



Article First-Principles Study of B Segregation at Austenite Grain Boundary and Its Effect on the Hardenability of Low-Alloy Steels

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Abstract: Addition of B is beneficial for the hardenability of low-alloy steels and the effect is further improved when combined with the addition of Mo. While experiments demonstrated that Mo reduces the $M_{23}(C,B)_6$ precipitation and indicated an interaction between the alloying elements at the grain boundary, the underlying mechanism remains unclear. In the present study, the segregation behavior of B and its interaction with C and Mo at an austenite grain boundary were investigated using first-principles calculations. It was demonstrated that B has a strong tendency to segregate to the grain boundary and leads to a remarkable reduction in grain boundary energy, which is considered to be responsible for the improvement in hardenability. A strong attractive interaction between B and Mo was revealed, consistent with the experimentally observed co-segregation. The partitioning energies of Mo and B from grain boundary into borocarbide were calculated, and it was found that Mo can suppress the precipitation by increasing the partitioning energy of B and destabilizing the $M_{23}(C,B)_6$ phase.

Keywords: metals and alloys; atomic scale structure; grain boundaries; segregation; first-principles calculations

1. Introduction

Hardenability is the ability of a steel to transform from austenite into hard phases during cooling by suppressing the formation of soft phase, i.e., ferrite. A sufficient hardenability allows for formation of a bainitic or martensitic microstructure under industrial cooling conditions. To improve the hardenability, a sufficient amount of alloying elements was often added to the steels. For example, for the bainitic rail steels, usually more than 2 mass% Mn was added to ensure a bainitic matrix [1]. For the purpose of conservation of alloying element resources and cost reduction, attention has been paid to boron, which is known to improve the hardenability of low-alloy steels even in a very small amount [2,3]. The beneficial effect of B on the hardenability is believed to be due to the decrease in grain boundary (GB) energy by B segregation, which retarded the nucleation of ferrite [4,5]. On the other hand, the precipitation of $M_{23}(C,B)_6$ results in a deterioration in hardenability as the precipitates act as nucleation sites for ferrite. Therefore, the effect of B on the hardenability is also influenced by the presence of other alloying elements [6–9]. The combined addition of Mo and B is known to have a synergistic effect on the hardenability, which was attributed to the suppression effect of Mo on the precipitation of $M_{23}(C,B)_6$ [6,8,9].

As an important alloying element widely used in steels, the segregation behavior of B and its interaction with other alloying elements have been extensively studied by first-principles calculations [10–15]. However, many of these studies focused on the behavior of B at the bcc-Fe GB in ferritic steels or at the GB and metal/oxide interface in



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). austenitic stainless steels. Although within the framework of DFT, the interfacial properties were estimated at 0 K, the results seemed able to explain phenomena observed at finite temperatures. Wang et al. predicted the spherical morphology of the Cu precipitate based on the DFT-calculated Fe-matrix/Cu-precipitate interfacial energies with different interface orientations, consistent with experimental observation [16]. The alloying element segregation at the Fe-matrix/Cu-precipitate interface and its effect on the kinetic of precipitate coarsening was also well captured by DFT calculation [17]. So far, there is no systematic study on the influence of B on the GB energy and its interaction with Mo at the fcc-Fe GB, which is relevant to the hardenability of steels.

The aim of this work was to understand the effect of B on the hardenability of steels from ab initio calculations. In this regard, the segregation behavior of B, C, and Mo and their interaction at the fcc-Fe GB as well as the effect of alloying elements on the stability of $M_{23}(C,B)_6$ were studied.

2. Methodology

First-principles calculations were performed based on density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) code [18,19] with the projector augmented wave (PAW) method [20,21] and the Perdew–Bruke–Ernzerhof (PBE) generalized approximation (GGA) [22]. A cutoff-energy of 450 eV was applied. The 3p3d4s states for Fe, 4p4d5s states for Mo and 2s2p states for B and C were treated as valence states. Full relaxation of the shape, volume of the supercells, and the ionic positions were allowed until the forces on each atom were less than 0.02 eV/Å. For the GB, the supercell volume was first optimized by stretching and compressing the supercell in GB normal direction under the condition of constant shape and volume [12] before full relaxation was performed, in order to ensure the finding of the most stable configuration. Periodic boundary conditions were applied and Monkhorst–Pack *k*-point mesh was used as listed in Table 1.

