Diffusion and surface segregation of carbon in α-Fe: Molecular-orbital theory

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The diffusion of dissolved interstitial C atoms in α-Fe and their surface segregation have been examined using the atom superposition and electron-delocalization molecular-orbital theory and large α-Fe cluster models in order to include relaxation. Interstitial C is found to bind most stably at a position near the octahedral site, and the diffusion barrier comes when it migrates through the octahedral site. Compression of surrounding Fe—Fe bonds is found to be the driving force for surface segregation, in contrast to our recent study of substitutional S in α-Fe, where the vacancy formation energy played a substantial role in its segregation to the surface.

INTRODUCTION

Carbon dissolved in transition metals is one of the most important nonmetallic impurities and has attracted considerable attention during the past few decades. Carbon is believed to be an interstitial element in cubic lattices and to diffuse through the interstitial sites because it is much smaller than host-metal atoms. Wert[1] developed an expression for the diffusion coefficient for interstitial solute atoms in terms of the enthalpy of activation and the absolute temperature. From the compilation of diffusion data, 0.87 eV was found for the activation enthalpy for C in α-iron. Other experimental work[2,3] has shown a similar activation energy, 0.83 eV, for C diffusion in α-iron. Similar to other impurities, the dissolved carbon in metals segregates to metal surfaces and to grain boundaries. Grabke et al. found 0.87 eV for the enthalpy of segregation of carbon to the (100) surface of α-iron by using a Langmuir-McLean isotherm plot.[4] It has been experimentally observed that carbon segregated to metal surfaces is displaced by sulfur at high temperature,[5] as expected because the segregation enthalpy of carbon is smaller than that of sulfur. In contrast to sulfur, carbon is known to enhance the bonding at grain boundaries.[6] Some theoretical studies have been performed to investigate the metal-carbon bonding character at grain boundaries[7] and in martensite.[8,9] Messmer and Briant[7] suggested from the charge-density maps calculated for small clusters by the self-consistent-field $X\alpha$ scattered-wave method that an impurity such as B, which forms covalent bonds with metal atoms, provides an added increment of bonding by sharing electrons between them, whereas an impurity such as S, which forms ionic bonds, draws the charge from the metal atoms, leading to

weakening of the metal-metal bonds. Other theoretical work[8,10] also showed the covalency of Fe—C bonds in α-iron. The strong covalent bond between Fe and interstitial C results from the Fe $3d$–C $2s,2p$ interactions.[8] Demangeat et al. found, using self-consistent calculations based on a tight-binding scheme,[10] an increase in bond ionicity on going from boron to oxygen.

Many questions concerning impurity diffusion and surface segregation are still unresolved. These include the cause of C segregation, why its driving force is weaker than that of S, the position of interstitial C in α-iron (octahedral or tetrahedral site), and the geometric structure around it. The purpose of this paper is to explain why segregation of C occurs by comparing the stabilities and electronic structures of C on the Fe(100) surface and in bulk iron as we have done recently for S segregation,[11] and to examine the diffusion mechanism by optimizing the geometric structures around C at several positions between the octahedral and tetrahedral sites.

THEORETICAL METHOD

As in the S segregation work, the atom superposition and electron-delocalization molecular-orbital (ASED-MO) theory and large cluster models are used. The parameters for Fe atoms are the same as in Ref. 11. The ionization potential input parameters for the C $2s$ and $2p$ orbitals are decreased by 1.5 eV from their atomic energy levels[12] because of charge transfer to C. The parameters are in Table I.

When a C atom is introduced into an interstitial site, not only does its interaction with neighboring Fe atoms affect the energy but also their relaxation around it. Therefore, the energy change, ΔE, can be divided into

TABLE I. Parameters used in the calculations: Principle quantum number, n; ionization potentials, $E_{\rm IP}$ (eV); and Slater exponents, ζ (a.u.), with linear coefficients, c, for double-zeta d orbitals.

Atom	n	$E_{\rm IP}$ (eV)	ζ	n	$E_{\rm IP}$ (eV)	ζ	n	$E_{\rm IP}$ (eV)	c_1	ζ_1	c_2	ζ_2
Fe	4	7.87	1.85	4	5.44	1.55	3	9.00	0.5366	5.35	0.6678	1.80
C	2	15.09	1.6083	2	9.76	1.5679						

two parts: ΔE_{Fe}, due to Fe atom relaxation and ΔE_C, due to Fe—C bonding. Thus

