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High temperature H and D behaviour in solid and liquid beryllium

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Abstract

We present the salient features and interpretations from a multi-technique study of the high temperature H isotope behaviour in Be, including liquid Be. The effects of the implantation of H or D ions in Be at 300 to 983 K as well as the effects of in situ annealing in the transmission electron microscope and annealing with a 30 ns laser pulse were investigated. Quantitative measurements of the gas release, ion-beam depth profiling, scanning electron and atomic force microscopy, and numerical modeling were used in the analysis. For H/Be $< 14\%$, the H trapping energy is 1.7 eV and diffusion out of the sample is effectively 10 times faster than anticipated from other work. The release is not connected with blister rupture. For H/Be $\geq 14\%$, the trapping energy is only 1.0–1.2 eV, but explosive release can take place under some circumstances. The implications for Be plasma facing components in tokamaks are discussed.

1. Introduction

Prediction of the recycling and tritium retention properties of Be as a plasma-facing material in future devices is not straightforward. The reported hydrogen (D,T) diffusivities differ by many orders of magnitude [1–3]. The solubilities are not much better known [1,4,5]. There is agreement that ion-implanted H is trapped with an activation energy of about 2 eV [6–9]. Nevertheless, extrapolation to reactor conditions is risky because it requires an understanding of the nature of the barrier to release, about which there is no consensus. It is also important to take into account the wide temperature excursions sustained by limiters or divertor plates in tokamaks; Be limiters have been known to melt on the surface. In this paper we present the salient features and interpretations from our multi-technique investigations of H isotope behaviour at high temperature in Be (PF-60 from Brush–Wellman); detailed aspects will appear elsewhere [10–13].

2. Approaches to high temperature simulation

Permeation experiments (e.g. Ref. [2]) are conducted at high temperature (T), but the achievable incident fluxes ($< 10^{16}$ ions/cm^{2}s) are much weaker than the particle fluxes on tokamak limiters and divertors (10^{18} cm^{-2}s^{-1}). Trapping energies are usually determined by low T implantation followed by thermal annealing. Because of the relatively slow anneal, diffusion is then not rate-limiting for desorption. Also, this does not simulate high T operation since the last causes defect annealing and H release *during* implantation. A factor to consider for realistic simulation is the steady state H concentration resulting from the competition between incident flux and release. For Be, a typical detrapping time at 1000 K would be 10 ms (with a 2 eV trap). With an incident flux of 10^{18} cm^{-2}s^{-1}, oversaturation (10^{16} Hcm^{-2} [14]) could be maintained in Be plasma-facing components during tokamak shots, even at high T. These conditions cannot be matched with ion beams.

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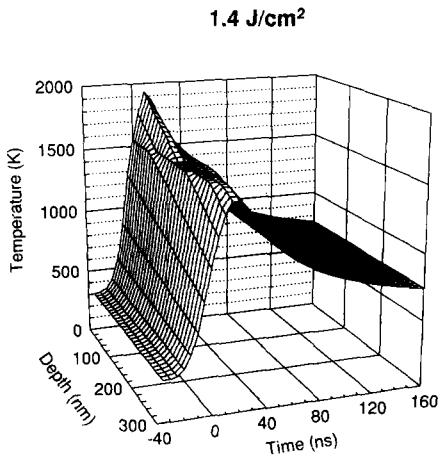

Fig. 1. Computed evolution of temperature profile in Be annealed by a 30 ns, 1.4 J/cm^2 ruby laser pulse. Note the plateau at the Be melting point of 1551 K.

An alternative approach is pulsed laser annealing (PLA) because it allows, if for a brief time, the coexistence of a very high mobile H concentration with a very high T. PLA was accomplished with a 30-ns ruby laser pulse. The usual procedure was to perform a "ramp" in which the same spot (2.5 mm^2) was subjected to increasingly powerful pulses until all the H isotopes, detected by a quadrupole mass analyser (QMA), were desorbed. Occasionally, the process was interrupted in view of further analysis of partly desorbed samples by other techniques. A finite difference code (DTRLAS) [15] is used to compute the evolution of the temperature profile. The code also does a kinetic calculation of H evolution (trapping and detrapping, diffusion, adsorption and desorption), according to a chosen model whose parameters can be varied to fit the data. Fig. 1 shows the evolution of T for a pulse with $E_{\mathrm{LASER}} = 1.4$ J/cm^2. A 140-nm-thick layer melts for 40 ns. The melting threshold at $E_{\mathrm{LASER}} = 1.1$ J/cm^2 was confirmed by scanning electron microscopy (SEM) observation. Unfortunately, the calculation is not correct in the liquid phase, because the liquid Be thermal conductivity is not known; based on other liquid metals [16], the error on $\mathrm{d}T/\mathrm{d}E_{\mathrm{LASER}}$ in the liquid phase is $\leq 40\%$.

