



THERMODYNAMIC EFFECTS ON THE KINETICS OF VACANCY-GENERATING PROCESSES

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Abstract—The inhibiting effect of vacancies on the very process in which they are generated is considered from a thermodynamic viewpoint. Examples of such processes treated here in some detail are grain growth and pore dissolution. It is shown that these processes are inhibited due to vacancy generation. A particular scenario discussed implies intermittent “locking”. After a period of uninhibited kinetics the process comes to a halt due to a thermodynamic back force “locking” it. It can only re-start once the vacancies produced are removed by diffusion. This repetitive cycle leads to an overall reduction in the rate of the kinetic process in question. Specific predictions with regard to grain growth in fine-grained (particularly nanocrystalline) materials and void dissolution kinetics in sintering are made. A third example considered is vacancy drag on a moving individual grain boundary. The magnitude of the drag is re-assessed by taking into account the Gibbs free energy of the vacancies generated. © 1999 Acta Metallurgica Inc. Published by Elsevier Science Ltd. All rights reserved.

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1. INTRODUCTION

It is a very common situation in materials science that vacancies are generated as a by-product of a kinetic process. Vacancy production by moving jogs on dislocations during plastic deformation, by migrating grain boundaries in grain growth, by a progressing solid/liquid interface in solidification or by shrinking voids in sintering are but a few examples. The excess free volume the system has to get rid of in such kinetic processes is released as vacancies which have to be accommodated by the crystal bulk. While the emergence of vacancies in these or similar processes has been appreciated in the literature, see, e.g. Refs [1–5], one aspect of vacancy assimilation remains largely neglected. It is the contribution of the vacancies generated to the total free energy of the system. This may produce a generalized thermodynamic force which influences the very kinetic process by which vacancies are generated. The aim of this paper is to emphasize the significance of this effect in general and to consider examples of particular kinetic processes where it can be of importance.

In most general terms, the Gibbs free energy G of a system with vacancies can be written as

$$G = G_{\text{non-vac}} + G_{\text{vac}} \quad (1)$$

where $G_{\text{non-vac}}$ is the non-vacancy part of the Gibbs free energy and G_{vac} is the contribution due to vacancies. The latter quantity can be calculated as the free energy of an ideal solution of vacancies in the crystal written as

$$G_{\text{vac}} = nH_v^f - kT \ln \frac{N!}{(N-n)!n!} \quad (2)$$

Here n and N are the number of vacancies and the number of atomic sites per unit volume, respectively, H_v^f is the vacancy formation enthalpy, k is the Boltzmann constant and T the absolute temperature. If one is interested in vacancies of concentration c not too far from its thermodynamic equilibrium value c^{eq} , a series expansion of G with respect to $c - c^{\text{eq}}$ can be truncated after the quadratic term. The corresponding expression for G can be obtained in the following simple exercise. Applying the Stirling formula for large values of N , $N - n$ and n , one has

$$\frac{dG_{\text{vac}}}{dn} = H_v^f + kT \ln \frac{n}{N-n} \quad (3)$$

and

$$\frac{d^2G_{\text{vac}}}{dn^2} = \frac{kT}{n} \left(1 + \frac{n}{N-n} \right) \quad (4)$$

In thermodynamic equilibrium, when $dG_{\text{vac}}/dn = 0$, one has from equations (3) and (4)

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$$\begin{aligned} \left(\frac{d^2 G_{\text{vac}}}{dc^2}\right)^{\text{eq}} &\equiv N^2 \left(\frac{d^2 G_{\text{vac}}}{dn^2}\right)^{\text{eq}} \\ &= \frac{NkT}{c^{\text{eq}}} \left[1 + \exp\left(-\frac{H_v^f}{kT}\right) \right] \cong \frac{NkT}{c^{\text{eq}}}. \end{aligned} \quad (5)$$

Accordingly, one has for the Gibbs free energy

$$G = G_{\text{non-vac}} + G_{\text{vac}}(c^{\text{eq}}) + \frac{1}{2} \frac{NkT}{c^{\text{eq}}} (c - c^{\text{eq}})^2. \quad (6)$$

As mentioned above, higher terms in $c - c^{\text{eq}}$ have been neglected. It should be stressed that this compact formula for the vacancy part of the free energy embraces both the vacancy formation enthalpy term and the entropy contribution.

The above formulation makes it possible to look at the kinetic processes involving vacancies from a viewpoint of their thermodynamic feasibility. Obviously, a kinetic process will be permitted thermodynamically if the derivative of G with respect to time, t , (denoted by a dot) is negative. This criterion reads

$$\dot{G} = \dot{G}_{\text{non-vac}} + \frac{NkT}{c^{\text{eq}}} (c - c^{\text{eq}}) \dot{c} < 0. \quad (7)$$

The time derivative of the vacancy concentration, \dot{c} , can be written as

$$\dot{c} = \dot{c}^+ - \dot{c}^- \quad (8)$$

representing a competition between the vacancy production (\dot{c}^+) and the vacancy removal (\dot{c}^-) rates. While the latter quantity can be expressed in a generic form

$$\dot{c}^- = -\frac{D_v}{d^2} (c - c_{\text{sink}}) \quad (9)$$

where D_v is the vacancy diffusivity, d is the sink spacing and c_{sink} the vacancy concentration at a sink, the vacancy production rate depends on the particular mechanism of vacancy generation and is related to the rate of variation of the first, “non-vacancy”, term of the free energy, \dot{G} . In what follows, kinetic processes which are significantly affected by this coupling with their “by-product”, i.e. the vacancies produced, will be investigated.

