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Coarsening of particles connected by dislocations

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This work theoretically reinvestigates the coarsening of particles controlled by diffusion through a dislocation network, when the dislocation spacing of the network is larger than the maximum particle size and the volume fraction of the particles vanishes. Both a three-dimensional network and a plane one, such as that which might be encountered at a low-angle grain boundary, are treated. It is considered here that the number of dislocation pipes for diffusion increases with distance away from the particle. Under certain reasonable assumptions, a $t^{1/4}$ steady-state coarsening kinetics is found. The origin of the differences between the present kinetic results ($t^{1/4}$) and those predictions previously reported in the specialized literature ($t^{1/5}$), for similar dislocation geometries, are discussed. The effect of the dislocation annihilation phenomenon on the growth kinetics is also examined qualitatively.

Nomenclature

A	cross sectional area of the pipe dislocations
$b_i (i = 1, 2, \ldots)$	constants
c	fractional concentration of solute at a given point at pipe dislocations
c_m	mean fractional concentration of solute in the matrix
c_r	fractional concentration of solute in the matrix in the vicinity of a particle of radius r
c_∞	fractional concentration of solute in the matrix in the vicinity of a plane particle/matrix interface
d	dislocation spacing
D_d	coefficient of solute diffusion along pipe dislocations, (moles per unit time, unit length and unit fractional concentration differential)
$g(u)$	steady-state distribution function of the normalized sizes of the particles
j	a positive integer
m	kinetic exponent
$N_i (i = 1, 2, \ldots)$	number of pipe dislocations contributing to the diffusion area within different ranges of x specified in the text
p	a positive integer
$q_i (i = 1, 2, \ldots)$	constants
r	radius of a given particle
R	gas constant
r^*	critical radius
r_0^*	critical radius at the onset of coarsening
t	time
t_0	time at the onset of coarsening
T	absolute temperature
$u(= r/r^*)$	normalized size of a given particle
u_m	maximum allowable normalized size in the steady-state for particle coarsening
x	radial distance measured from the centre of a given particle
γ	specific interfacial free energy
η	a function of ϕ
ϕ	volume fraction of the particles
Ω	molar volume of the particles
v	a function which tends asymptotically to a constant value as time tends to infinity
ξ	the sum of an infinite series, defined in the text
τ	pseudo-time

1. Introduction

The equilibrium concentration of solute in a matrix, in the vicinity of a pure-solute spherical particle of radius r, is given by the Gibbs–Thomson equation:

$$c_r = c_\infty \exp\left(\frac{2\gamma\Omega}{RTr}\right) \qquad (1)$$

This equation states that solubility increases as the particle size decreases. Hence, a distribution of particles in a matrix tends to coarsen by transfer of the atoms of solute from the smaller particles, which tend to dissolve, to the larger ones, which tend to grow.

The coarsening of particles controlled by different solute-diffusion mechanisms has been analysed previously. Accordingly, a specific value of the kinetic exponent m, in an $r^* \sim t^{1/m}$ kinetics, has been associated with each one of such mechanisms: $m = 2$ for matrix/precipitate interface reaction [1]; $m = 3$ for matrix diffusion [1, 2], and $m = 4$ for grain-boundary diffusion [3–5]. For coarsening controlled by diffusion through a plane array of pipe dislocations, such as that which defines a low-angle grain boundary, and for the case when the dislocation spacing of such an array is much smaller than the particle size, a value of $m = 4$ has been also derived [5]. On the other hand, for coarsening controlled by diffusion through either a plane [5] or three-dimensional [6] array of pipe dislocations, when the corresponding dislocation spacing is larger than the maximum particle size, a value of $m = 5$ has been obtained. As noted by Kreye [6], the physical situation associated with the problem of coarsening through pipe dislocations may correspond to that of second-phase particles nucleated at dislocation lines that were present in the matrix phase. Moreover, pipe-diffusion-controlled coarsening might also be important in materials which are experiencing plastic deformation, as in the case of fatigue loading [7].

