Acta Materialia 96 (2015) 284–291

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Preferential void formation at crystallographically ordered grain boundaries in nanotwinned copper thin films

Thomas LaGrange [a], Kazuto Arakawa [b,c], Hidehiro Yasuda [d], Mukul Kumar [a,*]

[a] Lawrence Livermore National Laboratory, 7000 East Avenue, L-342, Livermore, CA 94550, USA
[b] Department of Materials Science, Faculty of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan
[c] CREST, JST, 7, Gobancho, Chiyoda-ku, Tokyo 102-0076, Japan
[d] Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, 7-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

A R T I C L E I N F O

Article history:
Received 18 December 2014
Revised 4 June 2015
Accepted 6 June 2015
Available online 24 June 2015

Keywords:
Grain boundary networks
Radiation defects
Grain boundary migration
Triple junctions

A B S T R A C T

Nanocrystalline materials are expected to have improved radiation resistance as the high density of grain boundary area is thought to act as an effective sink for radiation-induced defects. However, continued absorption of defects can alter the structure of grain boundaries and/or enhance their mobility, eventually leading to microstructural degradation in the form of grain coarsening, thus negating their initial radiation tolerance. Hence, an ideal microstructure might be one with a mix of boundaries that are effective sinks and limit grain coarsening. We show through *in situ* electron irradiation experiments, however, that this is an insufficient condition. Our observations indicate that even a high density of low energy coherent twin boundaries, supposedly stabilizing the microstructure against grain coarsening, can be a detriment in that it biases the mobility of vacancies accumulating during irradiation thereby resulting in preferential void nucleation near twin boundaries. These observations highlight the fact that radiation induced grain boundary migration depends greatly on the topology of the grain boundary network and that the migration of high-angle grain boundaries can be hindered when coordinated at triple junctions composed of at least two low-energy boundaries, e.g., coincidence site lattice boundaries.

1. Introduction

Most structural materials used in nuclear reactors are prone to radiation damage that degrade their mechanical properties and limit their service life. High-energy particle irradiation produces defects in these materials that are mobile at high temperatures and are influenced by stress fields associated with pre-existing extended defects. After an initial relaxation phase, the defects, that do not recombine, aggregate to produce defect clusters or diffuse rapidly to interfaces and other defects, inducing detrimental microstructural evolution [1]. For example, interstitials, being more mobile than the vacancies, are quickly absorbed by nearby dislocations, inducing creep by dislocation climb and dislocation multiplication that result in work hardening and embrittlement. Likewise, a small excess of remnant vacancies can agglomerate, leading to the formation of voids that cause swelling [1–6], an increase in residual stresses, microcrack formation, and the eventual failure of the material. The long-term stability of a microstructure under irradiation depends on its neutrality toward defect absorption. Even a small imbalance in defect mobility and absorption at sinks can eventually lead to a dramatic degradation of strength and structural integrity. This could be particularly true under high radiation doses and dose rates, where the balance between the rate of defect production and absorption may overwhelm even a highly efficient defect sink [1,7]. Development of materials with a high density of sites that can act as sinks for the point defects produced by high-energy particles would thus be an enabling technology for reliable and clean nuclear energy.

Polycrystals with nano-sized grains have a high interfacial areal density and have been considered to possess an ideal microstructure for radiation resilience [8]. Extensive research on the void nucleation and swelling produced by high energy electron and fission neutron irradiation has shown that in materials with submicron grain sizes, void formation is greatly reduced [7,9–12]. The main supposition of these studies is that grain boundaries (GB) are efficient sinks for vacancies and that as the average grain size decreases below 1 μm vacancy concentrations dramatically diminish thereby reducing the tendency to form and grow voids. (The assumption that all grain boundaries behave alike regardless of their crystallographic identity is implicit in these studies.) Thus the use of nanocrystalline materials should be an adept solution

* Corresponding author.

http://dx.doi.org/10.1016/j.actamat.2015.06.015
1359-6454/

to reduce irradiation induced swelling. However, at elevated temperatures the grain boundary area per unit volume in most nanocrystalline materials tends to decrease with time, potentially negating its initial advantages for radiation resilience. Remarkably, with our current knowledge of the basic physics of coarsening in high dose radiation environments, it is difficult to predict whether a given nanostructured material will have adequate radiation resistance. Moreover, nanocrystalline structures have a distinct topological character that is different from conventional micron-sized polycrystalline microstructures [13,14], which may significantly influence the defect dynamics during the cascade relaxation phase. And, like the case of grain coarsening, the topological characteristics of the grain boundary network (GBN) may well be an important factor in the radiation resistance of nanostructured materials.

Here, we examine the effect of GBN topology on radiation induced grain boundary migration (RIGBM) and on void formation using nanotwinned copper (nt-Cu) foils. The nt-Cu samples are composed of regions with a high density of coherent twin boundaries (CTB) and have a moderate fraction of random high angle grain boundaries (HAGB). With such topologically distinct microstructures, we are able to contrast different GB types and gain better understanding of their influence on the radiation induced coarsening and void formation (see Fig. 1A and B). Being low energy, a high density of CTBs and triple junctions (TJ) composed of low angle boundaries (LAGB, angular misorientation <15°) and CTBs can limit thermal coarsening in nanocrystalline materials [15,16], but the sink efficiency of such microstructures is poor. Conversely, a mixture of random HAGB and CTBs is prone to destabilization if the majority of the TJs have only one low energy component (out of three), with incoherent twin boundary (ITB) segments readily nucleating and causing the hitherto low mobility interfaces to migrate at a faster rate [13]. This is unlike the case of conventional polycrystalline microstructures where a high density of CTBs and ITBs in a well-organized topological network substantially reduced the coarsening rate [17].

