



ON THE KINETICS OF GRAIN GROWTH INHIBITED BY VACANCY GENERATION

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1. Introduction

In recent papers [1,2] we investigated the inhibiting effect of vacancy generation on grain growth. It was shown that vacancies produced as a result of the reduction of the grain boundary (GB) area, i.e. of the elimination of the excess volume, increase the free energy of the system. Therefore, the ‘injection’ of vacancies into the bulk of the material acts as an inhibiting factor leading to a decrease in the grain growth rate. In the approach proposed uninhibited grain growth was considered to occur only during a limited time, t^* . It was assumed that after that time, on reaching the condition when the time derivative of the Gibbs free energy becomes positive, ‘locking’ of grain growth occurs. It was further assumed that grain growth remains arrested for a time $\tau = d^2/D_v$ it takes the excess vacancies to be removed by diffusion. (Here D_v is the vacancy diffusivity and d is the characteristic vacancy sink spacing.) A sequence of such locking-unlocking events was considered to represent the grain growth kinetics. The effective grain growth rate V_{eff} following from that approach is given by the following equation:

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

which is valid below a certain critical grain size,

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

Here V is the ‘unperturbed’ rate of grain growth driven by the boundary energy; γ , δ , β and m are GB characteristics: free energy per unit area, thickness, the relative excess free volume, and mobility, respectively; R is the average grain size (radius), D_{SD} is the bulk self-diffusion coefficient, N is the number of atoms per unit volume and Z is the coordination number; kT has the usual meaning.

Smoothing the discontinuous solution by replacing V_{eff} with the time derivative of the average grain size, dR/dt , and solving eq. (1) yields the time law for the grain growth model of Refs. 1 and 2:

$$\frac{1}{R_0} - \frac{1}{R} = \frac{1}{24} \cdot \frac{\gamma D_{SD} t}{NkTZ(\delta\beta)^2 d^2}, \quad (3)$$

where R_0 is the initial grain size.

The model picture outlined above appears to account for the inhibiting effect of vacancies on grain growth, but, of course, it is not more than an approximation of the real continuous process of grain growth. Guided by the principle that *natura non facit saltus*, the present authors suggested a description of grain growth as a continuous process [3]. The continuous growth model that was applied for the case of thin films will be used here in order to show that the intermittent locking-unlocking representation of grain growth given in Refs. 1 and 2 is a reasonable approximation. The main goal of this paper is an analysis of stability of nanocrystalline materials against grain growth. To that end, the continuous growth model will be used.

2. Continuous Growth Model

By analogy with Ref. 3, we can write an equation expressing the balance of energy associated with an increment of grain size, dR :

$$-\frac{d}{dR} \left(\frac{3\gamma}{2R} \right) dR = \frac{3}{2} \cdot \frac{1}{R} \cdot \frac{(dR/dt)^2}{m} dt + \frac{NkT}{c^{eq}} (c - c^{eq}) \frac{6\delta\beta}{R^2} dR. \quad (4)$$

where c and c^{eq} are the actual and the equilibrium vacancy concentrations, respectively. Equation (4) expresses the energy balance: the energy release associated with the reduction of the GB area [the LHS of eq. (4)] is distributed between the dissipation due to the drag forces [first term on the RHS of eq. (4)] and the vacancy sub-system [second term on the RHS of eq. (4)]. The variation of the vacancy concentration is described by

$$\dot{c} = \frac{6\delta\beta}{R^2} \cdot \frac{dR}{dt} - \frac{D_v}{d^2} (c - c^{eq}). \quad (5)$$

The evolution of the system is now given by the set of coupled equations, eqs. (4) and (5), which can be re-written in a dimensionless form:

$$\xi \frac{d\xi}{dt} + A\Psi C - A = 0, \quad (6)$$

$$\frac{dC}{dt} = \frac{p}{\xi^2} \frac{d\xi}{dt} - C \quad (7)$$

Here $\xi = R/d$, $C = c - c^{eq}$, $A = m\gamma/D_v$, $\Psi = \frac{4NkT(\delta\beta)}{c^{eq}\gamma}$, $p = 6\beta \frac{\delta}{d}$; the time t is now non-dimensional and is measured in the units of d^2/D_v .

