In Situ TEM Concurrent and Successive Au Self-Ion Irradiation and He Implantation

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The development of advanced computational methods used for predicting performance lifetimes of materials exposed to harsh radiation environments are highly dependent on fundamental understanding of solid-radiation interactions that occur within metal components. In this work, we present successive and concurrent in situ TEM dual-beam self-ion irradiation of 2.8 MeV Au4+ and implantation of 10 keV He1+, utilizing a new facility at Sandia National Laboratories. These experiments, using a model material system, provide direct real-time insight into initial interactions of displacement damage and fission products that simulate damage from neutron exposure. In successive irradiation, extensive dislocation loop and stacking fault tetrahedra damage was formed and could be associated with individual ion strikes, but no evidence of cavity formation was observed. In contrast, concurrent irradiation to the same dose resulted in the onset of cavity formation at the site of a heavy-ion strike. This direct real-time observation provides insight into the complex interplay between the helium and vacancy dynamics.

1. Introduction

The neutron irradiation of cladding metals during nuclear reactor operation, for example, leads to microstructural evolution that alters mechanical properties.1 For many decades, ion irradiation has been used to simulate the displacement damage of a material under neutron irradiation. Ion irradiation rarely leads to the splitting of atoms, thus the material remains inactive. The material is therefore safe to investigate and radiation environments are simplified to merely the displacement of atoms. This oversimplification leads, naturally, to focused studies of displacement cascades and damage accumulation. These displacement experiments have certainly increased the understanding of the cascade component of radiation, especially when performed in situ,2 and lead to advances in materials development.3,4 A review of the facilities capable of real-time irradiation investigations at the nanoscale, as of 2009, can be found elsewhere.5 However, it has been shown that many of the advantages of ion irradiation studies, increased dose rate and no activation, affect the evolution and type of damage accumulation in the material, and hence the resulting microstructures.6 Attempts have been made to better simulate neutron radiation environments, with the addition of helium implants, a surrogate for alpha particles. There are several ways to include helium in the simulated irradiation process: ex situ pre- or co-implantation of helium, or in situ transmission electron microscopy (TEM) pre- or co-implantation.

When simulating neutron irradiation with ex situ irradiation, often the resulting ion dose and dose rate are high enough for cascade overlap, sample heating, and other complications that limit understanding or correlation to neutron irradiation.7,8 Nevertheless, these ex situ studies show the very different effects successive and concurrent helium implantation have on the resulting microstructure, such as cavity refinement and inception.5,10

In situ TEM has the distinct advantage of direct observation of irradiation processes at the nanoscale, making direct comparison to atomistic modeling efforts possible.11 Due to experimental difficulties in achieving dual-beam irradiation in a TEM, the majority of in situ TEM irradiation studies focus on pre-implantation of helium and a single ion species for irradiation or concurrent helium with another light-ion species such as hydrogen.

Many of the experimental difficulties in achieving truly concurrent heavy- and light-ion irradiation and implantation have been overcome at the Ion Beam Laboratory (IBL) at Sandia National Laboratories (SNL). This work presents in situ TEM studies carried out on the newly developed In situ Ion Irradiation TEM (I2TEM).12 These experiments investigate the feasibility of a dual-beam experiment using Sandia’s new facility to compare defect production and evolution in He1+ and Au4+ self-ion, successive and concurrent ion exposed Au thin films.

To better predict the structural evolution and associated change in mechanical properties that occur in cladding metals during irradiation, a fundamental understanding is needed of defect interactions. Interactions between defect structure with both initial microstructure as well as other radiation defects produced during the lifetime of the reactors must be understood. This study provides insight into both the nucleation of radiation defects and the initial interactions of displacement damage with a supersaturation of helium in a model face-centered cubic (FCC) system.

