Acta Materialia 133 (2017) 186–199

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

The grain-boundary structural unit model redux

Jian Han [a], Vaclav Vitek [a], David J. Srolovitz [a, b, *]

[a] Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA
[b] Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, USA

ARTICLE INFO

Article history:
Received 22 February 2017
Received in revised form
27 April 2017
Accepted 1 May 2017
Available online 3 May 2017

Keywords:
Grain boundaries
Structural unit model
Metastability
Simulation

ABSTRACT

Properties of grain boundaries (GBs) and their underlying structures are key to understanding polycrystalline material phenomena. The most widely used model for GB structure is the structural unit model (SUM), introduced ~ 50 years ago. The SUM represents GB structure as a combination of structural units (SUs); this combination evolves systematically with GB misorientation. Despite its successes, many observations suggest the SUM does not completely describe the GB structure; its utility for predicting GB properties is limited. There has been a growing realization that, even for fixed misorientation, multiple stable/metastable structures are common (corresponding to different microscopic degrees of freedom). We generalize the SUM by considering the effect of such metastable structures. While the SUM can describe GB structure evolution between a pair of delimiting boundaries, there will be many such evolutionary paths, corresponding to SUs associated with the metastable structure of the delimiting boundaries. The equilibrium GB energy vs. misorientation does not necessarily correspond to one of these paths, but will have contributions from many. Recognizing this, we propose a new approach to predict GB structure and energy, allowing for accurate determination of the GB energy vs. misorientation based on a very small number of atomistic simulations. For example, we predict the GB energy vs. misorientation for [100] and [111] symmetric tilt boundaries in BCC tungsten over the entire misorientation range to a mean error of <2 % based on atomistic simulations at only three or four misorientations. Our approach allows for the trade-off between computational cost and prediction accuracy.

1. Introduction

The central goal of materials science is to establish the link between structure and properties. In a polycrystal, many properties may be traced to the properties/behavior of grain boundaries (GBs). Hence, the link between polycrystal properties, GB properties/behavior, and GB structure has been a recurring theme in materials science for nearly a century [1]. This paper focuses on a predictive model for GB structure and the link between the structure and GB properties, especially GB energy. Our approach is based upon some simple properties of single crystals, crystallography and minimal application of atomistic computer simulations (the number of such simulations is set by the desired overall accuracy of the prediction).

Starting from the early days of the study of GBs, there have been two distinct classes of GB structure models. The first class is the amorphous-cement model for high-angle GBs [2,3] which posits that high-angle GBs are structureless. Although this model naturally leads to glass-like GB behaviors, intuitively consistent with the experimental measurement of viscous GB sliding [4], it contradicts direct observations in high-resolution microscopy [5,6] that routinely show highly ordered GB structures on the atomic scale. The second class of GB models is the dislocation model, such as those used to describe low-angle GBs [7–9]. Such models were extended to high-angle GBs by superimposing a dislocation structure onto a high-symmetry reference structure, rather than superimposing a set of isolated lattice dislocations on a single crystal [10–12]. In this model, we can think of the GB as consisting of a core, associated with the reference structure, and the elastic deformation associated with the elastic field of the dislocation array (this language is similar to that for a lattice dislocation, where we distinguish the long-range elastic field from a nonlinear core). The inherent weakness of such models for high-angle GB structure is associated with the need to identify an appropriate reference structure (the choice of which is not unique). Although some reference structures are better than others, the dislocation model cannot guide such choices. For example, for a high-angle GB with a

---

[*] Corresponding author. Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA.

E-mail address: srol@seas.upenn.edu (D.J. Srolovitz).

http://dx.doi.org/10.1016/j.actamat.2017.05.002

misorientation angle close to that of a coherent twin boundary, we can choose either a single crystal or the coherent twin boundary as the reference structure. Observation of the atomic structure of this GB shows that this boundary is almost identical to that of the coherent twin boundary except for the addition of widely separated dislocations. Clearly, in this case, the coherent twin boundary provides a much better reference than does the single crystal. Identification of a good reference structure can only be made by considering the atomic structure of a GB. For low-angle GBs, the obvious reference structure is the single crystal and hence the dislocation model can be directly applied; however, the predictability of the dislocation model for high-angle GBs is limited (without knowledge of the atomic structure of the GB core).

The inherent weakness of the dislocation model for high-angle GBs is mitigated by the structural unit model (SUM) [13–16], which explicitly accounts for the atomic structure of the GB core. The SUM supplements the dislocation model through knowledge of the atomic structure of several specific GBs, which often posses high symmetry, as determined through atomistic simulations or experiments. These specific GBs, called "delimiting boundaries", serve as the reference structures for all other GBs. The structure of a GB that is geometrically between two delimiting boundaries can be described as a combination of the SU associated with these two delimiting boundaries; the minority units simply corresponds to the (secondary) dislocations in the dislocation model for high-angle GBs.

