Acta Materialia 141 (2017) 427–433

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

Step-controlled Brownian motion of nanosized liquid Pb inclusions in a solid Al matrix

T. Radetic [a], E. Johnson [b], D.L. Olmsted [c], Y. Yang [d], B.B. Laird [e], M. Asta [c, f], U. Dahmen [g, *]

[a] Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia
[b] Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark
[c] Department of Materials Science & Engineering, University of California, Berkeley, CA 94720, USA
[d] Physics Department, School of Physical and Material Science, East China Normal University, Shanghai 200062, China
[e] Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA
[f] Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
[g] National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Lab, 1 Cyclotron Rd., Berkeley, CA 94720, USA

ARTICLE INFO

Article history:
Received 13 July 2017
Received in revised form
17 September 2017
Accepted 18 September 2017
Available online 19 September 2017

Keywords:
Embedded particle diffusion
Brownian motion
Step nucleation
Arrhenius slope
Roughening transition

ABSTRACT

We have made direct observations of the Brownian motion of individual nanosized liquid lead inclusions in solid aluminum by in-situ transmission electron microscopy. The process was found to depend strongly on the size of the inclusion and the anisotropy of the interfacial energy. The rate controlling mechanism was the nucleation of steps on facets of the equilibrium shape and the diffusion of Al along the liquid-solid interface. Because the Al-Pb interface undergoes a roughening transition at $T_r \approx 820$ K, the step nucleation barrier decreases with increasing temperature and vanishes completely at T_r. By including the temperature dependence explicitly, we demonstrate that the contribution of the step energy to an Arrhenius plot of the data has a slope greater than the actual activation energy at temperature T by a factor $T_r/(T_r - T)$. In addition, we show that the diffusion barrier for interfacial transport makes a substantial contribution. Our analysis reconciles a large discrepancy between activation energies obtained from the temperature and size dependences of the process and solves the apparent paradox posed by the observation that some particles are frozen in non-equilibrium shapes while nearby smaller particles are sufficiently mobile to undergo rapid Brownian motion.

1. Introduction

Since the original observation of Brownian motion [1] a large number of thermally excited microscopic random-walk phenomena have been reported [2]. Advances in scanning tip microscopy, synchrotron X-ray diffraction and electron microscopy have made it possible to observe such events as the Brownian motion of vacancy islands [3,4], dislocations [5], nanotubes [6], cantilevers [7], molecules [8] or nanoparticles in a liquid [9,10]. Evidence for random motion of gas bubbles or voids [11] in solids has been found by transmission electron microscopy (TEM) starting with investigations of swelling in a nuclear reactor environment due to coalescence and associated expansion of gas bubbles [12,13]. More quantitative evidence for Brownian motion was based on an analysis of bubble size distributions [14] or mean square displacement [15]. Random motion of small inclusions trapped on grain boundaries [16] or dislocations [17,18] has illustrated the effect of confinement to two- or one-dimensional displacements. However, these studies have not been able to determine unambiguously the rate and mechanism of motion, features that are particularly important for our understanding of the stability of microstructures during coarsening and coalescence [13] and that control the thermodynamic and dynamic behavior of nanoscale materials embedded in a solid medium.

In the present study, we investigate the Brownian motion of liquid Pb inclusions in solid Al at elevated temperature using a detailed frame-by-frame analysis of in-situ TEM observations recorded at video rates. The ability to accurately monitor the trajectory of individual inclusions allows us to distinguish random from biased motions and thus eliminate effects such as coalescence or trapping.

* Corresponding author.
E-mail address: UDahmen@lbl.gov (U. Dahmen).

https://doi.org/10.1016/j.actamat.2017.09.040
1359-6454/

1.1. Methods and materials

Nanosized Pb inclusions in Al were produced by rapid solidification of Al-0.5 at.% Pb alloys of 99.999% purity. The specimens were annealed at 280 °C for 2 h in an Ar atmosphere to equilibrate the solid inclusions and anneal out defects. TEM foils were prepared by punching 3-mm discs from the ribbons followed by twin jet thinning using an electrolyte of 25% HNO_3 in methanol at −40 °C and 55 mA. In-situ observations were made in a JEOL 200CX microscope with LaB_6 electron source operating at an accelerating voltage of 200 kV. A water-cooled Gatan double tilt heating holder was used. The temperature reading was calibrated externally and verified by observing the melting point of unconstrained Pb assembled at the edge of the foil during re-heating. Standard tests to check for effects of the electron beam during in-situ experiments were conducted, including varying the current density, blanking the beam between exposures, and shifting the beam to neighboring areas between exposures. Radiation damage can be neglected because vacancies are mobile in Al at temperatures above 200 °C, thus minimizing defect formation [19]. In addition, the effects of the electron beam on the motion of particles due to sample heating and momentum transfer are negligible for heavy Pb particles confined in a solid Al matrix [9,10].

