Radiation-induced grain subdivision and bubble formation in U₃Si₂ at LWR temperature

Tiankai Yao a, Bowen Gong a, Lingfeng He b, Jason Harp b, Michael Tonks c, Jie Lian a, *

a Department of Mechanical, Aerospace & Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States
b Idaho National Laboratory, Idaho Falls, ID 83415, United States
c Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, United States

ABSTRACT

U₃Si₂, an advanced fuel form proposed for light water reactors (LWRs), has excellent thermal conductivity and a high fissile element density. However, limited understanding of the radiation performance and fission gas behavior of U₃Si₂ is available at LWR conditions. This study explores the irradiation behavior of U₃Si₂ by 300 keV Xe⁺ ion beam bombardment combining with in-situ transmission electron microscopy (TEM) observation. The crystal structure of U₃Si₂ is stable against radiation-induced amorphization at 350 °C even up to a very high dose of 64 displacements per atom (dpa). Grain subdivision of U₃Si₂ occurs at a relatively low dose of 0.8 dpa and continues to above 48 dpa, leading to the formation of high-density nanoparticles. Nano-sized Xe gas bubbles prevail at a dose of 24 dpa, and Xe bubble coalescence was identified with the increase of irradiation dose. The volumetric swelling resulting from Xe gas bubble formation and coalescence was estimated with respect to radiation dose, and a 2.2% volumetric swelling was observed for U₃Si₂ irradiated at 64 dpa. Due to extremely high susceptibility to oxidation, the nano-sized U₃Si₂ grains upon radiation-induced grain subdivision were oxidized to nanocrystalline UO₂ in a high vacuum chamber for TEM observation, eventually leading to the formation of UO₂ nanocrystallites stable up to 80 dpa.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

U₃Si₂, combining with advanced claddings, is being considered as a promising ATF concept under active development by Westinghouse Electrical Company LLC, collaborating with multiple national labs and universities. U₃Si₂ displays a high fissile element density up to 11.3 g U/cm³, 17% more uranium loading than UO₂ fuels. U₃Si₂ also displays high thermal conductivity at elevated temperatures (e.g., –25 W/m·K at 1673 K [1]) and a melting temperature of 1665 °C. The superior uranium loading and thermal properties of U₃Si₂ can potentially reduce the operation temperature, enable power uprates, extend fuel cycle, and improve safety margin of the LWR reactor operation.

U₃Si₂ fuel pellets have been fabricated in large quantity through arc melting, atomization, and subsequent sintering [2]. BISON code simulations [3] suggests a significant reduction of fuel temperature as compared with standard UO₂ fuels at all of the investigated burnup conditions. However, simulated temperatures for U₃Si₂ at LWR conditions are higher than 300 °C, necessitating a reevaluation of the available knowledge regarding the irradiation behavior of U₃Si₂ since most radiation data available for U₃Si₂ were obtained at temperatures lower than 250 °C [4]. Historically, U₃Si₂ has been used as a dispersed phase in aluminum plate-type reactor fuel, and the knowledge of radiation behavior under relatively low temperatures (<150 °C) to very high fission density is available [5]. U₃Si₂/Al plate-type dispersed fuel after a burn up of 5.2 × 10²¹ f/cm² showed uniformly-distributed separate small-sized fission gas bubbles and a stable swelling behavior in U₃Si₂ [6]. However, a temperature dependence of bubble morphology was found in U₃Si₂/Al plate fuel irradiated at Advanced Test Reactor (ATR) [4]. At a local life average fuel temperature of 160 °C, there is an appearance of inter-connected abnormally-enlarged fission gas bubbles up to 40 μm after a comparable fission density of 6.1 × 10²¹ f/cm³ [4]. Limited ion beam bombardment experiments were performed on U₃Si₂ at low-temperature regimes [7] with key observations including follows: (1) U₃Si₂ is sensitive to radiation-induced amorphization at...
low temperatures, and the critical amorphization dose is 0.38 dpa (1.5 MeV Kr⁺ irradiations) or $1.1 \times 10^{23}$ fissions/cm³ (neutron irradiation) at 30 °C; (2) A 2.2% volume contraction observed for U₃Si₂ upon radiation-induced amorphization, potentially beneficial for suppressing fission gas mobility; (3) a threshold temperature of 250 °C existing at a dose rate of $1.5 \times 10^{-3}$ dpa/s, above which no amorphization can occur. Very recently, Miao [8] studied irradiation of U₃Si₂ using 1 MeV Kr²⁺ ions at 350 °C and 550 °C, temperatures predicted by BISON code [9] respectively for U₃Si₂ pellet rim and center in LWR condition at a burnup of 30–50 MWD/MTU.

