In-Situ TEM Ion Irradiation Investigations on U₃Si₂ at LWR Temperatures

Yinbin Miao^{a,*}, Jason Harp^b, Kun Mo^a, Sumit Bhattacharya^c,
Peter Baldo^a, Abdellatif M. Yacout^a

^aArgonne National Laboratory, Lemont, IL 60439, United States

^bIdaho National Laboratory, Idaho Fall, ID 83415, United States

^cNorthwestern University, Evanston, IL 60208, United States

Abstract

The radiation-induced amorphization of U₃Si₂ was investigated by *in-situ* transmission electron microscopy using 1 MeV Kr ion irradiation. Both arc-melted and sintered U₃Si₂ specimens were irradiated at room temperature to confirm the similarity in their responses to radiation. The sintered specimens were then irradiated at 350°C and 550°C up to 7.2×10^{15} ions/cm² to examine their amorphization behavior under light water reactor (LWR) conditions. U₃Si₂ remains crystalline under irradiation at LWR temperatures. Oxidation of the material was observed at high irradiation doses.

Keywords: nuclear fuel, accident tolerant fuel, uranium silicide, ion irradiation, *in-situ* TEM

1. Introduction

The tsunami and subsequent nuclear accident in Fukushima stimulated global efforts to search for nuclear fuels with enhanced accident tolerance. The accident tolerant fuel (ATF) program aims to replace the conventional UO₂-zirconium alloy solution with a novel fuel design that can withstand a loss of coolant accident (LOCA) for a significantly longer period of time[1]. Having superior thermal conductivity and uranium density compared to UO₂[2], U₃Si₂ has been widely regarded as a promising ATF candidate[3, 4]. To evaluate the qualification of U₃Si₂ as a LWR fuel, its fuel performance, especially fission gas behavior, must be experimentally examined. In addition, development of advanced fuel performance codes that can precisely predict the fuel behavior of U₃Si₂ in LWRs calls for experimental microstructural references and validations of fission gas behavior. Previous studies on arc-melted U₃Si₂ at research reactor temperatures (<250°C) show that ion irradiation completely amorphizes U₃Si₂ at a very low dose level (approximately 0.3 dpa)[5]. As amorphization significantly alters the microstructure of the material, and therefore interferes with the evolution of fission gas bubbles[6, 7], the radiation-induced amorphization behavior of U₃Si₂ at LWR temperatures (from approximately 350°C to 800°C) must be well characterized. In addition, when cold pressing and sintering technique is used in fabrication, the microstructure of produced U₃Si₂ fuel pellets features reduced

*Addr: 9700 S. Cass Ave., Lemont, IL 60439, United States Tel: 630-252-7448 Email: ymiao@anl.gov (Y. Miao)

grain size, and precipitation of secondary phases such as USi and UO₂[8]. This difference in microstructure may also lead to amorphization behaviors different from those in the arc-melted fuel material. Therefore, it is important to understand and characterize any difference in irradiation behavior of the U₃Si₂ samples fabricated by the aforementioned methods. Although in-pile irradiation tests are essential to provide reliable experimental data describing material behavior in nuclear reactors, ion irradiation provides an inexpensive and time-saving option to obtain valuable qualitative information about irradiation effects on nuclear materials. In this regard, the combination of transmission electron microscopy (TEM) and *in-situ* ion irradiation makes it possible to capture the kinetics of radiation-induced microstructural modifications[9], including amorphization[5, 10, 11, 12], in materials. Therefore, an *in-situ* TEM ion irradiation technique was utilized in this study to characterize the amorphization behavior of U₃Si₂ at LWR conditions.

