First-principles study on the effects of co-segregation of Ti, B and O on the cohesion of the α-Fe grain boundary

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Abstract
The effects of Ti, B and O co-segregating on the α-Fe Σ5 [001]/(010) grain boundary are studied by a first-principles method, DMol. We found that (Ti + B) acts as an enhancer, but O can completely offset the beneficial effect of Ti. Based on the segregation energy analysis, it is also found that Ti can effectively prohibit O from segregating to the grain boundary and therefore eliminate the embrittlement of grain boundary induced by O. Thus, Ti is a kind of desirable addition in α-Fe to improve the mechanical properties.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The fracture behaviour of ultra-high strength steel has been intensively studied both experimentally and theoretically for decades. To date, it has been well known that the intergranular embrittlement is often the most important factor that limits the ductility and strength of structural steel. Alloy elements and metalloid impurities segregating to the grain boundary (GB) can dramatically affect intergranular embrittlement. Some impurities such as B, C, and Re, act as cohesive enhancers when segregating to the GB; some others, such as H, P, and Si, reduce the ductility of the GB [1–5]. Although many works have been presented, the underlying mechanism of the segregation effects is still an open question.

A thermodynamic theory developed by Rice and Wang [6] describes the mechanism of impurity-induced embrittlement, which is indicated by the competition between brittle interfacial separation and crack blunting. The potency on embrittlement of impurities can be predicted by the equation

$$2\gamma_{\text{int}} = 2\gamma_{\text{int0}} - (\Delta g_{\text{gb}} - \Delta g_{\text{s}})\Gamma, \tag{1}$$

where $2\gamma_{\text{int}}$ and $2\gamma_{\text{int0}}$ are the ideal cleavage works of an interface with and without impurity atoms, respectively, and Γ is the GB concentration of the impurities; Δg_{gb} and Δg_{s} are the Gibbs free energies of the GB and free surface (FS) segregation. The impurity is considered

as an embrittler in the case of $\Delta g_{gb} - \Delta g_s < 0$, and as a cohesive enhancer otherwise. By ignoring the entropy terms, Wu and Freeman replaced Δg_{gb} and Δg_s by ΔE_{gb} and ΔE_s, which indicate the change of binding energy of the cluster with and without the impurity in the GB and FS case, respectively [7]. They gave a coincident criterion: a negative $\Delta E_{gb} - \Delta E_s$ value indicates the embrittlement effect of the impurity, and a positive one means that the impurity is a cohesive enhancer[3]. A first-principles study is thus highly desired for understanding the mechanism of the effects of segregants on the GB because of high accuracy and in-depth description at electronic level.

Ti is believed to enhance the cohesion of the Fe GB at low concentration [8]. B is the most common cohesive enhancer while O is regarded as a detrimental impurity since it increases the ductile–brittle transformation temperature and embrittles the Fe GB [9–11]. Although the effects of these three kinds of impurity has been studied separately, the co-segregation behaviours of Ti–B or Ti–O are not well understood and the relevant research is rarely established. It is important and interesting to identify the role of the co-segregation of two kinds of impurity, whether they are cohesive enhancers or not. In the present paper, we employed the first-principles method DMol [12] to investigate the co-segregation effects of Ti, B or O on the α-Fe $\Sigma 5$ [001]/(010) GB. The paper is organized as follows: the cluster model and computation details are described in section 2, the energy results are presented and discussed in sections 3 and 4, the density of states (DOS) analysis is provided in section 5, and finally the conclusion is given in section 6.

2. Model and computation details

The DMol code [12] is employed to optimize the atomic configuration and to calculate the electronic structure of the GB and FS with and without Ti, B and O. The local density approximation functional proposed by Vosko *et al* [13] is adopted for the exchange–correlation potential. Double numeric basis sets are used with the 4p polarization function for Fe/Ti and 3d polarization function for B/O, and the frozen-core approximation is used.

