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CRITICAL RADIUS AND CRITICAL NUMBER OF GAS ATOMS FOR CAVITIES CONTAINING A VAN DER WAALS GAS*

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The effect of gas on void nucleation and growth is particularly important for structural materials in fusion reactors because of the high production of helium by neutron-induced transmutation reactions. Gas reduces the critical radius for bias driven growth and there is a critical number of gas atoms, n_g^* , at which the critical radius is reduced essentially to zero. The significance of this is that the time interval to the accumulation of n_g^* gas atoms may determine the time to the onset of bias driven swelling where n_g^* is large. In previous papers these critical quantities were given for an ideal gas. Recently, we presented the results for a Van der Waals gas. Here the derivation of these relations is presented and further results of calculations are given. At low temperatures (high pressures) the results depart from those of the ideal gas, with the critical number affected more strongly than the critical radius. Comparisons are made with earlier calculations.

1. INTRODUCTION

The formation of cavities in structural materials under irradiation leads to swelling and degradation of mechanical properties. Understanding cavity nucleation and growth has been the objective of extensive research. Early it was recognized that gas is necessary to stabilize small vacancy clusters. We now know that the the onset of bias driven cavity-growth may be achieved by two qualitatively different paths. The cavity may exceed the critical size for bias driven growth by stochastic fluctuations. Alternatively, the cavity may accumulate more than a critical number of gas atoms, whereby bias-driven growth is insured; no fluctuations are required. These two possibilities merge continuously into each other, since any contained gas decreases the critical radius. A review and further development of these concepts is contained in a recent publication.¹

Several theoretical efforts treat the gas in the cavities as an ideal gas. Since the

most common gas treated is helium formed by transmutation reactions, the use of the ideal gas law has provided valuable insight. Several previous investigations recognized that even for helium, the ideal gas law gives inaccurate results at the pressures required to stabilize cavity embryos.²⁻⁵ The obvious choice for another gas law is the modified Van der Waals equation of state. This equation was chosen for our work. More complicated equations of state are available.⁵⁻⁷ However, since as we have shown,¹ analytical solutions for critical radius and critical number of gas atoms can be obtained using the Van der Waals gas law, and numerical refinements in these results are expected to be small in the regimes of most interest, this is the relation employed here. In our previous paper we presented some comparisons of results using both ideal and Van der Waals gas laws, based on both numerical calculations and on derived analytical solutions. In the present paper we describe the

*Research sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

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derivation of those solutions for the Van der Waals gas law. Further comparisons are made between results for the two gas laws. Comparisons of the present results also are made with results reported previously.²⁻⁵

2. THEORY

The growth rate of a cavity embedded in a material containing diffusing point defects and other sinks can be described using the algebraic solutions of the point defect continuity equations.⁸ In this framework the growth rate of a cavity is

$$\frac{dr_c}{dt} = \frac{\Omega}{r_c} [Z_V^C D_V C_V - Z_I^C D_I C_I - Z_V^C D_V C_V^e(r_c)] \quad (1)$$

where r_c is the cavity radius, Ω is the atomic volume, and Z_V^C and Z_I^C are the capture efficiencies of cavities for vacancies and interstitials, respectively. The symbols D_V , D_I , C_V , and C_I are the diffusion coefficients and defect concentrations for vacancies and interstitials in the material. $C_V^e(r_c)$ is the equilibrium vacancy concentration at the surface of a cavity of radius r_c ,

$$C_V^e(r_c) = C_V^0 \exp \left[- \left(P_g - \frac{2\gamma\Omega}{r_c} \right) \frac{\Omega}{kT} \right] \quad (2)$$

