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A THEORY OF SWELLING AND GAS RELEASE FOR REACTOR MATERIALS

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The physical mechanisms deduced from the direct observation of inert gas bubbles in the electron microscope are used to evolve a model, or theory, for swelling. The model assumes the insolubility of the inert gases and the bodily migration of the gas bubble and relies upon the equation of state for the gas, upon the surface energy, the surface self-diffusion coefficient, and the lattice parameter of the solid and upon some internal driving force, which is believed to be related to the line tension of dislocation lines. With values for these parameters and for irradiation and annealing conditions, estimates for the bubble size (r) and number/cm³ (n) are made. From these the swelling ($\Delta V/V$) can be calculated, and the effect of grain size, grain boundary migration, and other structural features of the solid must be considered.

The model is tested against several experimental results from a variety of solids and satisfactory agreement obtained. The model is thought to be valid for all solids, including non-metals, and can account for boundary swelling and gas release. The limitations of the model, which is a very simple one, are discussed.

On a utilisé pour élaborer une théorie du gonflement, les renseignements mis en évidence par l'observation au microscope électronique des bulles de gaz inerte dans le microscope électronique. Le modèle suppose l'insolubilité des gaz inerts et la migration corporelle des bulles de gaz, et se fonde sur l'équation d'état des gaz, sur l'énergie de surface, sur le coefficient de diffusion superficielle, du solide et d'une force interne liée à la tension des lignes de dislocation. Une fois connues les valeurs de ces paramètres dans des conditions d'irradiation et de chauffage, on peut estimer la taille (r) des bulles et leur nombre par cm³. De là on peut calculer le gonflement

$\Delta V/V$, mais on doit tenir compte de l'effet de la taille des grains, de la migration des joints de grains et autres caractéristiques structurales du solide.

Le modèle est confronté avec plusieurs résultats expérimentaux obtenus à partir de différents substances et on aboutit à un accord satisfaisant. On pense que le modèle est applicable à tous les solides, y compris les corps non métalliques, et peut expliquer le gonflement inattendu et dégazage. On discute les limites de ce très simple modèle.

Die physikalischen Vorgänge die von direkter elektronenmikroskopischer Beobachtung von Gasblasen stammen, werden benutzt um ein Modell des Aufschwellens zu formulieren. Dieses Modell geht aus von der Unlöslichkeit der Edelgase und der Wanderung von ganzen Gasblasen, und verlässt sich auf Zustandsgleichungen für Edelgase, Oberflächenenergie, Oberflächendiffusionskoeffizient, Gitterparameter des Materials, und auf eine gewisse innere Treibkraft, welche wahrscheinlich von der Linienanspannung der Versetzungslinien herrührt. Wenn diese Parameter bekannt sind und man auch die Bestrahlungs- und Erhitzungsumstände berücksichtigt, kann man Blasen gröÙe (r) und Anzahl der Blasen/cm³ errechnen. Hieraus kann das Aufschwellen ($\Delta V/V$) errechnet werden, aber der Einfluss der KorngröÙe, Korngrenzenwanderung und anderer Struktureigenschaften der Materie müssen auch berücksichtigt werden.

Das Modell wird mit mehreren experimentellen Ergebnissen mit verschiedenen Feststoffen verglichen, und zufriedenstellende Übereinstimmung wurde gefunden. Das Modell dürfte auf alle Feststoffe anwendbar sein, inbegriffen Nichtmetalle, und kann "plötzliches Aufschwellen" und Gasabgabe erklären. Die Begrenzungen dieses sehr einfachen Modells werden diskutiert.

Ne, Kr, or Xe, but it is in the fuel materials where the effects of these gases have been of most concern. In ceramic fuels the main problem has been the release of the gas, but in metallic

fuels the problem has been one of dimensional instability, caused by the internal formation of bubbles, which has come to be called *swelling*.

Much experimental work has been done to establish the general influence of the many irradiation, annealing, and material variables upon swelling, but the pattern of behaviour has not been understood. The object of this paper is first to outline the behaviour of inert gases in solids as determined from direct experiments and from this to construct a simple model, or theory, of swelling, and incidentally of gas release. This will then be used to interpret some of the experimental observations.

2. The Behaviour of the Inert Gases in Solids

The inert gases are known to be extremely insoluble (e.g. Rimmer and Cottrell¹), Johnson and Shuttleworth²) and atoms injected into the crystal from transmutations rapidly supersaturate the solid and precipitate to form embryo gas bubbles on any suitable nuclei. Because the supersaturation (c/c_0) can be very high, the Gibbs relation

$$\frac{2\gamma}{r_0} = kTN \ln \left(\frac{c}{c_0} \right)$$

(where γ is the surface energy, k Boltzmann's constant, N the atomic density and T the absolute temperature) indicates that the radius r_0 of these nuclei can be extremely small. It has been shown that vacancy clusters less than 100 Å in diameter, and dislocation loops, formed during the irradiation, together with previously existing dislocation lines and grain boundaries are effective bubble nuclei³).

