

Atomistic Simulations of Carbon and Hydrogen Diffusion and Segregation in Alfa-Iron Deviant CSL Grain Boundaries

Mohamed A. Hendy¹, Tarek M. Hatem¹, Jaafar A. El-Awady²

¹ Centre for Simulation Innovation and Advanced Manufacturing, the British University in Egypt, El-Sherouk City, Cairo 11837, Egypt

² Department of Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland 21218, USA

ABSTRACT

Polycrystalline materials' mechanical properties and failure modes depend on many factors that include diffusion and segregation of different alloying elements and solutes as well as the structure of its grain boundaries (GBs). Segregated solute atoms to GB can alter the properties of steel alloys. Some of these elements lead to enhancing the strength of steel, on the other hand others can degrade the toughness of steel significantly. It is well known that carbon increases the cohesion at grain boundary. While the presence of hydrogen in steel have a drastic effects including blistering, flaking and embrittlement of steel. In practice during forming processes, the coincidence site lattice (CSL) GBs are experiencing deviations from their ideal configurations. Consequently, this will change the atomic structural integrity by superposition of sub-boundary dislocation networks on the ideal CSL interfaces. For this study, the ideal $\Sigma 3$ (112) structure and its angular deviations in BCC iron within the range of Brandon criterion are studied comprehensively using molecular statics simulations. The GB and free surface segregation energies of carbon and hydrogen atoms will be quantified. Rice-Wang model is used to assess the strengthening/embrittlement impact variation over the deviation angles.

INTRODUCTION

Solute segregation to grain boundaries (GBs) alters the mechanical properties of metallic alloys significantly [1,2]. Generally, the segregation of solute elements at GBs largely depends on the structure and character of these boundaries [3]. Some solutes increase the cohesive strength of the GBs while others have embrittlement effect [4]. Many studies have showed that Carbon segregation to GBs of α -iron increases the cohesive strength of these interfaces [5–7], while others have showed that carbon can increase slightly the embrittlement [8]. On the contrary, hydrogen segregation to GBs of α -iron always reduce the cohesive strength of the material's interface causing premature intergranular fracture [9–13].

Coherent twin boundaries (CTBs) have been shown to display good corrosion resistance in many engineering alloys [14]. It has been frequently observed that many GBs in real materials deviate from the ideal coincidence site lattice (CSL) symmetry plane [15–17]. Hence, The classification of a GB can be identified based on its proximity to a CSL structure, which allows for small angular deviations from the ideal symmetry plane determined by Brandon criterion [18]. The deviation is accommodated by secondary GB dislocations which affect the diffusivity and segregation behaviour of impurity atoms along the GB. Herbig et al. [15] have also shown experimentally that slight deviations from ideal CSL GB configurations in ferritic steels lead to unexpectedly high levels of segregation at those GBs.

In this paper the effect of small deviation from the ideal CSL structure on carbon and hydrogen segregation is studied. Accordingly, a common CTB in α -iron $\Sigma 3$ (112) is studied in the term of the effect of the deviation angle from their ideal structure GB on the change in cohesive energy due to carbon and hydrogen segregation respectively. Molecular statics (MS) simulations are used to evaluate the segregation energies of carbon/hydrogen at the studied ideal CSL GBs, their deviations and free surface. The results are then analyzed in terms of the effect of deviation angle on potency for carbon strengthening effect and hydrogen embrittlement effect on those interfaces.

METHODOLOGY

MS simulations were performed using LAMMPS [19] with EAM potential developed by Becquart and Ramasubramaniam [20, 21] for carbon and hydrogen respectively. Both potential has been widely accepted and used in similar studies [22, 23]. The simulation cell is relaxed using Polak-Ribière conjugate gradient energy minimization process [24]. The GBs is placed at the middle of the cell normal to the Y direction. All the simulations are done with bi-crystal cells of size of $20\text{nm} \times 20\text{nm} \times 20\text{nm}$. Since the periodicity cannot be achieved for CSL-GBs with small deviation angles, free surface boundary conditions are applied to all surfaces of the simulation cell. It should be noted that according to the Brandon criterion [15] for preserving CSL densities along the special GB planes the permissible deviation angle limit is:

$$\phi_{\text{limit}} = \phi_0 \Sigma^{(-\frac{1}{2})} \quad (1)$$

where ϕ_0 is Brandon limit constant ($\sim 15^\circ$) and Σ is the reciprocal value of the CSL density. Thus, to quantify the effect of the slight deviation from the symmetrical tilt plane of ideal CSL-GBs on carbon/hydrogen energetics, the GB plane is deviated from the ideal symmetry plane by varying the misorientation angle (Θ) between the two grains by a small deviation angle (ϕ), as shown in Fig 1. The exact deviation angles used in the current study equal to $0^\circ, 3^\circ, 5^\circ, 7^\circ$ and 9° .

