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Random vibration movements of liquid nanosized Pb inclusions in Al

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Abstract

Transmission electron microscopy has been used to study the behavior of liquid nanosized Pb inclusions in Al ribbons made by rapid solidification. In situ heating experiments carried out in the temperature range from around 375 to 450 °C have shown that liquid inclusions with sizes from around 10–50 nm, that are trapped on dislocations, perform random vibrations around their positions of attachment with vibration periods of some fractions of seconds. The amplitudes of the vibrations in directions perpendicular to the dislocations are a few nanometers, while the motion in directions parallel to the dislocations can be more than an order of magnitude larger. Under conditions where two or more inclusions, attached to a dislocation line, display one-dimensional random motion the inclusions are rarely seen to coalesce. Movement of the inclusions has been monitored by video and shorter sequences have been digitized and analyzed frame-by-frame. The analysis shows that the step lengths have Gaussian distributions indicative of random walks. Fractal analysis of the paths shows that the fractal dimension is close to two which agrees well with the observations that the inclusions carry out linear random walks in a confined space.

Keywords: Liquid lead inclusions; Inclusions on dislocations; In situ TEM; Random oscillations; Fractal analysis

1. Introduction

The mutual solubilities of Al and Pb are extremely low in the solid phases. The liquid phase area is characterized by a large miscibility gap that extends up to a temperature as high as 1566 °C [1] that prevents easy conventional processing of alloys with a fine microstructure. In small amounts such alloys can be made by non-equilibrium or metastable processes such as rapid solidification [2–4] ball milling [4] or ion implantations [5–7]. The microstructure of the alloys with low contents of lead consists of dense distributions of nanometer-sized inclusions of Pb embedded in the Al matrix. The solid Pb inclusions have fcc structure and they grow in parallel cube alignment with the matrix. They have cuboctahedral shape bounded by larger {1 1 1} and smaller {1 0 0} facets and the smallest inclusions display magic size behavior and a size dependent aspect ratio [8,9]. The low mutual solubilities mean that a Pb inclusion—solid or liquid—to a good approximation can be considered as an isolated system that is ideal for studies of melting and solidification. Melting of the inclusions is associated with a significant size dependent superheating [2–4,10], and when the inclusions melt they abruptly change shapes so that the smaller inclusions become spherical while larger inclusions retain a cuboctahedral-like shape with flat {1 1 1} facets and rounded {1 0 0} segments [11]. Rounding of the larger inclusions takes place at temperatures around 420–480 °C [2,3,9,11] and at the same time the inclusions begin to move around in the matrix either as free particles in a manner resembling a random walk or trapped to dislocations in a manner resembling random oscillations in a confined space [12]. These movements have been studied by digitized frame-by-frame image sequences obtained from in situ TEM video recordings and analyzed in the framework of random walk processes.

2. Experimental

TEM Al samples containing nanosized Pb particles were prepared from high-purity ribbons of Al with 0.65 at.% Pb obtained by rapid solidification from a temperature above the Al–Pb liquid miscibility gap. In situ TEM studies of the

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behavior of the inclusions were carried out at temperatures around 375–450 °C in a 200 kV Philips CM 20 microscope using a Gatan single tilt heating stage. The observations were recorded on videotape (25 video frames/s). Particle trajectories projected into the plane of view were obtained from measurements of the positions of the centers of the Pb inclusions using sequences containing 1000–3000 digitized images. The drift of the sample as a whole during the time of recording was ascertained from fixed points in the images.

3. Results and analysis

Fig. 1 shows a micrograph from a video sequence where two small inclusions (1 and 2) attached to a dislocation that is out of contrast were observed to move in random-like oscillations along the dislocation line. The much larger inclusions at the end of the invisible dislocation are virtually immobile and serve as reference points. Analysis of the movement of the inclusions was made on a video sequence containing nearly 2800 images corresponding to a total time of about 110 s. Six video frames from the middle of the sequence covering 1.25 s (Fig. 2) clearly show the vivacity of the movement of the two inclusions. This can also be seen in Fig. 3 where high-magnification binary inclusion images from the sequence in Fig. 2 have been superimposed. For convenience in the analysis, the images in Figs. 2 and 3 have been rotated so that the movement of the inclusions can be easily separated into a horizontal *y*-component parallel to the invisible dislocation and a vertical *x*-component perpendicular to the dislocation. The *x*- and *y*-components of the movement of the inclusions during the 110 s sequence are shown in Fig. 4 together with a plot of the *y*-distance between the inclusions. Both movements appear to be in the form of random oscillations with amplitudes that are much larger parallel to the dislocation than perpendicular to it. If the statistical standard deviations from the distributions of positions are used as a measure of the random amplitudes, the values for the parallel and perpendicular motions are about 11.5 and 1.3 nm, respectively. The periods of the movements are also randomly distributed with values that are fractions of seconds. Fourier analysis of the position versus time distributions shows a recurring frequency around $0.5\,s^{-1}$ in the parallel component of the movement.