In this study, the irradiation behavior of U₃Si₂ was investigated by 300 keV Xe⁺ ion beam at 350 °C and the microstructure evolution was studied by in-situ TEM observation. U₃Si₂ experienced a radiation-induced grain subdivision initiating at a relatively low dose of 0.8 dpa. A competition between irradiation induced grain polygonization and oxidation of U₃Si₂ was observed due to the high sensitivity of the nano-sized uranium silicides to oxidation. Xe-gas bubbles formed and grow with increased Xe concentration and radiation damage levels. The volumetric swelling of U₃Si₂ was estimated based purely on Xe gas bubble formation and coalescence. Results reported here demonstrate that U₃Si₂ fuel may experience grain subdivision, similar to the rim structure formed in UO₂ oxide fuels in LWR conditions.

2. Experiments

The bulk uranium silicide pellets were prepared through a powder metallurgy method by arc melting of constituent uranium metal and pure silicon and consolidation by conventional high-temperature sintering. The lamella sample for ion beam irradiation was prepared by focused ion beam (FIB) with a uniform thickness of ~100 nm. 300 keV Xe ion irradiation was performed using IVEM-Tandem facility at Argonne National Laboratory, and the ion flux is $6.25 \times 10^{11}$ ions/cm²·s. Irradiation temperature was carefully controlled at 350 °C through a GATAN double-tilt heating stage. After the irradiation temperature was reached, the FIB lamella sample was held for ~30 mins before ion beam irradiation. Microstructure evolution, structural transformation and bubble formation of uranium silicides upon irradiation were closely monitored through bright field transmission electron microscopy (BFTEM) imaging and selected area electron diffraction (SAED) on clean area with little FIB damage. A Hitachi H900 NAR intermediate voltage electron microscope (IVEM) operated at 300 KeV was used for microstructure characterization, and electron beam was turned off during irradiation experiment.

Radiation damage profile and Xe ion distribution were calculated by SRIM 2013 using a quick Kinchin-Pease model SRIM 2013 [10] (Fig. 1), and 61 eV and 15 eV were chosen as the atom displacement energy for uranium atoms as reported in references 5 and silicon atoms, respectively. An incidence angle of 15°, the same as the charged heavy ion incident angle with respect to the normal direction of TEM FIB lamella, was used for the SRIM damage calculation. The calculated damage rate on U₃Si₂ irradiated by 300 keV Xe⁺ ions is 5.03 $\times 10^{-3}$ dpa/s. Xe atomic concentration has a peak value of ~2.78% at a depth of 50 nm for 300 keV Xe⁺ irradiation in U₃Si₂ at an ion fluence of $1 \times 10^{18}$ ions/cm².

