation of Be-hydride/-hydroxide can be enhanced at slightly elevated temperatures. For implantation at 523 K (Fig. 5b), both the 550–570 K and 670–700 K desorption features became depopulated, meaning that the D trapping in states (2) (hydride formation) and (3) (hydroxide formation) is significantly reduced. On the other hand, the high temperature peaks (4) increase roughly by a factor of 3 compared to the case of implantation at 398 K, which indicates the trapping in defects can be enhanced at this temperature. In



**Fig. 5.** D<sub>2</sub> desorption profiles from Be implanted at (a) 398 K, (b) 523 K and (c) 623 K. Note that the desorption rate is shown on a linear scale. Open circles are the experimental data and the solid lines are fits by Gaussian functions. The profile consists of different desorption peaks. The number attributed to each peak corresponds to the different D trapping states described in the text.



**Fig. 6.** D<sub>2</sub> desorption from samples D-irradiated at 523 K during the isothermal annealing at 513 K (240 °C). The temperature program consists of a linear ramp up to 513 K with a heating rate of 0.25 K/s followed by isothermal annealing at 513 K for 20 h. Note that the scale of desorption rate for (c) is different from the others.

this context we would like to add the remark that the contribution of this implantation-induced defect to the D retention could be significantly lower for Be-D co-deposition if the uptake of D is dominated by low-energy D species.

The NRA results (Fig. 1) show that D retention in the Be/W layer is lower than in Be. In agreement with those results, the TPD spectra also show a significant reduction of the desorbed D amounts. It appears that low W fractions in Be can somewhat reduce the formation of D trapping states in Be. On the other hand, O impurities slightly increase the D retention in O-related traps, which is clearly confirmed by the increase of the 670–700 K desorption peak in the Be/O layer implanted at 398 K. This also leads to a slight increase of the total retention compared to pure Be at this temperature. The Be/O layer with high O concentration shows a continuous desorption up to high temperatures without a distinct peak structure (see Fig. 4(a)). The measured D desorption agrees qualitatively with desorption from Be-oxide [32].

In Be/C layers, it is expected that D is predominantly bonded to carbon. C-H chemical bonds are generally quite stable with binding energies in the range of 3–4 eV, which requires D de-trapping temperatures above 600 K. As anticipated, the Be/C layers show the highest desorption rates at release temperatures higher than about 700 K. In particular the Be/C layer with high C concentration releases D up to 1000 K. This high temperature release in Be/C layers is attributed to C-related bonds.

TPD spectra measured after loading at 513 and 623 K shown no desorption for release temperatures below the implantation temperature. In general, the total released amounts are lower than for implantation at 398 K which is in agreement with the NRA results. It is interesting to note that for pure Be the amount of D retained in the high temperature release peaks is higher than for the sample implanted at 398 K (see also Fig. 5b and c). A more detailed comparison of total D amounts measured by NRA and TPD is presented further below.

