



Diffusion in Solids and Liquids XI

Edited by
A. Öchsner, G.E. Murch, A. Shokuhfar
and J.M.P.Q. Delgado

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Diffusion in Solids and Liquids XI

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Edited by

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and J.M.P.Q. Delgado**



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CONCENTRATION DEPENDENCE OF GRAIN BOUNDARY DIFFUSION

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Abstract. According to different experimental data the grain boundary diffusion the triple product (P) can change in opposite directions after alloying. In this paper the analysis of the effect of alloying for different systems is proposed. It was shown that in Al-based system (Cu diffusion in Al, Zn diffusion in Al) the P value increases with alloying while the solidus temperature according to the phase diagram decreases, in other systems no such tendency can be seen. Estimations based on the segregation factor value demonstrate that some structural effect must be proposed in addition to describe the experimental results.

Introduction

To predict the behavior of diffusing elements in real material it is necessary to take into account not only the mobility of diffusing element in pure materials, but the dependence of the diffusion parameters on concentration of all elements in the system. If for bulk diffusion the main effects are already described and, on the base of that, some approaches for the complete description of diffusion process in multi-component system have been elaborated, the concentration dependence of grain boundary diffusion (GBD) parameters is much more complicated. To analyze the situation, here the main effects for concentration dependence of bulk diffusion coefficient are described. The main approach includes data about the thermodynamic activity of the components (e.g. using the CALPHAD approach) and atomic mobility for each diffusing components (see e.g. the DICTRA approach). The more or less complicated treatment of the diffusion problem has allowed to obtain good agreement with the experimental results.

The grain boundaries in polycrystals are less studied objects. It is evident that it is practically impossible to get all the necessary data. That is the reason why it is interesting to look on qualitative description of this question and what can be taken from the approach developed for bulk diffusion to describe GB diffusion.

First of all, it is necessary to be precise about the mechanism of diffusion (vacancy or interstitial). Metal/metal systems is characterized mainly by vacancy diffusion mechanism in the bulk and here, special attention will be paid to such systems:

For elements forming a substitutional solution the pre-exponential factor of bulk diffusion coefficient D_0 weakly depends on concentration being equal approximately $10^{-4} \div 10^{-6}$ m²/s for different systems. It can be easily explained by the fact that the structure of the solution does not change significantly and only the lattice parameters (connected directly with diffusion jump length) change in some limits. On the other hand the diffusion activation energy mainly follow the solidus line (see e.g. dependence of concentration dependence of diffusion coefficient in Ti-Nb [1], Cu-Au [2]). It gives as a general result the decreasing of diffusion coefficient with concentration if the solidus line goes up.

Taking into account that the diffusion driving force is not exactly the gradient of concentration, but the gradient of the thermodynamic activity (more precisely the gradient of chemical potential) the diffusion equation must be rewritten. For example, in dilute solution it is easy to show that instead of changes of diffusion equation the diffusion coefficient can be expressed in the Darken form [3]

$$D_i^{non-ideal} = D_i^{tr} \cdot \left(1 + \frac{\partial \ln \gamma_i}{\partial c_i} \cdot c_i \right) \quad (1)$$

where $D_i^{non-ideal}$ is the diffusion coefficient of the i -th component in a non-ideal solution; D_i^r is the diffusion coefficient of the i -th component in an ideal solution, obtained, for example from radiotracer experiments; γ_i is activity coefficient of the i -th component in the solution with concentration c_i .

Note, that this substitution take into account only the change of thermodynamic driving force and does not include the change of atom mobility. Sometimes, this effect is of great importance, but for the binary system, even with a high value of mixing enthalpy, we can neglect by this term because of small concentration (see e.g. [4]).

The situation became more difficult if we speak about grain boundary diffusion (GBD). It concerns not only the measurement of diffusion parameters (mainly the results are obtained in the so called 'B' regime of GBD according to Harrison's classification). Unfortunately, neither the GBD mechanism nor the thermodynamic properties of the GB solution are determined for a non-special GB. As for kinetic parameters the so called GBD triple product ($P = s\delta D_b$) can be determined from experiments and this value is used to describe the process. Here $s = c_b/c$ is the GB enrichment coefficient (ratio of GB concentration to bulk concentrations near the GB), δ is the GB width and D_b is the GB diffusion coefficient [5]. These three factors can change independently, but, they can change simultaneously because of some more general changes e.g. if the GB structure changes (such a change with temperature was demonstrated [6], and change of chemical composition of GB can play the same role).

Description of Experimental Results.

Acceleration of GBD. The effect of the GBD triple product increasing after preliminary alloying was observed only in several systems. These are: Zn diffusion in Al and Al-Zn alloys [7]; Cu diffusion in Al, Al-Cu alloys and in Al doped by Ce [8, 9], by Si and by Mg [10]; Fe diffusion in Al and Al-Cu [11, 12] alloys. In Figure 1 the results of the works [7-9] are presented as Arrhenius plots.

