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Acta Materialia 60 (2012) 1038–1047

Acta MATERIALIA

www.elsevier.com/locate/actamat

Observations of grain boundary impurities in nanocrystalline Al and their influence on microstructural stability and mechanical behaviour

F. Tang [a], D.S. Gianola [b], M.P. Moody [a], K.J. Hemker [c], J.M. Cairney [a,*]

[a] *Australian Centre for Microscopy and Microanalysis, University of Sydney, NSW 2006, Australia*
[b] *Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA*
[c] *Mechanical Engineering, Johns Hopkins University, Baltimore, MD 21218-2682, USA*

Received 11 August 2011; received in revised form 31 October 2011; accepted 31 October 2011
Available online 15 December 2011

Abstract

The exceptional properties of nanocrystalline materials lend themselves to a wide range of structural and functional applications. There is recent evidence to suggest that grain boundary impurities may have a dramatic effect on the stability, strength and ductility of nanocrystalline metals and alloys. In this study, transmission electron microscopy and atom probe tomography were used to characterize specimens deposited at different base pressures, thus providing a direct comparison of impurity content with microstructural stability and mechanical behaviour. Atom probe measurements provide clear experimental evidence of grain boundary segregation of oxygen in samples deposited at higher base pressures. It is proposed that these oxygen atoms pin the boundaries, preventing stress-assisted grain growth and resulting in increased strength and loss in ductility. This study provides the first direct experimental evidence that boundary impurities play a critical role in determining the microstructural stability and deformation behaviour of nanocrystalline metals.

Keywords: Nanocrystalline; Impurity segregation; Deformation; Aluminium; Atom probe tomography

1. Introduction

Nanocrystalline and nanostructured materials offer properties that are vastly different from and often superior to those of conventional microcrystalline materials. Improvements include, but are not limited to, higher strength, enhanced hardness [1], greater diffusivity and self-healing of radiation-induced damage through the absorption and recombination of point defects [2]. Processing difficulties have inhibited their use as bulk structural materials, but nanocrystalline thin films, membranes, laminates and coatings are becoming very common in micro- and nanoscale structures and devices.

The unique properties of nanocrystalline materials are directly related to the ubiquitous presence of grain boundaries. These grain boundaries are often thought of as static obstacles to dislocation or magnetic boundary motion, pathways for atomic and thermal transport, and sinks and sources of point defects and dislocations. Their existence and stability are crucial to the long-term performance of nanocrystalline devices, but they are not nearly as static as is generally assumed. Nanocrystalline materials are inherently metastable, since thermally or mechanically driven grain growth leads to a reduction in overall grain boundary content and energy. In some instances abnormal grain growth has been associated with exposure to elevated temperatures, but many experimental observations suggest that thermally assisted grain growth in nanocrystalline materials is modest at intermediate temperatures [2,3]. This unexpected thermal stability has been attributed to a

* Corresponding author. Tel.: +61 2 9351 4523; fax: +61 2 9351 7682.
E-mail address: julie.cairney@sydney.edu.au (J.M. Cairney).

1359-6454/$36.00
doi:10.1016/j.actamat.2011.10.061

number of hypothetical factors, including solute and pore drag, chemical ordering and geometric frustration. By contrast, the mechanical stability of nanocrystalline materials has been shown to be much lower than originally expected. Mechanically induced room temperature grain growth in nanocrystalline metals has been associated with indentation [4–6], compression loading [7,8], tensile loading [9–12] and mechanical fatigue [13]. Experiments quantifying the growth in terms of temperature [6], strain rate [12], proximity to crack tips [14] and testing mode [7] also point to applied stress as the driving force for grain growth.

A recent study by Gianola and coworkers [15] supports the hypothesis that small amounts of impurities can have a dramatic effect on the strength and ductility of nanocrystalline metals. Micro-tensile testing of nanocrystalline Al (nc-Al) films revealed that the deposition base pressure, and presumably the attendant impurity concentration, have a dramatic influence on the mechanical behaviour. As shown in Fig. 1, samples deposited at higher base pressures (10^{-5} torr) showed a stable microstructure and a strong-but-brittle response, while those deposited at lower base pressures (10^{-7} torr) showed remarkable thermal stability, but a very different deformation response, namely moderate strength and over 15% strain to failure. Grain growth was only observed in the films deposited at lower base pressures. Stress-coupled grain growth is therefore thought to be affected by impurities at the grain boundaries, where a critical O impurity concentration appears to be required to pin or immobilize grain boundaries against the coupling of applied stress [15]. Recent molecular dynamics (MD) simulations of an Al tilt grain boundary decorated with O atoms [16] also support the notion of a changing critical stress required for coupled grain boundary motion due to an impurity pinning atmosphere.