The cluster models are shown in figure 1. The pure α-Fe GB is constructed with a coincidence site lattice (CSL) model. We select a cluster of 91 atoms in five stacking layers along the [010] direction. To consider the co-segregation, a Ti atom is assumed to substitute Fe1 atom on the GB core and FS, while the B(O) impurity occupies the interstitial site in the triangular prism formed by Fe and Ti atoms. The local atomic configuration is sufficiently optimized by fixing the outermost atoms of the cluster, and adjusting vertical components of positions of Fe atoms which are not on the GB plane [14], and horizontal components of the position of B(O) and those Fe atoms which are on the GB plane according to the atomic force approach [15, 16]. The C_{2V} symmetry of the cluster is held within the optimization process and the force is converged to less than 10^{-2} eV Å^{-1}. We consider six systems including Fe, B/Fe, O/Fe, Ti/Fe, (Ti + B)/Fe, and (Ti + O)/Fe, which correspond to the pure Fe GB (FS), and the Fe GB (FS) with B, O, Ti, Ti–B, and Ti–O, respectively. The last two are co-segregation cases.

3. Binding-energy difference and segregation energy

3.1. Binding-energy difference

When segregating to pure Fe or the Ti/Fe GB, both B and O push away Fe2, Fe3, and Fe6–Fe9 slightly from their original positions. This is mainly attributed to the size of the available

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[3] Readers should keep in mind that, rigorously, this criterion only works at $T = 0$ K. This condition is fulfilled by the first-principles calculation based on the DFT, which is a ground-state theory corresponding to 0 K.
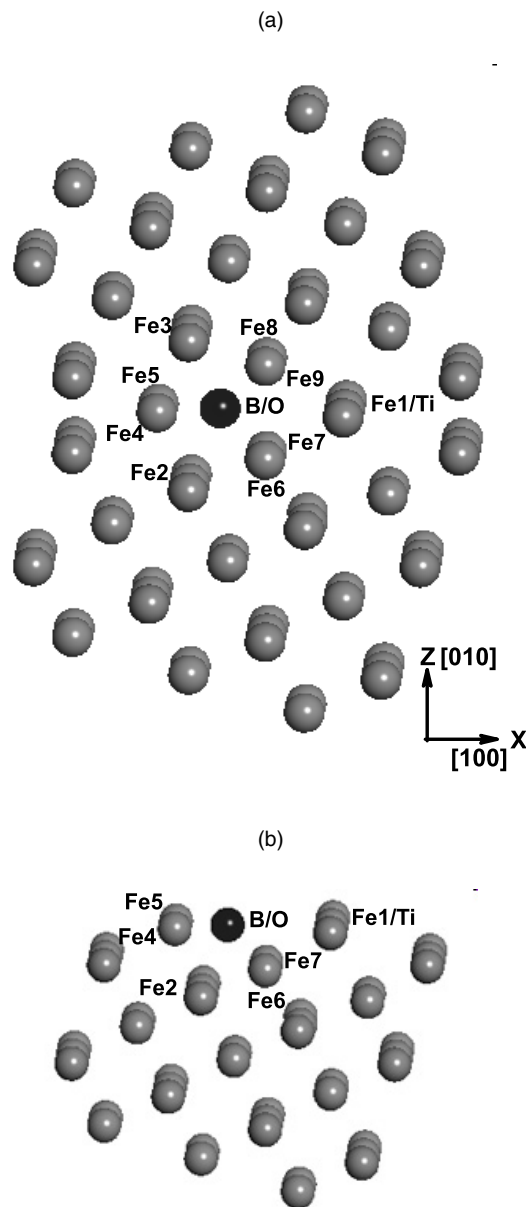
(a)

(b)

Figure 1. The 3D atomic cluster model and notation for the structure of α-Fe $\Sigma 5$ [001]/(010) grain boundary and corresponding free surface. The grey balls denote Fe and/or Ti atoms, and the smaller black ball denotes B or O atoms. (a) is a model of the grain boundary, and (b) is that of free surface. The notation in (a) and (b) is kept consistent.

interstitial volume. The volume of the GB hole (V_{GB}) is 4.3 Å^3, 36.2% of the volume of α-Fe bulk [17] ($V_{bulk} = 11.8$ Å^3). When an impurity atom enters the GB hole, V_{GB} will expand to decrease the elastic energy. The distance between Fe6 and Fe7 depends on the type of impurity. It decreases in Ti/Fe, B/Fe, and (Ti + B)/Fe systems but increases in O/Fe and (Ti + O)/Fe systems with respect to that in the pure Fe GB system.