$$\Delta E = \Delta E_{Fe} + \Delta E_C . \qquad (1)$$

ΔE_{Fe} should be positive since Fe atoms move away from their equilibrium position toward surrounding Fe atoms of the lattice and ΔE_C is expected to be negative since C binds to its neighboring Fe atoms. ΔE_{Fe} is determined from the comparison of unrelaxed and relaxed systems without C atoms, and ΔE_C comes from subtracting ΔE_{Fe} from ΔE. Since in the ASED-MO theory the total energy is the sum of the two-body repulsion energy, E_R, and the molecular-orbital stabilization energy, E_{MO}, the following formulas can be written:

$$\Delta E = \Delta E_R + \Delta E_{MO} , \qquad (2)$$

$$\Delta E_{Fe} = \Delta E_{R,Fe} + \Delta E_{MO,Fe} , \qquad (3)$$

$$\Delta E_C = \Delta E_{R,C} + \Delta E_{MO,C} . \qquad (4)$$

At equilibrium ΔE is at a minimum.

It is assumed that the change in spin polarization of the Fe atoms is induced only by coordination of C to neighboring Fe atoms, not by the relaxation of Fe atoms. The spin-polarization rule of Ref. 11(a) is used.

RESULTS

C on the Fe(100) surface

A low-energy electron-diffraction (LEED) study[5] has revealed that C adsorbs at the fourfold sites on Fe(100). The large four-layer $Fe_{42}(100)$ and the smallest $Fe_5(100)$ cluster models in Fig. 1 are used to study the adsorption of C on the (100) surface. Fe atom relaxations and coverage effects are not included in the model.

The height of C from the $Fe_{42}(100)$ surface layer is calculated to be 0.64 Å. No experimental value is available but it can be compared with the height of O, which is 0.53 ± 0.06 Å on the Fe(100) surface obtained from LEED analysis.[13] The distance between C and the second-layer Fe atom directly below is 2.07 Å, which is shorter than 2.13 Å between C and the surface layer Fe atoms. The binding energy (BE) of C on the $Fe_{42}(100)$ surface is calculated to be 7.89 eV. This is close to the value of 7.56 eV deduced from the segregation enthalpy and the relative partial enthalpy of carbon in α-iron.[4,14] No direct measurement is available. When the same height of C is used on the $Fe_5(100)$ surface, the BE is calculated to be 7.23 eV.

The molecular-orbital diagram for the large $Fe_{42}(100)C_{ad}$ cluster model is expected to be close to the bulk limit for isolated C atom adsorption. For the MO analysis, only the $Fe_5(100)C_{ad}$ cluster is used and the MO diagram for a-symmetry orbital interactions is shown in Fig. 2. The C $2p_z$ orbital interacts mainly with Fe $3d$ orbitals and stabilizes them. The C $2s$ orbital undergoes a bonding stabilization by mixing with Fe $4s + 3d$ orbitals but also pushes up the stabilized C $2p_z + $ Fe $3d$ bonding orbitals by antibonding mixing with the C $2p_z$ orbital. When the interaction of the C $2s$ orbital with Fe orbitals is removed by moving down the C $2s$ level to -50 eV and shrinking the orbital by using a Slater exponent of 30 a.u., the BE of C on the $Fe_{42}(100)$ surface becomes 7.79 eV, which is 0.10 eV, less than when the C $2s$ orbital in-

FIG. 1. Top and side views of $Fe_5(100)C_{ad}$ and $Fe_{42}(100)C_{ad}$ cluster models.
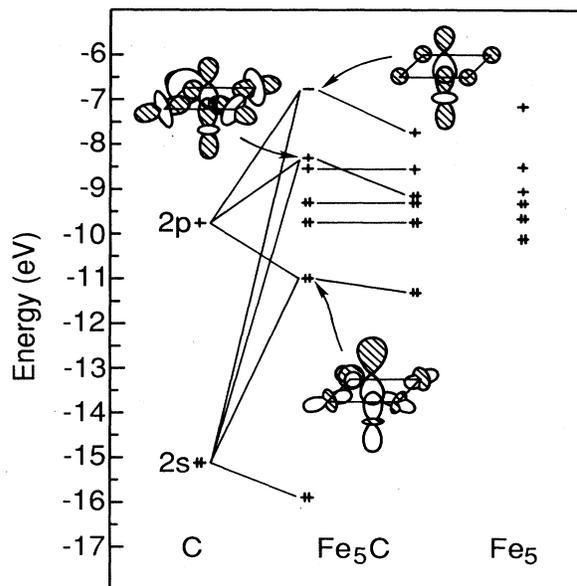
FIG. 2. Interactions of C $2s$ and $2p_z$ orbitals with surrounding metal orbitals in the $Fe_5(100)$ surface cluster. The third column of levels has the C $2s$ interaction removed, and comparison with the Fe_5 column shows bonding stabilization caused by mixing with the C $2p_z$ orbital.

