Thermal Stability of Fission Gas Bubble Superlattice in Irradiated U-10Mo Fuel

J. Gan*, D.D. Keiser, Jr.; B.D. Miller; A.B. Robinson, D.M. Wachs, and M.K. Meyer

Nuclear Fuels and Materials Division, Idaho National Laboratory
P. O. Box 1625, Idaho Falls, ID 83415-6188 U.S.A.

*Corresponding Author Contact Information:

Dr. Jian Gan
Nuclear Fuels and Materials Division
Idaho National Laboratory
P.O. Box 1625
Idaho Falls, ID, 83415-6188 U.S.A.
Phone: 1 (208) 533-7385
Fax: 1 (208) 533-7863
E-mail: Jian.Gan@inl.gov

For submission to *Journal of Nuclear Materials*
March 2014

This manuscript has not been published elsewhere
and has not been submitted simultaneously for publication elsewhere.

© Battelle Energy Alliance, LLC, 2011

© 2015. This manuscript version is made available under the Elsevier user license
<http://www.elsevier.com/open-access/userlicense/1.0/>

KEYWORDS

Bubble superlattice; transmission electron microscopy; U-10Mo; in-situ heating; stability

ABSTRACT

To investigate the thermal stability of the fission gas bubble superlattice, a key microstructural feature in both irradiated U-7Mo dispersion and U-10Mo monolithic fuel plates, a focused ion beam-transmission electron microscopy (FIB-TEM) sample of irradiated U-10Mo fuel with a local fission density of 3.5×10^{21} fissions/cm³ was used for an in-situ heating TEM experiment. The temperature of the heating holder was raised at a ramp rate of approximately 10°C/min up to ~700°C, kept at that temperature for about 34 min and further increased to 850°C with a reduced rate of 5°C/min. The result shows a high thermal stability of the fission gas bubble superlattice. The implication of this observation on the fuel microstructural evolution and performance under irradiation is discussed.

1. INTRODUCTION

The formation of a gas bubble superlattice (GBS) in metals irradiated with gas ions has been investigated extensively by Johnson and others in the past [1-14]. The modeling efforts on the mechanisms of the development of self-organization nanostructures as a result of irradiation are outlined by Ghoniem et al [15]. GBS formations are reported in body-center-cubic (bcc), face-center-cubic (fcc), and hexagonal metals irradiated with noble gas helium, neon, and krypton ions. The degree of ordering varies depending on the material, ion species, and irradiation condition. The work on helium-irradiated Mo indicates that the development of a GBS occurs between the irradiation temperatures of $\sim 0.15T_m$ and $0.35T_m$ (T_m the melting point) [13]. For Mo the melting temperature and the corresponding irradiation temperature window are 2623°C and 161-741°C, respectively. GBS formation of Xe bubbles from Xe ion irradiation has not been reported in the open literature. The development of a 3-dimensional highly-ordered GBS consisting of mostly Xe (e.g., Xe/Kr ~ 10) in the U- χ Mo ($\chi = 7-10$) fuels irradiated in reactors was discovered in recent years using TEM in post-irradiation examination [16-19]. The typical fuel plate centerline temperature under irradiation in a research or test reactor is in the range of

90-150°C. At a relatively low fission density of 1.41×10^{21} fissions/cm³, a GBS already developed with an average size of ~2 nm. At an intermediate fission density of 3.3×10^{21} fissions/cm³, the GBS is identified to have an fcc structure in the bcc host material of U-7Mo with an average bubble size and superlattice constant of ~3.1 nm and ~12 nm, respectively. This is contradictory to the GBS found from noble gas ion irradiations where all the GBS have the same structure as their host material. None of the current models can explain the development of an fcc GBS in a bcc host material.

