ELSEVIER

Journal of Nuclear Materials 290–293 (2001) 211–215

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Tritium retention in neutron-irradiated low-Z materials for use as plasma facing materials

F. Scaffidi-Argentina [a,*], C. Sand [a], C.H. Wu [b]

[a] *Forschungszentrum Karlsruhe, Institute fur Kern- und Energietechnik, Postfach 3640, D-76021 Karlsruhe, Germany*
[b] *EFDA-CSU, c/o Max-Planck-Institut für Plasmaphysik, Boltzmannstr. 2, 85748 Garching, Germany*

Abstract

Among the presently available low-Z materials, graphite, carbon-based composites (CFC) and beryllium represent the primary candidate materials to be used as protection for both the first wall and the high heat flux components (e.g., the divertor) in the next-step fusion reactor. Research and evaluations are underway to study the characteristics of several graphite and CFC as well as beryllium grades associated with safety, tritium release, heat transfer, thermal-mechanical and irradiation stability. Several types of graphite and CFC samples were irradiated in the high flux reactor (HFR) at different temperatures but with the same irradiation damage, while beryllium samples were irradiated in the BR2 reactor at low temperature but with a very high neutron fluence. In this paper, the result of a series of out-of-pile annealing tests aiming at investigating the tritium release kinetics after both neutron irradiation and tritium-loading from three graphite grades (i.e., A05, RGTi(91), CL5890), two DunlopCFC grades (i.e., Concept 1, Concept 2) and four SepCarbCFC grades (i.e., N312C, NS11, N112, N312B) are presented. Furthermore, the tritium and helium release behavior in a beryllium grade (i.e., S-200E) produced by the Kawecki Berylco Industries is also presented.

Keywords: Beryllium; Carbon; Neutron irradiation; Tritium

1. Introduction

The knowledge of the tritium and helium release kinetics as a function of neutron fluence, temperature and damage dose represents an important issue for any plasma facing material (PFM) to be used in a next step fusion reactor. However, the tritium and helium behavior in neutron-irradiated PFMs like beryllium and carbon-based materials is usually a complex function of both the irradiation history (e.g., flux, irradiation temperature, time at temperature, etc.) and of the material grade.

In general, there are three main processes leading to tritium retention in carbon-based materials exposed to a tritium plasma [1], namely: (a) the formation of a surface layer, saturated with the implanted tritium; (b) the co-implantation of tritium with eroded carbon; (c) the atomic diffusion of the implanted/co-implanted tritium to trapping sites usually located well beyond the implantation/co-implantation zone.

On the other hand, tritium produced/implanted in beryllium diffuses at a significant rate to sites of lower free energy (i.e., He bubbles) and/or chemically reacts with impurities for which it has a particular affinity (e.g., beryllium oxide). If tritium is trapped in a helium-filled bubble, it follows the destiny of the bubble and will be released only if the bubble is vented into an open porosity network, through which the gas can escape with effectively no activation energy. On the other hand, tritium chemically bound in form of beryllium hydroxide ($Be(OH)_2$) at oxide inclusions is energetically stable with respect to single tritium atoms and therefore, requires a sufficiently high thermal energy to be released. Due to the two different tritium trapping mechanisms in beryllium,

* Corresponding author. Tel.: +49-7247 822 047; fax: +49-7247 824837.
E-mail address: francesco.scaffidi@iket.fzk.de (F. Scaffidi-Argentina).

0022-3115/01/$ - see front matter
PII: S0022-3115(00)00565-1

the release kinetics is therefore, expected to be dependent on the particular trapping mechanisms and, in particular, to be hindered both by structural sinks and by beryllium oxide impurities.

2. Experimental details

2.1. Samples and irradiation conditions

2.1.1. Graphite and carbon fiber composites

Both graphite and carbon-based material specimens analyzed in the frame of the present work consist of cylindrical bars with a diameter of 5 mm and a length of 15 mm. They include three graphite grades (i.e., A05, RGTi(91) and CL5890), two DunlopCFC grades (i.e., Concept 1, Concept 2) and four SepCarbCFC grades (i.e., N312C, NS11, N112, N312B). A description of the specimens and their properties can be found in [2].

The samples were irradiated between December 1995 and February 1996 at the high flux reactor Petten (Netherlands) as a part of the PARIDE D 302 experiment[3]. A first set of samples was irradiated at a nominal temperature of 335°C up to a neutron dose of 0.31 displacements per atom (dpa) during two reactor cycles (i.e., 49.64 effective full power irradiation days) with a fast ($E_n \geqslant 0.1$ MeV) neutron fluence up to 3.34×10^{24} m^{-2}, while a second set of samples was irradiated at a nominal temperature of 775°C up to a neutron dose of 0.35 displacements per atom (dpa) during one reactor cycle (i.e., 23.75 effective full power irradiation days) with a fast ($E_n \geqslant 0.1$ MeV) neutron fluence up to 4.0×10^{24} m^{-2}.