The chemical composition of the Xe-irradiated sample was analyzed using a Cameca SX-100 electron probe micro-analyzer (EPMA). Interaction of electron beam with U₃Si₂ FIB lamella is simulated with Casino [11], a software package based on a Monte Carlo simulation of electron trajectories in solids. An operation voltage of 10 keV was selected based on simulation results as electrons generated by the selected accelerating voltage have sufficient energy to penetrate the 100 nm thick FIB U₃Si₂ lamella with limited interaction with the sample holder underneath. Energy dispersive spectrum (EDS) in a large area was also obtained by the EPMA to verify that there are no counts from the holder materials. Five locations were randomly selected through the 10 × 20 μm sample area, and the elemental distribution was averaged to reveal the chemical composition of the sample. The standard deviation of the measured values from 5 locations was estimated as the experimental uncertainty. The standard used for O element was UO₂ and ThSiO₄ was used for O and Si elements.

Post-irradiation TEM images were acquired to further reveal the size and distribution of Xe gas bubbles in the Xe-irradiated U₃Si₂ in complementary to Fresnel contrast imaging from the same area. Under-focused and over-focused TEM images were imported into MATLAB® and converted to RGB values at each pixel and consequently converted to a grayscale value at each pixel. Since gas bubbles show the white contrast in under-focused images and black contrast in over-focused images, the generated images enable us to reveal the location and size of gas bubbles by subtracting gray values at each pixel. Despite this, when analyzing these images, gas bubbles were found to be close to each other, making it hard for the image-processing software to analyze them automatically. Therefore, we manually counted the numbers of bubbles and measured bubble sizes in several randomly-selected regions using ImageJ. Volumetric swelling induced by Xe bubbles was calculated based on the number of Xe bubbles and size measured in 2-dimensional TEM images. We also assume that the Xe gas bubbles are the only source for volumetric swelling and no radiation-induced dimensional change was considered when reporting the volumetric swelling [12].

3. Results and discussion

Due to extreme conditions of high temperature and intensive radiation, it is expected that nuclear fuels experience drastic microstructure evolution and restructuring induced by radiation damage from energetic neutrons (up to 5 MeV) and highly ionizing fission fragments (with energy up to 100 MeV). Materials subjected to intensive displacive damage, e.g., by charged heavy particles, will also experience radiation-induced amorphization and structure transformation under relatively low temperatures, and radiation-induced defects can be recovered at higher temperatures due to a dynamic annealing process. A critical value in determining materials radiation resistance against amorphization is the critical amorphization temperature, above which all of the defects can be recovered and no amorphization can occur anymore. LWR fuel UO₂ and its isostructural oxides with a simple fluorite structure, such as CeO₂ and ZrO₂, exhibit excellent structural stability and resistance against radiation-induced amorphization [13]. Different from oxide fuels, U₃Si₂, an intermetallic compound with a tetragonal crystal
structure, is sensitive to radiation-damage-induced amorphization at low temperature. Both heavy ion and neutron irradiations confirm that $U_3Si_2$ loses its crystal structure and is readily amorphized at a low dose of ~0.3 dpa at room temperature. However, the critical amorphization temperature is as low as ~240 °C due to the thermal recovery of irradiation damage [14].

Since the relevant LWR operation temperature (both inlet and outlet temperatures) is high enough to ensure the temperature of the fuel rim above the critical amorphization temperature of $U_3Si_2$, it is expected that $U_3Si_2$ fuel will be stable against radiation-induced amorphization. This is confirmed by in-situ TEM observation of the 300 keV Xe-irradiated $U_3Si_2$ at 350 °C. Before irradiation, a SAED pattern showing single crystalline features for the FIB lamella was obtained (Fig. 2a), which can be well indexed by $U_3Si_2$ with a tetragonal structure along [010] zone axis. No diffuse halos were observed in the SAED patterns with increased radiation damage levels up to 64 dpa (Fig. 2e), 200 times of the critical dose required to fully amorphize $U_3Si_2$ at room temperature. These results indicate that complete amorphization does not occur in $U_3Si_2$ upon intensive displacive damage, and $U_3Si_2$ as the leading ATF concept is likely stable against radiation-induced amorphization upon energetic neutron damage at reactor conditions.

