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Thermal stability of helium bubble superlattice in Mo under TEM in-situ heating

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Abstract

Although the temperature window of helium ion irradiation for gas bubble superlattice (GBS) formation was found to be in the range of approximately 0.15–0.35 melting point in literature, the thermal stability of He GBS has not been fully investigated. This work reports the experiment using an in-situ heating holder in a transmission electron microscope (TEM). A 3.0 mm TEM disc sample of Mo (99.95% pure) was irradiated with 40 keV He ions at 300 °C to a fluence of 1.0E+17 ions/cm^2, corresponding to a peak He concentration of approximately 10 at.%, in order to introduce He GBS. In-situ heating was conducted with a ramp rate of ~25 °C/min, hold time of ~30 min, and temperature step of ~100 °C up to 850 °C (0.39T_m homologous temperature). The result shows good thermal stability of He GBS in Mo with no noticeable change on GBS lattice constant and ordering. The implication of this unique and stable ordered microstructure on mechanistic understanding of GBS and its advanced application are discussed.

Keywords: Helium; Ion irradiation; Gas bubble superlattice; Transmission electron microscopy; In-situ heating

1 Introduction

Gas bubble superlattice (GBS) in metals irradiated with inert gas ions has been investigated extensively by Johnson and others in the past [1–14]. The formation of helium GBS in body-center-cubic (bcc) metal appears the most successful among all the inert gas ion irradiations. The possible mechanisms of the self-organization nanostructures as a result of irradiation are outlined by Ghoniem et al. [15] with a few recent additions [16,17]. GBS formations are reported in 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 although in general the degree of bubble ordering is considered to be low. The work on helium-irradiated Mo indicates that a GBS occurs between the irradiation temperatures of ~0.15 T_m and 0.35 T_m (T_m the melting temperature in K) [13]. For Mo the melting temperature and the corresponding irradiation temperature window to form He GBS are 2623 °C and 161–741 °C, respectively. The recent discoveries of highly-ordered GBS consisting of mostly fission gaseous atom Xe (Xe/Kr ~ 10) in the U-Mo fuels irradiated in reactors stimulated great interest on the GBS [18-21]. The degree of ordering in Xe GBS in irradiated U(Mo) fuel is significantly better than that reported in He GBS in pure metals in the literature. Xenon GBS is identified to have an fcc structure in the bcc host material of U-7Mo with an average bubble size and bubble lattice 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 reported so far have the same structure as their host material. The exceptional performance of U-Mo fuel in geometrical stability, mechanical integrity and fission gas retention is attributed to the high stability of Xe GBS under extreme irradiation conditions up to intermediate fission density.

In addition to radiation stability, thermal stability of a GBS is equally important. The thermal annealing study on the GBS may lead to a better understanding of the development of this unique self-organized microstructural feature and its potential application to be used as a functional material over a broad temperature range. In-situ heating in TEM is a popular technique to investigate the dynamic response of the microstructure or chemical process as a

function of temperature [22–28]. It allows tracking the thermal response of microstructural features such as defect clusters, bubbles, voids, loops, precipitates, dislocation, and grain boundary down to nanometer scale. The previous work on TEM in-situ heating of Xe GBS in the irradiated U-Mo fuel revealed exceptionally high thermal stability up to 850 °C (0.72 T_m) [29]. Contradictory result for thermal annealing of He GBS in copper foil indicated bubble growth and coalescence at 325 °C (0.44 T_m) and the formation of blisters at higher temperatures [30]. The objective of this work is to investigate the thermal stability of the He GBS in Mo under TEM in-situ heating. The result will be compared with literature to gain the insight of GBS thermal stability.