teraction is permitted. Consequently, the C 2*s* orbital interaction with the Fe surface band is bonding, unlike in the S case, though very weak (0.10 eV). Taking into account the 1.5-eV two-body repulsion energy, the contribution of C 2*p* orbitals, including $2p_x$ and $2p_y$, to the BE turns out to be 9.29 eV. The interaction of a C atom with Fe is dominated by the C 2*p* orbitals and the Fe valence-band orbitals. This may be expected to be true for iron's neighbors in the transition series too, as well as for carbon's neighbors, B, N, and O.

C at interstitial sites in α-iron

In bcc α-iron the interstitial C atom has been believed to occupy either an octahedral (O) site or a tetrahedral (T) site and diffuse from one site to the other. The O site has two Fe atoms at a distance of 1.43 Å and four Fe atoms 2.02 Å away from the center. The much shorter distance of the two Fe atoms from the center, compared to the shortest distance between C and Fe atoms in cementite,[15] 1.85 Å, and the distance of 1.91 Å predicted from covalent radii[16] of C and Fe atoms, should cause large Fe atom relaxations away from the C atom. The T site has four equivalent Fe atoms at a distance of 1.60 Å, so Fe relaxation away from C in this site will be important too.

An Fe_{92} cluster model, as shown in Fig. 3, is used for studying C at interstitial sites. This enables relaxations of surrounding Fe atoms to be included. The structures around C are optimized by relaxations of 16–26 surrounding Fe atoms, depending on the sites of a C atom, in 0.02 Å steps for five C positions between the O and T sites. The five sites for an interstitial C atom are O, T, one-fourth (O-M), one-half or middle (M), and three-fourths (M-T) of the distance between the O and T sites. The spin polarization of the cluster is assumed to change linearly for C migrating from the O site through the T site.

The optimized structures for C at the O, T, and O-M sites are shown in Fig. 4. In the O structure, the two
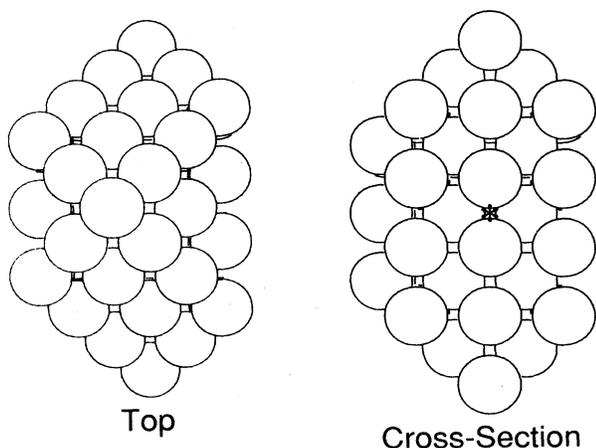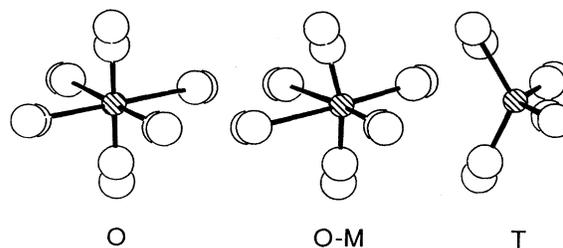
FIG. 4. The optimized structures for an interstitial C atom at the O, O-M, and T sites. Fe atom positions before and after relaxation away from the C atom are shown.

nearest-neighboring Fe atoms move away 0.46 Å and the next-nearest four Fe atoms move 0.11 Å away from their original lattice points. The distance between C and the nearest Fe atoms is 1.89 Å and between C and the next-nearest ones it is 2.13 Å. An x-ray investigation[17] of N in bcc iron showed a similar structure: 0.51-Å expansion of the two nearest Fe atoms but a slight contraction (about 0.01 Å) of the four next-nearest-neighbor Fe atoms. This contraction may be a result of the ionicity of the Fe—N bonds, causing the Fe to become cationic and shrink in size and attract neighboring Fe atoms by charge donation bonding. Another predicted structure for C at the O site of bcc iron is based on overlap analysis[8] and predicts a relaxation of about 0.57 Å for the two nearest Fe atoms. In the T structure, four Fe atoms adjacent to C expand by 0.37 Å to a distance of 1.97 Å. Twenty more Fe atoms are relaxed. Eight of them move away 0.18 Å from their original lattice points and the rest of them move 0.04 Å. When C occupies the O-M site, the two Fe atoms at apexes of the O structure expand 0.47 Å to a distance of 1.91 Å. The two Fe atoms close to C at corners of the square move 0.18 Å away to a distance of 2.09 Å and the other two Fe atoms at corners of the other side also relax 0.12 Å away. The four Fe atoms surrounding the two Fe atoms at the apexes move 0.18 Å. The other four atoms surrounding the two Fe atoms close to C move 0.13 Å. Twelve more surrounding Fe atoms relax < 0.07 Å.