In an effort to elucidate the optimal microstructure that combines resistance to both microstructural coarsening and radiation damage we use high-energy electron irradiation *in situ* in a 2 MeV transmission electron microscope (TEM). This allows us to probe the influence of GB character and network topology on the point defect annihilation and agglomeration processes attendant in nanocrystalline materials with a high density of CTBs (to provide coarsening resistance) and random HAGB (for radiation sink efficiency). By irradiating with high-energy electrons, that produces Frenkel defects (vacancy-interstitial pairs), we can isolate and observe the microstructural evolution solely associated with point defect agglomeration dynamics. We also contrast the microstructural evolution under ambient and high temperature electron radiation to evaluate the influence of GB character on damage accumulation behavior that leads to void formation. Through *in situ* observations of the microstructural evolution and the differences under irradiation of various grain boundary types, we are able to formulate a better correlation between grain boundary character, radiation sink efficiency and radiation defect dynamics in nanotwinned metals.

2. Methods

2.1. nt-Cu sample preparation

High-purity (99.999%) nt-Cu samples used in these studies were fabricated via DC magnetron sputtering implementing a "multilayer" process method that yields thick (>25 μm), uniform foils with a nanotwinned, columnar structure. The growth twin density in nt-Cu samples is governed by the deposition rate [18]. Depositing the foils at rates of $\sim$2.5 nm s^{-1} resulted in high twin area densities per volume of >10^{7} m^{-1}. Cross-sectional TEM samples were prepared by focused-ion-beam (FIB) method (FEI Nova 600 Dual-Beam FIB, Oregon, USA) and FIB sections were taken from the as-deposited nt-Cu films, which have a high density of CTBs (see orientation and bright-field images in Fig. 1). The FIB sectioning creates a thin damage layer due to the high-energy ion bombardment. To remove this amorphous damage layer, the samples were subjected to a final polishing step in a Gatan precision ion polishing system (PIPS) using a modified low energy Ar gun at 500 eV.

2.2. Electron irradiation conditions

In-situ electron irradiation experiments on the nt-Cu foils were conducted on the Hitachi H-3000 ultra high voltage (UHV) transmission electron microscope (TEM) located at the Research Center for High Voltage Electron Microscopy in Osaka University. The TEM was operated at a voltage of 2 MeV and the electron beam was focused to a spot 1 μm in diameter, producing electron dose rates of 2.4×10^{24} e^{-} m^{-2} s^{-1} in the region of interest on the specimen. Images were taken sequentially as a function of irradiation time and during the imaging itself the electron beam was defocused to give effective electron doses of $\sim$1–2 $\times 10^{23}$ e^{-} m^{-2} s^{-1}. Electron irradiation during image acquisition itself, though minimal, was also included in these dose calculations. In-situ observations of microstructural evolution during electron irradiation were made at ambient temperatures and at higher temperatures around 573 K. These conditions were chosen based on the prior research by Niwase et al. [19] who observed significant void formation in copper at these temperatures under electron irradiation. Defect evolution and void formation were tracked as a function of irradiation time and calculated dose. The position of individual GBs was also tracked during irradiation to compare the influence of GB type on their observed radiation induced migration.

2.3. Crystallographic orientation acquisition and analysis

Automated crystallographic orientation mapping (ACOM) data of the nt-Cu TEM foils and irradiated materials were acquired using the NanoMEGAS ASTAR system attached to a field-emission FEI CM300 transmission electron microscope (TEM). The ASTAR system collects and indexes nanodiffraction patterns over a total scan area of a few square micrometers, and thus provides statistically relevant information of the grain orientation, texture and GB character (i.e., GBs and TBs in general) [20]. As the thickness of TEM samples is on the order of $\sim$100–150 nm, the dynamical (multiple scattering) diffraction effects influence the intensity of the diffraction spots and complicate the determination of the local crystal orientation. By precessing the electron beam about the TEM optical axis, which effectively wobbles the Ewald's sphere about the microscope axis, more diffraction spots are present in the diffraction patterns and quasi-kinematical diffraction intensities are obtained, greatly assisting orientation determination and increasing data reliability. The ACOM data displayed in Fig. 1B were collected with a precession angle of 0.5°, a probe size of 6 nm, and a scan step size of 4 nm, which provides oversampling and increased reliability. The orientation data shown in Fig. 4 was acquired with a 1 nm probe size, scan step of 0.88 nm and a precession angle of 0.5°. The technique is not entirely free of artifacts; in particular, ambiguities in orientation indexing arise for regions aligned close to a high symmetry axis or when two crystals (grains) significantly overlap. These regions are infrequently encountered and are easily identified and eliminated from the statistics by partitioning the