In the irradiated U-7Mo fuel, while the majority of the GBS collapses as the large bubbles become dominant at the high fission density of 5.2×10^{21} fissions/cm³ as a result of grain subdivision, remnant GBS is still present, with an average bubble size and superlattice constant of ~3.6 nm and ~12 nm, respectively [19]. Note that the dominant radiation damage to the microstructure of a nuclear fuel is generated by high energy fission products since an average of ~169 MeV is released as the kinetic energy of the daughter nuclei from each fission event. Despite the range of several μm for fission products including Xe and Kr, a GBS develops under extremely aggressive irradiation and violent dynamic conditions with significant amount of atomic displacements, Xe precipitation, and re-resolution of Xe back to the U-Mo matrix. It is a great challenge, from both experiment and modeling aspects, to capture the complete processes of GBS nucleation, growth, and collapse in irradiated U-Mo fuel. The stability of the GBS in U-Mo fuel under extremely harsh irradiation conditions from low to intermediate fission density is believed to be largely responsible for its exceptional fuel performance in geometrical stability, mechanical integrity and fission gas retention.

Equally important to the radiation stability of a GBS in the U-Mo fuel is its thermal stability. Although U-Mo fuel plate operation temperature for research and test reactors is limited to be below 250 °C due to corrosion of Al alloy cladding in the coolant, the thermal annealing study on the irradiated fuel may provide insight to a better understanding of the U-Mo fuel performance as well as to its potential to be used as an alternative fuel for other types of reactors at higher temperature. On the other hand, the microstructural stability of U-Mo fuel itself is controlled by the γ -phase (bcc) stability. There is a great interest in investigating the thermal stability of the GBS in relation to U-Mo γ -phase stability. In-situ heating TEM is a popular technique to investigate the dynamic response of the microstructure or chemical process as a

function of temperature [20-26]. It allows tracking the thermal stability of microstructural features such as defect clusters, bubbles, loops, precipitates, dislocation, and grain boundary down to nanometer scale. The objective of this work is to investigate the thermal stability of the GBS under in-situ heating to see if there is a threshold temperature where the GBS starts to collapse.

2. EXPERIMENT

A thermal stability study of the GBS was conducted using a Gatan double-tilt TEM heating holder (Model 652-Ta) on a TEM sample prepared from an irradiated U-10Mo/Al monolithic fuel plate (L1F040) using an FEI Quanta 3D dual-beam FIB system. The local fission density and irradiation temperature is estimated to be 3.5×10^{21} fissions/cm³ and $\sim 140^\circ\text{C}$, respectively. A JEOL-2010 TEM/STEM 200kV microscope, with a LaB₆ filament and a Gatan UltraScan 1000 digital camera, was used. The experimental setup is illustrated in Figure 1. The Gatan heating holder has a type-R thermocouple spot-welded to the miniature furnace body to sense the furnace temperature. The actual temperature of the specimen in a heating holder tends to be lower than the measured furnace temperature. This is because heat transfer under vacuum is mainly by conduction; therefore, the specimen temperature is controlled by the uncertain quality of the mechanical contact between the furnace and the specimen. However, at high temperature, it is anticipated that the difference between the thermocouple reading and actual temperature on the specimen tends to diminish since heat transfer by thermal radiation starts to predominate.

Figure 1. Illustration of TEM in-situ heating experiment showing heating holder (left), a schematic of FIB-TEM Cu grid on the heating holder (center), and a magnified view of the FIB-TEM specimen of the irradiated U-10Mo fuel mounted on the Cu grid finger-D (right).

The temperature ramp rate was approximately 10°C/min before reaching ~ 700°C. The heating holder temperature was raised from room temperature to 700 °C in about 90 min, kept at 700 °C for approximately 34 min, and further increased to ~850 °C at a reduced ramp rate of ~ 5 °C/min. The temperature vs. elapsed time is shown in Figure 2. During the in-situ heating experiment, the TEM column pressure is in the range of $(0.65 - 1.5) \times 10^{-5}$ Pa, depending on the temperature. As a result of thermal drifting, Cu grid softening and finger sagging, and thermal expansion under heating, frequent adjustments of the specimen z-height and tilt are necessary to maintain the GBS image clarity under the right imaging condition for the same area of a TEM sample. Note that the entire FIB-TEM sample is about $10 \times 15 \mu\text{m}^2$ in size.

Figure 2. Temperature vs. elapsed time during TEM in-situ heating experiment.