A distinct feature observed in the SAED for unirradiated $U_3Si_2$ is the existence of weaker diffraction spots of (100), (200) and (300) as indexed in Fig. 2a which can be attributed to the structural modulation and existence of superstructure. The superstructure is typically observed in materials with complex compositions (e.g., minerals) with multiple cations in which a chemical ordering exists due to the distribution of cations on equivalent crystallographic sites. Such an ordered structure is possibly associated with non-stoichiometry of $U_3Si_2$ recently suggested by a DFT study [15]. It still remains open for the structural modulation and chemical ordering of the superstructure observed.

Upon radiation, uranium silicide experiences a rapid order-disorder structural transition as evidenced by the disappearance of the superstructure diffraction spots in SAED patterns at a relatively low dose (~0.8 dpa). In fact, Al$_2$Zr, which share the same crystal structure prototype ($Cu_3Au$) with $U_3Si_2$, readily experience the similar order-to-disorder transition under the exposure to neutron and heavy ion irradiations at a low radiation level of ~1 dpa [16]. Therefore, the order-to-disorder transition does not have appreciable effects on the radiation response of $U_3Si_2$ fuels [17].

In addition to the superstructure, additional subsets of diffractions were also identified that can be indexed to different zone axis [122] (Fig. 2b) and [12T] (Fig. 2c) of $U_3Si_2$. The additional subset diffractions may be due to the existence of the second grain within the FIB lamella or the sample bending from Xe$^+$ irradiation satisfying additional diffraction conditions. Sample bending and appearance of additional subset diffractions were observed by in-situ TEM for CeO$_2$ upon Kr$^+$ irradiation [18]. A close-up look of the SAED pattern for $U_3Si_2$ irradiated to 0.8 dpa shows diffuse spots distinctively on (210) and (011) planes (Fig. 3a), indicating the appearance of sub-grains within the starting $U_3Si_2$ grains. A narrow distribution of extra spots on the arching indicated that those newly formed sub-grains may share small-angle grain boundaries. Similar features on SAED patterns have been reported for HBS in spent UO$_2$ fuel [19], and the variation of sub-grains orientation is very small.

Radiation-induced grain subdivision and polygonization were also observed in Xe-irradiated $U_3Si_2$ at 350 °C, and the grain subdivision initiated a very low radiation level of ~0.8 dpa as evidenced by the diffuse SAED spots (Fig. 3a), the characteristics of nanostructured materials. The grain subdivision as indicated by the appearance of polycrystalline diffraction rings is clearly revealed in the sample irradiated by 24 dpa (Figs. 2c and 3b). The polycrystalline rings were indexed by the tetragonal structure of the $U_3Si_2$ as labeled in Fig. 3b. Accompanying with radiation-induced grain subdivision and polygonization, oxidation of nano-sized $U_3Si_2$ also occurred during ion beam irradiation and in-situ TEM observation, resulting in the appearance of the polycrystalline diffraction rings that can be indexed to UO$_2$ nanocrystals (Fig. 3b). Due to the similarity of some inter-plane spacing between these two compounds, overlaps of the polycrystalline rings from both $U_3Si_2$ and UO$_2$ nanocrystals were observed. Such small lattice mismatch of specific d-spacings between $U_3Si_2$ and UO$_2$ is consistent with the susceptibility of $U_3Si_2$ against oxidation. However, characteristic diffraction rings exist exclusively from $U_3Si_2$, e.g., the (221) plane (see Figs. 2d–e and 3b) which cannot be indexed by

![Fig. 2. Selected area electron diffraction (SAED) patterns of $U_3Si_2$ after irradiation by 300 keV Xe$^+$ at 350 °C at various doses of (a) as received; (b) 0.8 dpa; (c) 24 dpa; (d) 48 dpa; (e) 64 dpa; and (f) 80 dpa.](image-url)
structural parameters of UO₂ or other uranium silicide compounds (e.g., U₃Si₅). This enables the exclusive determination of the nanosized U₃Si₂ and radiation-induced grain subdivision process. The radiation-induced grain subdivision continues with the radiation damage level beyond 64 dpa as evidenced by the fact that the diffraction pattern (Fig. 2e) consists of residual diffractions (e.g., (421) spot and (221) ring) of U₃Si₂.

