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Journal of Nuclear Materials 258–263 (1998) 798–802

journal of nuclear materials

Influence of loading method on hydrogen retention and release from beryllium

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Abstract

Analysis of experimental data and modeling of processes of hydrogen isotope retention, diffusion and release from beryllium irradiated in two fission reactors were carried out. The activation energies of hydrogen release for five TDS peaks were calculated according to the mechanism of second order desorption. An attempt was made to describe high-temperature peak by bulk diffusion from beryllium with surface oxide layer.

1. Introduction

When a fusion reactor is operating, berylluim, as a material of plasma facing components will be exposed to high intensity fluxes of neutrons and γ-photons, additionally to a flux of neutrals. In the present work an attempt was made to estimate the influence of neutrons and γ-photons on hydrogen isotope retention and release behaviour for beryllium irradiated in the hydrogen isotope environment. Fission reactors were used as irradiation sources. Its radiation spectra strongly differs from that of a fusion reactor therefore ITER irradiation conditions can hardly be stimulated comprehensively using fission reactors as a source of irradiation. Nevertheless, obtained results can be interesting for fusion application because investigations carried out revealed the processes connected with the influence of a fraction of the fusion reactor irradiation spectrum being typical for fission reactors upon hydrogen isotope behavior in beryllium. These processes are concerned with the peculiarities of BeO formation in the presence of hydrogen isotopes and under the influence of n, γ irradiation.

2. Modeling of experimental data on hydrogen isotope releases from beryllium samples

To understand the processes, connected with the influence of neutron and γ-photon irradiation on the parameters of hydrogen isotope retention and release from beryllium, the series of experiments on EHP-56 beryllium in-pile loading have been carried out [1]. It was observed, that hydrogen release from the samples loaded with hydrogen at the temperature 1150 K in IVG.1M reactor (irradiation time – 6 h, the pressure of hydrogen 10^5 Pa) is much more in comparison with control samples loaded under the same conditions without irradiation and with that loaded after irradiation in nitrogen atmosphere.

The first five peaks of thermodesorption spectroscopy (TDS) curves obtained in these experiments, cannot be simulated according to diffusion mechanism using the resonable values for diffusion coefficients in Be and BeO, and consequently, for their correct description it is necessary to use other mechanisms. One can try to describe these peaks within the framework of second order desorption model, where flux of desorbing particles can be written down for the case when two chemisorbed atoms recombine and then desorb from the surface as [2]

$$J = N\nu^2 \exp\left(-\frac{2E_{\mathrm{des}}}{kT}\right) = kN^2, \tag{1}$$

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where k is the recombination coefficient, N the concentration of particles on a surface, atoms/cm^2, v the oscillation frequency of an atom on the surface, 10^{13} s^{-1}, α the lattice parameter, $\approx 2.7 \times 10^{-8}$ cm, E_{des} the activation energy of desorption, as a rule it equals the difference in activation energy of adsorption and the heat of chemisorption.

When calculating all the frequency factors of the recombination coefficients have been taken as equal to 7.3×10^{-3} cm^2/s, as in the expression for the flux (1) that is written down as va^2.

The results of such modeling are shown in Fig. 1, where an attempt was made to describe the sixth hydrogen release peak ($T_{\mathrm{peak}} \approx 1100$ K) by diffusion mechanism. Analysis of experimental data on hydrogen diffusion coefficients in polycrystalline beryllium and in beryllium oxide [3–7] and numerical modeling of hydrogen isotopes released from a cylindrical beryllium sample (∅ 3 mm with the thickness of surface oxide film $l = 5$ nm), have shown, that only the sixth peak can be fitted within the framework of diffusion mechanism from the bulk of beryllium sample.

The temperature dependence of hydrogen diffusion coefficients in Be and BeO, obtained as the fitting results, nevertheless are a little bit outside the range of experimental data of the various authors being available for us and are the following:

$$D_{\mathrm{Be}} = 3 \times 10^{-7}\ \exp(-28\ \mathrm{kJ/mol})\mathrm{m}^2/\mathrm{s},$$

$$D_{\mathrm{BeO}} = 8 \times 10^{-5}\ \exp(-192\ \mathrm{kJ/mol})\mathrm{m}^2/\mathrm{s}.$$

The hydrogen amount, released from beryllium sample only according to the given mechanism, exceeds the equilibrium solubility of hydrogen in beryllium under our loading conditions, if we use the data on hydrogen solubility in Be from the work of Shapovalov [8]. It assumes initially high concentration of hydrogen in beryllium, obtained during the process of its manufacturing.