Table 1. The calculated binding-energy difference (in eV) for grain boundary (ΔE_{gb}), unrelaxed free surface (ΔE_s^0), and relaxed free surface (ΔE_s) of all six systems.

	ΔE_{gb}	ΔE_s^0 unrelaxed	ΔE_s relaxed	$\Delta E_{gb} - \Delta E_s^0$ chemical comp.	$\Delta E_s^0 - \Delta E_s$ mechanical comp.	$\Delta E_{gb} - \Delta E_s$ total
B/Fe	−1.03	−0.06	0.93	−0.97	−0.99	−1.96
O/Fe	−0.03	−0.05	−1.09	0.02	1.04	1.06
Ti/Fe	−1.00	−0.06	0.97	−0.94	−1.03	−1.97
(Ti + B)/Fe	−1.05	−0.10	0.88	−0.95	−0.98	−1.93
(Ti + O)/Fe	−0.07	−0.09	−0.10	0.02	0.01	0.03

The calculated binding-energy difference of each system is listed in table 1. For Ti/Fe and B/Fe systems, $\Delta E_{gb} - \Delta E_s$ are −1.97 and −1.96 eV, respectively, indicating that Ti and B are GB cohesive enhancers. The latter is consistent with other references [18, 19]. The (Ti + B)/Fe system also displays a negative $\Delta E_{gb} - \Delta E_s$ value, which is −1.93 eV, higher than that of Ti/Fe or B/Fe. Thus, the co-segregation of Ti and B will slightly offset the beneficial effects of each other. In contrast, $\Delta E_{gb} - \Delta E_s$ in the O/Fe system is 1.06 eV, so O can be considered as an embrittler. For the (Ti + O)/Fe system, the small $\Delta E_{gb} - \Delta E_s$ value, 0.03 eV, indicates that substituting Ti for Fe on the GB can alleviate the detrimental effect of O, but cannot change the case completely.

In general, the effects of impurity on the GB can be divided into chemical and mechanical components. According to Yang [20] and Freeman [21], the process of GB fracture can be considered in two steps. First, the GB cracks into two separated FSs without any relaxation; the binding-energy difference in this stage, $\Delta E_{gb} - \Delta E_s^0$, is the chemical component. Then, these two separated FSs are fully relaxed, and $\Delta E_s^0 - \Delta E_s$ is the mechanical component.

All the mentioned quantities are calculated, and the results are listed in table 1. The chemical components are −0.97, −0.94, and −0.95 eV for B/Fe, Ti/Fe, and (Ti + B)/Fe systems, respectively, and are comparative to corresponding mechanical components, which are −0.99, −1.03, and −0.98 eV, respectively. These negative values indicate that both chemical and mechanical effects are beneficial to the GB cohesion, and FS relaxation is crucial. In contrast, the mechanical component in the O/Fe system possesses a positive value 1.04 eV, and becomes the dominant factor, which reveals that the cracking of the GB into two FSs is energetically more favourable. In the (Ti+O)/Fe system, although the chemical and mechanical components are both positive (0.02 and 0.01 eV, respectively), it is hard to conclude that (Ti + O) is detrimental to the GB cohesion, because the accuracy of the present calculation is only to 10^{-2} eV due to the approximations we employed (LDA, frozen-core and finite cluster). Nevertheless, it should be noticed that the mechanical component for the (Ti + O)/Fe system is much less than that for the O/Fe system, which is 1.04 eV. It can be concluded that Ti reduces the detrimental effect of O by almost completely offsetting the mechanical component.