Specimens were tilted to a <110> zone axis, where four {111} facets of the Pb inclusions are seen edge-on, thus allowing direct observation of facet roughening [22]. Video recordings of moving Pb inclusions were made at 30 frames/s and digitized for image processing. Typical data sets comprised more than 1000 individual images. For drift correction, large inclusions, which remained immobile, or defects in the vicinity of a moving particle were used as a reference. Automated image processing included extraction of the region of interest, background fitting, Gaussian convolution and thresholding to allow an accurate measurement of the center of mass of a moving particle. The resulting data files were exported and analyzed using standard statistical methods.

A random motion in three dimensions can be characterized by measuring the root mean square displacement in two dimensions [e.g.29]. The main effect of the third dimension in our experiments was the occasional escape of a particle from the free surface. However, this effect was found to be independent of the electron beam.

2. Results

The Al-Pb system has a monotectic phase diagram with a miscibility gap in the liquid state and no measurable solubility in the solid state. Both components have a face-centered cubic crystal structure. Despite a 22% difference in lattice parameter, solid Pb inclusions adopt the cube-on-cube orientation relationship with the Al matrix, forming strongly faceted shapes. These shapes can be described as cuboctahedra, i.e. {111} octahedra truncated by {100} facets. A large difference in melting point of the two components makes it possible to observe melting and solidification of Pb inclusions well below the melting point of the Al matrix at temperatures where large concentrations of vacancies in Al are freely mobile [19].

Previous work has shown nanoscale Pb inclusions in Al to exhibit a number of remarkable phenomena that are due to their small size and their confinement within a solid matrix: solid Pb inclusions follow a sequence of magic sizes [20] and shapes [21] due to residual strain energy; nanoscale solid Pb inclusions are found to superheat by as much as 100 K relative to the bulk melting point [22]; Pb inclusions at grain boundaries show clear evidence for premelting that depends on interface structure and curvature [23]; liquid Pb inclusions adopt shapes that reflect the anisotropy of the interfacial energy between liquid Pb and solid Al [24,25,22]. Once such particles are melted they are often observed to move rapidly in an apparently random fashion [26]. In the present work, this random motion of liquid Pb inclusions a few nanometers in size is followed by direct observation in a transmission electron microscope in the temperature range between 695 and 752 K.

A typical field of liquid Pb inclusions is shown in Fig. 1a. With increasing temperature, the smallest particles carried out local vibrations or began to move rapidly while the larger particles remained stationary and often retained a highly faceted, non-equilibrium shape. From video recordings of dynamic observations, it was possible to analyze images frame by frame, extract the center of mass and subsequently plot the trajectory of an individual particle. Fig. 1b shows a composite graph of the path of a single particle during observation at five different temperatures. For each temperature, the trajectory represents data from about 1000 video frames. These data could then be used for detailed statistical analysis of the motion. Histograms of the displacements over time intervals of 0.03 s and 1 s are shown in Fig. 2. The inset normal distribution illustrates that particle displacements follow Gaussian statistics with a zero mean and a standard deviation that corresponds to the root mean square displacement.

For a random walk, the mean square displacement in two dimensions is $\langle x^2 \rangle = 4Dt$, where D is the diffusion coefficient [29]. Fig. 3 shows a plot of the mean square displacement of a particle

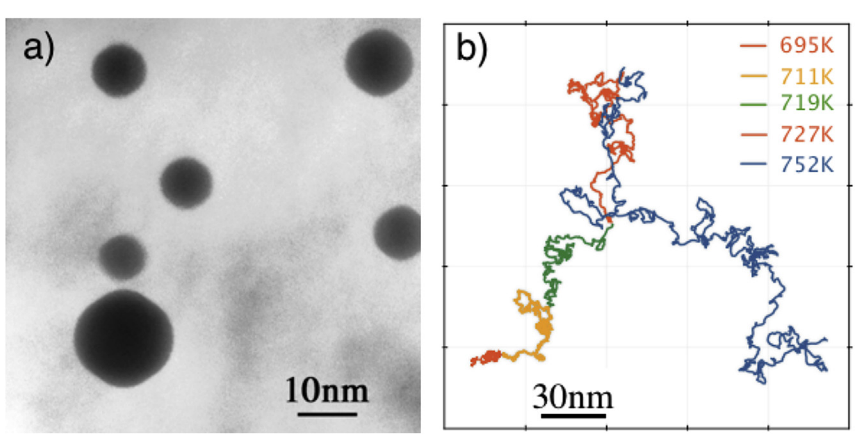

Figure 1. Field of liquid Pb inclusions viewed along a <110> direction, and trajectory of a single particle, extracted from sequences of about 1000 video frames recorded at temperatures ranging from 695 to 752 K.