3. RESULTS and DISCUSSIONS

The GBS microstructure was monitored during an in-situ heating experiment under bright field imaging conditions at zone [110]. GBS images were recorded at various points of the heating experiment as a function of time and temperature for evaluation of its thermal stability as shown in Figure 3. At high temperature, the specimen was kept at a relatively constant temperature of 700°C for approximately 34 min, and multiple TEM images were taken at different times as shown in Figure 4. Note that the images on the left and right are taken from the area close to zone [110], while the two images in the middle are taken from an adjacent area close to zone [121]. The heating current was turned off after reaching approximately 850°C, and the sample temperature quickly returned to room temperature.

Figure 5 shows a comparison of GBS images at zone [110] taken at room temperature before and after the in-situ heating experiment. There is no significant change in GBS lattice constant and bubble size. The slight difference between the two images is likely caused by small deviation in the imaging condition.

Figure 3. TEM bright field images of fission gas bubble superlattice in irradiated U-10Mo fuel at zone [110] at the temperature of 199, 400, 603, and 793°C.

Figure 4. TEM bright field images of gas bubble superlattice in irradiated U-10Mo fuel kept at a temperature of $\sim 704^{\circ}\text{C}$ for approximately 34 min. Pictures on the left and right are taken close to zone [110], and the two pictures in the middle are taken from an adjacent area close to zone [121].

Figure 5. TEM bright field images of gas bubble superlattice at zone [110] at room temperature before and after TEM in-situ heating experiment up to $\sim 850^{\circ}\text{C}$. The scale bar is 20 nm.

The images shown in Figures 3-5 demonstrate the high thermal stability of the GBS in irradiated U-10Mo fuel up to 850°C. Bubble migration and coalescence were not observed during the heating experiment. No evidence was found for the development of large bubbles or shrinkage of GBS bubbles. The fcc structure of the Xe GBS in U-Mo, developed at an irradiation temperature of 140°C (T_{irr}), remains stable at the highest heating temperature of 850°C (T_{ht}). Since the melting point of U-10Mo is approximately 1175°C, estimated from the U-Mo phase diagram [27], the corresponding homologous temperature for irradiation and the highest heating temperature is $0.29T_m$ and $0.78T_m$, respectively. Note that the irradiation temperature for the GBS in U-Mo is in good agreement with the temperature windows for GBS formation identified from He ion irradiated Mo ($T_{irr}/T_m = 0.15 - 0.35$) [13]. The observed high thermal stability of the Xe GBS up to an annealing temperature of $0.78T_m$ was a surprise. It is speculated that helium GBS in irradiated Mo may not survive at an annealing temperature of $0.78T_m$. Yun et al. found that strain energy in UO_2 for Xe is much larger than that of He as a result of a large difference in atomic radius (2.15 Å for Xe vs. 0.3 Å for He) [28]. Therefore, it is anticipated that, for an insoluble noble gas atom, Xe mobility shall be much lower than that of He in metal as well. The low mobility of Xe in U-Mo fuel may contribute to the observed high thermal stability of the Xe GBS.

After annealing at a temperature of approximately 700°C for 34 min, there is no significant change of the GBS as shown in Figure 4. It appears that the mobility of Xe in the irradiated U-10Mo remains low, even at this high annealing temperature ($0.67T_m$). Weber et al. reported on the effect of a 30-min annealing on the Xe distribution profile in polycrystalline Al irradiated with Xe ions at room temperature [29]. They found that Xe is immobile at annealing temperatures below 260°C ($0.57T_m$) and becomes highly mobile at a temperature of 290°C ($0.60T_m$). The high thermal stability of the Xe GBS demonstrated by annealing at ~700°C ($0.67T_m$) in this work may be related to the reduced Xe mobility in the irradiated U-10Mo fuel due to solid fission products (SFP) in solution. Since no SFP precipitates were found in the U-Mo matrix filled with GBS, it is speculated that the SFP at high concentration, while kept in solution in U-Mo fuel, create a large strain field that may significantly increase the diffusion barrier for Xe compared to ion irradiation without SFP.