However, a group of inert gas atoms, whether they be interstitial or substitutional, do not constitute a gas bubble. Before the atoms can behave as a gas, their separation must be increased by the removal of surrounding matrix atoms. This process only occurs at temperatures where vacancies can flow into the embryo bubbles⁴). The flow will continue until the gas pressure (P) in the bubble is balanced by the surface energy (γ), i.e. until $P = 2\gamma/r$, where r is the radius of the bubble, if it is spherical. The

bubble is then in equilibrium. (If the material will have increased in volume by time. Firstly, as a consequence of the mutation which increases the number of (this effect will always occur and can be important but, for clarity, it will not be shown here to be a part of "swelling") and because these vacancies, which can be trapped have been trapped in the bubbles and for the space of one atom each.

Fig. 1 illustrates how the size of an helium bubble in copper, in equilibrium

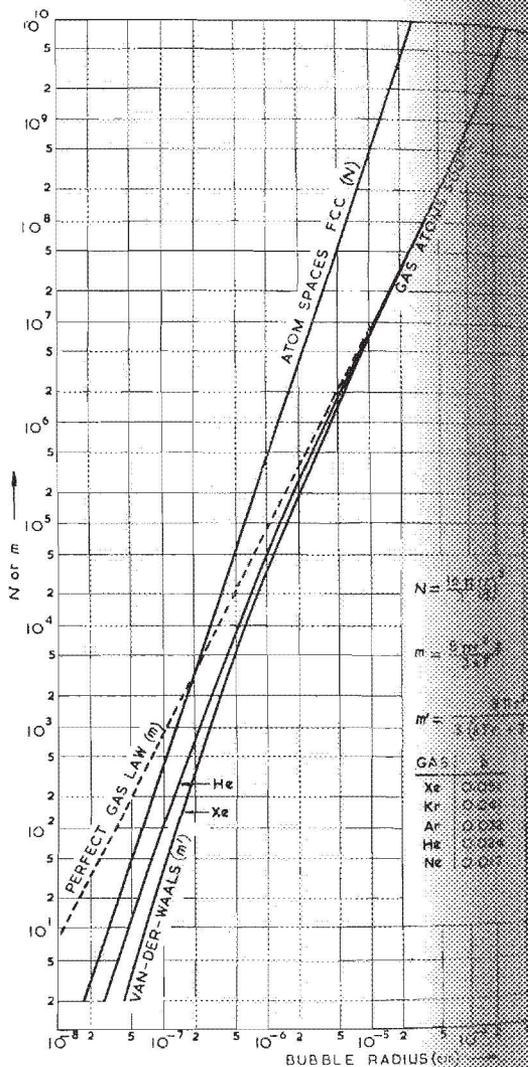


Fig. 1. The relative number of inert gas atoms in bubbles of various sizes, $P = 2\gamma/r$.

TABLE I

Influence of bubble size upon the number of atomic spaces per helium atom and the swelling

r (cm)	m' He atoms	N atom spaces	N/m'	$\Delta V/V$ (%) for an atomic concentration of 10^{-3}
10^{-7}	10^2	4×10^2	4	0.4
10^{-6}	5×10^4	4×10^5	8	0.8
10^{-5}	8×10^6	4×10^8	50	5
10^{-4}	8×10^8	4×10^{11}	500	< 50

surface energy (which throughout, for convenience, will be taken to be 10^3 erg/cm²), varies with helium content. The graph shows, for a temperature of 500° C, the number of helium and xenon atoms (m) a bubble of radius r will contain for the above equilibrium situation. The dotted line is based on the assumption of perfect gas behaviour, and of course, these values become quite unrealistic for small bubbles. The continuous line is for the Van der Waals correction of the form $P(r) = m'kT - m'kT/r$. Assuming this is sufficiently accurate, some values of the equilibrium helium content (m') of bubbles of various size are given in table I, together with the number of atom spaces (N) the bubble contains; these latter values are also shown in fig. 1†.

The nature of the gas determines the extent of the deviation from the straight line and curves for helium and xenon are both shown in fig. 1 together with values of the correction- $m'kT/r$ in e.r.u./mol, for other inert gases. The percentage volume increase resulting from a helium atomic concentration of 10^{-3} is also given in the last column of table I. Thus volume increases can readily be estimated from fig. 1 if the average radius of the bubbles r is known, together with the total gas content.

For bubbles with a radius greater than $\sim 10^{-4}$ cm, the Van der Waals correction is of little consequence (for all inert gases) and then if the helium atoms arrived as interstitial atoms, m' represents the number of vacancies the bubble has available if they arrived while in substitutional positions. The number is $(N - m')$.

the simple expressions⁵) for a perfect gas can be used, where the particular gas has no influence upon its equilibrium size.

3. The Migration of Gas Bubbles

Swelling can be minimised either by depriving the bubbles of vacancies or by maintaining a large number of bubbles. Frequently the scale upon which the bubbles first form is very fine, and if this large number of bubbles was maintained there would be few gas atoms (small m') in each bubble, and little swelling would result. However, there are processes which permit a coarsening of the inert gas bubbles so that their number reduces and the swelling increases, the bubbles attaining new equilibria by acquiring more vacancies.