2. VACANCY EFFECTS ON THE KINETICS OF VACANCY-GENERATING PROCESSES

2.1. Grain growth in fine-grained materials

Following Ref. [9], we start our consideration by looking at the grain boundary migration as a main mechanism of grain growth. The process is driven by the tendency of the system of grain boundaries to reduce the total grain boundary area. As a “by-product” of this process vacancies are released into the crystal bulk. Indeed, the density of a grain boundary is lower than that of the bulk, see e.g. Refs [6, 7]. The excess free volume released during the reduction of the grain boundary “phase” has to

be accommodated by the bulk. It is natural to assume that this excess volume is assimilated by the bulk, primarily in the form of vacancies. This assumption is supported by recent computer simulations of grain boundary motion [8]. The supply of vacancies by moving grain boundaries may produce a vacancy supersaturation in the bulk increasing the Gibbs free energy and producing a thermodynamic force on the boundary. As can be expected intuitively, particularly by analogy with the Le Chatelier principle, this thermodynamic force will *resist* grain boundary migration. Under certain conditions considered below this effect may be as strong as to temporarily suppress grain growth altogether.

The free energy of the grain boundary sub-system can be written as

$$G_{\text{GB}} = \frac{3}{2} \cdot \frac{\sigma}{R}. \quad (10)$$

This is a particular expression of the quantity $G_{\text{non-vac}}$ for the case under consideration. Here σ is the free energy per unit area of grain boundary and R is the average grain size. Substituting G_{GB} for $G_{\text{non-vac}}$ in equation (7) we obtain

$$\dot{G} = -\frac{3}{2} \frac{\sigma}{R^2} V + \frac{NkT}{c^{\text{eq}}} (c - c^{\text{eq}}) \dot{c} < 0. \quad (11)$$

The grain boundary velocity, or the grain growth rate $V = dR/dt$, is considered to be positive.

The vacancy generation rate can be represented as

$$\dot{c}^+ = \frac{6\beta\delta}{R^2} V \quad (12)$$

where β is the relative excess free volume of the boundary associated with a decreased density of a boundary as compared with the bulk, and δ is the boundary width. Substituting equations (9) and (12) into equation (8) yields

$$\dot{c} = \frac{6\beta\delta}{R^2} V - \frac{D_v}{d^2} (c - c_{\text{sink}}). \quad (13)$$

In the problem under consideration, sinks can be identified with dislocations, grain boundaries themselves, or (particularly in thin films) the outer surface.

The solution of equation (13) reads

$$\begin{aligned} c - c_0 &= (c_1 - c_0) \exp(-D_v t/d^2) + 6\beta \left(\frac{d}{R}\right)^2 \\ &\times \left(\frac{V\delta}{D_v}\right) [1 - \exp(-D_v t/d^2)] \end{aligned} \quad (14)$$

where c_1 denotes the initial vacancy concentration in the bulk, which in the following will be taken to be equal to the equilibrium vacancy concentration c^{eq} . For the case of $t \ll \tau = d^2/D_v$ of interest here (see below), equation (14) can be linearized in time and reduces to

$$c = c_i + 6\beta\delta Vt/R^2. \quad (15)$$

Substitution of equation (15) into inequality (11) yields

$$-\frac{\sigma}{R^2}V + \frac{24NkT}{c^{eq}}\left(\frac{\beta\delta V}{R^2}\right)^2 t < 0. \quad (16)$$

Evidently, this inequality is satisfied, i.e. grain growth can occur, for sufficiently small t . However, the inequality is violated for

$$t \geq t^* = \frac{1}{24} \cdot \frac{\sigma c^{eq} R^2}{NkT(\beta\delta)^2 V} \quad (17)$$

which means that grain growth gets arrested at $t = t^*$.

The assumption that $t^* \ll \tau = d^2/D_v$ used above can be rewritten as

$$\frac{1}{24} \left(\frac{R}{d}\right)^2 \frac{R}{NkTZ(\beta\delta)^2} \frac{D_{SD}}{m} \ll 1. \quad (18)$$

Here $D_{SD} = Zc^{eq}D_v = D_0 \exp(-H_{SD}/kT)$ is the coefficient of bulk self-diffusion, Z being the coordination number and H_{SD} the corresponding activation enthalpy given by the sum of the activation enthalpy for vacancy migration and vacancy formation; the intrinsic grain boundary velocity V has been replaced with $m\sigma/R$ where m is the grain boundary mobility [10]. The validity of this inequality for fine-grained materials was demonstrated in Ref. [9].

With the above results the following scenario of grain growth was suggested in Ref. [9]. Once started, grain growth will be arrested after a time

t^* . Grain boundaries will remain stationary (“locked”) for a time $\tau - t^* \cong \tau$ during which time grain growth induced vacancy concentration will relax back to c^{eq} . The thermodynamic inhibition of grain growth will thus be removed and grain boundary motion will re-start. The sequence of grain boundary “locking”, relaxation of vacancy concentration in the bulk, and grain boundary motion will then be repeated cyclically. In other words, the motion of grain boundaries will occur in a jerky way. The intrinsic grain growth rate V , which in the absence of “vacancy self-locking” would be determined by the driving force on the grain boundaries (that is, by the capillary force), will be modified. The *effective* grain growth rate will be given by $V_{eff} = (t^*/\tau) \cdot V$. This is the overall average grain growth rate which would be observed in the experiment if the detail of grain boundary motion (i.e. its jerky character) was not resolved. The kinetics of grain growth and the corresponding variation of the vacancy concentration in the bulk are illustrated by a schematic diagram in Fig. 1.

