

Deuterium absorption in reduced activation ferritic/martensitic steel F82H under exposure to D₂O vapor/water at room temperature

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Abstract

Eight samples of F82H ferritic/martensitic steel were irradiated at 300 K with 20 MeV W ions to the damage level of 0.54 displacements per atom at the damage peak. Three samples were afterwards annealed in vacuum at 423 K for 72 h and then at 373 K for 106 h. Three other samples were annealed in H₂ atmosphere at 100 kPa at the same annealing temperatures and durations. All samples were exposed at room temperature to D₂O vapor at the partial pressures in the range from 3 to 6 kPa for 365 to 1181 days. After termination of the D₂O vapor exposure, the surfaces of the samples were partly covered by small (≤ 1 mm in diameter) drops of D₂O water. Thus, the damaged samples were exposed to a mixture of D₂O vapor and water. Trapping of deuterium at the ion-induced defects in the damage zone was examined by the D(³He, p)⁴He nuclear reaction. It has been found that the W-ion-induced defects generated in the F82H samples are decorated by deuterium diffusing from the surface.

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Highlights

- F82H steel samples were irradiated at 300 K with 20 MeV W ions
- The damaged F82H samples were exposed at room temperature to D₂O vapor/water for 365 – 1181 days
- Deuterium was accumulated in the ion-induced damage zone

1. Introduction

Hydrogen has been and always will be a source of various problems within production, storage and application of steels because of its generally detrimental effects on processing characteristics and service performance of steel products. Just a few parts per million (ppm) of hydrogen dissolved in steel can cause hairline cracks (flakes), hydrogen embrittlement, hydrogen blistering and loss of tensile ductility, particularly in large steel castings ingots, blooms and slabs [1, 2]. Thus, the control of hydrogen content in steels products during storage in air is thought to be an important task.

Reduced Activation Ferritic/Martensitic (RAFM) steels are the primary candidate material for first wall and breeding blanket structural application in future fusion power plants [3, 4]. As probable blanket structural materials, RAFM steels will be exposed to gaseous tritium bred in a blanket under neutron irradiation [5]. A part of the tritium implanted from the plasma into the armor material will permeate to RAFM steels. Therefore, the evaluation of tritium retention in RAFM steels under neutron irradiation is an important issue for safety assessment of fusion reactors. It is conceivable that the tritium retention will be also affected by the amount of impurity protium accumulated in the steel bars during storage in air after steel fabrication.

The goal of this work was to reveal accumulation of hydrogen isotope in the RAFM steel F82H exposed to water vapor at room temperature by using deuterated water D_2O . Just to create a ‘reservoir’ to accumulate absorbed deuterium, the displacement damage was generated in the steel near-surface layer. It has been shown recently [6, 7] that in tungsten (W) and RAFM steels F82H and EUROFER97 beforehand irradiated with MeV-range heavy ions and then exposed to D_2 gas at elevated temperatures, the ion-induced defects become occupied with deuterium to a depth depending on the exposure time. Thus, it can be said with assurance that the W-ion-induced defects in RAFM steels serve as saturable strong traps¹ being filled by D atoms

¹Saturable traps are traps having finite capacity. Traps where D in solution becomes trapped when it encounters unoccupied traps are denoted as strong traps.

diffusing from the surface.

2. Experimental

The RAMF steel F82H (Japan) [8, 9] was used in this work. Rectangular-shape F82H steel samples, $10 \times 10 \text{ mm}^2$ in size and 1 mm in thickness, were cut from the same F82H slab followed by mechanical polishing to a high finish and cleaning in an ultrasonic bath.

To generate ion-induced defects, the F82H samples were irradiated with 20 MeV W ions at 300 K to a fluence of $8 \times 10^{17} \text{ W/m}^2$. To simulate the damage profile in the F82H sample, the damage profile in a pure iron (Fe) target was calculated for the same irradiation conditions using the program SRIM-2008.03 [10], ‘full cascade option’, with a displacement energy of $E_d = 40 \text{ eV}$. As a result, the sub-surface layer of the Fe target was damaged to 0.54 displacements per atom (dpa) at the damage peak situated at a depth of 1.8 μm .

