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First-principles calculation of tetragonality and atomic interactions in Fe-C systems

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Abstract: Tetragonality and atomic interactions in Fe-C systems have been evaluated by first-principles calculation in Fe-C systems. Three kinds of supercells, $Fe_{54}C_1$, $Fe_{54}C_2$ and $Fe_{128}C_1$ are used for the calculation of tetragonality. Tetragonality of Fe-C system obtained by first-principles calculation increases linearly with increasing carbon content and agrees well with experimental results. In $Fe_{54}C_2$, tetragonality changes with the configuration of two carbon atoms. The value of tetragonality is either 0.981, 1.036 or 1.090. When the two Fe-C-Fe pairs are parallel, calculated tetragonality is 1.036 and agrees well with experimental data. Mechanical energy, which can be obtained using first-principles calculation and corresponds to the strain energy, is low in comparison with that of perpendicular Fe-C-Fe pairs. Formation enthalpy is also low. Thus, the existence probability under the assumption of a Boltzmann distribution is high. On the other hand, when the two Fe-C-Fe pairs are perpendicular, calculated tetragonality is 0.981 and does not agree with experimental data. Mechanical energy and formation enthalpy are high, and the existence probability is low.

1. INTRODUCTION

An Fe-C martensite is a very important topic both for basic research and practical application, and has been intensively studied for a long period of time. Among the variety of research topics of Fe-C martensite, atomic position of carbon, tetragonality, and mechanism of martensitic transformation are very important and have attracted special attention of many researchers. There are so many studies about these topics, and these studies are reviewed in some textbooks and papers[1-5]. In spite of these researches, we still have some unsolved issues. One of these issues is tetragonality. Why tetragonality appears in Fe-C systems, and how alloying elements affect the tetragonality, are not clarified yet. Tetragonality has a remarkable influence on the material properties of steels. For example, the shape memory effect is improved by increasing the tetragonality of martensite in Fe-based shape memory alloys. This is because high tetragonality produces thin plate martensites, the mobility of the austenite/martensite interface is increased with increasing tetragonality, and the shape memory effect is improved[6]. Ohtsuka and Kajiwara[7] reported that the addition of carbon to an FeNiCoAl alloy coupled with aging treatments increases the tetragonality of martensite and improves the shape memory effect. Moreover, it is expected that high tetragonality makes it difficult for slip deformation to occur, and tetragonality has a considerable influence on the mechanical properties of materials. Therefore, tetragonality is very important as regards understanding the mechanical properties of materials, but very few studies have been conducted on tetragonality from this perspective. In this study, the tetragonality of Fe with various carbon content has been calculated and the effects of carbon atom position on the tetragonality and atomic interactions in Fe-C system have been investigated with first-principles calculation.

2. CALCULATION

The plane-wave base Vienna Ab-initio Simulation Package (VASP) with the pseudo potential method was used for the calculation[8,9]. The density functional theory was applied using the projector-augmented wave (PAW) method based on the generalized density gradient approximation (GGA-PBE) with spin polarization. Two kinds of supercells, a $3 \times 3 \times 3$ supercell with 54 Fe atoms and 1 or 2 interstitial carbon atoms and a $4 \times 4 \times 4$ supercell with 128 Fe atoms and 1 interstitial carbon atom, were used for the calculation. The former supercell consists of $3 \times 3 \times 3 = 27$ bcc cubic cells and is

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abbreviated as $Fe_{54}C_1$ or $Fe_{54}C_2$, while the latter consists of 4 × 4 × 4 = 64 bcc cubic cells and is abbreviated as $Fe_{128}C_1$. The K-point meshes for these two supercell types are 6 × 6 × 6 and 4 × 4 × 4, respectively, and the cut-off energy is 400 eV. These supercells are appropriate for use in the first-principles calculation, as confirmed by Sawada et al[10]. That is, the atomic interactions are sufficiently small and the calculation cost is reasonable. If the supercell is overly small, the carbon atom interaction is large, which affects the calculation results. Further, if the supercell is extremely large, the calculation time cost is also large. Both the shape and size of the supercell can be varied during calculation and, therefore, a full relaxation calculation was performed in this study.

