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Embedded-atom study of low-energy equilibrium triple junction structures and energies

S.M. Eich*, G. Schmitz

Institute of Materials Science, University of Stuttgart, Heisenbergstraße 3, D–70569 Stuttgart, Germany

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ABSTRACT

We present an atomistic study of the structures and defect energies of triple junctions (TJs) in polycrystalline materials. A new concept to calculate the excess energy of isolated TJs is proposed and applied to a molecular dynamics (MD) study of iron tricrystals. Line energies of bulk TJs (merging three grain boundaries (GBs)) and surface TJs (merging one grain boundary and two surfaces) are found to be very low. In absolute value they amont to only a few 10^{-10} Jm^{-1}. Remarkably, defined as a correct excess energy relative to the GBs, the bulk TJ energy is determined to be negative in all studied configurations with an average value of -2.8×10^{-10} Jm^{-1}. These quantitative results are in contrast to various experimental attempts, but they fully agree with simple geometric estimates and broken-bond models, which prompts a re-interpretation of reported measurements.

1. Introduction

In nanocrystalline materials, the volume fractions of grain boundaries (GBs) and triple junctions (TJs) gain significance, justifying these defects as a major research topic [1]. However, only a few experimental and theoretical works have been published on the actual energy of TJs and they are contradictory even in the sign of the TJ energy [2–8].

In the 1870's, Gibbs already discussed the possibility that TJs among fluid phases can exhibit either positive or negative line energies [2]. For a negative line energy, he explicitly mentioned the "case with respect to a line in which three surfaces of discontinuity are regarded as meeting, but where nevertheless there really exists in stable equilibrium a filament of different phase from the three surrounding masses" and gave the example of two adhering soap bubbles [7,9].

Initial experimental studies on solid materials were performed by Nishimura in 1973, investigating thermal etching at TJs [3]. The geometrical analysis presumed a tetrahedron and isotropic surface energies in describing the edge pit at the TJ. The evaluation revealed that, without assigning any TJ line energy, the surface depression at the TJ is already about one third deeper than the depth of the adjacent GB grooves. The same concept was continued by Fortier et al. in 1991 using scanning tunneling microscopy [4]. They indeed found that, on average, TJ depressions are about one third deeper than those of the GB grooves. Significant deviations from this approximate value were ascribed to the specific line energy of the TJs. The minimum triple line energy was found positive and quantified to about 5×10^{-7} Jm^{-1}.

However, those early attempts did not include the contributions of the three surface TJs formed along the adjacent GB grooves. King pointed out in 2007 that for a complete description, not only the bulk TJ energy, but also the three surface TJ energies need to be taken into account [10]. A consequent extension of the tetrahedron model was used by Kim et al. in 2009 when investigating TJ surface pits in nanocrystalline zirconia using energy-filtered transmission electron microscopy [5]. Now, also accounting for the surface TJs, they found that some TJs exhibit deeper pits than expected, indicating positive (bulk) TJ energy, but no case of a reduced TJ depth was observed. Still their model relies on isotropic interface energies.

In 2010, Gottstein et al. proposed that the depression at the quadruple point of a copper tricrystal [6] is exclusively controlled by the equilibrium of the four TJ line tensions [11]. The line tensions of the three surface TJs are determined by their curvature in the roots of the GB groovings, assuming isotropic surface energies, and so the remaining unknown, the line tension of the (bulk) TJ, can be quantified. They concluded that the bulk TJ energy is

* Corresponding author.
E-mail address: Sebastian.Eich@imw.uni-stuttgart.de (S.M. Eich).

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$(6.3 \pm 2.8) \times 10^{-9}$ Jm^{-1} and the surface TJ energies are $(16.8 \pm 7.0) \times 10^{-9}$ Jm^{-1}[6].

Thermal TJ grooving was also considered by Génin et al. in 1992 in an explicit diffusion model also assuming isotropic surface energies [12]. They found that the TJ pit is always deeper than the groovings at the adjacent GBs already without any particular contribution of TJ line energies. So, the actual depth ratio predominantly varies with the GB grooving angles, which are related to the GB energies. Even more complex, Zhang and Gladwell concluded that the "depth ratio between the TJ pit and the groove root is sensitive to the level of interface anisotropy and can deviate significantly from the isotropic case" [13]. Therefore, the anisotropy of the surface energies plays a dominant role in TJ grooving and must likely be included in an accurate model. Thus, all experimental attempts to measure the TJ energy show a certain lack in the correct thermodynamic description of TJ grooving.

On the theoretical side, two studies applied molecular dynamics (MD) simulations in order to extract the TJ energy directly. In 1999, Srinivasan initially used a Lennard-Jones model potential to investigate a system consisting of several TJs [7]. He concluded that "at least one of the trijunctions must have a negative excess energy". The second work was performed by Caro and van Swygenhoven in 2001 [8]. On the basis of finite GB widths, they evaluated the TJ energy to be 14.1×10^{-10} Jm^{-1}. However, they used the bulk energy instead of GB energies as a reference and thus, the TJ energy would likely be always positive.