2 Experiment

The Mo sheet with a thickness of 250 µm and purity of 99.95 wt.% was acquired from GoodFellow. Helium ion irradiation for 3.0 mm TEM disc samples was performed at Los Alamos National Laboratory using an ion implanter with beam energy of 40 keV and an ion flux of 7.6×10^{12} ions·cm^{-2}·s^{-1} to a fluence of 1.0×10^{17} ions·cm^{-2} at an irradiation temperature of 300 °C. A JEOL-2010 TEM/STEM 200 kV microscope, equipped with a LaB_6 filament and a Gatan UltraScan 1000 digital camera, was used. TEM samples were prepared using twin-jet electrical polishing in a 12.5% sulfuric acid and 87.5% methanol solution at temperature of 5 °C to perforation. Fig. 1 shows the TEM bright field images of He GBS at zone [001] in over-focus and under-focus conditions along with the insets showing the selected area diffraction (SAD) from Mo at zone [001] and the Fast Fourier Transformation (FFT) where four faint spots and their orientation indicate bubble ordering coherent to the host material Mo.

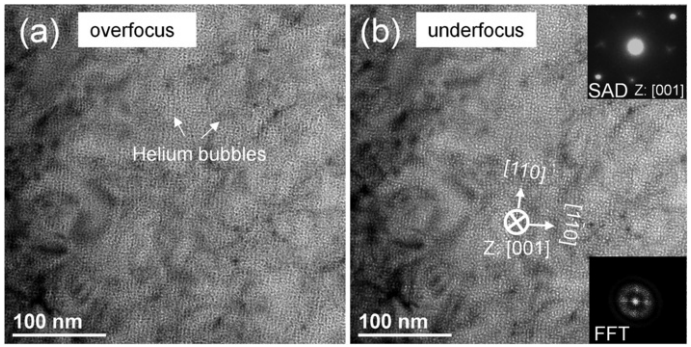

Fig. 1 TEM bright field images of helium gas babble superlattice imaged at zone [001] in (a) over-focus and (b) under-focus condition. Insets show the selected area diffraction (top) and fast Fourier Transform (bottom) that confirms the bubble ordering.

alt-text: Fig. 1

The Gatan double-tilt heating holder (Model 652-Ta) used in this experiment has a type-R thermocouple spot-welded to the miniature furnace body to measure the furnace temperature. The actual temperature of the 3.0 mm Mo disc specimen in a heating holder is likely to be slightly lower than the measured furnace temperature. This is because heat transfer under vacuum is mainly by conduction and specimen temperature is affected by the uncertain quality of the mechanical contact between the furnace and the specimen. At high temperature, it is anticipated that the difference between the thermocouple reading and actual temperature on the specimen diminishes since heat transfer by thermal radiation starts to predominate. The in-situ heating was conducted with a TEM column vacuum of ~8.0×10^{-6} Pa (~6×10^{-8} torr), temperature ramp rate of ~25 °C per minute and a hold time of ~30 min starting at 300 °C with a step of 100 °C and finished at 850 °C which is the maximum safe operation temperature for this holder. The temperature vs. time along with the homologous temperatures for Mo is shown in Fig. 2.

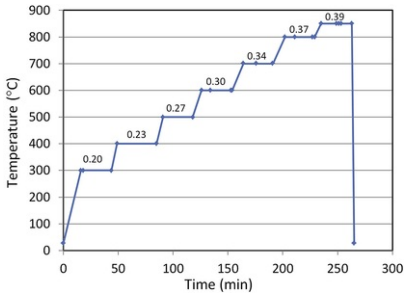

Fig. 2 TEM in-situ heating profile (temperature vs. time) and the corresponding homologous temperatures for Mo.

alt-text: Fig. 2

3 Results and discussions

The He GBS microstructure was monitored during the in-situ heating experiment under bright field imaging conditions near zone [001]. 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 Fig. 3. All the TEM images were recorded in over-focus condition from the same region of the sample at different times and temperature using a reference mark shown as a dark circular feature in the pictures. Note that at high temperatures the contrast of this circular feature is significantly reduced but still discernable. The heating current was turned down to zero at the end of heating at 850 °C and the sample temperature quickly returned to room temperature. Fig. 4 shows the bright field images of He GBS near zone [001] in under-focus condition at room temperature before and after TEM in-situ heating experiment. There is no noticeable change in bubble size and ordering. The in-situ heating experiment reveals good thermal stability of He GBS up to 850 °C ($0.39\,T_m$). This is in agreement with the result of in-situ heating for Xe GBS in irradiated U-10Mo which is thermally stable up to 850 °C ($0.78\,T_m$). The significance of this thermal stability for He GBS is on its potential for broad applications such as for 3D patterning for advanced functional material and the design of the future advanced nuclear fuels with inherent property for the development of thermally stable fission gas bubble superlattice with high gas inventory capacity and significant delay on break-way swelling.

