Journal of Nuclear Materials 479 (2016) 542–547

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Combined effects of radiation damage and He accumulation on bubble nucleation in $Gd_2Ti_2O_7$

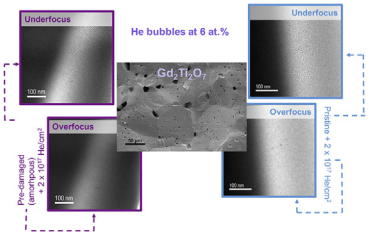
Caitlin A. Taylor [a, *], Maulik K. Patel [a], Jeffery A. Aguiar [b, c], Yanwen Zhang [d, a], Miguel L. Crespillo [a], Juan Wen [e, f], Haizhou Xue [a], Yongqiang Wang [f], William J. Weber [a, d]

[a] Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996, USA
[b] Fuel Performance and Design Department, Idaho National Laboratory, Idaho Falls, ID 83415-6188, USA
[c] Material Science Center, National Renewable Energy Laboratory, Golden, CO 80220, USA
[d] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[e] School of Nuclear Science and Technology, Lanzhou University, Lanzhou, Gansu 730000, China
[f] Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

HIGHLIGHTS

- He bubbles not formed in amorphous $Gd_2Ti_2O_7$ implanted with 2×10^{16} He/cm^2, even after additional irradiation at 300 to 700 K.
- He bubbles, 1.5 and 2.1 nm diameter, respectively, observed in amorphous and pristine $Gd_2Ti_2O_7$ implanted to 2×10^{17} He/cm^2.
- The critical He dose for bubble nucleation is estimated to be 6 at.% He.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 March 2016
Received in revised form
24 May 2016
Accepted 19 July 2016
Available online 22 July 2016

Keywords:
Pyrochlore
Helium bubble
Radiation damage
Nuclear waste

ABSTRACT

Pyrochlores have long been considered as host phases for long-term immobilization of radioactive waste nuclides that would undergo α-decay for hundreds of thousands of years. This work utilizes ion-beam irradiations to examine the combined effects of radiation damage and He accumulation on bubble formation in $Gd_2Ti_2O_7$ over relevant waste-form timescales. Helium bubbles are not observed in pre-damaged $Gd_2Ti_2O_7$ implanted with 2×10^{16} He/cm^2, even after post-implantation irradiations with 7 MeV Au^{3+} at 300, 500, and 700 K. However, He bubbles with average diameters of 1.5 nm and 2.1 nm are observed in pre-damaged (amorphous) $Gd_2Ti_2O_7$ and pristine $Gd_2Ti_2O_7$, respectively, after implantation of 2×10^{17} He/cm^2. The critical He concentration for bubble nucleation in $Gd_2Ti_2O_7$ is estimated to be 6 at.% He.

1. Introduction

Nuclear waste from reactors and legacy weapons programs contains actinides, such as ^{239}Pu, ^{237}Np, ^{241}Am, and ^{244}Cm. Long-lived actinides (e.g. ^{239}Pu with a half-life of 24,100 years and ^{237}Np with a half-life of 2.1 million years) pose the greatest health threat [1]. In addition, substantial quantities of excess Pu from retired weapons [2] and Pu separated from commercially-generated spent fuel currently exist in several countries [3]. One potential solution involves immobilization of the actinides in nuclear waste-forms, which are then deposited in a geological repository for long-term storage. Current host matrices under

* Corresponding author.
E-mail address: ctayl105@vols.utk.edu (C.A. Taylor).

http://dx.doi.org/10.1016/j.jnucmat.2016.07.043
0022-3115/

consideration for use as nuclear waste-forms include glasses and crystalline ceramics. Glasses provide the simplest approach to actinide immobilization, as fewer separation steps are required; however, actinide solubility in glasses is a concern for separated actinides [2]. Multiphase crystalline waste-forms can be tailored for complex nuclear wastes, with one or more phases acting as host phases for actinides. In the case of separated actinides, both single-phase and multiphase waste-forms have been proposed [2,3]. Crystalline ceramics, while more difficult to fabricate, provide improved chemical durability over glass waste-forms due to actinides being incorporated and bonded into lattice site positions. In addition, crystalline ceramics offer a more predictable landscape for actinide immobilization than less durable materials that rely heavily on engineered barriers and the geological repository mineralogy itself to contain the radioisotopes. Natural analogues to crystalline ceramics provide validation data on the performance of mineral-like ceramics under long-term storage conditions. Complex ceramics, e.g. pyrochlore, zirconolite, and monazite, are particularly useful as they offer a variety of lattice sites, allowing for incorporation of actinides of varying size and valence state [1,4].

