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CLUSTERING OF CARBON ATOMS IN α -IRON*

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ABSTRACT

Binding and migration energies and atomic configurations have been calculated for small carbon clusters in α -iron. A mathematical model was used which consisted of a spherical crystallite containing about 530 atoms which were treated as individual particles, surrounded by an elastic continuum with atoms imbedded in it. A two-body central force was used to simulate the interaction between nearest and next nearest neighboring iron atoms in the crystallite and another was used for the iron-carbon interaction. The dicarbon, tricarbon, and tetracarbon binding energies were 0.14, 0.36, and 0.66 eV respectively, and the binding energy continued increasing for larger clusters by approximately 0.31 eV per additional carbon atom. The most stable configurations for clusters were very thin platelets on $\{001\}$ planes in which the individual carbon atoms occupied octahedral sites. The axes of the carbon atoms were parallel to each other and perpendicular to the platelet. The migration energy of the platelets was higher than the single carbon migration energy, and the migration mechanism consisted of peripheral atoms moving around the edges of the platelet.

INTRODUCTION

The properties of point defects in metals have been studied recently by carrying out "computer experiments"--lattice calculations in which defect configurations and energies are investigated by treating the atoms as individual particles which interact with two body forces. Most calculations have been concerned with vacancies and interstitials in f.c.c. metals, but some calculations have been carried out for b.c.c. metals ^(1,2) and recently the problem of impurities has been studied. ^(3,4) The impurity calculations have been concerned primarily with carbon interstitials in α -iron ⁽³⁾ and in iron martensite ⁽⁴⁾, although the structure and energy of Fe_3C (cementite) were also investigated ⁽³⁾. These calculations have been extended to the case of carbon clustering in α -iron, and the results of this study are given in the present paper.

In calculations such as this, a model is devised which matches various known physical properties of a metal and which, one hopes, can be extrapolated to yield results about unknown properties of the metal. The solid is represented by a crystalline in which the atoms interact with two-body central forces surrounded by an elastic boundary which is meant to simulate the remainder of the lattice. An energy equation is written in terms of the interatomic forces and the boundary forces, and the parameters in this equation are adjusted to yield a reasonable approximation of the perfect lattice. Then an impurity is inserted and its interaction with the host lattice is adjusted to match some known properties of this system. The energy equation is then investigated in a region of configuration space in which it represents the configurations under study, i.e. the whole process may be thought of as very complicated curve fitting to one section of configuration space and extrapolation to another section. The curve fitting process is not unique however: any

number of quite different models can do a reasonably good job. Also, there is the question of whether or not the forces which describe the perfect lattice are adequate to describe the defect state, i.e. whether extrapolation is physically meaningful. The earlier calculations for vacancies, interstitials, and carbon interstitials⁽²⁻⁴⁾ gave results which appear to be realistic, and thus the extension to more complex configurations is warranted.

The physical interest in studying carbon clusters in α -iron arises because these clusters must be involved in the precipitation of carbides from solid solution, and especially in the poorly understood nucleation processes for the precipitation. There is an abundance of experimental information pertaining to carbide precipitation in iron, but it is extremely difficult to know or control all the factors involved in the precipitation process, and therefore there are many conflicting data. As a result, no clear understanding of the precipitation process has emerged from the available data. The present calculations were carried out with the hope that they would help clarify the situation rather than simply add more confusing information to this already complex problem.

MODEL

The model used in the present calculations has been discussed in detail earlier⁽²⁻⁴⁾ and only a brief summary will be given here. A spherical set of 531 atoms was treated as a crystallite of independent particles and the atoms outside this set were treated as though they were imbedded in an elastic continuum. A two-body central interaction between first-nearest and second-nearest neighboring atoms was used to simulate the iron-iron interaction and a similar but shorter ranged

interaction was used to simulate the iron-carbon interaction. The interatomic potentials are given in Table I. The atoms imbedded in the elastic continuum were allowed to relax radially with a displacement field which decreased as $1/r^2$. The iron elastic moduli were used as a basis for obtaining the iron-iron interaction, and the elastic continuum was "pre-stressed" to give the proper perfect lattice stability. The iron-carbon interaction was obtained primarily from the carbon migration energy, but since this was not sufficient to specify the interaction in the context of this model, the experimental values of the carbon activation volume for migration and the binding energy of a carbon atom to a vacancy were also used.