Supercell	Number of Atoms	k-Point Mesh
$1 \times 1 \times 3 \text{ GB}$	120	4 imes 2 imes 4
$1 \times 1 \times 2 \text{ GB}$	80	4 imes 2 imes 6
$M_{23}(C,B)_{6}$	116	4 imes 4 imes 4

Table 1. *k*-point mesh sampling of different supercells.

An accurate treatment of paramagnetic state of fcc-Fe is rather challenging for DFT calculations and the most straightforward approach is to use ordered magnetic arrangements to approximate the paramagnetism [23,24]. In this study, non-magnetic (NM) calculations and double-layer antiferromagnetic (AFMD) calculations were performed to calculate the segregation energies, which were most commonly used in DFT calculations for fcc-Fe grain boundaries [14,15,24,25]. The latter was considered as a reasonable approximation to the true paramagnetic state [23,26,27] and the former was computationally more feasible. As will be discussed later, the segregation energies seemed to be affected only slightly by the magnetic approximation. Therefore, NM calculations were used throughout the study unless otherwise specified. The equilibrium lattice constant *a* obtained by NM calculation is 3.44 Å, in good agreement with previous first-principles calculations [14,15,23,28]. Spin-polarized calculations were performed for the ferromagnetic [29] 116-atom $M_{23}(C,B)_6$ supercell (Figure 1c). The four Wyckoff sites 4a, 8c, 32f, and 48h are distinguished by different colors.



Figure 1. Atomic structure of Σ 5(210) fcc-Fe GB supercell (**a**), perspective view of the structural units (**b**) and M₂₃(C,B)₆ supercell (**c**).

The $1 \times 1 \times 3 \Sigma 5(210)$ fcc-Fe GB supercell (Figure 1a) was applied for the NM calculation, which contains 120 Fe atoms and 6 interstitial sites at the center of the capped trigonal prism (CTP) structural unit, as shown in Figure 1b. Mo and C were treated as substitutional and interstitial atom (Mo(s) and C(i)), respectively, while B can occupy both the interstitial and substitutional sites in Fe [12]. Therefore, both possibilities (B(i) and B(s)) were examined in this study. In the following, interstitial and substitutional solute atoms will be denoted as X (X = B, C) and Y (Y = B, Mo), respectively. According to Ref. [24], the most stable segregation site for substitutional alloying elements resides either in the GB 'core' plane, or in its neighboring atomic plane, denoted as S0 and S1 site in Figure 1a, respectively. Both sites were examined for substitutional B and Mo, and it was found that B and Mo prefer to occupy S1 and S0 site, respectively.

The average solution energy of interstitial atom X at the GB in Fe-X binary system was defined as

$$E_{\rm sol}^{\rm GB}(X) = \frac{E_{\rm tot}^{\rm Fe-X} - E_{\rm tot}^{\rm clean} - m\mu_X}{m} \tag{1}$$

and the solution energy of substitutional atom Y in Fe-Y binary system was defined as

$$E_{\rm sol}^{\rm GB}({\rm Y}) = \frac{E_{\rm tot}^{\rm Fe-{\rm Y}} - E_{\rm tot}^{\rm clean} - n\mu_{\rm Y} + n\mu_{\rm Fe}}{n} \tag{2}$$