The jerky grain growth scenario outlined above only applies if the ratio t^*/τ is small. If t^* is comparable with τ , the grain boundary motion will become continuous. The condition expressing this change in the character of the grain boundary motion reads

$$\frac{1}{24} \cdot \frac{\sigma D_{SD}}{NkTZ(\beta\delta)^2 V} \cdot \left(\frac{R}{d}\right)^2 \cong 1. \quad (19)$$

Below the critical grain radius R_c which can be obtained from equation (19) the grain growth is

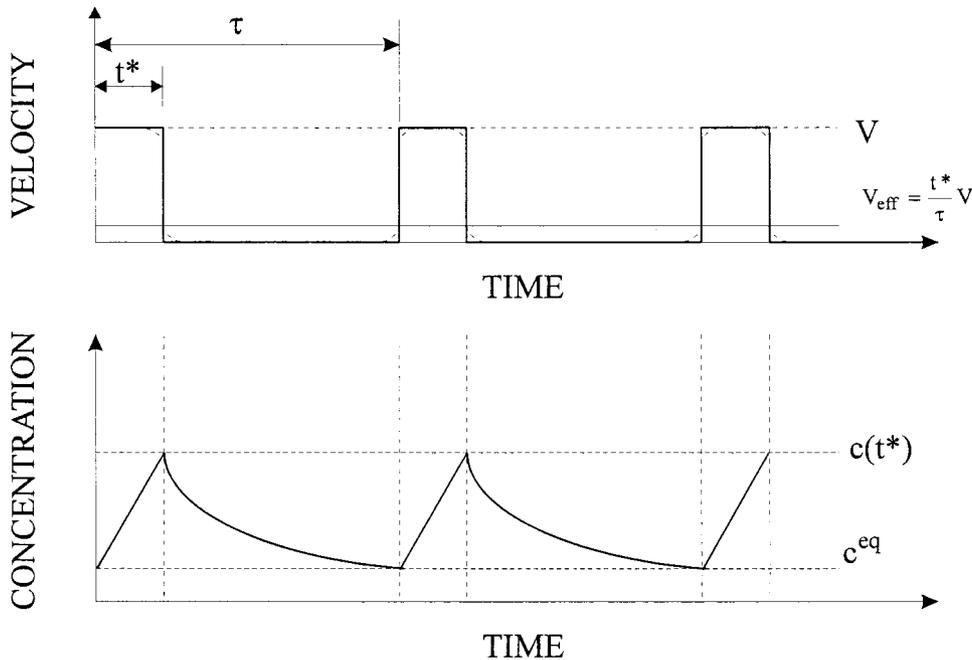


Fig. 1. Variation with time of the grain growth rate V (a) and the vacancy concentration c (b) (schematic). The dashed lines show a “smoothed” grain boundary velocity profile in a real situation.

affected by the self-locking described; above this grain size, the ordinary grain growth driven by capillary forces will prevail. As seen from equation (19), the critical radius depends on the vacancy sink spacing d which may be determined by the average distance between dislocations or the dislocation cell size. However, for ultrafine grain sized materials, where R can be identified with d , the critical radius can be written as

$$R_c = 24NkTZ(\beta\delta)^2 \frac{m}{D_{SD}}. \quad (20)$$

The above considerations implied tacitly that vacancies generated during grain growth form a “solid solution”, rather than a second phase, i.e. voids. Using equations for the time to void nucleation [11], it can be demonstrated that even with the highest vacancy concentration produced, namely $c(t^*)$, the time to form a stable nucleus of a void is much larger than the time t^* itself.

Several predictions regarding the jerky motion regime made in this section (see also Ref. [9]) deserve special mention:

1. The temperature dependence of the effective velocity V_{eff} introduced above

$$V_{\text{eff}} = \frac{t^*}{\tau} \cdot V = \frac{1}{24} \cdot \frac{\sigma D_{SD}}{NkTZ(\beta\delta)^2} \cdot \left(\frac{R}{d}\right)^2 \quad (21)$$

is primarily determined by that of the coefficient of self-diffusion. In other words, different activation enthalpies should be observed for small and large grain sizes. Indeed, for small grain size where jerky motion prevails, the activation enthalpy for self-diffusion should be observed, while for large grain size corresponding to continuous grain boundary motion the activation enthalpy for the intrinsic grain boundary mobility will be found. The latter is generally different from the activation enthalpy for self-diffusion [10].