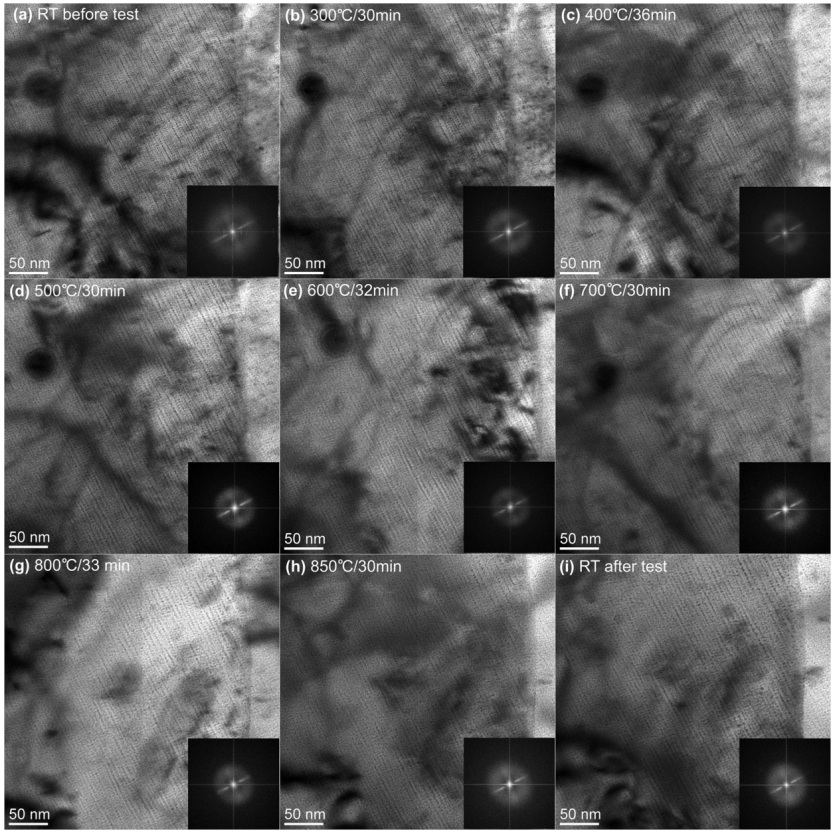

Fig. 3 TEM bright field images (over-focused) of He gas bubble superlattice in pure Mo near zone [001] from the same area at temperatures of 25, 300, 400, 500, 600, 700, 800, 850 and then 25 °C through (a) and (i). The inset of FFT indicates the presence of He GBS with no noticeable degradation on bubble ordering.

alt-text: Fig. 3

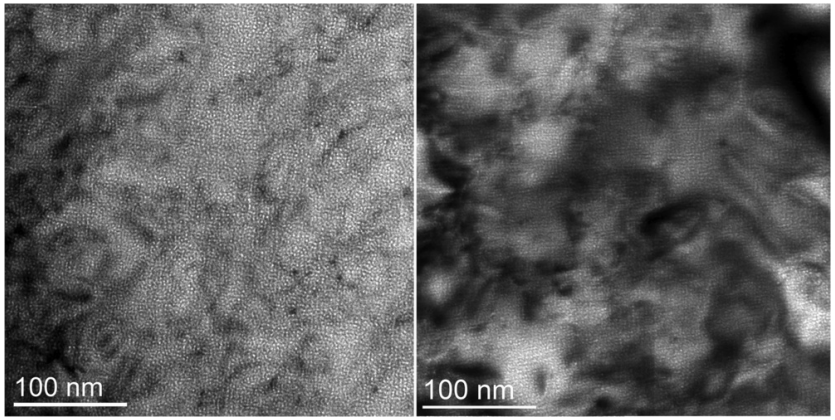

Fig. 4 TEM bright field images (under-focused) of He gas bubble superlattice in pure Mo near zone [001] at room temperature before (left) and after (right) TEM in-situ heating experiment revealing no noticeable change on bubble size, ordering and morphology.

