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Assessment of the CSL and SU models for bcc-Fe grain boundaries from first principles

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ABSTRACT

We present a systematic first principles investigation on a group of representative low-Σ ($\Sigma \leqslant 11$) symmetric tilt grain boundaries in bcc-Fe. The grain boundary (GB) structures were constructed using both the coincident site lattice (CSL) and structural unit (SU) models. Calculations are performed to address the relation and applicability of the two models. Results suggest that on some of the GBs, the CSL and SU models may yield different atomistic structures. In these cases, their structures differ only by one vacancy, and the SU model always predicts a much lower GB formation energy than the CSL does. Further calculations on GB vacancy formation suggest that the SU model is more appropriate for describing the low-Σ bcc GBs.

1. Introduction

The development of nuclear energy as an environmentally clean energy source has been consistently stimulated in recent decades, for it not only reduces our reliance on fossil fuels, but also promisingly offers an eventual solution to the world's energy crisis. The viability of nuclear energy ultimately depends on the development of high performance structural materials that can support extended component lifetime under extremely hostile conditions in fission and fusion reactors [1]. Ferritic alloys are among the most promising candidates for such applications [2]. During service, high energy neutrons ($E > 1$ MeV) produced from (n,α) transmutation reactions generate an ultra-high number of insoluble helium atoms, vacancies, and self-interstitial atoms in the ferrite matrix [3]. The reliability and lifetime of ferritic alloy components in nuclear applications suffer seriously from the segregation and enrichment of these defects at grain boundaries (GBs), leading to the severe loss of toughness at lower irradiation temperatures, and degradation of creep rupture properties at higher temperatures [4].

Grain boundary defines the interfacial region between two adjacent grains, with a crystallographic structure distinct from the grain interiors. Since the concept of "grain boundary design" was proposed by Watanabe [5], GBs have attracted increasing research attention in recent years. By acting as sinks and sources of point defects, GBs can play critical roles in atom diffusion and dislocation motion in metallic matrix, and thus greatly influence grain growth, recrystallization, creep, superplasticity, as well as the radiation damage effects [5–7]. Historically perhaps due to the experimental difficulties in GB characterization, numerous theoretical efforts have been made to model GB structures in proper manners, and further to assess the relevant energetics and properties. The employed models are rather diverse, being mostly the coincident-site-lattice (CSL) model [8,9] or the structural-unit (SU) model [10,11], and in fewer cases, the dislocation model [7,12], the disclination model [13,14], the O-lattice model [15,16], or the displacement-shift-complete (DSC) model [17]. In particular, the CSL model is constructed by rotating one grain lattice against the other about a rotation axis by a certain angle, so as to achieve a number of coincident lattice sites [9]. The degree of fit (Σ) between the two adjoining lattices is described by the reciprocal of the ratio of coincidence sites to the total number of sites. Thus a lower Σ boundary corresponds to a boundary plane that contains a higher density of coincident sites. Deviations from the ideal CSL orientation may be accommodated by local atomic

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relaxation or the inclusion of dislocations into the boundary. While in the SU model, those grain boundaries with certain misorientation angles correspond to "favored" structural units (typically with a low Σ value), and each structural unit can be seen as a favored symmetric tilt grain boundary (STGB). All other boundaries with long periods can be characterized as a combination of structural units comprising one or several neighboring favored boundaries with shorter periods [18].

It is surprising to know from the literatures that, the predicted formation energy of a given GB can be very different when using different GB models, even by the same research group. For some of the $\langle 1\,1\,0\rangle$ and $\langle 1\,0\,0\rangle$ tilt Fe-GBs, the CSL and SU models can predict almost the same formation energy by first principles calculations [19–26], but for the others, the CSL predicted formation energies are always 30–50% higher than the SU counterparts [22,23,27]. To our best knowledge, there has never been a first-principles study aimed to evaluate the relation between the two mainstream models. To calculate a given GB, it is still not clear which model shall be more appropriate to use. Moreover, no first-principles study has been performed based on the same one model that thus allows a direct comparison between the two representative STGBs of bcc phase, for example, the $\langle 1\,1\,0\rangle$ and $\langle 1\,0\,0\rangle$ tilt Fe-GBs. The interaction of GBs with point defects such as vacancies is also far from being understood. The aim of the present work is to make up for these loopholes. The paper is organized as follows. The methodologies for GB modeling and calculations are described in Section 2. In Section 3, intensive DFT calculations are performed: (i) to predict the stable GB configurations and the corresponding formation energies for a group of low-Σ ($\Sigma \leqslant 11$) special GBs within the $\langle 1\,0\,0\rangle$ and $\langle 1\,1\,0\rangle$ symmetric tilt grain boundary systems; (ii) to clarify the relation between the CSL and the SU models for bcc-Fe GBs; (iii) to manifest the vacancy interaction with some exemplary GBs. In Section 4, we summarize all our major results and findings. The obtained knowledge will be very helpful in guiding our future study on the GB-related problems in ferritic alloys for nuclear applications.