In what follows the W-ion-irradiated F82H steel samples will be designated as “damaged” samples. The damaged samples were exposed to D_2O vapor after distributing over three sets:

(i) The samples ## 64 and 65 from the first set were exposed to D_2O vapor without any additional treatment. In what follows, for the sake of convenience, these samples will be indicated as F82H[dam].

(ii-iii) To remove residual protium from the damaged steel and to reveal an effect of the isotopic exchange under D_2O vapor exposure, the samples ## 1, 3, and 5 from the second set were annealed in vacuum (about $2 \times 10^{-5} \text{ Pa}$) at 423 K for 72 h and then at 373 K for 106 h (these samples will be indicated as F82H[dam+ann]). In turn, the samples ## 2, 4, and 6 from the third set were annealed in protium (H_2) atmosphere at a pressure of 100 kPa at temperature of 423 K for 72 h and then at temperature of 373 K for 106 h. As this took place, protium was trapped at defects in the damaged zone, as shown in Ref. [7] (these samples will be designated by F82H[dam+annH₂]). The heat treatment was chosen so that protium saturates all the traps in the

damage zone of the samples from the third set. Note that the temperature treatment was identical for all the samples from the second and third sets.

The damaged samples and an open plastic bottle with frozen deuterated water (D_2O , deuterium purity - 99.9 at.%) were placed in a small vacuum container, and after that the container was instantly evacuated and hermetically sealed. The container was kept at room temperature (RT), i.e., at temperatures in the range from 290 to 300 K, depending on the season. Thus, once the deuterated ice thawed, the damaged samples started to be exposed to D_2O vapor at a pressure in the range of 3 to 6 kPa, depending on the temperature of the container. The data on the temperature dependence of the D_2O vapor pressure were taken from [11, 12]. There is a need to note that after termination of the D_2O vapor exposure, the surfaces of the samples removed from the container were partly covered by small (≤ 1 mm in diameter) drops of D_2O water. Thus, it can be said that the damaged samples were exposed to a mixture of D_2O vapor and water.

After exposure to the D_2O vapor/water for certain time interval (365 – 1181 days, history of the F82H samples is given at the end of this Section), the deuterium depth profiles in the samples were determined by nuclear reaction analysis (NRA). An analyzing beam of 3He ions with energies varied from 0.69 to 4.0 MeV was used. The total 3He ion charge acquired on a spot of size 1×1 mm² was 10 μC for 0.69 MeV 3He ions and 5 μC for 3He ions at energies varied from 0.8 to 4.0 MeV.

The D concentration within the near-surface layer (at depths of up to about 0.1 μm) was measured by means of the $D(^3He, \alpha)H$ reaction at a 3He energy of 0.69 MeV. The α particles were energy-analyzed with a small-angle surface barrier detector at the laboratory scattering angle of 102°. The α spectrum was transformed into a D depth profile using the program SIMNRA [13].

To determine the D concentration up to a depth of 6.3 μm , protons arising from the $D(^3He, p)^4He$ nuclear reaction at 3He ion energies from 0.69 to 4.0 MeV were counted using a

wide-angle detector placed at a scattered angle of 135° . The program SIMNRA was used for the deconvolution of the measured proton yields. The D depth distribution was established by a sequence of layers with thicknesses equivalent to the depth resolution calculated using the code RESOLNRA [14]. A concentration of deuterium as a function of depth was assumed taking into account the near-surface D concentration profile obtained from the α particle spectrum, and the proton counts resulting from the assumed D depth profile was calculated for the different ^3He ion energies. The assumed D depth profile was iteratively adjusted until the calculated proton yield curve matched the experimentally measured proton yield data set [15].

It should be noted that the samples #65 and 64 were analyzed by NRA at different points on the surface, and positions of these points were marked.

History of the F82H samples is shown below. It should be noted that during storage of the samples in air between W ion irradiation (damaging) and D_2O vapor/water exposure, and between D_2O vapor/water exposure and NRA measurement, the samples were exposed to H_2O vapor. The partial pressure of the H_2O vapor could vary in the range of 0.4 to 1.5 kPa, depending on the temperature and the relative humidity [11].

