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Journal of Nuclear Materials 283–287 (2000) 1419–1423

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Tritium release from neutron-irradiated Li_2O sintered pellets: porosity dependence

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Abstract

The tritium release behaviour from sintered Li_2O pellets of various densities (71–98.5% theoretical density, T.D.) has been investigated by heating tests at a constant rate. It is shown that the tritium release rate depends on porosity at densities above 87% T.D., while no dependence was observed at densities below 86% T.D. The tritium release process is thought to consist of three stages described as follows: (1) the liberation of tritium trapped at point defects due to their recovery (peak at around 570 K); (2) the advection through interconnected pores via adsorption and desorption on their inner walls and diffusion in the gas phase of interconnected pores (peak at around 620 K); (3) the dissolution and release of tritium trapped in closed pores (peaks at around 700, 830 and 1000 K).

1. Introduction

Li_2O is one of the principal candidates for tritium breeding materials in a fusion reactor system. In our previous studies [1,2], the diffusion coefficient of tritium in Li_2O single crystals was evaluated, and the influence of fast neutron irradiation on the diffusion coefficient was disclosed. The investigation of tritium release behaviour from sintered porous Li_2O pellets [3] showed that the desorption process from the Li_2O surface is the rate determining step for tritium release. A great body of data referring to tritium adsorption behaviour on the surface of Li_2O has been reported elsewhere [4–6].

The tritium release behaviour from sintered ceramic breeding materials is markedly affected by open, closed and interconnected pores. Therefore, it is important to investigate the tritium behaviour in the pores, especially its transport from bulk to surface through interconnected pores [7–11]. It is thought that the latter process consists of the advection of tritium to the surface via adsorption/desorption on the inner walls of the interconnected pores and diffusion of tritium in the gas phase of interconnected pores [10]. By this means, the tritium behaviour is affected by the tortuosity and the size of interconnected pores, the distribution of pores in the material, the pore size and the grain size. The tritium generated is considered to be trapped in closed pores of ceramics. It is also thought that the tritium is trapped by various kinds of defects in the materials, such as grain boundaries, impurities, vacancies, dislocations, micro voids, point defects generated by irradiation, and so on.

In the present study, the effect of pore network on the tritium release behaviour from sintered Li_2O pellets has been investigated. The tritium release experiments from the specimens of various densities in the range of 71–98.5% theoretical density (T.D.) have been performed to obtain a detailed knowledge of the porosity dependence of the tritium release behaviour.

2. Experimental

The specimens were sintered Li_2O pellets of 71–98.5% T.D. The preparation method of the pellets has been described in detail elsewhere [12,13]. For pellets with densities 71–92.5% T.D., 99% pure Li_2O powder prepared by Cerac Co. was heated in vacuum at 970 K for 4 h to decompose Li_2CO_3 and LiOH. After the heat

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0022-3115/00/$ - see front matter
PII: S0022-3115(00)00323-8

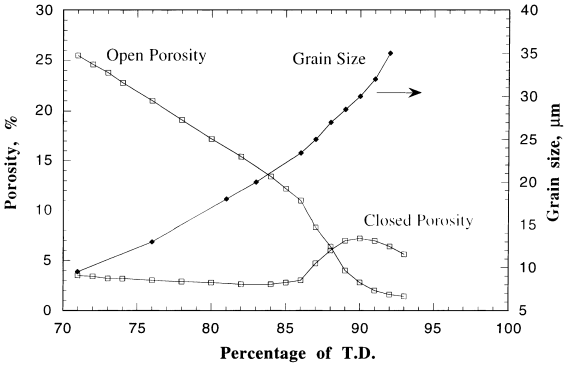

Fig. 1. Grain size and porosity of sintered Li_2O pellets versus the percentage of T.D.

treatment, the powder was pressed without binder in the pressure range of 9.8×10^7–4.9×10^8 Pa followed by sintering in a vacuum in the temperature range of 1370–1570 K for 2–4 h. Fig. 1 shows the volume fraction of closed and open pores in the pellets obtained. For densities greater than 86% T.D., the closed porosity rapidly increases with theoretical density and reaches a maximum at 90% T.D. The grain size of the sintered pellets increases with theoretical density as shown in Fig. 1, i.e., 9.5 μm at 71% T.D. and 60 μm at 92.5% T.D. Only the 98.5% T.D. specimens were prepared by hot isostatic pressing at a pressure of 1000 atm and a temperature of 1320 K. The preparation method of these specimens and their characteristics have been described elsewhere [14].