where *m* and *n* represent the number of interstitial and substitutional atoms, respectively. $E_{\text{tot}}^{\text{Fe}-\text{X}}$ and $E_{\text{tot}}^{\text{Fe}-\text{Y}}$ are the total energies of the GB supercell containing alloying element atoms, and $E_{\text{tot}}^{\text{clean}}$ is the total energy of the pure Fe GB supercell. The 1/6 monolayer (1/6 ML = 1 solute atom/interface) and 1 monolayer (6 solute atoms/interface) were considered to represent dilute limit and high concentration, respectively. Therefore, *m* and *n* are either 2 or 12 in Equations (1) and (2) for the NM calculations. For AFMD calculations, the 1 × 1 × 2 GB supercell was applied, so that there were four atomic layers along the [001] direction (*z* direction in Figure 1a), with two layers spin up and the next two layers spin down. With such a magnetic configuration, all four available interstitial/substitutional sites in the 1 × 1 × 2 supercell are symmetrically equivalent. μ indicates the atomic energy of elements in their crystal form (fcc-Fe, bcc-Mo, graphite, and α -B), which will be cancelled

out during the calculation of segregation energy. The segregation energy was defined as the energy gain by moving the alloying element atom from grain interior (GI) to the GB [17],

$$E_{\rm seg} = E_{\rm sol}^{\rm GB} - E_{\rm sol}^{\rm GI} \tag{3}$$

where GI was modeled with the GB supercell where a solute atom was placed at the octahedral site on the atomic layer farthest from the GB plane. A negative segregation energy indicates that the solute atom is prone to segregation.

The interaction energy (per interface) associated with combining two systems A and B with the chemical composition [(120- n_1)Fe, m_1X_1 , n_1 Mo] and [(120- n_2)Fe, m_2X_2 , n_2 Mo] was defined as [12]

$$E_{\text{interact}}^{A,B} = \frac{E_{\text{tot}}^{C} + E_{\text{tot}}^{\text{clean}} - E_{\text{tot}}^{A} - E_{\text{tot}}^{B}}{2}$$
(4)

where the chemical composition of the combined system C is $[(120-n_1-n_2)Fe, m_1X_1 + m_2X_2, (n_1 + n_2)Mo]$. A and B are binary systems with either m = 0 or n = 0. The factor 2 in Equation (4) accounts for two grain boundaries in the supercell. The interaction energy represents the energy change by bringing all the solute atoms from two separate GBs into one GB and leaving the other one clean. A positive interaction energy indicates a repulsive interaction and vice versa.

The GB (formation) energy of a binary system Fe-X (Fe-Y) at dilute limit was defined as the energy required to glue two crystals and form interfaces following Ref. [17]:

$$\gamma_{\rm GB} = \frac{E_{\rm tot}^{\rm GB}(120{\rm Fe}, 2{\rm X}({\rm Y})) - 2E_{\rm tot}^{\rm GB/2}(60{\rm Fe}, 1{\rm X}({\rm Y}))}{2A}$$
(5)

where *A* is the area of the interface.

According to Ref. [30], the partitioning energy, i.e., the energy required for an alloying element atom M to partition from the matrix to the precipitate, is a good indicator for the stabilizing/destabilizing effect of M on the precipitate. The partitioning energy of both B and Mo were considered in the present study. The energy required for a B atom to partition from a clean and Mo-segregated GB into the Fe₂₃C₆ phase was defined as

$$E_{\rm p}^{\rm B(i)} = \left(\frac{E_{\rm tot}^{\rm GB}[120{\rm Fe}, 2{\rm C}]}{2} + E_{\rm tot}^{\rm ppt}[92{\rm Fe}, 1{\rm B}, 23{\rm C}]\right) - \left(\frac{E_{\rm tot}^{\rm GB}[120{\rm Fe}, 2{\rm B}]}{2} + E_{\rm tot}^{\rm ppt}[92{\rm Fe}, 24{\rm C}]\right)$$
(6)

and

$$E_{\rm p}^{\rm B(i)} = \left(\frac{E_{\rm tot}^{\rm GB}[108\rm Fe, 12\rm Mo, 2\rm C]}{2} + E_{\rm tot}^{\rm ppt}[92\rm Fe, 1\rm B, 23\rm C]\right) - \left(\frac{E_{\rm tot}^{\rm GB}[108\rm Fe, 12\rm Mo, 2\rm B]}{2} + E_{\rm tot}^{\rm ppt}[92\rm Fe, 24\rm C]\right)$$
(7)

