

Anomalous Helium Bubble Diffusion in Dilute Aluminum Alloys

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Remarkably rapid Brownian motion of helium bubbles in aluminum alloyed with very low concentrations of lead and of indium has been observed *in situ* by hot-stage transmission electron microscopy. Bubble diffusion is enhanced as the impurity coats the bubble surfaces at annealing temperatures above the melting point of the impurity. The bubble diffusion coefficients calculated from video images of the bubble motion, and the corresponding surface diffusion coefficients, are orders of magnitude larger than diffusion coefficients determined from helium bubble growth experiments in pure aluminum.

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Helium atoms, being essentially insoluble in all metals [1], will agglomerate into bubbles that cause a deterioration of material properties. As such, the behavior of helium and other inert gases in fusion and fission reactor materials [where helium and heavier gas atoms are produced by the (n, α) reaction and as fission products, respectively] is of considerable interest [2], particularly as reactor lifetimes are determined entirely by the structural damage due to gas bubbles and voids. Under such extreme conditions, bubble growth occurs as diffusing gas atoms, which produced continuously during irradiation, are captured, and by thermal-gradient-induced bubble migration and coalescence. In the absence of a continuous source of gas atoms and without temperature gradients, however, growth occurs by random bubble migration and coalescence, and, to a lesser extent, by Ostwald ripening [3].

In this Letter we report *in situ* observations by hot-stage transmission electron microscopy (TEM) of anomalously rapid helium bubble diffusion in aluminum containing a low concentration of lead, and in aluminum with a low concentration of indium, at annealing temperatures above the melting point of the impurity species. This work was motivated by recent TEM and positron lifetime spectroscopy measurements indicating surprisingly rapid helium bubble growth in aluminum containing approximately 1 ppm by weight of lead [4,5]. Figure 1, adapted from Ref. [4], shows bubble growth as a function of annealing time at 823 K for both the Pb-containing and Pb-free samples, and suggests that the accelerated bubble growth in the case of the dilute alloy may be due to extension of the migration-coalescence growth regime to much larger bubble sizes. Electron micrographs and energy dispersive x-ray spectra taken at room temperature show the lead to be present as small precipitates at preferred facets of the helium bubbles.

To verify this hypothesis, samples of 99.999%-pure aluminum alloyed with 200 ppm by weight of lead, and separately, with 1000 ppm by weight of indium, were thinned to electron transparency and subsequently irradi-

ated with 50-keV alpha particles at the HVEM-Tandem Facility at Argonne National Laboratory to produce a helium concentration of approximately 20 atomic ppm. The implanted samples were then annealed at 723–743 K for several minutes, during which time video recordings were made of spherical helium bubbles undergoing Brownian motion and eventually coalescing or disappear-

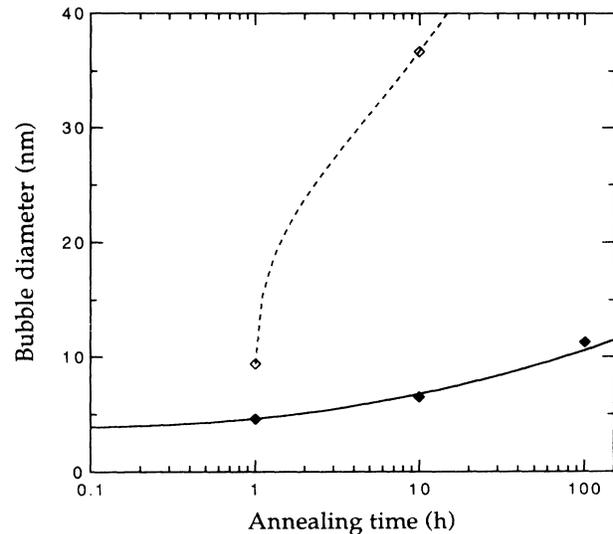


FIG. 1. Average bubble diameter (in nanometers) plotted against annealing time (in hours) at 823 K, for helium bubbles in aluminum containing a low concentration of lead (open diamonds) and in pure aluminum (solid diamonds) [4]. Additional measurements could not be taken for the alloy, as the bubbles quickly attained a size comparable to the sample thickness required for electron transparency. The dashed and solid curves are fits of these data by the migration and coalescence bubble growth equation given by Farrell, Chickering, and Mansur [6], which assumes a bubble size-independent surface diffusion coefficient D_s . The D_s values corresponding to the dashed and solid curves are 1.13×10^{-9} and $2.0 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, respectively.