The GBS images, acquired at room temperature before and after the in-situ heating experiment, demonstrate the high thermal stability of the GBS. The high radiation stability of the GBS is apparent since it was developed in the U-Mo fuel under very aggressive bombardment from fission fragments (~ 90 MeV) to very high atomic displacement damage. With respect to the thermal stability of the γ -phase U-Mo (bcc), the temperature-transformation-time (TTT) diagram shown in Figure 6 indicates that for U-10Mo it may take up to 5 hours to start decomposing its γ -phase at 500°C . Once passing 580°C , the U-10Mo will be stable in its high temperature γ -phase (bcc). A logical question is: Will GBS collapse once γ -phase becomes decomposed? To better understand the correlation between the γ -phase stability and the GBS stability in irradiated U-Mo fuel, it is desired to conduct an in-situ heating TEM experiment on irradiated U-7Mo fuel instead of the U-10Mo fuel since the former may start the phase transformation in ~ 1 hour at 525°C , which is much sooner than U-10Mo fuel at 500°C (~ 6 hours). Note that although GBS has a high thermal stability, the overall stability of GBS in irradiated U-Mo fuel may be strongly influenced by the interaction between the U-Mo and Al matrix for dispersion fuels or Al cladding for monolithic fuels at much lower irradiation temperatures.

Figure 6. Time-Temperature-Transformation diagram of U-10Mo alloy (after [30]).

It is important to keep in mind that the high thermal stability of the Xe GBS in irradiated U-10Mo heating up to $0.78T_m$ does not **imply** that the development of GBS can occur at this high irradiation temperature. **However, if the GBS is not stable at a given annealing temperature, the GBS development is most probably not feasible at that temperature under irradiation.** It is well known that U-10Mo oxidizes quickly in air, even at room temperature. **In addition to the possible effect of SFP in solution on suppressing Xe mobility in irradiated U-Mo, the surface oxide formed on both sides of a FIB-TEM sample is speculated to reduce the surface sink strength and prevent Xe loss from the near surface region.** This may compensate the effect of preferential loss of Xe and small defect clusters to the surface under heating due to the large surface to volume ratio for a TEM sample. As a general concern for the in-situ heating TEM particularly for a FIB-TEM sample, the small sample dimension plus the technical difficulty in verifying the FIB-TEM specimen temperature for the TEM heating holder, the observation from this work needs to be verified by a furnace annealing experiment of a bulk irradiated fuel sample followed by TEM characterization. This work has been planned, and the results will be provided in a future publication or conference.

4. CONCLUSIONS

In U-Mo fuels with Al alloy matrix or cladding, if the diffusion reaction between the U-Mo and Al can be suppressed, the result from in-situ heating TEM of an irradiated U-10Mo fuel demonstrates the extraordinary thermal stability of the fission GBS consisting of mostly xenon atoms. No significant changes in the bubble superlattice could be identified after the specimen was kept at a temperature of $\sim 700^\circ\text{C}$ for ~ 34 min. The γ phase (bcc) of U-10Mo appears stable after exposure to a high temperature ($500\text{-}846^\circ\text{C}$) for an accumulated time of ~ 80 min. The U-Mo fuel has the potential to be used at irradiation temperatures higher than that of U-Mo fuels in the research and test reactors.

Acknowledgments

Many thanks to Francine Rice for her assistance on the experiment and James Madden for FIB-TEM sample preparation. This work was supported by the U.S. Department of Energy, Office of Nuclear Materials Threat Reduction (NA-212), National Nuclear Security

Administration, under DOE-NE Idaho Operations Office Contract DE-AC07-05ID14517. This manuscript was authored by a contractor for the U.S. Government. The publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for U.S. Government purposes.