Many workers have assumed that this coarsening process is one where the inert gas atoms dissolve and diffuse from one bubble to another (as in a normal precipitate coarsening process); however, there is no direct evidence for such a process, and there are many arguments against it. It had been suggested⁶) that gas bubbles could *migrate* by a surface diffusion process and that their coarsening resulted from collisions. Recently direct observation of helium bubbles in copper has shown that they do indeed migrate and collide so that their number steadily reduces and their size increases⁷). These experiments were performed *inside* the electron microscope upon films of copper ≈ 2500 Å thick and it was apparent that the migration was caused by large temperature gradients (estimated to be $\sim 10^5$ °C/cm)

occurring during the heating pulses, which lasted only a few seconds. However, the velocities (v) were consistent with the known surface self-diffusion coefficient (D_s) given by Choi and Shewmon⁸), and the formula

$$v = \frac{1}{8\pi} \frac{D_s}{kT} \left(\frac{a_0}{r} \right)^4 F \quad (1)$$

(Mullins, private communication) where a_0 is the lattice parameter of a face-centred cubic crystal, and F the force which acts upon the bubble to produce its directed motion.

In the above experiment F was proportional to the volume of the bubble and produced observed bubble velocities which were inversely proportional to their radii. However in bulk material the driving force F will be different because such large temperature gradients cannot persist but recent experiments (Barnes and Mazey, to be published) have shown that migration still occurs in furnace-heated films where there is no temperature gradient. It is not difficult to infer what the controlling features of bubble migration will then be. With no driving force, the bubbles will vacillate and perform a Brownian motion, but this motion will normally be constrained because the bubbles lie on dislocation lines (or on some less mobile crystal defect). If the dislocation is stressed it will attempt to drag the bubble with it and so exert a driving force (F) upon the bubble which will migrate at a velocity (v) determined by equation 1. Any mechanical stress will cause the dislocation to slip and bow out between bubbles and so exert a force $2T \cos \theta$ on the bubble, where 2θ is the angle between the dislocations leaving the bubble surface and T is the dislocation line tension. A chemical stress will be exerted whenever there is a non-equilibrium of vacancies and these will cause the dislocation to climb and bow out on the climb plane between bubbles⁹). For the same θ , the same force will be exerted upon the bubble. The force resulting from dislocation climb will occur whenever the bubbles are not in equilibrium and vacancies are demanded by the bubbles, e.g. when collisions occur. The absolute

maximum force that a dislocation can exert on a bubble is $2T$, i.e. μb^2 where μ is the shear modulus and b the Burgers vector of the dislocation line. The value of this force is of the order of 10^{-4} dynes for most metals.

With any constant and uniformly applied stress (mechanical or chemical) the radius of curvature of the dislocation line will be constant and close neighbours on a dislocation line will be subject to convergent resultant forces and will eventually collide, as the diagram in Fig. 2

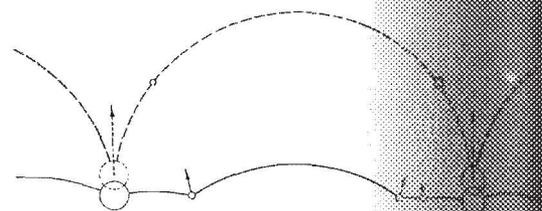


Fig. 2. The motion of bubbles on a stressed dislocation line.

illustrates. The largest force would be exerted on the bubble most separated from its neighbours on the same dislocation line. The smaller bubbles would rapidly migrate and eventually increase the force upon their larger neighbours. Eventually it would be these latter which would set the pace, and the driving force would increase until it became equal to its maximum value when approximately $\frac{1}{2} \frac{2T}{\sigma}$ where σ is the applied stress and 2 is the distance between the centres of neighbouring bubbles on the same dislocation line. For values of 2 greater than this, the dislocation would be able to break free from the bubbles and slip through the crystal, being intermittently impeded when it intersected bubbles which were close together. Similar considerations would apply to dislocations

4. The Model

If we construct a simple model of a solid containing n spherical bubbles/cm³ each of radius r , and acted upon by a driving force

† Because swelling is defined as the increase in volume divided by the original volume of the solid, the unit of volume is always taken as that of the original, unswollen, solid.

assuming for simplicity that the gas obeys the perfect gas law

$$PV = nkT$$

where n is the number of gas atoms/cm³, then

$$\frac{8\pi}{3} \gamma r^2 n = mkT \quad (2)$$

and that there are ample vacancies to keep the bubbles in equilibrium with γ the surface energy (i.e. if $P = 2\gamma/r$). These bubbles will each move with a velocity v given by eq. (1).

Any moving bubble will collide with any other bubble which lies within a distance $2r$ of its own centre, i.e. with any whose centre lies within the volume shown diagrammatically in Fig. 1 where the time considered is dt . Conse-

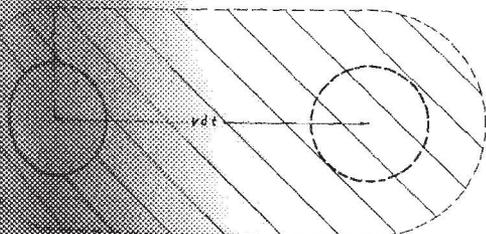


Fig. 1. Diagram showing the collision volume of a bubble moving with a velocity v . If there are two bubbles in a volume of the solid equal to

$$\frac{4}{3}\pi r^3 vt + \frac{4}{3}\pi(2r)^3 - 2 \times \frac{4}{3}\pi r^3$$

there will be one collision, i.e. if there is one bubble in a volume equal to $2\pi r^2 [v dt + 2r]$.

only if the centres of two bubbles lie in this volume there will be a collision between them.

