Diffusion Kinetics in an Ensemble of Intersecting Grain Boundaries.  
The Role of a Size Factor  

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INTRODUCTION  

In [1], we used the Fisher quasi-steady state model [2] and derived equations to describe grain boundary diffusion (GBD) in an ensemble of three grain boundaries formed at triple junction. Diffusion proceeds successively along the grain boundaries so that the diffusion fluxes merge in the triple junction point (configuration of a grain boundary ensemble (GBE) of version I) or the diffusion fluxes are separated (GBE configuration according to version II). In contrast to [3] (where enhanced (as compared to GBD) diffusion was studied along a triple junction line, which was considered as a specific lattice defect in [3]), the problem studied in [1] belongs to another class of diffusion problems, namely, to diffusion kinetics characterized by different diffusion stages. From this standpoint, a triple junction point is a singular point in space in which the diffusion fluxes along the grain boundaries included in a GBE merge (or separate). The description of GBD in a GBE containing a triple junction point is directly related to the problem of damage of a metal during electromigration (i.e., diffusion under the effect of a direct high-density electric current) in thin metal films, which play the role of current-carrying layers in microelectronic devices [4, 5].  

In the approach proposed in [1] for describing GBE diffusion, each grain boundary from the ensemble has its specific GBD coefficient \( D_\alpha \) (\( \alpha \) is the grain boundary number) and, correspondingly, its Fisher diffusion length \( D_\theta \). An expression for the Fisher diffusion length is given in an explicit form in [6]. A triple point is at depth \( L_0 \) from a surface containing a diffusion source. Quantity \( L_0 \) is an important structural characteristic of GBE: it can be considered as an analog of the grain size in a polycrystal. In order to simplify the problem, it was assumed in [1] that the tilt angle of grain boundaries in the GBE to the surface containing diffusion source is the same and that these grain boundaries (i.e., tilted at an angle to the surface) have the same diffusion properties. In a GBE of version I, tilt boundaries have number 1; in a GBE of version II, they have number 3. The expressions obtained in [1] for diffusing matter (DM) concentration distributions in the grain boundaries of an ensemble have the form of functional parametric dependences in which the main argument is the ratio \( y/L_0 \) (\( y \) is the coordinate axis normal to the surface containing the diffusion source). The parameters of the problem are the ratios \( L_i/L_0 \) (\( i = 1, 3 \)), the angle \( \theta = \pi/2 - \phi \) (where \( \phi \) is the tilt angle to the surface containing the diffusion source), and the ratio \( \alpha = 0.5(D_{gb3}/D_{gb1})^{1/2} \). The DM concentration distribution in each grain boundary in the ensemble depends on the GBD coefficient of the grain boundary, the GBD coefficients of the other grain boundaries, and the structural characteristics of GBE (i.e., angle \( \theta \) and \( L_0 \)).  

In [1], we compared the DM concentrations in boundary 1 of an ensemble and in a single boundary (i.e., in bicrystal) and estimated the diffusion rate in GBE of versions I and II for the case \( L_1 = L_0 \) and \( \theta = 60^\circ \), which corresponds to an equilibrium state of a polycrystal with a triple junction angle of 120°. The comparison was preformed for a parameter \( \alpha = 0.125-2 \). The choice of the minimum value of parameter \( \alpha \) was based on the variation of the double product \( \delta D_{gb} \) (where \( \delta \) is the boundary width) fixed in experi-
ments on studying the GBD of zinc in aluminum bicrystals containing tilt ⟨100⟩ and ⟨111⟩ grain boundaries with different angles of misorientation [7]. It was shown that it is impossible to obtain a diffusion rate in any boundary of the considered GBEs that is higher than in a single boundary at \( \alpha = 0.5 \) (i.e., for the same GBE coefficients in all grain boundaries of an ensemble, which is the most often case for a polycrystal). The condition for enhanced diffusion (as compared to a single boundary) in grain boundary 1 of a version II GBE is the inequality \( \alpha < 0.25 \). In a GBE of version I, it was impossible to effect diffusion along grain boundary 1 of the ensemble that is faster than the diffusion in a single boundary at \( \theta = 60^\circ \) and \( L_1 = L_0 \) even in the hypothetic case of \( \alpha = 0 \).

The decrease in the diffusion rate in the GBE of version I at \( L_1 = L_0 \) and \( \theta = 60^\circ \) as compared to the diffusion rate in a single boundary is caused by the length of grain boundary 1, i.e., by the distance to be traveled by a diffusing atom to achieve the triple point. This distance is much longer than the corresponding distance in the bicrystal. The two channels providing diffusion of a matter to the triple junction in the GBE in version I do not provide the delivery of the required amount of matter per unit time as compared to the case of a single boundary. The aim of this study is to find the conditions imposed by a change in the ratio \( L_1/L_0 \) that provide faster diffusion in a version I GBE as compared to the diffusion in a single boundary at \( \theta = 60^\circ \), i.e., at a triple junction angle of 120°.

**ROLE OF A SIZE FACTOR**

At a fixed angle \( \theta \) (in our case \( \theta = 60^\circ \)), it is possible to change the conditions of DM delivery to a triple point only by changing the ratio \( L_1/L_0 \). If a polycrystal is considered as a “mosaic” composed of GBEs by according to versions I and II, a change in the ratio \( L_1/L_0 \) means that the relation between the GBD length and the grain size changes; i.e., the role of the corresponding size factor should be taken into account to analyze the diffusion kinetics. It should be noted that standard approaches to the description of GBD in a single boundary [2] or in a polycrystal [8] make such an analysis impossible. Taking into account that the Fisher model of GBD is quasi-steady state and \( L_1 \) depends weakly on time, a physically grounded change in the \( L_1/L_0 \) ratio is represented by a change in triple junction point depth \( L_0 \). To understand the character of the change in the distances traveled by DM atoms in grain boundary 1 in a version I GBE when the \( L_1/L_0 \) ratios changes, we juxtapose the diffusion “wedge” in a single grain boundary (SGB) characterized by diffusion length \( L_0 \) with the triple point of the GBE. Various positions of the triple point in the GBD zone in the bicrystal corresponding to a change in \( L_0/L_0 \) are shown in Fig. 1. It is seen that, as the ratio \( L_S/L_0 \) increases, the length of grain boundary 1 in the version I GBE decreases and, correspondingly, the efficiency of DM delivery to the triple point increases. Since the comparative analysis of the concentration distribution in grain boundary 1 of GBE and in the SGB is performed on condition that \( L_1 = L_S \), the length of grain boundary 1 decreases as the ratio \( L_1/L_0 \) will increases, as in the case of an increase in the \( L_S/L_0 \) ratio.

In general form, the effect of the size factor on the rate of DM delivery to the triple point can be estimated if the DM concentration at triple point \( c_{\text{gb}}^* \) is compared to the DM concentration in the single boundary \( c_{\text{gb}} \) at a depth \( y = L_0 \). Under the condition \( c_{\text{gb}}^* > c_{\text{gb}} \) \((y = L_0)\), the diffusion rate at the triple point of version I is higher than the diffusion rate in the SGB at a depth \( y = L_0 \); otherwise, the diffusion rate is lower. According to [1], the concentration at the triple point in a GBE of version I characterising by \( \theta = 60^\circ \) is

\[
c_{\text{gb}}^* = \frac{2c_0\exp[2(L_1/L_0)^{-1}]}{1 - \alpha + (1 + \alpha)\exp[4(L_1/L_0)^{-1}]},
\]

where \( c_0 \) is the DM concentration on the surface.