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## DETERMINATION OF GRAIN BOUNDARY WIDTH AND GRAIN BOUNDARY Cu DIFFUSIVITY IN Al-5% Cu

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### Abstract

Changes in Cu concentration, both along the grain boundary and in the surrounding matrix, was measured in an Al-5 wt % Cu alloy. The size evolution of  $\theta$  phase ( $\text{CuAl}_2$ ) grain boundary allotriomorphs, as a function of time, was concurrently examined to allow investigation of both the grain boundary width and diffusivity. Kinetics of precipitate growth were modeled using the Brailsford and Aaron treatment of the collector plate mechanism. Diffusion of Cu from the matrix to the grain boundary allotriomorphs was modeled using Fisher's treatment of grain boundary diffusivity. The results of these models were used to assign values to both the width of a grain boundary and the Cu diffusivity within the boundary. It was determined that a grain boundary having a misorientation of 20 degrees has a diffusivity of  $D_b = 17.0 \exp\left(\frac{-10833}{T}\right) \text{cm}^2 / \text{sec}$  and a width of 0.85 nm.

### Introduction

Polycrystalline materials, to a large extent, are affected by their grain boundaries. Metallurgical processes, such as Coble creep, sintering, recrystallization, and diffusion-induced grain boundary migration are just a few of the processes that are greatly influenced by grain boundaries. There remains much to be learned about the relationship between grain and interface boundaries, their boundary structure and resultant effects on the mechanical and thermal phenomena.

Diffusion in polycrystalline materials has long been known to occur more rapidly along grain boundaries than through the interior of crystals. To facilitate quantitative investigation of grain boundary diffusion, Fisher has presented a mathematical analysis of the problem [1]. In his model, Fisher demonstrated that the problem of grain boundary diffusion is analogous to the diffusion of heat along a thin copper foil embedded in cork. Fisher was able to obtain good agreement with experimentally determined grain boundary self diffusion of silver [2].

It has been shown that the growth of  $\theta$  ( $\text{CuAl}_2$ ) at grain boundaries proceeded faster than volume diffusion would allow. This led to the development of the 'collector plate' mechanism of growth by Aaron and Aaronson [3] later modified by Brailsford and Aaron [4]. In the collector plate mechanism, the grain boundary acts as a fast diffusion path for the solute and gives the precipitate

a much larger collection area for solute than just the grain boundary precipitate's own surface area.

In all previous work, when accounting for the effect of grain boundary diffusion on material properties, it has not been possible to isolate the effect of the grain boundary diffusivity from the effect of grain boundary width. Usually a grain boundary width is assumed (e.g., 1 nm), allowing the grain boundary diffusivity to be estimated. In the present investigation a method has been formulated by which the grain boundary width and the grain boundary diffusivity may be arrived at simultaneously.

### Experimental Procedure

A high purity Al-5 wt. % Cu alloy was solutionized at 550 °C for 2 hours. Samples were then isothermally transformed at 200 °C for 18 seconds, 1, 30, and 60 minutes. Following heat treatment, the material was sectioned with a low speed saw and 3 mm disks were spark-cut from the sample. A twin-jet electropolisher was used to prepare the samples and precipitate lengths and widths were measured in a 120 keV Transmission Electron Microscope (TEM).

The time dependencies of lengthening and thickening were determined by measuring the largest allotriomorph for each misorientation studied. The misorientation for this work is defined as the minimum angle about an axis that one lattice must be rotated in order to bring it into complete coincidence with the second lattice [6,7].

The Cu concentration was measured using a 200 keV TEM with a field emission gun. This allowed a highly focused beam to give spatial resolutions of approximately +/- 1 nm. The most effective concentration measurements were made along an axis perpendicular to the grain boundary. The measurements ranged from the bulk value in the matrix far away from the grain boundary in one grain, to the value in the grain boundary, and then ranging out to the bulk value in the second grain. When possible the measurements were taken starting from the precipitate grain boundary interface and going out along the grain boundary to half the distance between precipitates.