An analysis of numerical solutions of the set of eqs. (6) and (7) for a broad range of parameters has shown that for sufficiently small initial grain size $\xi_0 = R_0/d$ the grain growth uninhibited by vacancies is preceded by an incubation time during which the growth rate is substantially reduced, the time dependence of the grain size exhibiting a plateau-like behaviour, cf. Fig. 1a. For large values of ξ_0 no incubation time is observed. By analogy with Ref. 3, the incubation time is defined as the time at which the grain growth rate is a maximum. This time corresponds to the termination of the plateau-like behaviour and a transition to uninhibited, parabolic grain growth, cf. Fig. 1a. Over the incubation time,

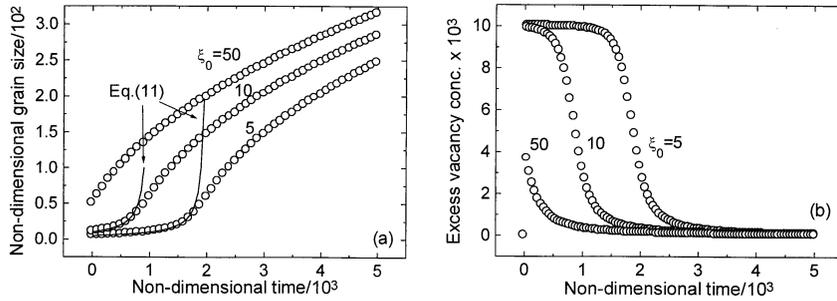


Figure 1. Dependence of non-dimensional grain size (a) and of excess vacancy concentration (b) on the non-dimensional time calculated from eqs. (6)-(7) for the following values of parameters: $A = 10$, $\Psi = 100$ and $p = 100$.

the vacancy concentration stays at an approximately constant, increased level, cf. Fig. 1b. Numerical results show that the non-dimensional incubation time is inversely proportional to ξ_0 and can be represented by the following formula:

$$\tau_{incubation} = \frac{p\Psi}{\xi_0} \quad (8)$$

or, in dimensional form

$$t_{incubation} = 24 \frac{NkT(\delta\beta d)^2}{c^{eq}\gamma R_o D_v} \quad (9)$$

Within the incubation time, an approximate analytical solution of the set of eqs. (6) and (7) can be obtained as follows. Using the fact that the excess vacancy concentration C is nearly constant and the rate of grain growth is slow, one can neglect the first term in eq. (6) which yields for the vacancy concentration

$$C = 1/\Psi \quad (10)$$

(The validity of the assumption that the first term is negligible can be proved *a posteriori*.) Substitution of this expression into eq. (7) and integration lead to

$$\frac{1}{\xi_0} - \frac{1}{\xi} = \frac{t}{p\Psi} \quad (11)$$

which, when rewritten in the dimensional form, coincides with eq. (3). This demonstrates that the approximation [1,2] based on the intermittent locking-unlocking scheme with smoothing, provides a quantitatively adequate representation of continuous grain growth in the regime where the inhibiting effect of grain growth induced vacancies is operative. Indeed, Fig. 1 demonstrates an excellent match between the $\xi(t)$ dependencies over the incubation period given by eqs. (11) and (3).

