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## INTERACTION BETWEEN PRECIPITATES AND MIGRATING GRAIN BOUNDARIES

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**Résumé :** Nous étudions l'interaction entre un joint de grains mobile et des précipités. A cause de l'existence d'un profil de concentration qui comporte une zone de déplétion en avant du joint, les précipités peuvent être dissous pendant la migration, si toutefois celle-ci est suffisamment lente.

**Abstract :** We analyse the interaction between a moving grain boundary and precipitates. Because of the existence of a concentration profile which exhibits a depletion zone ahead of the boundary, we argue that if the interface moves slowly enough, the precipitates can be dissolved during its migration.

### INTRODUCTION

It is well known that grain boundaries may modify the kinetics of precipitation. The case which has been studied in detail is the acceleration of the growth of precipitates at an immobile boundary [1]. However, when grain boundaries move in an alloy which contains precipitates, a great variety of situations can arise. Recently, relatively uncommon observations have been made in two different systems. These can be described as follows.

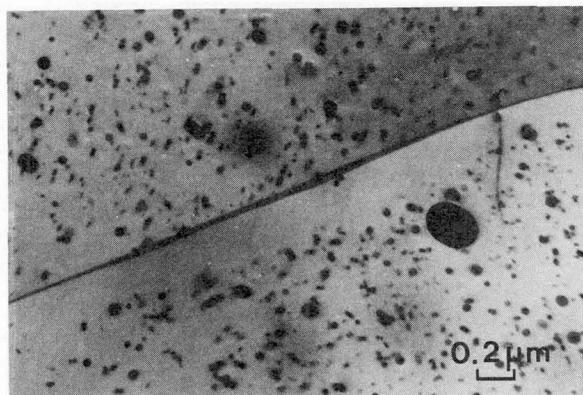
During a heat treatment performed on a rapidly solidified Al-Cr-Zr alloy [2], very fine (a few nanometers), homogeneous and coherent  $\text{Al}_3\text{Zr}$  precipitates appear. Then, behind the grain boundaries that have migrated, three different morphologies of coherent (or semi-coherent) precipitates are observed. The higher the velocity of the boundary, the finer is the precipitation. Finally, it should be noted that the characteristics of the finer precipitates are similar to those of the initial one.

The other system that we have studied is a Ti-Y-O alloy [3] containing yttria precipitates in epitaxy with the titanium matrix. After recrystallization, we observe precipitates which have the same characteristics, on both sides of the grain boundaries that have moved. However, it is important to note the presence of an asymmetrical precipitate free zone, as shown in figure 1. We have interpreted these observations in terms of a dissolution/reprecipitation process during the migration of the grain boundary through the preexisting precipitates.

These two experiments, as well as some other observations [4,5,6], show that many different situations can arise when parameters such as the grain boundary velocity, the diffusion rate of the solute atoms, the initial size of the precipitates and the surface tension between these and the matrix are varied.

In the following, we will attempt to model the Ti-Y-O experimental situation. In fact, we shall consider a simpler system, i.e. a matrix containing only one atomic species in solid solution as well as precipitates formed by compact aggregates of these atoms.

We will first recall some results reported by Cahn [7] and by Lücke and Stüwe [8] concerning the solute atoms concentration profile in the vicinity of a migrating grain boundary (G.B.). The existence of such an asymmetric concentration profile will allow us to construct a model of dissolution of the precipitates ahead of the moving boundary. We will then discuss two limiting cases, which give some useful orders of magnitude. Finally, a more refined theory will be also briefly mentioned.



**Figure 1 :** The precipitation behind the grain boundary has the same characteristics as the initial one (average radius : 100 Å). Note the presence of an asymmetrical precipitates free zone, the width of which is close to 2000 Å. The direction of the grain boundary movement will be discussed in the conclusion.

## 1. THE CONCENTRATION PROFILE IN THE VICINITY OF A MOVING GRAIN BOUNDARY

It is generally admitted that G.B.s often exert an attractive force on the atoms of the solid solution (generally of an elastic origin). This short-range, attractive interaction leads to a symmetric concentration profile in the vicinity of a static interface (see figure 2a).