2. Experiments

Fine uranium powder (92.5 wt.%) and silicon powder (7.5 wt.%) were mixed and pressed at 225 MPa. The powder mixture was then arc melted to produce U₃Si₂ ingots. To fabricate U₃Si₂ pellets, the arc-melted ingots were further comminuted into fine powder. The U₃Si₂ powder was then cold pressed and sintered in an Ar atmosphere to form fuel pellets using the same technique as for samples irradiated in-pile for the ATF-1 campaign. The details of this fabrication can be found in Ref. [8]. The arc-melted ingot are relatively pure, containing only 1.5 vol.% U₃Si precipitates, whereas the sintering technique introduced USi and UO₂ secondary phases comprising approximately 14 vol.%. Both arc-melted (ingots) and sintered (pellets) samples were investigated in this study. TEM thin foils were prepared from each material by focused ion beam (FIB) technique using an FEI HELIOS NanoLab 600 DualBeam FIB/SEM. *In-situ* TEM ion irradiation investigations were performed at the IVEM-Tandem facility at Argonne National Laboratory (ANL); the TEM thin foils were irradiated with 1 MeV Kr ions. SRIM[13] was used to estimate the Kr ion radiation dose following the approach described by Stoller et al.[14] The displacement energy of uranium was selected to be 61 eV as predicted by Beeler et al. using low-energy cascade simulation[15, 16], while a trivial value of 15 eV was used as the displacement energy of silicon. According to the SRIM simulation, for a 50 nm thick U₃Si₂ TEM foil, 1 dpa radiation damage is achieved at an ion influence of 3.6×10^{14} ions/cm². To evaluate the radiation responses of the arc-melted and the sintered samples, ion irradiation was first carried out at room temperature for comparison with previous studies by Birtcher et al. on arc-melted U₃Si₂[5]. Thereafter, two typical LWR temperatures, 350°C and 550°C, were selected to apply on U₃Si₂ specimens according to the BISON simulation[4]. The responses of sintered U₃Si₂ TEM specimens to ion irradiation were examined at both temperatures.

3. Results and Discussion

Before ion irradiation, the arc-melted specimen contains stacking faults as shown in Fig. 1(a). The tetragonal U₃Si₂ crystal structure[17] is clearly illustrated by the diffraction pattern at the [110] zone (Fig. 1(b)). During room temperature irradiation, the majority of the arc-melted U₃Si₂ TEM foil becomes amorphous at merely 3.6×10^{13} ions/cm² (0.1 SRIM dpa); only a residual (2 $\bar{2}$ 0) spot can be distinguished (Fig. 1(c) and (d)). When the ion fluence increases to 1.08×10^{14} ions/cm² (0.3 SRIM dpa), the specimen is completely amorphized (Fig. 1(e) and (f)). After Kr irradiation to 3.6×10^{13} ions/cm², the diffraction contrast from the stacking faults vanishes due to

the loss of long-distance order. The only contrast in TEM images comes from the mass-thickness contrast at a thin area (see the yellow circles in Fig. 1). The approximately 0.3 dpa amorphization threshold at room temperature is consistent with previous studies on arc-melted U_3Si_2 using 1.5 MeV Kr ions[5].

Figure 1: Amorphization of arc-melted U_3Si_2 irradiated by 1 MeV Kr at room temperature: (a)/(b) Prior to ion irradiation, the arc-melted specimen contains stacking faults and shows clear U_3Si_2 diffraction pattern; (c)/(d) the majority of the U_3Si_2 phase becomes amorphous at 3.6×10^{13} ions/cm² (0.1 SRIM dpa), eliminating the preexistent stacking faults; (e)/(f) full amorphization occurs at 1.08×10^{14} ions/cm² (0.3 SRIM dpa).

Due to their reduced grain size and fabrication-introduced secondary phases, the sintered U_3Si_2 TEM foil irradiated at room temperature contains at least three grains (G1, G2, and G3) and a precipitate (P1), as shown in Fig. 2(a). Electron diffraction patterns (Fig. 2(b)) confirm that all three grains belong to the U_3Si_2 matrix phase, and that the precipitate is UO_2 . At 3.6×10^{13} ions/cm² (0.1 SRIM dpa), two of the matrix grains (G1 and G3 in Fig. 2(c) and (d)) become fully amorphous. Due to the amorphization, the grain boundary between G1 and G3 disappears. Meanwhile, the other matrix grain (G2) only becomes partially amorphous; its diffraction pattern can still be distinguished. As the ion fluence arrives at 1.08×10^{14} ions/cm² (0.3 SRIM dpa), all three of the U_3Si_2 grains become fully amorphous (Fig. 2(e) and (f)). The diffraction contrast of the three grains fades during amorphization, leaving mass-thickness as the only major source of the image contrast. Matrix grain G2 still appears brighter than G1 and G3 after full amorphization, which implies that G2 is thinner than the other two grains. This difference in thickness may originate from preferential etching of the different crystallographic orientations during FIB milling. This orientation variance and consequent directional dependence of threshold displacement energy/channeling effect could also account for the different amorphization rates of the three grains. Namely, the specific orientation of G2 could result in a channeling effect during ion irradiation, leading to slightly lower effective radiation doses (dpa values). Due to the nature

of sintering, there are preexisting voids in the sintered U_3Si_2 specimen. Those voids were found to remain stable during the amorphization process (Fig. 2(a), (c), and (e)). The UO_2 precipitate also remains crystalline throughout the ion irradiation experiment, which is consistent with the excellent radiation tolerance of UO_2 . The comparable amorphization threshold (approximately 0.3 dpa) of the two types of U_3Si_2 samples confirms that U_3Si_2 fabricated through these two different techniques has similar irradiation-induced amorphization behavior. The subsequent high-temperature experiments, performed on the cold pressed and sintered U_3Si_2 pellet samples, can therefore be assumed to represent U_3Si_2 fabricated by either technique.