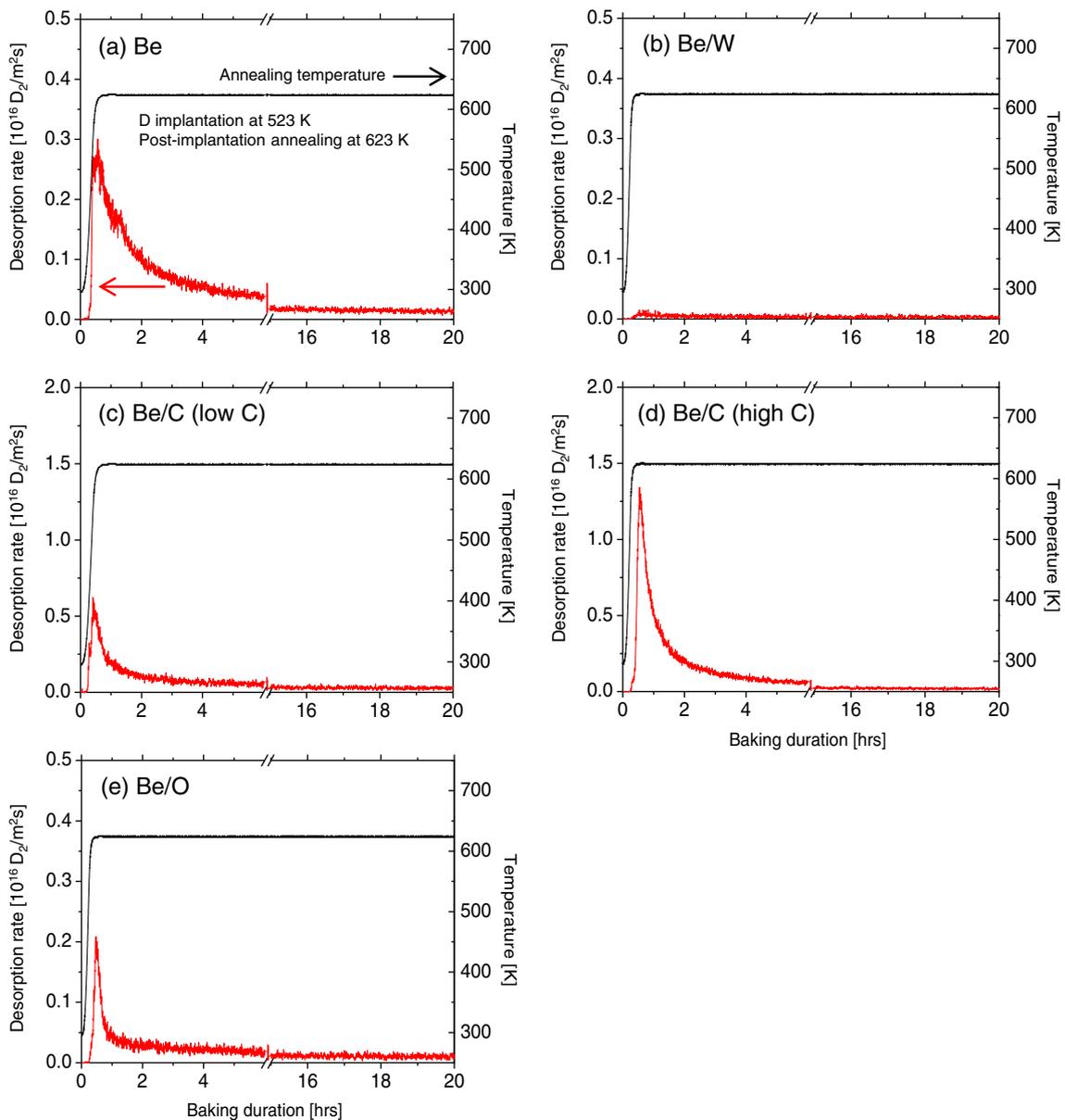
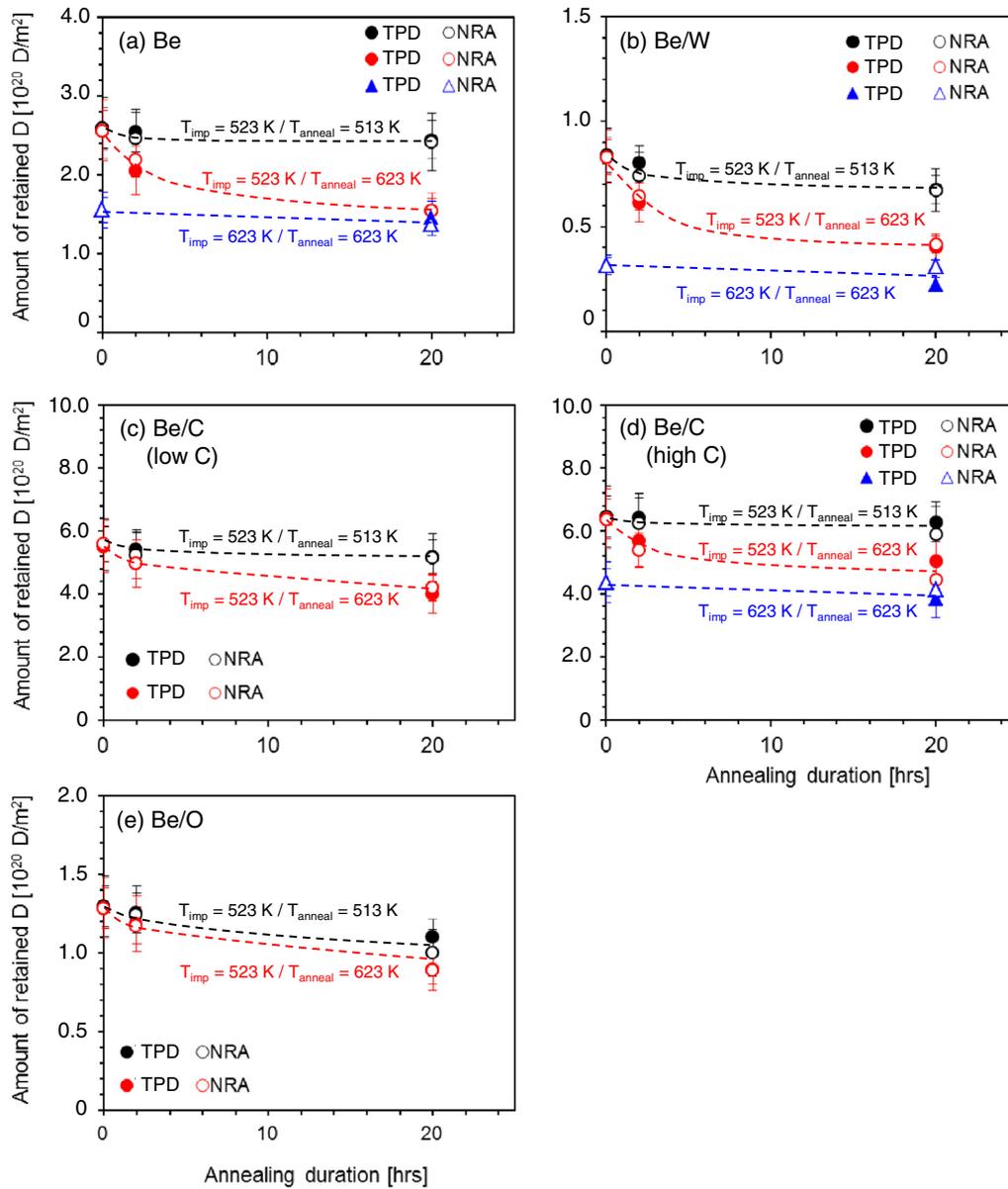