2. As long as R remains smaller than R_c , an acceleration of grain growth can be expected, as suggested by equation (21) showing a quadratic dependence of the grain growth rate on R . However, on approaching the critical grain radius R_c , the “normal” regime of continuous grain growth driven by the surface tension will set in leading to the inverse R dependence of the grain growth velocity.
3. In nanocrystalline materials no vacancy sinks are available in the bulk of the grains due to the absence of dislocations there. The sink spacing d is to be identified with the grain size R yielding a time independent value of the average grain growth rate V_{eff} , cf. equation (21)

$$V_{\text{eff}} = \frac{1}{24} \cdot \frac{\sigma D_{SD}}{NkTZ(\beta\delta)^2}.$$

This indicates that in the initial stage of grain

growth when R is smaller than R_c , the rate of growth is time-independent, i.e. the grain size should be linear in time. This prediction is supported by experiments on grain growth in nanocrystalline iron [12]. Moreover, the critical grain size R_c estimated for different temperatures using the present model is in good accord with the measured values [12] of the grain size limiting the linear range of the R vs t curve.

It should be noted that the discontinuous character of grain growth may not be the only mode of the growth kinetics. An alternative would be continuous growth, with a rate reduced by vacancy generation effect, following a first “self-locking” event. This “degenerated” jerky motion variant will be analysed elsewhere.

2.2. Kinetics of void dissolution

Dissolution of voids is a classical problem in the theory of sintering. The foundations of the theory were established by Frenkel, Pines and Geguzin (see Refs [5, 13] for a review). However, the vacancy inhibition effect discussed above appears to have been overlooked by previous workers. Such an effect may also be operative in the case of void dissolution which is accompanied by a massive release of vacancies into the surrounding bulk of the material. In this section the conditions for intermittent temporary arrest of the void dissolution process leading to an effective decrease of the rate of dissolution is considered following the treatment of the problem in Ref. [14]. The essence of the effect can be studied for an ensemble of identical voids of radius R_{void} in an otherwise uniform solid. The number of voids per unit volume, n_{void} , is assumed not to change during the process. The void sizes R_{void} and n_{void} are related to the volume fraction, f , of voids (porosity) through

$$f = \frac{4\pi R_{\text{void}}^3 n_{\text{void}}}{3}. \quad (22)$$

Introducing the surface energy per unit area, σ^s , one can rewrite equation (6) for the Gibbs free energy of the system of voids and vacancies, G , as [3]

$$G = 4\pi R_{\text{void}}^2 \sigma^s n_{\text{void}} + G(c^{\text{eq}}) + \frac{1}{2} \frac{NkT}{c^{\text{eq}}} (c - c^{\text{eq}})^2. \quad (23)$$

For the rate of variation of G it follows

$$\dot{G} = 8\pi R_{\text{void}} \sigma^s n_{\text{void}} \dot{R}_{\text{void}} + \frac{NkT}{c^{\text{eq}}} (c - c^{\text{eq}}) \dot{c}. \quad (24)$$

In order to consider the rate of variation with time of the radius of an individual void, \dot{R}_{void} , we write for the vacancy flux into the bulk:

$$j = -D_v N \frac{c_s - \bar{c}}{R_{\text{void}}}. \quad (25)$$

Here c_s and \bar{c} are the vacancy concentrations in

close proximity of the void surface and in the bulk far away from it, respectively. It is assumed that the voids are not located at such vacancy sinks as dislocations or cell, subgrain or grain boundaries. An individual void and its vacancy atmosphere are sketched in Fig. 2.

The rate of change of the void radius follows from the balance of volume lost by the void and transferred to the bulk by the vacancies emitted:

$$-D_v N \Omega \frac{c_s - \bar{c}}{R_{\text{void}}} 4\pi R_{\text{void}}^2 = 4\pi R_{\text{void}}^2 \dot{R}_{\text{void}} \quad (26)$$

or

$$\dot{R}_{\text{void}} = -D_v N \Omega_{\text{vac}} \frac{c_s - \bar{c}}{R_{\text{void}}}. \quad (27)$$

Here Ω_{vac} denotes the volume of a vacancy.

To calculate the vacancy concentration in the bulk, \bar{c} , we introduce the radius of the ‘‘catchment region’’ $L \gg R_{\text{void}}$ of an individual void which is defined by

$$\frac{4\pi}{3} L^3 n_{\text{void}} = 1. \quad (28)$$

The vacancy concentration \bar{c} within this catchment region is assumed to be uniform. The variation of \bar{c} with time can be considered to result from a competition between vacancy ‘‘injection’’ from the void and vacancy losses to bulk sinks. The rate of increase of the vacancy content in the bulk due to vacancy injection from the void, $\dot{\bar{c}}^+$, is obtained from the balance equation

$$\frac{4\pi}{3} L^3 \dot{\bar{c}}^+ = 4\pi R_{\text{void}}^2 D_v \frac{c_s - \bar{c}}{R_{\text{void}}} \quad (29)$$

which, using equation (27), yields

$$\dot{\bar{c}}^+ = 4\pi R_{\text{void}} n_{\text{void}} D_v (c_s - \bar{c}). \quad (30)$$

The rate of decrease of \bar{c} due to vacancy annihilation at sinks (e.g. edge dislocations or grain boundaries) is given by

$$\dot{\bar{c}}^- = -\frac{D_v}{d^2} \bar{c} \quad (31)$$

cf. equation (9). The difference is that the vacancy concentration at sinks has been assumed to be zero implying sinks of infinite strength. The sinks may be associated with dislocations as well as with cell, subgrain or grain boundaries. Finally, the equation for the time derivative of \bar{c} reads

$$\dot{\bar{c}} = 4\pi R_{\text{void}} n_{\text{void}} D_v (c_s - \bar{c}) - \frac{D_v}{d^2} \bar{c}. \quad (32)$$

