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Tritium localisation and release from the ceramic pebbles of breeder

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Abstract

Magnetic field (MF) effects on the radiolysis and tritium release from Li_4SiO_4 (FZK) and Li_2TiO_3 (CEA) ceramic pebbles were investigated. The tritium chemical forms in Li_4SiO_4 were estimated by means of lyomethods. In the case of the neutron fluence $F_n \leqslant 10^{18}$ n m^{-2}, the tritium is mostly in the T^+ form, but in the case of $F_n \approx 10^{25}$ n m^{-2}, the T^+ form accounts for 86–95% of the tritium. A high subsurface concentration of tritium is characteristic of a separate pebble and correlates with the distribution of radiation-induced defects. The MF increases the radiolysis of Li_4SiO_4 by 20–25%. Irradiation with electrons to 1000 MGy at 1200 K increases the grain size by 5–10%, decreasing the parameters of tritium release. The increased grain size was observed for the Li_4SiO_4 pebbles irradiated in EXOTIC-8. A considerable tritium detention (up to 40%) was observed after annealing to 1120 K in the MF of 2.4 T.

1. Introduction

The main function of ceramic breeder materials in the HCPB (helium cooled pebble bed) is to regenerate tritium continuously in fusion reactors, particularly in DEMO or industrial facilities. Li_4SiO_4 or Li_2TiO_3 ceramic pebbles, which are the European reference material of HCPB, will be subjected to high temperatures (up to 1120 K), intense fluxes of fast neutrons (up to 10^{18} n m^{-2} s^{-1}), and intense magnetic (up to 7–10 T) and electric fields. Not only lithium burn-up but also radiolysis, radiation-induced chemical processes, and phase transitions, etc. will take place in the ceramic materials. All this can cause irreversible changes in the composition and structure of the materials affecting parameters of tritium release from the pebbles. Up to now, both the separate and combined long-term action of high temperatures and radiation in fission reactors on the ceramics of various compositions (e.g., the EXOTIC experiments) have been investigated. The action of magnetic (MF) and electric fields is less studied, mostly in laboratory-scale experiments. (e.g., [1]). These experiments demonstrate that the MF affects both the radiolysis of Li_4SiO_4 or Li_2TiO_3 and the parameters of tritium diffusion inside the ceramics. As different radiation-induced defects (RD) and products of radiolysis (RP) form as a result of radiolysis, the MF can change the parameters of the tritium release at the different concentrations of RD. Of great importance is the formation of colloid lithium, which acts as an effective tritium scavenger forming LiT having a high decomposition temperature (about 1000 K). The delaying action of MF on tritium release is explained by MF lengthening the diffusion path of charged tritium forms inside the ceramic grains, which is proportional to the grain size [2]. Both the destruction of ceramic grains (mostly due to the lithium burn-up) and radiation-induced recrystallisation can be expected during the long-term operation (≈20 000 h) of the ceramic pebbles [3]. The recrystallisation can increase the grain size, the diffusion path of tritium, and the delaying action of MF on tritium release.

The possible chemical forms of tritium localisation in the irradiated pebbles, the MF effects on the formation

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of RD and RP, and on the tritium release from the irradiated pebbles were investigated in this paper.