Microstructural evolution of the Xe-irradiated U₃Si₂ was also closely monitored by BFTEM imaging as a function of irradiation doses (Fig. 4). Throughout the investigated irradiation dose range up to 80 dpa, there is a constant evolution of band contours with irradiation due to irradiation-induced strain. The high density of nano-sized grains showing dark diffraction contrast in the BFTEM image formed upon irradiation dissociated from the original large-sized grains, which become more noticeable with the dose above 24 dpa (Fig. 2c). The formation of nano-sized grains can be attributed to the radiation-induced grain subdivision of U₃Si₂ and oxidation of the nanocrystalline silicides to oxides. It is difficult to differentiate silicide nanocrystals from oxide nanocrystals due to similar diffraction contrast in the BFTEM image as both silicide and oxides coexist as evidenced by the SAED patterns (Fig. 3). These nano-sized grains experience a moderate radiation-induced grain coarsening with the size increasing up to 20 nm at the highest dose of 80 dpa (as shown in Fig. 4f). Radiation-induced grain subdivision and polygonization are well documented in UO₂ oxide fuels at the rim region of the fuel pellets with higher burn-up [20]. The rim structure or high burn-up structure (HBS) is typically characterized as a mesoporous material in which micron-sized pores embedded into the nanocrystalline UO₂ matrix with an average grain size of several hundred nm. The formation mechanism of the HBS is generally considered as a competition between irradiation-induced grain polygonization and grain recrystallization/growth at reactor working temperatures. Fission gas bubbles may also play an important role in which an optimized ratio of grain size/pore size may exist for the formation and stabilization of the HBS. Radiation-induced grain subdivision and polygonization observed here suggest a possible formation of rim structure in U₃Si₂ as the leading ATF fuel during reactor operation. Similar to oxide fuels, the nanostructure remains stable without dissociation or drastic size increase upon high dose radiation (up to 64 dpa) at 350 °C.

Fig. 3. SAED patterns of U₃Si₂ after irradiation by 300 keV Xe⁺ at 350 °C at various doses of (a) 0.8 dpa; (b) 24 dpa; and (c) 80 dpa. Irradiation induced grain polygonization of U₃Si₂ occurs at 0.8 dpa. At 24 dpa, diffraction rings for nano-sized UO₂ grains (red colored) coexist with one for nano-sized U₃Si₂ (green colored). At 80 dpa, nano UO₂ is the dominant phase. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. In-situ bright field TEM images of U₃Si₂ after irradiation by 300 keV Xe⁺ at 350 °C at various doses of (a) as received; (b) 0.8 dpa; (c) 24 dpa; (d) 48 dpa; (e) 64 dpa; and (f) 80 dpa.
The 300 keV Xe\(^{+}\) irradiation-induced grain subdivision at 350 °C observed in this study is consistent with an earlier study of radiation-induced polygonization of U\(_3\)Si\(_2\) by 1.5 MeV Kr\(^{2+}\) at 350 °C [14]. In their study, the starting microstructure was completely refined into a subdivided grain structure at a radiation dose of ~10 dpa; however, the dose to initiate the grain subdivision was not provided. We also performed 1 MeV Kr\(^{2+}\) ion beam irradiation at the same temperature, and the radiation damage-induced grain subdivision also occurs in U\(_3\)Si\(_2\) with the initial dose for grain subdivision between 3 and 4 dpa (data not shown here), which is substantially higher than the 0.8 dpa reported here for 300 keV Xe\(^{+}\). The difference of required dose levels for the onset of grain subdivision could be attributed to the effects of different ion types and energy. For 1.5 MeV Kr ion irradiation, all of the Kr ions penetrated through the TEM samples, and the radiation-induced microstructure evolution is mainly due to the defect accumulation. However, the 300 keV Xe\(^{+}\) beam used in this study will be implanted inside the TEM samples, and the accumulated Xe fission gas atoms lead to the formation of high density nano-sized bubbles (as discussed later). The coupled effects from both Xe atoms and radiation defects may lead to a lower onset dose for grain subdivision.