3.RESULTS AND DISCUSSION

As was already mentioned in the previous section, the tetragonality of martensite in Fe-C alloys has been determined experimentally in a large number of studies and, so, a considerable amount of data clearly indicates that the tetragonality is proportional to the carbon content. In order to confirm that the first-principles calculation can reproduce these data, the tetragonality of Fe-C is calculated in supercells with three different carbon content compositions. The $Fe_{54}C_1$ supercell realizes Fe-0.40 mass%C (Fe-1.82 at%C) and is important as a practical structural steel. For steel with lower and higher carbon content, $Fe_{128}C_1$ was used as Fe-0.17 mass%C (Fe-0.78 at%C) and $Fe_{54}C_2$ was used as Fe-0.79 mass%C (Fe-3.57 at%C), respectively. For the first two supercells listed above, which contain a single carbon atom only, all the octahedral sites have the same energy and the tetragonality can be uniquely determined. However, the last supercell contains two carbon atoms and the energy of the octahedral site differs according to the carbon atom configuration. The energies were calculated for all of these conditions. When the second carbon atom is at the center of the cube that is formed by the eight first carbon atoms, the total energy is at a minimum and this tetragonality value is accepted as the tetragonality for $Fe_{54}C_2$. The $Fe_{54}C_2$ tetragonality is plotted in Fig.1[11] in addition to the $Fe_{128}C_1$ and $Fe_{54}C_1$ tetragonality. The calculated data agrees very well with the experimental data. Here, the experimental data are approximated using the linear fit of Cohen et al[12].

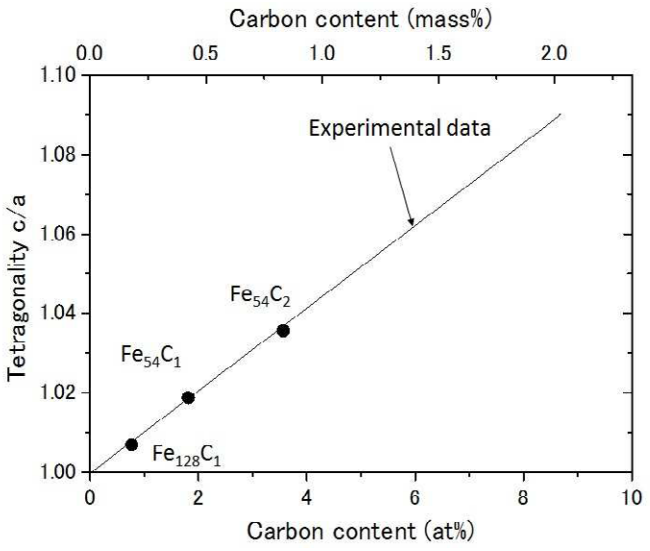

Fig.1 Tetragonality of Fe-C as a function of carbon content. The solid symbols represent the calculated results, while the line indicates the experimental data approximated as a linear relationship[11].

In $Fe_{54}C_2$ supercell, the total energy and tetragonality change according to the configuration of two carbon atoms. So in this section, all the tetragonality data for $Fe_{54}C_2$ is investigated in detail. Note that a carbon atom is in an unstable position if the energy is not at a minimum, but investigation of all the tetragonality and energy data will clarify how the tetragonality value is uniquely determined by the carbon content. It is an advantage of the first-principles calculation that we can obtain the energies of unrealistic states through this approach.

