

Segregation of H, C and B to $\Sigma = 5$ (0 1 3) α -Fe grain boundary: A theoretical study

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Abstract

The ASED-MO theory is used to study the effects of H and the H–C and H–B pairs in the electronic structure of a Fe grain boundary (GB). The results obtained for H in a GB model are consistent with its behavior as a chemical embrittler. The total energies calculated for FeH, FeC and FeB clusters indicate that all interstitials segregate to the GB. C has the lowest energy, followed by B, and could compete with other impurities for the site location on the GB.

The results obtained for FeCH and FeBH are consistent with the observed behavior of C and B as cohesion enhancers. A strong repulsive interaction between C and H and B and H atoms is developed if they occupy the nearest interstitial site on the GB. When C or B are present, the total energies are similar to that obtained for the FeH cluster. This indicates that H is displaced from the capped trigonal prism (CTP). Also, we do not detect any C–H or B–H interaction.

Density of states (DOS) and crystal orbital overlap population (COOP) curves are used to shed more light on the interstitial-Fe GB interaction. The existence of strong metal–metalloid bonds is shown, which are primarily due to Fe 3d, 4s and C (or B) 2s, 2p interactions.

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1. Introduction

Intergranular embrittlement in metals is usually caused by impurities segregating towards the GBs [1]. The larger the grain size, the smaller amount of impurity is needed to saturate the GB. Fine-grain polycrystals are known to be less brittle. It should be noted that BCC crystals, being not as close packed as FCC or HCP, are particularly prone to GB embrittlement by impurity segregation [2]. A problem such as this is very complex. The full process of intergranular fracture undoubtedly involves dislocation motion and pile ups, plastic deformation, work hardening and bond breaking [3]. In this paper we focus on the chemical bonding aspect of this problem. If we can understand why the segregated impurities weaken the bonds at the grain boundaries, then we will be one step closer to a complete description of intergranular fracture.

It is well known from experiments that H cause embrittlement [4,5] while B and C improve the GB cohesion in Fe. In

fact, in Fe, C and B are known to displace harmful impurities such as P, Sn and S from the GB and thus reduce the detrimental effects of these impurities [6–11].

Using surface-analytical methods, Grabke [12] studied the GB segregation of C in ternary Fe–P–C and Fe–S–C alloys and conclude that C has two effects: (1) upon increasing GB concentration the P is displaced from the GB; (2) C decreases the tendency for intergranular fracture and increases the cohesion of the GB. Similar effects have been observed for B and N.

On the theoretical side, Wu et al. [13] investigated the effect of C on the Fe GB cohesion and determined that C is a cohesion enhancer. Comparisons with earlier results obtained for B, S and P show that the number of the hybridized p electrons and the resulting spatial anisotropy of bonding with the surrounding Fe atoms is the key factor determining the relative embrittling or cohesion enhancing behavior of a metalloid impurity.

The interaction of BCC Fe with defects and H as an interstitial atom has been investigated in preliminary works by our group. In all cases, we have found that the total energy of the system decreases when the H atom is located near the defect

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void, making it a possible region for H accumulation. The H atom bond to their closet neighbor Fe weakening the bond between Fe atoms. In general, the H effect is limited to its first Fe neighbors. H–H interaction was also analyzed. Although same H–H association is revealed, no bond is formed between the impurity atoms [14–18].

We have also studied the Fe–C and the Fe–S interaction. Both interstitials weaken Fe–Fe bonds perpendicular to the GB plane and simultaneously form new interstitial-Fe bonds, although C shows the possibility of connecting the two halves of the crystal with a bridge Fe–C–Fe bond. Such “connection” makes C a cohesion enhance [19].

In the present work we study the $\Sigma = 5$ (0 1 3) 36.9° [1 0 0] symmetrical tilt GB in BCC Fe and model H, C and B impurities in interstitial positions, trying to elucidate the bonding character of the segregated impurities at the GB. We use the atom superposition and electron delocalization molecular orbital (ASED-MO) method, which is described in Appendix A.

