

Growth of inert-gas bubbles in solids; behaviour of non-uniform size distributions

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An analytical study of the effects of non-uniform sizes on the growth kinetics of inert-gas bubbles in solids is presented. Assuming ideal-gas behaviour and gas-diffusion-controlled growth, it is found that for out-of-reactor conditions, the size distribution undergoes pure translation in bubble-radius space, the growth kinetics being independent of the details of the size-distribution function. On the other hand, for in-reactor growth in fissile materials, it is found that kinetic re-solution of fission gas causes any arbitrary subset of the overall size distribution to become increasingly "narrow" as bubble growth proceeds, as long as all bubbles within the subset are described by the same given kinetic behaviour.

1. Introduction

The growth of inert-gas bubbles in solids, resulting from the precipitation of sparingly soluble inert-gas atoms, is a subject that has received widespread attention during recent years. The focus of much of this attention has been upon the behaviour of fission-gas bubbles in fissile materials, since these cause nuclear-reactor fuel elements to swell macroscopically [1], leading to premature failure. In addition, it has also been found that studies of gas bubbles in solids can yield important information regarding such properties as impurity diffusivities [2], surface self diffusivities [3, 4], and surface energies [5, 6].

One particular area, to which considerable theoretical effort has been applied, is the growth kinetics of gas bubbles from super-saturated solution, both under in-reactor conditions [7, 8] and during postirradiation heat-treatment [9-11]. Of course, in-reactor bubble growth is complicated by such effects as "kinetic re-solution" of the gas [12, 13] which results from the disruptive influence of energetic fission fragments, as well as the directed migration of bubbles in, say, a temperature gradient [14].

A simplification that is often made in analyses of bubble growth [8-10], is that the size distribution of bubbles is uniform, an assumption which is often not physically realistic. Since size-distribution effects can potentially exert a strong influence on bubble-growth kinetics, we shall here examine, from an analytical point of view,

a number of the consequences, upon bubble behaviour, resulting from the assumption of a non-uniform size distribution. In particular, for out-of-reactor growth (e.g., corresponding to the growth of fission-gas bubbles during postirradiation heat-treatment), effects of non-uniform sizes on growth kinetics will be considered, whereas for in-reactor growth, the influence of kinetic re-solution upon the "shape" of the size distribution will be evaluated.

The basic assumptions we shall make regarding various other properties of the system will be essentially the same as those used elsewhere [8, 10, 11], that is: (1) The bubbles are spherical, intragranular, and stationary (in co-ordinate space). (2) The bubble system is disperse, such that each bubble can be regarded as being situated at the centre of a spherically symmetric concentration field of dissolved gas [15]. (3) Gas diffusion occurs under quasi-stationary conditions. (4) The equilibrium solubility of the gas in the solid is zero. In addition, we shall assume that the bubbles are sufficiently large such that the gas they contain behaves ideally. (We note that some size-distribution effects, for very small bubbles, have been considered elsewhere [11].) Then, if the supply of vacancies is rapid enough to maintain the gas pressure virtually equal to the surface tension restraint (in other words, assuming gas-diffusion-controlled growth kinetics) the radius R of a gas bubble is related to the number N of gas atoms it contains through the expression

$$8\pi \gamma R^2/3 = NkT, \quad (1)$$

where γ is the surface tension of the solid (assumed to be independent of crystallographic direction), k the Boltzmann constant, and T the absolute temperature.

These assumptions yield an analytically tractable problem, the solution of which describes some important aspects of size-distribution phenomena, aspects which can, however, be quantitatively evaluated without requiring detailed knowledge of the "shape" of the distribution in bubble-radius space.