The change in energy for C moving from the O site through the T site is shown in Fig. 5. The O and T sites are comparable in energy to each other but both of them are predicted to be less stable than the O-M site. The changes in energy for an interstitial C atom at various sites are analyzed using Eqs. (1)–(4) and presented in Table II. The largest energy barrier for the migration of C is about half of the experimental estimates for diffusion in α-Fe.[1−3] The BE of C, 7.05 eV, is comparable with the dissolution energy,[18] 6.79 eV, at the eutectoid temperature, derived thermodynamically from the heat of solution of cementite in α-iron. As shown in Table II, the molecular-orbital stabilization from the interaction of the C atom with neighboring Fe atoms, $\Delta E_{MO,C}$, is greatest at the O site but the two-body repulsion energy between the C and surrounding Fe atoms, $\Delta E_{R,C}$, is largest here too. Both results follow from the larger number of neighboring Fe atoms and shorter Fe—C bonds at the

FIG. 3. Top and cross-section views of Fe_{92} cluster model for the interstitial C atom diffusion study; * denotes the octahedral site.
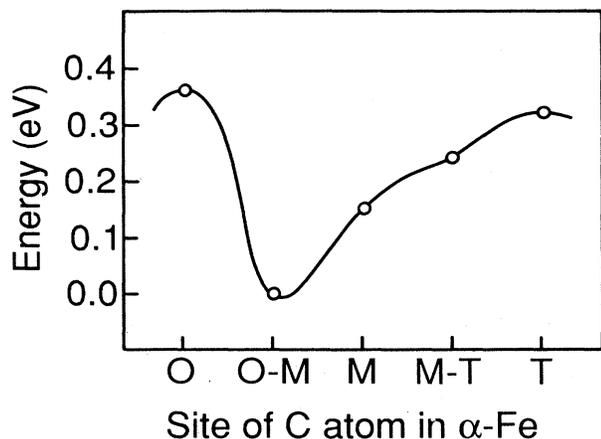
FIG. 5. Calculated energy change for various positions of the interstitial C atom using the Fe_{92} cluster.

FIG. 6. Mo energy levels for the interaction of an interstitial C with surrounding Fe atoms using the small clusters defined in Fig. 4. Only the MO energy levels where the C contribution to the density is greater than 1% are drawn.

O site. However, the sum of $\Delta E_{MO,C}$ and $\Delta E_{R,C}$ is minimum at the O-M site. Also at this site the destabilization due to relaxations of Fe atoms is the least; it is greatest at the O site. As a result, the O-M site turns out to be the most favorable for an interstitial C atom.

Using the clusters shown in Fig. 4, the comparison of MO energy levels for the interaction of C with surrounding Fe atoms at the O, O-M, and T sites is made in Fig. 6. No conspicuous change in MO levels for the different sites of C can be found except for the C $2p$ +Fe d bonding orbitals. At the T site these levels are less stabilized compared to those at the other two sites. The C $2s$ orbital is greatly stabilized and splits far from its empty antibonding counterparts because of the large overlap resulting from the short Fe—C distance. When the contribution of C $2p$ orbitals to molecular-orbital energies is estimated by lowering the level of the C $2s$ orbital to -50 eV and shrinking it with a Slater exponent of 30 a.u., it is 10.57 eV at the O site, 10.31 eV at the O-M site, and 9.96

eV at the T site. The C $2s$ orbital interaction with the Fe orbitals is bonding and almost constant, about 0.4 eV at each site, as expected from the MO energy levels in Fig. 6.

DISCUSSION

The bonding of a C atom to Fe atoms is achieved predominantly through the overlap of C $2p$ orbitals with Fe $4s$ +$3d$ band orbitals irrespective of the position of C in the Fe matrix. The MO energy gain is about 1 eV greater in interstitial sites than on the (100) surface. The result of the C $2s$ orbital interaction with the Fe $4s$ +$3d$ band depends on the position of C; it is almost nonbonding on the surface and weakly bonding at interstitial sites.