2. Atomic structure

A cluster formed by 196 atoms of Fe was used as a model of the $\Sigma = 5$ (0 1 3) tilt grain boundary [20]. The atomic configuration, projected on the (1 0 0) plane is shown in Fig. 1. The boundary contains a stack of capped trigonal prisms (CTP). The nine-atom CTP is the fundamental unit of this boundary that are shown in Figs. 1 and 2a. In Fig. 2b can be seen the atomic configuration of the (0 1 3) BG plane.

In order to find the GB structure corresponding to a minimum of energy, the interplanar distances were varied while the structure within the (0 1 3) planes were fixed [21,22]. It was found that the interplanar distances oscillate as a function of the distance from the GB, decreasing the oscillation amplitudes with the departure from the GB. Then, starting with the minimum energy structure for pure Fe boundary, an impurity atom was located at the center of a CTP and the structure was relaxed again. The atomic relaxation is found to extend mainly over the first five planes from GB. The (0 1 3) planes that contain iron atoms like Fe₁ increases the separation of the grains while that planes that contain iron atoms like Fe₃ are moved toward the GB plane in the minimum energy structure. It

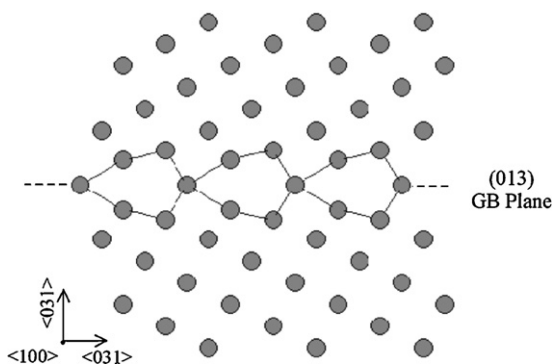


Fig. 1. Model of the symmetric tilt grain boundary in α -Fe, with [1 0 0] tilt axes which forms a twin about the (0 1 3) plane, viewed parallel to tilt axes.

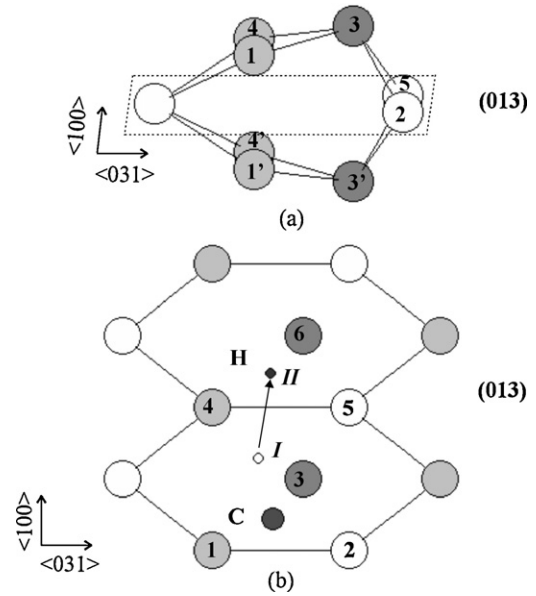


Fig. 2. (a) Capped trigonal prism (CTP) and the (0 1 3) GB plane. (b) Atomic configuration of the GB plane in the cluster with C and H as interstitials. The white, light grey and dark grey mark atomic positions of Fe atoms in alternating (0 1 3) planes, parallel to the GB plane. I and II correspond to H site of highest stability in the FeH and FeCH clusters, respectively.

is interesting to note that the relaxed interface with carbon interstitial has a smaller Fe₁–Fe_{1'} distance than the relaxed clean GB (2.10 versus 2.27 Å). This is an evidence that there is a significant bonding interaction between the carbon interstitial and its near neighbor Fe atoms. The separation between the grains is reduced by this C–Fe interaction. Similar results were reported by Braithwaite et al. [23] using first principles quantum mechanical calculations. For this author, the shortest Fe–Fe distance across the GB with interstitial C is 1.99 Å.

The nearest neighbor distances in the bulk BCC Fe lattice (2.477 Å) are the distances between nearest atoms in the $\langle 1 1 1 \rangle$ direction, while the shortest distances are the one between atoms across the GB plane (see Fe₁–Fe_{1'} in Fig. 2a). The BCC lattice parameter was taken as 2.866 Å [24].

