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Numerical Study of Grain Boundary Diffusion: Size Effects

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1. Introduction

Enhanced diffusivities along grain boundaries (GBs) are highly relevant for the preparation as well as for the performance of many polycrystalline materials. The importance of GBs is even further increased, if materials are characterized by a high density of interfaces. In such cases, for example in nanocrystalline materials, experiments to determine diffusion coefficients are not straightforward, because diffusion lengths have to become extremely small. In this contribution we analyze effects related to small diffusion lengths in the bulk (grain). First, a modified "Le Claire's constant" is calculated on the basis of an isolated boundary model [1] by integrating Whipple's solution [2] and, second, the microcrystalline network (e.g. square grains) is taken into account, when calculating the diffusion profiles in the kinetic regimes of type B and A [3] by using a finite element approach.

2. Results and discussion

Different aspects should be discussed, when size effects come into play in the analysis of diffusion profiles in polycrystalline materials.

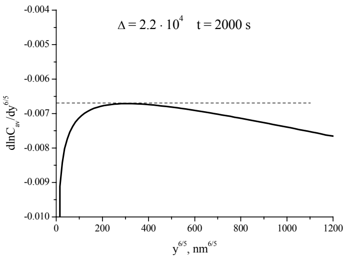

Fig. 1. A typical dependence of the derivative

i) The GB diffusion coefficients are often evaluated from the slope of $\ln C_{av} = f(y^{6/5})$ with y being the penetration depth and C_{av} denoting the concentration integrated along the coordinate parallel to the surface. We show that nonlinear profiles arise for a strongly reduced diffusion annealing time. In this case the derivative of the dependence has a maximum (fig. 1). If the used part of the profile exceeds the position of the maximum, errors in the deduced GB diffusivity result, when fitting the profile by a straight line according to the findings of Levine and MacCallum [4] and Le Claire [5].

ii) The parameter $w = \frac{y}{\sqrt{D_g t \beta}}$ was successfully used by Le Claire in order to suggest an expression for the product δD_{gb} [5], where δ and D_{gb} are the GB thickness and diffusivity, respectively (D_g: the grain diffusivity and t: the annealing time). The dimensionless quantity β shows the diffusion process is mostly due to the direct diffusion from the source and/or GB contribution. The derivative $d\ln C_{av}/dw^{6/5}$ was found to be constant (≈ -0.78), if $\Delta = D_{gb}/D_g \to \infty$ can be applied along the integration [1, 5]. We compared the results of integration of the exact Whipple's solution and Whipple's solution under condition $\Delta \to \infty$. As clearly seen in fig. 2 the solution with $\Delta \to \infty$ gives the value around –0.78, but the exact solution may be very far from this value. In fact, the derivative of the exact solution approaches "Le Claire's constant", if the diffusion annealing time increases. To generalize the problem we observed the dependence of the derivative as a function of $\alpha = \delta/2\sqrt{D_g t}$. The criterion found is that α should be less than at least 0.02 to apply Le Claire's relation, what is consistent with the results of Szabo et al. [6]. Moreover, the relation $d\ln C_{av}/dw^{6/5} \approx -0.77-0.71\alpha$ was found numerically, if $\alpha > 0.02$. We suggest the following evaluation procedure of D_{gb}: 1) take the maximum of the derivative $d\ln C_{av}/dy^{6/5}$, 2) calculate α and take the maximum of the derivative $d\ln C_{av}/dw^{6/5}$ properly, 3) put both derivatives in the expression for the δD_{gb} – product [5].

iii) In the conditions of small diffusion lengths in the bulk the spatial GB orientations with respect to the diffusion direction play a role, giving rise to additional changes in the profile slope, because the material cannot be further considered as a system of parallel boundaries. Each perpendicular GB leads to spikes in the profile (fig. 3), increasing the slope on average. Nevertheless, if one increases the annealing time, the differences between the models of square grains and parallel boundaries vanish. As a consequence, diffusion in both geometrical situations can be characterized by very similar effective diffusivities in the A – regime.

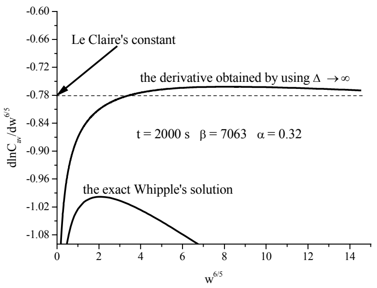

Fig. 2. Comparison of two solutions.

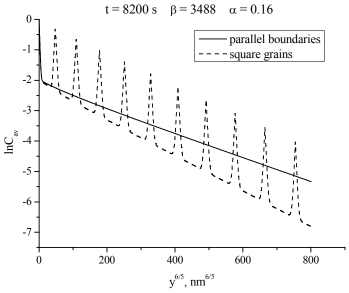

Fig. 3. Comparison of two models in the B – regime.

3. Conclusions

We have shown that a significant reduction of annealing time (small bulk diffusion length) gives rise to a nonlinearity of the diffusion profile and extremely large values of α. Perpendicular GBs in realistic microcrystalline polycrystals become important for short annealing times, leading to a possible underestimation of D_{gb}, applying the conventional procedure in the type B – kinetics.

References

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