2. Experimental Procedures

Gold was chosen as a model material system since it has no oxide and low stacking fault energy. Gold thin-film was
evaporated from 99.99% purity Alfa Aesar gold foil in a tungsten boat onto a freshly cleaved sodium chloride (NaCl) substrate at 423 K. The contamination level and grain size of the film was optimized by maintaining a pressure of $6 \times 10^{-5}$ Pa during deposition and maintaining at temperature 4 h under vacuum. Scanning electron microscopy (SEM) confirmed the thickness of the film to be approximately 100 nm. TEM samples were prepared by dissolving the NaCl substrate in deionized water then floating the thin film onto a standard copper TEM grid.

Both Au$^{4+}$ and He$^{1+}$ ion beams were introduced into the heavily modified JEOL 2100 TEM, along the same path, nominally orthogonal to the electron beam and at a 30° angle to the sample. The TEM was operated at 200 keV, which is well below the knock-on threshold of gold. The choice of 2.8 MeV Au$^{4+}$ self-ion species was made for three reasons: chemical interactions were eliminated, it has a large scattering cross-section, and the damage-thickness profile is nearly flat throughout the TEM foil. 10 keV He$^{1+}$ was chosen to maximize the helium concentration near the mid-plane of the thin film and thus minimize surface effects. The damage-thickness profiles per ion and sputter at both entry and exit surfaces were calculated for both ion species using the Stopping and Range of Ions in Matter (SRIM) calculation with a 30° incident angle and a layer thickness of 100 nm. The number of sputtered atoms throughout the experiment was found to be negligible by SRIM simulation and was therefore assumed to play no role in the experimental observations.

Three experiments will be discussed herein, successive He$^{1+}$ implantation then Au$^{4+}$ irradiation, successive Au$^{4+}$ irradiation then He$^{1+}$ irradiation, and concurrent Au$^{4+}$ irradiation and He$^{1+}$ implantation at room temperature. The total dose and dose rate of each species were held nominally constant. Respectively, the Au$^{4+}$ dose rate and dose were $2 \times 10^{10}$ ions cm$^{-2}$ s$^{-1}$ and $3 \times 10^{10}$ ions cm$^{-2}$. These irradiation parameters result in a calculated damage-depth profile with an average displacement damage of $1.3 \times 10^{-3}$ dpa and a maximum of $1.6 \times 10^{-3}$ dpa. The He$^{1+}$ dose was taken during the same time interval to $2 \times 10^{15}$ ions cm$^{-2}$ at a dose rate of $1 \times 10^{15}$ ions cm$^{-2}$ s$^{-1}$. This is a calculated average displacement of 0.16 dpa with a maximum of 0.41 dpa near the mid-plane. 

In situ video was recorded at 15 fps with a 1k x 1k TVIPS CCD camera in frame transfer mode and micrographs were taken with a 4k x 4k TVIPS camera.

### 3. Results and Discussion

Both orders of successive helium implantation and gold self-ion irradiation can be seen in Fig. 1. With a dose rate set at $2 \times 10^{10}$ ions cm$^{-2}$ s$^{-1}$ for the Au$^{4+}$ beam, the in situ video appeared to show single ion events with occasional interaction with the pre-existing microstructure, as well as radiation damage produced by previous cascade events. The final defect structures observed, in Fig. 1(b), are either dislocation loops or stacking fault tetrahedra (SFT), as would be expected from previous studies. Several of these small vacancy clusters in the cascade path appear to undergo structural evolution after the ion strike. Although the details of these interactions could not be resolved during this experiment, it is thought that this is due either to the formation of SFTs from initial dislocation loops and/or the Brownian motion of dislocation loops. These experiments were run at room temperature and negligible ion beam heating is expected, due to the low dose rate. This premise was substantiated with a post-experiment tilt series of the sample. There appeared to be minimal interaction of the cascade events with the initial and previously created microstructure, despite often overlaying each other in the observed projection of the in situ video.

It was expected, based on measured global dose rate, that ion strikes should occur every 2–3 s in the region of study. However, the observable Au$^{4+}$ ion strikes occur every 7 s, on average. The discrepancy between expected and observed strike rate could stem from either a fraction of ion strikes not producing large enough displacement cascades or local variations in flux within the ion beam spot. SRIM simulations suggest that nearly all ion strikes should create Frenkel pairs that are expected to collapse to visible vacancy clusters. Thus it is assumed this difference is primarily due to local variations in ion flux at the nanoscale within the continuous ion beam.