3. Results and discussion

3.1. Location of the hydrogen and carbon in the grain boundary

Let us discuss first the most stable localization for the H atom within the CTP. We have performed calculations locating the H atom on different sites of two different planes. This is, on the (1 0 0) plane, perpendicular to the GB plane, located in the middle of the CTP, and on the (0 1 3) plane. Fig. 3a and b shows the total energy contours lines for that two options, with minimum of -6.72 and -6.76 eV, respectively. We can see that the H atom achieve the higher stability on the GB plane, over a large stability zone within only 0.02 eV of broadening.

In the second stage, we have performed calculations for a C atom located on the (0 1 3) plane. The contour energy lines are shown in Fig. 4. Two minimum energy regions of -16.36 eV

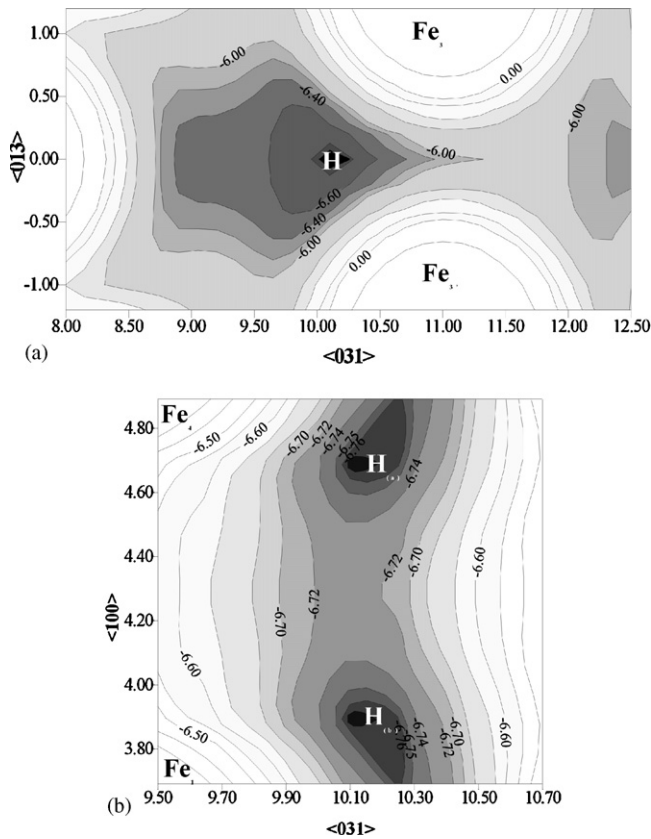


Fig. 3. Contour lines corresponding to the energy of the FeH system: (a) (1 0 0) plane, $E_{\min} = -6.72$ eV at (10.10, 0.00, 4.29), (b) (0 1 3) plane, $E_{\min} = -6.76$ eV at (10.10, 0.00, 4.69) and (10.10, 0.00, 3.89) indicated by $H_{(a)}$ and $H_{(b)}$. The regions of higher stability are darker.

were found, which are symmetrical with reference to the (1 0 0) plane in the middle of the CTP. This site is 0.76 eV more stable than a site in the middle of the CTP. If we compare both minimum of energy, this is, that for the FeH and for FeC

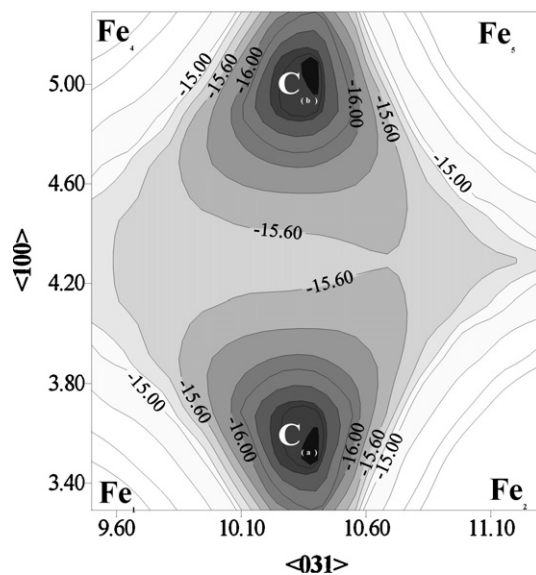


Fig. 4. Contour lines corresponding to the energy of the FeC system. There are two energy minimum of -16.36 eV at (10.40, 0.00, 3.49) and (10.40, 0.00, 5.09), indicated by $C_{(a)}$ and $C_{(b)}$.