Figure 2: Amorphization of cold pressed and sintered U_3Si_2 irradiated by 1 MeV Kr at room temperature: (a)/(b) prior to ion irradiation, three crystalline U_3Si_2 grains (G1, G2, and G3) and one UO_2 precipitate (P1) were identified in the specimen; (c)/(d) at 3.6×10^{13} ions/cm² (0.1 SRIM dpa), G1 and G3 become completely amorphous, whereas G2 has distinguishable diffraction pattern, showing various amorphization rates depending on crystallographic orientation; (e)/(f) At 1.08×10^{14} ions/cm² (0.3 SRIM dpa), all three grains become completely amorphous, while the UO_2 precipitate remains stable and crystalline during the ion irradiation at room temperature.

Previous *in-situ* TEM ion irradiation experiments[5] showed that arc-melted U_3Si_2 preserves its crystal structure up to 1.6 dpa at approximately 250°C. In order to confirm this resistance to amorphization at LWR temperatures, the sintered U_3Si_2 TEM foils were irradiated at 350°C and 550°C, respectively. Each specimen contains at least two U_3Si_2 grains, as shown in Figs. 3(a) and 4(a). At both typical LWR temperatures, the U_3Si_2 phase maintains its crystalline structure up to 1.8×10^{15} ions/cm² (5.0 SRIM dpa). This indicates that after the recovery mechanism is activated at approximately 240°C[5], the U_3Si_2 phase continues to have resistance to irradiation-induced amorphization up to 550°C. Amorphization is therefore not expected to be a significant concern for U_3Si_2 LWR fuel material at low dose, especially for the sintered U_3Si_2 pellets investigated in this study. To examine the amorphization behavior of U_3Si_2 at high irradiation dose that corresponds to the typical LWR cycle length, in-pile irradiation (e.g. ATF-1 campaign) or

high-energy *ex situ* ion irradiation experiments[18, 19] are necessary.

Figure 3: Cold pressed and sintered U₃Si₂ specimens irradiated by 1 MeV Kr at 350°C: both U₃Si₂ grains remain crystalline up to 1.8×10¹⁵ ions/cm² (5.0 SRIM dpa).

Figure 4: Cold pressed and sintered U₃Si₂ specimens irradiated by 1 MeV Kr at 550°C: both U₃Si₂ grains remain crystalline up to 1.8×10¹⁵ ions/cm² (5.0 SRIM dpa).

It was observed that at these elevated temperatures (350°C and 550°C), nanoscale crystalline domains start to form within the TEM foils at the beginning of ion irradiation (Figs. 3 and 4) and become prominent beyond approximately 1.8×10¹⁵ ions/cm² (Fig. 5(a) and (b)). Electron diffraction patterns indicate that this nanocrystalline phase is solely UO₂ (Fig. 5(f)), implying oxidation of the U₃Si₂ specimens at high temperatures under ion irradiation. At 7.2×10¹⁵ ions/cm² (20 SRIM dpa), the electron diffraction patterns indicate that the TEM foils irradiated at both LWR temperatures become completely oxidized. That is, UO₂ is the only distinguishable crystalline

Figure 5: The oxidation of U_3Si_2 irradiated at high temperatures: (a)/(b) bright field TEM images of U_3Si_2 TEM foils irradiated to $7.2 \times 10^{15} \text{ ions/cm}^2$ (20 SRIM dpa) at 350°C and 550°C , respectively, showing nanocrystalline grains; (c) the bright field TEM image of both unoxidized and oxidized regions of a TEM foil irradiated at 550°C , showing that oxidation only occurs in the irradiated region; (d) electron diffraction pattern of the U_3Si_2 TEM foil irradiated at 350°C ; (e)/(f) electron diffraction patterns of the unoxidized and oxidized regions in the U_3Si_2 TEM foil irradiated at 550°C .

