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On the theory of diffusional shrinkage of a pore in real crystals

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Driving forces and diffusional mechanisms of a pore shrinkage in a crystal, containing other sources (sinks) of vacancies are considered. The finite length of a diffusional path of an excess vacancy in the bulk of a crystal and the difference in the atomic chemical potential on a plain surface and that on the considered sources in the bulk of a crystal are taken into account as is the finite rate of a formation of vacancies on the surface of a pore. An expression describing the duration of the shrinkage of a spherical pore is obtained. This interval is essentially (by 30 times and more) smaller than that for a pore in an ideal crystal.

1. Introduction

A spherical pore is a convenient model for the investigation of different diffusional processes which take place in non-equilibrium systems in particular during sintering and joining of materials. The diffusional shrinkage of a pore in a crystal free of other sources and sinks of vacancies has been theoretically investigated previously [1, 2]. The shrinkage of a pore, intersected by block boundaries and dislocation lines (pore size is supposed to exceed the period of a dislocation net or block size), when conditions for the quasi-equilibrium on the surface of a pore are fulfilled, was theoretically investigated by Slyozov [3]. There, only the diffusion along the block boundaries and the dislocation cores was taken into account.

Surface tension, γ, is usually regarded as the only driving force of pore shrinkage. However, other driving forces of the relaxation of non-equilibrium systems containing pores are well-known. Let us consider, for example, a crystal, containing pores of a radius r_0 and dislocation loops of the vacancy type of a radius ρ_0. It is well-known that for the given parameters (in particular ρ_0) there exists a critical value of pore radius $r_c \propto \gamma$, such that if $r_0 > r_c$ the pores grow inspite of the surface tension. They also grow if $\gamma = 0$. On the other hand, if the dislocation loops are of the interstitial type, then the pores shrink even if $\gamma = 0$. The driving forces are determined by the difference in the atomic chemical potential (ACP), μ, on the line of a dislocation loop and on the surface of a pore in a non-equilibrium crystal.

The vacancy concentration in a thin layer near the pore surface is usually supposed to be equal to the equilibrium concentration in respect of the formation of vacancies on the surface of a pore. This is so only if the time interval, during which a vacancy is formed on the surface of a pore, is essentially smaller than that during which a vacancy is present in the layer concerned. This condition is usually fulfilled in a crystal free of other sources and sinks of vacancies, because diffusional currents are sufficiently small in such a crystal. Diffusional currents in a real crystal may be so intensive that the equilibrium vacancy concentration in a particular layer cannot be achieved. The rate of an approach of a vacancy concentration near the pore surface to the equilibrium concentration depends on the density of sources (sinks) of vacancies (surface defects) on the pore surface. If this density is sufficiently high, the alleged rate of an approach is considerable and the diffusional process is quick. In the opposite case, the rate of the motion of the surface is slow.

Pore shrinkage due to bulk diffusion in a crystal, containing other sources (sinks) of vacancies, is treated in the present paper. The nature and the

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values of parameters of the bulk sources (sinks) of vacancies are regarded as different from those of sources (sinks), situated on the pore surface. The possibility of vacancy depletion in a thin layer surrounding the pore surface is also taken into account.

2. Theory

If there is no temperature gradient, the vacancy current $\mathbf{J}$ in the framework of the linear theory depends only on the gradient of the ACP:

$$\mathbf{J} = \frac{N_e D_v}{kT} \nabla \mu, \qquad (1)$$

where D_v is the vacancy diffusion coefficient, N_e is the equilibrium (with respect to the bulk sources – sinks) average vacancy concentration, kT is the absolute temperature in the energy units. The process of pore shrinkage is so slow that the corresponding process of vacancy diffusion may be described by the stationary continuity equation, which may be written (for the case of one type of sources (sinks) of vacancies in the bulk of a crystal) by analogy to [4] as:

$$(\nabla, \mathbf{J}) + \frac{N(\mathbf{J}) - N_e(1 - \phi/kT)}{\tau} = 0, \qquad (2)$$

where $N(\mathbf{J})$ is the average vacancy concentration in a small "representative volume", situated around the position $\mathbf{J}$, $\phi \ll kT$ is the interaction energy of the vacancy and the stress field, $N_e(1 - \phi/kT)$ is the equilibrium concentration of vacancies near the relevant position $\mathbf{J}$, and τ is the time interval required for the distribution of vacancies in the bulk of a material to approach the equilibrium distribution. This interval depends on the properties of the sources (sinks), their density and the vacancy mobility. If there are several types of sources (sinks) of vacancies in a crystal, the second term on the left-hand side of Equation 2 ought to be written as [5]:

$$\sum_i \frac{N - N_e^i(1 - \phi/kT)}{\tau_i},$$

where N_e^i and τ_i refer to the sources (sinks) of the i-type, respectively. However, the sum may be written as $[N - N_e(1 - \phi/kT)]/\tau$ if we put

$$\frac{1}{\tau} = \sum_i \frac{1}{\tau_i}$$

and

$$N_e = \tau \sum_i (N_e^i/\tau_i).$$

Thus one may also use Equation 2 in this case.