U. S. Department of Energy Disclaimer

This information was prepared as an account of work sponsored by an agency of the U.S. Government. Neither the U.S. Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

Reference

1. S.L. Sass and B.L. Eyre, *Phil. Mag.* 27 (1973) 1447.
2. P.B. Johnson, D.J. Mazey, *Nature* 276 (1978) 595.
3. P.B. Johnson, D.J. Mazey, *J. Nucl. Mater.*, 93-94 (1980) 721.
4. W. Jager, J. Roth, *Nucl. Instr. And Meth.* 182-183 (1981) 975.
5. P.B. Johnson, D.J. Mazey, *J. Nucl. Mater.* 111-112 (1982) 681.
6. H. Van Swijgenhoven, G. Knuyt, J. Vanoppen, L.M. Stals, *J. Nucl. Mater.* 114 (1983) 157.
7. D.J. Mazey, J.H. Evans, *J. Nucl. Mater.* 138 (1986) 16.
8. J.H. Evans, D.J. Mazey, *J. Nucl. Mater.* 138 (1986) 176.
9. P.B. Johnson, A.L. Malcolm, D.J. Mazey, *J. Nucl. Mater.* 152 (1988) 69.
10. P.B. Johnson, A.L. Diprose, D.J. Mazey, *J. Nucl. Mater.* 158 (1988) 108.
11. P.B. Johnson, Bubble lattices in metals, in: J.H. Evans, S.E. Donnelly (Eds.), *Fundamental Aspects of Inert Gases in Solids*, Plenum, New York, 1991, p. 167.
12. P.B. Johnson, K.L. Reader, R.W. Thomson, *J. Nucl. Mater.* 231 (1996) 92.
13. F.E. Lawson, P.B. Johnson, *J. Nucl. Mater.* 252 (1998) 34.
14. P.B. Johnson, F. Lawson, *Nucl. Instr. and Meth. in Phys. Res. B*, 243 (2006) 325.
15. N.M. Ghoniem, D. Walgraef, S.J. Zinkle, *Journal of Computer-Aided materials Design*, 8: (2002) 1-38.

16. S. Van den Berghe, W. Van Renterghem, A. Leenaers, J. Nucl. Mater., 375 (2008) 340-346.
17. J. Gan, D.D. Keiser Jr., D.M. Wachs, A.B. Robinson, B.D. Miller, T.R. Allen, J. Nucl. Mater., 396 (2010) 234-239.
18. J. Gan, D.D. Keiser Jr., B.D. Miller, A.B. Robinson, J.F. Jue, P. Medvedev, D.M. Wachs, J. Nucl. Mater., 424 (2012) 43-50.
19. J. Gan, B.D. Miller, D.D. Keiser Jr., A.B. Robinson, J.W. Madden, P. Medvedev, D.M. Wachs, J. Nucl. Mater., 454 (2014) 434-445.
20. J.W. Kim, J-P Ahn, D.H. Kim, H-S Chung, J-H Shim, Y. W. Cho and K.H. Oh, Scripta Materialia, 62 (2010) 701.
21. R. Sharma, Micron 43 (2012) 1147-1155.
22. D. Kiener, Z. Zhang, S. Sturm, S. Cazottes, P.J. Imrich, C. Kirchlechner and G. Dehm, Philosophical Magazine Vol. 92, No. 25-27 (2012) 3269-3289.
23. S.L. Shrestha, K.Y. Xie, S.P. Ringer, K.R. Carpenter, D.R. Smith, C.R. Killmore and J.M. Cairney, Scripta Materialia 69 (2013) 481-484.
24. S.J. Yoo, C.-Y. Kim, J.W. Shin, S.-G. Lee, J.-M. Jeong, Y.-J. Kim, S.-H. Lee, J.-G. Kim, Materials Characterization 78 (2013) 31-36.
25. N. Dalili, P. Li, M. Kupsta, Q. Liu, D.G. Ivey, Micron 58 (2014) 25-31.
26. A.M. Thron, P. Greene, K. Liu, K. van Benthem, Ultramicroscopy 137 (2014) 55-65.
27. Okamoto H., ASM International, Alloy Phase Diagram Section, Diagram # 901671, Binary Alloy Phase Diagrams, II Ed., Ed. T.B. Massalski, Materials Park, Ohio, U.S.A.
28. Y. Yun, O. Eriksson, P.M. Oppeneer, H. Kim, K. Park, J. Nucl. Mater. 385 (2009) 364-367.
29. T. Weber and K-P. Lieb, Nucl. Instr. And Meth. In Phys. Res, B44 (1989) 54-60.
30. P.E. Repas, R.H. Goodenow, and R.F. Hehemann: Trans. ASM, 57 (1964) 150-163.