Sample # 64: damaging + 29 days in air + 726 days of D_2O vapor/water exposure + 9 days in air + NRA (pos.# 1) + 13 days in air + 455 days of D_2O vapor/water exposure + 29 days in air + NRA (pos.# 2);

Sample # 65: damaging + 29 days in air + 365 days of D_2O vapor/water exposure + 8 days in air + NRA (pos.# 1) + 54 days in air + NRA (pos.## 2, 3) + 106 days in air (the sample was fixed on the NRA target holder) + NRA (pos.## 2, 3, 4);

Samples ## 1, 3, 5: damaging + 25 days in air + annealing in vacuum + 803 days of D_2O vapor/water exposure + 29 days in air + NRA;

Samples ## 2, 4, 6: damaging + 25 days in air + annealing in H_2 + 803 days of D_2O vapor/water exposure + 29 days in air + NRA.

3. Results and discussion

The deuterium depth profiles for the samples F82H[dam] ## 64 and 65 exposed to D₂O vapor/water at room temperature for 365, 726, and 1181 days are shown in Fig. 1. All profiles show a surface peak which probably comes from adsorbates on the surface. A thickness of the surface peaks cannot be resolved with the present technique but the amount of deuterium with the peaks can be determined to be in the range from 3.5×10^{18} to 1×10^{19} D/m². Beyond the surface a practically constant deuterium concentration extending to a depth of 2.7 μm is found. Note that the deuterium depth profiles coincide practically with the calculated damage profile (Fig. 1) indicating that the W-ion-induced defects are decorated by deuterium diffusing from the surface. The D concentration observed at a depth of the damage peak is different for the different samples and for different locations on one sample varies from 1×10^{-2} to 5×10^{-2} at.%. Note that values of the D concentration do not correlate both with the duration of exposure to the D₂O vapor/water (365 – 1181 days) and with the duration of following air storage before the NRA measurement (8 – 168 days). The significant variation in the D concentration measured at different points on the surface of the samples #64 and 65 is likely due to inhomogeneity in the exposure conditions – during exposure to D₂O vapor some surface areas were exposed to D₂O water.

The D depth profiles shown in Fig. 1 allow determination of the amount of deuterium accumulated in the samples F82H[dam] ## 65, 64 exposed to D₂O vapor/water for 365 – 1181 days. This amount is varied from 3.1×10^{19} to 1×10^{20} D/m², depending on a point of the NRA measurement on the sample surface. Assuming that the damage zone was saturated with deuterium at the exposure for 365 days, the minimal estimate of the D accumulation rate for the F82H steel averaged over the exposure time lies in the interval from 1×10^{12} to 3×10^{12} D/m²s.

After storage in air for 62 days, the sample F82H[dam] # 65 was analyzed by the NRA technique at two positions labeled # 2 and # 3, and as it was shown in Fig. 1, deuterium was accumulated on defects within the W-ion-induced damage zone, i.e., at depths of up to 2.7 μm.

The sample was fixed on the NRA target holder, and after storage in air for the next 106 days the position # 2 and # 3 were analyzed by the NRA technique again. The results are shown in Fig. 2. Deuterium was detected in this case far beyond the damage zone, at depths of up to 6.3 μm . In addition, D concentration in the W-ion-induced damage zone was slightly reduced. Note that in the course of the first NRA measurement with the analyzing ^3He ions having energies in the range from 0.69 to 4.0 MeV, displacement damage at depths of up to 8 μm was generated, as calculated with the use of the program SRIM-2008.03 [10] for Fe target. Obviously, over a period of time between the first and second NRA measurements (106 days), deuterium was redistributed between strong traps in the W-ion-induced damaged zone (0 – 2.7 μm) and strong traps created in the ^3He -ion-induced damage zone (0 – 8 μm). The ^3He -ion-induced damage profile calculated for Fe target is also shown in Fig. 2.