ACP is determined by the formula:

$$\mu = -\phi - kT \ln \frac{N(\mathbf{J})}{N_0} \equiv \mu_e + (\mu - \mu_e),$$

where $\mu_e \equiv -kT \ln (N_e/N_0)$, and N_0 is the number of the atoms per unit volume of the crystal material. The inequality $|\mu - \mu_e| \ll \mu_e$ permits us to use the linear theory.

Using Equations 1 and 2 one may obtain an equation for $(\mu - \mu_e)$:

$$(\Delta - l^2)(\mu - \mu_e) = 0, \qquad (3)$$

where $l = (D_v\tau)^{1/2}$ is the average length of a diffusional path of an excess vacancy in the bulk of a crystal, containing sinks of vacancies. Let us consider a spherical pore of radius r_0. Equation 3 has the following solution of the spherical symmetry:

$$\mu - \mu_e = -\frac{AkTr_0}{N_e\, r} \exp \frac{r_0 - r}{l}, \qquad (4)$$

where r is the distance from the centre of a pore. Constant A is determined by the boundary condition, which may be found using the following reasons. Let us consider a thin layer of thickness a surrounding the pore. The number of vacancies going through the outer surface of the layer per unit time is $4\pi r_0^2 \mathbf{J}(\mathbf{J}_0)$. As vacancies leave the layer, the vacancy concentration near the pore surface $N(r_0)$ does not attain equilibrium, corresponding to the value of ACP on the surface of a pore, value N_p. Hence the sources, situated on the surface of a pore, emit vacancies, the number of which may be written:

$$4\pi r_0^2 a [N_p - N(r_0)]/\tau_1$$

(here τ_1 is time interval which characterizes properties of an ensemble of the surface sources (sinks) of vacancies. This interval is a mean duration of the presence of an excess vacancy within a particular thin layer when the vacancy is drifting along the surface of a pore). It is obvious that τ_1 is proportional to the thickness of the layer: $\tau_1 = a/v$ (here v is a parameter which characterizes the ability of the ensemble of the surface sources to supply deficient vacancies). The number of vacancies, leaving the layer per unit time, is equal to that emitted from the pore surface. Thus we obtain the boundary conditions:

$$J(r_0) = v[N_p - N(r_0)]. \qquad (5)$$

Using Equations 1, 4 and 5, one obtains:

$$A = vr_0 l(N_p - N_e)/[vr_0 l + (r_0 + l)D_v]. \quad (6)$$

If $v \to \infty$, Equation 5 yields:

$$A = N_p - N_e.$$

This corresponds to the case when the vacancy concentration near the pore surface attains equilibrium value (with respect to the formation of vacancies on the pore surface) [4].

2.1. Rate and duration of pore shrinkage

Vacancy current is determined by Equations 1, 4 and 6. The rate of pore shrinkage is obviously determined by the formula:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = -\frac{1}{N_0}\int_s (\mathbf{J}, \mathbf{n})\,\mathrm{d}s, \quad (7)$$

where V is the volume of a pore, $\mathbf{n}$ is a unit vector, normal to the pore surface s, directed outward.

Using Equations 1, 4 and 7, one may obtain:

$$\frac{\mathrm{d}r_0}{\mathrm{d}t} = -\frac{D_v}{N_0}\frac{A}{l}\left(1 + \frac{l}{r_0}\right). \quad (8)$$

Here, as before, μ_e denotes the ACP on the bulk sources and $\mu - \mu_1$ denotes that related to the surface sources (without consideration of the contribution of the surface tension). The effect of the surface tension is to reduce the ACP on the pore surface by $2\gamma/r_0 N_0$. This yields:

$$N_p = N_e \exp\frac{\mu_1 + (2\gamma/r_0 N_0)}{kT}. \quad (9)$$

The exponential index in Equation 9 is usually small. Expanding the exponent and retaining the first term of the series in Equation 9, and using Equations 6, 8 and 9, one may obtain:

$$\frac{\mathrm{d}r_0}{\mathrm{d}t} = -\frac{Dv}{kTN_0}\,\frac{N_0\mu_1 r_0^2 + (2\gamma + l\mu_1 N_0)r_0 + 2\gamma l}{(lv + D_v)r_0^2 + lr_0 D_v}. \quad (10)$$