The energy minima and saddle-point configurations were found using a high speed digital computer (IBM 7094).

RESULTS

The input data used for obtaining the carbon-iron interaction were⁽³⁾: activation energy for carbon migration in α -iron $E_C^M = 0.86$ eV, activation volume for carbon migration in α -iron $V_C^M = 0.00\Omega$, where Ω is an α -iron atomic volume, and binding energy of a carbon atom to an α -iron vacancy $E_{V-C}^B = 0.41$ eV. The migration mechanism was found to be from the site with octahedral symmetry, O, through the site with tetrahedral symmetry, T, to another O site. The O-T-O path is straight and the jump distance is $\frac{a}{2}$, where a is the α -iron lattice constant.

Three dicarbon configurations were found to be stable: $E_{2Ca}^B = 0.14$ eV, $E_{2Cb}^B = 0.11$ eV, and $E_{2Cc}^B = 0.08$ eV. Configuration 2Ca consists of two parallel 0 configurations a distance $\sqrt{3}/2$ apart (the nearest neighbor distance in the α -iron lattice), and 2Cb consists of two parallel 0 configurations a distance $\underline{a}$ apart (the second neighbor distance in the α -iron lattice) with the line joining their centers perpendicular to their orientation. The third configuration does not play any role in larger clusters and will not be discussed.

A tetracarbon cluster is shown in Fig. 1, where the open circles are iron atoms and the closed circles are carbon atoms. The most stable triplet, 3Ca, can be found by removing any one of the four carbon atoms, and may be thought of as being comprised of two 2Ca "bonds" and one 2Cb "bond." The binding energy was $E_{3Ca}^B = 0.36$ eV. The most stable tetracarbon, with a binding energy $E_{4Ca}^B = 0.66$ eV, is the one shown in Fig. 1, and is formed by adding another carbon to the tricarbon configuration such that two more 2Ca and one more 2Cb bonds are formed. This process is continued for larger clusters--the additional carbon is added so that the maximum number of 2Ca and 2Cb bonds are formed.

The energies for a given configuration can be found to a reasonable degree of accuracy with this scheme also. Another dicarbon, 2Cd, which consists of two parallel 0 configurations a distance $\sqrt{2} \underline{a}$ apart with the line joining their centers perpendicular to their orientation, should also be considered. If each 2Ca and 2Cb bond contributes 0.11 eV, and each 2Cc bond contributes -0.02 eV, the energy from simple bond counting for 21 different possible cluster configurations with up to 9 carbon atoms in a cluster never is in error by more than 0.04 eV. The calculated binding energy for the 2Cd configuration was $E_{2Cd}^B = -0.026$ eV, so the cluster configurations and energies are to a very close approximation the superposition of the individual dicarbon configurations and binding energies. A closer fit to the values calculated with the computer can be obtained by somewhat more

complicated schemes, but this very simple method of bond counting is satisfactory for all practical purposes.

It must be emphasised that the dicarbon binding energies arise from the interaction of the strain fields: No explicit carbon-carbon interaction was used. The existence of a carbon-carbon interaction, as long as it is weak, will alter the energy scale somewhat, but should not change the basic pattern of the results. The assumption that the explicit carbon-carbon interaction is small is not unreasonable considering the small size of the carbon atoms and their separation distances in the iron lattice. If there is an electric field associated with a single carbon impurity, there will be an additional repulsion between the carbon atoms, but the effects of screening would reduce this interaction rapidly with separation distance.

The most stable cluster with 9 carbon atoms is shown in Fig. 2. A platelet is being formed on a $\{001\}$ plane: There are 5 carbon atoms in one (001) plane and 4 in the (001) plane a half lattice constant above it. The tendency to form $\{001\}$ platelets continues for larger clusters with an average binding energy of 0.306 eV per additional carbon atom. Fig. 3 shows the total binding energy as a function of cluster size, and it is seen that for clusters larger than the tetracarbon, the points lie on a straight line. The slope of this line defines the average binding energy per additional carbon atom.