3.2. Segregation energy

To investigate the mechanism of co-segregation and mutual effect of the impurities, we define the segregation energy of an impurity i, E_{seg}^i, as follows:

$$E_{seg}^i = E_b(GB + i) - E_b^{ref}(GB), \qquad (2)$$

where $E_b(GB + i)$ and $E_b^{ref}(GB)$ indicate the binding energies of the GB system with impurity and the corresponding reference system (pure Fe or Ti/Fe system), respectively. E_{seg}^i can indicate whether the impurity tends to segregate into the GB hole or not. The calculated

Table 2. The calculated segregation energy (in eV) of each kind of impurity for both the interstitial and substitutional doping case. i indicates impurity, and $E_b^{\text{ref}}(\text{GB})$ means the binding energy of the reference system. It should be noticed that for the (Ti + B)/Fe and (Ti + O)/Fe systems, the reference system is Ti/Fe.

	$E_b(\text{GB} + i)$	$E_b^{\text{ref}}(\text{GB})$	E_{seg}^i
B/Fe	−4.90	−3.87	−1.03
O/Fe	−4.00	−3.87	−0.13
Ti/Fe	−4.87	−3.87	−1.00
(Ti + B)/Fe	−4.92	−4.87	−0.05
(Ti + O)/Fe	−3.94	−4.87	0.93

segregation energies of the six systems are listed in table 2. $E_{\text{seg}}^{\text{B}}$, $E_{\text{seg}}^{\text{O}}$ and $E_{\text{seg}}^{\text{Ti}}$ are −1.03, −0.13 and −1.00 eV, respectively, when they segregate to the pure Fe GB. It is interesting that $E_{\text{seg}}^{\text{B}}$ increases remarkably to −0.05 eV and $E_{\text{seg}}^{\text{O}}$ reverses to a large positive value 0.93 eV when Ti substitutes Fe1 at the GB. The sign of $E_{\text{seg}}^{\text{B}}$ keeping invariant means that B still tends to segregate to the Ti/Fe GB system, while the reversal of the sign of $E_{\text{seg}}^{\text{O}}$ implies that Ti can effectively prevent the O segregation to the GB, improving the mechanical properties of α-Fe.

These analyses suggest that more knowledge of the binding-energy difference is required to provide an accurate understanding of co-segregation effects.

4. Local site energy

The local site energy E_l is an important quantity implying the local effect of an impurity. It is defined as [22]

$$E_l = \int_{-\infty}^{E_F} E \sum_\alpha \rho_{\alpha l}(E)\, \mathrm{d}E, \tag{3}$$

where l indicates the lth atom and $\rho_{\alpha l}$ indicates the density of states (DOS) of the αth atomic orbital of the lth atom; E_F is the Fermi level of the system. There is a constrained condition

$$N_l = \int_{-\infty}^{E_F} \rho_{\alpha l}(E)\, \mathrm{d}E. \tag{4}$$

N_l means the total number of electrons of the lth atom. It should be noticed that, theoretically, we need to sum over all the atomic orbitals of a given atom, including inner-core orbitals such as 1s2s. Because of the frozen-core approximation that we employed, only the valence orbitals and valence electrons are concerned. Thus, E_l actually means 'valence energy on the lth site' and N_l means the number of valence electrons of the lth atom. The relative difference between the values of E_l of different atoms is thus more important than the absolute value of E_l.

Table 3 shows the calculated E_ls of several given atoms in different systems. When B or Ti segregates on the GB, the E_ls of all atoms on the interface decrease. In the case of a separated free surface, the effect of B is anisotropic: the values of E_l of the atoms nearest to B increase about 2 eV except E_{Fe2}, the change of which is 1.1 eV, only half that of the others. This is because Fe2 does not lie on the surface, thus only the chemical component contributes to the difference of E_l. Ti behaves similarly to B in the case of FS. It can be concluded that the B/Fe and Ti/Fe systems tend to keep GB integrated rather than be separated into FSs. The co-segregation of Ti and B does not show a significant difference on E_ls compared with B/Fe and Ti/Fe. Thus it can be expected that (Ti + B) does not enhance the cohesion of α-Fe GB more in comparison with Ti or B alone.

Table 3. The calculated local site energies (in eV) of the given lattice in all six systems. (a) shows those in the GB case, and (b) shows those in the FS case.