3. Moderate concentrations

We define moderate doses (few at%) as giving bubbles but no blisters. Fig. 2 shows three sets of PLA data for D implanted in Be at 0.5, 1.5 and 5 keV, at the same average D/Be of 5%. The cumulative D desorbed (D_2 and some HD) by all preceding pulses, up to E_{LASER}, is plotted versus E_{LASER}. The curves are the best fits to the data with the code DTRLAS. Only the solid Be PLA results were used in fitting, but the curves are extrapolated in the liquid Be regime. The three sets were fitted with the same parameters, and so were other data (not shown) for D/Be of 2%, 9% and 11%. The desorption rate is limited at the same time by detrapping and diffusion, as we expected from the short time scale. On the other hand, a surface-limited process does not fit. This is confirmed by the D depth profiles obtained by elastic recoil detection (ERD) in partly desorbed samples: these profiles remain peaked, they do not flatten as expected from a surface barrier. The best fits for detrapping are an energy of 1.7 ± 0.2 eV with a pre-exponential of $(1.0 \pm 0.5) \times 10^{13}$ s^{-1} (assuming 1st order), or an energy of 1.7 ± 0.1 eV with a pre-exponential of $(1.5 \pm 0.5) \times 10^{-9}$ cm^{3}s^{-1} (2nd order). This trap energy is similar to those deduced by Wampler [6,7]. The diffusivity found is $D = (8 \pm 1) \times 10^{-4} \exp(-0.32 \pm 0.02\ \mathrm{eV}/kT)$ cm^{2}s^{-1}. Its pre-exponential factor is an order of magnitude larger that the largest value found in other work [2], while the activation energy is similar to that found therein, but larger than in Refs. [1,3]. The data are incompatible with the suppressed D permeation inferred by Wampler [6].

It is possible that D migration is somehow facilitated under our conditions. Electron microscopies were used to study this. A sample implanted at RT with 6 at% H/Be was mounted in the transmission electron microscope (TEM) and annealed in situ in steps of 100 K × 15 min, from 300 to 800 K. In Fig. 3, the unannealed sample (300 K) shows a high density of spots which have been identified as defect clusters. As T was raised, these transformed into dislocation segments

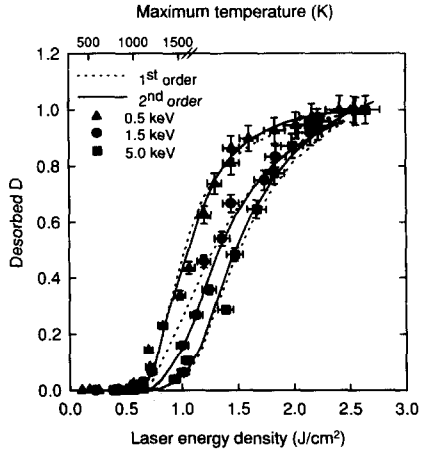

Fig. 2. Normalized cumulative D release from 3 samples implanted at RT with 5 at% D at different ion energies, as a function of the laser energy. The curves are model fits. The top abscissa shows the peak surface temperature reached during the anneal.

until, at 800 K, numerous dislocation lines were seen to terminate on grain boundaries (top right of bottom panel). These dislocations may provide channels for H migration to grain boundaries. This hypothesis appears to be confirmed by SEM of the surface topography. In samples implanted at high T to oversaturation (e.g. 773 K, 3×10^{17} D/cm^2 at 1.5 keV, saturation retention = 2×10^{16} cm^{-2} = 7 at% [14]), one observes scattered blisters remarkably aligned on the grain boundaries

