



# A molecular dynamics study of heterogeneous nucleation at grain boundaries during solid-state phase transformations



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## ARTICLE INFO

### Article history:

Received 9 September 2015  
Received in revised form 19 January 2016  
Accepted 21 January 2016  
Available online 15 February 2016

### Keywords:

Heterogeneous nucleation  
Solid-state  
Classical nucleation theory  
Wulff shape  
Winterbottom construction  
Molecular dynamics

## ABSTRACT

The study of solid-state nucleation through experiment is often limited by its tiny length range and short time scale. In this study, molecular dynamics (MD) simulations in a quasi 2D geometry are used to study the process of a BCC ferrite phase in pure Fe nucleating at a grain boundary (GB) in an FCC austenite polycrystalline system. In the MD simulations the critical nucleus can be identified, the bulk free energy difference between FCC and BCC is known for the Fe interatomic potential used and all relevant interface and GB energies are computed using a Gibbs–Cahn formulation. For nucleation events that exhibited low energy facets completely contained within the parent FCC phase, the results agreed well with predictions from classical nucleation theory (CNT) in terms of both the size and shape of the critical nucleus. For systems where the emerging nucleus contains facets that cross the GB plane the agreement with classical theory is less convincing and the observed nucleus does not exhibit parallel facets as predicted from the Winterbottom construction. The latter nucleation case involves a so-called pucker mechanism of the FCC grain boundary to accommodate the emerging nucleus and the effect of GB puckering on the incubation time is discussed.

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## 1. Introduction

Nucleation of secondary phases in solid-state crystalline materials is significant fundamental interest and practical importance due to its impact on the macroscopic mechanical, and transport properties of polycrystals. In many phase transformation and recrystallization processes the final microstructure is influenced to a large extent by the nucleation event and accurate models of microstructural evolution require a thorough understanding of the nucleation barrier, the nucleation rate and the crystallographic orientation relationship (OR) between the emerging and parent phases.

According to classical nucleation theory (CNT), the nucleation rate can be written in terms of the activation energy barrier, or work of formation, of a critical nucleus and the energy barrier, in turn, is a result of an interplay between the surface area and volume of the critical nucleus shape. Therefore the first step in the application of CNT is the determination of the critical shape. In the case of homogeneous nucleation the shape can be found from the Wulff construction. For nucleation occurring at planar defects the construction is complicated by additional contact angle

conditions that must exist at the grain boundary (GB) and inter-phase boundary intersections. By minimizing the sum of the total interfacial energy while maintaining force balance and connectivity of the interfaces, the equilibrium shape of a heterogeneous nucleus can be reached, which is Winterbottom construction [1]. The Winterbottom construction is performed by a  $\gamma$ -plot, hence the magnitude of vectors drawn from the origin do not correspond to actual lengths but instead correspond to the interfacial energies associated with the surface normal in that vector direction (see Appendices A, B and C). For a detailed description of the Winterbottom construction and the derivation of an equilibrium shape the reader is referred to [2,3].

In the 1950s, Clemm and Fisher [4] were the first to propose a geometric model (spherical cap model) to describe the nucleation of precipitates at a GB face, which can be considered as the overlap of two separate Winterbottom plots meeting at the GB. By assuming all interfacial energies are isotropic, Clemm and Fisher extended the critical energy calculation for different defect sites and showed that the critical work of formation decreases in the order of GB faces, triple lines (edges), and quadruple points (corner) [4].

In later years it was recognized that the assumption of isotropic surface energies was not particularly realistic, and in the 1970s Lee and Aaronson proposed that certain crystallographic relationships

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between the nucleus and the initial bulk grain were favored during the solid-state nucleation process [5,6]. The authors combined the spherical cap model with an anisotropic Winterbottom construction [7] to create a faceted-spherical cap model, and demonstrated that a facet exhibiting a low energy orientation relationship (OR) between matrix and nucleus phase can dramatically decrease the critical energy for the nucleation process. Other than the work of Aaronson and co-workers, additional studies have confirmed that, for interphase boundaries during the austenite to ferrite transformation in steel, some special crystallographic ORs can create small portions of the interphase boundary that are coherent, which significantly reduces the interfacial energy [8–10].

The traditional experimental techniques for nucleation studies measure average nucleation rates, and then compare with values calculated from the proposed geometric model according to CNT. Lange et al. [11] used electron microscopy to count ferrite nucleation diffraction spots arising from nucleation on austenite grain boundaries in steel. They detected a very high ferrite nucleation rate on the order of 1–100 nuclei per  $\text{m}^2$  of unreacted grain boundary area per second, which was too high to be explained by the faceted-spherical cap model of Lee and Aaronson. Lange et al. found that in order to match with the high nucleation rate, a disk-shaped “pillbox” nucleus has to form where all interfaces around the pillbox are coherent with its matrix phase. However, this assumption conflicts with the crystallography between the BCC and FCC lattices and implies the pillbox shape must be limited to a thickness of 2–5 atomic layers. In a more recent study, Offerman et al. monitored the ferrite nucleation process with a 3-dimensional synchrotron X-ray diffraction (3DXRD) technique [12]. They also reported an extremely high nucleation rate, especially at the initial stage of the nucleation process. Offerman et al. indicated that the activation energy related to the high nucleation rates was even lower than the prediction of the full coherent pillbox nucleus model. Thus, they assumed that a portion of the observed initial nuclei formed via a barrier-free nucleation mechanism. However, since none of the geometrical models of the critical nucleus have been successfully confirmed in real experiments, most heterogeneous solid-state nucleation studies report a huge discrepancy of nucleation rate between the experimental value and the CNT prediction [12,11,13].