In this paper we theoretically reinvestigate the problem of coarsening of spherical particles of pure solute connected by a pipe-dislocation array when the dislocation spacing is larger than the maximum particle size and the volume fraction of the particles vanishes. Both plane and three-dimensional arrays of dislocations are taken into account. The particle-dislocation geometries treated here are similar to those previously assumed, when analysing the above problem, by Ardell [5] for the plane case and by Kreye [6] for the three-dimensional one. Unlike the developments of Ardell and Kreye, in our approach it is considered that the number of dislocation pipes for diffusion increases with distance away from the particle.

Our main result is that for a dislocation network that remains unaltered during particle growth, the coarsening process is found to obey, under reasonable assumptions, a $t^{1/4}$ kinetics. This kinetic result ($t^{1/4}$) differs from other theoretical predictions ($t^{1/5}$) usually referred to in the specialized literature. The effect of the dislocation annihilation phenomenon on the coarsening kinetics is also discussed qualitatively.

2. Theory

In this section, the kinetic equation for the growth of a pure solute spherical particle which coarsens by solute diffusion through a network of pipe dislocations, when $\phi = 0$, is first derived. Then, the steady-state coarsening kinetics and the corresponding distribution function of the particle sizes are determined.

Because it is assumed that the dislocation spacing is larger than the maximum particle size, we can consider that the number of dislocations intersecting a particle, N_1, remains constant throughout its growth. For an illustrative purpose only, let us consider the situation of a dissolving particle. As the solute atoms emitted from such a particle move away from it, the dislocations contributing to the effective area of diffusion increase with the distance from the centre of the particle, x. In this work, it will be supposed that the number of dislocations contributing to the effective area of diffusion increases abruptly from N_i to N_{i+1}, at a distance x_i from the centre of the particle, for $i = 1, 2, \ldots$. Moreover, for simplicity, it will be assumed that the solute flux is always radially oriented with respect to the centre of the particle. As the particles are assumed to be infinitely apart (because $\phi = 0$), then, from the condition of the constancy of the flux of the solute atoms, either absorbed or emitted by a given particle, we can write the solute concentration at dislocations, c, as

$$c = b_i + q_i x \qquad x_{i-1} \leqslant x < x_i \tag{2}$$

for $i = 1, 2, \ldots$. We shall take x_0 as equal to the radius of the particle, r, whereas x_i will be taken as equal to id, for $i = 1, 2, \ldots$, where d is a measure of the dislocation spacing of the dislocation network. This latter choice is related to the fact that it is assumed here that the dislocation network considered possesses properties of periodicity, the corresponding period (that is, the dislocation spacing) being roughly the same in all directions. It is also clear from the condition of the constancy of the flux of the solute atoms, that we must have

$$q_i = \frac{N_1}{N_i} q_1 \tag{3}$$

for $i = 1, 2, \ldots$. Thus, the solute concentration at a distance x_j from the centre of the particle, for $j \geqslant 2$, can be expressed as

$$c_j = c_r + q_1 (d - r) + d \sum_{i=2}^{j} q_i \tag{4}$$

where c_r is the solute concentration at the particle/matrix interface. As j tends to infinity, the solute concentration must tend to the value of the average solute concentration in the matrix, c_m. Then, from Equations 3 and 4 we have:

$$q_1 = \frac{(c_m - c_r)}{N_1 d\xi - r} \tag{5}$$

where ξ is the sum of the infinite series:

$$\xi = \sum_{1}^{\infty} \frac{1}{N_i} \tag{6}$$

Equation 5 corresponds to the solute concentration gradient at the particle/matrix interface. Notice that such a gradient could also have been obtained by assuming that solute diffusion takes place along N_1 dislocations, up to a distance $N_1 d\xi$ from the centre of the particle, where the solute concentration is set equal to c_m.

So, from Equation 5, and by use of the first Fick's law, we can write the rate equation for the growth of a particle, in moles per unit time, as

$$\frac{4\pi r^2}{\Omega} \frac{dr}{dt} = D_d N_1 A \frac{(c_m - c_r)}{N_1 d\xi - r} \tag{7}$$

We shall now suppose that all positions of the dislocation network at which particles are situated, are geometrically equivalent, in such a manner that it can be considered that both N_1 and ξ have values which are the same for all particles. Also, if the dislocation array remains unaltered during particle coarsening, then N_1, d and ξ can be supposed to be constants. The above assumptions will be employed in the following.