A further complication arises when the mechanism of cluster formation is considered. The iron atoms near the platelet are displaced in a $\langle 001 \rangle$ direction from their normal lattice sites, i.e. the body-centered cubic structure is made somewhat body-centered tetragonal. Thus the environment a carbon atom sees when approaching a platelet is similar to that in martensite. For the same reasons that the carbon migration energy in martensite was found to be higher than in α -iron,⁽⁴⁾ the migration energy for a carbon atom approaching a platelet is higher than the single carbon migration energy.

This effect is strongest at the edges of the platelet and therefore creates a barrier towards forming the most stable cluster. There are more loosely bound clusters in which the atoms lie in $\{110\}$ planes which are more easily formed. The amount a given cluster will have $\{100\}$ character and the amount it will have $\{110\}$ character will be determined by the kinetics of the nucleation process. Individual platelets will not thicken by more than the two carbon planes, but it may be possible for platelets to stack up if separated by several lattice constants.

The computations involved in studying the migration of clusters become very involved, and only a few were carried out. Even so a pattern for the migration energy was found: The clusters move by steps in which single carbon atoms jump via the normal mechanism, and the energy required for the step is the single carbon migration energy plus $\frac{1}{2}$ the change in energy between the original and final configurations. This rule gives a slight underestimate because the jumping carbon atom sees a somewhat body-centered tetragonal lattice structure and since it was shown in the martensite calculations⁽⁴⁾ that this increases the migration energy, the single carbon migration energy in the appropriate martensitic environment should be used rather than that for α -iron. It is difficult to estimate this factor for each given case, but the calculated values indicate that it should be in the range of 0.05 eV to 0.10 eV. The results show that the clusters migrate by the peripheral atoms moving around the edge of the platelet, and the energy above the single carbon migration energy, 0.86 eV, is e.g. about 0.06 for dicarbons, 0.20 for tetracarbons, and 0.18 for most stable cluster of 6 carbon atoms. The migration energy increases, but not monotonically, with cluster size, and the total mechanism for migration of the larger clusters becomes so complex that the probability of their migration becomes very small. Also, since the binding energy per additional atom is about 0.3 eV, larger clusters will start to break up at energies lower than their migration energy.

DISCUSSION

These calculations should be most applicable to very small carbon clusters and it is questionable whether conclusions can be drawn pertaining to carbon clusters of measureable size, i.e. a size by which they can be seen by electron microscopy. There is both agreement and disagreement with various experimental interpretations, however, and a discussion is justified.

There are two known precipitates of carbon in α -iron: ϵ -carbide and Fe_3C (cementite). Which form is found in a given case depends upon the details of the experimental treatment. Fe_3C is the more stable phase, and its structure is quite well known.⁽⁵⁾ There is disagreement concerning the energy of a carbon atom in solution in α -iron relative to Fe_3C however, with values ranging from 0.4 to 0.8 eV.⁽⁶⁾ The structure of the metastable ϵ -carbide is thought to be hexagonal,⁽⁷⁾ and recent calorimetric experiments by Arndt and Damask⁽⁸⁾ have given a value of 0.27 eV for the energy of a carbon atom in solution in α -iron relative to some metastable phase which they presume to be ϵ -carbide. The original work in identifying ϵ -carbide as a hexagonal structure⁽⁷⁾ was carried out for decomposition of martensite, and it is not certain that the same phase is formed during the precipitation of carbon from a supersaturated solution of α -iron. Doremus and Koch⁽⁹⁾ report another carbide phase in partially aged samples (the precipitation was stopped when perhaps only half of the carbon had left solution) which they tentatively identified as an expanded α -iron lattice (body-centered tetragonal) with about 0.7 at % carbon. The treatment of their samples was the same as that for which ϵ -carbide had been reported after more complete aging. It is generally agreed however, that the metastable phase seen in most experiments forms platelets on $\{100\}$ planes and preferentially nucleate at dislocations, although nucleation within the matrix can occur with the proper conditions.^(10,11)