Cahn [7], and later on Lücke and Stüwe [8], dealt with the case of a moving grain boundary. The stationary diffusion equation to be solved can be written in the following way, in the moving frame:

$$D \left[ \frac{DC(x)}{dx} + \frac{C(x)}{kT} \frac{dU(x)}{dx} \right] + vC(x) = vC \quad (1)$$

where  $x$  is the distance from the interface in a moving reference frame (velocity  $v$ ).  $U(x)$  is the attractive potential acting on the solute atoms, the diffusion coefficient of which is  $D$ .  $C(x)$  and  $C$  are respectively the solute atom concentration at a distance  $x$  from the G.B., and the average concentration in the matrix. Finally,  $T$  and  $k$  are the absolute temperature and the Boltzmann constant.

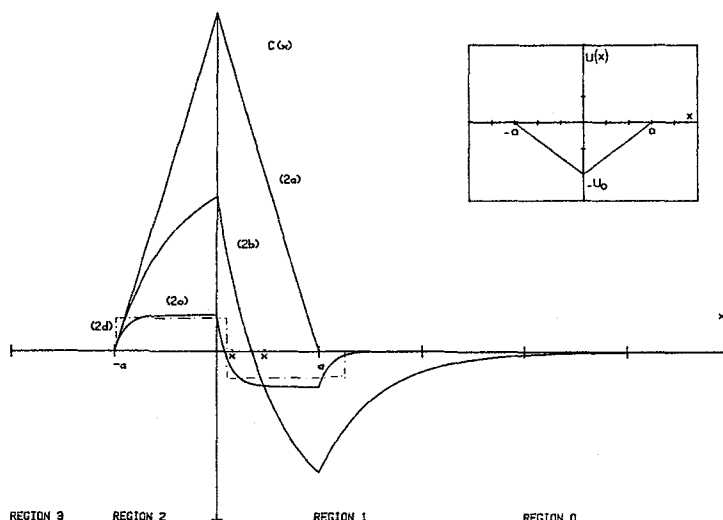
Introducing the dimensionless parameter :  $\Phi = a v / D$  (where  $a$  is a microscopic length of the order of the interatomic distance), we can write the solution of equation (1) in the following general form:

$$C(x) = \frac{\Phi C}{a} \exp \left( -\frac{U(x)}{kT} - \frac{\Phi x}{a} \right) \int_{-\infty}^x \exp \left( -\frac{U(x')}{kT} - \frac{\Phi x'}{a} \right) dx' \quad (2)$$

One of the simplest potentials one can choose is the triangular well, schematized on the insert of figure 2. It is convenient to introduce the dimensionless parameter :  $\eta = U_0 / kT$ .

$C(x)$  is shown in figure 2 for different values of  $\Phi$ .

When  $v$  is no longer equal to zero, the concentration peak is lower, which reflects the fact that the atoms have less time to diffuse to the attractive interface. But the most striking feature of this asymmetrical concentration profile is the existence of a solute depleted zone ahead of the G.B. This can be interpreted as a "remembrance" of the transient profile, where atoms come from both sides to feed the concentration peak. In the stationary case, only the depleted zone ahead of the moving G.B. still exists : there, since the diffusion is not fast enough, the concentration cannot attain to the value of the grain interior. Because of the existence of this region, one can suppose that a precipitate initially in equilibrium with the solid solution of concentration  $C$  will have a tendency to dissolve until, if it has not dissolved completely, it can grow again when the concentration peak region arrives in its vicinity. Obviously, the easiest situation to describe is the single precipitate one. It is also the most favourable situation as far as the dissolution is concerned, because the dissolution of a single precipitate (zero volume fraction) will in no means affect the value of the concentration of the solid solution. Thus, this value can be assumed constant (in the moving reference frame), and if this concentration is appropriate for the dissolution of the precipitate, nothing will stop it before the concentration peak arrives. On the contrary, in the case where many precipitates are taken into account, their dissolution increases the concentration of the surrounding solid solution, and the size of the particles ceases to evolve when equilibrium is reached. In this context, the most "pessimistic" approximation, as far as the dissolution is concerned, is the one which assumes that there is no atomic flow between the different regions (interior of the grains, depleted region, concentration peak zone), because, in this assumption, the atoms released by the dissolution remain in the initial region of depletion, and increase the concentration much more quickly. This is why we strongly believe that both kinds of approximation must be considered. These limiting cases are described in the following two sections.