At higher dose irradiation of 80 dpa, only weak diffraction spots with dim contrast exist for U\(_3\)Si\(_2\), and the dominant diffraction ring patterns can only be indexed to nano-crystalline UO\(_2\) (Fig. 3c), suggesting that almost all of the nano-sized silicides were oxidized to nano-sized UO\(_2\). Using electron microprobe analysis, a substantial amount of oxygen was found in the Xe-irradiated U\(_3\)Si\(_2\) at a dose of 80 dpa at 350 °C (Fig. 5), and the average U/Si ratio is close to stoichiometric U\(_3\)Si\(_2\) confirming the oxidation of the silicide under current experimental conditions. In dry oxidation condition, U\(_3\)O\(_8\) and UO\(_2\) are major oxidation products [21]. While in the appearance of water, hydrogen gas is proposed to form [22]. In low oxygen partial pressure, i.e. high vacuum or protecting environment such as helium gas, the oxidation behavior remains unclear so far with limited oxidation behavior of the silicides.

The transition of micron-sized U\(_3\)Si\(_2\) to nano-sized UO\(_2\) was also observed upon different ion irradiations (e.g., 1 MeV Kr\(^{2+}\)) in the same facility at the same temperature [8]. In their experiment, the formation of nano-sized UO\(_2\) from U\(_3\)Si\(_2\) upon irradiation was attributed to irradiation enhanced/induced oxidation due to the fact that part of the sample which was shielded from irradiation by sample grid remains as crystalline U\(_3\)Si\(_2\). Surrogate Ce\(_3\)Si\(_2\) [2] was also oxidized by proton irradiation with oxides built up on the sample surface at a comparable vacuum level as the TEM utilized here; whereas bulk Ce\(_3\)Si\(_2\) is not oxidized at the same experimental condition. These results suggest that irradiation enhanced/induced oxidation as proposed in Ref. [7] may not be the dominant mechanism for the formation of high-density nano-sized UO\(_2\). Oxidation may occur in U\(_3\)Si\(_2\) at temperature of 350 °C on the timescale of minutes albeit in a low oxygen environment (e.g., 0.2 atm oxygen) [21]. Radiation-induced grain subdivision may play an important role to the oxidation process. It is expected that U\(_3\)Si\(_2\) nano-crystalline maybe more susceptible to oxidation due to the greatly increased density of surfaces and grain boundaries and thus maybe easily be oxidized even in a high vacuum TEM chamber.

In addition to radiation-induced microstructure evolution, fission gas behavior and gaseous swelling of nuclear fuels are also critical for evaluating fuel performance. Fission gas behavior was extensively studied on U\(_3\)Si\(_2\)/Al dispersion fuels with the focus on bubble formation and volumetric fuel swelling. At low temperatures, stable swelling occurs in U\(_3\)Si\(_2\) even at a very high fission density (i.e. burn-up), in contrast to the breakaway swelling observed in many other intermetallic phases including U\(_3\)Si. Visible fission gas bubbles first start to form on grain boundaries and grow slowly as more fission gas atoms are produced. This stable swelling behavior was explained as a result of relatively small and uniform fission gas bubbles that do not have a tendency to coalesce under these conditions. Fission gas behavior in U\(_3\)Si\(_2\) is affected significantly by fission rate, uranium-to-silicon ratio, and temperature. At a very high fission density, the population of bubbles increases and becomes bimodal. At a temperature of 160 °C, large fission gas bubbles with size up to ~40 μm were observed at a fission density of 6.1 × 10\(^{21}\) f/cm\(^3\) as a result of bubble growth [41]. Bubble interconnection also occurred, leading to the breakaway swelling of the fuel particles. However, fission gas behavior in monolithic silicide fuels at relevant reactor operation temperatures has not been reported.