Small pieces ($2 \times 2 \times 2$ mm^3) were cut from Li_2O sintered pellets and heated in vacuum at 970 K for 4 h. After heat treatment, the specimens were irradiated by thermal neutrons to fluences up to 4×10^{20} n/m^2 using the JRR-4 reactor at JAERI.

The tritium release from the irradiated samples was measured by a proportional counter in a flow (180 cm^3/min) of ammonia (NH_3) sweep gas at atmospheric pressure during a constant heating rate of 2 K/min. By using an ammonia sweep gas, the adsorption of HTO on Li_2O surfaces and the production of LiOT is prevented [15]. In addition, the adsorption of HTO on the inner walls of the piping and counter is also precluded and this reduces the background level. The proportional counter was kept at about 400 K to suppress its contamination due to adsorption of tritium.

3. Results and discussion

3.1. Porosity dependence

Fig. 2 shows the tritium release curves of the samples with various theoretical densities (71–86% T.D.) during a temperature ramp of 2 K/min. The open and closed

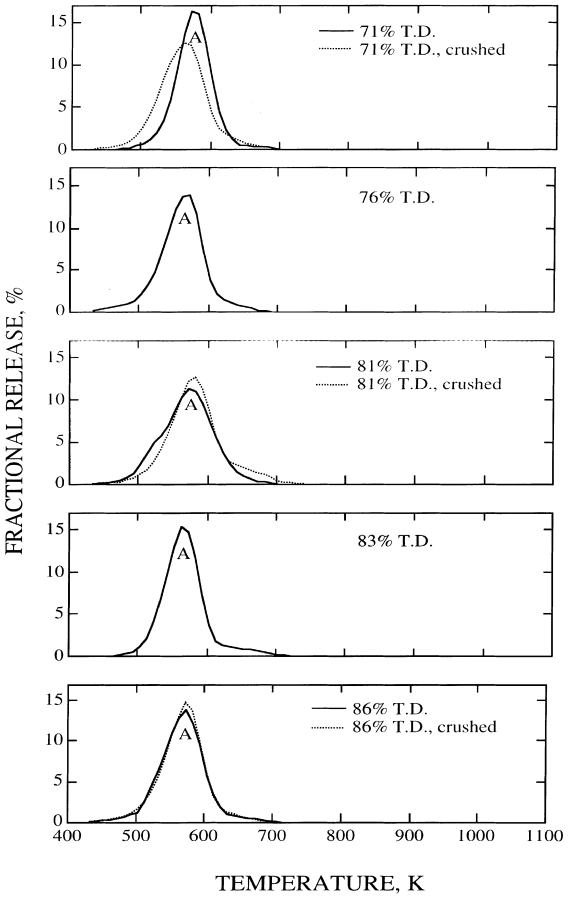

Fig. 2. Tritium release from sintered Li_2O pellets of 71–86% T.D. during a temperature ramp of 2 K/min. The dashed lines represent the tritium release from the same samples crushed into powders.

porosity of the 71% T.D. sample are 25% and 3.5%, respectively, and those of the 86% T.D. sample are 11% and 3%, respectively [12]. The average grain size of 71% and 86% T.D. specimens are 9.5 and 24 μm, respectively [13]. In spite of these distinctions in the porosity and grain size among specimens, the tritium release peaks appear at almost the same temperatures, around 570 K for all specimens. It is believed for all specimens that the tritium advection through the interconnected pores is not the rate determining step of tritium release and the trapping effect in the closed pores is negligible in this density region because of the large ratio of open to closed porosity.

Fig. 3 displays the tritium release curves for specimens of 87%, 88% and 89% T.D. for a temperature ramp of 2 K/min. The open and closed porosity of the 87% T.D. specimen are 8.3% and 4.7%, respectively, and those of 89% T.D. specimen are 4.0% and 7.0%, respectively. The average grain size of the 87% and 89%

