Solute drag and wetting of a grain boundary

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ABSTRACT

A recently observed increase of the grain-boundary (GB) mobility in Al by adding Ga impurities is in contrast with classical solute drag theories. This abnormal behaviour can be explained by the formation of a quasiliquid layer at the GB, which enhances diffusion and mobility. We present here a model including these various aspects which explains the experimental results.

§ 1. INTRODUCTION

Owing to a recent development in the experimental techniques the grain-boundary (GB) mobility can be measured by *in-situ* experiments performed on bicrystals (Gottstein, *et al.* 1995). The long-standing question of the effect of solute atoms on GB migration has been renewed by the development of such a direct technique. Motivated by macroscopic grain growth experiments on Al–Ga alloys (Straumal *et al.* 1995), which exhibited a non-trivial dependence of the grain growth kinetics with respect to the Ga content, such bicrystal experiments were performed on this system.

It has been shown (Molodov *et al.* 1995, 1996) that the addition of a few parts per million (10 ppm) of Ga in Al increases the mobility of a $\langle 111 \rangle$ tilt GB with a tilt angle close to the special $\Sigma = 7$ GB, where the Σ value is the inverse density of the coincident sites. This surprising result contradicts all the classical solute drag theories (Cahn 1962, Lücke *et al.* 1972), which predict a slowing down of grain boundaries by adding solute elements. The purpose of the present letter is to propose a model to explain this surprising result.

It has been known for a long time that Ga embrittles Al alloys by the formation of a low-temperature eutectic at the grain boundaries (Pugh 1991). It has been suggested that a similar phenomenon may be the origin of the present acceleration of GBs in Al–Ga (Molodov *et al.* 1996). This interesting qualitative idea underlies the model that we present here. Our aim is both to investigate the order of magnitude of the acceleration of the GBs which would result from this assumption and to make further predictions on the dependence of the behaviour with respect to experimental parameters (solute content and temperature) which could lead to experimental validation of the idea.

§ 2. Modification of the classical theory for solute drag to account for the presence of a quasiliquid layer on the grain boundary

The classical paper by Cahn (1962) describes the influence of solute atoms on GB motion. For the idealized situation of two semi-infinite grains separated by a GB, the diffusion problem is solved and the drag force is obtained by integrating over the diffusion profile the interaction forces between the GB and impurities. The solute drag P_i is a function of the GB velocity v, the solute bulk concentration c_0, the diffusion constant $D(x)$, where x is the direction of the normal of the GB, and the interaction potential $E(x)$ of the solute with the GB.

In order to obtain quantitative results a number of assumptions have to be made especially concerning the diffusivity of solute atoms in the GB, the mobility of the GB and the shape of the interaction potential. In Cahn's approach all these quantities are assumed to be independent of the solute content. As a consequence, adding solute atoms can only increase the dissipation and therefore slow down a moving GB (Hillert 1969).

The occurrence of a liquid-like layer associated with the segregation of Ga at the GB as suggested by various workers (Molodov *et al.* 1995, Straumal *et al.* 1995) is expected to modify the diffusivity across the GB and as a consequence the mobility of the GB. The magnitude of this effect would be of course a function of the solute content and this dependence will lead to a non-trivial behaviour of the solute drag as a function of the solute content.

Following Cahn, the velocity v of the moving GB under the driving force F is given by

$$v = M[F - P_i(c_0, v)],\qquad(1)$$

where P is the solute drag given by

$$P_i = -N_v \int_{-\infty}^{\infty} [c(x, v) - c_0]\frac{\mathrm{d}E}{\mathrm{d}x}\mathrm{d}x.\qquad(2)$$