In Eq. (2), C_V^0 is the equilibrium concentration of vacancies in an otherwise perfect lattice, P_g is the gas pressure in the cavity, γ is the surface energy of the cavity-matrix interface, k is Boltzmann's constant, and T is the absolute temperature. The role that gas plays in promoting cavity growth is described in Eq. (2). The gas pressure counteracts the surface energy. For a given number of gas atoms in the cavity, different gas laws predict different pressures. For a modified Van der Waals gas the pressure is increased above that for an

ideal gas because of the volume correction term and equals

$$P_g = n_g k T / \left(\frac{4}{3} \pi r_c^3 - n_g B \right) \quad (3)$$

The constant B has been determined as a function of temperature for helium,⁹

$$B = 6.65 \times 10^{-27} [4.5 \times 10^{-4} + 5.42/(1890 + T)] \quad (4)$$

The expression gives a value of 1.6×10^{-29} m³/atom at 600°C.

The growth rate of a cavity containing a fixed number of gas atoms can now be evaluated from Eq. (1) by using the defect concentrations described in ref. 1 along with Eqs. (2) and (3). A plot of dr_c/dt versus r_c shows the following properties. For a fixed number of gas atoms below a critical number n_g^* , very small cavities are overpressured and grow by absorbing vacancies until reaching a stable radius, r_c^S , where r_c^S is always somewhat above the corresponding thermal equilibrium value, r_c^{eq} , for the same number of gas atoms. Large cavities above a critical size, r_c^C , also grow because of the defect bias in the material formed by the preferential attraction of interstitials to dislocations. Cavities of intermediate size shrink to r_c^S . Cavities containing more than n_g^* gas atoms have positive growth rate at all sizes. At n_g^* gas atoms the critical radius r_c^C and the stable radius r_c^S coincide at the minimum critical radius r_c^{C*} .

The values of r_c^S and r_c^C can be determined by finding the roots to the equation¹⁰

$$r_c = \frac{2\gamma}{P_g + \frac{kT}{\Omega} \ln \left[\frac{1-Z}{C_V^0} \frac{C_V}{C_V^0} + Z \right]} \quad (5)$$

Equation (5) results from Eq. (1) when thermal vacancy emission negates radiation-induced

growth, $dr_c/dt = 0$. The quantity Z denotes $Z^d Z^i / Z^v Z^g$, where Z^d and Z^i denotes the dislocation capture efficiencies for vacancies and interstitials. Further restrictions are necessary to obtain the simple form of the argument of the logarithm in Eq. (5): dislocations, cavities, and mutual recombination are the only modes of point defect loss; and dislocations are the dominant of the two sinks. Using the definition $f = (kT/\Omega) \ln[(1-Z) C_v/C_v^0 + Z]$, and substituting Eq. (3) for P_g , Eq. (5) may be written

$$g(r_c) = r_c^4 - \frac{2\gamma}{f} r_c^3 + \frac{3n_g(kT - Bf)}{4\pi f} r_c + \frac{3\gamma n_g B}{2\pi f} = 0 \quad (6)$$

Equation (6) has four roots, two of which are r_c^s and r_c^c . The remaining roots are non-physical. An important special case is where r_c^s and r_c^c are equal. This occurs when $g' = dg/dr_c = 0$. Taking the derivative of Eq. (6), setting it equal to zero, solving it for n_g and substituting into Eq. (6) gives the quadratic

$$r_c^2 + \left[\frac{8\gamma B}{3(kT - Bf)} - \frac{4\gamma}{3f} \right] r_c - \frac{4\gamma^2 B}{f(kT - Bf)} = 0 \quad (7)$$

The roots of Eq. (7) give the minimum critical radius r_c^{c*}

$$r_c^{c*} = \frac{2\gamma}{3f} \left[\frac{kT - 3Bf}{kT - Bf} \right] \left(1 \pm \sqrt{1 + \eta} \right) \quad (8)$$

where

$$\eta = \frac{16B}{f(kT - Bf)} \left/ \left[\frac{8B/3}{kT - Bf} - \frac{4}{3f} \right]^2 \right. \quad (9)$$

The critical number of gas atoms is obtained from Eqs. (8), (9), and $dg/dr_c = 0$ from Eq. (6) as

$$n_g^* = \frac{8\pi r_c^{c*2}}{3(kT - Bf)} (3\gamma - 2f r_c^{c*}) \quad (10)$$

This solution for r_c^{c*} and n_g^* approaches the ideal gas solution as B approaches zero. For finite values of B , however, care must be taken to choose the correct root. For high temperatures the positive sign is taken but, as the temperature is lowered to the condition where $kT = 3Bf$, a singular point is reached where the correct root becomes the negative one.