2. Experimental

The following EFDA reference Li_4SiO_4 (FZK) and Li_2TiO_3 (CEA) pebbles were studied in this paper: Li_2TiO_3 pebbles having natural Li-6 content, Li_4SiO_4 pebbles enriched with Li-6 up to 20%, and Li_4SiO_4 pebbles synthesised in FZK (batch OSi-42/93-2) and irradiated in the EXOTIC-8/8 experiment in HFR (Petten) to the lithium burn-up of 11%. High-temperature radiolysis was performed by a flux of fast electrons (5 MeV) at the temperature 1173–1273 K to the dose 1000–1200 MGy ($P = 70$–100 MGy h^{-1}). In order to mark the samples with tritium after high-temperature radiolysis, the pebbles were irradiated in a photoneutron setup to 10^{17}–10^{18} n m^{-2}. In order to estimate the MF effect on the radiolysis, an irradiation rig with the MF intensity up to 1.4 T was used. RD and RP in the Li_4SiO_4 pebbles were analysed by the method of chemical acceptors [4]. RD and RP in the Li_2TiO_3 pebbles were analysed by electron spin resonance (ESR) as the Li_2TiO_3 pebbles are practically insoluble. The possible chemical forms of tritium (T_2, T^0, T^+, T^-) were determined by dissolving the irradiated Li_4SiO_4 pebbles in the following 3 systems of acceptors – 0.4 M H_2SO_4 + 1 M CH_3CH_2OH, 0.4 M H_2SO_4 + 1 M $NaNO_3$, and 1 M $ClCH_2COONa$ under flowing helium, and measuring the tritium activity both in the solution by the liquid scintillation method (LSM) and in the gas phase by means of the gas-flow proportional counter TMH 2. The spatial distribution of tritium in separate Li_4SiO_4 pebbles was determined by dissolving many pebbles of the same size under the kinetic dissolution regime in H_2O, and simultaneously measuring the electrical conductivity of the solution to determine the dissolved layer and the increase in tritium concentration in the solution and the gas phase [5]. The distribution of RD in a pebble was determined from their recombination luminescence on the pebble surface during the dissolution.

The MF effect on tritium release from the irradiated pebbles was investigated by means of a thermoannealing setup using a linear temperature increase at the heating rate $\beta = 2$–10 K min^{-1}. The activity of the tritium retained in the pebbles was determined by LSM. Changes in the ceramic composition were investigated by X-ray diffraction (XRD), and changes in structure by scanning electron microscopy (SEM). The number of RD in the samples was determined by a thermostimulated luminescence method, and the presence of colloid lithium by the ultrathin ESR line [6].

3. Results and discussion

3.1. Localised tritium forms in the Li_4SiO_4 pebbles

The tritium forms localised in the ceramic pebbles are little studied; mostly the released forms of tritium (HTO, HT) have been determined. As the MF affects only the volume diffusion of charged tritium forms (T^+, T^-), it is important to determine their distribution in the ceramic pebbles irradiated under various conditions (Table 1). The distribution of tritium forms changes under annealing – T_2 (HT) releases first, and T^- disappears at 1000 K.

3.2. The tritium distribution in the volume of a pebble

The radial distributions of tritium and RD in the Li_4SiO_4 pebbles are shown in Fig. 1. The distributions are not uniform. Approximately 80% of tritium and 70% of RD localise in a subsurface layer of thickness 50 μm. The distribution of tritium correlates with the distribution of RD as RD act as scavenging centres for tritium. An increased subsurface concentration of RD is possibly caused by an increased surface concentration of intrinsic structure defects and a different chemical composition (an increased SiO_2 and Li_2SiO_3 content) of the subsurface layer due to rapid quenching of the surface at the melting-spraying fabrication process of pebbles.

Table 1
Distribution of the chemical forms of tritium in the Li_4SiO_4 pebbles

No.	Irradiation and its conditions	Fractions of T forms (%)			
		T^+	T^-	T^0	T_2 (HT)
1	Irradiated with neutrons to 10^{17}–10^{18} n m^{-2} at room temperature	100	–	–	–
2	Irradiated with electrons (5 MeV) to 1000 MGy at 1100 K, neutrons to 5×10^{17} n m^{-2}	95 ± 2	2 ± 1	–	3 ± 1
3	Irradiated with neutrons (>1 MeV) to 2.4×10^{25} n m^{-2} in HFR (EXOTIC-8)	86 ± 3	5 ± 1	–	9 ± 2

