MASTER

THEORETICAL CONSIDERATIONS OF MIGRATION AND
COALESCENCE OF PORES IN SOLIDS BY SURFACE
DIFFUSION

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Prepared for:

International Conference on Radiation-Induced Voids in
Metals, State University of New York, Albany, New York,
June 9-11, 1971

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THEORETICAL CONSIDERATIONS OF MIGRATION AND COALESCENCE
OF PORES IN SOLIDS BY SURFACE DIFFUSION

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INTRODUCTION

The first analysis of swelling due to random migration and coalescence of gas-filled pores in solids by surface diffusion was carried out by Greenwood and Speight¹. The time rate of change of the mean radius, and hence the volume change or swelling, were calculated by considering the mean time required for all bubbles to coalesce to form the next larger bubble size. The conclusion of their argument was that swelling should be proportional to the $2/5$ power of time for the case of in-pile swelling. The case of post-irradiation annealing was later treated by Speight,² who predicted that the mean radius and swelling should vary in this case as the $1/5$ power of time.

A more detailed approach to the post-irradiation annealing problem was included in a subsequent analysis by Gruber;³ finite-difference techniques were adapted to calculate the complete bubble size distribution as a function of time, using a digital computer. This treatment was based on a relation given by Chandrasekhar⁴ in a discussion of colloid coagulation. The results confirmed those obtained by Speight,² except for a relatively small difference in the numerical coefficient. The results further showed that the distribution approached a limiting "self-preserving" shape, and that the shape of the distribution was such that the volume change was about 15% larger than that calculated from the mean radius.

These results were confirmed by analytical computations by Baroody,⁵ who also pointed out a numerical error in the example given for swelling by random migration. The predicted values for swelling and mean radius should have been 6% and 1340 Å for the case of a one-month, 1000°K post-irradiation anneal of copper containing 10^{20} helium atoms per cubic centimeter. This example was considered at that time to be an extreme case; the purpose of the example was to illustrate the conclusion that swelling due to random migration should be small relative to other possible mechanisms. However, in more recent discussions of swelling, particularly in the case of fast breeder reactors, the projected irradiation conditions make this formerly "extreme" example appear much less severe by comparison. A more complete treatment of the random migration problem is therefore appropriate.

ANALYSIS

The same assumptions and approximations will be used here as in the previous case;³ we consider the problem of random migration of bubbles in a perfect, infinite crystal containing a constant concentration m of gas atoms per unit initial volume. The gas is assumed for convenience to behave ideally, and vacancy diffusion in the solid is assumed to equilibrate the pressure in the bubbles with the surface tension of the solid. Coalescence and equilibration are assumed to occur "instantaneously" when two bubbles collide; that is, the collision process is considered to be the rate-controlling step.

Consider a function $F(n,t)$, which represents the frequency distribution of bubbles containing n atoms as a function of time t . Let F_i denote the (time dependent) value of this function at $n = n_i$. The appropriate solution to the diffusion equation was given by Chandrasekhar in a discussion of the analogous problem of colloid coagulation;⁶ the number of collisions ΔF_{ij} between bubbles

containing n_i gas atoms and those containing n_j gas atoms in a time increment Δt is

$$\Delta F_{ij} = 4\pi D_{ij} R_{ij} F_i F_j \{ 1 + [R_{ij}/(\pi D_{ij} t)^{1/2}] \} \Delta t. \quad (1)$$

The diffusion coefficient D_{ij} is given by $D_i + D_j$, and the interaction radius R_{ij} is taken as the sum $r_i + r_j$. The approximation was made in the earlier analysis, following Chandrasekhar, that the interaction radius would be small relative to the mean distance travelled by the two coalescing bubbles. On this basis the second term in brackets in Eq. (1) was neglected, and the distribution function $F(n,t)$ was calculated on the basis of the simplified equation. The purpose of the present work is to investigate the validity of this approximation.

First we note several useful relations from the previous work. The diffusion coefficient of a pore is given by

$$D_p = 3\Omega^{2/3} D_s / 2\pi r^4 \quad (2)$$

or, for the particular case of a face-centered cubic lattice,

$$D_p = 0.301 D_s (a_0/r)^4, \quad (2a)$$

where Ω is the atomic volume, D_s the surface diffusion coefficient, r the pore radius, and a_0 the interatomic distance. For an ideal-gas bubble, in equilibrium so that $p = 2\gamma/r$, where p is the gas pressure and γ is the surface tension of the solid, we have

$$r_i^2 = (3kT/8\pi\gamma)n_i, \quad (3)$$

where, as before, n_i is the number of gas atoms contained in the bubble. Finally, the results of the analysis showed that the mean radius varied as the $1/5$ power of time. Thus if we consider only the mean bubble size and calculate the time

dependence of the second term in Eq. (1), we find that the magnitude of this term should increase as $t^{1/10}$. Thus after "sufficiently long" time, this term should dominate the collision kinetics.