3. Analysis of Stability Against Grain Growth

A comparison of the inhibited grain growth with the common, parabolic grain growth behaviour can be used to formulate a condition for the occurrence of the vacancy-induced stabilization against grain growth. Parabolic growth occurs if the vacancy effect can be neglected, i.e. if the vacancy concentration is sufficiently close to its equilibrium value. From eq. (6) it then follows

$$\xi^2 - \xi_0^2 = 2At. \quad (12)$$

(Under these conditions eq. (7) becomes obsolete.) Obviously, the solution of the set of eqs. (6) and (7) coincides with the parabolic law given by eq. (12) for time tending to zero and also for times much larger than the incubation time, when C tends to zero, cf. Fig. 1. A real inhibition of grain growth means that the rate of growth in the plateau region, described by eq. (11), is much smaller than that corresponding to 'free', uninhibited growth described by eq. (12). This condition reads

$$\xi \ll (Ap\Psi)^{1/3}. \quad (13)$$

Since we are interested in a situation when no significant grain growth occurs over the incubation time, a representative value for ξ is ξ_0 . For the values of parameters used in Fig. 1 inequality (13) transforms to $\xi_0 \ll 46.4$. Indeed, as can be seen from Fig. 1a, the $\xi(t)$ dependence for $\xi_0 = 50$ does not exhibit any incubation period. Also the maximum excess vacancy concentration does not reach the value given by eq. (10), cf. Fig. 1b. Inequality (13), re-written in the dimensional form, reads

$$R_0 \ll R_c^* = \left[24NkTZ(\delta\beta)^2 d^2 \frac{m}{D_{SD}} \right]^{1/3}. \quad (14)$$

A striking observation is that this condition is not very material sensitive, particularly due to the fact that the ratio of the GB mobility and the coefficient of bulk self-diffusion is not strongly material dependent, and also due to the power of 1/3. However, the sink spacing d related, e.g., to the inverse of the square root of the dislocation density ρ , may bring about some variability of the quantity on the right hand-side of inequality (14).

One particular case needs to be considered separately, though. It is the case when the initial grain size is so small that no other vacancy sinks but the GBs themselves are available, so that d is to be identified with the grain size R . It should be noted that a vacancy generated at a particular GB cannot be readily reabsorbed by the same GB, since some local vacancy supersaturation had to prevail inside that GB for vacancy generation to occur there in the first place. The vacancy generated may be absorbed at another GB facet without a decrease of that facet's length, e.g. due to a topological constraint. This would give rise to the special case $d = R$ we consider. Equation (7) then changes to

$$\frac{dC}{dt} = \frac{1}{\xi^2} \left(6 \frac{d\xi}{dt} - C \right). \quad (15)$$

Equation (6) remains unchanged. However, the meaning of the non-dimensional grain size and the non-dimensional time are different now: $\xi = R/(\delta\beta)$, and time is measured in units of $(\delta\beta)^2/D_v$.

Solving the set of equations (6) and (15) numerically, one can see that the temporal behaviour of the grain size in this case is different from the behaviour in the case of constant sink spacing d . After a short initial period of time t_{trans} the rate of vacancy-inhibited growth slows down considerably, cf. Fig. 2a. After that, the grain growth effectively stays inhibited for very long times. The growth rate is thus always lower than the respective rate of usual parabolic growth (cf. Fig. 2b). Again, using the fact that after the transient period t_{trans} the vacancy concentration is sustained at an approximately constant level and that the grain size does not change significantly, one can obtain an approximate solution of the set of eqs. (6) and (15) which reads

$$R - R_0 = \frac{1}{24} \cdot \frac{\gamma D_{SD} t}{NkTZ(\delta\beta)^2}. \quad (16)$$

A comparison with eq. (1), where d is set equal to R , shows that the solutions provided by the continuous growth model and the locking-unlocking approximation are identical for this case, too. From