**Figure 2:** Concentration profile in the vicinity of an attractive G.B. ( $\eta = 0.1$ ;  $Ca^3 = 5 \cdot 10^{-3}$ ;  $a = 1.8 \text{ \AA}$ ) :

Region 3 :  $x < -a$  :  $C(x) = C$

Region 2 :  $-a < x < 0$  :  $C(x) = C \{ \eta e^{(\eta - \Phi)(x+a)/a} - \Phi \} / (\eta - \Phi)$

Region 2 for  $0 < x < \tilde{x}$  and region 1 for  $\tilde{x} < x < a$  :  $0 < x < a$  :  $C(x) = C \{ \Phi + K e^{-(\eta + \Phi)x/a} \} / (\eta + \Phi)$

Region 1 for  $a < x < a/\Phi$  and region 0 for  $x >> a/\Phi$  :  $a < x$  :  $C(x) = C \{ 1 + K' e^{-\Phi x/a} \}$

with :  $K = -\Phi + (\eta + \Phi) \{ \eta e^{(\eta - \Phi)(x+a)/a} - \Phi \} / (\eta - \Phi)$

and:  $K' = \{ -\eta + (-\Phi + (\eta + \Phi) \{ \eta e^{(\eta - \Phi)(x+a)/a} - \Phi \} / (\eta - \Phi)) e^{-(\eta + \Phi)x/a} \} / (\eta + \Phi)$

In each case  $x$  is defined by:  $C(x) = C$  ( $0 < x < a$ ).

(2a):  $\Phi = 0$ : immobile grain boundary

(2b):  $\Phi = 1$

(2c):  $\Phi = 5$

(2d): Approximation of the case (2c) with the square profile.

**Insert :** The triangular potential well : the precise shape of this potential is in fact unknown and meaningless, because of its short-range character. The only relevant parameter is  $\eta$ , which represents a measure of the strength of interaction.

## 2. THE SINGLE PRECIPITATE CASE:

Let us now consider a single spherical precipitate of radius  $R_0$ , in equilibrium with the solid solution of concentration  $C$ . Furthermore, we assume that this precipitate is small enough to be present at any time in a homogeneous environment. This is generally true in the solute depleted zone, because its width ( of the order of  $a/\Phi$  ) is much greater than  $a$  ( see the legend of figure 2 ) for small values of  $\Phi$ , and this case will be considered in the following. The dissolution (or the growth) of the particles will be described within the framework of the Lifshitz and Slyozov's quasi-stationary theory [9]:

$$\frac{dR}{dt} = \frac{D\alpha C_\infty a^3}{R} \left[ \frac{C(t) - C_\infty}{\alpha C_\infty} - \frac{1}{R} \right] \quad (3)$$

where  $R$  is the particle's radius at time  $t$ , and:  $\alpha = 2\gamma a^3 / k T$  is a length involving the surface tension  $\gamma$  between the precipitate and the matrix.  $C_\infty$  is the equilibrium concentration in the vicinity of a plane interface separating the two phases, and  $C(t)$  is the actual concentration of the solid solution which surrounds the particle at time  $t$ , i.e.  $C(x_0 - vt)$ , where  $x_0$  is the initial distance to the G.B..