phase in the specimen, as shown in Fig. 5(d) and (f). Meanwhile, the bright field images (Fig. 5(a) and (b)) show nanocrystalline UO_2 grains included in an amorphous matrix. Both diffraction contrast images and diffraction patterns imply that the U_3Si_2 turns into UO_2 nano-grains and a Si-enriched amorphous phase. Previous corrosion studies on U-Si compounds indicate that U and Si oxidize simultaneously, forming silicon oxide, residual silicon, and various uranium oxides at different temperatures[20, 21]. Both silicon and its oxide readily amorphize under ion irradiation at room temperature[22, 23], whereas silicon oxide has a considerably lower amorphization threshold dose at elevated temperatures[24, 25]. Therefore, the Si-enriched amorphous phase is more likely to be silicon oxide. The measured UO_2 nano-grain size in the specimen irradiated at 550°C is larger than that in the foil irradiated at 350°C (approximately 85 nm vs. 40 nm). In the TEM thin foil irradiated at 550°C, around one third of the area was blocked by the sample grid during the ion irradiation (Fig. 5(c)). As a result, the area that was not irradiated maintains its crystalline U_3Si_2 phase throughout the experiment. Thus, it is clear that the oxidation of the TEM foils is not solely due to the elevated temperatures. Instead, the oxidation is either radiation induced or radiation enhanced. In a TEM chamber, the typical vacuum is approximately 1.5×10^{-5} Pa. Assuming that the gas composition within the TEM chamber is similar to air, the oxygen content in the chamber is approximately 2.77×10^8 molecules/cm³. A typical $5 \mu\text{m} \times 5 \mu\text{m} \times 50 \text{ nm}$ TEM foil contains approximately 3.6×10^{10} uranium atoms. Therefore, while the oxygen content in the TEM chamber is low, it is still enough to oxidize the entire TEM thin foil. This phenomenon indicates that U_3Si_2 can readily oxidize into nanocrystalline UO_2 and a Si-enriched amorphous phase under irradiation at LWR temperatures, even in this environment with low oxygen partial pressure. At LWR temperatures (400°C and 800°C), similar oxidation behavior was observed on the surfaces of bulk Ce_3Si_2 (a non-radioactive surrogate of U_3Si_2) pellets irradiated by 2 MeV protons at a background vacuum of 8×10^{-4} Pa[26], implying that surface oxidation of fuel pellets may be an issue for U_3Si_2 during normal operation of LWRs. Thus, this finding may illuminate future studies of the corrosion behavior of U_3Si_2 fuel material under irradiation.

4. Conclusions

In this study, *in-situ* TEM ion irradiation investigations were conducted to characterize the response of U_3Si_2 to 1 MeV Kr ion irradiation. The cold pressed and sintered U_3Si_2 was proven to have similar amorphization behavior to the arc-melted U_3Si_2 samples. The amorphization behavior is also consistent with previous studies on arc-melted U_3Si_2 [5]. In contrast, the U_3Si_2 was found to remain crystalline up to 5 SRIM dpa at LWR temperatures, implying that amorphization is not a major concern at low dose for U_3Si_2 as a LWR fuel material. Additionally, at LWR temperatures, ion irradiated U_3Si_2 was observed to readily oxidize into a mixture of nanocrystalline UO_2 and a Si-enriched amorphous phase even in the TEM vacuum. This finding may direct future study on the corrosion resistance of U_3Si_2 under irradiation.

5. Acknowledgment

This work was funded by the Accident Tolerant Fuel High-Impact Problems (ATF HIP) of the U.S. Department of Energy (DOE)'s Nuclear Energy Advanced Modeling and Simulation (NEAMS) program. The efforts involving Argonne National Laboratory, including the use of the IVEM-Tandem Facility, were sponsored under Contract no. DE-AC02-06CH11357 between

UChicago Argonne, LLC and the U.S. Department of Energy. This work made use of the EPIC facility (NUANCE Center-Northwestern University), which has received support from the MRSEC program (NSFDMR-1121262) at the Materials Research Center; the Nanoscale Science and Engineering Center (NSFEEC-0647560) at the International Institute for Nanotechnology; and the State of Illinois, through the International Institute for Nanotechnology.

Fabrication of the samples used in this work was supported by the U.S. Department of Energy, Office of Nuclear Energy. Fabrication was part of a collaboration led by Westinghouse Electric Company comprising several national laboratories, vendors, and universities awarded in response to the DE-FOA-0001063 funding opportunity. The authors would like to acknowledge the assistance of the support staff associated with the Fuels Applied Science Building at Idaho National Laboratory specifically Rita Hoggan for preparing samples for FIB liftouts.