Despite the successes of the SUM, experimental and atomistic simulation results accumulated over the half-century since its introduction show that there is a large (and growing) set of cases for which the SUM simply does not work. For example, even for pure tilt GBs with low-index rotation axes, the structures of the intervening boundaries cannot be predicted based on the structures of the delimiting boundaries [17,18]. Perhaps these discrepancies between the SUM and the experimental/simulation observation is the result of not choosing the correct reference structures. By initially examining more conceivable reference structures, it may be possible to provide the correct prediction. Another possible source of the discrepancy is associated with the fact that for many boundaries a single, unique structure does not exist; i.e., there are multiple, metastable structures [19–24]. Unfortunately, identifying more potential delimiting boundaries or determining more structures for each GB would require additional (and often expensive/time consuming) simulations or measurements. Hence, this implies an inherent trade-off between accuracy and efficiency. Finally, we note that GB structure can change with temperature or in the course of some dynamical processes (e.g., absorption of point defects during irradiation, absorption of dislocations during plastic deformation, or GB sliding). In fact, examination of GB kinetic effects (such as GB sliding) seems to support the amorphous-cement model [25–27] rather than the SUM, which is inherently based upon crystallography. Despite these challenges, the SUM remains the most widely used approach for describing/predicting GB structure (e.g. Ref. [28]) and GB properties (e.g. Refs. [29–31]).

Grain-boundary metastability or multiplicity is a unifying feature associated with the issues raised above. GB metastability refers to the existence of different microscopic or atomic structures for a fixed set of macroscopic GB descriptors (i.e., rotation axis, misorientation angle and GB plane normal). We note that at high temperature or during dynamical processes, the GB does not necessarily occupy only its ground state (structure with the minimum energy) but may explore many metastable states [24]. Inclusion of GB metastability in the SUM is key to understanding the observed GB structure/properties and how these evolve with the GB geometry, as well as glass-like GB behavior which is normally thought of as a feature of the amorphous-cement model and a failure of the SUM.

In this paper, our goals in revisiting the SUM are two-fold: (1) to generalize the SUM to address why it leads to frequent erroneous predictions of GB structure/energy and (2) to develop an approach to predict GB structure and energy as a function of crystallographic variables with an accuracy that can be iteratively improved with increasing number of atomistic simulations. In the next section, we discuss GB geometry and the method we employ in atomistic simulations of GB structure. Then, we describe the atomic structure of the GBs in terms of a generalized SUM. In the following section, we develop a practical, efficient approach for predicting the GB energy (and other properties) in terms of the generalized SUM and a small set of atomistic simulations.

2. Macroscopic geometry and atomistic simulation method

For the sake of simplicity and clarity, we focus our discussion on the case of symmetric tilt grain boundaries (STGBs) in cubic metals. In addition, we further focus on those STGBs which have a periodic atomic structure (i.e., coincidence-site-lattice (CSL) GBs). This is a relatively weak assumption since any non-periodic (irrational) GB can be approximated as a periodic boundary to any degree of accuracy required.

We create any such STGB in a cubic crystal as follows. First, construct a cubic crystal, choose a mirror plane, and establish a Cartesian coordinate system $\widehat{\mathbf{o}} \times \widehat{\mathbf{p}} \times \widehat{\mathbf{n}}$, where $\widehat{\mathbf{o}}$ and $\widehat{\mathbf{p}}$ are parallel and $\widehat{\mathbf{n}}$ is perpendicular to the mirror plane. We define $\widehat{\mathbf{o}}$ to be the tilt axis. Rotate the crystal by $\theta/2$ about the $\widehat{\mathbf{o}}$-axis (i.e., the tilt axis). Repeat this procedure for another (identical) crystal but rotate it by $-\theta/2$ about the $\widehat{\mathbf{o}}$-axis. Remove all of the atoms from the first crystal below the mirror plane and those from the other crystal above the mirror plane. Join the two half-crystals to create the GB. This mirror plane is the GB plane and the GB has a misorientation angle of θ about the $\widehat{\mathbf{o}}$-axis.

When the crystallographic indices of the $\widehat{\mathbf{o}}$- and $\widehat{\mathbf{p}}$-directions are rational, there are an infinite number of discrete values of the misorientation angle θ such that the two lattices coincide at a subset of the lattice sites. The GB formed in this way is called a CSL GB. The reciprocal of the fraction of sites which are coincident is denoted Σ. A CSL GB is periodic in both the $\widehat{\mathbf{o}}$- and $\widehat{\mathbf{p}}$-directions. Denote the period vector along the $\widehat{\mathbf{o}}(\widehat{\mathbf{p}})$-axis by $\mathbf{o}$ ($\mathbf{p}$), with magnitude o (p) equal to the boundary period.

While the SUM approach we describe in this paper is applicable to all crystalline materials, for concreteness, we choose our examples to be GBs in a body-centered cubic (BCC) metal; in atomistic studies a many-body Finnis-Sinclair interatomic potential developed for tungsten [32] has been used. Although this potential is indeed able to produce many properties of tungsten, it is considered here as a representative model of a BCC metal. The first step in our atomistic simulations is to construct bicrystal supercells for [100] and [111] tilt axes and several misorientations, as listed in Table 1. In order to explore possible metastable GB structures, we construct supercells for each misorientation in which we displace the upper crystal relative to the lower crystal by a displacement vector that lies within the GB plane. We explore a sufficient number of possible shifts to ensure that we capture nearly all possible metastable GB structures, as described in detail in Ref. [24]. Starting from each of these initial structures (we explore the cases for two tilt axes, 162 misorientations, and many shifts corresponding to a total of $130,000$ structures), we relax the structures via a conjugate-gradient energy minimization procedure. These simulations represent the data set against which we compare our predictions.

We emphasize that different atomistic simulation methods may