### Results

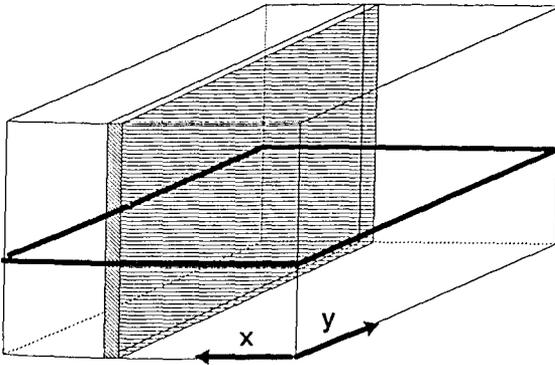
The modeling of the precipitate growth results from the Brailsford-Aaron calculations give a solution to the grain boundary diffusivity in the form of  $D_b \delta = \text{CONSTANT}$  [4,5], where  $D_b$  represents the grain boundary diffusivity and  $\delta$  represents the grain boundary width. These precipitate growth results were taken from the same grain boundaries as the Cu concentration measurements, and have been previously published [5]. Table 1 summarizes the results obtained for  $D_b \delta$  as a function of misorientation. For the following calculation the diffusivity and the width of a 20 degree grain boundary will be examined applying the initial conditions for Cu concentration employed by Brailsford and Aaron. Specifically these are:

- (1) The grain boundary is assumed to have the same initial composition as the matrix, in the present case 2.2 atomic %.
- (2) The matrix:precipitate and the grain boundary:precipitate interface is assumed to have a composition given by:

Table 1 Results of  $D_b \delta$  Calculation from Brailsford-Aaron Model of Grain boundary precipitate growth [5].

Misorientation	$D_b \delta$
20 degrees	$2.495 \times 10^{-10}$
30 degrees	$5.972 \times 10^{-10}$
40 degrees	$8.951 \times 10^{-10}$

a)



b)

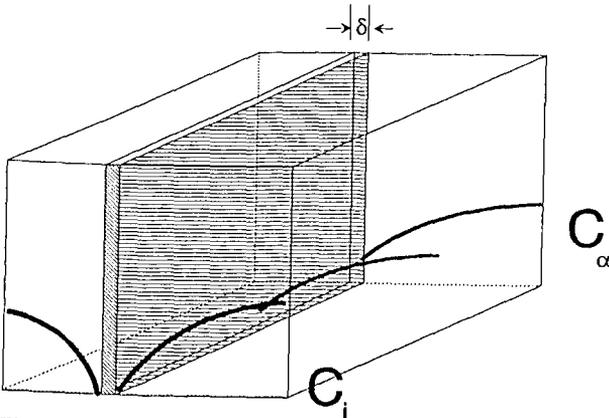


Figure 1. a) qualitative demonstration of the initial conditions used for Brailsford and Aaron's growth calculation and for the solution to Cu concentration employing Fisher's time dependent grain boundary diffusion expression. b) qualitative demonstration of the Cu concentration profile after 1 min. at 200C.

$$C_{\alpha 0} = 5.15 \exp(-4671/T) \quad (1)$$

These same initial conditions used by Brailsford and Aaron will be adopted with Fisher's equations to model the Cu concentration in the area of the grain boundary. Fisher gives the variation of solute in and around the grain boundary as:

$$\frac{\partial C}{\partial t} = D_b \left( \frac{\partial^2 C}{\partial y^2} \right) + \left( \frac{2}{\delta} \right) D_v \left( \frac{\partial C}{\partial x} \right) \quad (2)$$

where  $y$  is the distance along the grain boundary,  $x$  is the distance perpendicular to the grain boundary,  $D_b$  is the grain boundary diffusivity,  $D_v$  is the matrix diffusivity,  $C$  is the Cu concentration and  $t$  is the time (figure 1). Brailsford and Aaron presented a detailed solution to the problem of a growing grain boundary allotriomorph and obtain the expression for  $D_b \delta$ :

$$D_b \delta = \frac{(C_0 - C_{\alpha 0}) \lambda^3}{(C_{\alpha} - C_{\alpha 0}) t_0}, \quad (3)$$

where  $\lambda$  is simply a scale factor that they used for the half length of the precipitate, and  $t_0$  is a dimensionless fitting parameter determined by fitting the volume change of the precipitate as a function of time.  $C_0$  is the composition in the precipitate,  $C_{\alpha 0}$  is given by equation 1, and  $C_{\alpha}$  is the bulk composition in the matrix. At any given temperature the solution to (3) is a constant. Table 1 summarizes the results obtained from this calculation as a function of misorientation. Using the solution to this equation at 200°C allows  $D_b$  to be expressed solely in terms of  $\delta$ . This information, used with Fisher's equation (equation 2), allows all variables to be determined except for grain boundary width and Cu concentration at 200°C.