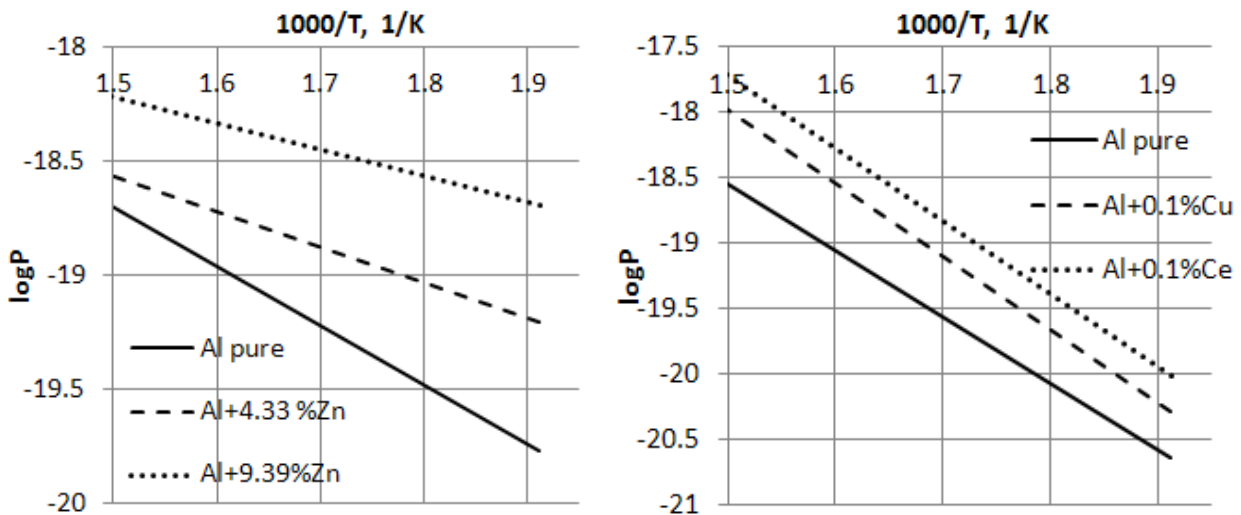


Fig. 1 The temperature dependence of the grain boundary diffusion triple product for Al-Zn/Zn (a), Al-Cu/Cu and Al-Ce/Cu (b) systems.

We can see the difference in these two pictures. At the first of them the decreasing of the activation energy can be seen. On the second plot the obtained data correspond to almost equal value of activation energy (the increasing of EA value was less than 10%). It should be noted that the calculation of the P value for Cu GBD in pure Al made by EDX analysis in concentration region 0.2-3 % and by measuring the angle of iso-concentration profile at the concentration level less than 0.01% did not show any concentration dependence [13]. But the diffusion in preliminary alloyed Al at the level of 0.1 % is 2-3 times faster. It means that GB in preliminary alloyed Al and in pure Al are not the same.

Slowing down of the GBD. One can find a number of results, demonstrated the depletion of the GBD by alloying. The largest set of the results was obtained on Cu, and here some of them will be included for the following discussion.

One of the first (historically) result was decreasing of the S diffusion rate in Cu after alloying of small quantity of Fe [14]. Later, it was shown that:

- the addition of Fe slows down also the diffusion of Ag [15] and Fe [16].
- Small addition of sulfur changes by 2-3 times the self-diffusion of Cu, and also diffusion of Ni in Cu [17, 18].
- Ag preliminary added to Cu changes by 2-3 times Ag diffusion [19].

Note, that these results are interesting because the same macroscopic effect can be seen in the systems with different types of interaction between diffusing and alloying elements, e.g. Fe atoms are neutral for a Fe-Fe pair, strong attractive in Fe-S and repulsive for Fe-Ag.

Ag is a segregated element on Cu GB while Fe is not. But both elements change significantly the diffusion rate of themselves.

It is important to mention that in all these cases (if reported) the activation energy in non-pure materials was of a higher value than for pure.

Discussion.

In almost all discussion about this question the main explanation is based on the role of segregation. The main approach was to take into account the change of the flux from GB to the bulk, because of non-equality of the GB and bulk concentration (near the GB). Starting from the work of Gibbs, the modification of Fisher model was made in the term, describing this flux (last term in the right part of equation):

$$\frac{\partial c_b}{\partial t} = D_b \frac{\partial^2 c_b}{\partial y^2} + \frac{2D}{\delta} \left(\frac{\partial c}{\partial x} \right)_{x=\pm \frac{\delta}{2}} \quad (2)$$

It was introduced by substitution $C = C_b/s$. Because of this fact the penetration depth, which can be described by Fisher's length $L = \sqrt{\frac{s\delta D_b}{2}} \sqrt{\frac{\pi \cdot t}{D}}$, increases proportionally to $s^{1/2}$. In the same way the different non-linear segregation effects were taken into account, e.g.:

-saturation effect in the Langmuir-McLean form, effect of chemical interaction in the Fowler form [20]

