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Defect evolution in heavy ion irradiated nanotwinned Cu with nanovoids

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ABSTRACT

Epitaxial nanotwinned Cu film with abundant nanovoids surrounding domain boundaries was subjected to Kr^{++} ion irradiation inside a transmission electron microscope at various dose rates. Irradiation-induced defect clusters distributed preferentially near domain boundaries during the early stage of radiation. Meanwhile, the pre-existing nanovoids continuously shrank. This study suggests that the defect network enabled by the unique combination of nanotwins and nanovoids may significantly enhance the radiation tolerance of metallic materials.

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1. Introduction

When metallic materials are subjected to irradiations by high-energy ions or neutrons, a large number of vacancy and interstitial clusters are induced in form of Frank (intrinsic or extrinsic) loops, perfect dislocation loops, stacking fault tetrahedrons (SFTs), voids and bubbles [1–10]. These irradiation-induced defects cause dramatic microstructural alteration, leading to the degradation of physical and mechanical properties in irradiated materials [3,11–13]. For instance, the irradiation-induced hardening and embrittlement in metallic materials have been frequently reported [14–16]. Therefore, it is of great significance to design advanced materials with excellent radiation tolerance. In general, irradiation tolerance of a material is largely determined by its capability to remove point defects [17–19]. Thus in principle the radiation tolerance of a metallic material can be enhanced by introducing sufficient defect sinks that are capable of annihilating defects and consequently suppressing radiation damage [20,21]. To date, various types of defect sinks have been investigated, including grain boundary [18,22–27], phase boundary [28–31], free surface [32,33] and twin boundary (TB) [34–36]. Among them grain boundary alleviated radiation damage has been intensively studied, and prior studies revealed that certain nanostructured materials, containing a large volume fraction of GBs, exhibit exceptional radiation resistance [37–42]. However, the grain coarsening of nanocrystalline materials often observed during irradiation at elevated temperature [43], compromises their radiation resistance.

Recently, nanotwinned (nt) metals have shown superior thermal stability and remarkable radiation tolerance compared to their nanograined counterparts [35,44–48]. *In situ* radiation studies in a transmission electron microscope unraveled that irradiated nt Cu and Ag, with a high density of TBs, contained a lower defect density than their bulk counterpart under the same radiation conditions [34,35,49]. The *in situ* observations also confirmed that SFTs, a dominant type of vacancy clusters in various irradiated metals with face-centered-cubic (fcc) structure, can be removed through their frequent interactions with TBs [34]. In addition, TB affected zones were observed in heavy ion irradiated nt Ag, providing direct evidence that TBs can act as an effective defect sinks [47]. Our recent studies on nt Cu showed that its radiation tolerance could be enhanced further by introducing nanovoids (nvs) at domain boundaries [50,51]. Nevertheless, as defect density evolves rapidly, the early-stage of defect-TB interactions has not yet been fully understood. To elucidate this issue, here we report a follow-up *in situ* Kr^{++} irradiation study on nanovoid-nanotwinned (nv-nt) Cu. The results show that irradiation-induced defect clusters were non-

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uniformly distributed inside the specimen at the early stages of irradiation process, lending further evidence for the enhanced radiation tolerance of nv-nt Cu.

2. Experimental

An epitaxial nt Cu film, ~1.5 μm thick, was deposited on HF etched Si (110) substrates at room temperature via DC magnetron sputtering technique. The chamber was evacuated to a base pressure of $<8 \times 10^{-8}$ torr prior to deposition, and the deposition rate was kept at ~0.6 nm/s. Plan-view transmission electron microscopy (TEM) samples were prepared by polishing, dimpling and low energy (3.5 keV) Ar ion milling.

In situ Kr^{++} ion irradiation was conducted at room temperature in the Intermediate Voltage Electron Microscope (IVEM), at Argonne National Laboratory. The Kr^{++} ion beam had a high energy of 1 MeV, and the microscope was operated at 200 kV. During radiation, a CCD camera was utilized to capture the microstructural evolution at 15 frames/s. The displacement damage inside TEM foil was estimated using the SRIM (Stopping and Range of Ions in Matter) simulation with the Kinch-Pease method [52,53].

The dose rate was controlled to be low in order to gain sufficient time for extracting more details on defect-TB interactions and the evolution of defect density during early stage (low dose) of radiation. The entire experiment consisted of two stages: stage 1 ranging from 0 to 0.025 dpa at a low dose rate $K_1 = 2.2 \times 10^{-4}$ dpa/s, and stage 2 over a dose of 0.025–0.1dpa at a higher dose rate $K_2 = 6.0 \times 10^{-4}$ dpa/s.

