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In Situ TEM and Molecular Dynamics Investigation of Grain Growth in Nanocrystalline Cu Nanoparticles

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The thermal stability of nanocrystalline Cu nanoparticles was investigated using a combination of in situ TEM annealing experiments and molecular dynamics (MD) simulations. Nanoparticles prepared by a gas aggregation source exhibit an average size of ~100 nm and are predominantly polycrystalline, with grains of ~25 nm. Upon annealing up to 600 °C, the particles preserve their external morphology without signs of sintering, while their internal structure evolves through progressive grain growth. Orientation mapping revealed an increase in Σ3 and other special boundaries, consistent with the tendency of grain boundary networks to evolve toward low-energy configurations. MD simulations partially reproduce the general coarsening process and the formation of nearly monocrystalline particles, but predominantly produce {111} stacking faults rather than Σ3 twins. This discrepancy is attributed to the limited timescale and idealized initial conditions of the simulations compared with the defect-rich experimental particles.

Keywords: Cu nanoparticles, Grain growth, Nanocrystalline grains, ACOM TEM, Molecular dynamics

1 Introduction

Nanocrystalline metals with grain sizes below ~500 nm are inherently unstable at elevated temperatures because of the high energy stored in their grain boundary network [1-4]. Even modest annealing can trigger grain coarsening, altering structure and properties [5, 6]. Copper is a technologically important metal used in electronics, interconnects, and catalysis [7-11], yet Cu nanostructures are particularly prone to microstructural change when heated [6, 12-14]. While most studies of Cu nanoparticles have focused on sintering and coalescence between particles [15-17], much less is known about the processes of intrinsic grain growth inside individual polycrystalline nanoparticles. While conventional nanocrystalline grain-growth models (usually derived for bulk-like, periodic networks) predict coarsening through curvature-driven boundary migration, they often fail in highly confined systems [6, 18-19]. In nanoparticles (~100 nm) composed of ~10–20 nm grains, proximity to free surfaces and finite geometry profoundly distort boundary motion and topological evolution—a fact existing theories overlook. Understanding how grain size and special boundaries evolve under these confined conditions is therefore essential both for the stability of functional nanoparticles and for advancing fundamental theories of recrystallization at the nanoscale [6, 20].

Previous in-situ TEM studies on nanocrystalline Cu thin films and foils have shown that grain growth proceeds not only by conventional curvature-driven boundary migration but also via mechanisms such as grain rotation, coalescence, and the formation of annealing twins [12, 21]. In face-centered cubic metals like Cu, Σ3 twin boundaries—equivalent to coherent twin planes—are essential because of their comparatively low energy, and they can either pin grain boundaries or facilitate their motion [22]. Atomistic simulations have similarly highlighted the roles of grain rotation and specialized boundary formation in nanocrystalline grain growth—for instance, MD results show grain rotation reduces boundary energy [23, 24]. Still, these predictions remain rarely tested in confined, three-dimensional geometries like nanoparticles. Thus, for polycrystalline nanoparticles—where the high surface-to-volume ratio and geometric confinement can fundamentally alter boundary stability—there is scant experimental data on how average grain size and special boundary (Σ3) fraction evolve during annealing.

Here, we investigate grain growth inside individual polycrystalline Cu nanoparticles during in-situ TEM heating up to 600 °C. Using bright-field imaging and ASTAR orientation mapping at selected temperatures, we quantify the evolution of the average grain size

and the fraction of Σ3 (twin) boundaries. These experimental observations are complemented by molecular dynamics simulations of heated Cu nanoparticles, which provide atomistic insight into the same structural descriptors under controlled conditions. By directly comparing experiment and simulation, we aim to clarify how grain size and special boundary populations evolve in confined nanoparticles, and to assess the influence of nanoscale geometry and surface proximity on grain growth.

2 Methods

A primary gas aggregation cluster source (GAS) was employed to generate Cu nanoparticles (NPs). The sputtering process was carried out from a Cu target using a DC planar magnetron that forms the central part of the GAS. Argon was introduced at a constant flow rate of 8 sccm, while the working pressure in the aggregation chamber was maintained at 43 Pa. More details about the used GAS can be found here [25].

