Materials Chemistry and Physics 179 (2016) 254–265

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Thermo-kinetic mechanisms for grain boundary structure multiplicity, thermal instability and defect interactions

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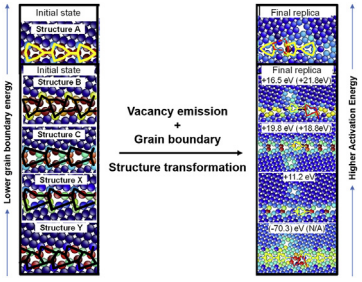
HIGHLIGHTS

- Influence of structural characteristics on vacancy emission from metastable Σ5 grain boundaries.
- Nudged elastic band analysis of grain boundary structure transformation from vacancy absorption.
- Effect of multiplicity on activation energy and mechanisms for vacancy and interstitial effects.
- Structural analysis of dislocation nucleation process from nudged elastic band transition replicas.
- Conceptual framework for defect-induced non equilibrium grain boundary structures.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 October 2015
Received in revised form
25 April 2016
Accepted 15 May 2016
Available online 21 May 2016

Keywords:
Metals
Crystal structure
Thermodynamic properties
Computer modelling and simulation
Dislocations
Interfaces

ABSTRACT

Grain boundaries (GBs) provide a source and/or a sink for crystal defects and store elastic energy due to the non-uniform atomic bonding structure of the GB core. GB structures are thermodynamically driven to transition to the lowest energy configuration possible; however to date there has been little evidence to explain why specific GB structures have a low energy state. Furthermore, there is little quantitative demonstration of the significance of physical and GB structure characteristics on the GB energy, thermal stability, and the effect of temporary local GB structure transformations on defect interactions. This paper evaluates the defect interactions and structure stability of multiple Σ5(310) GB structures in bi-crystals of pure aluminium, and systematically investigates the features at 0 K to characterise multiple metastable structures. Structure stability is evaluated by utilising unstable vacancy defects to initiate GB transformations, and using nudged elastic band simulations to quantify this with the activation energy. The emission of stable vacancy defects from the 'stable' and metastable grain boundaries is also evaluated in the same manner. A detailed analysis of dislocation nucleation at the atomistic scale demonstrates that local transformations of GB structure between stable and metastable intermediates can provide a mechanism to accommodate the generation of crystal defects. Kinetic (time-dependent) effects that compete with energetic driving forces for structural transformations of GBs are shown to cause a significant effect on the activation properties that may exceed the influence of GB potential energy. The results demonstrate that GB structural multiplicity can be associated with the generation and absorption of dislocations and vacancies. This paper demonstrates the suitability of atomistic simulations coupled with nudged elastic band simulations to evaluate fundamental thermodynamic properties of pure FCC metals. Overall, this paper demonstrates an inherent link between the atomic structure and the thermal,

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http://dx.doi.org/10.1016/j.matchemphys.2016.05.037

energy and structure stability properties of grain boundaries; and reveals the mechanisms for GB-defect interactions involving localised GB structure transformation.

1. Introduction

The thermal stability of grain boundaries (GBs) is directly linked to the energy, chemical and mechanical properties of polycrystalline metals. The bond structure and physical features at the atomic scale inherently determine the GB potential energy; however, the key causal factors that determine this relationship are not clearly defined [1,2]. Modelling the structure – property - energy relationships of grain boundaries provides considerable benefits for the understanding of the fundamental causes of the properties of polycrystalline materials. Molecular dynamics (MD) simulations are well-established as an effective tool to aid the modelling of fundamental thermodynamic and characterising structural characteristics [3]. Structure-property-energy models have a crucial role in the design and optimisation of modern materials, particularly for the developing sector of GB engineering with metals with nano-sized grains [4–7].

GBs significantly influence the chemical and thermodynamic properties of materials by acting as a source or a sink for crystal defects [8]. Analytical studies from first-principles have proven that there is a thermodynamically viable mechanism for the emission or absorption of point defects from high energy tilt GBs [8]. Furthermore, TEM studies have verified that the structure of the GB core can be an effective source of vacancies [9], and an effective sink for interstitials and vacancies [10]. A systematic simulation-based study found that the GB energy can be strongly correlated with vacancy absorption and emission [11], in agreement with a theoretical correlation [12]. However, the conceptual framework that can explain the mechanism of defect interactions with GBs remains incomplete. This paper investigates the process of GB structure transformation as a key mechanism for enabling defect–GB interactions [12].