It will happen if there is one bubble in a volume of the solid given by

$$2\pi r^2(v dt + 2r).$$

On average there is one bubble in a volume $1/n$ of the solid, so that the probability of a single bubble making a collision is n times the above volume, and the total number of collisions/cm³ in a time dt is

$$dn = 2\pi r^2 n^2 (v dt + 2r). \quad (3)$$

The number of bubbles halves in a time τ ,

i.e. if $dn' = -n$ when $dt = \tau$, eq. (3) can be modified to become

$$\tau = \frac{1}{v} \left[\frac{1}{2\pi r^2 n} - 2r \right]. \quad (4)$$

Except when the bubbles occupy an appreciable fraction of the volume, i.e. at large values of swelling, the term $2r$ is much smaller than $1/(2\pi r^2 n)$ and can be neglected. This will be done, but the significance of this term will be referred to later when "breakaway" phenomena are discussed.

Because at each collision one bubble disappears, dn' is equal to dn , the change in the number of bubbles. Equation (3) thus becomes

$$\frac{dn}{dt} = 2\pi r^2 n^2 v = \frac{n}{\tau^*}$$

and we can substitute for v and r using eqs. (1) and (2) respectively, obtaining

$$\frac{dn}{dt} = \frac{2\pi \gamma D_s F a_0^4 n^3}{3m(kT)^2}$$

which on integration gives

$$\frac{1}{n^2} - \frac{1}{n_0^2} = \frac{4\pi \gamma D_s F a_0^4 t}{3m(kT)^2} = \frac{2t}{\tau^* n^2} \quad (5)$$

where n_0 is the number of bubbles at the beginning of the anneal which lasts for t seconds. Once coarsening has begun, $(1/n^2) \gg (1/n_0^2)$ and $(1/n_0^2)$ can be neglected. Thus from eq. (2)

$$r^4 = \frac{3m D_s F a_0^4 t}{16\pi \gamma} = \frac{2r^4 t}{\tau^*}. \quad (6)$$

During an isothermal anneal of a solid containing many small bubbles, the bubbles will move very rapidly, making many collisions, and eventually become so large that movement almost ceases. τ^* represents the approximated time taken for the number of bubbles to halve and is proportional to r^4 and $1/n^2$. Thus τ^* will increase by a factor 4 each generation and the final generation of bubbles will have been present during the major part of the anneal.

The swelling $(\Delta V/V)$ is the volume of the

bubbles divided by the *original* volume of the solid and is given by the relation

$$\frac{\Delta V}{V} = \frac{4}{3}\pi r^3 n.$$

This can be expressed in terms of m and r , using eq. (2)

$$\frac{\Delta V}{V} = \frac{m k T r}{2\gamma}$$

and thus from eq. (6)

$$\frac{\Delta V}{V} = \frac{3^{\frac{1}{2}}}{4\pi^{\frac{1}{2}}} k T a_0 \left(\frac{m}{\gamma}\right)^{\frac{5}{4}} (D_s F t)^{\frac{1}{4}}. \quad (7)$$

The equations (5), (6) and (7) constitute a theory of swelling since the volume increase ($\Delta V/V$), the bubble size (r), or the number n of bubbles/cm³ can be calculated from the physical constants of the material, γ , D_s , and a_0 , the gas content m , and the annealing conditions t and T . The driving force F must be chosen according to the circumstances but, since it occurs to the $\frac{1}{4}$ power in eq. (7), approximations will be made, and we shall substitute a value of 10^{-4} dynes and assume it applies to any metal. (Here it is being assumed that the driving force F is an appreciable fraction of the maximum which a stressed dislocation could exert.)

The equations must be modified if the gas is being generated while the bubbles are migrating. This has been done in Appendix I.

5. Limitations of the Model

Some of the assumptions used in deriving the above model were that:

1. The gas obeys the perfect gas law. This breaks down for small bubbles and the size at which it breaks down (~ 500 Å radius) depends upon the particular gas, which is not otherwise considered. At the expense of some complication, the theory could be modified for any other equation of state.
2. The bubbles are spherical. However, frequently they are crystallographic polyhedra (Nelson, Mazey and Barnes, to be published),

and this would influence the values of $\Delta V/V$ to be used.

3. Surface diffusion determines the rate of migration of the bubbles. Above a certain temperature, volume diffusion will begin to augment surface diffusion but this will not happen with bubbles less than about 1 micrometer in radius (Mullins and Shewmon 1959).
4. The bubbles are all the same size. This is not true, as can be seen in electron micrographs. Nor would the assumed behavior lead to equal bubbles. The larger bubbles will dominate the migration rate (and the swelling) if all bubbles lie on dislocation lines, as is normally observed.
5. The driving force F is constant and the same for each bubble. This is most likely to have its maximum value at the largest bubbles.
6. There is no re-resolution of the gas. This model will be invalid if the bubbles contain gas which are highly soluble in the matrix (e.g. hydrogen).