Fig. 7.  $D_2$  desorption from samples D-irradiated at 523 K during the isothermal annealing at 623 K (350 °C). The temperature program consist of a linear ramp up to 623 K with a heating rate of 0.25 K/s followed by isothermal annealing at 623 K for 20 h. Note that the scale of desorption rate for Be/C samples is different from the others.



**Fig. 8.** Reduction of retained D amount by annealing at 513 and 623 K determined by TPD and NRA results. Here, “ $T_{\text{imp}}$ ” and “ $T_{\text{anneal}}$ ” indicate the D irradiation and annealing temperatures, respectively.

### 3.3. Deuterium release during isothermal annealing

Fig. 6 shows D desorption from samples implanted at 523 K during the isothermal annealing at 513 K (240 °C). For all samples, the D desorption rate slightly increased during the temperature ramp ( $\approx 0.25$  K/s), and dropped down as soon as the temperature reached 513 K. D desorption continued during the temperature holding at 523 K, but the desorption rate is quite low and close to the QMS detection limit. Increasing the annealing temperature to 623 K (350 °C) leads to a higher D release during the temperature ramp as shown in Fig. 7. For this case, the desorption rate during the holding phase was also slightly higher than that during the 513 K holding.

D desorption from samples implanted at 623 K and annealed at 623 K (not shown) exhibits a very similar behaviour as the samples implanted at 523 K and post-annealed at 513 K. During the temperature ramp up the D desorption rate slightly increases then dropping

to a more or less constant rate with very low level during the holding phase.

In Fig. 8, the reduction of the retained D amount by annealing at 513 and 623 K is summarized. In this figure, the value labelled as “TPD” means the amount calculated from the TPD results by integration of the HD and D<sub>2</sub> release rates over time. Plotted in the figure is the initial D amount measured with a normal TPD run up to 1000 K minus the integral over the TPD release rate for the corresponding spectra measured during isothermal annealing. The retained D after annealing was also cross-checked by NRA; this is labelled as “NRA”. As seen in the figure, the TPD and NRA results show in most cases good agreement. Because the desorption rate during the isothermal annealing was close to the QMS detection limit, the TPD values could be afflicted with a relatively large uncertainty. In these cases the NRA data are considered more reliable.