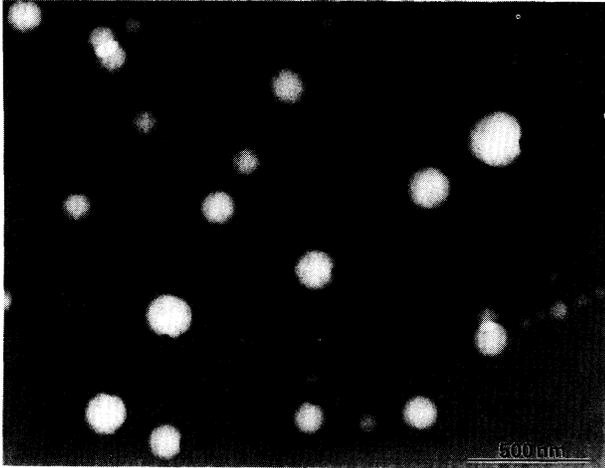


FIG. 2. Bright-field electron micrograph, taken after slow cooling to room temperature, showing solid indium precipitates attached to preferred facets of helium bubbles in the aluminum alloy. Also apparent, as collections of dark spots (presumably indium) superimposed on a lighter circular region, are remnants of helium bubbles that have reached a foil surface.

ing at a foil surface. The participation of the impurity, which is not visibly apparent at the annealing temperatures, was verified in each case by cycling the sample temperature between room temperature and the annealing temperature. Solid precipitates attached to helium bubble facets appeared during slow cooling at room temperature, as in Fig. 2, but did *not* appear during a rapid quench. In the latter case, the precipitates subsequently formed at approximately 520 K, and disappeared again above the melting temperature of the impurity, as the sample temperature was increased.

The video images were used to obtain bubble diffusion coefficients D_b at the annealing temperatures in the following manner. Spatial displacements transverse to the electron beam were measured for each of several lead- and indium-coated bubbles during successive 1-s time intervals. The collection of N measurements for each bubble must possess (in the limit of an infinite number of measurements) a Gaussian probability distribution, since the N measurements can be regarded as single measurements for N noninteracting, identical bubbles, all initially located together on a two-dimensional plane at $r=0$ at time $t=0$. Thus the radial distribution of measurements r at time t resembles

$$p(r) = 2\pi r \frac{N}{4\pi D_b t} \exp[-r^2/4D_b t],$$

so that integrating p over the entire plane produces the total N measurements. The number of displacements r between r_i and r_j (with $r_i < r_j$) is then approximately

$$n_{ij} = N \exp[-r_i^2/4D_b t] - N \exp[-r_j^2/4D_b t].$$

TABLE I. Measured diffusion coefficients D_b for observed helium bubbles of radius R in aluminum with a low concentration of lead or indium. The corresponding surface diffusion coefficients D_s are calculated under the assumption that bubble migration occurs by self-diffusion of aluminum atoms at the bubble surface.

	R (nm)	D_b (nm^2s^{-1})	D_s ($\mu\text{m}^2\text{s}^{-1}$)
Pb/He	5.15	2.0	0.70
	6.0	1.2	0.77
In/He	7.9	2.0	3.85
	16.0	7.0	227
	26.5	0.8	195

This expression provides the areas $n_{i,i+1}$ for Gaussian histograms that are compared to the histograms of measured bubble displacements. The bubble diffusion coefficient D_b that provides the best match, for each of the monitored helium bubbles, is presented in Table I. The accuracy implied by these values derives from a visual assessment of the histogram fit in each case, and accounts as well for errors in the displacement measurements.