Actinide-containing waste-forms must be able to withstand α-decay from the incorporated actinides for hundreds of thousands of years, with the rate of α-decay varying with actinide type and concentration. Each α-decay event will produce one α-recoil nucleus (~100 keV) and one α-particle, or He nucleus, (~5 MeV), resulting in significant damage and He accumulation over geological time. This work focuses on pyrochlores, an $A_2B_2O_7$ structure, where actinides can occupy the A-site (2+, 3+) and B-site (4+, 5+). The pyrochlore matrix has long been considered as a potential actinide immobilization host phase [5–8]. Ion-irradiation studies have shown that $Gd_2Ti_2O_7$, like all other titanate pyrochlores, amorphizes under irradiation [9–11]. Previous work on $Gd_2Ti_2O_7$ doped with ^{244}Cm showed that amorphization results from the overlap of amorphous tracks produced by α-recoils and spontaneous fission fragments [12]. $Gd_2Ti_2O_7$ becomes fully amorphous at a dose of ~0.2 dpa or within the first several hundred years of waste-form storage depending on actinide content [9]. The leach rates of Gd and Ti ions from irradiated $Gd_2Ti_2O_7$ placed in 90 °C nitric acid solution increased by a factor of 15 due to irradiation-induced amorphization [13]. While the amorphous state is stable, helium accumulation may result in bubble nucleation and growth over geological time, which could place additional stresses on the material that instigate crack formation. Cracks would provide a direct path for groundwater to enter the waste-form, potentially increasing the leach rate of radioactive material. Helium bubbles several nanometers in diameter have been observed in fluorite-structured materials (e.g. AmO_2 [14] and yttria-stabilized zirconia [15]) and in amorphous borosilicate glass [16,17]; however, to the best of our knowledge, He bubbles have not been previously studied in any pyrochlore composition. Transmission electron microscopy (TEM) measurements revealed bubble formation and growth after implantation of a few atomic percent He in nuclear glass [16,17], and similar behavior might be expected in amorphous $Gd_2Ti_2O_7$. In this work, various ion-beam irradiations and He implantation experiments were performed to study the effects of combined radiation damage and He accumulation on bubble nucleation and growth in the pyrochlore $Gd_2Ti_2O_7$ over relevant waste-form timescales.

2. Experimental methods

$Gd_2Ti_2O_7$ samples were prepared using conventional solid-state synthesis by mixing Gd_2O_3 and TiO_2 powders in stoichiometric ratios, ball milling, pressing the powders into individual pellets using a room temperature uniaxial press, and sintering in air. Samples were ~12.7 mm in diameter after sintering and estimated to be 94% theoretical density using the Archimedes method. The as-synthesized samples, which had a typical grain size of 50–80 μm (Fig. 1), were polished using diamond lapping film down to 1 μm and finished using a 0.02 μm colloidal silica solution to remove residual polishing damage. Table 1 summarizes all irradiation conditions utilized in this work. All samples were pre-damaged with 7 MeV Au^{3+} to a fluence of 2.2×10^{15} Au/cm^2 (6 dpa at the damage peak) using a 3 MV tandem accelerator at the University of Tennessee's Ion Beam Materials Laboratory [18]. The ion flux was kept constant (8.1×10^{11} ions/cm^2/s) during the Au irradiation, and the ion beam was rastered (at scanning frequencies of 517 and 64 Hz for the horizontal and vertical directions, respectively, and a current density of 3.89 nA/mm^2) over an irradiated area of 10.2 × 10.2 mm to ensure a uniform irradiation over a majority of the pellet surface. A glass scintillator and a CCD camera were used to accurately locate the ion beam. Following He implantations (described below), some samples were further irradiated at 300, 500 and 700 K under the same 7 MeV Au^{3+} conditions. In the case of high temperature irradiation of the He-implanted samples, the temperature was controlled using a HRN (LPS-800-1) heater controller from Thermionics Northwest Inc. The room temperature Au irradiations produced a beam heating of ~50 °C, as measured by a type K thermocouple at the sample surface. More details about the high temperature irradiations capability can be found in the description of the UT-IBML facility [18]. The Au irradiation dose in these samples exceeds that required for full amorphization (Fig. 2) and corresponds to the total damage accumulation expected over 50–1000 years in a waste form containing 5 wt% minor actinides and 1000–10,000 years in a waste-form containing 20 wt% ^{239}Pu [1,4], as shown in Fig. 2. This pre-damage step induces the pyrochlore to amorphous phase transformation that would occur due to α-recoil damage during interim or early storage times (several hundred to several thousand years); furthermore, this phase transformation will occur prior to any significant He accumulation in an actual nuclear waste-form. Samples were implanted with either 200 keV He^+ to fluences of 2×10^{15} and 2×10^{16} He/cm^2 (0.1 and 1.0 at.% He at the peak, projected range (R_p ~ 900 nm) or with 65 keV He^+ to a fluence of 2×10^{17} He/cm^2 (12 at.% He at the peak, R_p ~ 450 nm) using the 200 kV Danfysik Research Implanter at Los Alamos National Laboratory's Ion Beam Materials Laboratory. The ion fluxes utilized for the He implantations were 1.1×10^{13} ions/cm^2/s for the 200 keV implantations and 7.39×10^{12} ions/cm^2/s for the 65 keV implantations. Damage dose and He concentration values were simulated using full cascade mode in the Monte Carlo code Stopping and Range of Ions in Matter (SRIM) [19], with all

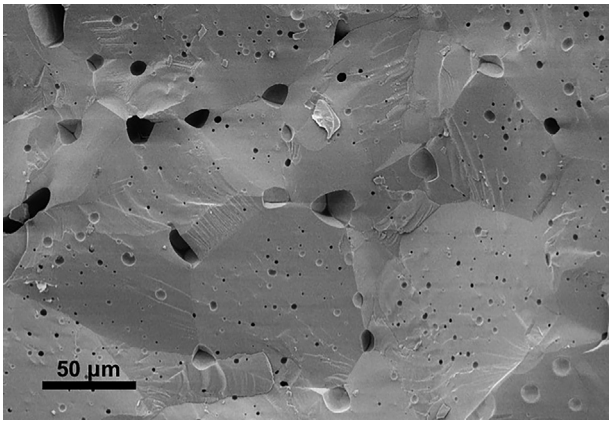


Fig. 1. SEM backscattered electron image obtained from a fractured as-synthesized $Gd_2Ti_2O_7$ pellet.