After irradiation the bars were axially cut in four parts the length of which was about 3.75 mm, and used for the post-irradiation examination (PIE) tests. A cutting method which did not severely heat the samples was used to prevent release of contained gases.

Since in a fusion reactor tritium is loaded in the first wall materials during irradiation, several graphite and CFC samples were out-of-pile loaded with tritium after neutron irradiation. The loading was performed in an alumina tube at 0.2 MPa (absolute) and 850°C for 6 h in a atmosphere of $H_2 + 50$ appm T_2. Details on the loading procedure can be found in [4].

2.1.2. Beryllium

The beryllium specimens analyzed in the frame of the present work consist of segments of a cylindrical bar with a diameter of 15 mm and a length of 100 mm produced by the Kawecki Berylco Industries by vacuum hot pressing (VHP) of impact attritioned powder of 100 mesh at least (S-200E grade) [5]. The average grain size is 10–13 μm, the total beryllium oxide (BeO) content is lower than 2% and the bulk density corresponds to 99.5% of the theoretical one.

The bar was irradiated at 40–50°C in the BR2 reactor in Mol (Belgium) for 2440 effective irradiation days with a fast ($E_n \geqslant 1$ MeV) neutron fluence of 3.925×10^{26} m^{-2}. The calculated helium content after irradiation amounted to 20 670 atomic parts per million (appm) while the tritium content amounted to 110 appm [5].

After irradiation the bars were ultrasonically treated to remove the outer oxide layer which is always present on the external beryllium surface. Then they were rinsed with water and dried, and appropriate samples were cut from the bars. A cutting method which did not severely heat the samples was used to prevent release of contained gases. During the cutting it was experienced that the irradiated material was rather brittle.

2.2. Gas release measurements

Annealing and gas-release measurements for both irradiated/loaded CFC and beryllium specimens were carried out with a flow-through tritium release facility installed at the Forschungszentrum Karlsruhe. The system essentially consists of an inlet gas manifold, a sample furnace chamber connected by a short, heated line ($T \approx 300$°C) to a zinc-reducer ($T \approx 390$°C) which transforms any tritium water to tritium gas, and an ionization chamber or a proportional counter downstream from the furnace for analysis of the purge gas tritium activity. The use of the zinc-reducer avoids problems with tritium water absorption on the inner wall of the release facility pipes, thus allowing quantitative tritium measurements. The total released tritium is determined by integrating the measured release rate over the time.

The release kinetics and total amount of released tritium are determined by annealing the specimens with temperature ramps up to 1100°C. For these annealing experiments, the thermal ramp from room temperature to annealing temperature consisted, in the case of beryllium, of two ramp segments (i.e., 7°C/min from room temperature up to 500°C and 15°C/min from 500°C up to 1100°C). On the other hand, in the case of graphite and CFC a single ramp of 15°C/min from room temperature up to 1100°C was applied. In both cases, the final annealing temperature of 1100°C was kept constant for about 3 h. A 50 cm^3/min high-purity argon with 1 vol% H_2 was used as a purge gas for the annealing experiments with beryllium, while a high-purity helium with 0.1 vol% H_2 was used for the annealing experiments with graphite and CFC.

Tritium release rate was measured with an in-line ionization chamber or a proportional counter. In order to determine the total retained tritium (i.e., inventory) in both graphite and CFC samples after the annealing, the specimens were afterwards totally burned in a pure oxygen atmosphere at 1500°C for 5–6 min. The released

tritium is trapped in a bubbler and then measured by means of liquid scintillation counting.

In the case of beryllium, the gas composition in the process line as well as the helium release rate were measured with a quadrupole mass spectrometer (QMS) connected downstream from the specimen furnace. QMS signature were mass-2 for H_2, mass-4 for ^4He and mass-40 for ^{40}Ar. Based on previous studies [6], the contribution of HT to the QMS mass-4 peak can be considered as negligible.

The QMS was calibrated with gas standard mixtures flowing in the process line, while the ionization chamber and the proportional counter were calibrated with a standardized tritiated gas mixture. A dummy release measurement is performed before a tritium release experiments is started, in order to determine the background of the system.