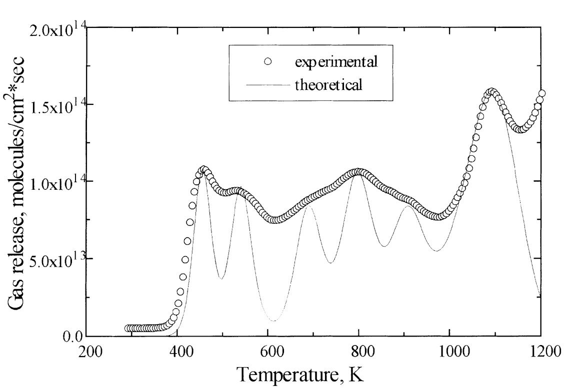

Fig. 1. Results of modeling of hydrogen release spectra from the beryllium samples, loaded with hydrogen in IVG.1M reactor at $T = 1150$ K for 6 h, $P_{(\mathrm{H_2})} = 10^5$ Pa. Temperature ramp rate is 20 K/min.

The activation energies of other gas release peaks, calculated earlier in the work of Tazhibaeva [9] using the model of the second order desorption, have been corrected and are represented in Table 1.

While it is possible to find in the literature reasonable explanations for the values of binding energies between atom and surface having been calculated for the first two peaks and connected with the energy of dissociation of Be(H) and Be(OH) compositions, for peaks 3–5 the existance of chemisorbed states with such high binding energies on BeO surface seems hardly probable. Therefore we assume, that for the first two peaks the recombination of two hydrogen atoms located on the surface takes place, and for peaks 3–5 the recombination occurs between the atom, located on a surface (in adsorbed state) and the atom, located near the surface region (in absorbed state), and the atom can be located in the sites having different energy levels. For such a process, assuming that for our case $E_{\mathrm{b-s}} > E_{\mathrm{des}}$, the flux of desorbing atoms can be written down as [2]

$$J = NC\ va^3\ \exp\left(-\frac{E_{\mathrm{des}} + E_{\mathrm{b-s}}}{kT}\right), \tag{2}$$

where C is the concentration of atoms near the surface layer, atoms/cm^3, $E_{\mathrm{b-s}}$ the activation energy of bulk–surface transition and, assuming that there is the same concentration of absorbed hydrogen atoms near the surface layer (recalculated to atoms/cm^2), as on a surface, it is possible to carry out modeling of gas release flux according to this mechanism using the expression for flux (1).

However, in this case the meaning of activation energy of recombination process changes. If for the first two peaks this energy represents twice the energy of desorption, for the other three peaks this energy is a sum of activation energy of desorption and the activation energy of hydrogen atom transfer from the bulk onto the surface. Here we make an important assumption, that during the growth of the oxide film in the atmosphere of hydrogen, under the influence of reactor irradiation there occurs an active oxide formation with the concentration of hydrogen inside significantly exceeding the equilibrium value [8]. The data, received from the experiments on IVG.1M reactor, where the increase of hydrogen retention was observed, confirm the high probability of the existence of such a mechanism.

To confirm that surface region of the sample plays a key role in hydrogen retention, the loading in RA

Table 1
Activation energies for TDS curve of Fig. 1

Peak number	1	2	3	4	5
E (eV/atom)	0.65	0.78	0.99	1.17	1.33

reactor was carried out in deuterium atmosphere, at the same pressure and temperature, as was done in IVG.1M reactor ($T = 1150$ K, loading time 50 h, deuterium pressure 10^5 Pa). Gas release spectra for these experiments are submitted on Figs. 2 and 3. It is necessary to note, that the effect, having been observed for the samples loaded in IVG.1M reactor, was not observed for the samples loaded in RA reactor, the reactor with less intensity of irradiation. In that case gas release was practically identical for irradiated and non-irradiated samples. It is clearly seen, that gas release in a high-temperature region, responsible for bulk diffusion, has low intensity.

As is seen from the data of Tables 1–3, the activation energies of gas release remain practically constant, and only the quantity of atoms released according to various mechanism, are changed. It is also seen, that the 6th peak, which was attributed to the diffusion mechanism of gas quantity, was not displaced with the decrease of released gas quantity, while the other peaks are shifted to higher temperatures. One can see from Figs. 1–3 that the gas release from the samples, irradiated in RA reactor, is one order of magnitude less than the gas released from the samples irradiated in IVG.1M reactor, even taking into account the greater time of irradiation, greater fluence and the same temperature of irradiation.