Following 2.8 MeV Au$^{4+}$ ion irradiation to a dose of $3 \times 10^{10}$ ions cm$^{-2}$, or 25 identifiable ion strikes, the same grain was implanted with 10 keV He$^{1+}$ to a global dose of $2 \times 10^{15}$ ions cm$^{-2}$ resulting in a maximum 0.41 dpa 10 nm below the incident surface. Despite this relatively high dose, no structural change was observed in the gold grain due to helium implantation, as seen in Fig. 1(c). The lack of observable structural change, the calculated 3,500 appm total helium implanted, and the low solubility of helium in gold suggest a supersaturation of helium is present near the incident surface of the gold film. The absence of visible cavity formation is not surprising for a room temperature experiment. In a similar fashion, comparison of Figs. 1(d) and 1(e) shows no observable cavities or other radiation defects formed during the helium implantation of the gold grain. Comparing Figs. 1(c) and 1(e) suggests the addition of dislocation loops and SFTs are not sufficient to nucleate cavities in this model system at room temperature and a global helium dose of $2 \times 10^{15}$ ions cm$^{-2}$.

In the second successive implantation experiment, following helium implantation, the implanted region was observed in situ during self-ion irradiation to the same global dose used in the first experiment, or 22 identifiable ion strikes. The structural evolution from this irradiation procedure includes dislocation loops and SFTs, but no observable cavities under any imaging condition can be seen in Fig. 1(f). The similarity between Figs. 1(c) and 1(f) indicates, under these experimental conditions, there are no observable differences between pre- and post-implantation of helium. This suggests that neither the thermal spike associated with each gold strike through a region of supersaturated helium in the gold foil, nor a wealth of defects for the cavities to nucleate are sufficient to produce the formation of cavities.

The unique capabilities of the I$^{3}$TEM permit the ability to concurrently implant and irradiate the same region of the same sample at the same incident angle. This capability was used to simultaneously irradiated and implant the gold film.
with 2.8 MeV Au$^{4+}$ and 10 keV He$^{1+}$, respectively, to the same total global dose and dose used in successive irradiation experiments. Similar to the successive series, this concurrent experiment resulted in dislocations loops and SFTs appearing as a result of self-ion irradiation, Fig. 2(b). In contrast to successive irradiation experiments, two sets of structures identified by Fresnel imaging to be cavities, are arrowed in Fig. 2(b). Due to the difficulty of validating the presence of helium$^{19,20}$ and the experimental conditions, it is assumed that the cavities observed contain helium. During the concurrent experiment, 17 heavy ion strikes were identified and are plotted in Fig. 2(c). Similar to the successive experiment, the rate of the defect strikes and the number of defects per strike appear nearly linear and there appear to be minimal interactions with initial defects. This indicates the number of defects produced in each cascade is similar. An exception to this is seen in Fig. 2(b), identified with a white arrow. In this region, the dislocation structure evolved from a line dislocation to a series of dislocation loops, SFTs, or both. This complex evolution also appears to result in cavity formation.

Nucleation of the defect structure, arrowed in black in Fig. 2(b), was observed during in situ TEM concurrent irradiation, as shown in a video frame set of the event (Fig. 3). The presence of cavities is seen with the initial cascade damage, which is formed in less than 1/15th of a second. Although the cavities observed in this study are assumed to be helium-filled, cavities can be created without
gas implantation, as reported in ex situ single- and dual-beam ion irradiation experiments in stainless steel.\textsuperscript{10} The reported cavities were observed in stainless steel irradiated with Ni ions to 1 dpa at 0.5T\textsubscript{m}. However, the amount of damage created in the present, room temperature, gold experiments amounts to one second of irradiation in the reported stainless steel study. The density of helium in the matrix at the cascade event is calculated to be 35,000 appm/dpa, so it is then fair to assume, due to the difficulties of verifying helium content,\textsuperscript{19,20} that the cavities are helium filled.

