Acta Materialia 96 (2015) 378–389

Contents lists available at ScienceDirect

Acta Materialia

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

Optimization of strength and ductility in nanotwinned ultra-fine grained Ag: Twin density and grain orientations

R.T. Ott [a,*], J. Geng [a], M.F. Besser [a], M.J. Kramer [a,b], Y.M. Wang [c], E.S. Park [a], R. LeSar [a,b], A.H. King [a]

[a] Division of Materials Sciences and Engineering, Ames Laboratory (USDOE), Ames, IA 50011, USA
[b] Materials Science and Engineering Department, Iowa State University, Ames, IA 50011, USA
[c] Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

ARTICLE INFO

Article history:
Received 12 February 2015
Accepted 14 June 2015
Available online 27 June 2015

Keywords:
Nanotwinned
Ultra-fine grained
Ag
Nanostructured
Synthesis

ABSTRACT

Nanotwinned ultrafine grained Ag thick films with different twin densities and orientations have been synthesized by magnetron sputtering with a wide-range of deposition rates. The twin boundary (TB) spacings and orientations as well as the grain size for the different deposition conditions have been characterized by both synchrotron X-ray scattering and transmission electron microscopy (TEM). Structural characterization combined with uniaxial tensile tests of the free-standing films reveals a large increase in the yield strength for films deposited at high deposition rates without any accompanying change in the TB spacing – a behavior that is not reported in the literature. We find that films deposited at lower deposition rates exhibit more randomly oriented grains with a lower overall twin density (averaged over all the grains) than the more heavily twinned grains with strong ⟨1 1 1⟩ fiber texture in the films deposited at higher deposition rates. The TB spacing in the twinned grains, however, does not show any significant dependence on the deposition rate. The dependence of the strength and ductility on the twin density and orientations can be described by two different soft deformation modes: (1) untwinned grains and (2) nanowinned grains that are not oriented with ⟨1 1 1⟩ along the growth direction. The untwinned grains provide relatively low resistance to slip, and thus decreased strength, while the nanotwinned grains that are not oriented with ⟨1 1 1⟩ along the growth direction are softer than nanotwinned grains that are oriented with ⟨1 1 1⟩ along the growth direction. We have revealed that an ultrafine-grained (150–200 nm) structure consisting of a mixture of nanotwinned (~8–12 nm spacing) and untwined grains yields the best combination of high strength and uniform tensile ductility.

1. Introduction

Nanotwinned (nt) materials have attracted considerable attention in recent years as an extension of work on nanocrystalline metals and alloys [1–19]. While nanocrystalline materials exhibit significantly improved mechanical properties over materials with more conventionally-scaled microstructures, they suffer from a number of challenges, including poor coarsening resistance and elevated electrical resistance [20–22]. Nanotwinned materials provide strength gains similar to those of their nanograined counterparts, but potentially with better coarsening resistance and improved electrical conductivity. The origins of the mechanical properties of nanotwinned materials, however, are not completely understood. Much has been learned about the effects of grain size on deformation. Strengthening of metals via the confinement of dislocations by grain boundaries can be described empirically by the Hall–Petch (H–P) relationship,

$$\sigma_y = \sigma_o + k_y d^{-1/2} \quad (1)$$

where σ_y is the yield strength, σ_o is related to the lattice friction, k_y is a constant and d is the grain size. This relationship has proven reliable over many orders of magnitude of the grain size, from the tens of microns down to nanocrystalline materials with grain sizes approaching 10–20 nm [23–26]. For smaller grain sizes, however, there is evidence from experiments and simulations that the H–P relationship breaks down, and there can be apparently "inverse H–P relationship" i.e., softening with decreasing grain size [27–32].

For face-centered cubic (fcc) metals that contain {1 1 1} coherent twin boundaries (CTB), the classic Hall–Petch equation in Eq. (1) has been modified to include the contribution of twins, which are now the smallest structural feature in the material. In this case, the revised H–P equation is [9]:

* Corresponding author.
E-mail address: rtott@ameslab.gov (R.T. Ott).

http://dx.doi.org/10.1016/j.actamat.2015.06.030
1359-6454/

$$\sigma_y = \sigma_o + k_y^d d^{-1/2} + k_y^t t^{-1/2} \quad (2)$$

where t is the average twin boundary spacing. For nt-Cu prepared by electrodeposition, Lu et al. reported that the tensile yield strength can be well-described by the H–P relationship in Eq. (2) down to a TB spacing of ~17 nm, at which point the films exhibit softening behavior [11]. Interestingly, nt-Cu films prepared by magnetron sputtering [6,7,15,33,34] appear to show lower yield strengths than films prepared by electrodeposition for TB spacings down to ~15 nm, but no softening with decreasing TB spacing. A key difference between the two findings is that the films prepared by sputtering have strong ⟨1 1 1⟩ fiber textures and columnar grains, while the electrodeposited materials have mostly equiaxed nt-grains with more random orientations albeit still with a ⟨1 1 1⟩ fiber texture. The strength of the films with columnar grains has been described in the context of the confined layer slip (CLS) model, which was initially developed to describe plastic deformation in multi-layer films [35]. Since the coherent TBs are predominantly parallel to the loading axis, according to the CLS model the yield strength should show a $1/t$ dependence [15,36].

