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Calculation of distribution of grain boundary energy over grain misorientations

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Introduction

Distribution of excess free energy over the network of grain boundaries in polycrystals is considered to be an important factor for properties and processes controlled by the boundaries. Assuming that grain boundary energy depends only on grain misorientations and is independent of the boundary orientation ("isotropic" case), the energy is equal to the magnitude of tension force. The equilibrium condition, understood as the balance of tension forces at a triple junction, determines relative values of energy for boundaries meeting at the junction. This method of estimating the distribution of energy over grain misorientations has been known since the Dunn and Lionetti experiments with tilt boundaries in silicon steel [1,2]. The main ideas of a similar experiment on much larger scale are described in [3]. It is based on using EBSP to determine grain orientations and on precision sectioning to obtain microstructural features, including true dihedral angles between boundaries at triple junctions. The ultimate goal is to take boundary orientations into consideration, but the first step is to get distributions over complete space of grain misorientations, without differentiating between boundary orientations. It means that an "average" energy over all boundary orientations is to be assigned to each misorientation. This paper presents a method to overcome the technical problem of tessellating the space of grain misorientations. We are particularly interested in homophase boundaries of materials with cubic (O_h) symmetry, and we will concentrate on this case.

Procedure

Let γ^i $(i = 1, 2, 3)$ denote the energy of the i-th boundary at the triple junction, and let $\mathbf{t}_i$ be a unit vector tangent to the i-th boundary (at the junction), perpendicular to the junction, and directed towards the boundary side of the junction. The Herring [4,5] equilibrium condition (without torque) has the form $\sum_i \gamma^i \mathbf{t}_i = \mathbf{0}$. By taking the scalar product of the Herring formula

and vectors $\mathbf{t}_j$, $(j = 1, 2, 3)$ one gets three equations

$$\sum_i (\mathbf{t}_i \cdot \mathbf{t}_j)\, \gamma^i = 0 \ . \tag{1}$$

The scalar product $\mathbf{t}_i \cdot \mathbf{t}_j$ is equal to the cosine of the dihedral angle between boundaries i and j. With known true dihedral angles and grain misorientations, one wants to calculate the distribution of γ over all possible grain misorientations. Each triple line provides equations (1) linear with respect to γ. The idea is to discretize the domain of the energy function so instead of a continuous misorientation g, the function depends on a discrete index, say m ($\gamma(g) \leftarrow \gamma(m) = \gamma_m$, $m = 1, ..., M$). Assuming N triple junctions are analyzed, this approximation of γ by a 'step function' leads to a system of $3N$ linear equations of the type (1) with respect to non-negative γ_m. They can be written as

$$\sum_m A_{km}\gamma_m = 0 \ , \qquad k = 1, ..., 3N \ . \tag{2}$$

The system is homogeneous, and we normalize the coefficients so for a given k they satisfy $\sum_m A_{km}A_{km} = 1$. Because of the homogeneity only relative values γ_m/γ_0 can be determined. From now on, the symbol γ_m denotes this ratio, not the absolute value of the energy. The constant γ_0 is chosen in such a way that the integral of the ratio over the 'misorientation space' is equal to 1, i.e., the distribution is normalized to 1.

To get the sought distribution, it is sufficient to solve the system (2) with respect to γ_m. It sounds simple but in practice, the procedure is complicated. The reason lies in difficulties with the discretization of the misorientation space and in symmetry requirements. The most obvious of these requirements is that the energy of the boundary between grains 1 and 2 is the same as the energy of the boundary between 2 and 1. Additional conditions arise from the crystal symmetry. The symmetries in the general case involving boundary orientations are considered elsewhere [6]. In the simplified situation, with γ depending only on grain misorientations, there must occur $\gamma(g) = \gamma(g^T) = \gamma(c_k g c_l)$, where g is the proper orthogonal matrix of grain misorientation, T denotes transposition, and orthogonal matrices c_k and c_l represent proper symmetry operations of the crystal point group. In the case of cubic symmetry, there are 24 proper (point) symmetry operations; hence, $k, l = 1, ..., 24$, and the number of equivalent misorientations at which the distribution must take equal values reaches $2 \times 24 \times 24 = 1152$.

A simple idea would be to use the asymmetric domain — a part of the space in which a physically unique misorientation is represented by a unique point. Such domains are known for all crystallographic symmetries in Rodrigues parameterization of rotations [7]. The problem is that even in Rodrigues parameterization the shape of the domain is relatively complex and all tessellations are rather awkward. Additional complications arise due to non-uniformity of the Rodrigues 'space'[1]. This makes the tessellation into cells of equal volume (which is most appropriate) even more difficult.

