KINETICS OF GASEOUS EXPANSION OF POROUS MATERIALS

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To a considerable extent the kinetics of gaseous expansion, i.e., the change in volume due to the release of gas phase from heavily supersaturated solid solutions of gaseous fission products, are determined by the fact that the processes of formation of grains of the new phase—gas pores—and the processes of growth and fusion of these pores are interrelated.

The pore size distribution function f (r, ρ, t) characterizing the porosity that develops when a supersaturated solid solution of gaseous fission products breaks down can generally be found from the equation [1]

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \rho}(f v_\rho) + \text{div}\,(f \mathbf{u}) = \Psi(r, \rho, t) + I_+ \qquad \left(v_\rho = \frac{\partial \rho}{\partial t}\right). \quad (1)$$

Here ρ is the pore radius, r is the radius vector giving the position of its center at moment t, v_ρ is the rate of growth of the pore radius, $\mathbf{u}$ $(\mathbf{v}, \rho)$ is the rate of displacement of the pore, Ψ (r, ρ, t) is the rate of creation of pores of radius ρ at time t at a point in the material r. The term I_+ takes into account the change in the distribution function due to the fusion of pores. In principle, this equation, together with the equations for v_ρ, $\mathbf{u}$, Ψ and I_+, makes it possible to find f (r, ρ, t), and hence the increase in volume. A solution of this system can always be found by numerical methods. On the other hand, in certain special cases the problem is so simplified that an analytic solution is possible.

Thus, for example, a very important special case is the expansion of porous materials, i.e., materials that even in the initial state have a pore density so great that the gas phase is mainly liberated into these pre-existing pores, while the processes of new pore formation do not play a very significant part. If the pore fusion processes are also on a small scale, the pore density may be regarded as fixed. Apart from materials which acquire considerable branched porosity as a result of the manufacturing process, this group includes materials that, though initially nonporous, have become porous in previous stages of expansion. In this case Eq. (1) will lack the still relatively obscure terms Ψ (r, ρ, t) and I_+. This considerably simplifies the determination of f (r, ρ, t). If we neglect the processes of pore displacement, Eq. (1) assumes the form

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \rho}(v_\rho f) = 0. \quad (2)$$

In this case the total number of pores does not change, and the change in the distribution function is related only with the change in pore size; therefore the solution of this equation can be expressed in terms of the initial distribution function $f_0(\rho°)$ as follows:

$$f(\rho, t) = f_0(\rho°)\frac{\partial \rho°}{\partial \rho}. \quad (3)$$

In this case the radius of each pore will be a function of time and the initial radius $\rho°$ and, generally speaking, this relationship will take the form

$$\rho(t) = \rho° + \int_0^t v_\rho[\tau, \rho(\tau)]\,d\tau. \quad (4)$$

In particular, as the initial distribution f_0 we can use the pore distribution observed in one of the previous stages of gaseous expansion. Moreover, to determine f (ρ, t), it is necessary, with the help of (4), to establish a relation between ρ, $\rho°$ and t. The specific form of this relation is determined by the mechanism controlling the growth of the pores, since this decides whether the quantity v_ρ is a function of the pore radius and time or of time only. When the gas in the pores may be considered perfect, and the growth of the pores is due to the now widely accepted mechanism of diffusion flow of vacancies,

correlated with the flow of gas atoms in such a way that the pore pressure is maintained at the pressure level of the surface tension forces [2],

$$v_\rho = \frac{3DkT}{4\gamma}c(t) \quad (5)$$

and does not depend on the pore radius [1]. Here D is the diffusion coefficient, c (t) is the concentration of gas atoms dissolved in the material, γ is the coefficient of surface tension for the material, k is Boltzmann's constant, and T is temperature. In this case from Eqs. (4) and (3) it follows that $d\rho = d\rho°$, and f $(\rho, t) = f_0(\rho°)$. We now go over to the dimensionless variables x ("radius") and Φ ("time").

$$x = \frac{\rho}{\rho_0}, \qquad \Phi = \frac{3DkT}{4\gamma\rho_0}\int_0^t c(\tau)\,d\tau. \quad (6)$$

Here ρ_0 is the minimum nonzero value of the radius encountered in the initial distribution. Relation (4) between the initial value of the pore radius and its value at time t may be written thus:

$$x = x° + \Phi. \quad (7)$$

In this case the distribution function corresponding to "time" may be expressed in terms of the initial distribution f_0 as follows:

$$f(x, \Phi) = f_0(x - \Phi). \quad (8)$$

In order to express this solution in terms of the variables Φ and t, it is necessary to determine c (t), which would make it possible to find Φ (t). When gas atoms are created at a constant rate a, the concentration c (t) will be the solution of the equation

$$\frac{dc}{dt} = a - 4\pi Dc(t)N\langle\rho(t)\rangle, \qquad N\langle\rho(t)\rangle = \int_0^\infty \rho f(\rho, t)\,d\rho. \quad (9)$$