Beyond size-dependent strengthening effects, texturing in polycrystalline materials is also known to strongly affect the strength of materials. For polycrystalline metals, the aggregate of grain orientations can be represented by the Taylor factor (M) [37], where,

$$\sigma = M\tau_{\mathrm{crss}} \quad (3)$$

For fcc metals with random grain orientations, the average value for M is 3.1, but ranges from 2.5 to 3.67 for materials with 100% ⟨1 0 0⟩ texture and 100% ⟨1 1 1⟩ texture, respectively [38]. Given the strong texturing often associated with films prepared by magnetron sputtering, the effects of the different grain orientations on the strengthening behavior need to be considered.

Although nanotwinned metals are known to have the ability to achieve both high strength and high ductility, the experimental demonstration of such a behavior has been limited to nt-Cu prepared by electrodeposition with random grain orientations [11], where a minimum grain size of 500 nm is considered prerequisite in order to avoid the longstanding strength–ductility tradeoff paradigm in nanostructured materials [39,40]. An outstanding question remains whether both strength and ductility can be achieved when the grain size decreases below 500 nm as twin boundaries act as the main strengthening agents. There are existing challenges to investigate and subsequently optimize the strength–ductility of nt-metals in this grain size region (i.e., 100–500 nm). First, a large quantity of the data in the literature for ultrafine-grained materials has shown an early necking behavior and low uniform tensile elongation (<~2%) when the grain size is only a couple of hundred nanometers [39]. Second, to optimize the strength and ductility, a wide range of processing parameters is required in order to fabricate materials with different twin densities and grain sizes. Third, it is difficult to address the ductility issue through molecular dynamics (MD) [41] due to spatial and temporal limitations, and thus, experimental exploration of this behavior is essential. Lastly, there are a limited number of metals (e.g., Ag, Cu and Pd), which form high-density growth twins during synthesis. Therefore, the material-of-choice for such study is very limited.

In this paper, the contributions of different strengthening mechanisms in nt-Ag films, e.g., grain size, twin density (averaged over all the grains) and orientation effects as well as their dependence on the processing conditions are examined. Specifically, we report on the strengthening associated with changing the TB density and orientation in free-standing nt-Ag films prepared by magnetron sputtering. Using a wide-range of deposition rates onto LN_2-cooled substrates, we are able to synthesize thick films (> 35 μm) in which the average grain size can be tailored from 150 to 300 nm and the twin density varied for a constant TB spacing. Moreover, the relative orientations of the grains (and hence the twins) can be controlled, with the highest deposition rates yielding films with highly {1 1 1} textured columnar grains and the lowest deposition rates providing films with much more randomly oriented grains relative to the growth direction. From these films, we have determined the important interdependence between the deposition conditions, the twin density, twin orientations and the bulk mechanical behavior. For the first time, we achieve high strength and high ductility in ultrafine-grained (150–200 nm) nt-Ag samples.

2. Experimental methods

Ag films were deposited onto ⟨1 0 0⟩ oriented Si wafers using magnetron sputtering. Three 50 mm diameter Ag targets were arranged in a confocal geometry to sputter onto the 152 mm diameter substrate, which was rotated at 15 rpm and cooled with liquid nitrogen, except where noted. The distance from the sputtering targets to the center of the substrate is 120 mm. For all of the sputtering runs, the base pressure was $<5 \times 10^{-8}$ torr and the working pressure was 5 mtorr of Ar. All three sputtering guns were operated at 100, 175 or 300 W for the different deposition runs. For convenience, we will identify films by the respective gun powers at which they were sputtered (100, 175, 300 W). Due to the confocal geometry of the sputtering guns, a gradient of deposition rates develops across the radius of the substrate. These deposition rates were determined by measuring the film thickness (using micrometer) and dividing it by the deposition time. Fig. 1(a) shows a schematic of the positions where samples were harvested for structural characterization and tensile testing. The sample positions are denoted by concentric circles (C1, C2, C3 and C4) of increasing radii from the center of the film that correspond to different deposition rates for a given sputtering power. Specifically, C1, C2, C3 and C4 correspond to radii of 10, 25, 40 and 55 mm, respectively, from the center of the substrate. For labeling purposes, we denote samples according to their location and deposition power as "Cx y W" (where x = 1, 2, 3, 4 and y = 100, 175, 300).

The as-deposited structures of the Ag films were examined using synchrotron X-ray scattering experiments performed at Sector 6-IDD of the Advanced Photon Source at Argonne National Laboratory. The experiments were performed in transmission mode with 100 keV (0.1234 Å) X-rays that were focused to a beam size of $70 \times 100\ \mu m^2$. The X-ray exposures were collected using a GE amorphous Si detector ($200 \times 200\ \mu m^2$ pixel size) positioned at 1434.6 mm from the samples. The camera length was determined by fitting the pattern of SRM Si powder using Fit2D software [42]. The scattering geometry coupled with the high-energy X-rays corresponds to scattering from planes that are essentially parallel to the film growth direction (in-plane scattering). Fig. 1(b) shows a schematic of the sample geometry and the diffracting planes that are examined in the synchrotron experiments.

The average twin boundary spacing and grain sizes and orientations of the samples were measured using an FEI Tecnai G^2 F20-XT transmission electron microscopy (TEM), a Phillips CM30 TEM with a double tilt sample holder and electron backscatter diffraction (EBSD) imaging. The TEM was performed on cross-sectional samples of the films that were prepared by wedge-polishing followed by dual-ion beam milling. The inverse pole figures were determined by EBSD on the top (free-side) of the films using a JEOL JAMP-7830F field-emission-gun scanning-auger microprobe equipped with EDAX detector and TSL OIM data acquisition system.

The mechanical behavior of the films was examined by testing the free-standing films in uniaxial tension at a constant strain rate