2. Out-of-reactor bubble growth

In order to facilitate our discussion of the growth kinetics of gas bubbles during heat-treatment, for which the total concentration of gas in the solid, m , remains essentially constant, we shall consider only times for which bubble nucleation is complete, so that the total concentration of bubbles, n , is invariant in time. Equating m to the sum of the average concentration of dissolved gas, C , plus the instantaneous gas content of the bubbles, we obtain, using Equation 1,

$$m = C + \frac{8\pi\gamma}{3kT} \int_0^\infty R^2 f(R, t) dR, \quad (2)$$

where $f(R, t)$ is the bubble size-distribution function, defined such that $f(R, t) dR$ is the concentration of bubbles, at time t , with radii within the incremental range dR measured about R . Now, from our assumptions regarding gas diffusion to bubbles, it follows that

$$dN/dt = 4\pi DRC, \quad (3)$$

where D is the diffusion coefficient for gas atoms in the solid. Combining Equations 1 and 3, we find that the "velocity" of a bubble, v_R , in bubble-radius space, is given by

$$v_R = (3kTDC)/(4\gamma). \quad (4)$$

Clearly, v_R is free from any explicit dependence upon R . This implies that all bubbles are instantaneously changing in size at the same rate (a result which is *not* valid for very small bubbles [11]). Consequently, if one were to observe the growth kinetics from within the bubble-radius space, he would see the size distribution undergoing pure translation to larger radii, with no simultaneous change of "shape" occurring. From another viewpoint, if the observer were to move along the bubble-radius axis at the time-dependent rate indicated by Equation 4, the bubble distribution would appear, to him, to be stationary.

Using the brackets $\langle \rangle$ to denote an average value with respect to $f(R, t)$, it follows, for example, that

$$\langle R^l \rangle \equiv n^{-1} \int_0^\infty R^l f(R, t) dR, \quad (5)$$

and hence, from Equations 2, 4, and 5, that

$$m = \frac{4\gamma}{3kTD} \frac{d\langle R \rangle}{dt} + \frac{8\pi\gamma n}{3kT} \langle R^2 \rangle. \quad (6)$$

Now, the variance of the bubble size distribution, μ , is given by

$$\mu \equiv \langle (R - \langle R \rangle)^2 \rangle = \langle R^2 \rangle - \langle R \rangle^2, \quad (7)$$

and it follows that μ is a time invariant, since v_R is independent of R . Equations 6 and 7 can be combined to yield

$$m \left(1 - \frac{8\pi\gamma n \mu}{3mkT} \right) = \frac{4\gamma}{3kTD} \frac{d\langle R \rangle}{dt} + \frac{8\pi\gamma n}{3kT} \langle R \rangle^2. \quad (8)$$

We observe, from Equation 8, that the variation of $\langle R \rangle$ with time is independent of any explicit functional form for $f(R, t)$, depending only upon certain integral properties of the distribution function, namely, n , μ , and of course, the value of the mean radius $\langle R \rangle_0$ at some reference time, which we choose arbitrarily to be $t = 0$. Of course, the values of n , μ , and $\langle R \rangle_0$ are determined during the interval prior to $t = 0$, during which the bubble system is being formed.

Equation 8 can be considerably simplified if expressed in terms of the following dimensionless quantities:

$$\begin{aligned} \xi &\equiv \left(1 - \frac{8\pi\gamma n \mu}{3mkT} \right)^{1/2}, \\ \rho &\equiv \langle R \rangle \left(\frac{8\pi\gamma n}{3mkT} \right)^{1/2}, \\ \tau &\equiv t \left(\frac{3\pi mkTnD^2}{2\gamma} \right)^{1/2}, \end{aligned}$$

in which case we obtain

$$\frac{d\rho}{d\tau} + \rho^2 = \xi^2. \quad (9)$$

Equation 9 can be easily integrated, subject to the condition $\rho(\tau = 0) = \rho_0$ where, of course,

$$\rho_0 \equiv \left(\frac{8\pi\gamma n}{3mkT} \right)^{1/2} \langle R \rangle_0.$$

We thus find that

$$\rho = \xi \tanh [\xi\tau + \tanh^{-1}(\rho_0/\xi)]. \quad (10)$$

The special case corresponding to $\rho_0 = 0$ and

$\xi = 1$ (i.e., a uniform size distribution with zero initial mean radius) has been treated elsewhere [9, 10]. One can also use Equation 4 to show that

$$C = m d\rho/d\tau$$

and differentiation of Equation 10 thus gives

$$C = m\xi^2 \operatorname{sech}^2 [\xi\tau + \tanh^{-1}(\rho_0/\xi)]. \quad (11)$$

Equations 10 and 11 describe the temporal behaviour of the mean bubble radius and the average concentration of gas dissolved in the solid in terms of the size distribution parameters, n , μ , and $\langle R \rangle_0$.