There are many other implicit assumptions. One is that *all* the gas is in mobile bubbles. Of course, there will be a temperature and gas content below which this is not true. Then gas atoms can escape singly to the surface. Another is that the bubbles do not migrate on such a coarse scale that they are rendered immobile. Also it is assumed that the bubbles are in vacancy equilibrium. At low temperatures this is not true either, particularly some distance from a vacancy source⁴). These conditions will not be discussed here, and will restrict the model to temperatures greater than the temperature at which vacancies can readily migrate (as a working value this can be assumed to be $\frac{1}{2}T_m$ where T_m is the melting temperature in degrees Kelvin).

At high temperatures the simple model does not apply because the bubbles within the grain become large, and can coalesce with any further movement. Also many gas bubbles will be trapped on grain boundaries lying in their path.

bubbles will then migrate under different conditions and will be restricted to migrate in the surface of the boundary. Coalescence of these grain boundary bubbles is likely to occur next. Both these "breakaway" phenomena will now be considered.

6. General Breakaway Swelling and Gas Release

If there is sufficient gas present all the bubbles in the grains will eventually touch (without any further need to migrate) and the major part of the gas contained in the sample will be released. This will occur at a volume increase which will depend upon the distribution of the bubbles¹¹). For instance, if equal sized, spherical bubbles were packed in a simple cubic array in the solid they would all touch when they occupied a fractional volume

$$\frac{\Delta V}{V} = \frac{\pi}{6 - \pi} = 1.1$$

at a swelling of 110%. For more realistic swelling gas release from the grains would occur at lower swelling values. Thus unless one swells the material to have foam-like plastic properties there must be a maximum swelling, $\Delta V/V$, which cannot be exceeded and at which virtually all the gas is released.

However, before the bubbles actually touch they will need far further migration there will be "breakaway swelling". This is not revealed in the simple model because the term $2r$ in eq. (4) and (4) was neglected, for the sake of simplicity. The bubbles will join irrespective of their velocity when $2r = 1/(2\pi r^2 n)$, i.e. when $\Delta V/V = 1/3$. If the bubbles are randomly distributed they should immediately touch another bubble when they enlarge until eventually all bubbles come to the surface. Rearranging this condition to become $\frac{1}{3} = \Delta V/V$ shows that the condition, where virtually all the gas is released, occurs at a swelling of 33.3%. A swelling of $\sim 30\%$ swelling has frequently been observed (e.g. refs. 12) and 13)). The prediction from the above model will thus be that $\Delta V/V \sim 0.1$, i.e. $\sim 10\%$

swelling. There will thus be an accelerated swelling at about this value, because then v will be less than that given by the approximate eq. (4), and as the swelling approaches 33.3% the velocity v needed for the bubbles to coalesce during the anneal approaches zero. The simple model can be modified to include this case of breakaway swelling as has been done in compiling figs. 5 and 6, below. Thus the model can be used to predict the onset of breakaway swelling and the stage at which general release of the gas occurs.

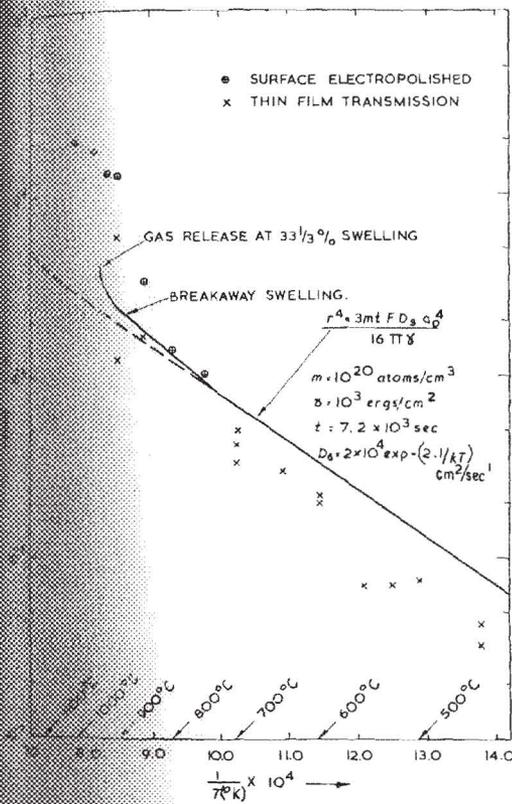
7. Grain Boundary Swelling and Gas Release

Large bubbles will form in the grain boundaries owing to the trapping of the bubbles there. Because coarsening of these bubbles does not increase the grain boundary area they occupy¹⁴) it is only by acquiring more gas in the grain boundaries that this can happen. When they all touch the grain boundary will become porous and the gas will escape. This phenomena will be called grain boundary gas release, and will occur when

$$\frac{\Delta A}{A} = \frac{\pi r^2 n_b d}{3} = \frac{m_b kT d}{8\gamma}$$

(where $\Delta A/A$ is the fraction of the grain boundary covered by n_b bubbles/cm³, which contain m_b atoms of inert gas/cm³, and d is the grain diameter). Using a similar criterion as before, that bubbles will generally touch when there are two bubbles on an area of $\pi(2r)^2$, i.e. that $\Delta A/A = \frac{1}{2}\pi$, then $m_b = 4\pi\gamma/kTd$.