To avoid these problems we used the parameterization by Euler angles. With the angles $(\varphi_1, \phi, \varphi_2)$ defined as in [8] and $\Phi = \cos\phi$, the complete domain for all possible rotations is given by $0 \le \varphi_1, \varphi_2 < 2\pi$ and $-1 \le \Phi \le +1$. The asymmetric domain for cubic case in Euler angles parameterization is known [9], but its very complicated shape prohibits any reasonable tessellations. In what follows, the complete domain can be used but it is more efficient to use

[1]Random misorientation distribution is represented by non–uniform density in the parameter space. In other words, cells of equal shapes confine different volumes.

the sub–domain D with parameters φ_1, φ_2 in the range from 0 to $\pi/2$ and $0 \le \Phi \le \Phi_0 (\le +1)$. If $\Phi_0 \ge 1/3$ the domain D containes the asymmetric domain. To make our consideration simple we take $\Phi_0 = 1$ throughout the rest of the paper.[2] The points of this region are related to equivalent points outside it via translations and mirrors in the space of Euler angles, so it is easy to reconstruct the whole space. The relations between equivalent points within the domain D are complicated. The maximal number of equivalent points within D is $1152/(4 \times 4 \times 2) = 36$.

The advantage of parameters $(\varphi_1, \Phi, \varphi_2)$ lies in the fact that the space is uniform. (The invariant volume is given by $\mathrm{const} \times \mathrm{d}\varphi_1 \, \mathrm{d}\Phi \, \mathrm{d}\varphi_2$.) Therefore, the complete space can be tessellated into cells of equal volume by suitably selected planes $\varphi_1 = \mathrm{const}$, $\Phi = \mathrm{const}$, $\varphi_2 = \mathrm{const}$. This is also the case for the sub–domain D. Moreover, because the cells have equal volumes, normalization of the distribution is trivial: $\gamma_m \leftarrow \gamma_m (M / \sum_l \gamma_l)$, where M is the number of cells in the domain. The only disadvantage is that there are still equivalent misorientations within that domain and one must keep track of them when solving the system of equations.

A simple iteration was applied to solve the system (2). In the ideal case, the right–hand side of the equations vanishes. However, for the approximation known in the n-th iterative step, the sum $\sum_m A_{km} \gamma_m^{(n)}$ is non–zero. The deviation is used to modify values of the distribution in the next iteration step. In order to involve all symmetries, we actually use the residual $r_k^{(n)} = \sum_m A_{km} \Gamma_m^{(n)}$, where for each considered misorientation the quantity $\Gamma_m^{(n)}$ is the arithmetic average of values of $\gamma_m^{(n)}$ at all symmetrically equivalent locations within D. The iteration step we applied had the form

$$\gamma_m^{(n+1)} \;=\; C^{(n)} \;\max \left\{ \; 0 \,, \;\; \gamma_m^{(n)} - \frac{1}{N_m} \sum_k A_{km} r_k^{(n)} \; \right\} \,,$$

where $C^{(n)}$ denotes a normalization coefficient, and N_m is equal to the number of equations involving γ_m. The initial value is $\gamma_m^{(0)} = 1$. The quantity $R(n) = \sum_k \mid r_k^{(n)} \mid$ is a measure of discrepancy between a correct solution of the system and its approximation in the n-th iterative step. Decrease of $R(n)$ with growing n indicates convergence of the iteration process.

Tests

The simplest way to test the whole procedure is to assume a valid energy distribution, generate misorientations at triple junctions, calculate the corresponding dihedral angles, and finally, recalculate the distribution from the misorientations and the dihedral angles.

Our model for testing is based on Read–Shockley type formula for energy of low angle boundaries with $\gamma \propto x(1 - \ln(x))$, where x is the ratio between misorientation angle to a fixed angle limiting the angular range of applicability of the expression [10]. We shaped all energy cusps by slightly modifying Read–Shockley formula. Let a function f be defined as

$$f(x,a) = ax(1-\ln(x)) + (1-a) \quad \text{for} \quad 0 < x \le 1, \quad f(0,a) = 1-a \quad \text{and} \quad f(x,a) = 1 \quad \text{otherwise.}$$

Parameter x determines the 'distance' from the center of a cusp, and a $(0 \le a \le 1)$ corresponds to its depth. To define the energy function properly, we need to include some more steps. The smallest rotation angle between rotations represented by matrices g_1 and g_2 is given by $\omega(g_1, g_2) =$

[2] It must be noticed, however, that for the tessellations we use, the diameter (misorientation angle between most distant points) of the cells increases with Φ approaching 1 and the reconstruction is better when Φ_0 is smaller than 1.