E_l	Pure Fe	B/Fe	O/Fe	Ti/Fe	(Ti + B)/Fe	(Ti + O)/Fe
			(a) GB case			
(Ti)Fe1	−6.0	−10.4	−5.4	−3.6	−3.7	−0.7
Fe2	−7.4	−12.3	−8.9	−10.7	−12.2	−8.8
Fe4	−6.8	−11.6	−8.0	−10.5	−11.5	−8.1
Fe6	−7.4	−12.0	−7.3	−10.7	−12.1	7.3
			(b) FS case			
(Ti)Fe1	−7.4	−5.4	−7.4	−0.6	−0.7	−1.2
Fe2	−10.7	−9.6	−12.1	−7.6	−9.6	−12.2
Fe4	−7.8	−5.1	−8.9	−4.7	−5.4	−9.0
Fe6	−9.4	−7.6	−9.8	−6.6	−7.5	−9.6

In the (Ti + O)/Fe GB, compared with the Ti/Fe GB, E_{Fe2}, E_{Fe4} and E_{Fe6} increase by 1.9, 2.4 and 3.4 eV, respectively. But in the (Ti + O)/Fe FS, E_{Fe2}, E_{Fe4} and E_{Fe6} decrease 4.6, 4.3 and 3.0 eV, respectively. The data suggest that if the (Ti + O)/Fe GB is divided into two separated FSs, the E_l of each site which is on the interface of the GB will decrease; thus separating into FSs is more favourable for the (Ti + O)/Fe system. It should be noticed that E_{Ti} increases dramatically from −3.6 to −0.7 eV when O segregates on Ti/Fe GB, while it decreases from −0.6 to −1.2 eV in the (Ti + O)/Fe FS. This suggests that the co-segregation of Ti and O is not favourable in the case of the GB; thus Ti can effectively prohibit the segregation of O. Besides that, the E_ls of O/Fe are similar to those of (Ti + O)/Fe, and O is an embrittler for the α-Fe GB.

5. Density of states

The local densities of states (LDOSs) have been introduced in section 4; they are obtained by broadening the discrete eigenvalue spectrum with sets of Lorentzian function. The calculated LDOSs are shown in figures 2 and 3.

In the case of B/Fe GB, the LDOSs of Fe2, Fe4, and Fe6 display some hybridization peaks associated to the B 2s orbital, which means that B bonds to its nearest-neighbour (NN) Fe atoms. The LDOSs of Fe1, Fe2, Fe4, and Fe6 shift to a lower energy range compared with those in the pure Fe GB. The anti-bonding peaks are below the Fermi level due to the B segregation. This is beneficial in lowering the system energy. The effects of Ti and (Ti + B) are similar to that of B. The LDOSs of relevant atoms in (Ti + B)/Fe GB and Ti/Fe GB coincide with each other. Thus, it can be expected that the co-segregation of Ti and B does not enhance the cohesion of the α-Fe GB further compared with Ti or B alone.

For the (Ti + O)/Fe system, the LDOSs of all the relevant atoms shift to higher energies in the GB case and to lower energies in the FS case compared with those of Ti/Fe. This indicates that the segregation of O will completely cancel the enhancive effect of Ti.