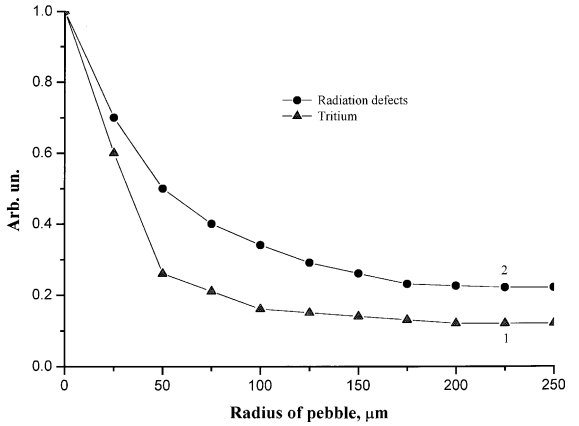

Fig. 1. The distribution of tritium and RD in the volume of a Li_4SiO_4 pebble (∅ 0.5 mm) irradiated at room temperature to 100 MGy: 1 – [tritium], 2 – [RD]. ('0' level is the surface).

3.3. Magnetic field effect on the tritium release

The tritium release from ceramic pebbles both in-pile and in post irradiation experiments is studied in numerous papers. There are fewer data about the effect of an intense MF on the tritium release. The MF can change both the efficiency of formation of RD and RP and the parameters of tritium diffusion in the ceramics.

The role of RD and RP (colloid Li, O_2, Si^0, etc.) of both electron and hole types on the tritium retention was demonstrated in numerous papers (e.g., [7]). The MF of 1.34 T increases the yield of RD and RP in Li_4SiO_4 and Li_2TiO_3 by 20–25% during irradiation at temperatures up to 800–900 K. That is related to the spin transformation of a primary exciton $(O^{=})^*$ ($S \rightarrow T$ process) [8]. During irradiation at temperatures above 900 K, the localisation of RD does not take place; only the stable RP such as O_2, Li_2SiO_3, etc. can form. Under the irradiation at temperature 400–600 K and at doses above 10–20 MGy, colloid lithium forms in Li_4SiO_4 ceramics. The formation and dissociation of LiT in the Li_4SiO_4 pebbles is confirmed by the appearance at 1000 K of an additional maximum in the tritium release from the samples, where colloid lithium was accumulated (the electron dose 150 MGy, the temperature 500 K) before the neutron irradiation. Thus the additional RD and RP formed as a result of the MF can only increase the time of tritium release by 10–20%.

The MF effect on the parameters of tritium (T^+, T^-) diffusion in the grain volume of ceramics appears as the lengthening of the diffusion path due to the Larmor effect. The delaying effect of MF on the tritium release was observed to increase as the grain size increases. As the initial grain size is within 1–3 μm for Li_2TiO_3 and 5–10 μm for Li_4SiO_4, the MF effect is not significant. The time for complete tritium release under annealing increases by 10–15% while not changing the total amount of tritium released. Irradiating these materials with fast electrons to the dose 1000–1200 MGy at the temperature 1100–1200 K, the grain size was observed to increase to 3–7 μm for Li_2TiO_3 and to 10–15 μm for Li_4SiO_4. The MF increased the time of complete tritium release from these samples under annealing by 15–20%. The curves of tritium release from the highly irradiated Li_4SiO_4 pebbles (the EXOTIC-8 experiment) at the heating rate $\beta = 2.7\ \mathrm{K\,min^{-1}}$ to 1100 K both without and within the MF of 2.35 T are shown in Fig. 2. We can see that the MF decreases the tritium release by 48% at 1100 K while does not change considerably the temperatures of maximum release rate. The tritium detention observed correlates with the average grain size 20–30 μm of the Li_4SiO_4 pebbles irradiated in EXOTIC-8, and the grain size of several grains increased even to 50 μm.