$\arccos((\mathrm{tr}(g_1\, g_2^T) - 1)/2)$. For misorientations of symmetric objects, the misorientation angle is $\omega_s(g_1, g_2) = \min_{k,l}\{\omega(c_k g_1 c_l, g_2)\}$. Moreover, to take into account the equivalence between g and g^T, we define $\Omega(g_1, g_2) = \min\{\omega_s(g_1, g_2), \omega_s(g_1^T, g_2)\}$. The energy function was assumed to have the form of the product

$$\gamma(g) \propto \prod_n f(\Omega(g, g_n)/W_n, a_n) \ ,$$

where g_n determines the location of the n-th cusp, W_n is its half–width, and a_n corresponds to its depth. We chose the cusps to be located at the misorientations defined by coincidence lattice relationships with Σ in the range from 1 to 49. They were enumerated in the standard order as Σ_n with $n = 1, 2, ..., 48$ (i.e., $\Sigma_1 = 1$, $\Sigma_2 = 3$, ..., $\Sigma_{48} = 49$). The half–widths of cusps are given by Brandon criterion $W_n = (\pi/12)\Sigma_n^{-1/2}$, and their depths are determined by $a_n = \Sigma_n^{-1/2}$ (Fig.1).

Figure 1. Sections through normalized model distribution. The first one corresponds to fixed misorientation axis $< 1\,1\,1 >$ and the angle changing from 0 to 120°. The second figure is the stereographic projection for fixed misorientation angle of 60° and axes covering hemisphere. The isolines are 0.70, 0.90, 0.97 and 1.00, with the latter constituting the external perimeter of each cusp. The symmetry of the model is clearly visible.

Random grain orientations were generated by taking random numbers within $[0, 1)$ as $\varphi_1/(2\pi)$, $(\Phi + 1)/2$ and $\varphi_2/(2\pi)$. With a known distribution of energy and grain misorientations, cosines of the dihedral angles at the triple junction were calculated by solving (1) with respect to $\mathbf{t}_i \cdot \mathbf{t}_j$; for $i \neq j$ one has $\mathbf{t}_i \cdot \mathbf{t}_j = (\chi^2/2 - (\gamma^i)^2 - (\gamma^j)^2)/(\gamma^i\gamma^j)$, where $\chi^2 = (\gamma^1)^2 + (\gamma^2)^2 + (\gamma^3)^2$.

The reconstruction procedure was applied to the generated data. The result displayed in Fig.2 corresponds to a set of 10^6 triple junctions. The cell dimensions were $\Delta\varphi_1 = (\pi/2)/90 = \Delta\varphi_2$ and $\Delta\Phi = 1/90$. The iteration process was terminated after 50 steps. The reconstructed distribution is in good agreement with the model.

We performed a test of the sensitivity of the procedure to experimental errors. Grain misorientations are determined with relatively high accuracy (of about 0.5°). The largest experimental errors will come from dihedral angles. Therefore, the directions of $\mathbf{t}_i$ vectors were disturbed by random angles (θ) generated according to von Mises distribution $\exp(\kappa \cos\theta)$, with the concentration parameter κ equal to 1000 (Fig.3a). The result of reconstruction from such inaccurate data is shown in Fig.4. Despite the errors the quality of the result is still good because the number of used triple junctions is large. (For this particular case, narrow cusps are indistinguishable if the number of junctions is smaller than about 10^5.)

Figure 2. Sections through the reconstructed distribution. Data were given in a mesh with the step size of 1°. The same levels as in Fig.1 are shown. The levels were smoothed by the drawing program we used.

Figure 3. (a) Part of von Mises distribution in the range from $-10°$ to $10°$. (b) The ratio $R(n)/R(0)$ versus n. Diamonds and stars correspond to reconstructions given in Figs 2 and 4, respectively.

Figure 4. Sections through the distribution reconstructed from inaccurate data. The isolines on the stereographic projection are 0.70, 0.90 and 0.97.

Real cases will be even more intricate. The system of equations (2) is expected to be seriously inconsistent and under–determined. Inconsistency appears not only because of experimental errors but also due to the dependence of γ on boundary orientation. For reasonable cell sizes, some cells may be empty due to non-uniformness of misorientation distribution. Extrapolation of the energy distribution over such regions is questionable because it is difficult to justify any assumptions concerning smoothness of this function. Resolution of the method is directly related to the cell size and determined by the number of available triple junctions and the level of experimental errors.

Summary

Details of the numerical procedure for reconstruction of distribution of grain boundary free energy over grain misorientations are considered. Efficiency of the procedure is tested on a model distribution and computer generated data. The model satisfies conditions caused by crystal symmetry. The conditions are also incorporated into the reconstructing procedure, so they are satisfied by the reconstructed function.

Let us also mention that an effort is under way to collect experimental data (orientations and true dihedral angles) for several thousand grains in polycrystalline MgO.

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