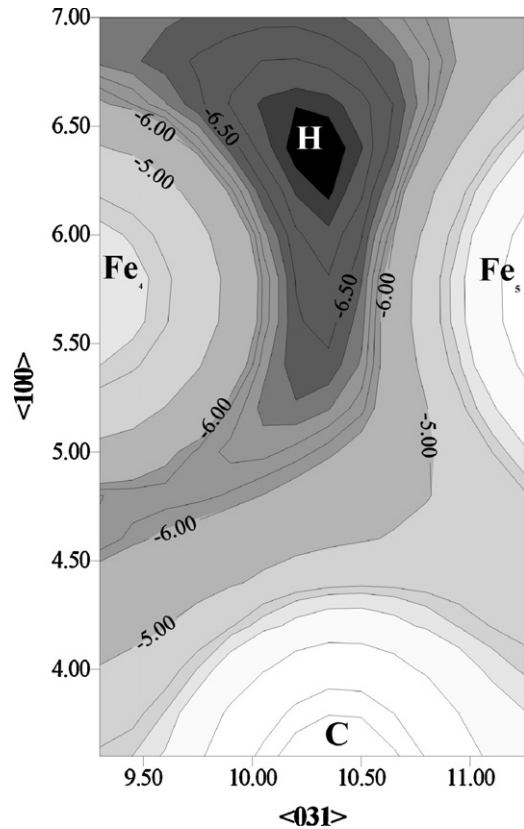


Fig. 5. Energy of the FeCH system. $E_{\min} = -6.75$ eV. The C–H distance is 2.91 Å.

systems, we can expect a site competition between H and C at the GB.

After that, while the C atom is located in its energetic minimum, which correspond to that shown in Fig. 4, an H atom was moved on the (0 1 3) surface, and the energy for this FeCH system was computed. The results are shown in Fig. 5, with a minimum energy of -6.75 eV, similar to that for the FeH (see Table 1). This is so, because the H atom is pushed away of the CTP that contain the C atom and found a new stable location in the neighbor CTP. The C–H distance is 2.91 Å. In Fig. 2b we can see the scheme for the C and H positions; (I and II of this figure correspond to H site of highest stability in the FeH and FeCH clusters, respectively).

The bond length for Fe–C in a C/Fe(1 0 0) surface, determined by LEED is 1.94 Å which is smaller than the sum of the covalent radii of the elements (2.02 Å), a result that could indicate a strong bond [25]. First-principles calculation for C in α -Fe (1 0 0) edge dislocation core indicate that the

Table 1
Total energies for FeH, FeC, FeB, FeCH, and FeBH systems

Structure	ΔE (eV)
FeH	-6.76
FeC	-13.36
FeB	-8.86
FeCH	-6.75
FeBH	-6.61

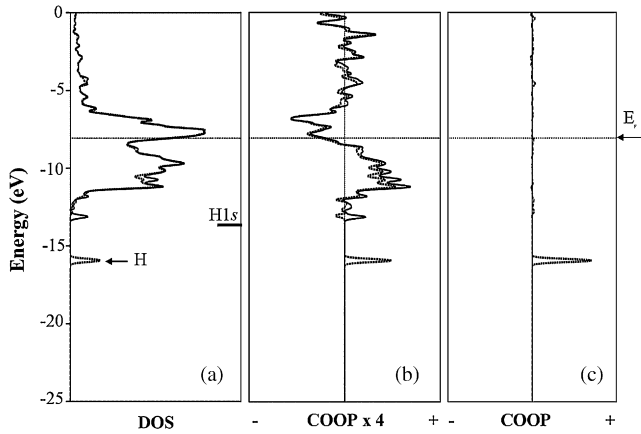


Fig. 6. (a) Contribution to DOS of Fe₃ in the Fe (solid line) and FeH (dotted line) clusters. (b) COOP curves for Fe₃-Fe₄ bond in the Fe (solid line) and FeH (dotted line) clusters. (c) COOP curves for Fe₃-H bond in the FeH cluster.

minimum interatomic distance for the Fe-C bond is 1.84 Å [26]. The results are shown in Tables 2 and 3.