Inclusions that are as small as those shown in Fig. 1 (14–15 nm in diameter) move readily parallel to the dislocation along distances that are large compared to their own sizes. The distances moved between consecutive video frames lie in the range from 0 to about 20 nm with root mean square distances of 4.2 and 3.7 nm respectively, corresponding to diffusivities of 22×10^{-16} and $1.7 \times 10^{-16}\,m^2\,s^{-1}$ that are comparable to the diffusion coefficients of non-trapped inclusions of similar sizes [12].

Despite the fact that the inclusions move such large distances and that they at various times enter each other's "territory" (Fig. 4) coalescence between inclusions is rarely observed. In the present case where the full video sequence covered more than 10 min it did not occur. The smallest distance between the inclusions in the sequence shown in Fig. 4 is about 25 nm, the mean is 50 nm, and the largest distance is nearly 100 nm. If the inclusions rarely coalesce it means that they must mutually repulse each other when

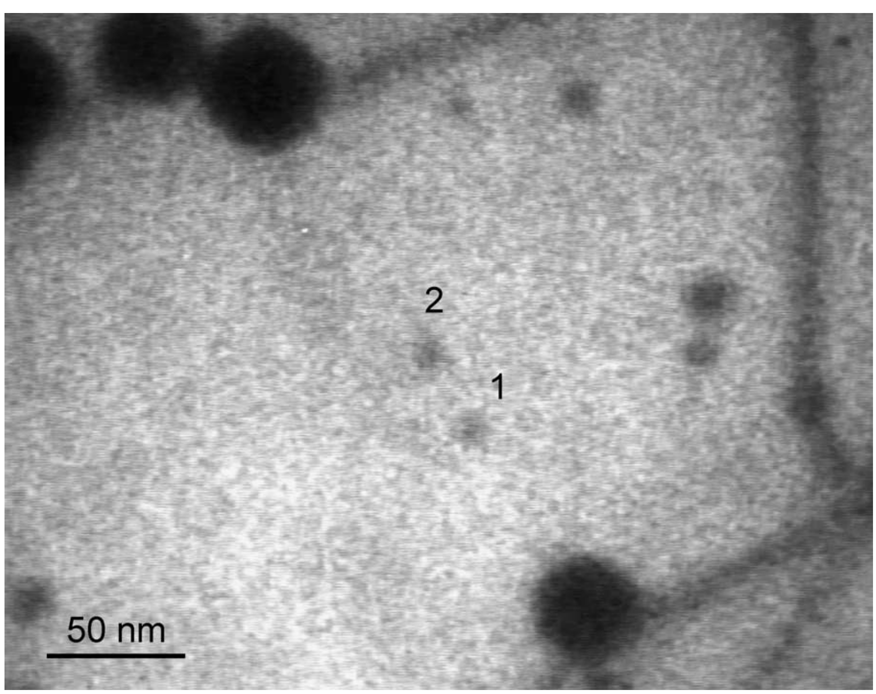

Fig. 1. TEM micrograph showing two liquid Pb inclusions attached to a straight dislocation that is out of contrast. The dislocation is terminated at the two large inclusions in the top and bottom of the picture. Labels 1 and 2 refer to the two inclusions whose movements have been studied.

