Computational Materials Science 86 (2014) 30–37

Contents lists available at ScienceDirect

Computational Materials Science

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

Molecular dynamics simulations of Al–Al_2Cu phase boundaries

V. Kokotin [b,1], U. Hecht [a,*]

[a] ACCESS e.V., Intzestraße 5, D-52072 Aachen, Germany
[b] ThyssenKrupp Steel Europe, Kaiser-Wilhelm-Straße 100, D-47166 Duisburg, Germany[1]

ARTICLE INFO

Article history:
Received 6 October 2013
Received in revised form 19 December 2013
Accepted 9 January 2014
Available online 8 February 2014

Keywords:
Molecular dynamics
Phase boundaries
Interface energy and anisotropy
Orientation relationship
Eutectics

ABSTRACT

Potential based molecular dynamics simulations were performed for Al–Al_2Cu phase boundaries (PBs) at a temperature of 50 K using a newly designed computation geometry that enables modeling hetero-interface configurations for an arbitrary pair of phases. The computational method and geometry were validated for symmetric grain boundaries in Al, both [001] and [110] tilt boundaries, followed by extensive simulations of Al–Al_2Cu PBs. For randomly oriented Al and Al_2Cu as well as randomly oriented phase boundary planes the average PB energy reaches $\gamma_{av.} = 0.456 \pm 0.002\ J/m^2$. Two special orientation relationships (ORs), known to prevail in Al–Al_2Cu eutectics after unidirectional solidification, were characterized in detail. For each OR the 3D phase boundary energy surface was mapped and the energy minima were carefully analyzed. Computational results were compared to experimental observations based on EBSD measurements and allowed concluding that lamellar eutectic interfaces select a shallow energy minimum $\gamma_{\alpha 4} = 0.407\ J/m^2$ for one OR, but a deep, cusp-like energy minimum $\gamma_{\beta 6} = 0.253\ J/m^2$ for the second OR. The calculations thus substantiate the experimentally observed behavior of lamellar eutectic interfaces, being nearly isotropic in the first case, but strongly anisotropic in the latter.

1. Introduction

Materials properties depend on both, the properties of the constituent phases and the properties of interfaces, grain boundaries and/or phase boundaries that are present within a given volume of interest. Phase boundary properties impact on mechanical and physical performance directly but also indirectly, since they play an important role during microstructure formation and effectively control microstructure stability during service. A multitude of research tasks emerge from this background being dedicated to the analysis of interfacial properties and specifically to the investigation of the interfacial energy and anisotropy for random and special configurations of grain or phase boundaries (hetero-interfaces). Research on coupled eutectic growth is one of the areas calling for quantitative data on interfacial properties of all hetero-interfaces, including the solid–solid interfaces formed between the crystalline phases in the eutectic phase mixture. In fact, the interfacial anisotropy and hence the Wulff plot of their interfacial energy determines not only the selection of orientation relationships within a eutectic grain but also impacts on the eutectic growth dynamics [1].

Within this paper we present and discuss molecular dynamics simulations (MD) of interfaces between the face-centered cubic Al (Pearson symbol cF4, space group no. 225) and the tetragonal intermetallic compound Al_2Cu (Pearson symbol tI12, space group no. 140). The simulation work aimed at providing quantitative 3D data for the energy and anisotropy of Al–Al_2Cu interfaces with special emphasis on two distinct orientation relationships that were observed to prevail in eutectic, polycrystalline samples after unidirectional solidification [2]. Potential-based atomistic modeling was chosen as a fast computational method that allows mapping a large number of interfacial configurations in a reasonable time, but also because the available interatomic potentials [3,4] seem reliable. The MD methodology based on the analysis of equilibrium fluctuations at solid–liquid [5] or solid–solid interfaces [6] has not been adopted for this work, mainly because of difficulties expected to arise from transition layers with intermediate composition between Al and Al_2Cu. Instead, the methodology commonly used for grain boundary simulations [7,8] was selected, however with a newly developed simulation geometry.

The paper is structured as follows: in Section 2 the simulation set-up, the computational procedure and simulation runs are described and assessed against benchmark data for grain boundaries in Al, in Section 3 computational results obtained for Al–Al_2Cu interfaces at 50 K are presented and interfacial properties are discussed in comparison with experimental observations. The main

---

* Corresponding author. Tel.: +49 2418098014.
E-mail address: u.hecht@access.rwth-aachen.de (U. Hecht).

[1] Present address.

http://dx.doi.org/10.1016/j.commatsci.2014.01.014

results and conclusions as well as an outlook on present and future applications of the results are summarized in Section 4.

2. MD simulation method and validation against benchmark data

Atomistic modeling of interfaces, either ab initio or based on interatomic potentials proved prolific in many areas of materials science [9] and has widely been applied to study the structure, energy and mobility of grain boundaries (GBs) [10,11]. The commonly used method for GB modeling consists of building a bi-crystalline model box that contains a single GB in it [7,8] and simulating the relaxation of the structure. For simplicity the GB plane is always placed in the middle of the box parallel to one of the box planes. For special symmetric GBs both crystal lattices have the same but mirrored orientation relative to the GB plane, such that periodic boundary conditions can be applied. For non-symmetric GBs or GBs with mixed tilt-twist character no periodicity and no symmetry can be observed [12] and in such cases periodic boundary conditions would lead to additional internal stresses, other than those arising at the GB. For phase boundaries (PBs) involving misfits, the application of periodic boundary conditions is equally problematic. To overcome these limitations, a new simulation design was developed and validated against benchmark data for selected GBs in Al, as described below.