We shall define the critical radius of a particle, r^*, as the radius of a particle which is instantly neither growing nor shrinking. Clearly, the solute concentration at the particle/matrix interface of such a particle must be equal to c_m. Then, by expanding Equation 1 into a series of the first order, we have

$$c_m - c_\infty = \frac{2\gamma\Omega c_\infty}{RTr^*} \tag{8}$$

Thus, by means of Equations 7 and 8 we can write

$$\frac{dr^4}{dt} = \frac{2D_d N_1 A\gamma\Omega^2 c_\infty}{\pi RT} \frac{(u-1)}{(N_1 d\xi - r)} \tag{9}$$

where c_r in Equation 7 has been obtained by expanding Equation 1 into a series of the first order, and

$$u = \frac{r}{r^*} \tag{10}$$

is the normalized size of the particle. We shall now suppose that the product $N_1 d\xi$ in Equation 9 is sufficiently large, so that little error is committed if we substitute $N_1 d\xi$ for $(N_1 d\xi - r)$ in the denominator of the right-hand side of such an equation. Then, from Equations 9 and 10 we have

$$\frac{du^4}{d\tau} = v\,(u-1) - u^4 \tag{11}$$

where

$$v = \frac{2D_d A\gamma\Omega^2 c_\infty}{\pi RTN_1 d\xi} \frac{dt}{dr^{*4}} \tag{12}$$

and

$$\tau = \ln(r^{*4}) \tag{13}$$

It is clear from previous work [5, 8], that in the present case a steady state for particle coarsening is possible if $du^4/d\tau$ is a function of u only, i.e. if v tends asymptotically to a constant value. Such a value and that of the maximum allowable normalized size of the particles, u_m, can be obtained in the usual manner, i.e. by making $(du^4/d\tau)$ and $d(du^4/d\tau)/du$ as equal to zero at $u = u_m$ [5, 8]. This latter procedure yields $v = 4(4/3)^3$ and $u_m = 4/3$. Hence, on integrating Equation 12, we can express the steady-state coarsening rate equation as

$$r^{*4} - r_0^{*4} = \left(\frac{3}{4}\right)^3 \frac{D_d A\gamma\Omega^2 c_\infty}{2\pi RTd\xi}(t - t_0) \tag{14}$$

The procedure for determining the corresponding steady-state distribution function of the normalized sizes of the particles, $g(u)$, has been previously presented in the Appendix of [5]. The expression derived there is

$$g(u) = -\frac{3u^3}{(du^4/d\tau)} \exp\left[\int_0^u \frac{3u^3 du}{(du^4/d\tau)}\right] \tag{15}$$

where, for the present case, $(du^4/d\tau)$ is given by Equation 11. In this way, the explicit expression for $g(u)$ associated with our problem is

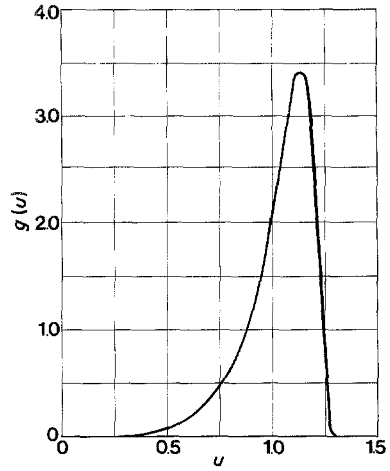

Figure 1 Theoretical steady-state distribution function of the normalized size of the particles, corresponding to Equation 16.

$$g(u) = (\tfrac{3}{4})^4 u^3 \left(1 - \frac{3u}{4}\right)^{-19/6} \left(1 + \frac{u}{2} + \frac{3u^2}{16}\right)^{-23/12} \times \exp\left\{\frac{1}{2} - \frac{2/3}{(4/3 - u)} - \frac{1}{2^{1/2}6} \times \left[\tan^{-1}\left(\frac{1 + 3u/4}{2^{1/2}}\right) - \tan^{-1}\frac{1}{2^{1/2}}\right]\right\} \tag{16}$$

for $u < 4/3$. Equation 16 has been represented graphically in Fig. 1.