Here $D = D_v N_e/N_0$ is the self-diffusion coefficient. Using Equation 10, one may obtain an expression for the duration of pore shrinkage:

$$t = kT\frac{vl + D_v}{Dv\mu_1} \times \int_{r_1}^{r_0} \frac{\{x^2 + [lD_v/(vl + D_v)]x\}\,\mathrm{d}x}{x^2 + [l + (2\gamma/\mu_1 N_0)]x + (2\gamma l/\mu_1 N_0)}, \quad (11)$$

where r_0 and r_1 are the initial and the final radii, respectively. From Equation 11 one obtains:

$$t = t_0 + \frac{kTN_0 l^3}{D(2\gamma - \mu_1 l N_0)}\ln\frac{r_0 + l}{r_1 + l} - \frac{kT}{D\mu_1 v}\,\frac{2\gamma}{\mu_1 N_0} \times \left(\frac{2\gamma v l}{2\gamma - \mu_1 l N_0} + D_v\right)\ln\frac{r_0 + (2\gamma/\mu_1 N_0)}{r_1 + (2\gamma/\mu_1 N_0)}, \quad (12)$$

where

$$t_0 = \frac{kT}{D}\,\frac{vl + D_v}{v}\,\frac{r_0 - r_1}{\mu_1}. \quad (13)$$

3. Discussion

We may easily see that Equation 13 yields an exaggerated duration of pore shrinkage at $v \to \infty$. In fact, at $v \to \infty$, retaining under the integral in Equation 11 only those terms proportional to x^2, one immediately obtains Equation 13. At arbitrary values of v the factor before the integral in Equation 11 exceeds its limiting value corresponding to $v \to \infty$. Remembering that the last term (proportional to D_v) in Equation 12 is always negative, one may conclude that Equation 13 always yields an exaggerated duration of pore shrinkage. But for sufficiently large pores, when $r_0, r_1 \gg (2\gamma/\mu_1 N_0)$, l, the shrinkage duration is determined chiefly by t_0. At $D_v \ll vl$ and $\mu_1 = 0$, Equations 12 and 13 yield the result received earlier [4] for the case when the value of the vacancy concentration near the pore surface is equal to the equilibrium concentration (see formula 4.3.17 in [4]). For the case when $D_v \ll vl$, $\mu_1 = 0$ and $l \gg r_0$ one may obtain a well-known formula for the duration of pore shrinkage in an ideal crystal [1, 2]:

$$t_i = \frac{kTN_0}{6\gamma D}(r_0^3 - r_1^3). \quad (14)$$

To estimate the role of the investigated mechanisms of pore shrinkage let us take $T = 1273$ K, $N_0 = 3 \times 10^{28}\ \mathrm{m}^{-3}$, $\gamma = 1.5\ \mathrm{N\,m}^{-1}$, $r_0 = 5 \times 10^{-6}$ m, $r_1 = 4 \times 10^{-6}$ m, $D = 10^{-15}\ \mathrm{m}^2\,\mathrm{sec}^{-1}$, $l = 10^{-6}$ m, $\mu_1 = 1.6 \times 10^{-22}$ J, $D_v = 10^{-11}\ \mathrm{m}^2\,\mathrm{sec}^{-1}$, $v = 10^{-4}\ \mathrm{m\,sec}^{-1}$. For such a case one may obtain from Equation 14 $t_i = 3.6 \times 10^6$ sec. Using Equations 13 and 14 one may obtain:

$$\frac{t_0}{t_i} = \frac{vl + D_v}{v\mu_1 N_0}\,\frac{6\gamma}{r_0^2 + r_0 r_1 + r_1^2}.$$

At the taken values of the parameters we have $t_0/t_i = 0.033$. At $\mu_1 = 0$ and at the values of other parameters taken as before, Equations 12 to 14 yield $t/t_i = 0.2$.

These estimations show that the investigated mechanisms of diffusional pore shrinkage are very effective. These mechanisms are particularly important for the processes of sintering a hardened powder, containing a considerable number of sources (sinks) of vacancies (for instance, dislocations).

It is worthwhile noting that from the results obtained one may see that the diffusional processes of a motion of a boundary may occur without surface tension forces if $\mu_1 \neq 0$. There are cases when the contribution of the surface tension in these processes is negligible, and the main contribution is due to the difference between the ACP on the sources in the bulk of a crystal and that on the surface, μ_1. In such cases the process may result in an increase in surface area. Using Equation 10, one may see that the rate of motion of that part of a surface of interest here depends essentially on the comparative values of l and D_v/v. The largest rate is achieved for plots where $vl \gg D_v$. At $vl \ll D_v$ the rate is smallest. If the plot with large v is surrounded by plots with small v (small number of surface defects), the advance of the plots is not uniform and this results in an increase in the total area of the surface. The latter is not essential when $\mu_1 \ll 2\gamma\kappa/N_0$ (κ is the curvature). These results offer an explanation for the often experimentally observed "germination" of large flat pores [6].

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