3.2. Electronic structure analysis

We now discuss the change in the electronic structure of Fe atoms next to the GB upon the introduction of an interstitial (see Tables 2 and 3). Fig. 6a compares the projected density of states (DOS) for a Fe atom of the clean GB and with H (dashed line). The curves are similar except for the small peaks at -15.93 eV corresponding to a DOS coming from H-based states. As a result of its interaction, H is stabilized when it is located near the GB, while the Fe-Fe bonding are modified (see Fig. 6b and Table 3). We can notice this effect observing the overlap population (OP) for different bonds in the cluster. The Fe₃-Fe₄ bond decreases its strength by 23% relative to the clean GB while the perpendicular bonds (Fe₁-Fe_{1'}) decreases only 15%.

The contribution to the DOS of Fe₂ in the clean Fe and FeC systems is presented in Fig. 7a. For the C segregation there is an extra small peak, comparing with that of pure Fe at -23.14 eV that correspond to C 2s (76%) bonded with Fe 4s orbitals. Another peak is located at -13.37 eV coming from C 2p (45%)

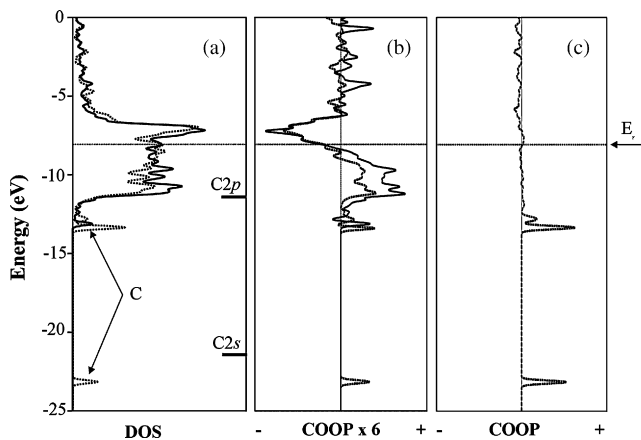


Fig. 7. (a) Contribution to DOS of Fe₂ in the Fe (solid line) and FeC (dotted line) clusters. (b) COOP curves for Fe₂-Fe₃ bond in the Fe (solid line) and FeC (dotted line) clusters. (c) COOP curves for Fe-C bond in the FeC cluster.

Table 2

Net charges for clean Fe, FeH, FeC, FeCH, FeB and FeBH systems

Atom	System					
	Fe	FeH	FeC	FeCH	FeB	FeBH
Fe ₂	1.153	1.196	1.576	1.568	1.259	1.252
Fe ₃	1.271	1.448	1.770	1.802	1.518	1.524
Fe ₄	1.101	1.255	1.140	1.293	1.379	1.528
H		-0.279		-0.273		-0.258
C			-1.437	-1.439		
B					-0.767	-0.730

mainly bonded with Fe 3d and 4s. From the COOP curves it is clear that both states are bonding (see Fig. 7b and c).

The interstitial atoms affect the electronic states of its surrounding Fe atoms causing a rearrangement of the electronic densities. In the FeC system, the Fe s orbital population of an atom nearest neighbor to C diminishes about 16% related to the same atom at the clean GB. The Fe p orbital population also decreases (14%) while the d orbital population decrease only (5%). This indicates a great participation of Fe 4s and 4p orbitals in the Fe-C bond. When we analyze the H effect on the electronic structure of the nearest neighbor Fe atoms, we found that the electronic densities decrease in a similar way for the FeH and FeCH systems, that is, Fe s, p and d orbital population about 8%, 7% and 1%, respectively. This is so due to the repulsive C-H interaction. Each interstitial is located at different CTP and can only interact with the nearest neighbor. In all cases, the interstitial atoms develop a negative charge that is transferred from their Fe closer neighbors (see Table 2). On the other hand, the Fe directly neighboring to the GB are less positive than those located in bulk positions which has a net charge of 1.237e⁻.