In these simulations, one carbon or hydrogen atom was inserted at the their most preferable interstitial site in α -Fe [25] which are octahedral site for carbon and tetrahedral site for hydrogen. The carbon/hydrogen GB segregation energy calculations are repeated >10 times at specific distance from the GB with different atoms positions to account for statistical errors.

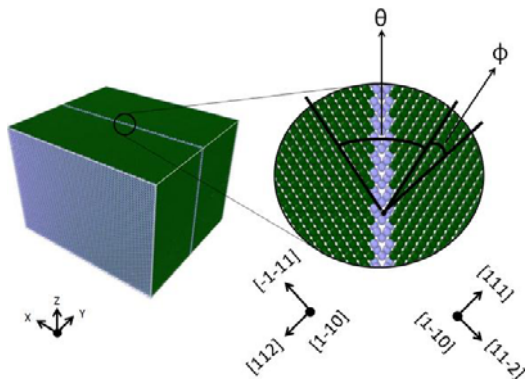


Fig. 1- Schematic diagram of the simulation cell for the ideal and deviated $\Sigma 3$ GB structures. The original misorientation angle (θ) between the $(\bar{1}\bar{1}\bar{1})$ plane normal and ideal (111) reference plane normal as well as the deviation (ϕ) are shown.

According to Rice-Wang model [26], the ability of an impurity atom to reduce the Griffith work of a GB is a linear function of the difference in the segregation energies at the grain boundary and free surface of this impurity atom. Generally, if the impurity atom tends to segregate to free surface rather than the GB, the impurity atom will cause the embrittlement of the material and enhance the intergranular fracture and vice versa. GB-cohesive energy is computed using as follows:

$$2\gamma_{int} = (2\gamma_{int})_0 - (E_{seg\ GB}^{\alpha} - E_{seg\ FS}^{\alpha}) \tau \quad (2)$$

where $2\gamma_{int}$ is the GB-cohesion energy in the presence of segregated impurity atom, $(2\gamma_{int})_0$ is the cohesion energy of the clean GB, and τ is the GB and free surface coverage constant.

The GB-segregation energy, $E_{seg\ GB}^{\alpha}$, is calculated as follows [27]:

$$E_{seg\ GB}^{\alpha} = (E_{GB}^{\alpha} - E_{GB}) - (E_{SC}^{\alpha} - E_{SC}) \quad (3)$$

where E_{GB}^{α} is the total energy of the simulation cell with a GB, free surfaces, and carbon/hydrogen atoms, E_{GB} is the total energy of the same system without the interstitial atom, E_{SC}^{α} is the total energy of the corresponding single crystal simulation cell with free surfaces and carbon/hydrogen atoms, E_{SC} is the total energy of the corresponding single crystal simulation cell without the interstitial atom. Accordingly lower segregation values indicates higher segregation tendency for the interstitial atom.

Similarly, the carbon/hydrogen free surface segregation energy, E_{FS}^{α} , is calculated as follows [27]:

$$E_{seg\ FS}^{\alpha} = (E_{FS}^{\alpha} - E_{FS}) - (E_{SC}^{\alpha} - E_{SC}) \quad (4)$$

where E_{FS}^{α} is the total energy of a single crystal simulation cell with free surface boundary conditions with carbon/hydrogen atoms, and E_{FS} is the corresponding system without interstitial atoms.

RESULTS AND DISCUSSIONS

In order to calculate GB-cohesive energy, both GB-segregation energy and free surface segregation energy need to be calculated [27]. Carbon/Hydrogen surface segregation energies are computed for the different orientations resulted from varying the deviation angle. The effect of the deviation angle, ϕ , on the carbon/hydrogen segregation energy within a 2 Angstroms from the GB plane is summarized in Fig. 2. All the segregation energies reported here are average values based on statistical analysis and mean estimation with a 95% confidence interval. It is observed that the average GB segregation energy value decrease as the deviation angle increases compared to the ideal structure. The most significant decrease in GB segregation energy is for the 9° deviation configuration (higher than Brandon limit) with mean value of -0.68 ev. GB segregation energy value at 9° is six times higher than the value for the ideal structure indicating that for $\Sigma 3$ (112) GB, exceeding Brandon limit alters the segregation properties considerably. Hydrogen segregation energy to GB showed lower sensitivity for changing the deviation angle.