Deuterium depth profiles in the damaged and annealed samples F82H[dam+ann] and F82H[dam+annH₂] exposed to the D₂O vapor/water for 803 days are plotted in Fig. 3. In the samples F82H[dam+ann] (## 1, 3, and 5) the D concentration observed at depths of up to 2.0 μm varies from 1×10^{-3} to 3×10^{-3} at.% (Fig. 3a). However, in the samples F82H[dam+annH₂] (## 2, 4, and 6) the maximum D concentration (1×10^{-3} to 2×10^{-3} at.%) extends to a depth of 1.3 μm (Fig. 3b).

The significantly lower D concentration in the samples F82H[dam+ann] (Fig. 3a), as compared with the D concentration in the samples F82H[dam] (Fig. 1), allows the conclusion that concentration of the W-ion-induced defects responsible for accumulation of deuterium reduces by about tenfold in the course of annealing at 423 K for 72 h and then at 373 K for 106 h.

Recall that after damaging and following annealing in H₂ atmosphere, the F82H[dam+annH₂] samples contain protium trapped by the W-ion-induced defects located in the damage zone. According to results reported in Ref. [7], the H concentration in the damage zone is estimated to be $\geq 1 \times 10^{-3}$ at.%. Under following exposure of these F82H[dam+annH₂]

samples to the D₂O vapor/water, the defects, initially occupied with protium, accumulate deuterium practically up to the same D concentration (2×10^{-3} at.%, Fig. 3b) as in the F82H[dam+ann] samples ($1 \times 10^{-3} - 3 \times 10^{-3}$ at.%, Fig. 3a) Besides, recall again that maximum D concentration is observed at depths of up to 2.0 μm for the F82H[dam+ann] samples and at depths of up to 1.3 μm for the F82H[dam+annH₂] samples. Thus, it can be said with caution that under exposure of F82H samples, beforehand damaged and annealed in H₂ atmosphere, to the D₂O vapor/water at room temperature, a certain portion of the previously accumulated protium is presumed to be replaced by deuterium due to the isotopic exchange processes occurring at the ion-induced defects.

A comparison of D depth profiles shown in Figs 3a and 3b gives grounds to speculate that only 1.3 μm thick sub-surface layer within the damage zone in the F82H[dam+annH₂] sample was subjected to process of H/D isotopic exchange under exposure to the D₂O vapor/water for 803 days. Obviously, in the H-containing sample the front of the H/D isotopic exchange moves from the surface into the bulk slower than in the sample that does not contain hydrogen.

It may be suggested that during transportation and storage of the D-containing F82H samples in air at ambient temperature, process of the D/H isotopic exchange took also place. However, compared to the H/D exchange rate maintaining under exposure to the D₂O vapor/water, the rate of the D/H exchange process under storage in air is believed to be relatively low due to lower values of the H₂O partial pressure in air (0.4 – 1.5 kPa) and shorter time interval of keeping in air (8 – 168 days). Note that the damaged F82H samples were saturated with deuterium after exposure to a mixture of D₂O vapor and water at higher D₂O partial vapor pressure (3 – 6 kPa) for 365 days.

What are possible mechanisms of penetration of deuterium into the damage zone? The F82H steel contains about 8 wt.% chromium (Cr) [9]. It is known that that chromium reacts with oxygen and moisture in the environment to form a protective, adherent and coherent, oxide film on the steel surface. Unfortunately, we can't find anything written on composition and

structure of the oxide films formed on the F82H surface at room temperature. However, there are results on chemical composition, structure and thickness of surface oxide film formed on high chromium (about 10.6 wt.% Cr) martensitic steel MANET at ambient conditions [16]. This surface oxide film was analyzed by X-ray diffraction, Rutherford backscattering spectroscopy and nuclear reaction technique. It has been found that the structure of the total oxide film could be described by three layers in the following sequence starting from the steel surface: M_2O_3 (triclinic unit cell, about 4.5 nm thick), M_3O_4 (spinel, about 4.5 nm thick), M_2O_3 (cubic unit cell, about 3 nm thick), where M is a mixture mainly of Fe and Cr [16]. Thus, it may be suggested with caution that that the uppermost layer of the oxide film formed on the F82H steel surface before D_2O vapor/water exposure consists of the Fe_2O_3 and Cr_2O_3 oxides.