Here N is the total number of pores in unit volume, and $\langle\rho(t)\rangle$ is the mean pore radius. The second equation relating the variables c (t) and $\rho(t)$ is Eq. (5). In this equation v_ρ may also be understood to represent, in particular, $d\langle\rho\rangle/dt$, since in the case in question this dependence of v_ρ on t holds for pores of any radius, and hence for $\langle\rho\rangle$. The equation then assumes the form

$$\frac{d\langle\rho\rangle}{dt} = \frac{3DkT}{4\gamma}c(t). \quad (10)$$

Eliminating c(t) with the help of (10) from Eq. (9), we get the nonlinear equation

$$\frac{d}{dt}\left(\frac{d\langle\rho\rangle}{dt} + \frac{\alpha}{2}\langle\rho\rangle^2\right) = \beta, \qquad \alpha = 4\pi DN, \quad \beta = \frac{3aDkT}{4\gamma}.$$

Integrating, we get

$$\frac{d\langle\rho\rangle}{dt} + \frac{\alpha}{2}\langle\rho\rangle^2 = \beta t + G \qquad \left(G = \frac{\beta}{a}c_0 + \frac{\alpha}{2}\langle\rho\rangle^2\right). \quad (11)$$

Here the constant of integration G is determined with the help of the conditions

$$\langle\rho\rangle = \langle\rho°\rangle, \qquad \frac{d\langle\rho\rangle}{dt} = \frac{3DkT}{4\gamma}c_0 \quad \text{for} \quad t = 0. \quad (12)$$

By means of the substitution

$$t = \left(\frac{2}{\alpha\beta}\right)^{1/3}x - \frac{G}{\beta}, \qquad \langle\rho\rangle = \left(\frac{4\beta}{\alpha^2}\right)^{1/3}\frac{1}{y}\frac{dy}{dx},$$

we can reduce Eq. (11) to a linear equation of the type $y'' - xy = 0$.

Its solution is expressed in terms of Bessel functions [3]. As a result, we have

$$\langle \rho(t) \rangle = \left(\frac{3akT}{8\pi\gamma N} \right)^{1/2} (t^\circ + \tau + t)^{1/2} \frac{I_{1/3}(s) + \varepsilon I_{-1/3}(s)}{I_{-1/3}(s) + \varepsilon I_{1/3}(s)} \cdot$$

$$(13)$$

$$s = \left(\frac{2\pi a D^2 N kT}{3\gamma} \right)^{1/2} (t^\circ + \tau + t)^{3/2}, \quad \tau = c_0/a, \quad t^\circ = \frac{8\pi\gamma \langle\rho^\circ\rangle^2 N}{3akT}.$$

Here τ and t° are the mean values of the time needed to create the initial numbers of gas atoms in the solution and in the pores, respectively; the constant of integration

$$\varepsilon = -\frac{\sqrt{2G/\alpha}\, I_{2/3}(s_0) - \langle\rho^\circ\rangle\, I_{-1/3}(s_0)}{\sqrt{2G/\alpha}\, I_{-2/3}(s_0) - \langle\rho^\circ\rangle\, I_{1/3}(s_0)}$$

is determined with the help of the first of conditions (12). Here s_0 is the value of s at $t = 0$.

From this, incidentally, it can be seen that asymptotically (at large s)

$$\langle\rho\rangle \sim (t^\circ + \tau + t)^{1/2}, \quad \Delta V \sim (t^\circ + \tau + t)^{3/2}.$$

Having found $\langle\rho(t)\rangle$, we can also find $\Phi(t)$, since, in accordance with relations (6) and (10), $\Phi(t) = (\langle\rho(t)\rangle - \langle\rho^\circ\rangle)/\rho_0$. If $\Phi(t)$ is known, $f(\rho, t)$ can be found from Eq. (8). However, the expansion can be found without having to first find $f(\rho, t)$, since the time dependence of the total pore volume is expressed directly in terms of $\Phi(t)$ and the first moments of the initial distribution function f_0:

$$\Delta V = \frac{4\pi\rho_0^4}{3} \left\{ \int_1^\infty y^3 f_0(y)\, dy + 3\Phi(t) \int_1^\infty y^2 f_0(y)\, dy + 3\Phi^2(t) \right.$$

$$\left. \times \int_1^\infty y f_0(y)\, dy + \Phi^3(t) \int_1^\infty f_0(y)\, dy \right\}.$$

If we take into account the fact that, starting from a certain stage of expansion, the material may be regarded as porous, then the results obtained enable us, in particular, to extrapolate experimental data from the region of small to the region of high burnup values.

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