The OP and interatomic distances for the clean Fe, FeH, FeC and FeCH systems are shown in Table 3. In all cases, the more

Table 3

Overlap population and distances for metal-metal and metal-interstitial interactions

Bond ^a	Distance (Å)	System					
		Fe	FeH	FeC	FeCH	FeB	FeBH
Fe ₃ -Fe ₄	2.34	0.299	0.230	0.252	0.238	0.190	0.187
Fe ₄ -Fe _{4'}	2.10	0.489	0.414	0.412	0.412	0.374	0.374
Fe ₂ -Fe ₃	2.22	0.381	0.358	0.183	0.185	0.308	0.305
Fe ₁ -Fe ₂	2.91	0.060	0.050	0.000	0.000	0.025	0.025
Fe ₁ -Fe ₃	2.34	0.299	0.264	0.140	0.141	0.190	0.190
Fe ₄ -Fe ₆	2.34	0.299	0.264	0.291	0.223	0.285	0.224
Fe ₁ -Fe _{1'}	2.10	0.489	0.430	0.328	0.327	0.374	0.374
Fe ₃ -Fe ₅	2.22	0.381				0.308	0.305
Fe ₄ -Fe ₅	2.91	0.060				0.025	0.000
Fe ₃ -H _I	1.74		0.208				
Fe ₄ -H _I	1.73		0.208				
Fe ₁ -C	1.72			0.528			
Fe ₂ -C	1.63			0.562			
Fe ₃ -C	1.75			0.517			
Fe ₄ -H _{II}	1.70				0.206		
Fe ₆ -H _{II}	1.75				0.194		
Fe ₄ -B	1.88					0.458	0.436
Fe ₃ -B	1.87					0.472	0.480
Fe ₆ -H	1.67						0.242

^a (') Indicate atoms perpendicular to the GB plane.

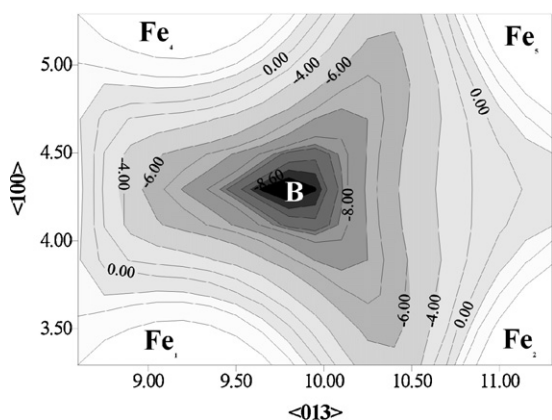


Fig. 8. Contour lines corresponding to the energy of the FeB system. $E_{\min} = -8.86$ eV at (9.8, 0.00, 4.29). The regions of higher stability are darker.

weakened bond result to be $\text{Fe}_3\text{--Fe}_4$ or $\text{Fe}_1\text{--Fe}_3$, that are bonds of the same grain. The $\text{Fe}_1\text{--Fe}_{1'}$ and $\text{Fe}_4\text{--Fe}_{4'}$ bonds, perpendicular to the GB plane, are also weakened. The main force that keeps the two halves of the crystal together are the one between $\text{Fe}_1\text{--Fe}_{1'}$ and between the Fe_3 atoms via the impurity (across the GBs).

3.3. Location of the hydrogen and boron in the grain boundary

In order to study the effect of B–H interaction we have performed calculations for a B atom located on the (0 1 3) plane to get the most stable location. The contour energy curves in Fig. 8 shows the energies for the FeB system, with a minimum of -8.86 eV. This minimum is located in the middle of the CTP, a different site to that obtained for FeH and for FeC systems. Again, this energy value could indicate that B compete with H atom for the site location at the GB, trying to displace it from the GB.