To assess the sign of the time derivative of G , the solutions of the set of differential equations for R_{void} and \bar{c} are substituted into equation (24) from equations (27) and (32). The vacancy concentration at the void surface, c_s , is taken in the form of the Gibbs–Thomson equation

$$c_s = c^{\text{eq}} \exp\left(\frac{2\Omega_{\text{vac}} \sigma^s}{kTR_{\text{void}}}\right). \quad (33)$$

The resulting equation for the rate of variation of G reads [14]

$$\dot{G} = 4\pi N n_{\text{void}} D_v R_{\text{void}} kT (c_s - \bar{c}) \Psi \quad (34)$$

where

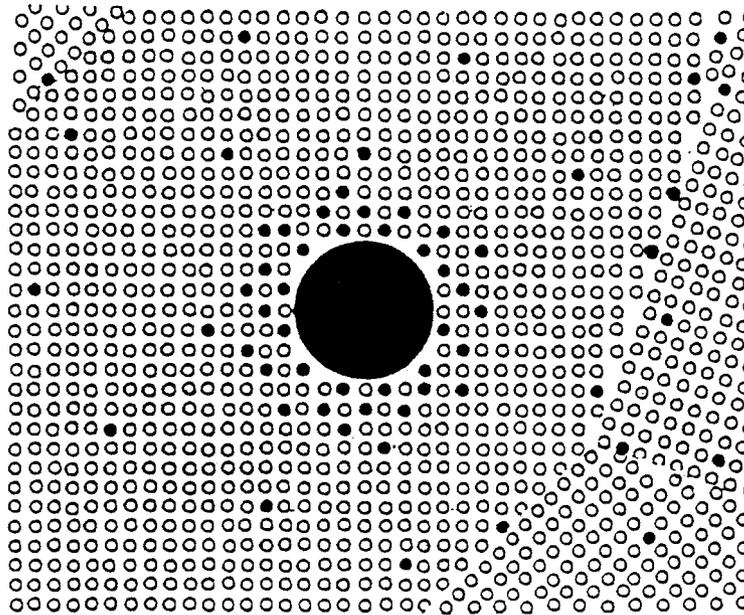


Fig. 2. A schematic picture of a void with a vacancy atmosphere (black dots). In this particular example, vacancy sinks are associated with the grain boundaries shown.

$$\Psi = \frac{2\Omega_{\text{vac}}\sigma^s}{kTR_{\text{void}}} + \frac{\bar{c} - c^{\text{eq}}}{c^{\text{eq}}} \left[1 - \frac{1}{4\pi n_{\text{void}}d^2 R_{\text{void}}} \cdot \frac{\bar{c}}{c_S - \bar{c}} \right]. \quad (35)$$

Obviously, the sign of \dot{G} is determined by that of Ψ . Under certain assumptions discussed in Ref. [14] [in particular, the assumption of the smallness of $2\Omega_{\text{vac}}\sigma^s/kT(R_{\text{void}})_0$ where $(R_{\text{void}})_0$ is the initial void radius] and for sufficiently small times, equation (35) can be rewritten as

$$\Psi \cong -\frac{2\Omega_{\text{vac}}\sigma^s}{kT(R_{\text{void}})_0} + \frac{D_v(\chi-1)^2}{d^2\chi} \cdot t \quad (36)$$

where

$$\chi = 4\pi n_{\text{void}}d^2 \frac{2\Omega_{\text{vac}}\sigma^s}{kT}. \quad (37)$$

Obviously, at very small times, Ψ is negative, and so is \dot{G} . However, after a time

$$t^* = \frac{2\Omega_{\text{vac}}\sigma^s}{kT(R_{\text{void}})_0} \cdot \frac{\chi}{(\chi-1)^2} \frac{d^2}{D_v} \quad (38)$$

the void dissolution will be blocked. Apart from the case when χ tends to unity (when the time to locking of void dissolution tends to infinity), t^* is smaller than the characteristic vacancy removal time d^2/D_v . As in the previous example, the kinetic process under consideration is expected to be discontinuous. It will take the system a time of the order of d^2/D_v to dispose of the vacancy supersaturation produced during the time t^* . Voids will be “locked” during this vacancy removal time. Then void dissolution will re-start leading to renewed injection of vacancies into the surrounding bulk. Repeated locking and unlocking of the process will thus occur. The system is “open” for the void dissolution process to occur within the time t^* , that is for a small fraction of the time d^2/D_v and “locked” for a time of the order of d^2/D_v . The inhibition of the void dissolution rate will thus be governed by a (typically small) factor I defined as

$$I^{-1} = \frac{t^*}{(d^2/D_v)} = \frac{2\Omega_{\text{vac}}\sigma^s}{kT(R_{\text{void}})_0} \cdot \frac{\chi}{(\chi-1)^2}. \quad (39)$$

(Indeed, it was shown in Ref. [14] that for $(R_{\text{void}})_0$ larger than 10^{-6} cm χ is small compared to unity.) While an ensemble of identical voids was considered for simplicity, the salient features of the phenomenon are captured by the model. In an ensemble of voids with a size distribution, the radius dependence of the void activity time t^* between two successive arrests of the dissolution process will change the evolution kinetics of an ensemble of voids and the void size distribution. It was stressed in Ref. [14] that the Lifshitz–Slyozov–Wagner kinetics of an ensemble of voids should be re-considered in this light.