As expected, the released D amount is very small if the annealing temperature is equal to or smaller than the implantation

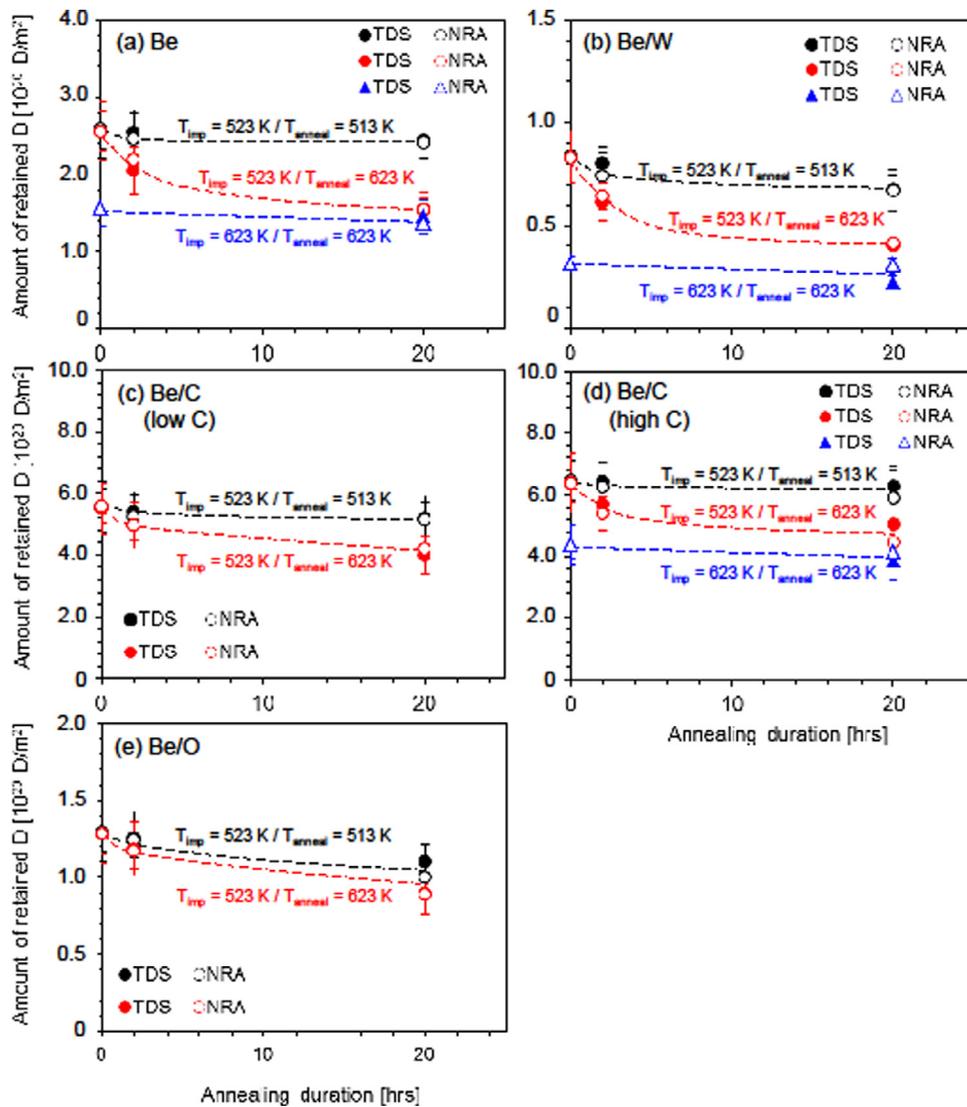


Fig. 9. Reduction of retained D amount by annealing at 513 and 623 K determined by TPD and NRA results. Here, “ $T_{\text{imp}}$ ” and “ $T_{\text{anneal}}$ ” indicate the D irradiation and annealing temperatures, respectively.

temperature. This can be seen in both “ $T_{\text{imp}} = 523 \text{ K} / T_{\text{anneal}} = 513 \text{ K}$ ” and “ $T_{\text{imp}} = 623 \text{ K} / T_{\text{anneal}} = 623 \text{ K}$ ” cases. On the other hand, the result for “ $T_{\text{imp}} = 523 \text{ K} / T_{\text{anneal}} = 623 \text{ K}$ ” shows a reasonable reduction of the retained D amount by the long-term annealing. This reduction is in agreement with what we anticipate from the TPD experiments, i.e., the remaining D amount after annealing at 623 K is comparable to that after D implantation at 623 K. This means the removal efficiency of isothermal annealing/baking will strongly depend on the implantation temperature. If the wall temperature during the plasma operation is already higher than the subsequent baking temperature (513 K or 623 K), one cannot expect high tritium removal efficiency by the wall baking procedure.