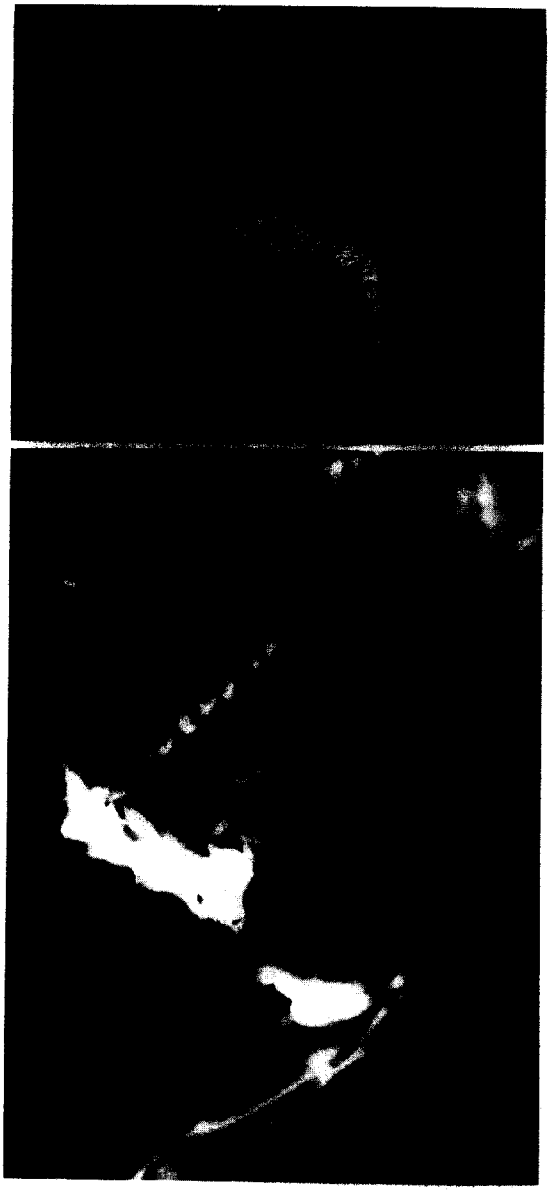

Fig. 3. Selected micrographs from an in situ anneal in the transmission electron microscope at temperatures up to 800 K. The sample had been implanted at RT with 2 keV H ions at H/Be = 6%.

Fig. 4. Scanning electron micrograph of a sample implanted at 773 K with 3×10^{17} 1.5-keV D ions/cm^2.

(Fig. 4). We are thus led to conclude that high T during implantation or annealing causes a preferential migration of detrapped H to grain boundaries, possibly along dislocation lines. A small fraction of that gas precipitates into blisters, while the major part desorbs into the intergranular interstices.

As we saw in Fig. 2, some of the D is released while the surface is liquid. There is no sharp break in the release curve when the surface melts and the same model curve reproduces the data. The DTRLAS simulations indicate that, at the melting temperature, D is strongly detrapped (mobile) and already has a high diffusivity of $\sim 10^{-4}$ cm^{2}s^{-1}. This may explain that melting does not change matters much despite the phase change.

4. High concentrations

For average D/Be $\geq 14\%$ (peak D/Be $\approx 30\%$), laser desorption occurs at quite lower E_{LASER} (i.e. T); for instance 50% release at $T_{\mathrm{PEAK}} = 1300$ K, compared with ~ 1800 K for D/Be = 11%. The high dose PLA data can be fitted by two models. The first is detrapping-limited (instantaneous migration) with two traps of 1.0 and 1.2 eV; the second is diffusion-limited with an activation energy of 0.18 eV. In the latter case, DTRLAS predicts substantially broadened profiles in partly desorbed samples. Fig. 5 shows a comparison of ERD measurements with the calculated profiles for two samples. While the experimental profiles are compatible with the detrapping model, they are not with the diffusion-limited model. Three more samples with varying doses and E_{LASER} were analysed. On average, the diffusion-limited model gives profiles that are twice as broad as the experimental ones, while the detrapping model agrees with experiment within 10%. The

