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# Experimental observations of twin formation during thermal annealing of nanocrystalline copper films using orientation mapping

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ABSTRACT

This study employed a TEM-based automated crystal orientation mapping technique that enables orientation mapping with nanoscale spatial resolution. This nanoscale orientation mapping technique was employed to study thermally-assisted grain growth and to quantify the attendant formation of nanotwins and twin junctions in nanocrystalline Cu. The grain size increased from 29 ± 14 nm to 57 ± 22 nm and the fraction of twin-containing grains increased from 0.18 to 0.70. Close inspection of the twins and twin junctions captured within orientation maps documented a frequency of junctions that was remarkably consistent with previous molecular dynamics predictions.

The physical and mechanical properties of metals are highly dependent on the type and density of interfaces that they contain. For example, tailoring microstructures with certain boundaries can result in materials with enhanced properties [1,2]. The study of special grain boundaries and the manufacture of materials with specific grain boundary character has been shown to provide enhanced properties (e.g. improved fatigue life and resistance to stress-corrosion cracking [1]) and is commonly referred to as grain boundary engineering. Grain boundary engineering has been applied to a number of coarse-grained material systems to great effect [3].

Nanocrystalline metals and alloys have been shown to possess yield strengths that are an order of magnitude greater than coarse-grained metals [4–6], but a major drawback of nanocrystalline metals is that this strength generally comes with an equally dramatic loss of tensile ductility [5]. Recent studies have sought to use boundaries to give nanocrystalline metals and alloys high strength while also maintaining ductility. For example, Gianola et al. have demonstrated that film purity can have a profound effect on stress-assisted grain boundary migration and the ductility of nanocrystalline films [7]. Lu et al. have shown that nanotwinned Cu possesses both high strength and ductility, demonstrating that the types of boundaries in a microstructure can have a profound effect on the ensuing properties [8–10]. Rather than being comprised of many random grain boundaries, as is the case in nanocrystalline Cu, nanotwinned Cu is coarse grained (~400 nm) with each grain containing closely spaced (~10 nm) twin boundaries [11]. These examples highlight the importance of characterizing and using the character and density of grain and twin boundaries as routes to producing nanoscale microstructures with enhanced properties.

Thermal annealing of nanocrystalline metals leads to grain growth of but can also alter the grain boundary character. This is especially true when annealing introduces twins into the microstructure [12]. Recent molecular dynamics (MD) simulations performed by Thomas et al. show the evolution of nanocrystalline Ni throughout annealing, focusing on the types of twins and twin junctions that form as a result of grain growth [13]. The MD simulations conducted by Thomas predicted 6 types of twin junctions, and these simulations were used to deduce atomic-level descriptions of how the twins are formed. The MD simulations also suggested that the twin junctions act to retard grain growth in the nanocrystalline microstructure, thus providing an example of the more global influence of twins.

To benchmark MD simulations like those performed in [13], characterization techniques with nanoscale resolution are needed. Grain boundary misorientation can be routinely obtained using orientation imaging microscopy, but determining grain boundary character requires knowledge of the shape and orientation of the grain boundary as well as the misorientation between grains. The spatial resolution of SEM-based electron backscatter diffraction (EBSD) techniques has improved in recent years but is generally still above what is needed to collect orientation maps of nanocrystalline metals and alloys. By contrast, the ASTAR system, recently developed by NanoMEGAS, facilitates collection and automated indexing of selected area electron diffraction (SAED) patterns from an array of locations across a sample [14]. By

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using this TEM-based automated crystal orientation mapping (ACOM) technique, orientation maps with a 2 nm step size can be routinely acquired. This results in many pixels per grain, producing well-defined grain shapes and boundaries. TEM-based ACOM maps do not directly yield information about the inclination of boundary planes perpendicular to the specimen surface and, thus, provide only 4 of the 5 required degrees of freedom to fully characterize a grain boundary. But, this effect is reduced in thin film specimens, where techniques sensitive to overlapping grains can provide estimates for the boundary inclination.

Nanocrystalline Cu thin films (60 nm thick) were fabricated via electron beam vapor deposition followed by modest thermal annealing at 300 °C for 30 min. A detailed fabrication procedure can be found in [15]. The microstructures of the as-deposited and annealed films were captured using TEM-based ACOM and a step size of 2 nm. These orientation maps were analyzed and transformed to a digital dataset using standard EBSD software developed by EDAX [16]. Fig. 1 compares the microstructure of the film before and after thermal annealing. The as-deposited film had an average grain size of 29 ± 14 nm, which after thermal annealing increased to 57 ± 22 nm. A cumulative distribution plot (Fig. 1a) shows the increase in grain size brought about by the annealing. In addition to growing the grains, many twins were introduced into the microstructure during the anneal. Orientation maps taken from the as-deposited and annealed films are shown in Fig. 1b and c, respectively. The grains containing Σ3 twin boundaries are highlighted, with parent grains colored blue and twinned regions colored red.