It is seen from Equation 14 that the main difference between the plane and three-dimensional cases lies in the value of ξ, or equivalently of the product $N_1\xi$. For instance, for a three-dimensional network we can crudely take N_i as $N_1 i^2$, and then the product $N_1\xi$ equals $\pi^2/6$ [9]. On the other hand, for a plane array of dislocations, such as those which might be encountered at low-angle grain boundaries, we can roughly take N_i as $N_1 i$, for $i < p$, where p can be considered as a measure of the sub-grain size in units of d. As long as in this latter situation the first p terms of the series $N_1\xi$ correspond to the first p terms of the harmonic series, and taking into account that the aforementioned series diverges as ln (p) [10], it is clear that for the plane case, the value of $N_1\xi$ will be chiefly determined by the value of p. Having in mind that the validity of Equation 14 is restricted to the case when the ratio $r/N_1 d\xi$ is sufficiently small for all the particles, it follows that particles which are situated on a three-dimensional dislocation network which remains unaltered throughout particle coarsening, may follow a $t^{1/4}$ kinetic if the particle size remains very small in comparison with the dislocation spacing. It is also concluded that particles which are located on a plane array of dislocations which remains stable during the coarsening process, may obey a $t^{1/4}$ kinetic either if the particle size is kept very small with respect to the dislocation spacing, or if the sub-grain size (or, equivalently, p) is sufficiently large, or both.

3. Discussion

In studying the coarsening of particles controlled by solute diffusion through a network of pipe dislocations, when the dislocation spacing is larger than the maximum particle size, a $t^{1/5}$ kinetic had been previously derived by Kreye [6] for the case of a three-dimensional network, and by Ardell [5] for the case of a plane network. We shall now explain the reasons why these results differ from the $t^{1/4}$ kinetics derived in this paper for the above problem.

Unfortunately, Kreye [6] did not describe in detail the solution of the aforementioned coarsening process. However, from inspection of the kinetic equation presented by him [6], it seems that Kreye assumed that solute emitted by a dissolving particle, for instance, diffused away from the particle along a constant number of dislocations, up to a distance from the centre of the particle equal to twice the radius of the particle. At this latter distance, the solute concentration was set equal to c_m [6]. So, seemingly Kreye attempted to represent the solute diffusion from or to a given particle through the three-dimensional dislocation network, by diffusion of solute along a constant number of dislocations, between the particle and an imaginary surface sink of source of solute atoms, located at a distance $2r$ from the centre of the particle of radius r. In fact, from Equation 7 in this paper, it follows that, when $\phi = 0$, the analogy described is indeed plausible, provided that the above sink or source of solute atoms is located at a distance $N_1 d \xi$ from the centre of the particle. This latter value depends only on the geometry of the array of dislocations, which in the present work is assumed to be the same for all particles. So, if in Kreye's formulation the above sink or source of solute atoms were located at a distance $N_1 \mathrm{d} \xi$ from the centre of the particle, then, for $N_1 d \xi \gg r$, a $t^{1/4}$ steady-state coarsening kinetic would be obtained.