The present calculations support the proposal by Doremus and Koch⁽⁹⁾ that a body-centered tetragonal structure is formed during the very early stages of precipitation of carbon from a supersaturated solution in α -iron. Such a structure is similar to martensite. The calculations indicate that this early stage is not a distinct phase but a clustering of carbon atoms within the α -iron lattice in the form of very thin platelets on $\{100\}$ planes. If ϵ -carbide is indeed formed as a later phase, this clustering would appear to set up the appropriate conditions. The structure reported by Doremus and Koch is also similar to that of Fe_{16}N_2 ⁽¹²⁾, an intermediate nitride which is found for both decomposition of nitrogen martensite and precipitation from supersaturated solid solution. The present model does not favor the Fe_{16}N_2 structure in bulk, but does yield about 0.16 eV for the energy of a carbon atom in solution relative to Fe_{16}C_2 in the form of a thin platelet. This structure is the same as the platelet reported in the present calculation except that all the carbons are twice as far separated. Thus if some repulsion does exist as a close interaction between carbon atoms, the Fe_{16}N_2 platelet structure could be energetically very important.

As mentioned above, Arndt and Damask⁽⁸⁾ report a value of 0.27 eV for the energy of a carbon atom in solution in α -iron relative to some metastable phase. This quantity corresponds to the average binding energy per carbon atom in the present calculations, and the calculations are in good agreement if it is assumed that they in fact were measuring body-centered tetragonal clustering rather than ϵ -carbide. In general the present results are thought more probably to err on the side of giving too large rather than too small a binding energy because the carbons more probably repel than attract each other. The dicarbon binding energies reported by Keefer and Wert⁽¹³⁾ are somewhat lower than those reported earlier using the present model,⁽³⁾ in agreement with this suggestion.

It was pointed out in the original carbon-iron report that for the purposes of this model, there is very little difference between carbon in iron

and nitrogen in iron. There were not sufficient data to arrive at an iron-nitrogen potential, but it should be similar to the iron-carbon potential. Thus it is difficult to explain the difference between carbon and nitrogen precipitation in α -iron with the present model. The relative stabilities of the various phases, as given by the model, are in general very close, and thus small differences between the iron-carbon and iron-nitrogen potentials or the existence of different non-negligible carbon-carbon or nitrogen-nitrogen interactions could account for the different structures. The only structure which is definitely energetically unfavorable is Fe_{16}N_2 , but as mentioned above, thin platelets with a Fe_{16}N_2 structure do have reasonable energies.

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TABLE I.

Interatomic potentials, in eV_1 , for the iron-iron interaction and the iron-carbon interaction. The range is given in Å.

RANGE	IRON-IRON INTERACTIONS
<2.40	$-2.195976 (r-3.097910)^3 + 2.704060 r - 7.436448$
2.40-3.00	$-0.639230 (r-3.115829)^3 + 0.477871 r - 1.581570$
3.00-3.44	$-1.115035 (r-3.066403)^3 + 0.466892 r - 1.547967$
>3.44	0

RANGE	IRON-CARBON INTERACTION
<2.523	$-3.365 (r-2.236)^3 + 0.886 r - 2.156$
>2.523	0

FIGURE CAPTIONS

Fig. 1. The most stable tetracarbon configuration, 4Ca. The open circles are iron atoms and the closed circles are carbon atoms. The binding energy for this configuration was $E_{4Ca}^B = 0.66$ eV. The most stable tricarbon configuration 3Ca is found by removing any one of the 4 carbon atoms and has a binding energy $E_{3Ca}^B = 0.36$ eV. Two of the carbon atoms a distance $\sqrt{3}a/2$ apart make a 2Ca configuration, with $E_{2Ca}^B = 0.14$ eV, and two a distance a apart make a 2Cb configuration, with $E_{2cb}^B = 0.11$ eV. Configuration 3Ca may be thought of as having two 2Ca "bonds" and one 2Cb "bond", and 4Ca as having four 2Ca "bonds" and two 2Cb "bonds". The displacement of the iron atoms from their perfect lattice positions is not shown.

Fig. 2. The most stable cluster with nine carbon atoms. This configuration shows the beginning of the formation of a platelet on a $\{001\}$ plane: There are 5 carbon atoms in one (001) plane and 4 in the (001) plane a half lattice constant above it. The displacement of the iron atoms from their perfect lattice positions is not shown.

Fig. 3. The total binding energy of carbon clusters as a function of cluster size. For clusters larger than the tetracarbon, the points lie on a straight line, and the slope of this line defines the average binding energy per additional carbon atom $\bar{B} = 0.306$ eV.

FIG. 1

FIG. 2

Fig. 3