Under exposure to air at ambient conditions, iron oxide surfaces react readily with water and become partially covered with molecular H_2O and/or hydroxyl groups [17, 18]. Generally it is believed that molecular H_2O binds to oxide surfaces as a Lewis base to the ionic charge [19]. However, the detailed mechanism of dissociative adsorption is poorly understood because oxide surfaces vary dramatically in geometry and electronic structures.

Adsorption and dissociation of water on different oxygen- and iron-terminated α - Fe_2O_3 surfaces at monolayer coverage have been studied by density-functional theory calculations [19, 20]. It has been found that the activation energy barrier for water dissociation process,



is less than 0.3 eV on all terminations. Moreover, for certain oxygen- and iron-terminations the H_2O dissociation can occur even spontaneously, i.e., without any detectable barrier. This fact strongly suggests that the iron oxide near-surface layer can be easily hydrogenated under exposure to water vapor/water at room temperature.

Unfortunately, we could not find the published data on hydrogen absorption in chromium oxides under interaction with H_2O . Only the data on the absorption of hydrogen inside Cr_2O_3

crystals under exposure to H₂ gas at temperatures from 373 to 723 K were reported for the first time in Ref. [21]. The interaction of H₂ with Cr₂O₃ involves the occurrence of two processes, the chemisorption of H₂ on the surface and the diffusion of chemisorbed hydrogen inside the structure of the oxide. The molar heat of chemisorption of H₂ is ~310 kJ/mol. The molar heat of absorption of H₂ into subsurface layers is ~165 kJ/mol. Hydrogen was found to be chemisorbed in the form of water and absorbed into oxide volume in the form of coordination bound atoms. The results of the H₂ chemisorption measurements show unambiguously that at least part of chemisorbed hydrogen diffuses into subsurface layers [21].

It may be suggested schematically that accumulation of deuterium in the damage zone of the F82H samples exposed to D₂O vapor/water at room temperature is the result of dissociative adsorption of D₂O molecules on the oxide surfaces, penetration of D atoms into surface oxide layers with following diffusion into the F82H matrix, and trapping of the D atoms by defects generated in the damage zone due to irradiation with 20 MeV W ions.

4. Conclusions

The goal of this work was to reveal accumulation of deuterium in the RAFM steel F82H exposed to deuterated water (D₂O) vapor at room temperature. To create a ‘reservoir’ to accumulate absorbed deuterium, F82H samples were irradiated with 20 MeV W ions to the damage level of 0.54 dpa at the damage peak situated at a depth of 1.8 μm. To remove residual protium from the damaged steel and to reveal the possible effect of isotope exchange under D₂O vapor exposure, some samples were additionally annealed in vacuum at 423 K for 72 h and then at 373 K for 106 h, whereas some samples were annealed in H₂ atmosphere (100 kPa) at the same annealing temperatures and durations. All the samples were exposed at room temperature to D₂O vapor at a partial pressure in the range of 3 to 6 kPa for 365 – 1181 days. After termination of the D₂O vapor exposure, the surfaces of the samples were partly covered by small (≤ 1 mm in size) drops of D₂O water. Thus it can be assumed that the damaged samples

were exposed to D₂O vapor/water.

It has been found that the W-ion-induced defects created in the F82H samples are decorated by deuterium diffusing from the surface. For the damaged F82 samples not subject to the annealing, the maximum D concentration in the damage zone varies from 1×10^{-2} to 5×10^{-2} at.%. The minimum estimate of the D accumulation rate for the F82H steel exposed to D₂O vapor/water at room temperature lies in the interval from 1×10^{12} to 3×10^{12} D/m²s.

In the samples subjected after damaging to the annealing in vacuum and in H₂ atmosphere, the maximum D concentration in the damage zone is significantly lower, 1×10^{-3} – 3×10^{-3} at.%, due to reduction of the defect concentration under the annealing process. Under D₂O vapor/water exposure of the damaged F82H samples subjected to the annealing in H₂ atmosphere, a part of the previously accumulated protium is presumed to be replaced by deuterium due to isotopic exchange processes occurring on the ion-induced defects.