The concentration profile around the GB is given by

$$c(x) = c_0 v \exp\left(-\frac{E(x)}{kT} - v\int_{x_0}^{x}\frac{\mathrm{d}\eta}{D(\eta)}\right)\int_{-\infty}^{x}\exp\left(\frac{E(\xi)}{kT} + v\int_{x_0}^{\xi}\frac{\mathrm{d}\eta}{D(\eta)}\right)\frac{\mathrm{d}\xi}{D(\xi)}.\qquad(3)$$
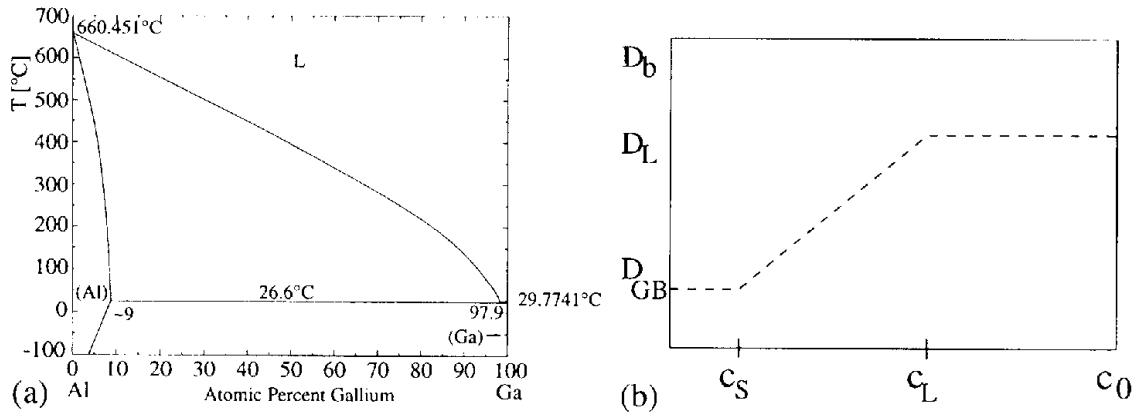
The mobility M can be related to the diffusion coefficient D_b across the GB by the relation proposed by Turnbull (1951):

$$M(D) = \frac{DV_m}{2\delta kT},\qquad(4)$$

where V_m is the atomic volume, 2δ is the width of the GB, k is the Boltzmann constant and T is the absolute temperature. In the absence of a liquid layer, D is equal to the standard GB diffusivity D_{GB}. In the case where a liquid layer covers completely the GB, D is identical with the diffusion coefficient D_L in the liquid state. For partial coverage of the GB, D will be approximated by a weighted average of the two diffusion coefficients. This amounts to assuming parallel paths through the GB across liquid-like and solid-like regions. The problem is therefore to determine the rate of coverage of the GB as a function of the solute content c_0.

In the phase diagram shown in fig. 1 (*a*), two critical concentrations can be identified for a given temperature T. When the concentration is between c_S and c_L there is coexistence of the liquid and solid phase, the volume fraction of each being

Fig. 1

700 |660.451°C
T[°C] 600
500
400 L
300
200
100
(Al)
0 /~9   26.6°C   97.9 29.7741°C
(Ga)—
-100
0 10 20 30 40 50 60 70 80 90 100
(a) Al   Atomic Percent Gallium   Ga

D_b
D_L
D_GB
(b) c_S   c_L   c_0

(*a*) Phase diagram of the Al-Ga system (Massalski *et al.* 1990). (*b*) The diffusion constant D_b in the GB as a function of the concentration c_0. c_S and c_L are the concentrations of the solidus and liquidus line respectively.

given by the lever rule. For simplicity and in the absence of more detailed evidence, we shall assume that this phase diagram still holds at the GB. Depending on the GB concentration c_{GB} (which is related to the nominal solute content c_0, the interaction energy and the GB velocity), the diffusion coefficient D will be different. The simplest possible assumption is to take a linear dependence as shown in fig. 1 (*b*) and a profile as shown in fig. 2 (*b*). Owing to segregation, the maximum solute concentration at the GB can exceed the concentration c_S of maximal solubility at a given temperature.