After that, while the B atom is located in its energetic minimum, an H atom was moved on the (0 1 3) surface, and the energy for this FeBH system was computed. The results are shown in Fig. 9, with a minimum energy of -6.61 eV, again similar to that for the FeH. The B–H interaction is repulsive and the H atom is displaced from the CTP to the neighbor one, locating in a equivalent site. The B–H distance is 2.37 Å, this is 0.54 Å shorter than C–H distance in the same environment.

3.4. Electronic structure analysis

When B is located in the GB, the DOS for a Fe atom neighbor to B is similar to that obtained for the cluster without B, except for two small peaks at -17.52 and -13.05 eV (see Fig. 10a). The first of these peaks appears right below the Fe d band (between -12 and -7 eV) and correspond to the interaction of Fe 4s with B 2s states (B 2s 65%). Another peak at -13.05 eV come from B 2p (B 2p 34%) mainly bonded with Fe 4s. The ΔE between this peaks (4.47 eV) is very similar to that found by photo-electron spectroscopy for Fe_2B crystal (4.5 eV) [27].

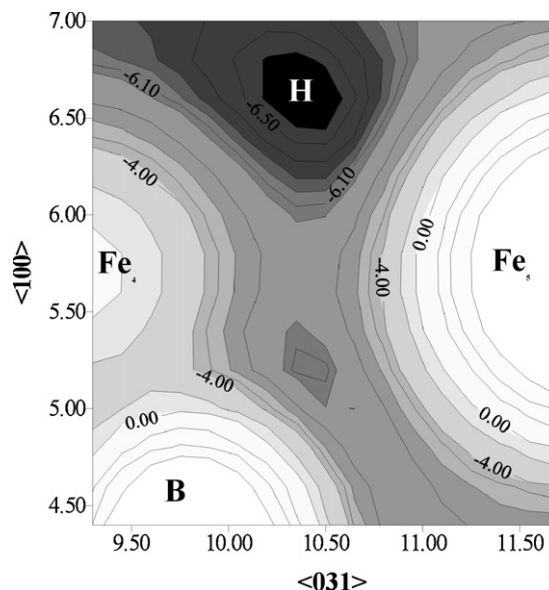


Fig. 9. Energy of the FeBH system. $E_{\min} = -6.61$ eV. The B–H distance is 2.37 Å.

In Fig. 10b we can see the COOP curves for a Fe–Fe bond first neighbor to B in the FeB and FeBH clusters.

Table 3 shows the OP for $\text{Fe}_3\text{--Fe}_4$ that decreases about 36% with B in FeB and FeBH systems. The perpendicular bonds (see $\text{Fe}_4\text{--Fe}_{4'}$) are also weakened.

On the other hand, the B interstitial has a bonding interaction with Fe atoms perpendicular in the GB forming strong a $\text{Fe}_3\text{--B--Fe}_{3'}$ bond that could increase the cohesion at the interface. The $\text{Fe}_2\text{--B}$ distance on the GB plane is longer than in the case of Fe–C system, C form strong bonds with Fe in all directions.

Electron transfer occurs from the Fe atoms to the B atom with an extent of about $0.7e^-$ for both clusters (see Table 2).

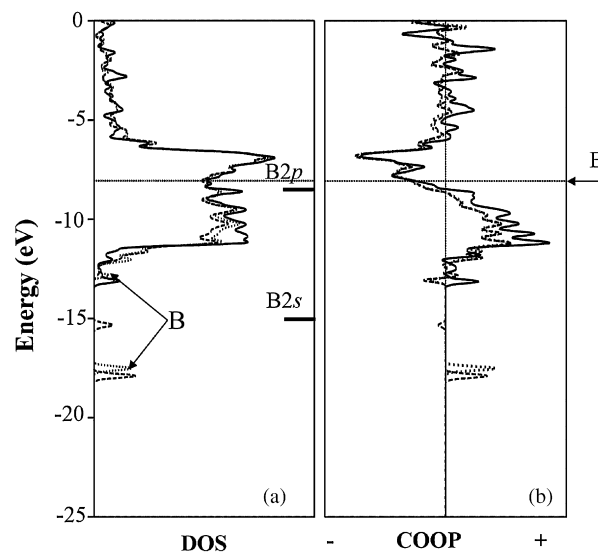


Fig. 10. (a) Contribution to DOS of Fe_4 in: the Fe cluster (solid line), FeB cluster (dotted line) and FeBH cluster (discontinuous line). (b) COOP curves for $\text{Fe}_3\text{--Fe}_4$ bond for FeB and FeBH clusters.