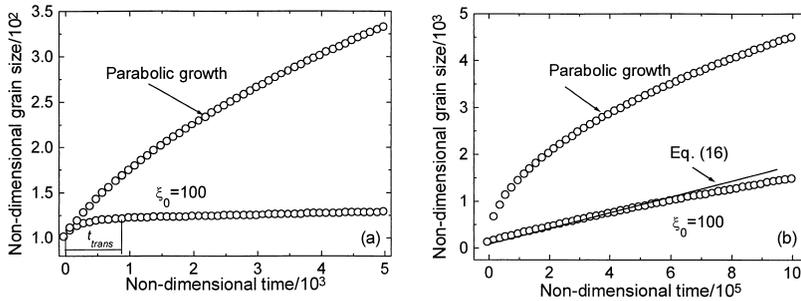


Figure 2. Dependence of non-dimensional grain size on the non-dimensional time calculated from eqs. (6) and (15) for the following values of parameters: $A = 10$, $\Psi = 100$ for two different time scales.

Fig. 2b it can be seen that eq. (16) indeed provides a good analytical approximation for sufficiently short times, which nevertheless should be longer than t_{trans} . However, with increasing initial grain size t_{trans} increases, too, and eq. (16) becomes less accurate. It should be mentioned that according to eq. (16) the dependence of the grain growth rate on temperature and hydrostatic pressure is determined by the bulk self-diffusion coefficient D_{SD} , rather than by GB parameters.

We can now check the stability of a nanocrystalline material against grain growth by requiring, as above, that the growth rate given by eq. (16) be much smaller than that corresponding to the parabolic law, eq. (12). The stability condition is then expressed by the inequality

$$R_o \ll R_c = 24NkTZ(\delta\beta)^2 \frac{m}{D_{SD}}, \quad (17)$$

(cf. eq. (2)). These results have an interesting interpretation: a nanocrystalline material cannot be stable if condition (14) or (17) (whichever is relevant) is violated. In that sense, the critical radius R_c or R_c^* can be regarded as a limiting stable grain size above which grain growth uninhibited by vacancies is possible. Obviously, as seen from (14) and (17) the critical grain size is temperature dependent. As the activation energies for GB mobility and the self-diffusion are generally different [4], the sense of the temperature variation of the critical grain size will depend on the interplay of the temperature dependencies of the mobility and the self-diffusion coefficient. It should be stressed that the GB mobility may depend very strongly on the type of the boundary, the texture in the material and its purity [4], which makes estimation of the critical radius to a fairly difficult task. Still, eqs. (14) and (17) make this possible in principle. To get a feel for the order of magnitude of the critical radius, we consider Al - the only material for which m is known with some confidence - at 300 °C. Taking $m = 2 \times 10^{-14} \text{ m}^4 \text{ J}^{-1} \text{ s}^{-1}$ and $D_{SD} = 1.3 \times 10^{-17} \text{ m}^2/\text{s}$ one obtains R_c of the order of 100 nm. As the two critical radii are related, $R_c^* = (R_c d^2)^{1/3}$, an estimate for R_c^* is readily obtained. For example, for the case when vacancy sinks are provided by dislocations, d^2 can be identified with the inverse of the dislocation density ρ . With ρ in the range of $10^{13} - 10^{15} \text{ m}^{-2}$, R_c^* is found to have the same order of magnitude as R_c , i.e. 100 nm. These estimates explain the relative stability of nanocrystalline materials against grain growth, as they fall in the subcritical range of R .

The grain growth inhibition by vacancies predicted is at least as important as the well known solute drag effect [5]. To demonstrate this, we compare the grain growth rates for Al of different purity, calculated according to eq. (12), with the prediction of the present model [eq. (16)]. For GB mobility, m , we used the recent data for migration of the $38.2^\circ \langle 111 \rangle$ tilt GBs in Al bicrystals of different purity [6]. The resulting time dependencies of grain size at 300 °C and for $R_o = 100 \text{ nm}$ are shown in Fig. 3. It can be seen that the mechanism considered is especially effective in impeding the grain growth at