Another important parameter for ITER wall baking will be the baking duration. Based on the results in this study using D-implanted layers, the difference between annealing for 2 h and 20 h is not significant, however in this case it has to be kept in mind that the D implanted layer is relatively thin. A recent investigation by Baldwin et al. showed that longer annealing enhances the D release from thick Be-D co-deposited layers [33]. In such thicker co-deposited layer, it requires more time for D retained deep in the layer to diffuse towards the surface due to the retardation of diffusion due to detrapping and retrapping processes. In this respect, it is also necessary to assess the D release behaviour from thicker Be-containing mixed layer.

#### 4. Summary and consequences for ITER baking operation

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 – D retention in and release from beryllium-containing mixed material layers were investigated, particularly, with focusing on the following issues:

- D retention and release with respect to the dependence on D irradiation temperature
- D release behaviour during long-term (up to 20 h) isothermal annealing at 513 and 623 K.

For most of the investigated mixed-material layers we found no indication of significant diffusion into the bulk during implantation at 398, 523, and 623 K (Fig. 2). The maximum D concentrations of all investigated mixed-material systems estimated from the NRA depth profiles agree reasonably with published values (Fig. 3). The D concentrations decreased with the D irradiation temperature in most cases, except for the Be/C layer with high C concentration which showed a more or less constant D/X value over the investigated temperature range. This result suggests that C-D chemical bonding becomes a dominant D trapping process in layers with high carbon concentration.

TPD analysis showed that D retention in the investigated Be layers is in good agreement with previous studies. D trapping natures in Be/W- and Be/O-mixed layers are quite similar to those observed in pure Be. Admixture of some fraction of O can slightly increase the retention at low to moderate temperatures, likely due to increase of D trapping by O-related traps, e.g. hydroxide formation. At elevated temperatures, D retention in Be/W- and Be/O-mixed materials is lower than in pure Be. However, carbon incorporation in Be seems to be critical. Carbon can introduce additional C-related binding sites, which require relatively high temperatures (above 600 K) for the D release.

It is obvious from the present study that the fuel removal efficiency of a baking procedure will strongly depend on the wall temperature during the operation. In case that D is loaded at moderate temperatures (300 to 400 K), which would correspond to the “cool divertor” scenario in ITER, a large fraction of the retained D is trapped in states with low release temperatures. Preceding studies have attributed these binding states to supersaturated Be and Be-hydride [27,29]. In such cases, wall baking will remove fuel retained in these trapping states and the removed fraction due to annealing at 623 K can reach values of 90 % for pure Be implanted at 300 K [12]. On the other hand, if D is loaded at temperatures above 500 K, corresponding to the “hot divertor” scenario, the amount of D trapped in states with lower trapping energies is already significantly reduced and the retained D is dominantly trapped in the states with higher trapping energy or C-related traps as shown in present “normal TPD” results (Fig. 4). The D concentration for implantation at 520 K is roughly a factor of 5–10 lower than for implantation at 320 K. In this case, however, even baking at 623 K is not sufficient to remove tritium with high efficiency. It should be kept in mind that, as mentioned above, implantation at higher temperature will lead to significantly reduced total fuel retention (see Figs. 1, 3, and 4), except for C-rich co-deposited layer. From the viewpoint of absolute in-vessel tritium inventory, the hot-divertor scenario would be preferable because the retention under high-temperature implantation condition is roughly comparable to or even less than the retention under low-implantation-temperature condition after baking.

An additional remark to be considered would be the baking duration. In the present study, we prepared the D containing samples by D ion implantation, resulting in the D trapping mostly at the near-surface region. In such case, the D release rate drops quickly

after it reaches the final baking temperature. However, this time constant can change for much thicker Be-D (–O or –C) co-deposited layer due to the longer diffusion time. This needs to be assessed in future work.

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