

COMPARATIVE STUDY OF Fe–C–H INTERACTION NEAR LINE AND POINT DEFECTS IN IRON STRUCTURES

S. SIMONETTI^{*,†,‡}, G. BRIZUELA[†] and A. JUAN[†]

**Centro de Investigaciones en Mecánica Teórica y Aplicada,
Universidad Tecnológica Nacional,
11 de Abril 461, 8000 Bahía Blanca, Argentina*

*†Departamento de Física,
Universidad Nacional del Sur,
Av. Alem 1253, 8000 Bahía Blanca, Argentina*

‡ssimonet@uns.edu.ar

Received 7 August 2007

The Fe–C–H interaction near defects in iron structures was studied using qualitative structure calculations in the framework of the atom superposition and electron delocalization molecular orbital. Calculations were performed using three Fe clusters to simulate an edge dislocation, a divacancy; both in bcc iron and a stacking fault in an fcc iron structure. In all cases, the most stable location for C atom inside the clusters was determined. Therefore, H atom was approximated to a minimum energy region where the C atom resides. The total energy of the cluster decreases when the C atom is located near the defects zone. In addition, the presence of C in the defects zone makes no favorable H accumulation. The C acts as an expeller of H in a way that reduces the hydrogen Fe–Fe bonds weakening.

Keywords: Defects; iron; carbon; hydrogen; computational simulation; embrittlement.

1. Introduction

Many phenomena such as gas–iron reactions, corrosion, catalysis, surface diffusion, sintering, recrystallization, adhesion, friction, etc. are influenced by the composition of surface and the presence of adsorbed non-metal impurities on the surface. Carbon and hydrogen atoms are common impurities or alloying elements in metals and they modify the physical and mechanical properties of them. Desirable reactions include the formation of carbon nanotubes from gaseous hydrocarbons, making gasoline from synthesis gas, etc.^{1–3} On the other hand, coke formation on the catalyst surface is undesirable as it poisons the catalyst.⁴ Engineers have intent to solve

technological problems such as protecting structure from hydrogen embrittlement,^{5–9} transporting of liquid hydrocarbons in the presence of hydrogen at high temperatures,¹⁰ storing hydrogen fuel at high densities without the danger of high pressures,^{11–13} and designing nuclear fusion reactors.¹⁴ In electronic materials hydrogen plays many roles, both beneficial and detrimental.¹⁵ It is therefore of interest to study how isolated carbon and hydrogen atoms bind near Fe defects, as the first step toward understanding the reactions involving carbon and hydrogen interactions. In this paper, we report the major findings in the study of the Fe–C–H interaction in defects such as an edge dislocation and a divacancy

[‡]Corresponding author.

in bcc structure and a stacking fault in the fcc Fe structures.

2. Computational Method

Energies and optimized positions for C and H were calculated with a cluster approximation using the atom superposition and electron delocalization molecular orbital (ASED-MO) formalism.^{16–19} This modification of the extended Hückel molecular orbital method (EHMO) include core–core repulsive terms to the energy.

The ASED-MO is a semiempirical method, which makes a reasonable prediction of the molecular and electronic structure.²⁰

The ASED theory is based on a physical model of molecular and solid electronic charge density distribution functions.^{19–21}

The adiabatic total energy values were computed as the difference between the electronic energy (E) of the system when the impurity atom/fragment is at finite distance within the bulk and the same energy when the atom/fragment is far away from the solid surface.

The total energy differences can be expressed as

$$\Delta E_{\text{total}} = E(\text{Fe}_m - \text{C}) - E(\text{Fe}_m) - E(\text{C}), \quad (1)$$

and

$$\Delta E_{\text{total}} = E(\text{Fe}_m - \text{C} - \text{H}) - E(\text{Fe}_m - \text{C}) - E(\text{H}), \quad (2)$$

where m is the size of the cluster.

To understand the bondings between the atoms, we performed electronic structure calculations using the YAHeMOP program.²² This program is also based on EHMO and includes Bloch SUMS as basic sets.

3. The Fe Cluster Models

The interaction of C and H atoms with lattice imperfections is important and often dominant in determining the influence of these impurities on the properties of solids. In this paper, we report the interaction, the electronic structure and bonding analysis between C and H and with defects in Fe clusters. We used three Fe clusters which simulate the defect structure environment: a bcc Fe₈₅ cluster containing an edge dislocation, a bcc Fe₁₂₄ cluster with a divacancy, and an fcc Fe₁₈₀ cluster containing a stacking fault.^{23–25} A section of these clusters is shown in Fig. 1. All of the calculations were performed at the central section of the clusters in order to avoid