For TEM analysis, the NPs were detached from the substrate using a razor blade, dispersed in methanol, and pipetted onto a TEM grid coated with ultrathin lacey carbon support film.

The specimens were examined using a JEOL 2200FS transmission electron microscope operated in TEM mode. Further characterization was done using automated orientation phase mapping (ACOM-TEM) with the JEOL 2200FS TEM equipped with "Spinning Star" electron precession with an ASTAR software package.

For molecular dynamics simulations, the LAMMPS software was used [26], implementing an embedded atomic potential for copper [27]. Polycrystalline Cu nanoparticles with a diameter of 10 nm were created in Atomsk [28] with grains constructed by Voronoi tessellation [29]. The simulations were performed at a temperature of 873 K using the Nosé–Hoover thermostat in the NVT ensemble, with a time step of 1 fs, as implemented in LAMMPS. Atomic configurations and grain sizes were determined using polyhedral template matching [30], as implemented in OVITO [31]. Special boundary areas were quantified with a custom Python script executed within OVITO.

3 Results

Figure 1 shows the initial state of the Cu nanoparticles prepared by a gas aggregation source. The particles exhibit a mean size of ~100 nm and are predominantly spherical. Diffraction contrast in the BF images (Figure 1a,b) reveals that most particles contain several grains with an average grain size of ~25 nm, while a few particles appear as single crystals. The polycrystalline nature of the nanoparticles is further confirmed by ACOM TEM maps (Figure 1c–e), which show large misorientations between the grains rather than subgrains.

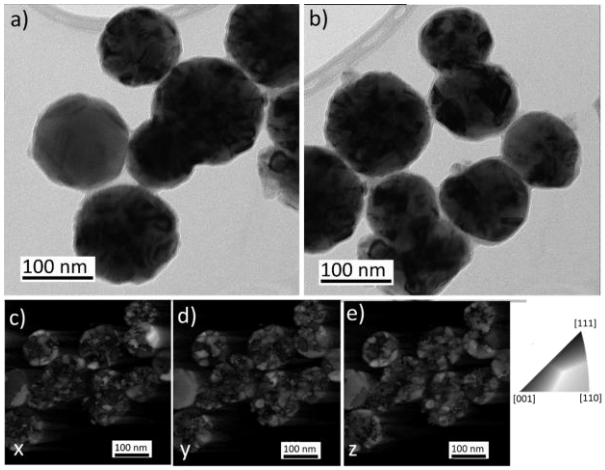

Fig. 1 *As sputtered nanoparticles a, b) TEM BF, c-e) ACOM TEM maps in x,y and z direction*

The particles were annealed in situ in the TEM from room temperature up to 600 °C, in steps of 100 °C, with each temperature held for 10 minutes. The evolution of the microstructure is shown in Figure 2. Up to 600 °C, the particles preserve their overall shape, and no signs of sintering are observed. The main changes occur within the internal nanostructure, where a gradual grain growth occurs in individual particles. Notably, one particle transforms into a single crystal at 400 °C, while at 600 °C, the majority of the particles become monocrystalline.

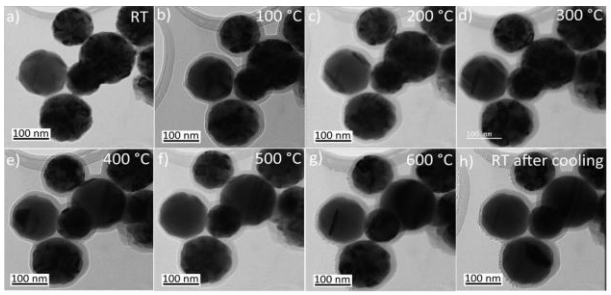

Fig. 2 *TEM BF of the in situ annealing in the temperature range from room temperature to 600 °C*

For further characterization, ACOM TEM maps were acquired at selected temperatures (Figure 3). At 400 °C, apart from the particles that became fully monocrystalline, most particles retained their initial nanostructure, with only occasional signs of grain growth (Figure 3b, arrows). At 600 °C, changes in the orientations of grains that remained polycrystalline were observed, likely caused by particle rotation. Progressive grain growth is also evident from the grain size histograms (Figure 3d–f).