The migrating bubbles will be held at a grain boundary because then the total surface energy is lower. A force F , given by $F_{\max} = 2\pi r\gamma_{gb}$ will be necessary to drag the bubble off the grain boundary where γ_{gb} is the interfacial energy of the grain boundary. Alternatively if the grain boundary is moving it can exert a maximum force of this value upon the bubbles. For a bubble 100 Å radius, this force would be $\sim 10^{-2}$ dyne, and even for the smallest bubble would be greater than the maximum force due to dislocations. Thus grain boundaries will be more effective in holding, or dragging bubbles,



8.3. EXTERNAL RESTRAINT

The model has for simplicity neglected any external pressure (P') which may be exerted upon the solid. It also neglected the intrinsic strength (σ') of the solid. Equation (2) should be modified to become:

$$\left(\frac{2\gamma}{r} + P' + \sigma'\right) \frac{4}{3}\pi r^3 n = m kT,$$

σ' is only important when it is comparable with $2\gamma/r$ and this only occurs when r is large. As this is the case only at high temperature, when σ' is itself small, we can generally neglect $\sigma' \dagger$.

Sometimes the swelling solid is restrained by a stronger solid which surrounds it, as for instance when a strong material is used to can a fuel rod. The restraint (P') is effective if it is comparable with $(2\gamma/r) + \sigma'$ and limits the swelling to a maximum value of $m kT/P' \dagger\dagger$, despite migration and coalescence of the bubbles. The bubbles will however enlarge until they become virtually immobile at the temperature of operation, their size being similar to that which they would have attained in the absence of the restraint, but each will contain more gas and consequently there will be fewer bubbles. If the sample is cooled the restraint may be removed, and if it is then reheated to the original temperature, vacancies will flow to the bubbles which enlarge until the gas pressure becomes equal to $2\gamma/r$. No further movement will occur since now the bubbles will be too large to be mobile, but the swelling will be larger than it would have been if the sample had been heated, without an intervening anneal under restraint.

The samples of irradiated uranium studied by Churchman, Barnes and Cottrell¹³ showed exactly this behaviour whenever an external pressure was applied. At the time the experi-

† The very early models for swelling neglected the term $2\gamma/r$ and thus only apply to very infrequent cases where large bubbles occur at low temperatures.

†† Swellings can on no account exceed this value where P' is the ambient pressure, and if for instance the external pressure P' is selected so that $\Delta V/V = m kT/P' < 0.33$ then general breakaway and gas release can be prevented.

The variation of bubble radius with annealing temperature of copper containing approximately 10^{20} helium atoms/cm³.

It can be seen that the experimental values show the same trend.

Values of n and r obtained microscopically constitute a better basis for testing the model because the complications introduced by bubbles in the grain boundaries can be avoided and a much wider range of values can be obtained than for swelling which normally only ranges from 1-20%.

The dotted curves relating the swelling and annealing temperature, shown in fig. 6, have been drawn using eq. (7) and an activation of 2.1 eV. Corrections have also been made on the basis of eq. 2. The importance of breakaway swelling and these corrected curves have been shown as full lines, these corrections being important for small gas contents or at low temperatures.

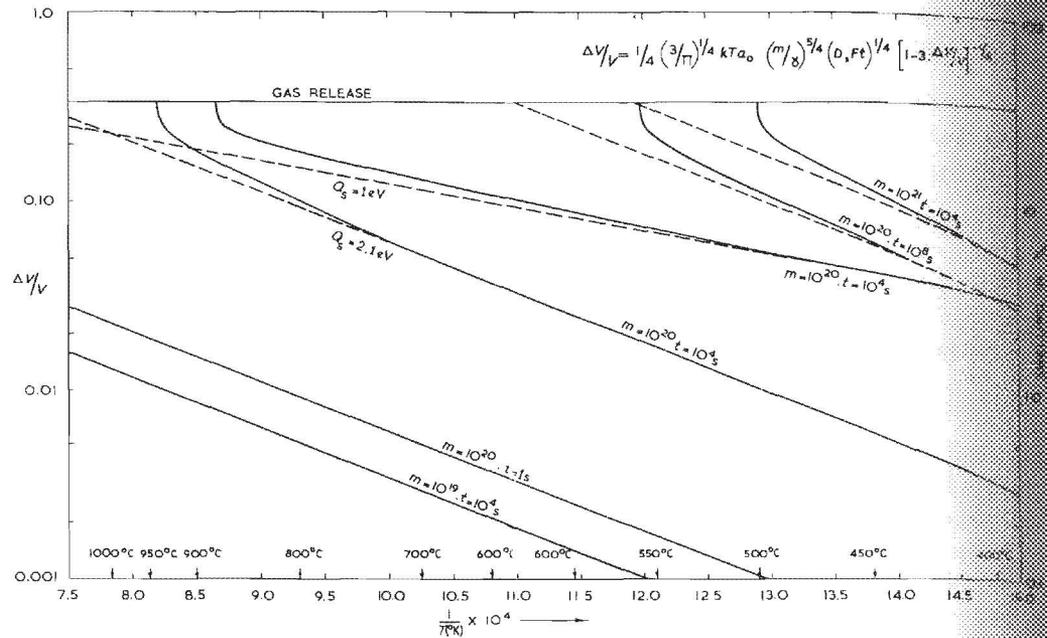


Fig. 6. Values, estimated using the model, of swelling at various temperatures for copper containing different quantities of an inert gas, and using the surface diffusion data of Choi and Shewmon. The importance of breakaway swelling is shown by the deviation of the solid lines from the broken ones. The effect of grain boundaries has been neglected and thus the results will only apply to large-grained materials.

ments were performed it was difficult to explain these results but the above explanation follows naturally from the model. The numerical values calculated in Appendix II, where it is assumed that increased mobility is given to a bubble when its size is reduced by an external pressure, are very near those for their sample E1.