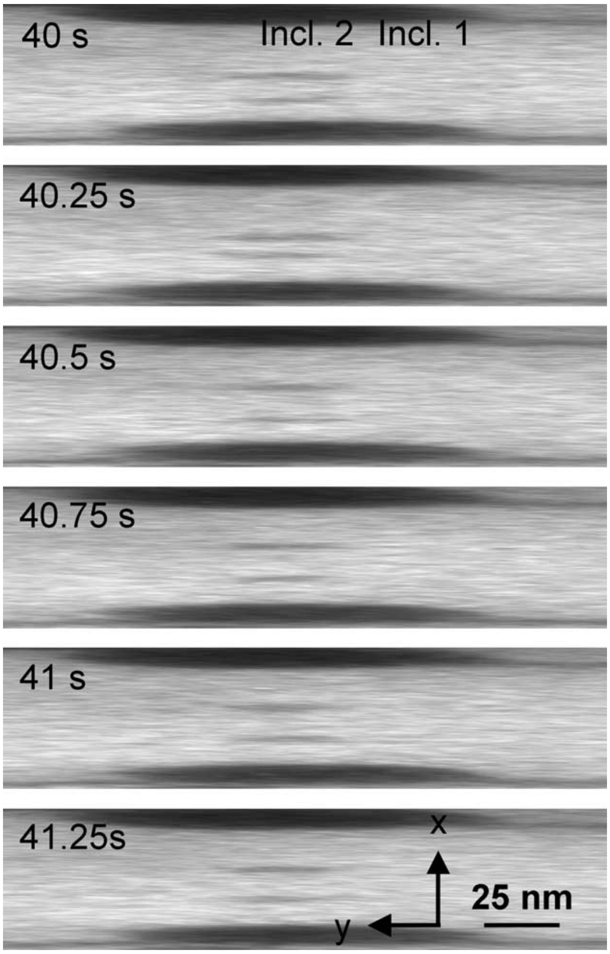

Fig. 2. A sequence of micrographs from the video shows the movement of the two inclusions labeled 1 and 2. The times of recording of the video frames in the sequence are indicated. The *x*–*y* coordinate system indicates the two components of the movements perpendicular and parallel to the dislocation, respectively.

they are close together and that their movements parallel to the dislocation should display a degree of correlation. A correlation analysis of the dataset shows a degree of both correlation and anti-correlation repeated with a frequency of around 0.5–1 s^{-1} comparable to the frequency seen in the Fourier analysis. If the probability of coalescence is suppressed it must be based on a mechanism that will prevent

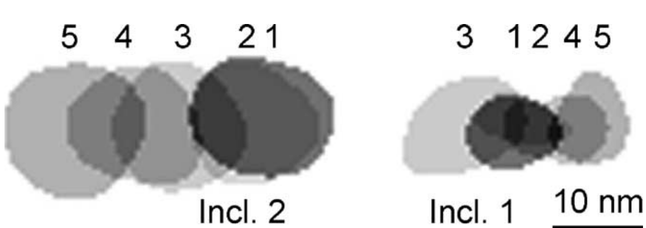

Fig. 3. A set of high-magnification overlaid binary pictures of the movement of the two inclusions shown in Fig. 2. The time between each picture is 0.08 s and number 1 refers to a time of 40.25 s. Note that the movement of inclusion 2 is an erratic shift to the left while inclusion 1 makes a small oscillation before it moves to the right.

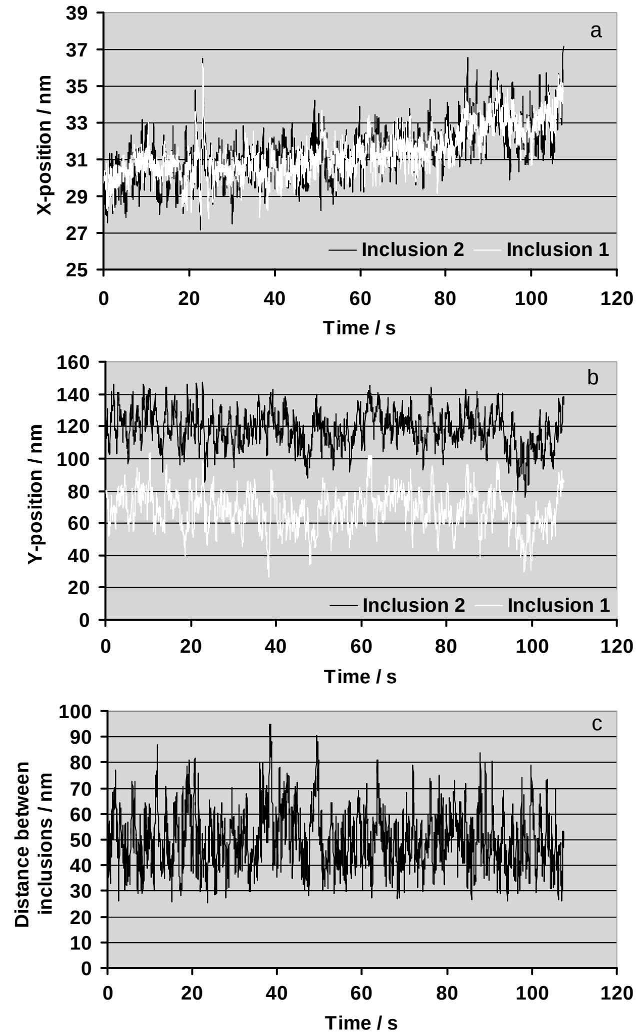

Fig. 4. The *x*-components (a), *y*-components (b), and *y*-distance (c) between the two inclusions for the full sequence covering 110 s. The slight increase in the *x*-values at the end of the time traces may indicate a small specimen drift that is not visible in the plots of the *y*-components. All the traces show random oscillatory behavior.

the inclusions from approaching each other when they get sufficiently close.