The energy required for a Mo atom to partition from a clean GB into the $Fe_{23}C_6$ and $Fe_{23}(C,B)_6$ precipitate was defined as

$$E_{\rm p}^{\rm Mo} = \left(\frac{E_{\rm tot}^{\rm GB}[120{\rm Fe}]}{2} + E_{\rm tot}^{\rm ppt}[91{\rm Fe}, 1{\rm Mo}, 24{\rm C}]\right) - \left(\frac{E_{\rm tot}^{\rm GB}[118{\rm Fe}, 2{\rm Mo}]}{2} + E_{\rm tot}^{\rm ppt}[92{\rm Fe}, 24{\rm C}]\right)$$
(8)

and

$$E_{\rm p}^{\rm Mo} = \left(\frac{E_{\rm tot}^{\rm GB}[120{\rm Fe}]}{2} + E_{\rm tot}^{\rm ppt}[91{\rm Fe}, 1{\rm Mo}, 1{\rm B}, 23{\rm C}]\right) - \left(\frac{E_{\rm tot}^{\rm GB}[118{\rm Fe}, 2{\rm Mo}]}{2} + E_{\rm tot}^{\rm ppt}[92{\rm Fe}, 1{\rm B}, 23{\rm C}]\right)$$
(9)

A negative partitioning energy E_p^{Mo} indicates that Mo is prone to partition from the Fe matrix into the precipitate and vice versa.

3. Results and Discussion

The calculated solution energies are listed in Table 2. Solution energies were usually calculated using cubic bulk supercells in literature while in our study, a bulk-like model, i.e., the GB slab with a solute atom placed in the atomic layer far from the GB plane (grain

interior) was applied. Theoretically, the two models should give the same result, as long as the supercell is sufficiently large. This was confirmed by the good agreement between the present study and Ref. [13] in the solution energy of both interstitial B and substitutional B, where NM calculations were applied. According to our calculation, the interstitial site is energetically more favorable than the substitutional site for B. Ponomareva et al. combined the magnetic sampling method and magnetic special quasi-random structure technique to simulate the paramagnetic state of fcc-Fe [31]. Jiang and Carter modeled fcc-Fe as a ferromagnetic high-spin phase [23]. These two studies yielded C solution energies with opposite signs, indicating that the calculated solution energy depends on the treatment of paramagnetism in fcc-Fe.

Alloying Element	Solution Energy	Segregation Energy
B(i)	0.26, 0.25 [13]	-1.93, -1.56 [13]
B(s)	0.45, 0.47 [13]	-1.44, -1.56 [13]
C	0.04, 0.20 [31], -0.17 [23]	-0.47, -0.24 [13]
Мо	0.28	-0.35, -0.44 [24]

Table 2. Solution and segregation energies of alloying elements in fcc-Fe (eV).

The calculated segregation energy and GB energy are plotted in Figure 2. Although the solution energy is affected by the magnetic treatment, the effect seems to be cancelled out during the calculation of segregation energy as it represents the change in energy by moving the solute atom from the bulk region to the GB. This was confirmed by the comparison between the NM- and AFMD-calculated segregation energy at dilute limit. Although the AFMD-calculated segregation energy was systematically lower, the difference in segregation energies between different alloying elements agree fairly well between the AFMD and NM results (Figure 2a). The more negative segregation energy of B(i) suggests that B prefers interstitial site to substitutional site while in both sites the segregation energy of B is significantly lower than that of C and Mo. The trend of segregation energy still holds at higher concentration (1 monolayer). The calculated segregation energy was compared with literature using the same definition, as listed in Table 2. While giving the similar solution energy, the present study and Ref. [13] show different results in segregation energies of interstitial and substitutional B. The AFMD-calculated Mo segregation energy in our study is -0.63 eV, while that reported in Ref. [24] is -0.44 eV. The reason for the discrepancies may be the different relaxation methods applied in these studies. Nevertheless, the general trend that B shows a stronger segregation tendency than other alloying elements seems unaffected.