8.4. THERMAL CYCLING AND GROWTH

If stresses play an important part in determining the motion of the bubbles as is implicit in the model, externally or internally applied stress should enhance swelling. Thus thermal cycling of anisotropic polycrystalline materials or irradiation growth should have such an effect. There are several instances cited in the literature where such an enhancement has been suggested (13,16,17).

9. The Release of Gas

Much of the gas generated within a few

microns of a truly free surface, i.e. a surface which does not have an adjacent surface to which the recoiling atom can embed itself, will always be released by recoil, but except in the sheets this will normally be a small amount. Some gas from near the surface will diffuse out, but once the gas has precipitated in bubbles there will be no such release unless the bubble itself drifts to a free surface, and this will be governed by the surface diffusion coefficient and the other factors already discussed. As has already been said there will be appreciable gas release, both due to the bubbles in the grain boundary joining and due to those in the grains joining. It is only in these circumstances that large amounts of gas will be released. Any process which restricts the swelling of fine precipitates which anchor the bubbles should also reduce the gas release. This is a direct consequence of the insolubility of the inert gases, and their behaviour is very different from soluble gases, like hydrogen.

Conclusions

The ability of the model to account for some aspects of swelling and gas release for various reactor materials suggests that the underlying assumptions are valid, and in particular that the inert gases do not diffuse atomically from one bubble to another and that the bubbles enlarge mainly by migrating bodily through the solid by a diffusion process. This leads to the conclusion that the particular inert gas involved is not of vital importance (as it would be in a process involving solution in the solid) and suggests that for a particular solid it is possible to infer from experiments using one inert gas the behaviour with another.

The model suggests that the most effective way to reduce swelling is to prevent the migration of the bubbles nucleated on a fine scale. This can be done by reducing the surface energy coefficient (perhaps by poisoning the internal bubble surfaces). However, the introduction of stable precipitates on a fine scale (as discussed in Appendix III) is perhaps the most effective way to reduce the swelling of a material, and its effectiveness adds support to the assumptions made for the model. This method also ensures that the bubbles do not nucleate on a scale so coarse that their migration would be of no consequence. Such methods which reduce swelling should also retard the release of gas.

The model can be tested against existing experimental results, but also it suggests detailed experiments which can be tested in more sophisticated experiments, and it is hoped that this paper will stimulate such experiments so that the model can be further tested and improved to give a clear understanding of swelling and gas release which have such practical importance to the use of nuclear energy.

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Appendix I

Irradiation at high temperatures

It has been implicitly assumed that the solid contains a constant amount of gas m . Thus the model described only applies to conditions where a solid is heated *after* irradiation. Numerical comparisons between the model and reality have therefore always been made using the results of post-irradiation annealing experiments. This has been done because it is experimentally easier to control the conditions in such experiments than in the more complex ones involving heating during irradiation. However, we shall now briefly consider this latter case. For simplicity we shall assume that the gas is produced at a constant rate of \dot{m} atoms/cm³·sec while the solid is at a constant temperature T . Equation 2 then becomes

$$\frac{8\pi}{3} \gamma r^2 n = \dot{m} t kT$$

where t is the irradiation (and therefore the annealing) time.

Essentially eqs. (1) and (3) remain unaltered and we arrive at the following equation:

$$\frac{1}{n^2} = \frac{4\pi \gamma D_s F a_0^4}{3 \dot{m} (kT)^2} \ln t. \quad (8)$$

We obtain from eq. (2)

$$r^4 = \frac{3 \dot{m} D_s F a_0^4}{16 \pi \gamma} t^2 \ln t \quad (9)$$

assuming that at each temperature the bubbles nucleate on a scale fine enough for appreciable coarsening to occur. There may be temperatures where this is not valid.

It should be noted that for a constant dose rate the number of bubbles n is dependent only upon the square root of the inverse logarithm of the irradiation time, and thus varies little during the irradiation.

The equation for swelling becomes

$$\frac{\Delta V}{V} = \frac{3^{\frac{3}{2}}}{4\pi^{\frac{3}{2}}} kT a_0 \left(\frac{\dot{m}}{\gamma}\right)^{\frac{5}{4}} (D_s F \ln t)^{\frac{1}{2}} t^{3/4}. \quad (10)$$

These equations are more difficult to test because for each experiment a separate sample is normally used, and variations in the solid itself are not easily excluded from the results. It will be noticed if eqs. (7) and (10) are compared that for the same gas content $\dot{m}t$ (i.e. for the same dose) the swelling for post-irradiation annealing at the irradiation temperature and for the irradiation time, differ only in the term $(\ln t)^{\frac{1}{2}}$ from those obtained on irradiating at temperature. There are already indications that such results are similar and if it is true, future experiments can be much simplified by concentrating upon those of the post-irradiation annealing type.