2. Calculation methods

To construct a GB structure using either model, the CSL or the SU model, two different approaches are often followed in the literatures. The first approach employs a supercell containing only one GB interface between two grain lattices, with a sufficient vacuum thickness to isolate the two extra, identical free surfaces at both ends [28] (see Fig. 1(a)). When evaluating the GB formation energy, the extra energy due to the two free surfaces must be dissociated from the total free energy of the supercell ensemble. Our many practices revealed that this approach can be problematic when the two free surfaces are highly unstable, say, with high Miller indices. Severe surface relaxation and even surface reconstruction may take place. Thus the calculated surface energy and, consequently, the GB formation energy can be very unfaithful. The second approach employs a "sandwich" supercell that contains two identical GB interfaces. The two interfaces are separated by a sufficient thickness of one grain lattice (see Fig. 1(b)), so that the vacuum and the two extra free surfaces can be avoided. The calculation accuracy can be also assured effectively, as long as a full relaxation is carefully performed both on supercell shape and volume. With this consideration, we employ the "sandwich" supercell approach for all calculations throughout this work. Furthermore, one study of Suzuki and Mishin [29] has suggested that the impact of point defects on GBs is rather short-ranged, being limited within only a few atomic layers from GBs. Thus, when constructing the sandwich supercell models, we feel comfortable to include only the nearest five to six layers from the GB interface, and regard it to be sufficient even for calculations of vacancy on GBs.

All calculations were performed in the framework of density functional theory (DFT) as implemented in the Vienna *Ab initio* Simulation Package (VASP) [30]. The electron–ion interactions were described by the projector augmented wave method (PAW) within the frozen-core approximation [31,32]. The exchange–correlation energy was treated in the spin-polarized generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [33]. A kinetic-energy cutoff of 350 eV was tested to be sufficient for plane-waves expansion to achieve good convergence. Bcc α-Fe was assumed in its ferromagnetic state. Our predictions on the equilibrium lattice constant and bulk modulus were 2.840 Å and 174.7 GPa respectively, both in good agreement with the experimental values of 2.867 Å [34] and 168 GPa [35]. The magnetic moment per Fe atom was predicted as $2.17\mu_B$, close to the experimental value of $2.22\mu_B$ [35] and other calculations of 2.13–$2.32\mu_B$ [26,36–39].

The GB energy (γ_{GB}) can be evaluated as

$$\gamma_{GB} = \frac{1}{2A}(E_{GB} - E_{bulk}), \tag{1}$$

where A is the area of the GB. E_{GB} and E_{bulk} are the total energies of the sandwich GB supercell and the perfect bulk lattice with the exactly same number of atoms, respectively. The two energies were calculated with the same k-mesh density to minimize numerical errors.

3. Results and discussion

3.1. Configurations and energies of different GB models

Table 1 summarizes our results for various low-Σ CSL GBs ($\Sigma \leqslant 11$) within the $\langle 1\,0\,0\rangle$ and $\langle 1\,1\,0\rangle$ STGB systems, as compared to all available results in literature. The comparison was made between the CSL and SU models and between DFT and molecular dynamics (MD) methods, in terms of GB configuration, misorientation angle (θ), GB model, total number of modeled atoms (N), and GB formation energy(γ_{GB}). Note that, no matter which model was used, MD methods always underestimated the GB formation energy. Our results agree well with all previous DFT results. Most notably, for the $\Sigma3\{1\,1\,2\}\langle 1\,1\,0\rangle$, $\Sigma3\{1\,1\,1\}\langle 1\,1\,0\rangle$, or $\Sigma5\{3\,1\,0\}\langle 1\,0\,0\rangle$ GB, the CSL and SU models yield the same GB structure and thus the exactly same values of γ_{GB}, while for the $\Sigma5\{2\,1\,0\}\langle 1\,0\,0\rangle$, $\Sigma9\{1\,1\,4\}\langle 1\,1\,0\rangle$, or $\Sigma11\{3\,3\,2\}\langle 1\,1\,0\rangle$ GB, the two models yield different structures, and the SU model always predict a much lower formation energy than the CSL does.

The above calculations involve many details that need to be carefully handled as we will address below. For the sake of brevity, we now demonstrate our practices on two representative coincident-site-lattice (CSL) modeled GBs, the $\Sigma5(3\,1\,0)[0\,0\,1]$ and the $\Sigma5(2\,1\,0)[0\,0\,1]$ STGBs (Fig. 2). Recall that the CSL and SU models predicted the same value of formation energy on the $\Sigma5(3\,1\,0)[0\,0\,1]$ STGB but failed on the $\Sigma5(2\,1\,0)[0\,0\,1]$ STGB. Following the standard procedure for CSL model construction [8], the $\Sigma5(3\,1\,0)[0\,0\,1]$ GB was created by rotating one bcc-Fe grain against the other around the [001] axis by 36.87°. The resulting supercell in Fig. 2(a) contains 80 atoms and has a dimension of $5.68 \times 8.98 \times 17.96$ Å^3. A Monkhorst–Pack [43] k-mesh of $3 \times 2 \times 1$ was employed for Brillouin zone integration. The $\Sigma5(2\,1\,0)[0\,0\,1]$ GB was created by rotating one grain by about 53.13°. The resulting supercell in Fig. 2(b) contains 40 atoms and has a dimension of $2.84 \times 6.35 \times 25.40$ Å^3. An $8 \times 4 \times 1$ Monkhorst–Pack k-mesh was employed. The separation between the two identical GB interfaces are 8.98 Å and 12.70 Å, respectively, which are sufficient to eliminate the GB-GB interaction along z-axis due to the imposed periodic boundary conditions.