Fig. 2

(a)   E(x)

-δ   δ   x

E_0

(b)   D

D_L

D_GB

D_S

-δ   δ x
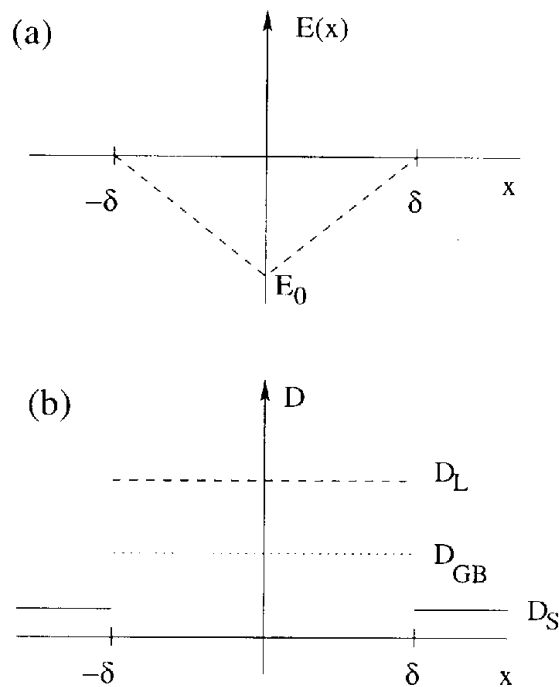
(*a*) The interaction potential of the impurities with the GB. (*b*) The diffusion constant in the GB.

If the concentration in the GB is between the solidus and liquidus concentrations, the diffusion constant increases linearly from the GB diffusion constant D_{GB} to the liquid diffusion constant D_L.

To illustrate our model, we have chosen typical values for the parameters adapted to diffusion in aluminium at $T = 700$ K which corresponds to the range of temperatures explored in experiments (Molodov et al. 1995). Reasonable values for the diffusion coefficients are $D_{GB} = 10^{-10}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ (Kaur et al. 1989) and $D_L = 10^{-8}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ (Kaur et al. 1995). The critical concentrations c_L and c_S were estimated from the phase diagram: $c_S = 0.05$ and $c_L = 0.4$ at $T = 700$ K. The estimation of the binding energy E_0 is not easy. A value of $E_0/kT = -4$ corresponding to a binding energy of 0.2 eV is in the range of admissible estimates. The detailed shape of the interaction potential $E(x)$ is even less known; following Cahn (1962) we have chosen a triangular attractive potential as shown in fig. 2 (a). The width b of the GB is taken to be equal to 0.5 nm.

To discuss our results, we shall consider on the one hand the variable c_0 which is the nominal solute concentration and on the other hand the energy parameter E_0 (which is poorly known). A systematic investigation of the expected GB behaviour as a function of both parameters is performed. In the E_0–c_0 plane, lines of equal GB concentrations can be drawn (fig. 3). In region 1 no quasiliquid phase is present. In region 3 the GB is covered by a quasiliquid phase and in region 2 a mixed situation is expected. In both region 1 and region 3 the mobility of the GB will be independent of the nominal solute concentration c_0: classical solute drag behaviour is then expected; for a given driving force the velocity will decrease with increasing solute content. In region 2, adding solute atoms has two effects: increasing the surface fraction of a quasiliquid GB and increasing solute drag. From these competing effects will result the unexpected concentration dependence of the velocity. The experimental results have been obtained with a driving force of capillary origin in either grain growth (Straumal et al. 1995) or bicrystal experiments (Molodov et al. 1995). As a

Fig. 3
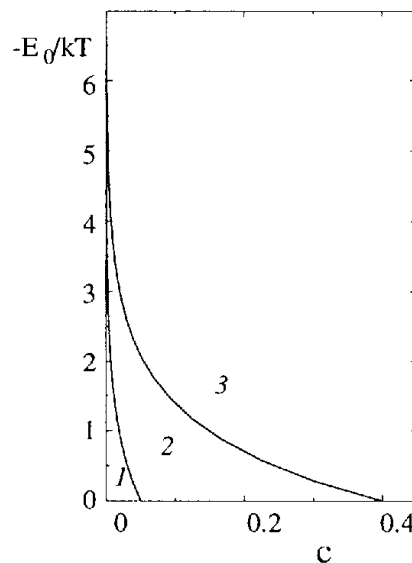
Lines of constant GB impurity concentration; $c_S = 0.05$ and $c_L = 0.4$.