The rapid bubble diffusion results from enhanced diffusion of aluminum atoms at the bubble/matrix interface. If the latter is assumed independent of bubble size, the corresponding surface diffusion coefficients D_s may be calculated from the standard relationship [7]

$$D_b = (3\Omega^{4/3}/2\pi R^4)D_s,$$

where R is the gas bubble radius and Ω is the volume of a matrix atom. These values are given in Table I, and are also presented in Fig. 3 together with D_s taken from other experiments showing helium bubble growth in pure aluminum at various annealing temperatures.

The mechanism by which atomic diffusion at the bubble surface is increased is unclear, however. It is important to note that the binary phase diagrams [10] for these aluminum alloys show negligible solubility of the impurity in the matrix material (so that the impurity will segregate to the free surfaces provided by the gas bubbles); an impurity melting temperature lower than that of the matrix and of the annealing temperature; and some solubility of the matrix atoms in the liquid impurity. These characteristics suggest a *liquid dissolution* process, whereby a liquid layer of impurity atoms at the bubble surface acts as a conduit for rapid transport of dissolved aluminum atoms. An equilibrium concentration in the liquid is maintained by continuous dissolution and precipitation of aluminum atoms at the solid matrix surface. Detailed calculations [11], assuming a monolayer of impurity atoms at the bubble surface, give bubble diffusion coefficients in good agreement with those in Table I, with the exception of the smallest indium-coated gas bubble. The much lower D_b in that case may be due to incomplete or thinner coverage at the gas/matrix interface: Be-

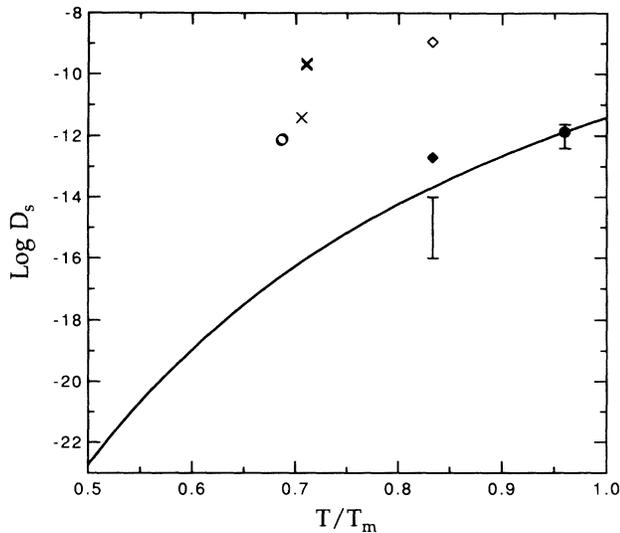


FIG. 3. Calculated surface diffusion coefficients D_s , plotted against the scaled annealing temperature T/T_m for helium bubble diffusion in aluminum. T_m is the melting temperature (933 K) of the aluminum matrix. The two open circles and three crosses indicate values of D_s for bubbles with attached liquid lead and indium precipitates, respectively, determined from direct observation of their Brownian motion at 723–743 K; the numerical values are given in Table I. The open and solid diamonds indicate the D_s (m^2s^{-1}) values for helium bubbles with and without attached lead precipitates, respectively, at 823 K, derived from the bubble growth data in Fig. 1. The solid circle shows the average value of D_s , determined by Farrell, Chickering, and Mansur [6] from measurements of coarsening of helium bubbles in neutron-irradiated, helium-implanted pure aluminum, during annealing at $0.96T_m$; the bars associated with that point indicate the range of five values. The solid curve is obtained from the expression $D_s = 0.86 \exp[-(2.1 \text{ eV})/kT]$ m^2s^{-1} , which is a fit to the data point reported by Farrell, Chickering, and Mansur, with the activation energy for surface diffusion taken from Smidt and Pieper [8]. The bars at $0.83T_m$ (823 K) indicate the estimate of D_s , by Chen and Cost [9] derived from similar measurements of bubble growth in helium-implanted pure aluminum.

cause bubble volume increases much faster than surface area when gas bubbles migrate and coalesce, there should be an effective bubble size threshold below which too little impurity has collected to allow such a liquid dissolution process to occur.