2.1. Simulation design and computational procedure

The simulation box consists of the two selected phases, called external and internal phase for simplicity, cut in cubic form and having the same geometric centers as shown in Fig. 1. The internal phase can rotate freely in order to meet any desired crystal orientation relative to the fixed external phase. The PB plane can have any orientation as well with one limitation: the distance between the PB plane and the geometric center of the box should be $L/2$ in order to fulfill the size ratio. The final simulation box is cut after the desired orientations (PB plane and phases) are set. This method insures that distinct PB plane positions can be probed systematically by cutting the internal phase parallel and perpendicular to the PB plane. Cutting of the PB plane is more demanding than cutting the free surfaces of the external and internal phases: thus atoms in the PB layer have been tested for overlapping with neighboring atoms from the other phase and removed, if necessary. Further PB refinement includes filling of bigger holes, being done after the first MD steps.

The total number of atoms in the simulation box is around 300.000 and the optimal size ratio of the internal (grey) and external (green) phases was found to be 0.5. For the chosen system size with $L = 10$ nm and for every position of the internal phase and the PB plane the distance between the corners of the internal phase and the external walls is higher than the cut-off parameter of the used potentials (0.65 nm). Due to this, the interaction between the two phases occurs at the PB only. The total contact area amounts to about 100 nm^2, giving good statistics for energy calculations.

The PB energy, γ, is calculated following the extended method described by Brown and Mishin [13] as the difference of the energy of the lattice regions containing the PB and the lattice regions containing an equal number of atoms in the bulk environment, divided by the PB area [14]. For a two-phase system consisting of several atom types Brown's original approach can be extended to:

$$\gamma = \frac{1}{S}\left(\sum_{i}\sum_{j=1}^{N_i^{\text{int.}}}(\varepsilon_{i,j}^{\text{int.}} - \varepsilon_{i,0}^{\text{int.}}) + \sum_{i}\sum_{j=1}^{N_i^{\text{ext.}}}(\varepsilon_{i,j}^{\text{ext.}} - \varepsilon_{i,0}^{\text{ext.}})\right), \tag{1}$$

where S is the PB area, $\varepsilon_{i,j}^{\text{int.}}$ and $\varepsilon_{i,j}^{\text{ext.}}$ are the energy of the individual atoms j of type i in the internal and external phases respectively, while $j = 0$ corresponds to the stable average value of the bulk sample without PB. Summation occurs over all atoms j of type i.

In order to avoid side effects from the free surfaces, the analyzed PB area was empirically reduced to the middle square of $L/2$ in the length.

Fig. 2 illustrates the dependence of the calculated PB energy, γ, on the parameter d, which represents the half-size of the box selected for the evaluation of $\varepsilon_{i,j}^{\text{int.}}$ and $\varepsilon_{i,j}^{\text{ext.}}$. As long as d is large enough, e.g. > 1 nm, the PB energy is independent on the choice of d. Naturally, d should not be excessively large, as to avoid surface effects. The $\gamma(d)$ dependence changes from the nearly constant to decreasing at low d values, when the selected box does not include all atoms associated with excess energy, representing the geometrical limits of the PB. According to this observation the PB thickness was determined from the point, where the $\gamma(d)$ dependence deviates from its linear approximation for high (>2.0 nm) d values by more than 0.01 J/m^2. The thickness of the PB was estimated to be around 0.10 nm for all simulated Al/Al$_2$Cu PBs, while the PB stretches for around 0.04 nm into Al$_2$Cu and for 0.06 nm into Al phase.

Since the excess energy of atoms may arise not only from the PB but also from elastic strain in the grains, and the latter contribution is linear in d, the apparent value of γ is also linear in d. Therefore, the true value of γ has been obtained by extrapolation from the region $d > 2.0$ nm to $d = 0$.

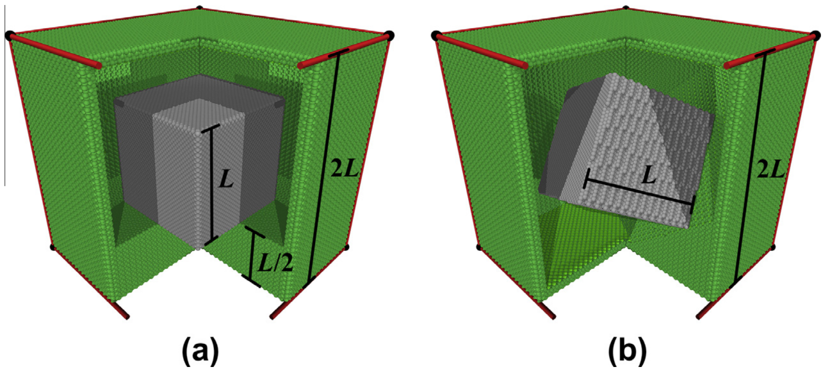

Fig. 1. The simulation box for (a) $\{(0\,0\,1)^{\mathrm{Al}}//(0\,0\,1)^{\mathrm{Al2Cu}}//\mathrm{PB}, [0\,0\,1]^{\mathrm{Al}}//[0\,0\,1]^{\mathrm{Al2Cu}}\}$ and for (b) $\{(1\,1\,1)^{\mathrm{Al}}//(2\,\bar{1}\,1)^{\mathrm{Al2Cu}}//\mathrm{PB}, [\bar{1}\,1\,0]^{\mathrm{Al}}//[1\,2\,0]^{\mathrm{Al2Cu}}\}$ phase boundaries. External phase – Al$_2$Cu (green), internal phase – Al (grey). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)