The approach adopted by Ardell [5] in analysing the same problem treated in this paper, for the case of a plane array of dislocations, is essentially the same which were seemingly employed by Kreye [6] in studying the case of a spatial network. More precisely, Ardell considered that solute diffusion emitted from a dissolving particle, for instance, moved away from the particle along a constant number of dislocations, up to a distance from the centre of the particle equal to $r + r^*/\eta$, where η is a function of the volume fraction of the particles, defined as $\eta = 4\phi^{1/2}/[\exp(4\phi)\,\Gamma(\frac{1}{2}, 4\phi)]$, with Γ denoting the incomplete gamma function. At the distance stated, the solute concentration was set equal to c_m by Ardell [5]. Hence, Ardell tacitally assumed that solute diffusion from or to a particle, through the plane dislocation network, was equivalent to that corresponding to diffusion along a constant number of dislocations, between the particle and an imaginary lineal sink or source of solute atoms, located at a distance $r + r^*/\eta$ from the centre of the particle. Therefore, we may now say that in the light of the derivation presented in Section 2, it follows that the approach adopted by Ardell is acceptable, at least when ϕ vanishes, provided that the imaginary surface sink or source of atoms is located at a distance $N_1 d \xi$ from the centre of the particle (see Equation 7). In this manner, when this latter result is introduced in Ardell's approach then, for $N_1 d \xi \gg r$, a $t^{1/4}$ steady-state coarsening kinetic is derived.

The analysis of the problem treated in this paper becomes much more complicated when the volume fraction of the particles is different from zero. In fact, the solute atoms are then absorbed after only a finite diffusion distance. The idea of Ardell [5] of introducing $\eta(\phi)$, as explained in the preceeding paragraph, for taking into account the influence of ϕ, should be considered as a guess only, especially in the light of the work of Brailsford and Wynblatt for matrix-diffusion-controlled coarsening [11]. These latter authors developed a fully consistent method for the analysis of the exchange of solute atoms, in a statistical averaged sense, for coarsening controlled by lattice diffusion. Such a method was found [11] to be more adequate to deal with matrix-diffusion-controlled coarsening than that employed by Ardell [12] for treating the said problem which, in turn, is analogous to the method used by the same author [5] to deal with pipe-diffusion-controlled coarsening.

Dislocation annihilation is a phenomenon frequently observed in the annealing of metallic materials as, for instance, in the case of previously cold-worked alloys. The effect of the dislocation annihilation phenomenon on the coarsening kinetics will be discussed here, within the frame of the theory presented in this paper. For this purpose, the values of d and ξ deduced in Section 2, will now be roughly considered as average values during the interval of time a solute atom diffuses through the dislocation network from a dissolving particle to a growing one. It is obvious that at any given time (or pseudo-time), different values of d and ξ should be considered for growing and dissolving particles. For simplicity, in the present approach the same functions $d(r^*)$ and $\xi(r^*)$ will be considered for all particles, by taking into account that the distinction stated above between growing and dissolving particles can be introduced in a rather crude manner, for example, by multiplying the right-hand side of Equation 7 by a suitable function of u. On the other hand, it will be supposed that the number of dislocations intersecting each particle, N_1, remains constant throughout the coarsening process. So we can see from the preceeding considerations that Equation 12 is still valid, but the product $d\xi$ can be now considered as an increasing function of r^*. For instance, if we suppose that the product $d\xi$ increases linearly with r^*, then it can be easily verified that in such a situation a $t^{1/5}$ steady-state coarsening kinetic is obeyed. So, it may be expected that the phenomenon of dislocation annihilation have influence on the value of the kinetic exponent of the coarsening kinetics.

The presence of dislocations connecting particles has been reported in previous works [6, 7]. Calderon *et al.* [7] studied the coarsening kinetics of particles connected by dislocations in an Fe–2.5% Ni–5.7% Al–2% Mo alloy, and a $t^{1/3}$ kinetic was encountered, thus suggesting matrix-diffusion-controlled coarsening. On the other hand, a number of cases has been reported where values of the kinetic exponent ranging from 4 to 5 have been found [13–16], which might be associated with a coarsening controlling mechanism such as pipe-diffusion of the solute. Nevertheless, detailed experimental observations on the characteristics of the dislocation network which might be present during particle coarsening are still lacking.

4. Conclusions

The particle coarsening controlled by diffusion through a three-dimensional and a two-dimensional network of pipe dislocations, when the dislocation spacing is larger than the maximum particle size and ϕ vanishes, was studied. It was considered that the number of dislocation pipes for diffusion increases with distance away from the particle. Under certain reasonable assumptions, a $t^{1/4}$ kinetic was derived. This kinetic result differs from other theoretical predictions usually referred to in the literature.

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