Because of the rather rapid variation of  $C(x)$  (exponential functions), it is possible to model the profile with step functions, which retain the following features : the new profile also exhibits four regions, the extension of the solute depleted zone being  $(a/\Phi - \tilde{x})$ , and the width of the concentration peak being  $(\tilde{x} + a)$ ; in each region,

the number of atoms is equal to the number of atoms defined by the profile described in the preceding section .

This case is analytically solvable, because the critical radius which can be defined in the following way (see equation (3)) :

$$R_c^i = \frac{\alpha C_\infty}{C_i - C_\infty} = \frac{R_0}{1 + \left(1 + \frac{R_0}{C}\right) \left(\frac{C_i}{C} - 1\right)} \quad (4)$$

is constant in region  $i$  ( $i=0, 1, 2$  or  $3$  : see figure 2 ). The solution of equation (3) reads in this case : ( $t_{i-1} < t < t_i$ )

$$t' = t_{i-1} + \frac{1}{2} (g^2(t') - g^2(t_{i-1})) - 2 (g(t') - g(t_{i-1})) + \ln\left(\frac{g(t')}{g(t_{i-1})}\right) \quad (5)$$

where  $t' = t D \alpha C R_0 / ((R_c^i)^3 (\alpha + R_0))$ ,  $g(t') = 1 - R(t) / R_c^i$  and  $t_i$  is the time when the precipitate leaves region  $i$  to enter region  $(i+1)$ .

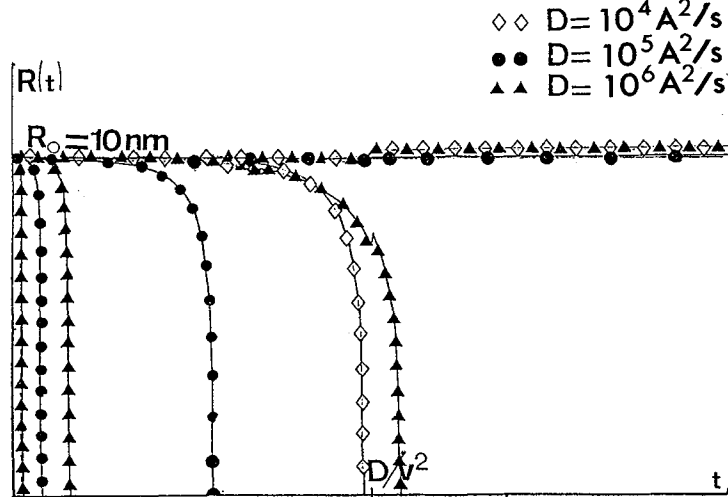
If we assume that  $v$  is of the order of  $1 \text{ A/s}$  (a few microns per hour), then  $\Phi$  is rather small, and consequently the deficiency in solute atoms in the zone of depletion is very small (on the order of  $\Phi^2$ ), and  $R_c^1$  is close to  $R_0$ . According to equation (5), the assumption that the precipitate dissolves in region 1 is self-coherent if  $\Phi$  is small enough, i.e.:  $\Phi < 10^{-6}$  for  $\alpha=10^{-3} \text{ A}$  or  $\Phi < 10^{-4}$  for  $\alpha=10 \text{ A}$ .

It means that, for a given  $D$ ,  $v$  must be small enough to ensure a sufficiently long stay of the precipitate in region 1, or that, for fixed  $v$ , the dissolution will not be complete until  $D$  has not reached a threshold value. Of course, this critical diffusion coefficient is lower when the interface energy is higher, or when the particles are initially smaller.

However, if the precipitate size has decreased enough in region 1, the particle can continue to dissolve even in region 2, provided that its radius has become smaller than  $R_c^2$ . Similarly, the dissolution can be achieved in region 3 if  $R(t_2) < R_0$ .

Figure 3 shows the evolution of  $R(t)$  when at  $t=0$ , the precipitate is at the threshold of region 1. Furthermore, let us add that these orders of magnitude are consistent with those that we determined by numerically solving the Lifshitz and Slyozov's equation with the concentration profile defined by equation (2).

In the following section, we consider the case where many precipitates evolve in separate regions.