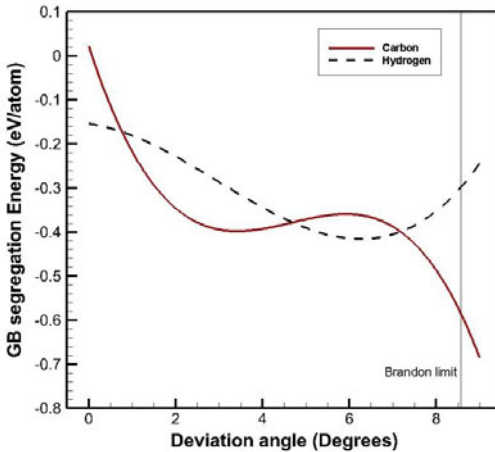


Fig 2 – Carbon/Hydrogen segregation energy within a 2 nm from the GB as a function of the deviation angle.

The free surface in the grain rotated with angle (ϕ), will change for the different deviations from the $\Sigma 3$ (112) ideal symmetry plane. Thus, different H-segregation energies would be expected for those free surface. The free surface calculations are shown in Fig. 3. The effect of different deviation angles from the ideal symmetry plane on the strengthening/embrittlement effect of Carbon/Hydrogen can be calculated from Eq. 2, and the results are shown in Fig. 4. As shown in Fig. 4 that for the studied GB and its deviated structures, carbon has strengthening effect to the studied GBs except for the ideal structure, while hydrogen reduces the cohesive energy at GBs and triggers intergranular fracture. The highest increase in cohesive energy is achieved for $\phi=9^\circ$ due to carbon segregation, while $\phi=9^\circ$ has the most decrease in the cohesive energy.

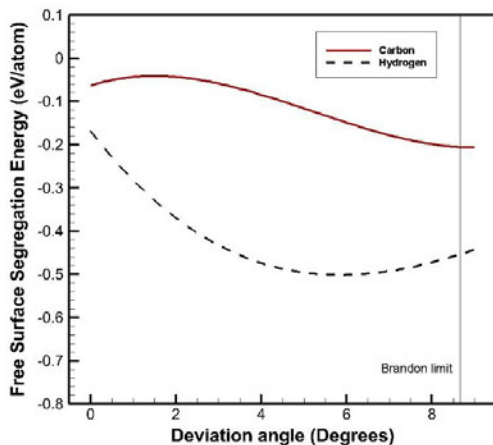


Fig. 3 – Carbon/Hydrogen surface segregation energy as a function of the deviation angle.

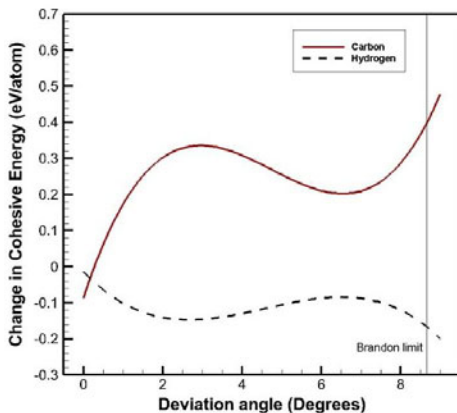


Fig. 4 - The change in cohesive energy due to the segregation of one carbon/hydrogen atom to $\Sigma 3$ (112) GB as a function of the deviation angle.

CONCLUSION

Carbon and Hydrogen segregation within $\Sigma 3$ (112) GB in αFe is analyzed using MS simulations. The results strongly suggest that angular deviations from the ideal CSL are

significantly affecting carbon and hydrogen segregation behaviour within the boundaries. Firstly, the average GB and free surface segregation energies showed a vast dependence on the sub-boundary network induced by angular deviations resulting in high atomic disorder and mismatch. The highest GB segregation tendency is shown at $\phi=9^\circ$ and $\phi=5^\circ$ for carbon and hydrogen respectively. By using Rice-Wang model, It has been shown that angular deviation structures increases the cohesive strength due to carbon segregation compared to the ideal structure. Furthermore, It could be concluded that all the tested GBs are vulnerable to hydrogen embrittlement through HEDE mechanism. The highest embrittlement resistance is recorded for the ideal while $\phi=9^\circ$ deviated structure showed the highest vulnerability to hydrogen embrittlement. Finally, this work is aimed to prove that interstitial atoms such as carbon and hydrogen behaviour in GBs are not only affected by the different special GB structures but also the small angular deviations from the ideal GB should be considered.

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