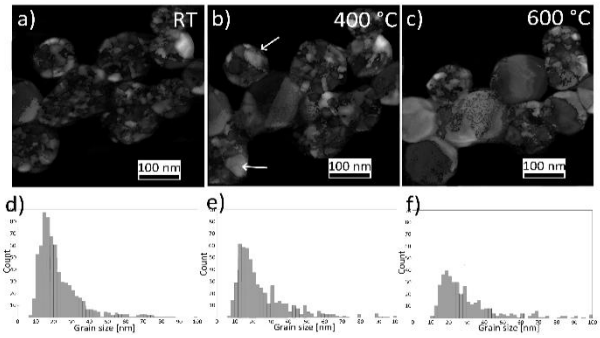

Fig. 3 *ASTAR maps images of the nanoparticles annealed to temperatures RT – 600 °C with corresponding grain size plots*

Information about the grain boundaries was extracted from the ACOM TEM maps (Figure 4). In particular, special boundaries such as Σ3, Σ5, Σ7, and others are highlighted. By tracking the fraction of the special boundary length relative to the total boundary length (Figure 4d–f), a significant increase in Σ3 is evident after annealing to 600 °C. The fractions of Σ7, Σ9, and Σ19a boundaries also increase, while the fraction of Σ5 decreases. Between room temperature and 400 °C, no significant changes are observed.

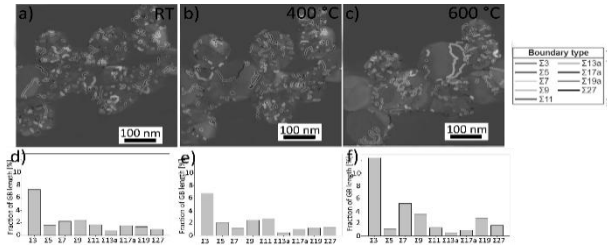

Fig. 4 *a- c) Overlap of ACOM TEM maps with special grain boundaries, d-f) corresponding histograms of special boundary length fractions*

Annealing was then simulated using MD on four particles with randomly oriented grains. Figure 5 shows an example of the results, visualized and colored according to grain orientation.

During the simulation, grain boundaries gradually disappeared as neighboring grains merged, leading to the growth of larger grains at the expense of smaller ones. In the final state, the nanoparticle became monocrystalline, but with planar defects (stacking faults). This outcome is consistent with TEM observations, where grain growth often produces nearly monocrystalline particles containing residual defects.

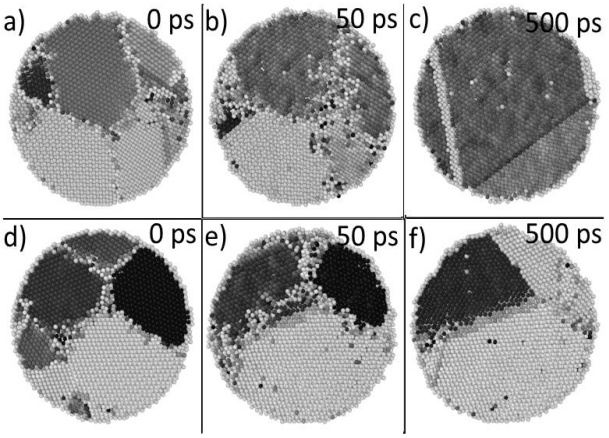

Fig. 5 *Example visualization of the result of the MD simulation of two different nanoparticles annealed to 600 °C at various time steps*

Special boundary areas were also extracted from the simulation results. Figure 6 compares their fractions in the initial state and after annealing for 0.5 ns at 600 °C. In contrast to the experimental observations, the Σ3 boundary area decreases after annealing, while only Σ11 and Σ9 increase in the selected particles.