Fig. 4
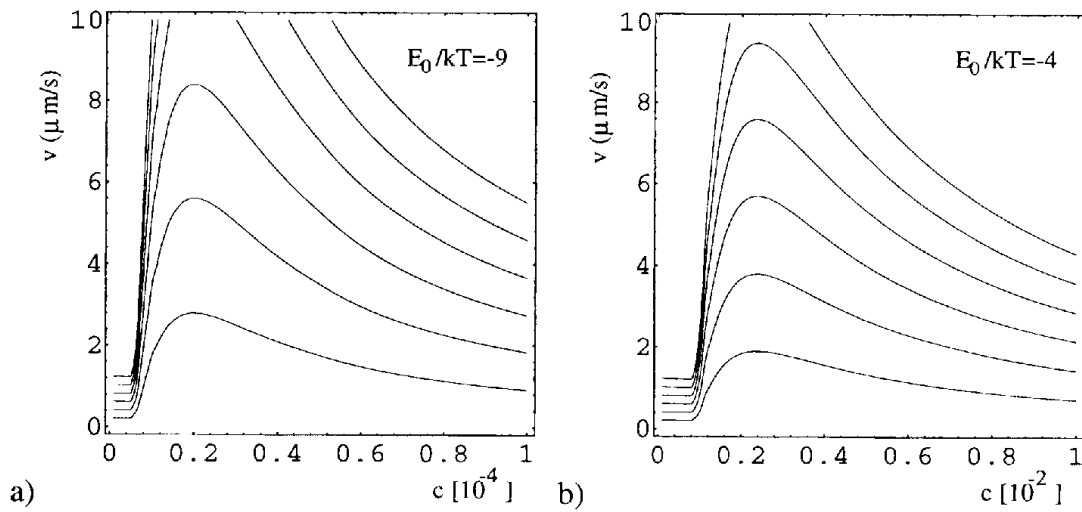
Lines of constant driving force with (*a*) $E_0/kT = -9$ and (*b*) $E_0/kT = -4$ and $T = 700$ K.

consequence the chosen values for *F* will range between 500 and 3000 N m^{-2}. Figure 4 (*a*) shows for this range of driving forces a non-monotonic dependence of the velocity as a function of the solute content for $E_0/kT = -9$. There is an acceleration of the GB velocity (of an order of magnitude) for solute contents lower than 10^{-5}, consistent with experimental observations (Molodov *et al.* 1995). For larger solute contents, standard solute drag behaviour is observed as suggested by grain growth experiments (Straumal *et al.* 1995). Figure 4 (*b*) shows for $E_0/kT = -4$ qualitatively identical results shifted in the direction of higher concentrations. When the temperature is increased (fig. 5), the maximum is less pronounced and tends to disappear since the difference between GB and liquid diffusion tends to disappear too.

Fig. 5
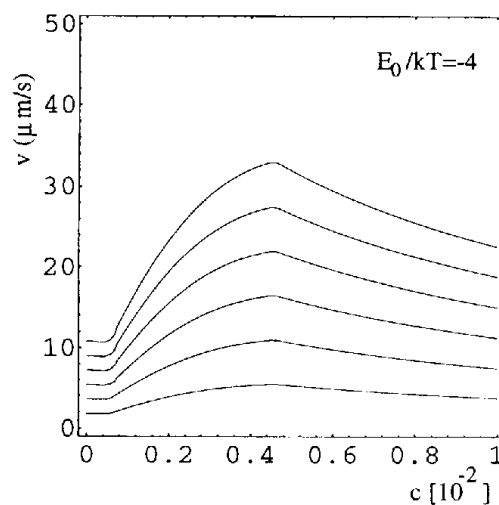
Lines of constant driving force with $E_0/kT = -4$ and $T = 800$ K.

§ 3. CONCLUSIONS

We have shown in the present contribution that the idea of a liquid-like phase at the GB proposed to explain the anomalous behaviour of grain velocity with a small addition of Ga can be made quantitative and can explain the order of magnitude of the effect. The present model allows to understand the qualitative non-monotonic behaviour of the grain growth kinetics as a function of the solute content and potentially predicts its dependence with respect to temperature. The experiments on bicrystals reported by Molodov *et al.* (1995) are probably the most direct way to check such predictions, provided that they are performed in a range of temperatures and solute concentrations c_0.

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