6. Conclusions

The co-segregation effects of (Ti + B) and (Ti + O), together with the effects of B, O, and Ti along, are studied by a first-principles method. The calculated results show that Ti and B are cohesive enhancers, and O is an embrittler. When the co-segregation of two kinds of
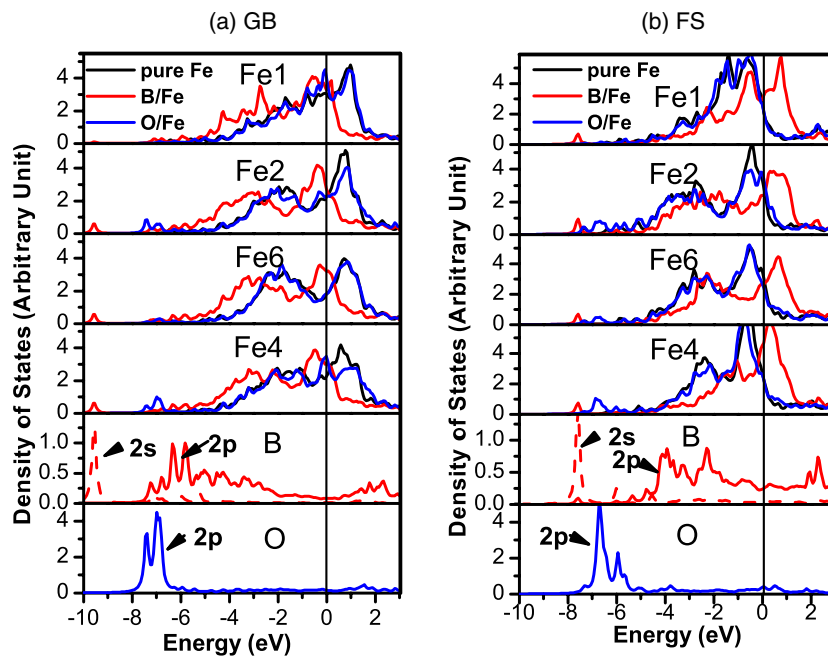
Figure 2. Local densities of states (LDOSs) of Fe1, Fe2, Fe4, and Fe6 atoms in (a) pure Fe, B/Fe, and O/Fe GB, (b) pure Fe, B/Fe, and O/Fe FS. The E_F is set to zero, and is represented by the vertical thin line.
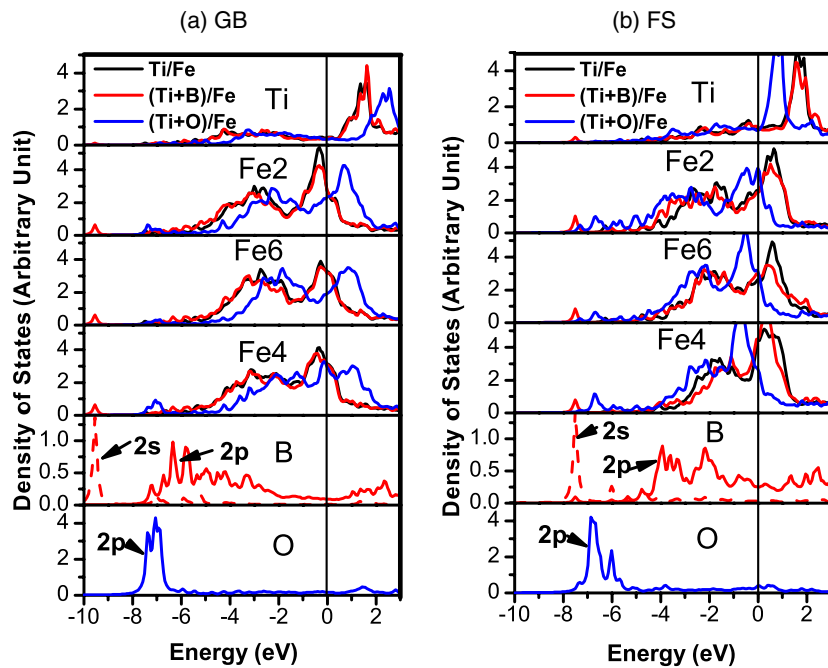

Figure 3. Local densities of states (LDOSs) of Ti, Fe2, Fe4, and Fe6 atoms in (a) Ti/Fe, (Ti + B)/Fe, and (Ti + O)/Fe GB, and (b) Ti/Fe, (Ti + B)/Fe, and (Ti+O)/Fe FS. The E_F is set to zero, and is represented by the vertical thin line.

the impurities occurs, (Ti + B) enhances the GB cohesion, but Ti can completely reduce the detrimental effect of O. Furthermore, based on the segregation energy analysis, we found that Ti additions can effectively prohibit the segregation of O to the GB, and therefore improve the cohesion of α-Fe. Thus, Ti is a kind of desirable addition in α-Fe.

Acknowledgments

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