Figure 2. Segregation energy (**a**) and GB energy (**b**) of different systems.

The GB formation energy without alloying elements was calculated to be 1.55 J/m^2 , in reasonable agreement with DFT results reported in other works (1.60 J/m² [13] and 1.75 J/m^2 [14]). Our calculations suggest that the GB energy is reduced significantly by B

segregation $(1.17 \text{ J/m}^2 \text{ for B(i)} \text{ and } 1.22 \text{ J/m}^2 \text{ for B(s)})$ and only decreased modestly by C and Mo (1.45 J/m^2) . It is believed that the reduced GB energy by B delays nucleation of ferrite at austenite GB [4,5] and thus increases the hardenability. The DFT results demonstrate a strong segregation tendency of B and its effectiveness in reducing the GB energy, which explains the improvement in hardenability by addition of a very small amount of B.

Figure 3 compiles the X_1-X_2 and Mo–X interaction energy at dilute limit. The interaction energy between interstitials is rather weak, oscillating within ± 0.04 eV. The calculated results indicate an attractive interaction between Mo and B/C atoms beyond an interatomic distance of 2.5 Å. It can be seen that B and C behave similarly in terms of interaction with Mo and with themselves at the GB. When the concentration of Mo and interstitial B was increased to 1 monolayer, the interaction energy between them was calculated to be -1.82 eV. The strong attractive interaction indicates the co-segregation of Mo and B at the austenite GB, consistent with experimental observation by atom probe tomography [32].



Figure 3. Interaction energy between interstitial solute atoms (a) and between Mo and interstitials (b).

The partitioning energies for B and Mo are plotted in Figure 4. The energy required for an interstitial B atom to partition from clean GB to $Fe_{23}C_6$ precipitate is 0.18 eV. The positive sign indicates that interstitial B is reluctant to form borocarbide. When a monolayer of Mo is present at the GB, the partitioning energy is further increased to 0.21 eV (Figure 4a). By definition, an increase in partitioning energy indicates that the partitioning from the GB into the precipitate becomes more difficult. As interstitial B atoms are strongly attracted by Mo atoms, they prefer to co-segregating with Mo at the GB, rather than entering the precipitate until all the interstitial sites have been occupied.



Figure 4. Energy required for B (a) and Mo (b) to partition from GB into $M_{23}C_6$ and $M_{23}(C,B)_6$.

Figure 4b presents the energy required for Mo to partition from the GB into the $M_{23}C_6$ and $M_{23}(C,B)_6$ precipitates with Mo occupying different Wyckoff sites. For each Wyckoff site, there may be several symmetrically inequivalent relative positions for Mo and B (blue bars). It can be seen that the partitioning energy of Mo is positive except at 8c-sites, which indicates that Mo destabilizes $M_{23}(C,B)_6$ phase and suppresses the precipitation. Due to the attractive interaction between B and Mo at the GB, the addition of Mo can further improve the hardenability via inhibiting the formation of borocarbides.

4. Conclusions

First-principles calculations indicate that both interstitial and substitutional B exhibit a strong segregation tendency and decrease the GB energy significantly. The reduction in GB energy is believed to suppress the nucleation of soft phase, i.e., ferrite, and thus improve the hardenability. The present study reveals a strong attractive interaction between Mo and B, which is responsible for their co-segregation observed by experiments. The calculated partitioning energies suggest that Mo destabilizes the $M_{23}(C,B)_6$ precipitates. Therefore, in the presence of Mo at the GB, the driving force for B to segregate is even larger and B feels reluctant to enter the precipitate. The interaction between B and Mo thus further increases the hardenability, which provides insight into the synergistic effect of Mo and B on the hardenability as reported in experimental studies.

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