alt-text: Fig. 4

To evaluate the possible change of GBS lattice constant as a function of the accumulated annealing effects, the inverse FFTs of the GBS images with mask before the annealing at room temperature and after annealing up to 850 °C are used to measure the GBS lattice constant. The results are shown in Fig. 5. It appears that He GBS lattice constant remains the same within the measurement uncertainty, indicating the GBS is thermally stable under the given annealing conditions. The visual inspection and measurement of GBS lattice constant on the inverse FFT between the room temperature and the annealed condition up to 850 °C reveals no noticeable difference as shown in the left of Fig. 5. Note that for the accumulated annealing at temperatures from 300 through 850 °C, only one set of GBS planes (aligned along [011] direction) was used for tracking and measurement of the GBS lattice constant. This is because it simplifies the tracking of GBS while maintaining the same imaging condition while the sample local region is undergoing thermal drifting and bending from the heating. The retaining of GBS alignment on the two orthogonal bubble planes for the annealed condition up to 850 °C, shown in Fig. 5 (left), confirms that the other set of bubble planes (aligned along [110]) is also retaining its original alignment and ordering.

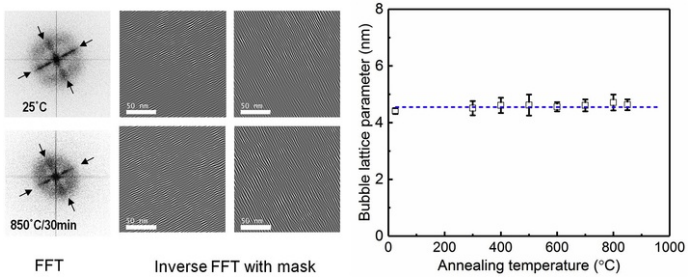

Fig. 5 The comparison of FFT and inverse FFT with mask before and after annealing for He GBS in Mo is shown on the left for evaluation of GBS lattice constant. The resultant GBS constant as a function of accumulated annealing temperature is shown on the right.

alt-text: Fig. 5

Although the temperature window of GBS development for He ion irradiation is reported to be 0.15–0.35T_m, the He GBS seems to remain thermally stable beyond its upper limit of irradiation temperature. Unfortunately, the in-situ heating holder used in this work only allows reaching the maximum homologous temperature of 0.39T_m for Mo. The previous TEM in-situ heating of Xe GBS in irradiated U-10Mo shows that GBS is stable even at 0.72T_m, significantly higher than the 0.35T_m upper limit of irradiation temperature identified from He ion irradiation. It remains an open question whether He GBS is stable at 0.72T_m (1812 °C). Considering the large surface sink effect in TEM in-situ heating, it is speculated that if a GBS can survive and remains stable under in-situ heating for a thin foil sample with large surface sink on both sides, it shall be stable under the same heating temperature in a bulk sample condition. Under extreme thermal annealing, a GBS may become disordered by coarsening and coalescence. The former requires emission of vacancies and gas atoms from bubbles, hindered by the high binding energies of vacancies and gas atoms [31]. The latter may take place by surface diffusion, which can be impeded by the presence of highly pressurized gas atoms in bubbles. Therefore, an existing GBS can remain stable at high temperatures likely due to the

sluggish coarsening and coalescence kinetics. Another possible scenario is that in anisotropic materials such as Mo, the elastic interaction between bubbles may favor an ordered pattern of bubbles, making the GBS a metastable state. In this case, coarsening and coalescence are suppressed in GBS with perfect ordering. An imperfect GBS will coarsen slowly towards better degree of ordering [32].