Accumulation of deuterium in the damage zone of the F82H samples exposed to D₂O vapor/water at room temperature is thought to be the result of dissociative adsorption of D₂O molecules on the oxide surfaces, penetration of D atoms into surface oxide layers with following diffusion into the F82H matrix, and trapping of the D atoms by the ion-induced defects.

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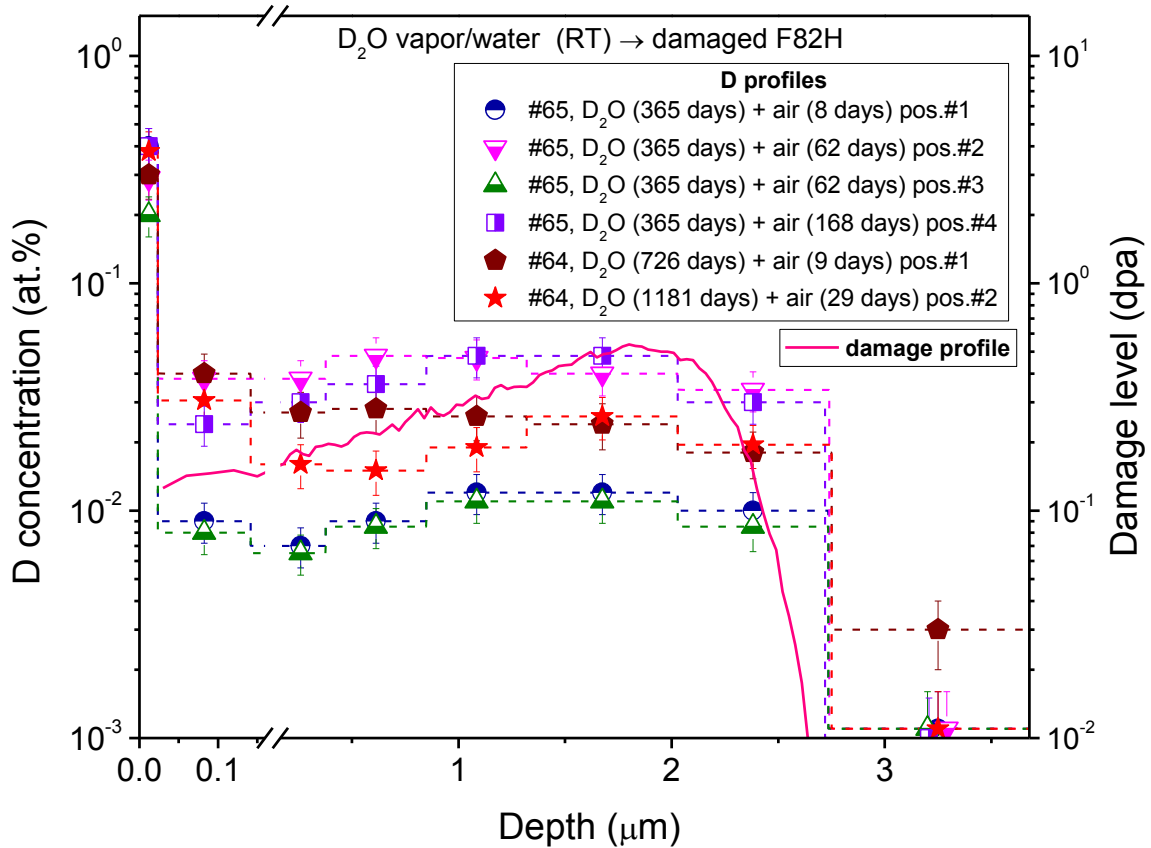


Figure 1. Depth profiles of deuterium retained in the damaged samples F82H[dam] ## 64 and 65 exposed to D₂O vapor/water at room temperature for 365, 725, and 1181 days. After the D₂O vapor/water exposures, the samples were kept in air and then analyzed by the NRA technique at different point positions on the surface. The duration of the D₂O vapor/water exposure and the duration of following air storage before the NRA measurement are indicated in the legend. In each of the eight layers used for the SIMNRA calculations, the D concentration is constant over the entire thickness of the layer. Damage profile calculated for Fe target with the use of the program SRIM-2008.03 [10] is plotted with the use of right ordinate axis.