TABLE II. Analysis of energy change (eV) due to the introduction of a C atom into various interstitial sites of α-iron.

Energy change	Sites of an interstitial C atom				
	O[a]	O-M[b]	M[c]	M-T[d]	T[e]
ΔE	-6.69	-7.05	-6.90	-6.81	-6.73
ΔE_R	5.77	5.93	5.79	5.88	5.87
ΔE_{MO}	-12.46	-12.98	-12.69	-12.68	-12.60
ΔE_{Fe}	1.22	0.96			0.98
$\Delta E_{R,Fe}$	2.73	3.22			3.21
$\Delta E_{MO,Fe}$	-1.51	-2.27			-2.23
ΔE_C	-7.91	-8.01			-7.71
$\Delta E_{R,C}$	3.04	2.71			2.67
$\Delta E_{MO,C}$	-10.95	-10.72			-10.37

[a]Octahedral site.
[b]Midway site between the O and M sites.
[c]Midway between the O and T sites.
[d]Midway between the M and T sites.
[e]Tetrahedral site.

With respect to this point, other theoretical work showed some ambiguity. Morinaga *et al.* performed calculations on the electronic structures of interstitial C and N atoms in martensitic iron using a discrete variational $X\alpha$ cluster method and suggested that the C (or N) $2s$ – Fe $3d$ interaction is also responsible for the strong covalent bond formation between the interstitial C (or N) atom and the surrounding Fe atoms.[8] In contrast, for C in the center of the substitutional site of bcc-iron, self-consistent spin-polarized calculations showed that C $2s$ orbitals do not strongly perturb any of the levels of the surrounding Fe atoms.[19]

Our predicted segregation energy, which is the difference between the adsorption energy, 7.89 eV, and dissolution energy, 7.05 eV, is 0.84 eV, which is in good agreement with the experimental value[4] of 0.87 eV obtained from a Langmuir-McLean isotherm plot in the temperature range of 496–838 °C. Since the C $2s$ orbital induces net bonding character, though very weak on the surface and at interstitial sites of α-iron, there is no closed-shell interaction, as was observed for sulfur. Rather, the interaction of a C atom with surrounding Fe atoms is stronger at interstitial sites than on a surface. Therefore, the driving force for C segregation is not the same as for S segregation. We can notice that ΔE for C on the (100) surface is about the same as ΔE_C for C at interstitial sites. The difference between two states amounts to ΔE_{Fe}, 0.96 eV, which is the destabilization energy of Fe atoms due to the relaxations. Therefore, the driving force for C segregation comes from the Fe-Fe repulsion energy.

Our calculated C migration barrier is 42% of the measured activation energy for C diffusion in α-iron. There are several factors affecting the calculated energy barrier for the diffusion. The static consideration gives several electrostatic factors for the barrier; the nuclear repulsion, nuclear-electron attraction, and electron-repulsion energies. The first two factors are calculated in terms of electrostatics and included in the two-body repulsion terms of the ASED-MO theory, but of the last factor interatomic electron-repulsion energy is not explicitly obtained. Therefore, the underestimate of the barrier for C

diffusion might result from this approximation of the theory. However, recalling the good agreements of the predicted segregation and dissolution energies of C with the experimental values, the interatomic electron-repulsion energy may be adequately represented in this theory. From a dynamic viewpoint, a nonequilibrium state may be produced during the diffusion process by not-fully-relaxed surrounding Fe atoms. It is believed that the simultaneous rushing of surrounding atoms towards a diffusant is relatively rare.[20] A dynamic analysis would clearly be interesting, but is beyond the scope of this work.

CONCLUSIONS

The strong bonding of C to Fe is achieved through the interaction of C $2p$ orbitals with Fe $4s + 3d$ band orbitals. The interaction of the C $2s$ orbital with the Fe $4s + 3d$ band is dependent on the position of C in α-iron. On the (100) surface it shows weak bonding and at the interstitial sites slightly stronger bonding. This is in contrast to substitutional sulfur, for which our past study found a significant closed-shell repulsive interaction between the S valence $3s$ orbital and the Fe valence band.

For an interstitial C atom in α-iron, it is predicted that the octahedral site is the least favorable and the off-octahedral site one-fourth towards a tetrahedral site is the most favorable. It is deduced from the comparison of energy components of C on the (100) surface and in the interstitial site that C atoms segregate to the surface because of the repulsive compression of Fe—Fe bonds surrounding the interstitial C.

The calculated migration energy of C through interstitial sites is 42% of the activation barrier for C diffusion in α-iron. This underestimate is probably due to approximations of the ASED-MO theory, though nonequilibrium effects may play a role.

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