Since there is no way to quantitatively determine this time, two approaches are available; either calculate the complete solution, using Eq. (1), or calculate the "long-time" approximation, using only the second term, and compare the result to the first treatment to determine the regimes of applicability of the two solutions. The second approach is used here, both because the solution can be given in general terms, so that one relation applies to all cases, and because the calculations are simpler. Before considering the calculations, however, we consider briefly a simplified model of the collision process by random walk.

Consider a random distribution of pores of various sizes. In a given small time increment Δt only those pores separated by small distances of about $(6D_{ij}\Delta t)^{1/2}$ will be likely to collide. Figure 1 shows an example of two pores initially close together. Consider the larger "j-pore" fixed, with the i-pore migrating by random surface diffusion. In time Δt the i-pore will sweep out a minimum volume corresponding to a cylinder of length Δx and radius r_i . As it does so, coalescence will occur with any j-pore lying in the shaded volume in Fig. 1. This volume is equal to the volume of a cylinder of length Δx and radius R_{ij} . Thus the probability of coalescence of one i-pore with a j-pore is

$$P_{ij} = F_j \pi R_{ij}^2 \sqrt{6D_{ij}\Delta t} \quad , \quad (4)$$

where now D_{ij} has been used to take into account the fact that the j-pore is also migrating. However, this results in an overestimate, since it implies that the two pores are migrating generally toward each other.

The predicted number of collisions of i - and j -pores in time Δt is given by $F_i P_{ij}$, or

$$\Delta F_{ij} = \pi F_i F_j R_{ij}^2 \sqrt{6D_{ij} \Delta t} \quad (5)$$

Two approximations were made in this derivation: each would be expected to affect only the numerical coefficient, and they tend to cancel one another; the first leads to an underestimate and the second to an overestimate of the interaction volume. We now consider Eq. (1) in relation to Eq. (5). If we ignore the first term in Eq. (1), we obtain for the "long-time" solution

$$\Delta F_{ij} = 4(\pi D_{ij})^{1/2} F_i F_j R_{ij}^2 \Delta t / t^{1/2} \quad (6)$$

Now if we consider that at any time t the distribution remains random, we can reset t to $t=0$ at the beginning of each time step. Then at the end of a time step, $t = \Delta t$, and Eq. (6) simplifies to the same form as Eq. (5). The only difference is that the numerical factor $\pi\sqrt{6}$ (~ 7.7) in Eq. (5) is replaced by $4\sqrt{\pi}$ (~ 7.1) from Eq. (6). The advantage of this approach is that it provides a basis for eliminating the t that appears in Eq. (1).

As in the previous treatment, the distribution function $F(n,t)$ can be normalized by dividing by the total number of gas atoms per unit volume. The resulting equation for collisions can be written

$$\Delta f_{ij} = f_i f_j (n_i^{-2} + n_j^{-2})^{1/2} (n_i^{1/2} + n_j^{1/2})^2 \sqrt{\Delta \tau_2} \quad (7)$$

where $\Delta \tau_2 = 24\Omega^{4/3} D_s m^2 \Delta t$ and f_i represents the normalized distribution function.

Finite-difference techniques were applied as discussed in the earlier work to determine the solution $f(n,\tau)$ that satisfies Eq. (7). In these calculations, a

value of $\sqrt{\Delta\tau_2}$ was chosen for each time step such that the largest fractional decrease in any value f_i was 10%. The calculated value was squared to give $\Delta\tau_2$, and the sum τ_2 was formed from the individual values.

As in the previous case, in order to determine the variation of the mean radius and swelling with time, the necessary moments of the calculated distribution were computed for each value of τ . Figure 2 shows the results on a logarithmic plot for the 3/2 moment (which determines swelling) and the ratio of the 1/2 moment to the zero moment (which determines the average radius). The curves approach linearity very quickly, near $\tau = 0.2$. This corresponds to a very short time for large m (for our usual example, copper with $m = 10^{20}$, $\tau \sim 6 \times 10^4$ at $t = 1$ sec). The calculated slope for both curves was 0.25 ± 0.01 after $\tau \approx 100$.