An example demonstrating the significance of the inhibiting effects of vacancies on void dissolution is an observation of an increase of the size and the number of voids in Cu which underwent a cyclic heat treatment [15]. Specimens of various diameter were repeatedly heated to 650°C with subsequent quenching into water. The following findings were reported in Ref. [16]: (i) the total volume of voids was linearly increasing with the number of cycles; (ii) the void density was monotonically decreasing towards the specimen surface, while a 2–3 mm thick layer near the surface was practically free of voids; (iii) in this surface layer, grain growth was enhanced, while in the middle part of the specimens grain growth was suppressed.

Our model can account for all these features. Indeed, the fact that voids which were found to form due to vacancies “quenched” from 650°C were not dissolving upon reheating lends itself as an illustration of the vacancy inhibition of void dissolution. Moreover, the vacancy supersaturation associated with the vacancy injection by voids into the bulk can be seen as a cause of grain growth suppression in the specimen bulk. The absence of voids in the near-surface layer can be explained by the proximity of the free surface which promotes efficient removal of vacancies that otherwise would suppress void dissolution. Finally, enhancement of grain growth in that layer is a further argument in favour of the concept outlined above, in particular with regard to inhibition of grain growth by vacancies (Section 2.1).

The effect discussed in this section is of special importance in the context of sintering as the knowledge of the factors determining the rate of void dissolution makes it possible to steer the dissolution kinetics. One such factor is the equilibrium vacancy concentration c^{eq} . As seen from equation (27) upon substitution of the solution of equation (32), the void dissolution rate during the time t^* is proportional to c^{eq} , while the inhibition factor I does not depend on c^{eq} [14]. Increasing c^{eq} by doping the material with solutes possessing a binding energy with vacancies would thus increase the void dissolution rate. Indeed, the solute effect on the equilibrium vacancy concentration can be expressed by a simple additivity rule: the total concentration of vacancies in a solid solution is given by the sum of the concentrations of the free vacancies and of those forming vacancy–solute pairs. The equilibrium concentration of vacancies in such a system is determined by the following expression, cf. Ref. [16]:

$$c_{\text{total}}^{\text{eq}} = c^{\text{eq}} \left[1 + Zc_{\text{sol}} \left(\exp\left(\frac{W}{kT}\right) - 1 \right) \right] > c^{\text{eq}} \quad (40)$$

where c_{sol} is the solute concentration and W the solute–vacancy binding energy. Thus, an overall enhancement of void dissolution rate due to alloy-

ing with vacancy-binding solutes is predicted by the present model. The effect of trace elements having a large binding energy with vacancies (particularly Sn) on the enhancement of densification of Al–Cu powders was observed by Sercombe and Schaffer [17].

3. VACANCY EFFECT ON GRAIN BOUNDARY MOTION

For processes considered above, the vacancies generated lead to a thermodynamic force inhibiting the process itself. Here a situation will be considered where this inhibition occurs as well, but is reduced due to the entropy of the vacancies generated. We are talking here about grain boundary motion which is accompanied with vacancy generation. Interaction of moving grain boundaries with point defects is one of the central problems of grain boundary migration [18–20]. Interaction of a moving grain boundary (GB) with vacancies it generates as a “by-product” of the motion was investigated in Refs [2–4]. The drag force on the boundary associated with a vacancy–boundary interaction was considered in Refs [3, 4]. However, entropy terms were not included. Below we shall re-visit the previous calculations taking the total Gibbs free energy into account.

Following Ref. [4] we consider a one-atomic model of a grain boundary moving at a velocity V . It is assumed that the GB produces vacancies at a rate

$$\dot{q}_B = -\frac{c_B - c_{B0}}{\tau_B} \quad (41)$$

with

$$c_{B0} = c^{\text{eq}} \exp(H_0/kT) \quad (42)$$

where c_{B0} is the thermal equilibrium vacancy concentration in the GB, respectively, c_B is the current vacancy concentration in the GB, τ_B is a characteristic “relaxation time” within the boundary and H_0 is the binding energy between a vacancy and the GB.

In the coordinate system moving with the boundary, the diffusion equation for vacancies outside of the boundary reads

$$\dot{c} = D_v c'' + Vc' - \frac{D_v}{d^2}(c - c^{\text{eq}}) \quad (43)$$

where c is the coordinate and time dependent bulk vacancy concentration. A dot and a prime denote a derivative with respect to time t and coordinate x , respectively. In steady state to be considered here, equation (43) is rewritten as

$$D_v c'' + Vc' - \frac{D_v}{d^2}(c - c^{\text{eq}}) = 0. \quad (44)$$

As the width of the vacancy profile around the GB is much larger than its thickness δ (of the order of

the atomic distance b), the space ahead of the boundary (region II) will be identified as $x > 0$ and that in the wake of the boundary (region I) as $x < 0$. While these regions are considered as two separate continua, the GB represents a discrete (but “infinitely thin”) object in between. This exactly follows the concept of Ref. [4], a difference being the inclusion of the bulk sink term in equation (44). Denoting the vacancy concentration on the right ($x = +0$) and on the left ($x = -0$) “edges” of the GB as c_2 and c_1 , respectively, and using the obvious boundary conditions

$$c(+0) = c_2; \quad c(-0) = c_1; \quad c(x \rightarrow \pm\infty) = c^{\text{eq}} \quad (45)$$

$$c - c^{\text{eq}} = (c_2 - c^{\text{eq}}) \exp\left[-\frac{x}{\tilde{x}_{\text{II}}}\right]; \quad (46)$$

for $X > 0$ (region II)

and

$$c - c^{\text{eq}} = (c_1 - c^{\text{eq}}) \exp\left[\frac{x}{\tilde{x}_{\text{I}}}\right], \quad (47)$$

for $X < 0$ (region I).