It should be noted from the definitions of ξ and ρ_0 that $0 < \xi \leq 1$ and $\xi \geq \rho_0$. In addition, if $\rho_0 = 0$, then $\xi = 1$.

The variation of both ρ and C with τ are illustrated in Fig. 1 for selected values of ξ and for the special case $\rho_0 = 0.3$. The tendency of the mean radius to "saturate" as C approaches zero can clearly be seen. Note also that the effect of decreasing the magnitude of ξ (equivalent to increasing μ), for given ρ_0 , is to cause the mean radius to saturate at a smaller value.

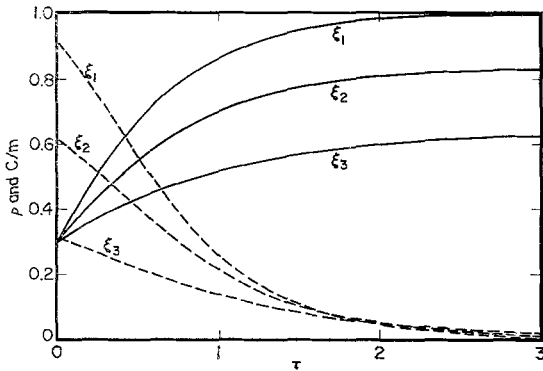


Figure 1 Variation of ρ (solid curves) and C/m (dashed curves) with τ for $\rho_0 = 0.3$, with $\xi_1 = 1.0$, $\xi_2 = \sqrt{0.7}$, $\xi_3 = \sqrt{0.4}$.

One can now easily describe the variation with time of a given bubble within the distribution. Let us thus consider a bubble having instantaneous radius $R(t)$. It follows from Equation 4 that

$$R(t) - R(0) = \langle R \rangle - \langle R \rangle_0,$$

where $\langle R \rangle$ is measured at the instant t . Therefore,

$$R(t) = R(0) - \langle R \rangle_0 + \left(\frac{3mkT}{8\pi\gamma n} \right)^{1/2} \rho,$$

where, of course, ρ is given by Equation 10. In particular, we note that $R(t)$ asymptotically approaches a limiting value, R_t , given by

$$R_t = R(0) - \langle R \rangle_0 + \left[\left(\frac{3mkT}{8\pi\gamma n} \right) - \mu \right]^{1/2}.$$

Hence, on the basis of this model, the level at which a given bubble radius saturates depends only upon a limited number of size-distribution parameters, i.e., the initial bubble radius, the initial mean radius, the variance of the size distribution, and the bubble concentration.

3. In-reactor bubble growth

As we have noted, a physically realistic description of the in-reactor behaviour of bubbles must include such phenomena as bubble migration and kinetic re-resolution, although we shall limit our discussion here to the effect of kinetic re-resolution, and continue to assume that the bubbles are stationary. One useful, albeit phenomenological, means for describing re-resolution is through the use of a parameter b , defined as the probability per unit time that a gas atom be re-injected, from a bubble, back into solution. Hence Equation 3 must be generalized to

$$dN/dt = 4\pi DRC - bN, \quad (12)$$

and the combination of Equations 1 and 12 yields

$$v_R = \frac{3kTDC}{4\gamma} - \frac{bR}{2}. \quad (13)$$

The fact that v_R now depends explicitly upon R implies that the size-distribution function does indeed undergo a simultaneous change of "shape" as it translates to larger radii. Our discussion here will be limited to analysing some aspects of this shape change. To this end, we describe the temporal behaviour of the i th central moment, $\sigma_i(t)$, which we define as

$$\sigma_i(t) \equiv \langle (R - \langle R \rangle)^i \rangle, \quad (14)$$

where, in the cases of interest, i is some positive integer. Note, for example, that $\sigma_2(t)$ is just the variance $\mu(t)$. If one differentiates Equation 14 with respect to time, he obtains

$$d\sigma_i(t)/dt = i\langle (R - \langle R \rangle)^{i-1} (v_R - d\langle R \rangle/dt) \rangle. \quad \dots (15)$$