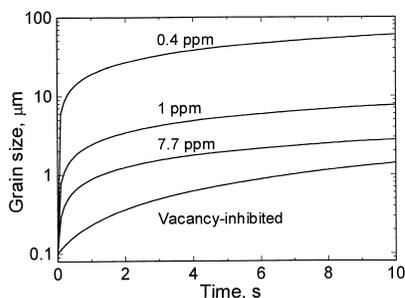


Figure 3. Time dependence of the grain size for Al of various levels of purity [7], compared with the prediction for the present mechanism (the lowest curve).

the most important, initial stage of the process. Even though the relative contribution of the vacancy inhibition effect depends on the grain boundary type (and may be not as pronounced for a general grain boundary as for the special grain boundary considered), this estimate demonstrates its significance vis-à-vis solute drag.

Recent experimental results on the grain growth kinetics in ultra-fine grained Fe in a range of temperatures [7] can be seen as a confirmation of the predictions of the present model.

4. Grain Refining Due to Vacancy Supersaturation

We would like to discuss the following aspect of the present kinetic description of the interaction between the process of grain growth and the evolution of the vacancy sub-system. The set of eqs. (6) and (7), or (6) and (15), admit solutions corresponding to a decrease of the average grain size for the case of initial vacancy supersaturation. In other words, it can be speculated that *grain refining* can be induced by high vacancy concentration, which can be created in different ways, e.g. by quenching from a high temperature, irradiation with energetic particles or plastic deformation. An example of the variation of the average grain size with time for three different initial excess vacancy concentrations is shown in Fig. 4. While the amount of grain size decrease is small, the very possibility of vacancy-induced grain refinement appears interesting.

The physical reason for this grain refinement is similar to the well known effect of grain refinement during the discontinuous precipitation (DP) [8], diffusion induced GB migration (DIGM) [9] and discontinuous ordering (DO) [10] reactions. In all cases the loss of energy associated with increase of GB area is compensated for by the energy profit in the bulk due to decomposition of supersaturated

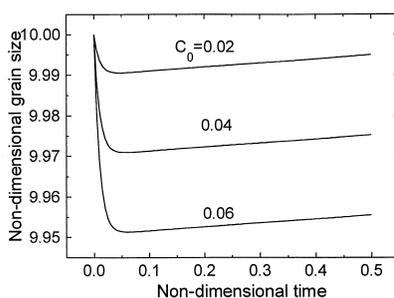


Figure 4. Dependence of non-dimensional grain size on the non-dimensional time calculated from eqs. (6)-(7) for various levels of initial vacancy supersaturation. (Parameter values are the same as in Fig. 1.)

solution (DP), formation of the solid solution (DIGM) or bulk ordering of the quenched disordered alloy (DO) behind moving GBs. However, true grain refinement can be achieved only in the late stages of these reactions. At the beginning, merely the morphology of GBs changes from planar to a wavy one, while the properly defined average grain size stays unchanged. Considering the small magnitude of the vacancy-induced grain refinement (see Fig. 4) one can conclude that also in this case the relaxation of excess vacancy concentration will probably be achieved by the changes of GB morphology rather than by grain refinement proper.

It should be noted that there is some similarity between grain refinement considered here and the osmotic pressure on the edge dislocations due to the vacancy supersaturation [11]. This pressure plays an important role in growth of vacancy dislocation loops by climb processes. In both cases, the system reacts to the vacancy supersaturation by migration of defects capable of absorbing the excess vacancies.

5. Conclusions

In this article, vacancy-induced inhibition of grain growth was considered. Conditions of stability of a polycrystalline material against grain growth were proposed. The analytical form of these criteria makes it possible to assess the stability of fine-grained, notably nanocrystalline, materials for specified experimental conditions. This can be viewed as the main result of the present paper.

In addition, the continuous grain growth model considered was used to verify the time laws for grain growth following from a previous idealized intermittent locking model.

Finally, a possibility of grain refinement due to vacancy supersaturation was discussed. It is hoped that this possibility, which at present is speculative, will motivate experimental studies into this effect.

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