3. Results

Fig. 1 displays the microstructure of as-deposited epitaxial nt Cu film before irradiation. To characterize nanovoids, most of the TEM images were recorded at the under-focus condition ($\Delta f \approx -500$ nm), when voids appear as predominantly white dots surrounded by a dark Fresnel fringes. The plan-view TEM micrograph examined from Cu <111> zone axis in Fig. 1a shows abundant nanovoids positioned along columnar domain boundaries, and the inserted selected area diffraction (SAD) pattern confirms the formation of single crystal Cu. The cross-sectional TEM micrograph examined from Cu <110> zone axis in Fig. 1b shows a high number density of growth twins with Σ3 {111} coherent twin boundaries (CTBs) and Σ3 {112} incoherent twin boundaries (ITBs). It is worth noting that most of the vertical ITBs are located around domain boundaries and are decorated with nanovoids marked by circles in Fig. 1b. Statistic studies in Fig. 1c–e show the average domain size D_{ave}, void size L_{ave} and twin thickness t_{ave}, are approximately 102, 7 and 7 nm, respectively.

A series of *in situ* TEM snapshots in Fig. 2 demonstrate the defect morphology evolution up to 0.1 dpa at low and high dose rate. These images were taken in a bright-field condition along Cu <111> zone axis to determine defect density. In order to investigate the influence of domain boundaries on defect accumulation and distribution, each domain is divided into three equal-area regions according to their distances to boundaries, Region I located between the red and blue lines is defined as the boundary region. Region II, the intermediate region, is delineated between the blue and green lines. In the center of each domain lies region III, the center region. The width of region I and II is ~9 and 21 nm, respectively. Qualitatively, the TEM micrographs show that a majority of the irradiation-induced defect clusters (black dots) were located near domain boundaries in boundary region II, especially in stage 1 of low dose radiation (Fig. 2a–c). More details related to the evolution of defect morphology can be found in Supplementary Video S1 (accelerated by 5 times).

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The quantitative analysis of defect evolution in each region is shown in Fig. 3. The defect density in all 3 regions accumulates nearly linearly with increasing dose, and the accumulation rate becomes greater in stage 2 of higher dose rate (Fig. 3a). A linear superposition of defect density in all 3 regions is shown in Fig. 3b. Fig. 3c shows the accumulative defect density is the highest in boundary region I, and the lowest in center region III. Fig. 3d shows the normalized fraction of defect density in each region over two radiation stages. As each region has identical area, a yellow dash line at 33% is shown to indicate the iso-fraction defects level. At stage 1, the density of defects reaches 50% in boundary region I, much greater than that in center region III, merely 20%. However, at stage 2 (a higher dose rate), such a large gap is considerably reduced and defects exhibit a tendency of more uniform distribution as indicated by arrows.

During irradiation, interstitial and vacancy clusters are produced simultaneously in nv-nt Cu. Previous TEM observations indicate that in Cu with low stacking fault energy, a majority of the irradiation-induced defects are SFTs, which can be identified by their well-defined triangular shapes in TEM studies [54,55]. *In situ* videos captured the morphology evolution of several SFTs as shown in Fig. 4. Before irradiation, the grain G1 in Fig. 4a was basically free from defects. By 198s (0.075 dpa) in Fig. 4b, a large number of defect clusters were generated, and two SFTs (SFT1 and SFT2) emerged in the center of G1. At 204s in Fig. 4c, the SFT1 reduced its footprint and another SFT, SFT3, was generated adjacent to the slightly enlarged SFT2. During further irradiation at 208 s, SFT1 was eliminated (Fig. 4d). At 213s in Fig. 4e, the two SFTs changed their shapes, and SFT2 appeared to be truncated. A few sec later at 217s (0.086 dpa), both SFT2 and SFT3 collapsed into smaller defect clusters (Fig. 4f). In comparison to the long-lived SFTs, interstitial loops usually have a shorter lifespan [35], and two small circular loops L1 and L2 marked in Fig. 4e were eliminated in merely several secs. More detailed information on the morphology evolution of SFTs can be found in Supplementary Video S2.

Meanwhile, a majority of nanovoids at domain boundaries contracted continuously during irradiation. Typical void shrinkage events captured by *in situ* TEM experiments are shown in Fig. 5. At 0 dpa, three representative voids (V1-V3 in red circles) with comparably large diameters of 12.4, 10.8 and 7.6 nm and two relatively small voids (indicated by white arrows) were tracked. After irradiation over 250 s to 0.1 dpa, the dimension of three large voids labeled in circles decreased to 9.4, 9.8 and 5.2 nm respectively, while the two smaller voids (by arrows) almost disappeared. Fig. 5e shows the variation of void size (L) with increasing time and dose for ten nanovoids of various dimensions, with an initial diameter ranging from 5 to 12 nm. The void size decreased slightly during radiation at low dose rate (stage 1), and the void shrinkage rate increased at stage 2 at higher dose rate. The correlation of this phenomenon with the interstitial diffusion and absorption will be discussed later.

4. Discussion

4.1. Defect formation, diffusion and distribution in nv-nt Cu

Under heavy ion irradiation, vacancy-interstitial (Frankel) pairs are created by the well-known collision cascade. Compared with vacancies, interstitials have lower migration energy, ~0.1eV for Cu at room temperature [3], and once produced they can diffuse rapidly in all directions until they are absorbed by defect sinks [17]. In general, defect sinks, such as high-angle grain boundaries can efficiently absorb and eliminate irradiation-induced defect clusters,