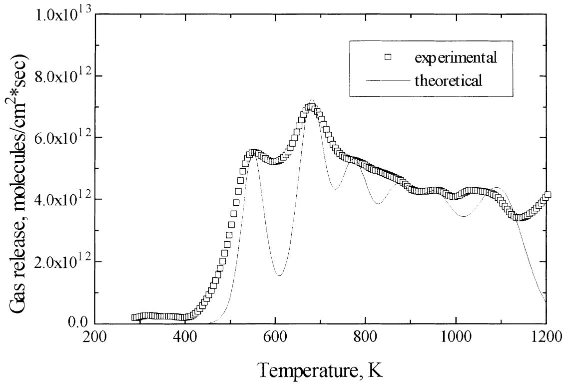

Fig. 2. Results of modeling of deuterium release from non irradiated beryllium samples, loaded in deuterium at $T = 1150$ K for 50 h, $P_{(D_2)} = 10^5$ Pa. Temperature ramp rate is 20 K/min.

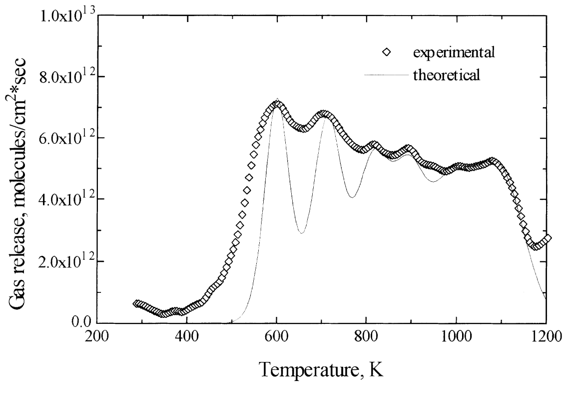

Fig. 3. Results of modeling of deuterium release from beryllium samples, irradiated in deuterium in RA reactor at $T = 1150$ K for 50 h, $P_{(D_2)} = 10^5$ Pa. Temperature ramp rate is 20 K/min.

Table 2
Activation energies for TDS curve of Fig. 2

Peak number	1	2	3	4	5
E (eV/atom)	0.72	0.9	0.99	1.14	1.27

Table 3
Activation energies for TDS curve of Fig. 3

Peak number	1	2	3	4	5
E (eV/atom)	0.79	0.95	1.08	1.18	1.3

As long as the total quantity of desorbed molecules, is about 10^{17} and 10^{16} molecules/cm^2, for the samples, loaded in IVG.1M and RA reactors, respectively, an assumption was made on the different degrees of surface fracturing for these samples [9]. The sample surface fractures, probably during the temperature increase or decrease, as a result of BeO film cracking on the surface. If we use a widely used simplified expression, having received in complete form in [10] for the estimation of stress, appearing in oxide film on the sample surface, it is possible to write down:

$$\sigma = \frac{(\alpha_{\mathrm{BeO}} - \alpha_{\mathrm{Be}}) \times \Delta T \times E_{\mathrm{BeO}} \times E_{\mathrm{Be}}}{(1 - \mu_{\mathrm{BeO}})E_{\mathrm{Be}} - \frac{h_{\mathrm{BeO}}}{h_{\mathrm{Be}}}(1 - \mu_{\mathrm{Be}})E_{\mathrm{BeO}}}, \tag{3}$$

where σ is the stress, arising in BeO when the temperature change is ΔT, μ_{BeO}, μ_{Be} and α_{BeO}, α_{Be}, Poisson's ratios and thermal expansion coefficients for BeO and Be, repectively, E_{BeO}, E_{Be}, their Young's modulus and h_{BeO}, h_{Be}, the thickness of the oxide and the radius of beryllium sample, respectively.

Though our samples have the cylindrical form, but, taking into account that $h_{\mathrm{Beo}}/h_{\mathrm{Be}} \ll 0.1$, it is possible to neglect by radial component of stress, i.e. not to take into account the bend of the surface and to use the expression (3).