Then, combining Equations 13 and 15,

$$d\sigma_i(t)/dt = -ib\sigma_i(t)/2,$$

from which one finds that

$$\sigma_i(t) = \sigma_i(0) \exp(-ibt/2). \quad (16)$$

We see, from Equation 16, that the size distribu-

tion tends to become increasingly "narrow" as time progresses.

In particular, setting $i = 2$,

$$\mu(t) = \mu(0) \exp(-bt),$$

so that the variance decreases exponentially with time, the "time constant" being b^{-1} . (It is helpful here to note that the square root of the variance, which is the standard deviation, is simply a measure of the *width* of the size distribution in bubble-radius space.) In addition, the coefficient of skewness, $S(t)$, is a dimensionless quantity which is a measure of the asymmetry of the size distribution, and is defined as

$$S(t) \equiv \sigma_3(t)/\sigma_2^{3/2}(t),$$

in which case, Equation 16 can be used to show that $S(t) = S(0)$; in other words, the coefficient of skewness is a time invariant, unaffected by kinetic re-solution.

Two important features of the analysis leading to Equation 16 need to be emphasized. First, the analysis is independent of the functional form of the size-distribution function. Second, unlike the analysis leading to Equations 10 and 11, nowhere was it necessary to demand that the brackets $\langle \rangle$ must necessarily include an average over the overall size distribution. Indeed, the analysis applies equally well to *any arbitrary subset* of the overall distribution, even if bubbles outside the subset are simultaneously being nucleated and/or annihilated. One need only require (a) that Equation 13 must apply to each of the bubbles under observation, and (b) that the observations must always cover the *same* set of bubbles.

The importance of requirement (a) lies in the fact that in a "real" material, no single growth-rate equation is likely to be applicable to all the

bubbles. (A good example of this fact is the manner in which bubbles on grain boundaries undergo different growth kinetics relative to bubbles within grains [16].) Consequently, for "real" materials, the *overall* size distribution, comprised of bubbles subjected to differing growth kinetics, may vary in an extremely complex manner.

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References

1. B. R. T. FROST, *Nucl. Appl. Technol.* **9** (1970) 128.
2. R. M. CORNELL, *Phil. Mag.* **19** (1969) 539.
3. F. A. NICHOLS, *J. Appl. Phys.* **37** (1966) 2805.
4. *Idem*, *Acta Metallurgica* **15** (1967) 365.
5. R. S. NELSON, D. J. MAZEY, and R. S. BARNES, *Phil. Mag.* **11** (1965) 91.
6. M. T. LILBURNE, *J. Mater. Sci.* **5** (1970) 351.
7. V. M. AGRANOVICH, É. YA. MIKHLIN, and L. P. SEMENOV, *Sov. At. Energy* **15** (1963) 1140.
8. A. J. MARKWORTH, *J. Appl. Phys.* **40** (1969) 1986.
9. M. V. SPEIGHT, *Metal Sci. J.* **2** (1968) 73.
10. A. J. MARKWORTH, *ibid* **3** (1969) 39.
11. A. J. MARKWORTH, and E. M. BAROODY, *ibid* **5** (1971) 55.
12. A. D. WHAPHAM, *Phil. Mag.* **23** (1971) 987.
13. M. O. MARLOWE, *Trans. Amer. Nucl. Soc.* **14** (1971) 146.
14. F. A. NICHOLS, *J. Metals* **21** January (1969) 19.
15. H. REISS and V. K. LAMER, *J. Chem. Phys.* **18** (1950) 1.
16. A. J. MARKWORTH, *J. Appl. Phys.*, **43** (1972) 2047.

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