Alternatively, the effect of the liquid coating may be limited to the dissolution of helium bubble facets, thereby eliminating the necessity for nucleation of new steps on those surfaces in order that the bubble migrate. Indeed, Willertz and Shewmon [12], Goodhew and Tyler [13], and other early investigators, noting that the surface diffusion coefficients they extracted from their bubble growth experiments were orders of magnitude smaller than those expected on the basis of Gjostein's [14] universal D_s vs T_m/T curve for fcc metals (T_m being the melt-

ing temperature), speculated that ledge nucleation may be the rate-limiting step in gas bubble growth by surface diffusion. In this regard, it is intriguing that the surface diffusion coefficients of the large indium-coated bubbles presented in Table I, and that derived from the bubble growth rate represented in Fig. 1 for the lead-containing alloy, are remarkably close to those predicted by Gjostein's curve for pure aluminum at temperatures of 743 and 823 K, respectively [11]. The lower D_s values determined for the smaller bubbles may then be due to thinner or less complete coverage of the bubble/matrix surface by the liquid impurity, so that facets are not entirely eliminated.

To conclude, we have observed anomalously rapid helium bubble migration at annealing temperatures of 723–743 K in aluminum alloyed with low concentrations of lead and, separately, of indium [15]. The bubble diffusion coefficients derived from the *in situ* TEM observations imply bubble growth rates far in excess of any reported for pure aluminum. This is consistent with our earlier results [4], and with our subsequent observations of much smaller size, and *no* apparent motion, of helium bubbles in control samples of pure aluminum, at the annealing temperatures given above. The corresponding surface diffusion coefficients, assuming thermally activated self-diffusion of aluminum atoms at the bubble/matrix interface, are similarly far higher (roughly 4 orders of magnitude) than any derived from bubble growth rates in pure aluminum. Consistent with the binary phase diagrams, the lead and indium impurities are present as precipitates at the helium bubble surfaces. Two liquid dissolution mechanisms for bubble diffusion, that rely on the properties of the attached liquid precipitates, are proposed. Volume diffusion of an equilibrium concentration of aluminum atoms through a thin layer of liquid impurity at the bubble surface produces bubble diffusion coefficients in good agreement with those derived from observation. Alternatively, the liquid coating may instead simply remove the bubble facets and permit surface self-diffusion of the aluminum atoms unhindered by the necessity to nucleate new facets; this would then resolve the vast discrepancy between the values of the surface diffusion coefficient derived from our observations and those derived by others from bubble growth experiments in pure aluminum. Further study is necessary to eliminate one or both of these proposed mechanisms; in particular, the quantity of impurity associated with a rapidly diffusing helium bubble must be accurately measured.

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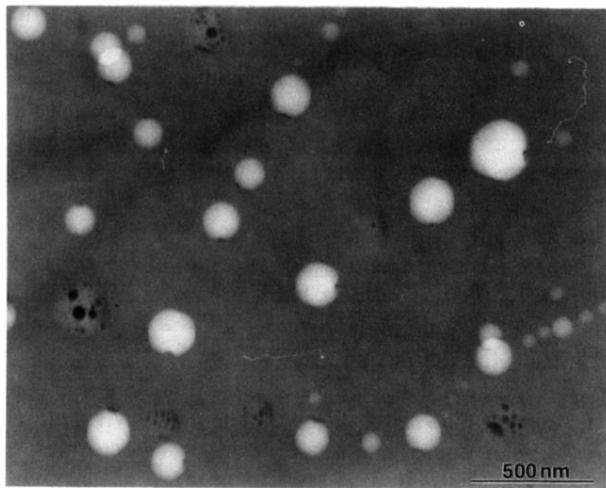


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