The results can be presented very concisely in terms of the self-preserving distribution shown in Fig. 3. This figure shows the function $f(n, \tau)$ normalized so that the resulting curve is independent of time. The normalizing procedure was described in the previous work; basically, it results from a separation of variables approach to the integro-differential equation corresponding to the finite-difference equation, Eq. (7). The results is that the distribution can be expressed as

$$F(n, t) = m\tau^{-2k} Z(u) \quad (8)$$

where $u = n\tau^{-k}$, and k is determined either from the integro-differential equation or from the finite-difference solution. The mean radius and volume change or swelling are proportional to $\tau^{k/2}$. In the present case, k was found to be 1/2; this value was used to calculate the self-preserving distribution shown in Fig. 3. This distribution was rather well-established at $\tau = 10$, and remained unchanged for all higher values considered (up to about 10^{14}).

DISCUSSION OF RESULTS

The purpose of these calculations has been to determine whether the approximation used in the earlier treatment was justified, or if the second term or both terms in Eq. (1) should be used in the analysis. A partial solution to this problem is attempted here by comparing the results of separate treatments of the two terms.

A simple comparison can be made by forming the ratio of the swelling predicted by the two calculations. The first analysis gave the result

$$\Delta V_1 = 0.82 A^{6/5} B^{1/5}, \quad (9)$$

and the present result is, substituting for τ_2 ,

$$V_2 = 2.8 A^{3/2} B^{1/4}; \quad (10)$$

in both equations we have substituted for notational convenience,

$$A = mkT/\gamma \quad \text{and} \quad B = \Omega^{4/3} D_s t.$$

The ratio of swelling of these two contributions is therefore

$$\Delta V_2 / \Delta V_1 = 3.4 A^{3/10} B^{1/20}. \quad (11)$$

This equation can be applied directly to determine the relative importance in a particular case. It is also apparent from this result that the parameters defining A influence this ratio more strongly than those defining B.

A more interesting quantitative result can be determined by considering the swelling ΔV_c at which $\Delta V_1 = \Delta V_2 = \Delta V_c$. From Eqs. (9) and (10),

$$\Delta V_c = 0.82 A_c^{6/5} B_c^{1/5} = 2.8 A_c^{3/2} B_c^{1/4}, \quad (12)$$

from which we obtain

$$A_c = 3.4^{-10/3} B_c^{-1/6} . \quad (13)$$

Substituting for A_c in Eq. (12) and simplifying, we obtain

$$\Delta V_c = 0.006 = 0.6\% . \quad (14)$$

This result is very interesting; it shows simply and quantitatively that, independently of the parameters involved, the second term begins to dominate the swelling kinetics at about the time swelling becomes significant. This result remains true whether swelling is due to a few large bubbles or to many smaller ones.

The swelling predicted by Eqs. (9) and (10) is shown as a function of time in Fig. 4 for two cases; $m = 10^{19}$ and $m = 10^{20}$, again for copper, post-irradiation annealed at 1000°K. The dashed lines indicate for comparison the results predicted in the earlier work for the case of biased migration; the cases shown correspond to the presence of a thermal gradient of 100°C/cm and a surface diffusion heat of transport of 10 kcal/mol.

These results confirm the earlier conclusion that "swelling is not likely to be significant if it occurs only as a result of random migration of bubbles in large-grained material,"³ except for rather extreme cases.

CONCLUSIONS

It has been shown that when swelling by random surface diffusion migration does become significant, at swelling above about 0.6%, the mean radius and swelling should increase as $t^{1/4}$ rather than $t^{1/5}$ as predicted in the approximate treatment. Although the critical swelling, 0.6%, is subject to a

more detailed investigation of the swelling behavior (where both terms are considered simultaneously), the fact that it exists and is relatively small is itself of value in further studies. For example, in the cases of random migration and coalescence on grain boundaries and on dislocations, analyses similar to that used in the derivation of Eq. (5) should be completely adequate, because in these cases swelling is due to larger bubbles with smaller separations than in the perfect matrix.

Preliminary calculations based on such equations indicate that the mean radius and swelling due to random migration by surface diffusion on grain boundaries and on dislocations vary respectively as $t^{1/6}$ and as $t^{1/8}$.

FIGURE CAPTIONS

- Fig. 1. Schematic representation of migrating pores for the case in which the sum of pore radii is greater than the pore separation.
- Fig. 2. Calculated variation of mean radius and swelling parameters as a function of τ .
- Fig. 3. "Standardized" or "self-preserving" distribution function.
- Fig. 4. Time dependence of swelling computed for copper, post-irradiation annealed at 1000°K for the indicated time. The upper curves correspond to a dose $m = 10^{20}$, and the lower dose to $m = 10^{19}$, helium atoms per cm^3 . The dashed lines show the results for biased migration corresponding to a thermal gradient of 100°C/cm for a heat of transport of 10 kcal/mol.

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