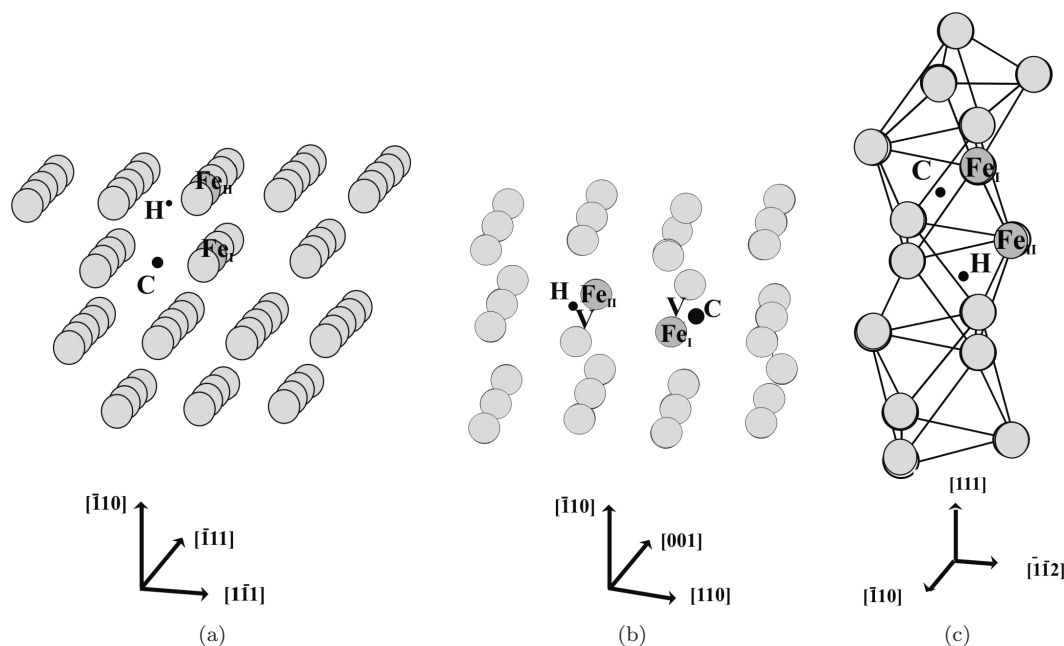


Fig. 1. Schematic section view of the impurities adsorption in the (a) Fe₈₅ cluster containing an edge dislocation, (b) Fe₁₂₄ cluster containing a divacancy (V–V), and (c) Fe₁₈₀ containing a stacking fault.

border effects. The impurities were located, one by one, in their positions of minimum energy in the following order: first the C atom and then the H atom. After determining the most stable position for the impurities in the zone near the defects, we studied the $\text{Fe}_{\text{matrix}}\text{-C-H}$ interactions and the impurity-impurity interactions.

4. Results and Discussion

First of all, we performed calculation for a single carbon atom (C) finding its most stable localization inside the clusters (see Fig. 1). The minimum in the dislocation, divacancy and stacking fault zones was found at 1.81 Å, 1.68 Å, and 1.79 Å of its first Fe neighbor (Fe_1), respectively.²³⁻²⁵ The defect regions

act as a tramp for the C atom and offer a favorable zone for the C location. That trapping of C with defects has also been reported in the literature. It is interesting to note that under our semiempirical approximation the C-Fe distances are quite similar to that of HF level calculations.²⁶⁻²⁹ The interstitial C atom affects the electronic states of its surrounding Fe atoms causing a rearrangement of the electronic densities. Then, a C-Fe bonding is achieved at the expense of Fe-Fe nearest neighbors bonds (see Fig. 2). The strength of the Fe-Fe bond diminishes after C location, but this atom also has the possibility to establish a Fe-C-Fe sort of bridge that provides additional strength to the Fe matrix. The C-Fe overlap populations (OP) in the dislocation, divacancy, and stacking fault zones are 0.726, 0.774 and