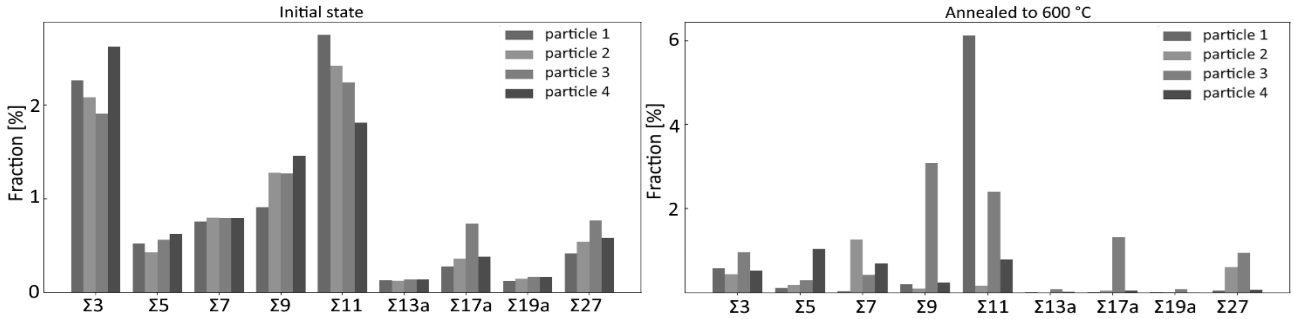

Fig. 6 *Area of special grain boundaries in MD – initial state and after annealing up to 600 °C for 500 ps*

4 Discussion

The experimental in situ TEM annealing demonstrated that Cu nanoparticles remain morphologically stable up to 600 °C, showing no evidence of sintering. Instead, the main microstructural evolution occurs internally, through grain coarsening and progressive reduction of grain boundary area. Grain growth in nanocrystalline metals has been widely reported during thermal treatment, where the driving force is the reduction of grain boundary energy [12, 32]. The increase in Σ3 and other special boundaries observed in the ACOM TEM analysis suggests that annealing promotes the formation of low-energy, energetically favorable boundaries, consistent with the concept of grain boundary engineering established in bulk materials [33, 34]. It should be noted that in the experimental

ACOM TEM maps, boundaries classified as Σ3 are not observed as extended, perfectly coherent twin planes, but rather as irregular or curved interfaces. This indicates that the Σ3 classification by MTEX likely includes incoherent twin-related segments or locally perturbed twin boundaries formed during boundary rearrangement, rather than long, defect-free coherent twins. Such irregular Σ3 features are typical in nanocrystalline systems, where the extremely short grain boundary length, high density of triple junctions, and nonequilibrium defect structures cause deviations from ideal, periodic boundary geometries [35, 36].

Experimentally, the Σ3 fraction (twins) increases upon annealing, consistent with the formation of low-energy coherent twins. In MD, however, planar defects manifest chiefly as {111} stacking faults rather than fully developed twins, likely due to the limited simulation timescale, the dominance of partial dislocation activity at free surfaces, and the smaller grain sizes compared to the experiment. Since coherent twins can emerge from successive faulting on {111}, longer simulation times, larger particle sizes, and/or additional thermal–mechanical activation may be required to reproduce the experimentally observed Σ3 enrichment. Another factor that may contribute to the discrepancy is the difference in initial conditions. The sputtered nanoparticles studied experimentally are formed under non-equilibrium growth, and thus contain a high density of defects and residual internal strains. These stored energies provide additional driving forces for grain boundary rearrangement and can favor the stabilization of low-energy Σ3 boundaries. Similar effects have been reported in nanocrystalline Ni, where thermomechanical treatments promoted Σ3 boundary formation through defect-driven boundary rearrangement [37]. In contrast, the MD simulations were initialized with idealized grain structures and without deposition-induced strains, limiting the available mechanisms for Σ3 enrichment.

5 Conclusions

In situ TEM annealing revealed that Cu nanoparticles remain morphologically stable up to 600 °C, without signs of sintering, while undergoing significant internal grain growth. The fraction of special boundaries, particularly Σ3, increased during annealing, indicating that the boundary network tends to evolve toward energetically favorable configurations. This behavior is consistent with concepts of grain boundary engineering in bulk systems.

Molecular dynamics simulations reproduced overall grain coarsening and near-monocrystalline end states but did not show the Σ3 enrichment observed experimentally. Instead, it produces primarily stacking faults. The differences in the evolution of special boundaries between experiment and simulation underline the importance of extending simulations to longer timescales and larger ensembles of particles to capture the statistical trends observed experimentally. These results contribute to the broader understanding of nanocrystalline Cu stability and annealing behavior.

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