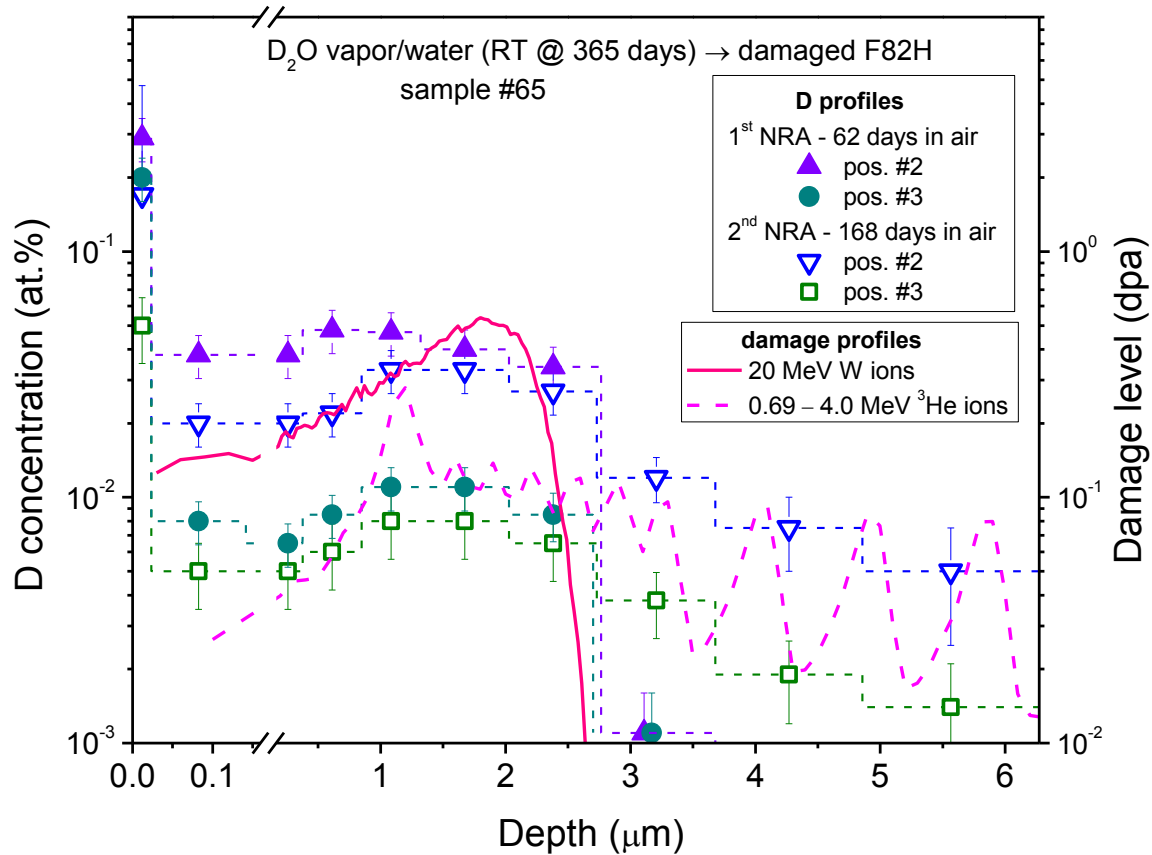


Figure 2. Depth profiles of deuterium retained in the damaged sample F82H[dam] # 65 exposed to D₂O vapor/water at room temperature for 365 and then measured by the NRA technique at the same point positions (#2 and #3) 62 and 168 days after storage in air. In each of the ten layers used for the SIMNRA calculations, the D concentration is constant over the entire thickness of the layer. Damage profiles calculated for Fe target with the use of the program SRIM-2008.03 [10] are plotted with the use of right ordinate axis. Note that during the first NRA measurement, the 0.69 – 4.0 MeV ³He-ion-induced defects were generated at depths of up to 8 μm.