3. RESULTS

In order to examine the effects of a Van der Waals gas on the critical radius, Eqs. (8) and (10) have been plotted for several different sets of conditions. In all cases, the diffusion coefficients, radiation parameters, and sink strengths are the same and are listed in Table 1. The curves shown are for a dislocation density of $L = 1 \times 10^{15} \text{ m}^{-2}$ unless otherwise specified. The remaining parameters are varied as described in the figure. The equivalent results for an ideal gas are also shown. Figures 1 and 2 show the minimum critical radius, r_c^{c*} , and the critical number of gas atoms, n_g^* , as functions of temperature for two different dislocation densities.

We also have evaluated r_c^s , the stable cavity radius under the same conditions. This was done by evaluating Eq. (1) for a range of gas contents, n_g , and finding the corresponding root r_c^s numerically. Figure 3 is a plot of r_c^s for several cases. Since the number of gas atoms changes from zero to n_g^* and since n_g varies several orders of magnitude, results were normalized by plotting r_c^s/r_c^{c*} vs n_g/n_g^* . For this normalization all the plots for an ideal gas fall on the same master curve. This is shown dashed Figure 3. The Van der Waals

TABLE 1
Parameters used for example calculations

Atomic volume, Ω	$1.095 \times 10^{-29} \text{ m}^3$
Surface energy, γ	1 J/m^2
Displacement rate	$1 \times 10^{-6} \text{ dpa/s}$
Recombination radius, r_0	$4 \times 10^{-10} \text{ m}$
Diffusion pre-exponential, D_0^i, D_0^v	$1 \times 10^{-6} \text{ m}^2/\text{s}$
Vacancy formation energy, E_v^f	1.6 eV
Vacancy migration energy, E_v^m	1.2 eV
Interstitial migration energy, E_i	0.15 eV
Sink efficiencies	$Z_i^d = 1.05$
	$Z_v^d = Z_i^i = Z_v^i = 1.00$

plots show some dependence on temperature and dislocation density.

4. COMPARISON WITH PREVIOUS RESULTS

Several other investigators²⁻⁵ have evaluated r_c^* and n_g^* for a Van der Waals gas or for more complicated equations of state. We compare our results with others by evaluating both results for the same set of parameters.

Parker and Russell² evaluated the effect of a Van der Waals gas on the kinetic analog of the free energy to form a void. The result was based on an earlier calculation by Russell¹¹ for a cavity containing an ideal gas. If we use the appropriate expressions for point defect arrival rates the effective vacancy saturation, S_e , in Russell's Eqs. (17) and (18) is $(1 - Z)v_c/C_v^0 + Z$. With this equation our results for an ideal gas agree with those of Russell. The Van der Waals result reported by Parker and Russell has the same general dependence on temperature but differs from ours throughout the range by a factor of about 40%. In addition, the minimum critical radius of Parker and Russell is independent of the Van der Waals constant and neither the minimum critical radius nor the critical number of gas

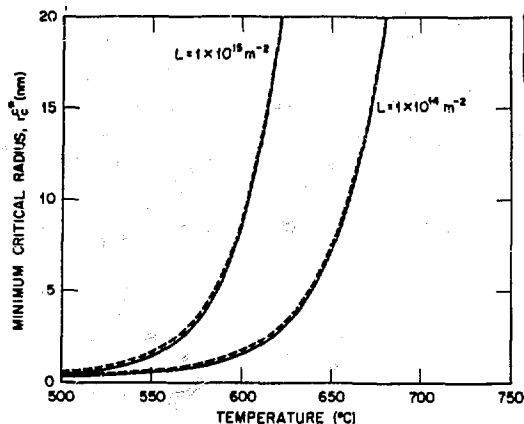


FIGURE 1
The minimum critical radius versus temperature. The solid curves are for an ideal gas while the dashed curves are for a Van der Waals gas.