Multiplicity of GB structures corresponds to the number of thermodynamically metastable energy states and has been observed in several studies of computer-simulated GBs at 0 K [12–15]. In the past, studies of GBs generally have generally assumed that the minimum energy structure alone is sufficient for studying the properties of the bi-crystal GB interfaces [14,16–18]. However, it is unlikely that the properties of real metals are only dependent on ideal GB structures. There are several examples of non-ideal GBs to support this, including non-equilibrium GBs [19], micro-faceted GBs [20], and local distortions due to dislocation-GB interactions [21].

The absorption and emission of point defects (i.e., vacancies) by GBs has been correlated with the GB structure stability, and the number of available metastable GB structural forms [12]. Evidence in support of this relationship stems from the relatively high source and sink strength of high energy “general” GBs (i.e., very high number of possible GB structures) [2]. Conversely, high stability GBs that exhibit minimal multiplicity of GB structure have proven to be inefficient vacancy sources and sinks in experiments [22]. The activation energy for transformations involving vacancies can quantify the associated thermodynamic barrier for point defect generation and interactions with the GB structure. This is indicative of the transition temperature for spontaneous irreversible transformation processes [23]. The nudged elastic band (NEB) method is a tool which is effective for evaluating the fundamental energy properties of materials, using atomic simulations at 0 K [24,25]. NEB simulations interpolate the atomic positions between a stable initial and an end state which are at a local energy minimum state [24]. The activation energy is the potential energy difference between the initial state and the maximum energy replica (i.e., “saddle point”) [27]. This study utilises an improved version, known ‘climbing image NEB’, which adds an additional stage to isolate the saddle point and improve the convergence of a realistic energy barrier [26].

This paper presents a study of the thermal and energy properties based on molecular dynamics simulations of Σ5(310) grain boundaries in pure FCC aluminium. Extensive structural analysis is used to characterise and classify the key GB structures, to provide a self-consistent basis for evaluating structural multiplicity effects. Results are provided to assess the relative source strength of the metastable and the stable GBs on the basis of nudged elastic band analysis of the emission of dislocations and vacancy defects. The mechanism of defect emission is discussed with respect to local changes in the atomistic structural transition states of the GB.

2. Theory

Understanding the ‘physical causes’ of the structure-property relationships at the atomistic scale has been the subject of considerable interest since the latter 1970s [2,29]. The ‘structure’ of the GB can be described as the shape of the free volume contained within the GB into a set of ‘deltahedra’ geometries [30]. Hence, the stable and ‘metastable’ GB structures obtained in atomic simulations are influenced by the initial free volume adjacent to the GB plane. The physical reasons for this set of structural configurations have been extensively described in an early study published by Asbhy et al., in 1978 [30]. The free volume is influenced by the cell dimensions and volume constraints, which results in a variety of possible distinctive metastable GB structures due to the geometrical constraints [30,31].

An extensive assessment of the factors that impact the GB energy was performed by Wolf and Jaszczak for equilibrium GB structures in static conditions [31]. The effects of multiple ‘independent’ structural variables were tested, including the free volume; the GB plane; the number of coincidental lattice sites (i.e., Σ number); and changes in the bond lengths. In static conditions, it was shown that the GB energy was most-strongly tied to the geometrical constraints of the simulation cell. The most-influential property was the proximity between the closest atoms within the configuration; indicating that the strong correlation with the free volume was an additional by-product and not a causal factor. The same observation was discovered for the effect of structure on the energy; and it was concluded that the physical GB properties are largely caused by size factors, not bonding or structure factors [31]. These results indicate that, in the absence of thermal effects or structural defects, the metastable (i.e., non-equilibrium) structures will be largely a consequence of the simulation cell constraints used during construction. Dislocation and vacancy interactions in real materials and/or thermal effects may cause non-equilibrium GB structures, in which case these metastable structures may play a role [32]. Furthermore, impurity atoms have been implicated in the process of GB structural ‘phases transformations’, causing