**Figure 3:** Evolution of  $R(t)$  in the single precipitate case, where the concentration profile is modelled by step functions. The various curves correspond to various diffusion coefficients ( $10^4 \text{ A}^2/\text{s} < D < 10^6 \text{ A}^2/\text{s}$ ) and various values of the surface tension ( $.01 \text{ A} < \alpha < 10 \text{ A}$ ), with  $v = 1 \text{ A/s}$ ,  $R_0 = 100 \text{ A}$ ,  $\text{Ca}^3 = 5 \cdot 10^{-3}$ ,  $a = 1.8 \text{ A}$ . For each symbol (eg.  $\Delta$ ), the values of  $\alpha$  for the different curves located from left to right, respectively correspond to  $10\text{A}$ ,  $1\text{A}$ ,  $0.1\text{A}$  and  $0.01\text{A}$ .

### 3. THE MANY PRECIPITATES CASE IN THE ABSENCE OF ATOMIC FLOW BETWEEN THE REGIONS:

In the case where a finite initial volume fraction  $f$  of precipitates is considered, one can no longer neglect the effect of their dissolution or their growth on the surrounding solid solution, as already mentioned. Thus we must add to equation (3) an equation of conservation of the total number of atoms. Considering, for the sake of simplicity, that all the particles have the same size  $R(t)$  at time  $t$ , this relation can be written :

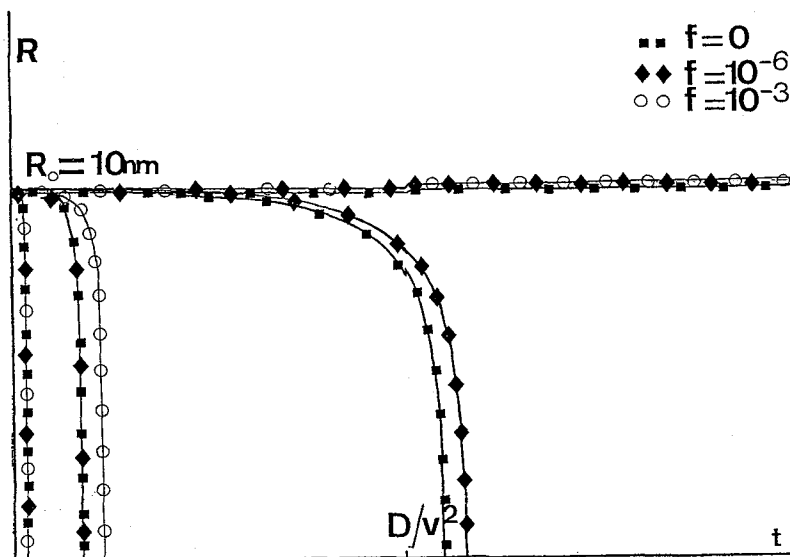
$$f + \frac{\alpha}{R_c(t=0)^3} = f \frac{\rho}{\rho_0} + \frac{\alpha}{R_c(t)^3} \quad (6)$$

where  $R_c(t)$  is the critical radius at time  $t$ , and :  $\rho(t) = R(t) / R_c(t=0)$ , while  $\rho_0 = \rho(t=0)$ .

Let us consider the case where  $R_c(t=0)$  is positive (which is the case when  $\Phi$  is small). Then, in equation (3),  $R_c(t)$  can be replaced by its expression in function of  $\rho(t)$ , which leads to:

$$\frac{d\rho}{dt} = \frac{\rho - 1}{\rho^2} + f \frac{R_c(t=0)^3}{\alpha \rho_0^3} \frac{\rho_0^3 - \rho^3}{\rho} \quad (7)$$

Note that the term which is proportional to  $f$  in the right-hand side of equation (7) is positive in the case of dissolution (i.e. when  $\rho$  is smaller than  $\rho_0$ ), and negative in the case of coalescence. This means that the absolute value of  $d\rho/dt$  is always diminished by a quantity proportional to  $f$ . Thus, as expected, the kinetics of dissolution or growth is slowed down in this case, and an equilibrium between the precipitates and the solid solution is rapidly reached. Nevertheless, figure 4 shows that it is still possible to dissolve precipitates for not too small volume fractions  $f$ , and reasonable values of the other parameters (e.g.  $D = 10^5 \text{ A}^2/\text{s}$ ;  $\alpha = 20 \text{ A}$ ;  $\text{Ca}^{3+} = 5 \times 10^{-3}$ ;  $R_0 = 100 \text{ A}$ ).