The number fraction of grains containing twin boundaries increased from 0.18 to 0.70 upon annealing. A summary of the length fraction of grain boundary characters, defined as the length of a specific GB type divided by the total observed GB length, for approximately 25,000 boundaries is given in Table 1. The thermal anneal resulted in a substantial increase in the Σ3 density with a commensurate decrease in the number of general high-angle boundaries. The density of Σ9 boundaries and low-angle boundaries was observed to be low and relatively constant for both. The amount of grain growth and twin density is comparable to that obtained in previous bright-field TEM observations of nanocrystalline Cu [12]; Simões et al. observed that grains in sputter deposited nanocrystalline Cu thin films grew from 43 ± 2 nm to 77 ± 4 nm when annealed for 1 h at 300 °C. They also reported a significant increase in twin density after the first hour of annealing [12].

**Table 1**
Grain boundary character comparison between as-deposited and annealed Cu thin films.

| Boundary type | As-deposited | Annealed |
|---|---|---|
| Low angle (5°–15°) | 0.045% | 0.090% |
| High angle (15°+) | 81.2% | 69.2% |
| Σ3 | 18.7% | 30.6% |
| Σ9 | 0.043% | 0.044% |
| Total # of boundaries observed | 2038 | 22,584 |

Thomas et al. described one effect twin junctions can have on the overall material properties as a reduction of overall grain boundary mobility [13]. Based on their MD simulations, Thomas identified six different types of twin junctions and referred to them as α, β, γ, δ, ε, and ζ [13]. They calculated the energy of each of these junctions and catalogued the frequency at which they appeared in their simulations of nanocrystalline Ni. In the as-deposited Cu films studied here, none of the aforementioned twin junctions were observed. Upon annealing, the increase in the population of Σ3 boundaries coincided with the formation of twin junctions that were observed with regularity. Orientation maps showing one set of junctions are presented in Fig. 2. Fig. 2a shows an example of a β junction: two coherent Σ3 boundaries intersecting at a 70.5° angle with a Σ9 boundary. Fig. 2b shows an

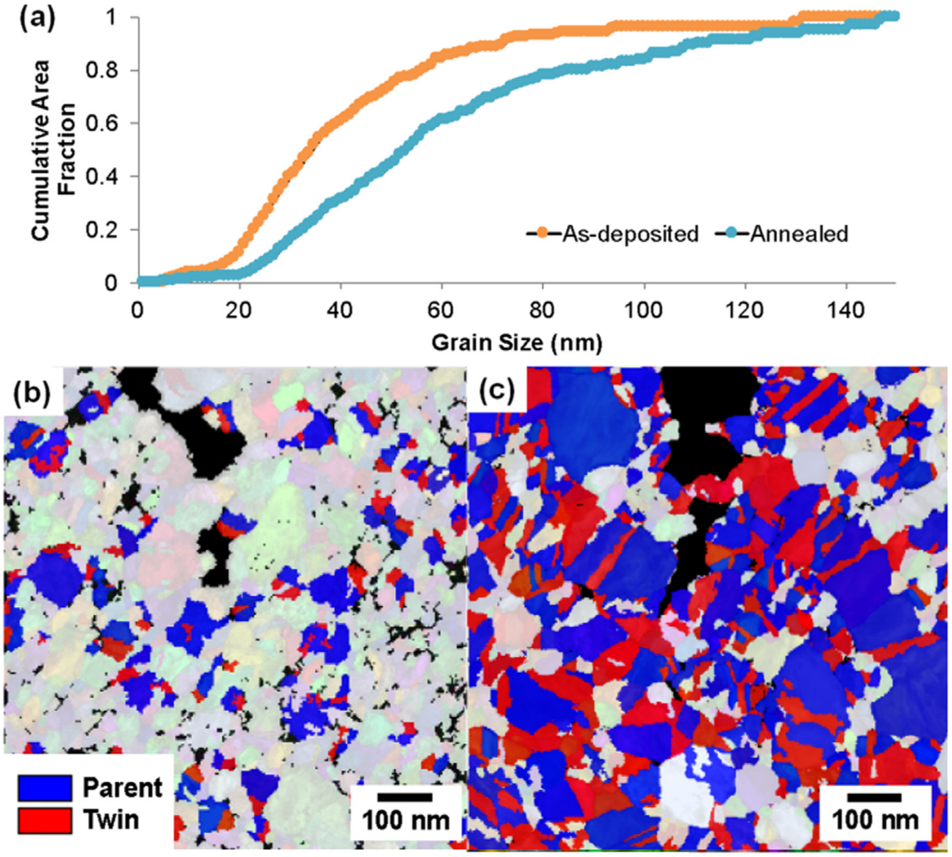

**Fig. 1.** (a) Cumulative distribution plot showing the grain size of the as-deposited and annealed Cu films. Orientation maps for (a) as-deposited and (b) annealed specimens. Grains in which twin boundaries are located are highlighted with parent grains colored blue and twinned regions in red. The fraction of twinned grains increases from 0.18 to 0.70 upon annealing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)