Thus, when concentration data are available, the grain boundary width is obtained by solving Fisher's equation for different grain boundary widths until a satisfactory fit of the Cu concentration data is obtained. The solution to Fisher's equation can be obtained using finite difference techniques.

The results from solving for the concentration around the grain boundary are compared directly with the experimental data collected. Figure 1 illustrates the problem setup for this calculation. It is assumed that each grain represents an equal source of Cu solute, making no allowances for anisotropy in volume diffusivity. The grain size is large ( $> 40 \mu\text{m}$ ) and it is assumed that each grain boundary acts independently of its neighbors. The grain boundary represents a plane of symmetry for the problem, and thus the solutions are calculated for the half-space of the grain boundary and one grain. It is further assumed that a plane of symmetry exists at half the distance between precipitates. Each precipitate is considered to act independently and equally as a sink for solute at the grain boundary. This gives a second plane of symmetry for the problem that is perpendicular to the grain boundary plane and located at one-half the distance between precipitates. Finally it is assumed that there is no height effect to be accounted for, the solution for the Cu concentration in any  $x$ - $y$  plane is considered to be equivalent, and thus the final solution for Cu concentration is calculated for the quarter space of one  $x$ - $y$  plane at a 20 degree grain boundary within the polycrystalline sample.

The results of calculating the Cu concentration along an axis perpendicular to the grain boundary, using the  $D_b \delta = \text{CONSTANT}$  determined by the Brailsford and Aaron calculation, are shown as a function of grain boundary width in Figure 2. The experimentally collected Cu concentration data are represented in the graphs with large symbols, and the calculated concentration curves are

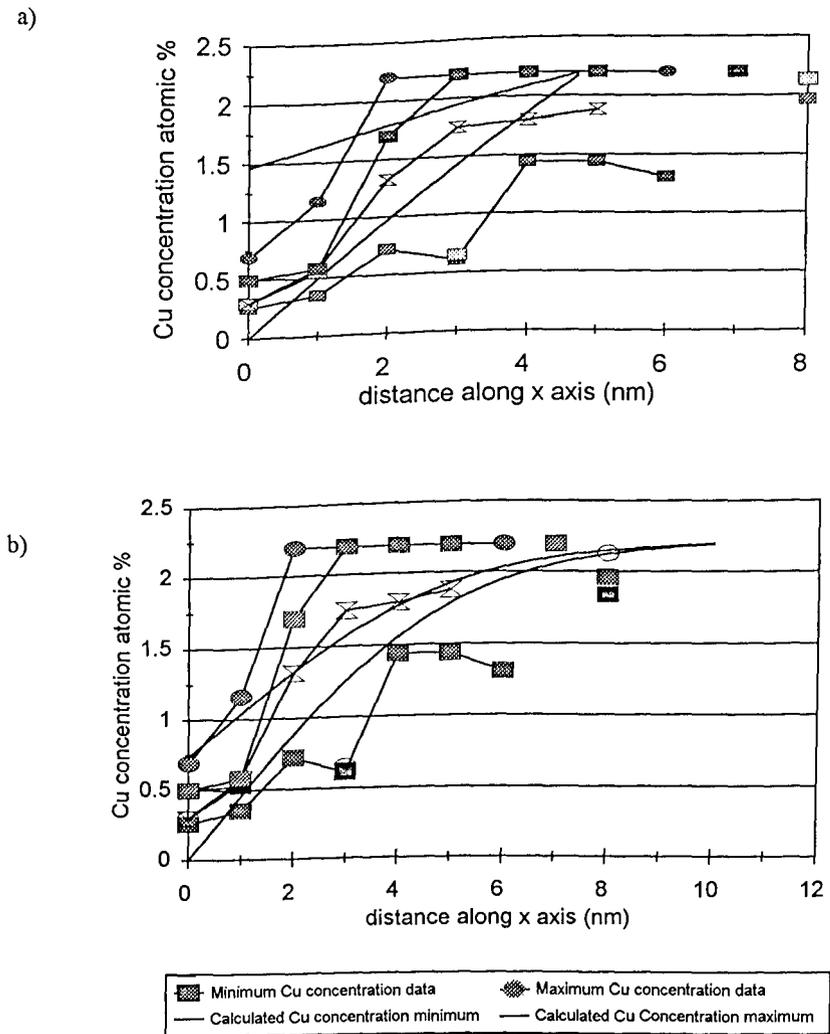


Figure 2. Comparison of Cu concentration data with calculated results. a) shows calculated concentration curves for a grain boundary width of 0.4 nm. b) demonstrates the concentration curves calculated for a grain boundary width of 0.85 nm.