**Figure 4:** Evolution of  $R(t)$  for three values of the initial volume fraction of precipitates:  $f=0, 10^{-6}, 10^{-3}$ . For each symbol (eg.  $\diamond$ ), the values of  $\alpha$  for the different curves located from left to right, respectively correspond to  $10\text{A}$ ,  $1\text{A}$ ,  $0.1\text{A}$  and  $0.01\text{A}$ . Note that for high values of  $\alpha$ , the kinetics of dissolution is not significantly modified by the presence of many precipitates. For high surfaces tensions, the equilibrium radius of the precipitates is slightly greater than  $R_0 = 100\text{A}$ .

## CONCLUSION:

This study is the first attempt to present a theoretical description of the dissolution of the precipitate particles through a moving grain boundary. It was carried out, in the framework of the classical Lifshitz and Slyozov's quasi-stationary theory, by taking into account the solute depleted zone created ahead of this grain boundary.

The two limiting cases presented in the last two sections allowed us to determine, for the complete dissolution of the particles, orders of magnitude of the physical parameters. Even in the many precipitates case in the absence of atomic flow between the regions (an unfavourable approximation), the complete dissolution occurs with certain values of the parameters which correspond to actual situations.

Furthermore, in the single precipitate case, calculations show the possible existence of a precipitate-free zone ahead of the moving grain boundary. This result is rather surprising; in our previous paper [3], the asymmetrical precipitate-free zone was supposed to be located behind the moving grain boundary, as in the case of the situation reported in some other systems [5,6].

In order to elucidate this situation, it is worth going beyond the study of these limiting cases by considering the differential system constituted by equation (3) and the following diffusion equation which contains a source term due to the dissolution or growth of the precipitates:

$$\frac{\partial C}{\partial t} = 0 = D \frac{\partial^2 C}{\partial x^2} + \frac{D}{kT} \frac{\partial}{\partial x} \left( C \frac{\partial U}{\partial x} \right) + v \frac{\partial C}{\partial x} + \frac{3fR^2}{R_0^3} \frac{\partial R}{\partial t} \quad (8)$$

with the assumption that  $R(t)$  varies in time only through the variation of :  $x = x_0 - vt$ .

If the initial volume fraction of precipitates is not too high :

$$f < \frac{1}{3} \left( \frac{\alpha \alpha_0^3}{\Phi R_0^2} \right)^2 \left| \ln \frac{\alpha \Phi^2}{\alpha + R_0} \right|^{-1} \quad (9)$$

it can be shown that the solution of this system of equations is not significantly different from the one we obtained from the single precipitate approximation [10].

Note that an extrapolation of the experimental data relative to the diffusion of some substitutional elements in  $\alpha$ -titanium [11] gives :  $10^5 \text{ A}^2/\text{s} < D < 10^9 \text{ A}^2/\text{s}$  (at the temperature of the experiment; see reference [3]). Figure 3 shows that, within the frame of the single precipitate theory, a complete dissolution of precipitates of radius 100 Å may occur, even for the lower value  $D=10^5 \text{ A}^2/\text{s}$ , if the value of  $\alpha$  is of the order of (or greater than) 1 Å. However, the single precipitate theory should not apply in the case of our experiment, because  $f$  is of the order of 1%, i.e. greater than the limit given by equation (9) for the lower diffusion coefficients ( $D < 10^6 \text{ A}^2/\text{s}$ ). Thus a more refined theory is necessary to describe this experimental situation.

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