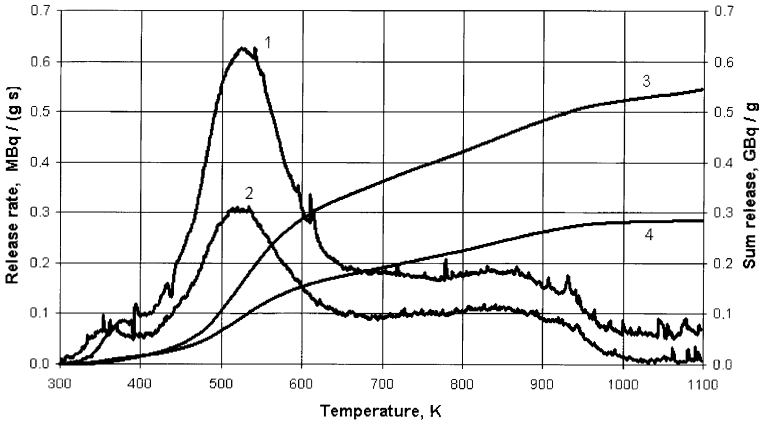

Fig. 2. The tritium release rate (1, 2) and sum release (3, 4) from the irradiated Li_4SiO_4 pebbles (the EXOTIC-8/8 experiment) during annealing ($\beta = 2.7\ \mathrm{K\,min^{-1}}$, the purge gas – He + 3.4%H_2): 1, 3 – without MF, 2, 4 – in the MF of 2.35 T.

4. Conclusion

Tritium localises in the ceramic pebbles mostly as T^+ (as T^+ in a cation vacancy, OT^-, etc.) even up to 100% at a small irradiation dose. Increasing the dose and temperature of irradiation, colloid lithium forms which binds tritium in the T^- form (LiT). At a very high irradiation dose ($>10^{25}$ n m^{-2}), tritium localises also in the molecular form (HT, T_2) in the pebble. The tritium distribution in the pebble volume is not uniform and correlates with the non-uniform distribution of RD. Approximately 80% of tritium localises in a subsurface layer of thickness 50 μm. The MF affects the parameters of the tritium release from ceramics, both increasing the number of RD and RP, which act as scavenging centres of tritium, and decreasing the diffusion parameters of charged tritium forms in the ceramic grains. The decrease in the diffusion parameters is proportional to the grain size, which can increase during long-term operation of HCPB.

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References

[1] J. Tiliks, S. Tanaka, G. Kizane, A. Supe, A. Abramenkovs, V. Grischmanovs, in: C. Varandas, F. Serra (Eds.), Proceedings of the 19th Symposium on Fusion Technology, Lisbon, Portugal, vol. 2, 16–20 September 1996, p. 1507.
[2] J. Tīliks, G. Ķizāne, A. Vītiņš, Ģ. Vītiņš, J. Meistars, Fus. Eng. Des. 69 (2003) 519.
[3] G. Piazza, J. Reimann, E. Günther, R. Knitter, N. Roux, J.D. Lulewicz, Fus. Eng. Des. 58&59 (2001) 653.
[4] J.E. Tiliks, G.K. Kizane, A.A. Supe, A.A. Abramenkovs, J.J. Tiliks, V.G. Vasiljev, Fus. Eng. Des. 17 (1991) 17.
[5] A. Abramenkovs, J. Tiliks, G. Kizane, V. Grischmanov, H. Werle, Fus. Technol. (1994) 1241.
[6] F. Beuneu, P. Vajda, G. Jaskierowicz, M. Lafleurielle, Phys. Rev. B 55 (1997) 11263.
[7] A. Abramenkovs, J. Tiliks, G. Kizane, V. Grishmanovs, A. Supe, J. Nucl. Mater. 248 (1997) 116.
[8] J. Tiliks, S. Tanaka, G. Kizane, A. Supe, V. Grischmanovs, A. Abramenkovs, J. Tiliks Jr., in: S. Casadio (Ed.), Proceedings of the 5th International Workshop on Ceramic Breeder Blanket Interactions, Rome, Italy, 23–25 September 1996, p. 143.