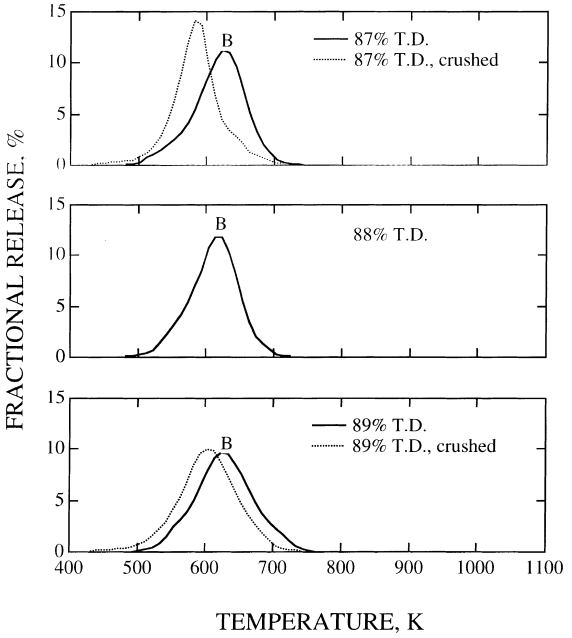

Fig. 3. Tritium release from sintered Li_2O pellets of 87–89% T.D. during a temperature ramp of 2 K/min. The dashed lines represent the tritium release from the same samples crushed into powders.

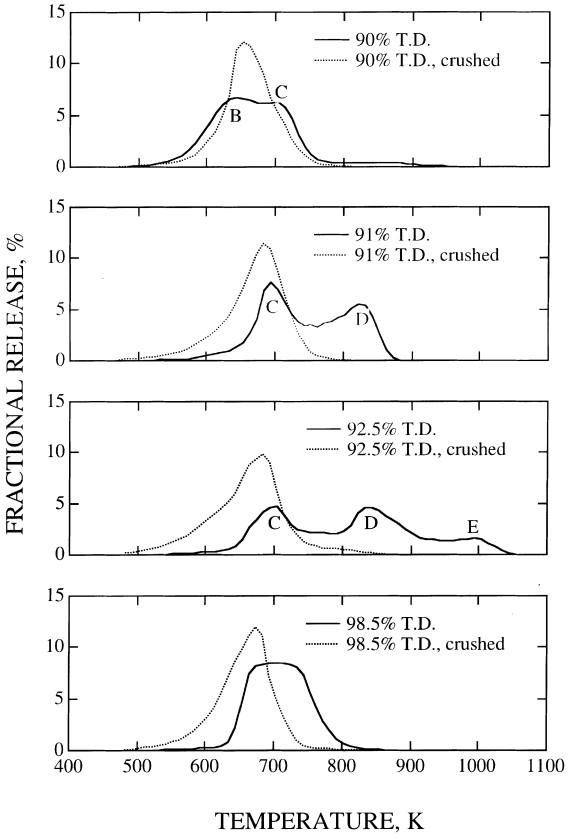

Fig. 4. Tritium release from sintered Li_2O pellets of 90–98.5% T.D. during a temperature ramp of 2 K/min. The dashed lines represent the tritium release from the same samples crushed into powders.

T.D. samples are 25 and 29 μm, respectively. The tritium release curves have maxima at temperatures of about 620 K. It seems likely that the rate determining step in the density region from 87% to 89% T.D. is different from that of the density region of 71–86% T.D. Since the open porosity is nearly equal to the closed porosity in this density range (the ratio of open to closed porosity is 0.57–1.8), it is thought that the rate determining steps of tritium release are the tritium advection through the interconnected pores and tritium diffusion in the gas phase of the interconnected pores.

Fig. 4 represents the tritium release curves for specimens of 90%, 91% and 92.5% T.D. during a constant heat rate of 2 K/min. The open and closed porosity of the 90% T.D. sample is 2.8% and 7.2%, respectively, and those of the 92.5% T.D. sample are 1.5% and 6.0%, respectively. The average grain size of the 90% and 92.5% T.D. are 30 and 60 μm, respectively. There are three peaks in the tritium release curves in the density range from 90% to 92.5% T.D. The tritium release peaks are at about 700, 830 and 1000 K. The ratio of open to closed porosity in this density region is in the range from 0.25 to 0.39. It is believed that the liberation of tritium trapped in closed pores causes the multiple peaks at high temperatures.

The tritium release curve for the 98.5% T.D. specimen during a temperature ramp of 2 K/min is shown in Fig. 4. The open and closed porosity of the 98.5% T.D. are 0.4% and 1.1%, respectively. The grain size of that specimen lies in the range from 60 to 100 μm. A plateau appears in the release curve for the 98.5% T.D. sample from 650 to 750 K.

3.2. The effect of pulverization on the tritium release kinetics

The irradiated specimens were pulverized into powder. The particle size of the typical pulverized samples which were observed by microscope photographs are all less than 100 μm. Tritium release behaviour has been subsequently investigated during a temperature ramp of 2 K/min.