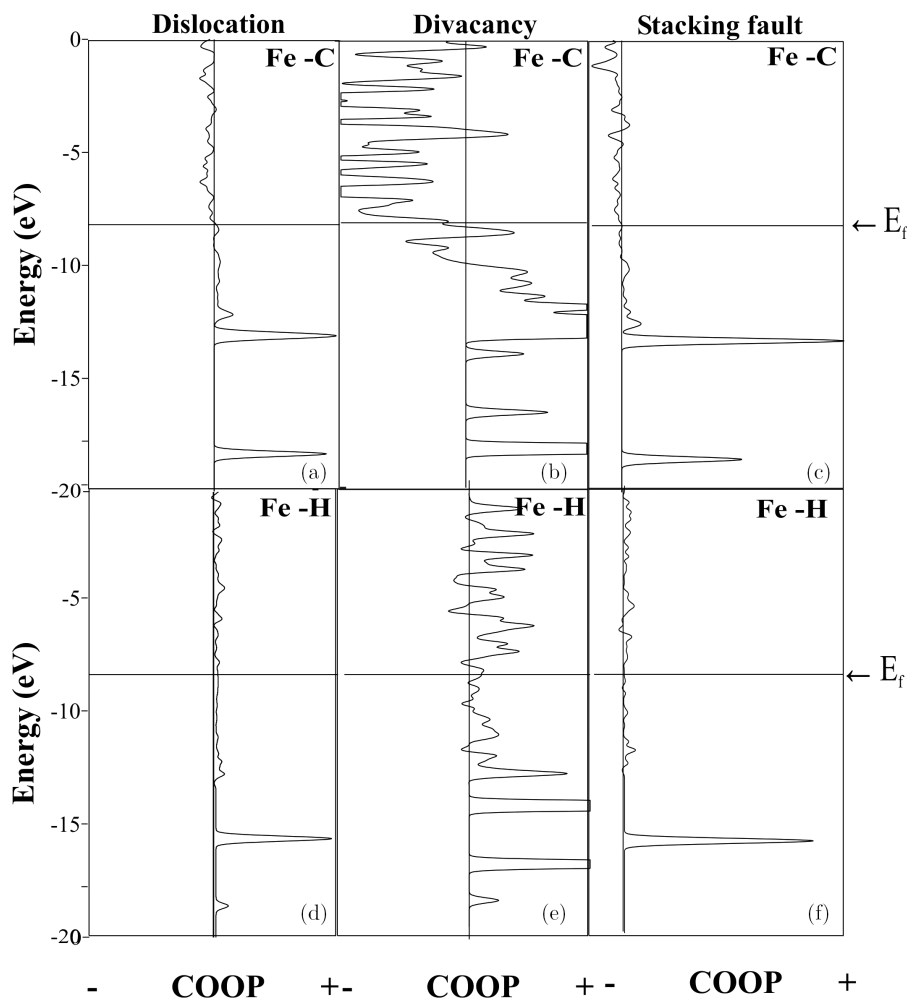


Fig. 2. Coop curves for Fe-C and Fe-H interactions in the Fe_{85} cluster containing an edge dislocation (a) and (d), Fe_{124} cluster containing a divacancy (b) and (e), and Fe_{180} cluster containing a stacking fault (c) and (f).

0.540, respectively. The values in the bcc structures are closer; while near an fcc stacking fault the Fe–C bond is lower (having similar distance).

In a second stage, we performed calculations for the hydrogen atom (H). While the fixed C atom resides in its minimum position, the H is moved along the defects regions (see Fig. 1). The stability decreases when the H atom is located in the Fe–C clusters. Figure 3 shows the energy contour plot for the Fe–C–H interaction in the clusters. The minimum Fe–H distances in the dislocation, divacancy, and stacking fault zones result to be 1.50 Å, 1.58 Å, and 1.73 Å of its first neighbor. The minimum C–H distances in the dislocation, divacancy, and stacking fault zones are 2.25 Å, 2.92 Å, and 3.26 Å, respectively. We can see that the H does not accumulate in the neighboring of the C atom. Then, there is no possible bonding between the H and C impurities at the distances of minimum energy within the Fe clusters. The long C–H distance prevents any interactions between the interstitials. When a diatomic C–H molecule is compared at the same distances in the vacuum the situation is similar. The presence of C does not make favorable any further H accumulation. The experimental information in Fe report that the C acts such as expeller of H and impede the hydrogen atom wreacking the Fe–Fe bond in the defect zone. It has been reported that 185 ppm carbon can prevent the intragranular fracture due to hydrogen.³⁰ The Fe–Fe bonds between atoms neighboring hydrogen reduce their OP after H location. The value of the Fermi energy (E_f) changes slightly with respect to the isolated metal cluster and more antibonding states are now filled for the Fe–Fe interaction. The Fe nearest neighbors OP decrease between 33% and 45%

with the introduction of the H atom in the defects zone. For the Fe cluster containing the dislocation, the Fe 4s orbital diminishes about 11% while the Fe 4p and 3d orbitals diminishes less than 5%. This indicates a participation of Fe 4s orbitals in the bondings. For the Fe cluster containing the divacancy, the Fe 4s population decreases about 16% when the impurities are present. The contribution of Fe 4p and Fe 3d orbitals are less important. For the Fe cluster containing the stacking fault, the Fe 4s and the Fe 4p populations decrease about 12% and 31%, respectively. The Fe 3d orbital participation is less than 8%. In all the cases, the H atom interacts with its Fe nearest neighbors from which it can obtain a negative charge acting as an acceptor of electrons in iron. In general, there is an electron transfer to the impurities from its Fe nearest neighbors and the impurities effect is practically non-extended to second neighbors. An H–Fe bonding is formed in all the studied structures. The H–Fe OP are 0.338, 0.366, and 0.197 in the cluster containing the dislocation, the divacancy, and the stacking fault, respectively.^{23–25} Table 1 summarizes the distances and OP for the major bondings in the Fe clusters. As we can see, the C–Fe OP are bigger than the H–Fe OP. Hydrogen is well known from both experimental and computer calculations as an embrittler. The C–Fe interactions could provide a compensation effect to the Fe matrix that could reduce the hydrogen detrimental effect on the Fe–Fe bonds. A strong bonding between C and Fe clusters arises because of the nearness of the C valence levels to the s–d band of Fe atomic levels and because of the availability of C 2p orbitals for better bonding interactions with Fe d orbitals.³¹ The resulting spatial anisotropy of bonding with the

