Journal of Nuclear Materials 511 (2018) 1–10

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Chemical imaging and diffusion of hydrogen and lithium in lithium aluminate

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HIGHLIGHTS

- STEM-EELS has been successfully applied to map Li in ion-irradiated γ-$LiAlO_2$ pellets.
- Direct evidence is found for preferred pathways of Li diffusion along the grain boundaries.
- Isolated voids are identified as possible Li trapping sites in pellets during irradiation.
- Possible lithium hydrides and/or hydrates are formed on the irradiated pellet surface.
- Possible H-bearing molecules or particles are precipitated along the grain boundaries.

ARTICLE INFO

Article history:
Received 15 May 2018
Received in revised form
30 August 2018
Accepted 30 August 2018
Available online 1 September 2018

Keywords:
Chemical imaging
Diffusion
Ion irradiation
Tritium breeder material
$LiAlO_2$

ABSTRACT

Tritium (^3H) must be replenished for strategic stockpile and fusion reactors. ^6Li-enriched γ-$LiAlO_2$ pellets have been used for ^3H production by thermal neutron irradiation. A fundamental study of ^3H and ^6Li diffusion processes in irradiated γ-$LiAlO_2$ pellets is needed to assess and predict the long-term material performance. This study focuses on identifying the trapping sites and diffusion pathways of ^1H (a surrogate for ^3H) and Li atoms in polycrystalline γ-$LiAlO_2$ pellets irradiated with both $^4He^+$ and $^1H_2^+$ ions. A combination of STEM-EELS, Nano-SIMS and APT is employed for chemical imaging at nanoscale resolution. There is direct evidence for preferred Li diffusion pathways along grain boundaries. Isolated voids are identified as possible Li trapping sites in the irradiated γ-$LiAlO_2$ pellets. Possible lithium hydrides and/or hydrates are precipitated on the surface of the irradiated pellets. This study improves our understanding of H and Li diffusion processes and provides data for modelling and simulation to predict material performance during neutron irradiation of γ-$LiAlO_2$ pellets.

1. Introduction

Tritium (^3H) has a radioactive half-life of 12.3 years. It must be continuously replenished to maintain a certain level for strategic stockpile [1] and in a fusion reactor during power generation [2]. ^6Li-enriched γ-$LiAlO_2$ pellets have been used for ^3H production in tritium-producing burnable absorber rods (TPBARs) by thermal neutron irradiation [1]. The neutron reaction with ^6Li emits 2.05 MeV ^4He and 2.75 MeV ^3H particles that collide with the host atoms and create point defects in the material. Interactions of the point defects and gas species lead to formation of extended defects, such as dislocation loops and cavities (including gas bubbles). Damage in the material accumulates with increasing dose over the time [3–5]. In addition, the $^4He^+$ and $^3H^+$ charged-particle irradiation also induces material decomposition and subsequent formation of cubic-phase $LiAl_5O_8$ precipitates [5,6]. As a result, the microstructure in the ^3H breeder material is subject to a significant change with irradiation dose, which is expected to affect ^3H and ^6Li diffusion kinetics.

Our previous studies [5,6] of ion-irradiated γ-$LiAlO_2$ have showed a number of phenomena, including the occurrence of damage saturation stages, surface amorphization, material decomposition, precipitation of $LiAl_5O_8$ nanoparticles, H and Li diffusion and release, formation of gas bubbles, and grain boundary

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https://doi.org/10.1016/j.jnucmat.2018.08.057
0022-3115/

effects on mass transport. While these observations help understand the general behavior of the ^{3}H breeder material during neutron irradiation, accurate assessment and prediction of the long-term material performance requires further investigation into how microstructural changes impact the ^{3}H and ^{6}Li diffusion processes. For neutron irradiated TPBARs with standard γ-$LiAlO_2$ pellets, a delay in the release of ^{3}H was observed for the first 100 effective full-power days (EFPDs) [7]. More recent TPBAR irradiation experiments indicate that ^{3}H release starts immediately after neutron irradiation of porous γ-$LiAlO_2$ pellets [8]. The incubation period of the ^{3}H release may be associated with the slower ^{3}H diffusion in more densified pellets. A fundamental study of ^{3}H and ^{6}Li trapping and diffusion processes in irradiated γ-$LiAlO_2$ pellets is needed for an improved understanding of this behavior. This study intends to identify the trapping sites and diffusion pathways of ^{1}H (a surrogate for ^{3}H) and Li atoms in polycrystalline γ-$LiAlO_2$ pellets irradiated with both $^4He^+$ and $^1H_2^+$ ions at the reactor operating temperature using a combination of high-resolution chemical imaging methods.