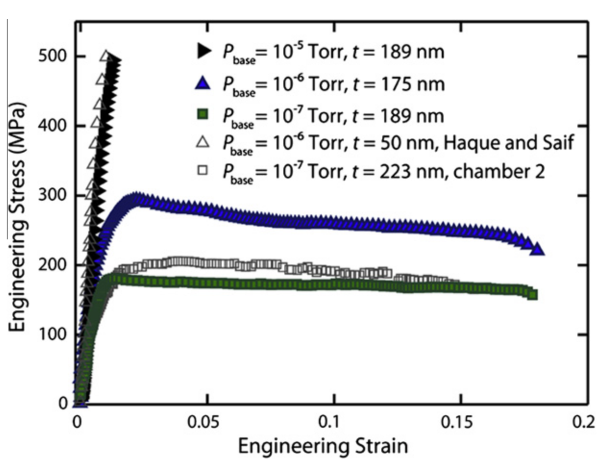

Fig. 1. RT tensile stress–strain curves for three batches of Al films, showing two distinct classes of mechanical behaviour. The transition from strong and ductile to stronger but brittle occurs at base pressures between 10^{-6} and 10^{-5} torr. For comparison, the stress–strain curves with open symbols represent the behaviour of nc-Al thin films deposited in other sputtering chambers, including a stress–strain curve for a similar nc-Al film deposited at relatively high base pressure [54].

Recent studies also suggest that impurities, in addition to affecting deformation behaviour, play a large role in the thermal stability of nanocrystalline microstructures, a critical issue in the development of commercial materials. For grains on the micron length-scale, the driving force for recrystallization (according to the Gibbs–Thompson equation), and therefore the recrystallization rate, is known to increase with decreasing grain size. However, studies have revealed that many nanocrystalline materials exhibit much better stability than predicted. For example, pure nc-Al prepared by mechanical attrition revealed grain size stability up to temperatures as high as $0.78T_m$ [17]. This stability has been attributed to the effect of solute atoms at the grain boundaries, either by impurity drag associated with grain growth [17,18] or by creating a state of metastable thermodynamic equilibrium which eliminates the driving force for grain coarsening [19].

Despite this evidence to suggest the importance of grain boundary impurities for both deformation and stability, a complete understanding of the role of trace-level impurities has been hindered by the technical difficulties involved with direct experimental measurements of grain boundary segregation. There are inherent challenges in the high-resolution microstructural analysis of nanocrystalline materials. Auger and secondary ion mass spectroscopy techniques require a fractured surface or, where mapping is possible, are limited by their low in-plane spatial resolution. Transmission electron microscopy (TEM) can provide information about the grain size and morphology. However, overlapping of grains in the thin foil precludes direct examination of the boundaries between the grains, and chemical analysis of small concentrations of impurities using electron energy loss spectroscopy is typically limited by the resolution of the instrument. Alternatively, atom probe tomography (APT) provides three-dimensional maps showing the elemental distribution at the atomic scale and may be used to characterize the segregation of elemental species to the grain boundary [20]. Light elements can be easily distinguished, and the detection limit is on the order of single atoms. It is therefore highly suited to the study of low-level grain boundary segregation. Unlike beam-based techniques, APT provides a means to directly determine interfacial segregation in three dimensions.

In the current study, both TEM and APT have been used to characterize the microstructure and segregation in samples that have been deposited at different base pressures. The samples investigated were the same as those used in the study of Gianola et al. [15], which allows for direct comparison of impurity levels with mechanical behaviour.

2. Experimental

For this study, three nc-Al films were prepared using magnetron sputtering at three different base pressures (to introduce different levels of impurities). The films were deposited on Si wafers by pulsed DC magnetron sputtering of a 99.999% pure Al target at base pressures of $\sim 1 \times 10^{-7}$,