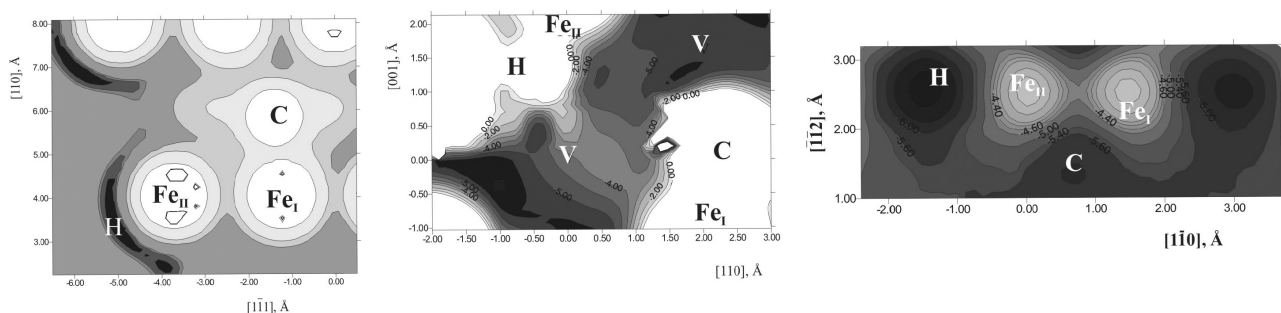


Fig. 3. Contour lines corresponding to the energy (eV) for the Fe–C–H system for (a) Fe_{85} cluster containing an edge dislocation, (b) Fe_{124} cluster containing a divacancy (V–V) and (c) Fe_{180} containing a stacking fault. The regions of lower energy are dark.

Table 1. Distances and overlap populations (OP) for the Fe–C–H interaction in the Fe clusters.

	Distance (Å)	OP
Fe ₈₅ –C–H (dislocation)		
C–Fe _I	1.81	0.726
H–Fe _{II}	1.50	0.338
C–H	2.25	—
Fe–Fe ^a	2.48	0.154
		0.242 ^b
Fe ₁₂₄ –C–H (divacancy)		
C–Fe _I	1.68	0.774
H–Fe _{II}	1.58	0.366
C–H	2.92	—
Fe–Fe ^a	2.48	0.164
		0.297 ^b
Fe ₁₈₀ –C–H (stacking fault)		
C–Fe _I	1.79	0.540
H–Fe _{II}	1.73	0.197
C–H	3.26	—
Fe–Fe ^a	2.54	0.104
		0.241 ^b

Fe_I: nearest neighbor to C atom.

Fe_{II}: nearest neighbor to H atom.

^aNearest neighbor interaction in the zone of the defect.

^bOP value for the metal–metal bond in a cluster free of impurities.

surrounding Fe atoms is the key factor determining the relative embrittling or cohesion enhancing behavior of a metalloid impurity.²⁷

5. Conclusions

The Fe–C–H interaction in three different crystal defects in two iron structures was studied using the ASED-MO method. Calculations were performed using three Fe clusters to simulate the defects of dislocation, divacancy, and stacking fault in the bcc and fcc Fe structures. The most stable position for C and H atoms inside the clusters was determined. According to our calculations the C–Fe interaction was favored in the defects region. The H does not reside in the vicinity of C. The presence of C does not make favorable for further H accumulation. No bonding is formed between interstitial atoms. Both impurities weaken the Fe–Fe bond and their bondings are achieved at the expense of their first Fe neighbors. The C atom also has the possibility to make a Fe–C–Fe bridge that could provide a compensation effect to the Fe matrix that could reduce the hydrogen detrimental effect on the Fe–Fe bonds.

The effect of H and the bridging effect of C depend on the spatial distribution of both impurities.

Acknowledgments

This work was supported by UTN-FRBB, UNS, PIP-CONICET, John Simon Guggenheim Memorial Foundation and Fulbright Commission. S. Simonetti, G. Brizuela, and A. Juan are the members of CONICET.

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