-effect of GB nonuniformity [21]

The modified solutions give the main effect in decreasing of the GB penetration depth and in curving of the concentration profile in semi-logarithmic coordinates. These models described the depletion of GBD in a qualitative way. But in a quantitative way they do not work well. It can be illustrated on the system Ag/Cu. The decreasing of P value is 2-3 times in dependence on the temperature. The estimation of segregation factor (Langmuir-McLean constant) in very dilute solution b is between 20 and 100 and we can take 100 as a maximal value. Estimation of the change of s value at the concentration of Ag 0.091% gives:

$$s = \frac{c_b}{c} = \frac{b}{1-c+bc} \approx 90 \quad (3)$$

It means that the change in P value must be around 10% but not 50%. Other factors give an even smaller effect.

Later, it was suggested to take into account the effect of chemical interaction in the form of complex formation [22, 23]. This model takes into account two different effects: the change of s factor as a function of concentration (change of the flux from GB to the bulk), and the modification of GB flux because not all atoms participate in the GB diffusion process (atoms which form the complexes are excluded from it). Application of this model for description of Cu GB diffusion in Al

gives reasonable results. In Fig. 2 the plots demonstrating the effect of complex formation on segregation and diffusion are presented. In this calculation the parameters b and K (b is the equilibrium constant for atomic segregation and K is equilibrium constant for atomic complex formation at GB) were varied. Increasing of K value increases the number of Cu atoms participated in atomic complexes formation and excluded from the diffusion process. The right picture demonstrates that the effective Fisher length (distance where the concentration decreases in 'e' times) decreases with increasing K value. The GB diffusion and bulk diffusion parameters were taken as for Zn GB diffusion at 400 °C) [24].

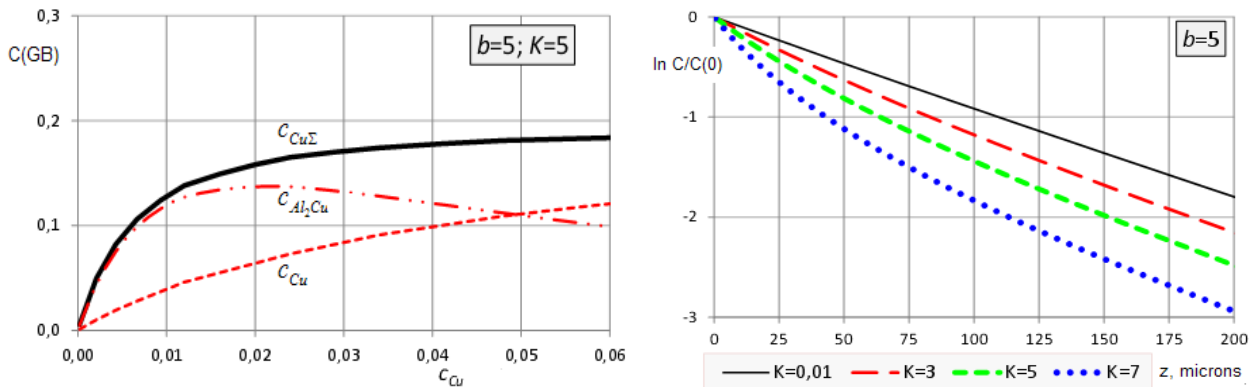


Figure 2. Distribution of Cu atoms on GB between Al_2Cu complexes and free Cu atoms (a) and concentration profile of Cu GB diffusion (b).

One more effect must be taken into account. The atoms involved in chemical interaction cannot participate in the diffusion process, but also, these atoms decrease the number of available sites for diffusion in GB. This effect description was suggested in [9] to describe the decreasing (in 1.5 times) the GB diffusion of Ag in Cu, alloyed by Fe. This effect can be described as pure geometrical decreasing of the effective GB diffusion coefficient.

As can be seen these effects cannot describe the increasing of P value after alloying. Decreasing of solidus line according to phase diagrams means the increasing of homological temperature for constant temperature of diffusion annealing, and in this case the increasing of triple product is understandable, although as a qualitative estimation only. For example, for the Al - based systems mentioned above the minimal solidus temperature correspond to eutectic temperature and it is 640 °C for Al-Ce, 546 °C for Al-Cu and 381 °C for Al-Zn. But no correlation between eutectic temperature and activation energy can be observed. But it can be supposed that in a system with positive segregation the change in GB chemical composition leads to increasing of atom mobility on GB.

Summary

To summarize the argument mentioned above it can be noted that to predict the concentration dependence of the GB diffusion process in the 'B' regime, several effects, which are determined by GB concentration and GB structure, must be taken into account:

- The change of the flux from GB to the bulk (GB enrichment factor);
- The change of the number of diffusing atoms and of the sites available for diffusion (factor of chemical interaction);
- The change in individual atoms mobility (diffusion coefficient).

These effects must be included separately in the GB diffusion equation and only their combination allows to describe the total changes.