The formation and redistribution of Xe gas bubbles in the 300 keV-irradiated U\(_3\)Si\(_2\) at 350 °C were also investigated and the bubble size/density with respect to irradiation doses was quantitatively analyzed. High-density nano-sized bubbles can be seen by high-resolution bright field TEM images (e.g., Fig. 6a) showing the bright contrast of cavities in the under-focused image (over-focused BFTEM images were not shown here). Xe bubbles with several-nm diameter become pervasive (Fig. 6) at a high dose regime above 24 dpa. However, strong diffraction contrast from high-density nano-sized nanoparticles upon radiation-induced polygonization makes it difficult in determining exact bubble morphologies. To clearly reveal bubble morphology and determine bubble sizes, through-focused BFTEM images were processed to align the under-focused and over-focused images at the exact location by MATLAB\textsuperscript®. As stated in the experiment section, a matrix containing grayscale values for each pixel can be created in MATLAB\textsuperscript®. By simply subtracting the matrix generated from the under-focused image and the over-focused image, a new matrix can be obtained, which contains the difference between these two images. This new matrix was then converted back to an image, which reflects the difference between the aforementioned two images. In the generated image, gas bubbles are in dark color while other regions are in bright color, which makes it much easier to distinguish gas bubbles. The diffraction contrast resulting from nanoparticles is removed such that the bubbles can be clearly revealed (see enhanced contrast images in Fig. 6d–f). Statistical analysis was performed by manually counting the number of bubbles and measuring its size from different areas of the enhanced contrast images, and uncertainties of the bubble size and density were derived based on the standard deviation of the distribution.
distribution of the bubble size can be identified for samples irradiated at different damage levels. It should be recognized the uncertainties are induced in discerning exact bubble morphologies due to small bubble size. In general, there is an appreciable shift of the peak size for Xe bubbles from ~2.0 nm to ~3.5 nm with increased irradiation doses, suggesting a minor bubble growth. In addition to bubble size increase, a decrease of number density at higher irradiation doses is observed due to radiation-induced bubble coalescence. Note that the bubble size studied here is generally smaller than 5 nm, well below the resolution limit of SEM (40 nm) used before for PIE observation of U3Si2/Al dispersed plate fuels shown in previous studies [23]. Interestingly, the sluggish bubble growth observed here with intense radiation at 350 °C is probably due to the low mobility of Xe in silicides. However, this is in contrast to the large size bubble formation/growth up to 50 μm and the breakaway of U3Si2/Al dispersed fuels observed at 160 °C [4]. A surface effect may occur leading to a minimized bubble growth in the 100 nm-thick TEM lamella.

The sluggish bubble growth behavior upon low energy 300 keV Xe+ irradiation in this study is consistent with a recent irradiation study on bulk U3Si2 by high energy 84 MeV Xe+ to 500 dpa at 300 °C [24] showing the formation and a uniform distribution of dense 10 nm Xe gas bubble. The formation of high density nano-sized bubbles with a uniform distribution suggests a favorable fuel gaseous swelling behavior of monolithic U3Si2 fuel in LWR conditions. Post irradiation examination of the ATF-1 U3Si2 fuel burn to ~6 × 1020 fissions/cm³ also shows no run-away swelling and the clear gap between U3Si2 and cladding [24]. These results all together by high energy and low energy Xe irradiations again imply a favorable fission gas behavior. The volumetric fuel swelling in ATF U3Si2 fuel might be different from the previously reported one in a low-temperature research reactor, necessitating a systematically revisist of the fuel swelling behavior at a boarder range of radiation conditions at different doses, rates, and temperature.