2. Experimental details

The samples used in this study are coupons (5 mm × 12 mm × 0.7 mm) sliced and polished from γ-$LiAlO_2$ pellet tubes, acquired from TPBAR fabricator WesDyne. Detailed procedures for the sample preparation were described elsewhere [6,9]. The design of the irradiation experiments was accomplished based on SRIM (Stopping and Range of Ions in Matter) simulations [10], where the specific gravity of the material is assumed to be $\rho = 2.615$ g/cm^3. The surface sputtering/monolayer collision step mode was chosen to eliminate sample damage artifacts caused by energetic light ions in the near surface region. In the simulation, the threshold displacement energies of E_d (Li) = 22 eV, E_d (Al) = 84 eV and E_d(O) = 37 eV were adopted from molecular dynamics (MD) simulations [11]. The surface binding energies were set to be equal to the threshold displacement energies on corresponding sublattices. In this study, ^{1}H is used as a surrogate for ^{3}H. 90 keV He^+ and 40 keV H^+ ions were chosen for irradiation at an incident angle of 60° off the surface normal. The SRIM simulation results are shown in Fig. 1 for an ion fluence of 2×10^{17} H^+/cm^2 that was applied in this study (see below). For 90 keV He^+ ion irradiation at 60° off normal, the peak dose is 5.0 dpa at 222 nm; the He profile is peaked at 312 nm with a maximum of 7.4 at.% He, as shown in Fig. 1(a). Similarly, the maximum dose in γ-$LiAlO_2$ irradiated at 60° off normal with 40 keV H^+ ions is 0.64 dpa at 150 nm, as shown in Fig. 1(b). The H peak is located at 215 nm with a maximum of 11.8 at.% H; the profile is spatially overlapped with the He damage profile peaked at 222 nm. In the ^{3}H production, ^{3}H atoms created from the thermal neutron reaction typically migrate in pellets with lattice disorder produced predominantly by He^+ ion irradiation. Thus, He^+ ion irradiation should be performed prior to H^+ ion irradiation.

A customized sample holder was designed and fabricated for ion irradiation in this study at elevated temperatures to eliminate Ag contamination that was found in our previous study [6] due to utilization of Ag paste for sample mounting. The sample holder was made of red brass with excellent thermal conductivity and a reasonably high melting point. A thermocouple was clamped onto the sample surface to measure the sample temperature. Three polycrystalline γ-$LiAlO_2$ pellets were mounted side by side at a time for sequential irradiation at 60° off the surface normal with 90 keV He^+ ions and t80 keV H_2^+ ions to an equal ion fluence of 2×10^{17} ions/cm^2 for each of the two ion species at 573 K (noted as 2×10^{17} He^++H^+/cm^2 below). The 80 keV H_2^+ beam is equivalent to 40 keV H^+ beam for ion irradiation, but has a beam current of about an order of magnitude higher. A magnetically rastering system was used for uniform irradiation over the entire sample surface (15 mm × 10 mm). The irradiation was manually interrupted once about every 15 min to check and correct the beam current, which was found to be fairly stable. The beam current is arithmetically averaged over the time period and the ion flux is typically on the order of 2×10^{13} ions/cm^2/s over the irradiation area (17 mm × 12 mm). In spite of this careful procedure, the absolute ion fluence is still subject to error of up to 10% or greater.

In-situ heating time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed in an interlaced mode to measure the depth profiles of Li and H in the as-irradiated and annealed polycrystalline γ-$LiAlO_2$. A non-interlaced mode would lead to a high H background by surface absorption from the ultrahigh vacuum chamber during ToF-SIMS because hydrogen has a high ionization efficiency. The irradiated sample was annealed in vacuum at 873 K for 30 min with both ramping-up and ramping-down rates of 1 K/s to study H and Li diffusion behavior. The sputtering conditions were described in previous reports [5,6]. The measurements were limited to a 2 mm × 2 mm area to ensure that the H_2^+ ion fluence was nearly the same in the analyzing spots. This approach allows for a quantitative comparison of H concentrations at different spots without a reference sample. Cross-sectional scanning transmission electron microscopy (STEM) specimens were prepared using a FEI Helios NanoLab dual-beam focused ion beam (FIB) microscope. A standard lift out procedure involving Ga^+ ions at 30 keV for cutting/thinning and 5 keV for polishing the specimen was used. High-angle annular dark field (HAADF) STEM was performed using an aberration-corrected JEOL JEM-ARM 200 C F microscope operating at an accelerating voltage of 200 kV with 20–27 mrad convergence and 82.6 mrad collection semi-angles. Cross-sectional composition

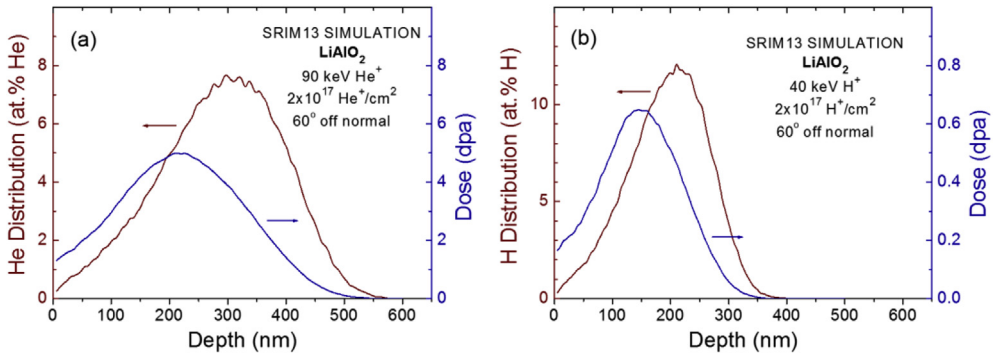

Fig. 1. SRIM simulation of the depth profiles of (a) He atoms and dose and (b) H atoms and dose in $LiAlO_2$ implanted to 2×10^{17} ions/cm^2.