Appendix II

Calculations showing the influence of an external restraint upon swelling

If a sample containing 3 cm³ of gas, measured at NTP per cm³ of solid, expands 6% on heating to a temperature of 810° C, while under no external pressure, the internal gas pressure must be 200 atmospheres, which, if $\gamma = 10^9$ ergs/cm², corresponds to a bubble radius of 1000 Å. If now at the same temperature, an external pressure of 400 atmospheres (6000 psi) is applied, the bubbles will reduce in size and rapidly coarsen until they regain a size of approximately 1000 Å, when the gas within them will be at a pressure of 600 atmospheres, and the volume it occupies will be 2%. Reheating under zero pressure will allow the bubbles to enlarge, without migration, until the internal pressure reduces to balance the surface energy pressure $2\gamma/r'$ where r' is the new radius. Because the number of bubbles does not change, the ratio of the new pressure (120 atmospheres) to the old pressure (600 atmospheres) is in the ratio of the old to new volumes. Thus the new bubble radius r' is 1700 Å and the new volume increase 10%. These values are very near those measured for the sample E1 of Churchman, Barnes and Cottrell¹³).

Appendix III

Effect of precipitates

The model incorporates the assumption that the solid is completely defined by the values of a_0 , γ , and D_s . This is, of course, a simplification; the detailed structural condition of the metal being very important, and the influence of grain size has been mentioned. Precipitates are known to greatly influence the migration of the bubbles⁷) and so they should influence swelling.

Bubbles will become attached to precipitates either they will nucleate there or, having nucleated on a finer scale will drift onto them. The attachment will depend upon the increase in surface energy needed to separate the bubble from the precipitate. Thus the attachment will be greatest when they have a large curved surface with low surface energy. A stress field around the precipitate would increase the adherence, as the bubble would normally release some of the stress.

If the driving force (F) is less than the force needed to detach the bubble (and this will generally be the case if dislocations provide the driving force), then the number of bubbles cannot reduce to much fewer than the number of precipitates (except by a breakaway process which does not depend upon the migration of bubbles). The number of bubbles will be stabilised at a higher number if several bubbles are anchored by one precipitate (plate-like precipitates will be most effective for this) if the precipitates lock the dislocations upon which the bubbles lie. In the latter case strings of bubbles would be held between precipitate particles but only if the stresses upon the dislocations were not high. Such behaviour has been observed in aluminium containing lead bubbles and iron impurity which forms precipitates⁷).

A modified, and much simpler, model can be constructed for the situation where a number of bubbles/cm³ is stabilised at a number which will be some factor times the number

TABLE 2

Approximate percentage swelling at 500° C for various helium contents in a solid containing a constant number of bubbles *N*

	<i>m</i>		<i>N</i> (bubbles/cm ³)	<i>m'</i> atoms per bubble	<i>r</i> (Å)	<i>N/m'</i> (from fig. 1)	$\Delta V/V$ (%)
	at %	cm ³ /cm ³					
10 ¹²	0.012	0.36	10 ¹⁴	10 ⁵	130	10	0.125
			10 ¹³	10 ⁶	400	20	0.25
			10 ¹²	10 ⁷	1200	100	1.25
10 ¹⁴	0.06	1.8	10 ¹⁵	5 × 10 ⁴	100	8	0.5
			10 ¹⁴	5 × 10 ⁵	300	20	1.25
			10 ¹³	5 × 10 ⁶	800	40	2.5
10 ¹⁶	0.12	3.6	10 ¹⁶	10 ⁴	60	7	0.87
			10 ¹⁵	10 ⁵	130	10	1.25
			10 ¹⁴	10 ⁶	400	20	2.5
10 ¹⁸	0.62	18	10 ¹⁶	5 × 10 ⁴	100	8	5.0
			10 ¹⁵	5 × 10 ⁵	300	20	12.5
			10 ¹⁴	5 × 10 ⁶	800	40	25
10 ²⁰	1.2	36	10 ¹⁷	10 ⁴	60	7	8.7
			10 ¹⁶	10 ⁵	130	10	12.5
			10 ¹⁵	10 ⁶	400	20	25.0
5 × 10 ²⁰	6.0	180	10 ²⁰	5 × 10	8	4	25
			10 ¹⁹	5 × 10 ²	18	4	25
			10 ¹⁸	5 × 10 ³	40	6	38

Number of atoms: $5 \times 10^{22}/\text{cm}^3$.

$$r^2 = \frac{3 m kT}{8 \pi \gamma N}, \tag{11}$$

$$\frac{\Delta V}{V} = \left(\frac{m kT}{2 \gamma} \right)^{\frac{1}{2}} \left(\frac{3}{4 \pi N} \right)^{\frac{1}{2}}. \tag{12}$$

better swelling resistance than normal uranium. This treatment gives a fine precipitate.

Table 2 gives some estimates, using fig. 1, of the swelling which will occur in a solid with various helium contents (expressed in atoms/cm³, in atomic percent and in cm³ of gas, measured at NTP, per cm³ of solid). Several values of *N* (the fixed number of bubbles) have been used. It can be seen, for instance, that by ensuring that the number of bubbles is greater than 10¹⁴, swellings greater than 25 % will not occur even with 5 × 10²⁰ gas atoms/cm³ present.

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