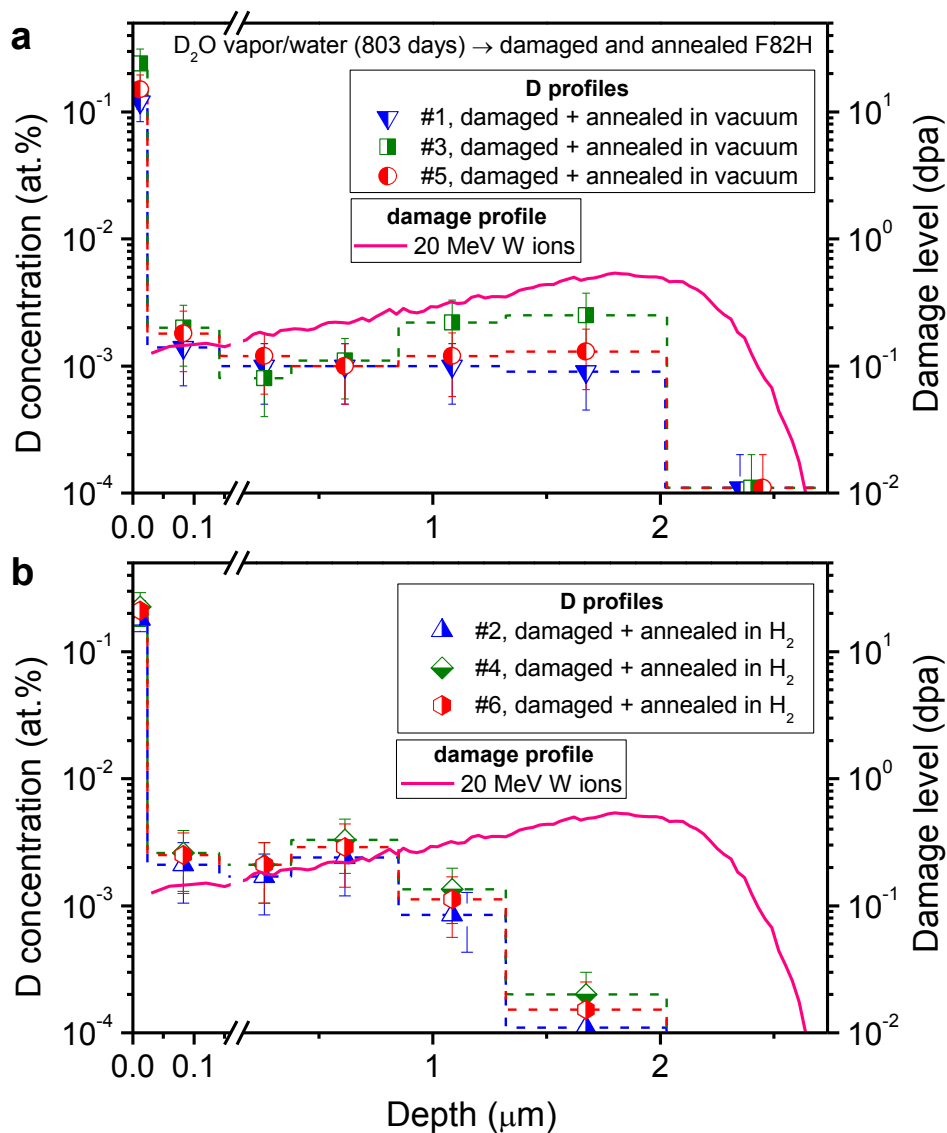


Figure 3. Depth profiles of deuterium retained in the damaged and then annealed samples F82H[dam+ann] ## 1, 3, and 5 (a) and F82H[dam+annH₂] ## 2, 4, and 6 (b) after exposure to D₂O vapor/water at room temperature for 803 days. NRA measurements were performed 29 days after termination of the D₂O exposure. In each of the seven layers used for the SIMNRA calculations, the D concentration is constant over the entire thickness of the layer. On both panels, damage profile calculated for Fe target with the use of the program SRIM-2008.03 [10] is plotted with the use of right ordinate axis.