3. Results and discussion

3.1. Graphite and carbon fiber composite

In order to increase the confidence in the obtained experimental data, the measurements were repeated at least two times. The tests showed a reproducibility ranging from 36% to 76% (average 56%) for the unloaded samples and from 1.9% to 51% for the tritium-loaded samples.

The first surprising result is that, contrary to any theoretical expectation, both graphite and CFC samples contain after irradiation a relatively high amount of tritium. A possible explanation is that during the irradiation some tritium coming from the reactor core was implanted in the samples and there trapped until they were out-of-pile annealed.

The kinetics of tritium release in both graphite and CFC in general depends on the irradiation temperature and damage dose. In agreement with previous studies [4,7] and independent from the irradiation temperature, both graphite and CFC tritium-loaded specimens do not show any tritium release at temperature of 700–750°C and below. In all cases, the tritium release rate starts to increase above about 700–750°C, reaches a maximum when the specimens first reach 1100°C and then starts to decrease monotonically with the time when the annealing temperature is kept constant at 1100°C. On the contrary, the not-loaded specimens irradiated at 335°C show a release rate which starts already at about 400–450°C, reaches a maximum at about 750°C and then monotonically decreases with the time. Furthermore, the not-loaded specimens irradiated at 775°C do not show any release at all temperatures, thus indicating that the tritium was probably already released during the in-pile irradiation. This fact seems to confirm the hypothesis that tritium in not-loaded samples is probably coming

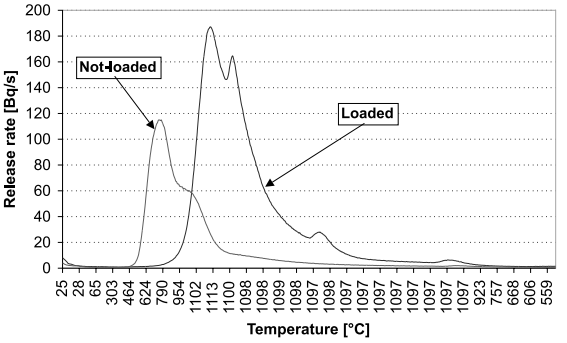

Fig. 1. Tritium release before and after the tritium loading from the SepCarb NS11 CFC samples irradiated at 335°C and out-of-pile heated on to an anneal temperature of 1100°C.

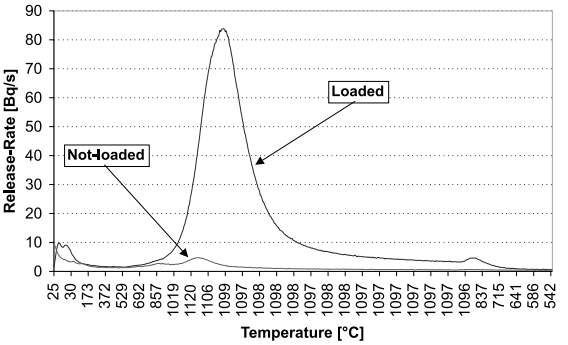

Fig. 2. Tritium release before and after the tritium loading from the SepCarb NS11 CFC samples irradiated at 775°C and out-of-pile heated on to an anneal temperature of 1100°C.

from the reactor core and therefore, weakly bound at the specimens surface. Figs. 1 and 2 show the tritium release before and after the tritium loading from the SepCarb NS11 CFC samples irradiated at 335°C and 775°C, respectively.

The not-loaded specimens release almost all the tritium during the annealing at 1100°C, except the SepCarbNS11 and SepCarbN112 CFC samples, and RGTi(91) graphite irradiated at 775°C, which show a tritium inventory of 32.6%, 62.7% and 20.1%, respectively. On the contrary, independent of the irradiation temperature all the tritium-loaded specimens release only about 50% of the tritium during the annealing at 1100°C, as shown in Figs. 3 and 4. The remaining tritium inventory is then released only after burning of the samples at 1500°C in a pure oxygen atmosphere.

Contrary to the SepCarb N312B which is a pure three-dimensional CFC material, the SepCarb NS11 has undergone during the production process a final infiltration of liquid silicon leading partially to the formation of silicon carbide (10–12 at% of silicon) [2]. In order

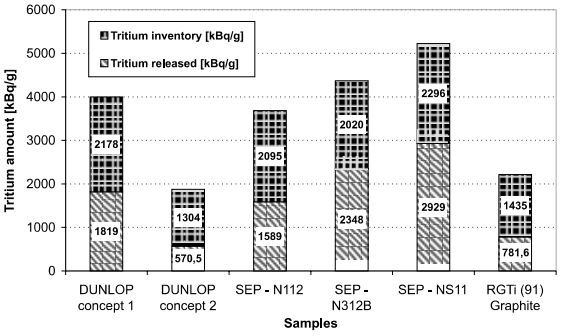

Fig. 3. Tritium inventory and release from tritium-loaded graphite and CFC samples irradiated at 335°C.