4. Conclusions

We have found that C or B and H prefer to occupy different interstitial sites rather than locating in the same CTP. This site-competition effect can be used in order to clean the GBs of the “harmful impurities” [2], such as H. Boron and carbon may be such a cleaning agent.

When the FeCH or FeBH systems are analyzed, the effect of each interstitial over the nearest neighbor metal atoms are almost the same. This is so because neither B and C do not interact with the H atom. When B or C atom occupies a site, there is a strong repulsive interaction between C–H and B–H atoms. As a result, the stable position for H in each case is in a neighbor CTP. It indicates that the B or C atoms would inhibit the diffusion of H atoms along the GB.

On the other hand, both C and B can strengthen the cohesion of the GB by forming bonds with their neighbor Fe atoms across the GB plane. In the clean GB, the interaction that keeps the two halves of the crystal together are Fe₁–Fe_{1'} or Fe₄–Fe_{4'} across the GB. When an impurity atom is present at the GB, the interatomic interaction changes. The Fe–Fe bonds, perpendicular to the GB, are weakened and the most important interaction is between the impurity atom and Fe₃. This interaction is actually responsible for the intergranular cohesion due to the formation of a Fe-impurity-Fe “bridge” bond.

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Appendix A

The calculations were carried out using the atom superposition and electron delocalization molecular orbital cluster method (ASED-MO) [28]. The ASED-MO is a semi-empirical method, which makes a reasonable prediction of molecular and electronic structures. This theory is based on a physical model of molecular and solid electronic charge density distribution functions, where by the latter is partitioned into a perfect following (with respect to the nucleus) atom part and an imperfect following bond charge part [28,29]. This method was described in a previous paper [14].

The total energy difference can be expressed as

$$\Delta E_{\text{total}} = E(\text{Fe}_m\text{X}) - E(\text{Fe}_m) - E(\text{X}) + \sum E_{\text{repulsion}},$$

X = H, C or B

or

$$\Delta E_{\text{total}} = E(\text{Fe}_m\text{XY}) - E(\text{Fe}_m\text{X}) - E(\text{Y}) + \sum E_{\text{repulsion}},$$

X = C or B, Y = H

where E is the electronic energy, m is the cluster size and X and Y is the interstitial atom. The repulsion energy ($E_{\text{repulsion}}$)

Table 4
Parameters for ASED-MO calculations

Atom	Orbital	Ionization potential (eV)	Slater exponent (au ⁻¹)	Linear coefficient	Pauling electronegativity
H	1s	13.60	1.000		2.1
C	2s	21.40	1.625		2.5
	2p	11.40	1.625		
B	2s	15.20	1.300		2.0
	2p	8.50	1.300		
Fe	3d	9.00	5.350	0.5366	1.8
			1.800	0.6678	
	4s	7.87	1.700		
	4p	4.10	1.400		

of nucleus B in the presence of a fixed atom A is calculated from

$$E_{\text{repulsion}} = \frac{1}{2} \sum_A \sum_{B \neq A} E_{AB}$$

where E_{AB} is a pairwise electrostatic energy term. The summation is extended over all Fe–Fe and Fe–X pairs [28]. The atomic parameters are listed in Table 4.

Throughout this paper, two conceptual tools: density of states (DOS) and crystal orbital overlap population (COOP) curves were used to shed more light on the Fe–X interactions computed with the YAHMOP program [30]. The DOS curve is a plot of the number of orbitals per unit volume per unit energy. The COOP curve is a plot of the overlap population weighed DOS versus energy. Integration of the COOP curve up to the E_f gives the total overlap population of the bond specified. Looking at the COOP, we may analyze the extent to which specific states contribute to a bond between atoms or orbitals [31].

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