Here the characteristic decay lengths

$$\tilde{x}_{\text{I}} = \frac{2}{\sqrt{1+4\alpha}-1} \frac{D_v}{V}; \quad (48)$$

$$\tilde{x}_{\text{II}} = \frac{2}{\sqrt{1+4\alpha}+1} \frac{D_v}{V}$$

with $\alpha = (D_v/Vd)^2$, have been introduced. The case considered in Ref. [4] corresponds to $\alpha = 0$. For non-zero but small values of α , it follows that

$$\tilde{x}_{\text{II}} = D_v/V; \quad \tilde{x}_{\text{I}} = \frac{Vd}{D_v}. \quad (49)$$

One can see that these lengths are vastly different, i.e. the vacancy profile is strongly asymmetrical, the decay in front of the GB being much faster than behind it. In the limit of $V \rightarrow 0$, the asymmetry vanishes, as seen from equation (50).

In order to find the GB vacancy concentration c_B and also determine the integration constants c_1 and c_2 , a flux balance across the GB should be considered, as done in Ref. [4]. The balance equations read:

$$\dot{q}_B \delta = j_{B/\text{II}} - j_{I/B}. \quad (50)$$

Requiring in addition continuity of the fluxes at the “edges” of the GB [4]

$$j_{B/\text{II}} = j_{\text{II}}|_{+0}, \quad j_{I/B} = j_{\text{I}}|_{-0} \quad (51)$$

(where $j_{B/\text{II}}$ and $j_{I/B}$ are the vacancy fluxes from the GB into the right “edge” and from the left “edge” into the GB, respectively, while j_{I} and j_{II} are the fluxes in the respective regions of the bulk), we come to a set of three equations:

$$\dot{q}_B \delta = \left[\frac{D_v}{b} \exp\left(-\frac{H_0}{kT}\right) c_B - \frac{D_v}{b} c_2 \right] - V c_2 - \left[\frac{D_v}{b} c_1 - \frac{D_v}{b} \exp\left(-\frac{H_0}{kT}\right) c_B \right] + V c_B \quad (52)$$

$$\left[\frac{D_v}{b} \exp\left(-\frac{H_0}{kT}\right) c_B - \frac{D_v}{b} c_2 \right] - V c_2 = -D_v \frac{\partial c}{\partial x} \Big|_{x=+0} - V \left(c_2 + \frac{\partial c}{\partial x} \Big|_{x=+0} \cdot b \right) \quad (53)$$

$$-D_v \frac{\partial c}{\partial x} \Big|_{x=-0} - V c_1 = \left[\frac{D_v}{b} c_1 - \frac{D_v}{b} \exp\left(-\frac{H_0}{kT}\right) c_B \right] - V c_B. \quad (54)$$

In these equations diffusional jumps of vacancies into and out of the GB as well as convection fluxes are included. In the expressions for the convection flux at the right “edge” of the GB, the vacancy concentration at the point one atomic distance ahead of the right “edge” should be taken in a discrete formulation. This gives rise to the last term on the right-hand side of equation (53) in the continuum formulation. The derivatives in equations (53) and (54) obtained from equations (46) and (47) read

$$\frac{\partial c}{\partial x} \Big|_{x=+0} = -\frac{c_2 - c^{\text{eq}}}{\tilde{x}_{\text{II}}}; \quad \frac{\partial c}{\partial x} \Big|_{x=-0} = \frac{c_1 - c^{\text{eq}}}{\tilde{x}_{\text{I}}}. \quad (55)$$

Substituting these expressions into equations (53) and (54) yields

$$c_1 = \frac{\frac{D_v}{\tilde{x}_{\text{I}}} c^{\text{eq}} + \left[\frac{D_v}{b} \exp\left(-\frac{H_0}{kT}\right) + V \right] c_B}{\frac{D_v}{b} + \frac{D_v}{\tilde{x}_{\text{I}}} + V} \quad (56)$$

$$c_2 = \frac{\left(\frac{D_v}{\tilde{x}_{\text{II}}} + V \frac{b}{\tilde{x}_{\text{II}}} \right) c^{\text{eq}} + \frac{D_v}{b} \exp\left(-\frac{H_0}{kT}\right) c_B}{\frac{D_v}{b} + \frac{D_v}{\tilde{x}_{\text{II}}} + V \frac{b}{\tilde{x}_{\text{II}}}}. \quad (57)$$