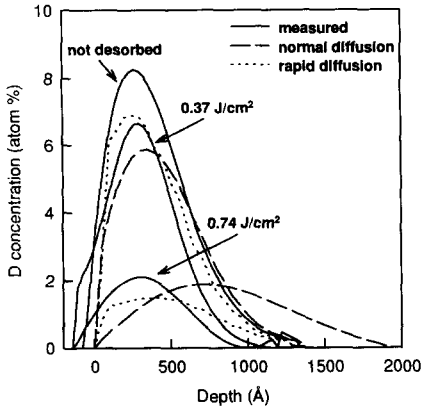

Fig. 5. Elastic recoil detection depth profiles after various stages for a sample implanted at RT with 1.1×10^{17} 1-keV D/cm^2: as implanted (not desorbed), after a single laser shot of 0.37 J/cm^2, and after a "ramp" (six shots) up to 0.74 J/cm^2. "Normal diffusion" refers to the diffusion-limited model, whereas "rapid diffusion" refers to the detrapping-limited case.

lower trapping energy at saturation suggests a change in the nature of trapping.

SEM of the samples before PLA shows abundant blistering but few punctured blisters. In situ annealing in the TEM showed the formation of bubbles at high T (or coalescence of small pre-existing bubbles that were invisible in our instrument). Half desorbed samples were studied by atomic force microscopy (AFM). Numerous deep craters varying in size from tens of nm's to μm's are seen in Fig. 6, so it is likely that some or all the gas was released from exploded blisters. In this case the transport modeling with DTRLAS has limited relevance. One should consider the increase in gas pressure and the weakening of the mechanical properties of Be at high T, in addition to transport and gas exchanges between bubbles and the solid matrix. 80% or more of the gas is released before melting. These PLA results are in sharp contrast with high T implantation which produced mostly unruptured blisters and non-explosive gas release – at least with our weak incident ion fluxes. As mentioned earlier, the intense particle fluxes on limiters or divertor plates may lead to oversaturation even at high T, with the concomittant possibility of blister explosion.

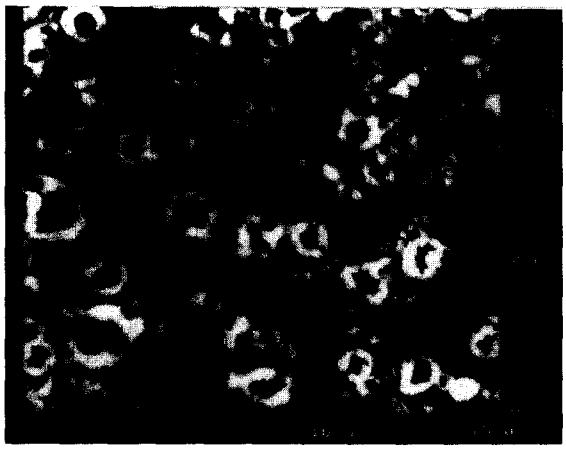

Fig. 6. Atomic force micrograph of a half-desorbed sample implanted at RT with 5-keV H ions at H/Be = 20 at%; a single laser shot was fired.

5. Conclusions

Pulsed laser annealing of Be implanted with H (D) at H/Be < 14% yields a value of 1.7 eV for the H trapping energy in Be, in good agreement with Wampler [6,7]. However, diffusive-like H release under PLA is enhanced by a factor of 10 or more compared with other data [1–3]. At D/Be ≥ 14%, the trapping energy is 1.0–1.2 eV, and "diffusion" essentially infinitely rapid. Desorption is never limited by a surface barrier (e.g. oxide). Evidence for a possible easy migration path along dislocations and between grain boundaries was found. It may help by recycling H isotopes more rapidly at high temperature and preventing blistering. Blisters are indeed not numerous and not punctured on samples implanted beyond saturation at 773 K and above. On the other hand, the unbroken blisters covering samples implanted at 300 K at high doses literally explode when subjected to PLA, releasing gas and solid material. It would be worthwhile to simulate disruptions in tokamaks on a realistic time-scale (ms) to see if this phenomenon can be a serious concern. Liquid Be does not appear to differ markedly from high temperature solid Be in its recycling properties. The results also raise the possibility that, due to the intense particle fluxes that impinge on limiters and divertor plates, an oversaturated concentration of H would be maintained even at high temperature, leading to blistering. Since it is known [17] that blistering is suppressed for shallow (i.e. low energy) implants, our results constitute yet another reason to reduce the plasma temperature in front of divertor plates.

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