Note that there is a large difference in atomic size and mobility between He and Xe. The degree of ordering and the type of GBS between He and Xe bubble lattice is known to be quite different. Judging from the significantly less degree of ordering in He GBS comparing to that of Xe GBS, it is believed that the thermal stability of He GBS is expected to be much less than Xe GBS. There is no Xe GBS formation from Xe ion irradiation reported in the open literature. This may be partially due to the difficulty of introducing Xe uniformly into the material and creating a dynamic environment to provide enough mobility for Xe atoms to develop bubble lattice. On the other hand, once a Xe GBS is developed such as that seen in the irradiated U-Mo fuel, the Xe GBS may remain exceptionally stable both under irradiation and thermal annealing condition. It is speculated that the difficulty of developing an inert gas GBS increases with the increase in gas atom size and the decrease in gas atom mobility, although the stability of a GBS may be higher with large atomic size of inert gaseous atoms. Since the mobility of inert gas atoms is closely associated with its partitioning with vacancies, it is anticipated that the rate of atomic displacement damage under irradiation may have a large impact to the GBS formation.

Future work is needed to investigate the temperature dependence of GBS through both in-situ and ex-situ heating experiment. The ex-situ heating experiment in high vacuum for a bulk sample can mitigate the artifact from the large surface sink effect for a TEM foil sample. The in-situ heating still has its unique advantage of allowing track the dynamic response of GBS evolution under heating. The comparison of microstructural response between the in-situ and ex-situ heating experiment and the comparison between He GBS and Xe GBS under heating at relevant homologous temperature will allow to investigate the mechanism that dictates the GBS thermal stability. This information are crucial to be used as input parameters for advanced modeling to further enhance the scientific understanding of GBS formation and ultimately to guide the design of functional materials or advanced nuclear fuels by utilizing the GBS microstructural features.

4 Conclusions

In conclusion, the He GBS developed in pure Mo under 40 keV He implantation at 300 °C to a fluence of 1×10^{17} ions/cm^2 with a local He peak concentration of ~10 at.%. Helium GBS has a bcc structure coherent with bcc Mo with a GBS lattice constant and average bubble size of 4.8 nm and 1.5 nm, respectively. TEM in-situ heating at 300 °C through 800 °C at 100 °C per step and a final heating at 850 °C with a hold time of approximately 30 min for each step reveals no noticeable change in GBS. This result indicates a good thermal stability of He GBS under heating up to at least $0.39T_m$, exceeding the upper limit of irradiation temperature ($0.35\,T_m$) for GBS formation.

Acknowledgments

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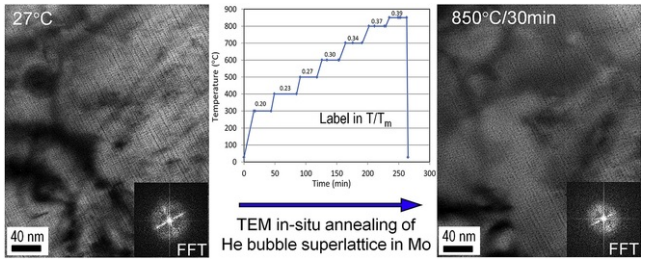
Graphical abstract



alt-text: Image 1

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Answer: Yes, my email address is correct

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Answer: acknowledged

Query: Could you please provide the grant number for (1) Idaho National Laboratory, (2) Office of Science, (3) U.S. DOE, (4) U.S. Department of Energy, (5) Los Alamos National Laboratory, (6) DOE-NE Idaho Operations Office Contract and (7) Basic Energy Sciences, if any?
Answer: The grant number for this project at INL is provided as FWP C000-14-003. There is no grant number associated for the irradiation support from LANL since that was accessed through user facility.

Query: Please confirm that given names and surnames have been identified correctly and are presented in the desired order and please carefully verify the spelling of all authors’ names.
Answer: The author names are checked and they are all correct.

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