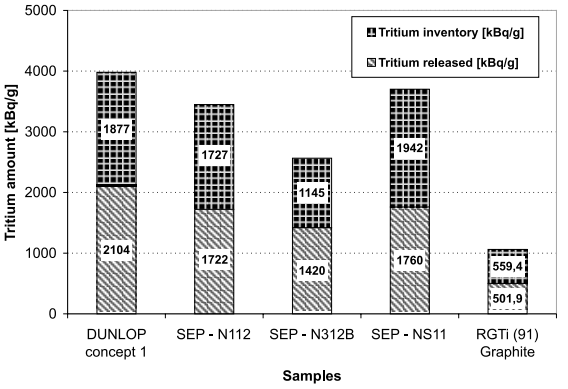

Fig. 4. Tritium inventory and release from tritium-loaded graphite and CFC samples irradiated at 775°C.

to investigate the effects that a silicon doping has on the tritium performance of the CFC samples, the behavior of tritium-loaded SepCarb N312B and SepCarb NS11 irradiated specimens has been compared. The result of the measurements showed that tritium is mainly released in form of HTO and therefore, the silicon doping does not have any significant effect on the tritium release kinetics either at 335°C or at 775°C irradiation temperature. In all cases, the largest peak of release rate is observed at 1100°C and the only minor effect that the silicon doping seems to produce on the specimens irradiated at 775°C is an earlier (about 30 min) release than in the case of a pure CFC, as shown in Fig. 5.

3.2. Beryllium

According to previous studies [7–9], the results of the measurements indicated that helium and tritium release behavior is a complex function of both irradiation temperature and time at temperature. Anyhow, in agreement with the studies reported in [7,8], the beryllium specimens do not show any tritium and helium

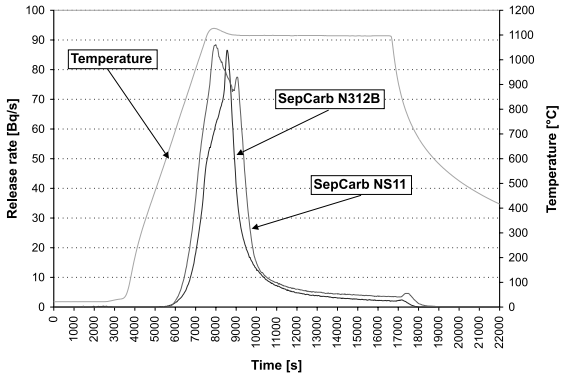

Fig. 5. Tritium release after the tritium loading from the SepCarb NS11 and the SepCarb N312B CFC samples irradiated at 775°C and out-of-pile heated on to an anneal temperature of 1100°C.

release at temperature of 600°C and below. Although tritium is released between 600°C and 900°C, no helium release is observed in that temperature range.

The tritium release rate has a rapid increase during the temperature ramp and a sharp peak is observed when the specimens first reach 1100°C. In agreement with a previous study [9] this sharp peak is probably related with the formation of micro-cracks at the specimen surface. Due to the very high neutron fluence (i.e., 3.925×10^{26} m^{-2}), in fact, the beryllium specimens has become very brittle and consequently they easily crack under thermal stresses during the heating-up phase of the annealing test. After reaching a maximum when the specimens first reach 1100°C, the release rate starts to decrease monotonically fast with the time when the annealing temperature is kept constant at 1100°C. At the time when the largest peak occurs, about 33% of the total tritium is released. Correspondingly, a strong and narrow peak of helium release is observed.

Fig. 6 shows quite clearly that tritium and helium are unambiguously released concurrently, thus leading to the conclusion that tritium and helium reside in common bubbles in the irradiated material. In fact, the burst release is due to the migration of the helium bubbles to form interconnected grain-edge tunnels to the specimen-free surfaces. Therefore, the tritium trapped in the helium-filled bubbles follows the destiny of the bubbles and will be released concurrently to the helium only after their migration and venting from an open-porosity network.