Further substitution of c_1 and c_2 from equations (56) and (57) into equation (55) yields a solution for the GB concentration c_B . This is a somewhat cumbersome expression and we present it here only for a natural limit case of sufficiently small relaxation time, τ_B , for the vacancy concentration in the GB. More specifically, it is assumed that the relaxation of the vacancy concentration in the GB to its equilibrium value occurs much faster than elsewhere, τ_B being much smaller than any other characteristic time of the problem, i.e. $\tau_B \ll \min\{d^2/D_v, D_v/V^2\}$. In that case $c_B = c_{B0}$. Furthermore, making use of the fact that both decay lengths \tilde{x}_{I} and \tilde{x}_{II} are much larger than the atomic spacing b , expressions (56) and (57) for the vacancy concentrations at the “edges” of the GB

can be simplified to

$$c_1 = \frac{1 + \frac{Vb}{D_v} \exp(H_0/kT)}{1 + \frac{Vb}{D_v}} c^{\text{eq}}; \quad c_2 = c^{\text{eq}}. \quad (58)$$

With the knowledge of the vacancy profile around the moving GB given by equations (46)–(49) we can calculate the vacancy drag force on the boundary. This is done by considering the change in the free energy of the system on a small virtual displacement of the boundary. The concentration dependence of the Gibbs free energy, G , is again taken in the form of equation (6). A boundary displacement to the right by an atomic distance b (the width of the boundary) produces a change in the Gibbs free energy of the system coming from three sources. First, the left “edge” of the GB, where the concentration was c_1 enters the region with concentration c_B . This produces a free energy change $G(c_B) - G(c_1)$. Second, the GB region proper, where the concentration was c_B , enters the right “edge” region, with concentration c_2 . The attendant change of free energy is $G(c_2) - G(c_B)$. Finally, the right “edge” region, where the concentration was c_2 , moves into the bulk where the concentration can be expressed as

$$c(b) = c_2 + \frac{\partial c}{\partial x} \Big|_{x=+0} \cdot b.$$

The associated change of the free energy is $G(c(b)) - G(c_2)$. Then the total change is

$$\Delta G = G(c(b)) - G(c_1) = G(c_2) + \frac{dG}{dc} \frac{dc}{dx} \Big|_{x=+0} \cdot b - G(c_1). \quad (59)$$

The change of the Gibbs free energy counted per unit volume can also be interpreted as the force per unit area of the GB. A negative ΔG thus implies a drag force, i.e. a force acting against the direction of the GB motion. Using equation (6) and noting that for the case under consideration the derivative in equation (59) is zero yields for the drag force P_{drag} :

$$P_{\text{drag}} = \Delta G = -\frac{1}{2} NkT c^{\text{eq}} \left[\frac{\exp(H_0/kT) - 1}{1 + Vb/D_v} \right]^2 \left(\frac{Vb}{D_v} \right)^2. \quad (60)$$

Using the inequalities $\exp(H_0/kT) \gg 1$ and

$$(Vb/D_v) \exp(H_0/kT) \ll 1 \quad (61)$$

equation (60) can be simplified to

$$P_{\text{drag}} = \Delta G = -\frac{1}{2} NkT c^{\text{eq}} \left(\frac{Vb}{D_v} \exp\left(\frac{H_0}{kT}\right) \right)^2. \quad (62)$$

Inequality (61) is safely fulfilled for *all* grain boundaries in Al investigated with regard to their mobility

even with an overestimated value of $H_0 = 0.3$ eV. (We refer here to Al as the only material for which a reasonably large set of data is available Ref. [21].)

It is interesting to note that the drag force calculated is significantly smaller than the one found earlier by Lücke and Gottstein [4] where the only term considered in the free energy was the enthalpy of the vacancies generated, yielding

$$P_{\text{drag}}^{\text{LG}} = -NH_v^f(c_1 - c_2) = -NH_v^f c_{\text{eq}} \frac{Vb}{D_v} \exp\left(\frac{H_0}{kT}\right). \quad (63)$$

Here H_v^f is the enthalpy of vacancy formation. The temperature dependence of the vacancy drag given by equation (62) is determined primarily by the activation enthalpies of grain boundary migration, vacancy diffusivity and vacancy formation, as well as the binding energy between a vacancy and a grain boundary. Depending on an interplay of these parameters for a given material and a particular grain boundary, the drag may increase or decrease with temperature.

4. CONCLUSIONS

In this paper, examples of vacancy-generating kinetic processes were considered in which the vacancies produced interact with the very process in which they have been created. The thermodynamic approach taken made it possible to assess the effect of this interaction on the rate of such processes. In two examples considered, namely grain growth in fine-grained materials and void dissolution, conditions were found when vacancy generation inhibits the underlying kinetic process. In both cases, repetitive cycles of uninhibited vacancy generation followed by a longer period of “locking” of the process (of grain growth or void dissolution) were predicted, its overall rate being reduced as compared to that associated with the primary driving force, i.e. grain boundary or surface energy. A number of predictions verifiable by experiment were made. The “degenerate” case of a single “locking” event followed by continuous kinetics will be considered elsewhere.

An example of a system in which ejection of vacancies occurs into both “phases” separated by an interface is a moving grain boundary. The vacancy drag associated with the asymmetry of the vacancy concentration profile around the grain boundary was reassessed by taking into account the entropy terms. A significant reduction of the drag force as compared to the one predicted by considering the enthalpy terms alone was found.

While the exposition of the vacancy generation effects in this article was limited to only three

examples of specific physical situations, further processes where similar effects may occur can be envisaged. A particular case is static recovery. Vacancy generation by jogs on moving dislocations as well as due to reduction of the total excess free volume associated with dislocations upon a decrease in their density may have an inhibiting effect on the recovery process itself. A detailed treatment of this case will be presented in a forthcoming paper [22].

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