After carrying out estimations with the values: $\alpha_{\mathrm{Be}} = 1.6 \times 10^{-5}$ 1/K, $\alpha_{\mathrm{BeO}} = 9.4 \times 10^{-6}$ 1/K; $\mu_{\mathrm{BeO}} = 0.18$, $\mu_{\mathrm{Be}} = 0.07$; $E_{\mathrm{BeO}} = 375$ GPa, $E_{\mathrm{Be}} = 243$ GPa; $h_{\mathrm{BeO}} = 5$ nm, $h_{\mathrm{Be}} = 1.5 \times 10^{-3}$ m, it turns out, that after the sample heating up to 313–393 K the compressing stress arises in the oxide film, $\sigma = 60$–300 MPa, exceeding the strength of beryllium oxide, 40–190 MPa [11] at these temperatures. Hence, it is reasonable to assume, that during the sample heating up to our temperature of loading and during the decreasing of temperature, the surface oxide film formed under these conditions, was cracked. Thus, depending on the conditions in which the oxide film was formed, its structure, mechanical properties and the character of its destruction were changed. This results in various degrees of surface fracturing for the samples, loaded in fission reactors with various spectra of radiation. This assumption, initially based on the data of TDS experiments, was then confirmed by the results of electron microscopy and X-ray structural microanalysis, which have shown the active growth of the oxide layer and the formation of cracks on the surfaces of beryllium samples, irradiated in hydrogen in IVG.1M reactor.

From the data obtained one can make a conclusion, that during the loading of beryllium samples with hydrogen in IVG.1M reactor the oxide film grows with the gas concentration exceeding the equilibrium value and this does not occur during the loading in RA reactor or without irradiation. The mechanism of this phenomenon is not quite clear.

For the explanation of effects occurring during interaction of hydrogen with beryllium in the process of reactor irradiation, it is necessary to know the parameters of their interaction with radiation. It is necessary for understanding the combined influence occuring as a result of irradiation and exposition in molecular hydrogen on hydrogen retention in IVG.1M reactor and absence of similar effect at irradiation in RA reactor. Comparison of results of influence of various spectra of radiation can allow one to allocate a part of the spectrum responsible for occurance of the effect observed.

The following main types of processes in Be under the influence of reactor irradiation that could result in the increase of hydrogen retention were calculated (see Table 4): the generation of α-particles (He nuclei) due to transmutation reactions (n,2n,n,α and γ,α) in beryllium, and generation of displacements under the neutron and γ-irradiation. Generation of recoil protons in hydrogen atmosphere, which could be implanted in beryllium surface and then be released as hydrogen during TDS experiments was also calculated. The number of such protons for IVG.1M reactor was 5–6 orders of magnitude less, than total number of hydrogen atoms released in the experiments. Ionization of molecular hydrogen (deuterium), energy transfer of hydrogen atoms and resulting dissociation of hydrogen complexes, change of electron states of metal and hydrogen in a metal, appearance of non-equilibrium excitations and creation of thermal peaks were also considered. It was shown that their influence in this case is negligible.

Table 4
Results of the calculation of radiation influence for Be samples being irradiated in hydrogen atmosphere in IVG.1M and RA reactors

	IVG.1M	RA
α/cm^3 s	0.2730×10^{12}	0.3474×10^{12}
α/cm^{3}for experiment	0.5897×10^{16}	0.1274×10^{17}
dpa/cm^3 s	1.8×10^{-8}	1.6×10^{-8}
dpa/cm^{3}for experiment	0.0004	0.0029
recoil protons(deutons)		
/s	9.6×10^{10}	2.4×10^{10}
/experiment	9.6×10^{10}	4.5×10^{15}

Comparision of two reactor's spectra revealed only one difference in irradiation characteristics for reactors used – the difference in the fluxes of γ-photons (one order of magnitude) and thermal neutrons (two orders of magnitude) that are greater for IVG.1M reactor. This part of radiation spectrum, according to a literary data, is responsible for the formation of so-called freely migrating defects [12], which, obviously, are of great importance for the formation of oxide film with high concentration of hydrogen. For example they are responsible for void swelling, radiation induced segregation, radiation enhanced diffusion, and radiation embrittlement.

3. Conclusions

Analysis of the earlier obtained TDS spectra for samples, loaded in H_2 and D_2 at $T = 1150$ K, $P = 10^5$ Pa in two different fission reactors, with different spectra of radiation has been carried out.

Activation energies of gas release were calculated, assuming, that the first five peaks can be described by second order desorption, and the sixth peak by bulk diffusion.

Assumption was made, that in the conditions of irradiation on IVG.1M reactor oxide, surface film grows in the process of irradiation with hydrogen concentrations, considerably exceeding equilibrium values.

It is shown, that the observed development of sample surface can be explained by the cracking of oxide film because of internal stresses arising in it at temperature changes of few tens of degrees. Thus the conditions of the oxide film growth can determine the concentration of hydrogen inside it and, accordingly, the character of its destruction.

Assumption was made that γ-radiation and thermal neutrons effects were responsible for the observed effects.

Acknowledgements

Part of this work was carried out under the sponsorship of International Agency of Atomic Energy.

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