4. Conclusions

The results of a series of annealing tests up to 1100°C for graphite and CFC specimens irradiated in the HFR reactor at different temperatures but with the same

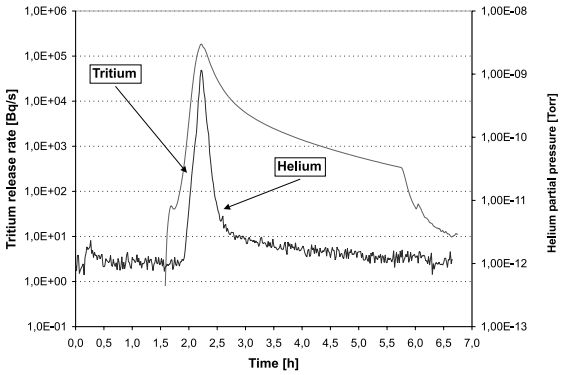

Fig. 6. Tritium inventory and release from a beryllium sample (S-200E grade) heated on a segmented ramp to an anneal temperature of 1100°C.

irradiation damage, as well as for beryllium samples irradiated in the BR2 reactor at low temperature but very high neutron fluence have been presented. The results include gas release measurements (for both loaded and unloaded samples) during thermal ramp out-of-pile annealing with the aim of investigating both tritium and helium release kinetics. Furthermore, results on the tritium inventory after the annealing in both graphite and CFC samples have been presented.

In agreement with previous studies, independent from the irradiation temperature both graphite and CFC tritium-loaded specimens do not show any tritium release at temperature of 700–750°C and below. In all cases, the tritium release rate starts to increase above about 700–750°C, reaches a maximum when the specimens first reach 1100°C and then starts to decrease monotonically with the time when the annealing temperature is kept constant at 1100°C. On the contrary, the not-loaded specimens irradiated at 375°C show a release rate which starts already at about 400–450°C, reaches a maximum at about 750°C and then monotonically decreases with the time. Furthermore, the not-loaded specimens irradiated at 775°C do not show any release at all temperatures, thus indicating that the tritium was probably released already during the irradiation. The not-loaded specimens release almost all the tritium during the annealing at 1100°C, except the SepCarb NS11 and SepCarb N112 CFC samples, and RGTi(91) graphite irradiated at 775°C, which show a tritium inventory of 32.6%, 62.7% and 20.1%, respectively. On the contrary, all the tritium-loaded specimens release only about 50% of the tritium during the annealing at 1100°C. In all cases, tritium is mainly released in the form of HTO and therefore, the silicon doping of the CFC samples does not have any significant effect on the tritium release kinetics either at 335 or at 775°C irradiation temperature.

With reference to beryllium, in agreement with previous studies neither tritium nor helium release was observed at a temperature of 600°C and below. Although tritium is released between 600°C and 900°C, no helium release is observed in that temperature range. However, the unambiguous concurrent release of helium and tritium observed at 1100°C leads to the conclusion that tritium and helium reside in common bubbles in the irradiated material.

Acknowledgements

This work was performed in the framework of the Forschungszentrum Karlsruhe Fusion Project and is supported by the European Union within the European Fusion Technology Program. The authors would like to thank E. Damm of the hot-cell laboratory of the Forschungszentrum Karlsruhe for performing the tritium loading of the samples, Mrs U. Hoeppener-Kramar and Mrs S. Kuhnmünch of the radiochemistry laboratory of the Forschungszentrum Karlsruhe for performing the tritium inventory measurements.

References

[1] P. Franzen et al., Nucl. Fus. 37 (10) (1997) 1374.
[2] J.P. Bonal, D. Moulinier, Thermal properties of advanced carbon fiber composites for fusion application, Report DMT/95-495, SEMI/LEMA/95-073, Commisariat à l'Energie Atomique, Direction des Réacteurs Nucléaires, Saclay, October 1995.
[3] R. Conrad, PARIDE: Irradiation of plasma facing materials for demo at the high flux reactor petten. Projects D 302.1 and D 302.2, Technical Memorandum HFR/4439, Joint Research Center, Institute of Advanced Materials, Petten, October 1997.
[4] H. Kwast et al., Phys. Scr. T64 (1996) 41.
[5] L. Sannen, Final report characterisation of irradiated beryllium, SCK-CEN Report FT/Mol/92-01, Mol, July 1992.
[6] R.A. Anderl et al., Fus. Technol. 28 (1995) 1114.
[7] R.A. Anderl et al., in: Proceedings of the Third IEA International Workshop on Beryllium Technology for Fusion, Mito City, Japan, 22–24 October 1997.
[8] F. Scaffidi-Argentina, H. Werle, in: Proceedings of the Second IEA International Workshop on Beryllium Technology for Fusion, Jackson Lake Lodge, Wy, 6–8 September 1995.
[9] F. Scaffidi-Argentina et al., in: Proceedings of the Fifth International Symposium on Fusion Nuclear Technology, Rome, Italy, 19–24 September 1999, to be published.