A random walk can be described and analyzed in terms of fractal analysis [13] in a variety of ways. In the Richardson plot, the length of the path is displayed as a function of step length using smoothing averages. In a log–log plot, the slope α is negative and the fractal dimension D of the path is obtained by $D = 1 - \alpha$; thus a free random walk with a fractal dimension of $D = 1.5$ should have a slope in the Richardson plot of $\alpha = -0.5$. Fig. 5 shows the Richardson plot for inclusion 1 together with a plot of the mean square displacement as a function of time. The Richardson plots for both inclusions have a slope $\alpha \approx -1$, and thus a fractal dimension of $D = 2$, characteristic for a random walk in a confined space. Likewise, the mean square displacements for the two inclusions are on average constant in time as it should be for movement in a confined space.

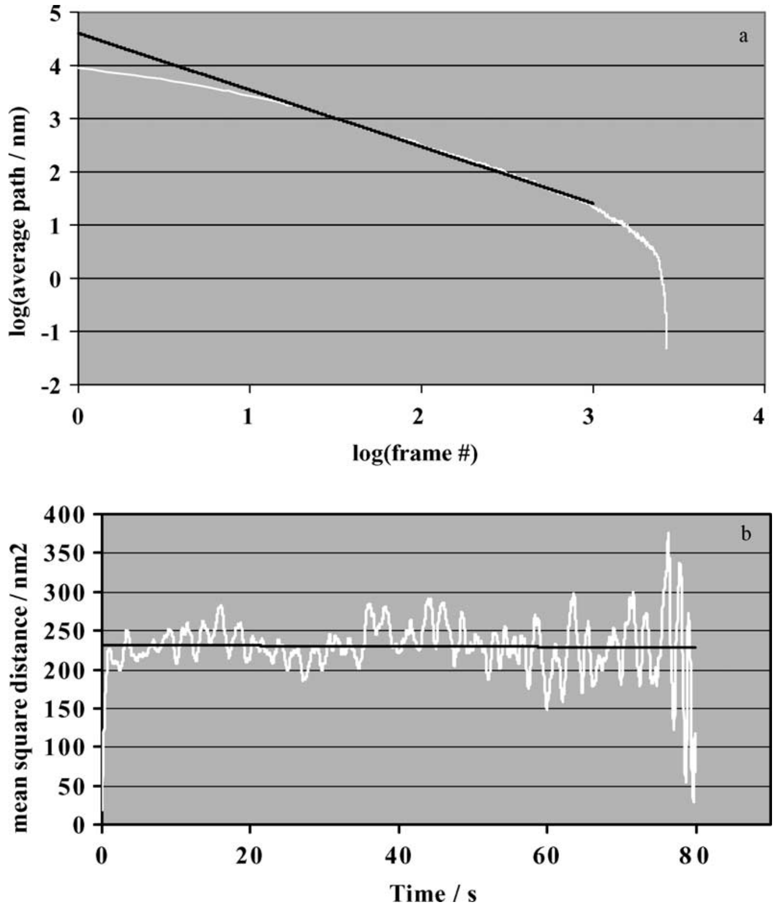

Fig. 5. Richardson plot (a) and a plot of the mean square displacement as a function of time (b) for inclusion 1. The slope of the Richardson plot is −1.06 indicating a fractal dimension of two. The mean square displacement is constant in time. Both results agree with the confined movement of the inclusion. White lines are experimental and black lines are linear fits.

4. Discussion

The concept of unconstrained random walk—or Brownian motion—was first analyzed by Einstein [14] who showed that the mean square displacement is proportional to the elapsed time. Later Smoluchowski analyzed constrained random motion of particles under the influence of an elastic force [15]. The vigorous movement of nanosized liquid Pb inclusions embedded in Al has been analyzed in terms of random walk processes. Free inclusions undergo unconstrained random walk while inclusions attached to dislocations are moving randomly along the dislocations or perpendicular to the dislocations. The component of the movement perpendicular to the dislocation line is in form of small amplitude random vibrations with a restoring force originating from the energy expense of extending the length of the dislocation line as it changes from a straight to a bent configuration [12]. The present analysis of the movement of the inclusions parallel to the dislocation lines shows that it is random oscillations with Gaussian distributions of step lengths. For the smallest inclusions, the random amplitudes are an order of magnitude larger than in the perpendicular movements showing that the constraints for movements parallel to the dislocation line are very weak. When two or more inclusions move together along the same dislocation they rarely coalesce, which implies that a repulsive force must exist between the inclusions when they get close together leading to a degree of correlation and anti-correlation in their movements.

5. Conclusions

Large-scale movements of nanosized liquid lead inclusions in aluminum have been studied by in situ TEM and recorded in real time by video. The movements have been analyzed in terms of random walk processes for free and constrained behavior. Further analysis of the temperature and size dependencies of the movements should provide information on activation energies and the atomistic processes causing the movements.

Acknowledgements

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