Studies of the nucleation process are limited by the tiny length range and short time scale. For example, the critical nuclei only exist for short periods of time with a size ranging from Å to a few nanometers (nm), which makes a quantitative comparison to CNT very difficult. In addition, the new nucleus often forms at defects or interfaces that are deeply buried in the material and therefore difficult to locate. Moreover, the nucleation process is controlled by many parameters that are very difficult to measure independently in any bulk material, e.g. the geometry of the nuclei, the boundary and interfacial energies, etc. To avoid the technical limitations encountered in experiment, this article introduces the molecular dynamics (MD) simulation method to investigate heterogeneous nucleation occurring in a polycrystalline material. There have been several atomistic simulation studies that computed the nucleation behavior of a crystal from the melt [14–16]. However, much less attention has been paid to simulations of crystal–crystal nucleation [17], especially in a polycrystalline environment. Among the benefits of the MD technique is the fact that the bulk energy, grain boundary energy, and interfacial energy can be individually captured during the simulations. In order to accurately predict the shape, critical size and nucleation energy of specific nuclei, the faceted-spherical cap model based on the Winterbottom construction is applied in the current study, where grain orientation and anisotropic interfacial energy are considered. Although the faceted-spherical cap model is appropriate in

instances where the facet plane does not cross the GB, an additional complication of heterogeneous nucleation at GB occurs when the model predicts a nucleus facet intersecting the GB plane. In these instances the necessary contact angle criteria at the GB–nucleus–matrix phase triple boundary cannot be satisfied unless the GB itself changes shape. The bowing of the GB during the nucleus process is referred to as puckering. Also in this study we investigate cases where this so-called pucker mechanism is relevant [18]. The main objective of this paper is to compare the size and shape of MD simulated nucleation events with classical theory for both puckered and flat GBs.

## 2. Simulation procedures and theoretical background

The system chosen for current nucleation study is pure Fe. It is well known that the equilibrium phase of Fe at high temperatures is BCC, it transforms to austenite (FCC) at intermediate temperatures and reverts back to BCC (ferrite) at low temperatures. For central force classical MD interatomic potentials the true phase equilibrium behavior of Fe has proven difficult to reproduce. Therefore, the choice of potential is important. The Fe–Cu EAM potential (Ac97) developed by Ackland et al. [19] is one of the few potentials that can stabilize two different crystal structures, BCC and FCC, in the solid phase. This potential has been utilized in a few Fe simulations [20,21], and showed a good agreement with the *ab initio* computed the lattice parameter and potential energy at 0 K [22–24]. Although the melting temperature predicted by Ac97 is off the experimental values, the energy barrier between the FCC and BCC structures is suitable to create a metastable FCC phase in the range of temperatures, where BCC is stable [25]. Besides, Lopasso and Caro et al. used MD to test the Ac97 potential by drawing a phase diagram [26]. They indicated that the Gibbs energy difference between the  $\gamma$  (FCC) and  $\alpha$  (BCC) phase predicted by the Ac97 potential at 1000 K was equivalent to that found in the CALPHAD database at a temperature around 700 K [27]. Therefore, pure Fe is selected as the basic element in this study to investigate  $\alpha$ -phase nucleation at the GB of the  $\gamma$ -phase matrix, and the Ac97 potential is applied in the simulation to describe the interatomic force of Fe–Fe bonds.

### 2.1. MD simulations

In a previous study, Song and Hoyt [28,29] successfully employed MD simulations to investigate the mobility of FCC–BCC interfaces during the pure Fe FCC to BCC phase transformation. Based on the Ac97 potential, the authors have calculated the melting points, lattice parameters, and Gibbs free energy difference of the  $\gamma$  and  $\alpha$  phases relative to that of the liquid (Table 1). All of the previous computed data will be directly employed in the present study, in particular the free energy difference between austenite and ferrite will be used as the volume driving force for nucleation according to CNT. The temperature that was selected for performing the nucleation simulation represents a trade off between low nucleation rates, and hence long simulation times, at low temperatures and grain boundary motion of the underlying austenite at high temperatures. Consequently, the major

**Table 1**  
Parameter for pure Fe based on Ac97 potential [28,23].

	Lattice parameter <sup>a</sup> (Å)	Melting point (K)	Potential energy <sup>b</sup> (eV/atom)	Gibbs energy <sup>a</sup> (eV/atom)
FCC	3.6911	2236	−4.261	−0.094
BCC	2.8946	2358	−4.305	−0.114

<sup>a</sup> At  $T = 1000$  K, refer to the liquid phase ( $G_{\text{liquid}} = 0$ ).

<sup>b</sup> At  $T = 0$  K.

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