Estimated volumetric expansion due to Xe gas bubbles indicates that there is a peak volumetric expansion with radiation damage levels (see Fig. 7b in which the radiation-induced coarsening of nanocrystals is also included). The estimated volumetric swelling increases with irradiation dose up to 64 dpa (0.8% for 24 dpa, and 2.2% for 64 dpa), and then slightly decreases to 80 dpa (1.3%). Note

**Fig. 6.** Xe gas bubble formation and evolution with irradiation doses of (a, d) 24 dpa; (b, e) 64 dpa; and (c, f) 80 dpa, where a, b, and c are under-focused BF TEM images; and d,e,f are processed images to show Xe bubbles size and distribution.

**Fig. 7.** Xe gas bubble size distribution (a) and size of nano-crystalline (b, open square) and estimated volumetric expansion (b, solid square) at various irradiation doses.
that the volumetric swelling is estimated only based on the measured bubble density and size from 2D images and extended to 3D geometry. The uncertainty in determining bubble size and density will propagate into the estimation of the volumetric swelling. In addition, radiation-induced volumetric change is not included, in which a 2.2% volumetric contraction was reported by Ref. [25] due to full amorphization of U3Si2. Volumetric change is also expected to result from the phase transformation from crystalline U3Si2 to nano-sized U3Si2 and eventually, amorphous UO2 since the unit volume of UO2 is 0.162 nm3 while that for U3Si2 with the same U content is 0.209 nm3. Such a reduced free volume is considered beneficial to fission gas retention as it suppresses the fission gas mobility. On the other hand, the incorporation of additional oxygen and other oxides will lead to volumetric expansion. Despite the estimated swelling is less quantitative with uncertainties, the relatively small volumetric swelling (~a few vol.%) resulting from fission gas accumulation only is encouraging. Further experiments performed at higher temperatures and in bulk samples mitigating surface effects are necessary to gain a complete understanding of the fission gas behavior (bubble formation, migration, and growth) in silicide fuels.

4. Conclusions

In this paper, radiation-induced microstructure evolution and fission gas behavior of U3Si2 irradiated by 300 keV Xe+ at 350 °C are studied by in-situ TEM. U3Si2 is resistant against amorphization at reactor operation temperatures even up to a very high dose of 60 dpa. Radiation-induced polygonization and grain subdivision occur in U3Si2 irradiated by 300 keV Xe at 350 °C. The polygonization begins at a low dose ~0.8 dpa and continues beyond 48 dpa. The radiation-induced polygonization leads to the formation of a high density of nanoparticles which experience a grain coarsening with radiation dose up to 80 dpa. Xe bubbles form in the Xe irradiated U3Si2 and a single mode size distribution was observed. A radiation-induced bubble coalescence is also identified, and the estimated volumetric swelling from gas bubbles only is low. Uranium silicide nanoparticles upon radiation-induced grain subdivision are easily oxidized even during in-situ TEM observation, eventually leading to complete oxidation to UO2 nanocrystals stable up to 80 dpa. These results indicated that at relevant reactor operation conditions, uranium silicide as the leading candidate of ATFs is stable against radiation—induced amorphization, but likely experiences a grain subdivision and possibly a rim structure, similar to UO2 fuels.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy under a Nuclear Engineer University Program (award number: DE-NE0008564) and a NSUF R&D award (award! number: 17-835) under DOE Idaho Operations Office Contract DE-AC07-05ID14517 as part of a Nuclear Science User Facilities Experiments. JL also acknowledges the support from a NSF Career Award (award #: DMR 1151028) for the study of radiation interaction with nanostructured oxides. This work is also part an collaboration lead by Westinghouse Electric Company comprising several national laboratories, vendors, and universities awarded in response to the DE-FOA-0000712 funding opportunity.

References