In this work, we present a detailed investigation of the energetic nature of TJs by means of atomistic studies in order not only to clarify the sign of the TJ energy, but also to provide accurate values. To this aim, we introduce a new relaxation scheme to obtain single TJs in low-energy equilibrium, avoiding unnecessary volume stress in the related grains. In addition, we show how to extract the TJ energies from the discrete and finite atomic configurations. All TJ configurations investigated here show a negative TJ excess energy with respect to the adjacent GB energies, i.e. the total energy of the GBs is effectively decreased in the vicinity of a TJ. For the MD simulations, we applied the embedded-atom method (EAM) [15,14], using the iron potential provided by Ackland [16].

2. Methodology

Before introducing the methodology, let us briefly review what has been stated on the properties of TJs in general, as the determination of TJ energies needs considerable care not only from the experimental point of view, but also in simulations [10]. King classified possible TJ properties into three categories [17]: i) properties that can be fully derived from the known properties of the joining GB interfaces, ii) properties that arise from the fact that the TJ modifies the nature of the related interfaces e.g. by terminating the interface at a given position, and iii) properties that represent a sole feature of the TJ, independent of the related interfaces. The assignment of the TJ line energy into these categories is delicate. Previous studies [19,18] based on dislocation models have revealed that the energy of TJs and GBs is fluctuating in correlation to the (quasi)periodic structure of the GBs. This, in turn, means that the actual termination of a GB by TJs also influences the TJ energies themselves. As a consequence, the contributions of all TJs to the total system energy cannot be strictly separated from one another. Assigning a specific energy to a sole TJ, interpreted as a line object according to the third category, although desirable, is *per se* not feasible. However, we will provide certain conventions with which such a classification could nevertheless be obtained as a convenient average.

2.1. Definition of grain boundary and triple junction energies

In the following we introduce GB and TJ energies on the basis of energy densities. To give general definitions, we assume that in every applicable model, there exists an energy density function $\varepsilon(\vec{r})$ so that for the total energy E of a system of volume V the expression

$$E(V) = \int_V \varepsilon(\vec{r})\mathrm{d}V \tag{1}$$

holds.

Considering a rectangular box with periodic boundary conditions in the x–z-plane with an area A and the GB plane located at $y = 0$ (right part of Fig. 1), the GB energy in terms of a Gibbsian excess is given by

$$\gamma_{\mathrm{GB}} = \frac{1}{A}\lim_{y\to\infty}\int_{-y}^{y}\int_A (\varepsilon(\vec{r}) - \varepsilon_0)\mathrm{d}V, \tag{2a}$$

where ε_0 is the bulk energy density. I.e. the GB energy is defined as the difference between a system (of infinite extent) containing a GB and a pristine system, normalized to the cross-sectional area of the GB.

Instead of collecting all excess energy across the GB plane in y-direction, one can also collect all energy, for instance, along the x-axis within the GB plane, which can easily be seen by rearranging the volume integration:

$$\begin{aligned}\gamma_{\mathrm{GB}} &= \frac{1}{x}\int_0^x \left(\frac{1}{z}\lim_{y\to\infty}\int_{-y}^{y}\int_0^z (\varepsilon(\vec{r}) - \varepsilon_0)\mathrm{d}z'\mathrm{d}y'\right)\mathrm{d}x' \\ &=: \frac{1}{x}\int_0^x \gamma_{\mathrm{GB}}(x')\mathrm{d}x'.\end{aligned} \tag{2b}$$

Here we have defined the *local* GB energy $\gamma_{\mathrm{GB}}(x)$.

If neither periodic boundary conditions can be applied in x-direction, nor it is possible to integrate over a strict GB period, the energy (of an infinite GB) must be obtained by averaging starting from arbitrary x_0:

$$\gamma_{\mathrm{GB}} = \lim_{x\to\infty}\overline{\gamma}_{\mathrm{GB}}(x) = \lim_{x\to\infty}\frac{1}{x - x_0}\int_{x_0}^{x}\gamma_{\mathrm{GB}}(x')\mathrm{d}x'. \tag{2c}$$

All definitions given in Equation (2a) to Equation (2c) are equivalent and the most suitable one for evaluation can be chosen.

If we consequently interpret the excess energy of a lattice defect relative to the objects which it joins, then the TJ energy must be chosen relative to the energy of the adjacent GBs. With regard to the dimensionality of a TJ [18], the TJ energy can be defined by reducing the dimension of Equation (2a) and this concept would even hold down to quadruple points. (To see the mathematical analogy, we may split the y-integration into two parts: $\gamma_{\mathrm{GB}} = \frac{1}{A}\lim_{y\to\infty}\sum_{i=1}^{2}\int_0^y\int_A(\varepsilon^{(i)}(\vec{r}) - \varepsilon_0)\mathrm{d}V$, where the y-integration now starts at the GB interface and extends into the two grains with respective energy density $\varepsilon^{(i)}(\vec{r})$.) By analogy, the excess energy of a TJ joining three GBs aligned along the z-axis under periodic boundary conditions is then given by