The initial indications of these helium cavities are indicated with black arrows in Fig. 3(b). The nearby radiation damage, that which is observed with strain-contrast and indicated with a black arrow in Fig. 3(d), is unstable until 200 ms after the initial ion strike. It is not clear in this movie frameset whether the defect is growing or moving (Figs. 3(c)–3(e)). However Fig. 3(f), taken in Fresnel imaging condition roughly 5 min after the conclusion of the experiment with the 4k \times 4k CCD camera, shows one of the cavities is no longer present. It is unlikely the defect was disrupted by a subsequent ion strike, as the cavity was under observation until a short time after concluding the irradiation. Speculating, the cavity could have migrated and escaped to the surface, which is an effective sink or it may have also migrated and coalesced with a nearby cavity, however, this is not likely, due to the low temperature and experimental conditions.\textsuperscript{21,22}

Significant insights into the initial formation of cavities can be gained from these in situ TEM experiments. It is of note that the first sign of structures assumed to be helium-filled cavities did not appear during similar dose and dose rate successive experiments, but did appear during the concurrent experiment. In addition, it should be noted that cavities did not appear at grain or twin boundaries, but in regions around accumulated cascade damage. This observation suggests that it is the complex dynamics of the heavy ion strike that lead to cavity formation rather than heterogeneous nucleation at grain boundaries or other initial defects. At these low dose rates, the global heating of the sample is negligible for each case, and particularly negligible when comparing successive and concurrent experiments. This would indicate the cavity nucleation is due to the coincident helium mobility and the immediate availability of mobile defects from the ion cascade, than increased sample heating. A subtle point is that a cavity is not formed during the helium implant followed by self-ion irradiation that has similar ion strike effects. This suggests that successive series gives the helium implanted in the sample time to stabilize in the structure prior to exposure of the cascade damage and associated thermal spike. In contrast, the concurrent experiment introduces approximately 160 appm helium between each strike that might aid in the development of cavities. These experiments raise many more questions regarding the fundamental understanding of initial microstructural evolution in a model FCC system due to a range of radiation defect structures and these suggest further studies are needed to fully understand the interplay of displacement damage and helium content in both model and industry-relevant systems.

![Fig. 3](https://example.com/fig3.png)

Fig. 3 72 \times 72 \text{nm}^2 cropped region from the in situ TEM concurrently 10 keV He\textsuperscript{1+} implantation and 2.8 MeV Au\textsuperscript{4+} irradiation experiment described in Fig. 2. (a) Still frame showing the initial defect structures observed in the region one frame before the ion strike. (b) First frame showing the cascade damage resulting from the ion strike. The majority of cascade damage, including cavities (black arrows), occurred in less than 1/15th of a second. (c) No significant change in the structure occurs in the next frameset. (d) At 133 ms after the cascade event was observed, defects (black arrow) are still mobile. (e) By 200 ms after the cascade event, the cascade damage appears stable for the remainder of the irradiation. (f) A post-experiment micrograph taken 5 min. After the event, in Fresnel imaging condition, shows only two remaining cavities.
4. Conclusion

Gold thin-films were successively and concurrently implanted and irradiated with 10 keV He$^{1+}$ and 2.8 MeV Au$^{4+}$ self-ions at room temperature, while under direct real-time TEM observation. This was achieved with the new I^3TEM facility at Sandia National Laboratory’s Ion Beam Laboratory. During either order of successive helium implantation and gold irradiation taken to a combined average damage level of 0.16 dpa, only displacement damage associated with individual heavy-ion strikes was observed. However, during concurrent implantation and irradiation, the formation of cavities was seen in the vicinity of cascade events. These real-time nanoscale observations of the initial structural evolution alludes to the complex interplay of helium and displacement damage expected in nuclear reactor cladding materials that cannot be sufficiently simulated by a single ion bombardment.

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