The tritium release curves of the crushed samples of 71%, 81% and 86% T.D. have one peak, like that of the specimens before crushing, at around 570 K (Fig. 2). Thus there is no effect of crushing on the tritium release in the density region from 71% to 86% T.D. and the processes of tritium release is identical for the samples

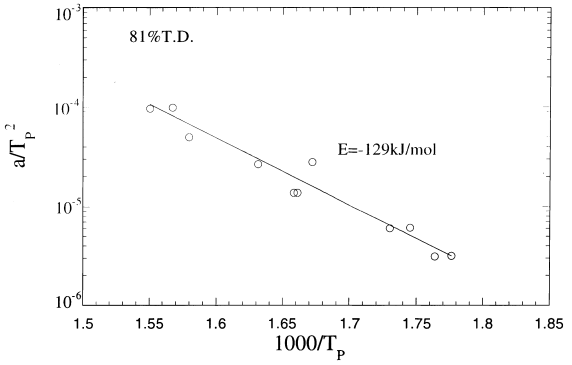

Fig. 5. Heating rate dependence of tritium release peaks from 81% T.D. sintered pellets.

before and after the crushing. The mechanism of tritium release will be discussed in detail in Section 3.3.

The peaks of the tritium release from the crushed specimens of 87% and 89% T.D (Fig. 3) are offset to lower temperatures by about 30 K than those from the uncrushed specimens. It is thought that the length of the interconnected pores became shorter by crushing.

The number of tritium release peaks decreased after crushing the specimens of 90%, 91% and 92.5% T.D. (Fig. 4). For crushed specimens of 90% and 91% T.D. only one peak appears at around 670 and 680 K, respectively. In contrast to that, two peaks were observed before crushing at around 630 and 700 K, and at about 700 and 830 K, respectively. Only one tritium release peak appears at around 680 K from the crushed specimen of 92.5% T.D., while three peaks at around 700, 830 and 1000 K were determined in the release curve of that specimen before crushing.

The sharp peak at about 680 K emerged instead of the wide plateau at around 650–750 K after crushing the 98.5% T.D. specimen.

3.3. Heating rate dependence

To evaluate an apparent activation energy for peak A in Fig. 2, tritium release experiments were performed at various heating rates (1, 2, 5, 10, 20 and 40 K/min) for 81% T.D. specimens. The relation between the heating rate (a) and the temperature of the tritium release peak (T_p) is described as

$$a/(T_p)^2 = C\exp(-E_0/kT_p),$$

where E_0 is the activation energy and k the Boltzman coefficient. C is expressed as $[\chi-(\chi-1)Q](k/E_0)\nu N_0^{(\chi-1)}$, where χ is the order of the reaction, ν the frequency factor and N_0 is the initial tritium concentration in the specimen. Q is expressed as $(1/x_m^2)\exp(1/x_m)H(x_m)$. $H(x_m)$ is expressed as $\int \exp(-1/y)\,dy$ and x_m expressed as kT_p/E_0 [16].

Fig. 5 shows the relation between the heating rate and the temperature of the tritium release peak a/T_p^2 and $1/T_p$. From the slope of the line in Fig. 5, the apparent activation energy of peak A is estimated at 129 kJ/mol. This value agrees well with the activation energy of the recovery of F^+ centers, about 135 kJ/mol [17]. It is thought that the appearance of peak A is associated with the evolution of tritium trapped at radiation defects, such as F^+ centers, due to the recovery of the latter at elevated temperatures.

4. Conclusions

The tritium release behaviour from sintered Li_2O pellets of various densities (71–98.5% T.D.) has been investigated by heating tests at a constant rate. It is shown that the tritium release rate is porosity dependent at densities greater than 87% T.D., while it is independent of porosity at densities less than 86% T.D. It is suggested that the tritium release process has three stages described as follows: (1) release of tritium trapped at radiation defects due to the recovery of the defects (peak at around 570 K), (2) the advection through interconnected pores via adsorption and desorption on the inner walls of the interconnected pores, and diffusion in the gas phase of the interconnected pores (peak at around 620 K), and (3) liberation of tritium trapped in the closed pores (peaks at around 700, 830 and 1000 K).

The tritium release behaviour is significantly affected by a slight porosity change. The results show the importance of tritium migration via pores in the tritium release behaviour. Further study of the influence of the pore network on the tritium release behaviour in Li_2O as well as in other tritium solid breeders is necessary.

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