atoms extrapolate to the ideal gas result as B approaches zero. The critical number of gas atoms normalized to that found for an ideal gas is plotted as a function of temperature for several cases in Figure 4.

More recently Townsend³ evaluated both r_c^* and n_g^* in an implicit solution contained in two equations. The solution was somewhat limited by the assumptions of no recombination of vacancies and interstitials. We compared our results for the same physical parameters and the agreement was very good (within a few percent). However, when the damage rate is increased or the dislocation density is lowered the solutions began to diverge. This is expected since, for these cases, defect recombination becomes more important.

A third approach to use a more accurate gas law was published by Stoller and Odette.^{4,5} They recognized the difficulty in depending on

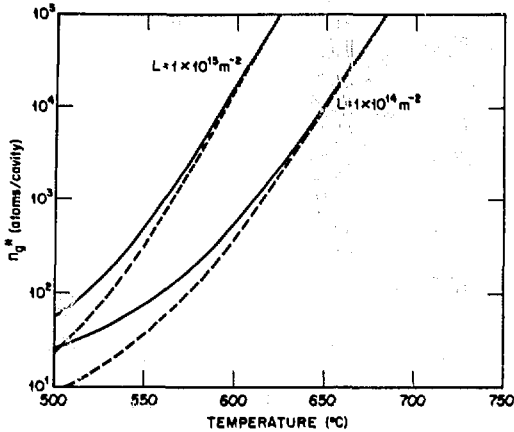


FIGURE 2

The critical number of gas atoms required to nucleate a bias-driven cavity plotted as a function of temperature. The solid curves are for an ideal gas and the dashed curves are for a Van der Waals gas.

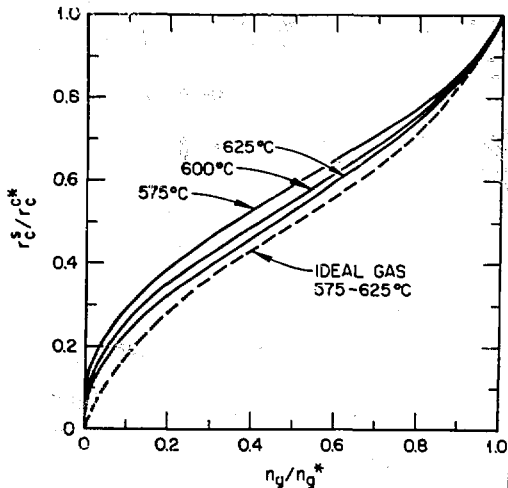


FIGURE 3

The stable bubble radius normalized to the minimum critical radius as a function of the number of gas atoms normalized to the critical number of gas atoms.

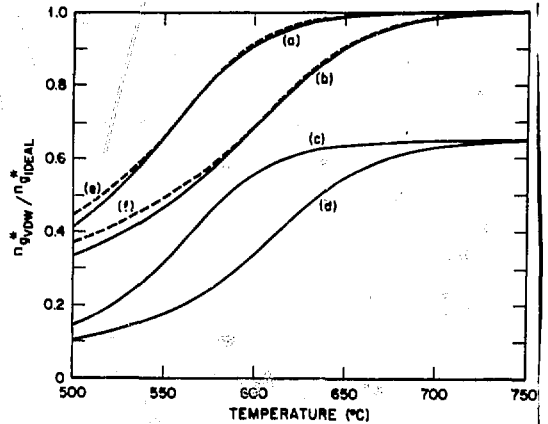


FIGURE 4

A plot of several different expressions for the ratio of n_g^* for a Van der Waals gas to that for an ideal gas as a function of temperature. (a), (c), and (e) are for a dislocation density, $L = 10^{14} \text{ m}^{-2}$ while (b), (d), and (f) are for $L = 10^{15} \text{ m}^{-2}$. Curves (a) and (b) are the results of the present work, (c) and (d) are those for Parker and Russell,² and (e) and (f) are those for Stoller and Odette.⁴