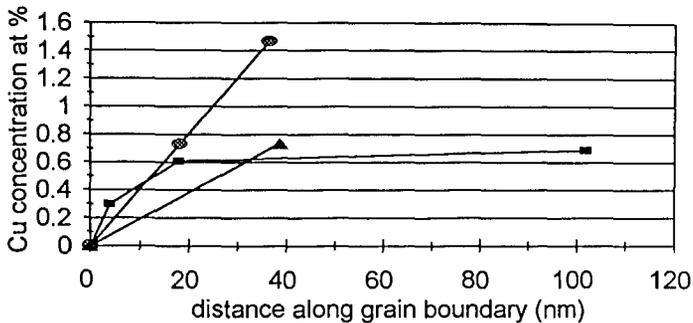


Figure 3. Experimental Cu concentration data in the grain boundary shown with theoretical Cu concentration values calculated for different grain boundary widths. Experimental data values shown with square symbol. Calculated Cu concentration values for a grain boundary width of 0.4 nm are shown with circles. Theoretical Cu concentration values for grain boundary width of 0.85 nm shown with triangles.

shown with lines. The bottom theoretical curve in each of the graphs represents the concentration along an axis perpendicular to the grain boundary plane and starting at the precipitate grain boundary interface. The top curve in each of the figures represents the calculated concentration at half the distance between precipitates. Thus the difference between the two curves represents the maximum theoretical difference in Cu concentration that can be obtained in the matrix as a function of position along the grain boundary.

The Cu concentration has also been calculated as a function of position in the grain boundary (Figure 3). The grain boundary assumed having a width of 0.4 nm is found to achieve a maximum Cu concentration of 1.5 atomic %. Cu concentration calculations using a grain boundary width of 0.85 nm have maximum Cu concentrations near 0.7 at %. The experimental concentration data are found to have a maximum Cu concentration value of 0.6 atomic %.

### Discussion

Table II. Diffusivity at 200° C as a function of grain boundary width.

Width	Diffusivity
0.4 nm	$6.237 \times 10^{-3} \text{ cm}^2/\text{sec}$
0.85 nm	$2.935 \times 10^{-3} \text{ cm}^2/\text{sec}$

A comparison of Figures 2a and b reveals that as the grain boundary width is increased, the difference between the maximum and the minimum Cu concentration curves decreases. This can be explained as increased Cu diffusing down the grain boundary channel as the grain boundary width is increased. Thus in a diffusion limited process such as grain boundary precipitate growth, less Cu is able to build up between precipitates in a wider grain boundary.

In Figure 3 it is seen that a grain boundary width of 0.4 nm allows the Cu concentration to build up to a maximum value of 1.5 atomic % between precipitates. When the grain boundary width is

given a value of 0.85 nm the maximum calculated Cu concentration value between precipitates is about 0.7 atomic %. The Cu concentration data collected at the grain boundary indicate that the maximum Cu concentration between allotriomorphs is about 0.6 atomic % Cu. Thus a grain boundary width of 0.85 nm is able to match the experimental Cu concentration data in the grain boundary much more accurately than can be achieved with a grain boundary width of 0.4 nm. Table 2 summarizes the calculated diffusivity for grain boundary widths of 0.4 nm and 0.85 nm.

### Conclusions

(1) Modeling the growth of grain boundary precipitates together with the resulting change in Cu concentration around the grain boundary allows simultaneous determination of the grain boundary width and the grain boundary diffusivity.

2) The grain boundary width for a 20° grain boundary at 200 C has been estimated to be 0.85 nm.

3) The grain boundary diffusivity for a misorientation of 20 degrees has been determined to be

$$D_b = 17.046 \exp\left(\frac{-10833}{T}\right) \text{cm}^2 / \text{sec.}$$

### Acknowledgments

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