References

- [1] S. J. Zinkle, K. A. Terrani, J. C. Gehin, L. J. Ott, L. L. Snead, *Journal of Nuclear Materials* 448 (2014) 374–379.
- [2] J. White, A. Nelson, J. Dunwoody, D. Byler, D. Safarik, K. McClellan, *Journal of Nuclear Materials* 464 (2015) 275–280.
- [3] J. Carmack, K. Barrett, H. MacLean-Chichester, *Light Water Reactor Accident Tolerant Fuels Irradiation Testing*, Technical Report, Idaho National Laboratory (INL), Idaho Falls, ID (United States), 2015.
- [4] K. Metzger, T. Knight, R. Williamson, in: *Proceedings of the International Congress on Advances in Nuclear Power Plants–ICAPP 2014*, Charlotte, NC.
- [5] R. Birtcher, J. Richardson, M. Mueller, *Journal of nuclear materials* 230 (1996) 158–163.
- [6] G. L. Hofman, *Journal of Nuclear Materials* 140 (1986) 256–263.
- [7] Y. S. Kim, G. Hofman, J. Rest, A. Robinson, *Journal of Nuclear Materials* 389 (2009) 443–449.
- [8] J. M. Harp, P. A. Lessing, R. E. Hoggan, *Journal of Nuclear Materials* 466 (2015) 728–738.
- [9] W.-Y. Chen, J. Wen, M. A. Kirk, Y. Miao, B. Ye, B. R. Kleinfeldt, A. J. Oaks, J. F. Stubbins, *Philosophical Magazine* 93 (2013) 4569–4581.
- [10] R. Birtcher, J. Richardson, M. Mueller, *Journal of nuclear materials* 244 (1997) 251–257.
- [11] L. Wang, S. Wang, R. Ewing, *Philosophical Magazine Letters* 80 (2000) 341–347.
- [12] J. Lian, J. Chen, L. Wang, R. C. Ewing, J. M. Farmer, L. A. Boatner, K. Helean, *Physical Review B* 68 (2003) 134107.
- [13] J. F. Ziegler, M. D. Ziegler, J. P. Biersack, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 268 (2010) 1818–1823.
- [14] R. E. Stoller, M. B. Toloczko, G. S. Was, A. G. Certain, S. Dwaraknath, F. A. Garner, *Nuclear instruments and methods in physics research section B: beam interactions with materials and atoms* 310 (2013) 75–80.
- [15] B. Beeler, C. Deo, M. Baskes, M. Okuniewski, in: *2012 ANS Annual Meeting and Embedded Topical Meeting: Nuclear Fuels and Structural Materials for the Next Generation Nuclear Reactors, NFSM 2012*; Chicago, IL; United States; 24 June 2012 through 28 June 2012;.
- [16] Y. Miao, B. Beeler, C. Deo, M. I. Baskes, M. A. Okuniewski, J. F. Stubbins, *Journal of Nuclear Materials* 456 (2015) 1–6.
- [17] K. Remschnig, T. Le Bihan, H. Noël, P. Rogl, *Journal of Solid State Chemistry* 97 (1992) 391–399.
- [18] M. Pellin, A. M. Yacout, K. Mo, J. Almer, S. Bhattacharya, W. Mohamed, D. Seidman, B. Ye, D. Yun, R. Xu, et al., *Journal of Nuclear Materials* 471 (2016) 266–271.
- [19] D. Yun, Y. Miao, R. Xu, Z. Mei, K. Mo, W. Mohamed, B. Ye, M. J. Pellin, A. M. Yacout, *Journal of Nuclear Materials* 471 (2016) 272–279.
- [20] S. Krummacher, D. Sarma, *Surface Science* 178 (1986) 842–849.
- [21] K. H. Kang, K. S. Kim, K. J. Kim, Y. C. Seo, Y. M. Park, *Journal of nuclear materials* 228 (1996) 220–226.
- [22] L. Pelaz, L. A. Marqués, J. Barbolla, *Journal of applied physics* 96 (2004) 5947–5976.
- [23] R. K. Eby, R. C. Ewing, R. C. Birtcher, *Journal of materials research* 7 (1992) 3080–3102.
- [24] L. Wang, S. Wang, W. Gong, R. Ewing, W. Weber, *Materials Science and Engineering: A* 253 (1998) 106–113.
- [25] R. Goldberg, J. Williams, R. Elliman, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 106 (1995) 242–247.
- [26] J. Blanchard, D. Butt, M. Meyer, P. Xu, *Development of Advanced High Uranium Density Fuels for Light Water Reactors*, Technical Report Project No. 11-3041, U.S. Department of Energy Nuclear Energy University Programs (NEUP) Final Report, 2016.