implicit functions or numerical solutions and devised empirical expressions which could be used for a reasonably wide set of parameters. The published version of their results contains a typographical error.¹² After making corrections, results using their expressions were plotted in Figure 4. The results agree very well for high temperatures where they approach ideal gas behavior. The results begin to deviate at lower temperatures where it is reasonable to expect differences between the Van der Waals equation of state we used and the different equation used by Stoller and Odette. Trinkaus⁷ has given expressions for r_c^* and n_g^* in terms of a parameter which expresses the power law dependence of gas pressure on contained number of gas atoms. Evaluating the expression for $\alpha = 1$, denoting an ideal gas, gives the identical results we obtained for an ideal gas.

5. DISCUSSION AND CONCLUSIONS

This paper is concerned with the more accurate evaluation of the minimum critical radius, r_c^* , and critical number of gas atoms, n_g^* , for bias driven cavity growth, and related quantities. A significant impetus for accurate evaluation of n_g^* is that at high temperatures or other conditions where n_g^* is large, and where residual gases are not sufficient, the time interval to the onset of bias driven swelling may be closely related to the time to accumulate n_g^* helium atoms in a cavity.

Analytical expressions have been derived for the minimum critical radius and for the critical number of gas atoms. For cavities containing less than this amount of gas, numerical methods are used to find the stable cavity radius and the critical cavity radius.

We found previously that the minimum critical radius is exactly 2/3 of the gas free critical radius for the ideal gas.¹ In the present case, this ratio is retained approximately for much of the range. At pressures so high (temperatures so low) that the Van der Waals solution for r_c^* , Eq. (8), is about to break down, the ratio of r_c^* to r_c^0 , the gas-free critical radius, is approximately 0.9. Therefore the present work shows that the ideal gas r_c^* is always a reasonable estimate of the critical radius. Another result we found previously for an ideal gas is that a cavity at the minimum critical radius containing n_g^* gas atoms has an internal pressure exactly 1/3 of the thermal equilibrium pressure for a cavity of the same size.¹ Again this ratio is preserved for a Van der Waals gas over much of the range of interest. For lower temperature, say 500°C for example, near where where Eqs. (8) and (10) break down, this ratio is decreased to 0.15. This means that for a cavity that has just enough gas to change from bubble growth to

bias driven growth the pressure is just 15% of the equilibrium pressure. This result should be considered when determining the helium inventory in irradiated materials.

Comparison of results with numerical calculations has demonstrated considerable advantage in working with the present analytical results, particularly for examining a wide range of cases of interest. Some significant differences with earlier calculations for Van der Waals gas stem from more restrictive approximations in the earlier work.

The strong dependence of critical radius and critical number of gas atoms on dislocation density, as illustrated in Figures 1 and 2 deserves highlighting. This sensitivity implies that the time to the onset of bias-driven swelling will vary significantly from point to point in a given material during irradiation. This would be expected to lead to patchiness of cavitation, especially in the early stages of swelling, a result often remarked in experimental studies.

It may also be of use to suggest that these analytical solutions may be extended to evaluate the effect of other more complex equations of state for which direct analytical solutions for r_c^* and n_g^* are not available.⁵⁻⁷ If such an equation of state can be cast in terms of a generalized Van der Waals equation with variable B, where B can be specified accurately over a certain range as a function of system parameters, then the minimum critical radius and the critical number of gas atoms can be obtained analytically from the present results.

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