Figure 2 [11] shows the calculated tetragonality value for $Fe_{54}C_2$ (Fe-0.79 mass%C) as a function of the distance between two carbon atoms. The tetragonality varies according to this distance and can be classified into three groups based on value: approximately 0.981 (open circle in Fig.2); 1.036 (solid circle), which agrees with experimental values; and 1.090 (open triangle). The tetragonality data points for the second carbon atom at the first, second, and third nearest neighbor sites of the first carbon atom are indicated by the numbers 1, 2, and 3 in the figure. The number in parentheses indicates that the given symbol represents that number of data points, but it is presented as a single point on this figure. The source of the division of the tetragonality value into three groups and the dependence of the tetragonality value on the carbon content are investigated

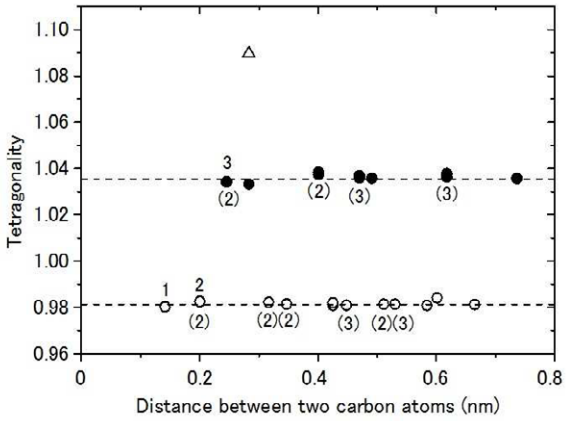

Fig. 2 Calculated value of tetragonality as a function of distance between two carbon atoms. Open circles: c/a =0.981, solid circles: c/a= 1.036, open triangle: c/a = 1.090. The number above the symbols indicates the first, second, and third nearest neighbor carbon atoms of the first carbon atom. The numbers in parentheses show that a single symbol includes that amount of data points[11].

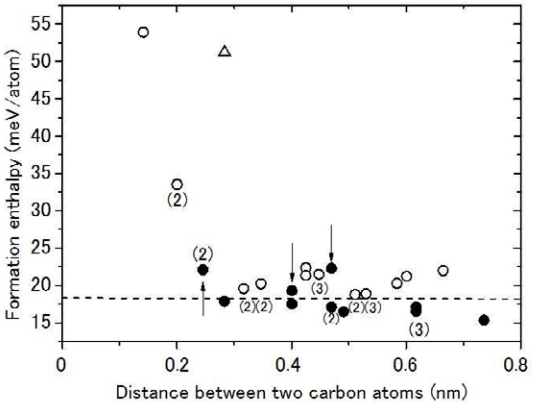

Fig.3 Formation enthalpy for $Fe_{54}C_2$ as a function of distance between two carbon atoms. Open circles: c/a=0.981, solid circles: c/a=1.036, open triangle: c/a = 1.090. The solid and open symbols are in the relatively lower and higher energy regions, respectively, and the arrows indicate exceptional cases. The numbers in parentheses indicate that a single symbol includes that number of data points[11].

through the first-principles calculation. When the Fe-C-Fe pair consisting of the first carbon atom and its two nearest neighbor Fe atoms is perpendicular to the second Fe-C-Fe pair, which is composed of the second carbon atom and its two nearest neighbor Fe atoms, the tetragonality is 0.981 and does not agree with experimental values. On the other hand, when the first Fe-C-Fe pair is parallel to the second pair, the tetragonality is 1.036, which agrees well with experimental data. The mechanical energy, the concept of which was proposed and calculated by Wu et al[13], is calculated for $Fe_{54}C_2$ system. The mechanical energy has been obtained as follows. First, the energy of $Fe_{54}C_2$ system, for which entire stress is almost zero, is calculated. A carbon atom is removed from this supercell and the energy of the $Fe_{54}C_1$ supercell, which still has a distortion caused by the interstitial carbon atom, is calculated. Then, the entire stress is relieved and the energy of the $Fe_{54}C_1$ supercell is calculated. The mechanical energy is the difference between the energies of distorted $Fe_{54}C_1$ system and undistorted $Fe_{54}C_1$ systems. The mechanical energy is very high when C-Fe-C dumbbell structure is formed or two carbon atoms are in the first nearest neighbour sites with each other. In the latter case, two carbon atoms have a strong repulsive interaction. The interaction between two carbon atoms decrease with increasing distance between these atoms.

Figure 3[11] shows the formation enthalpy of $Fe_{54}C_2$ as a function of the distance between the two carbon atoms. The formation enthalpy was calculated from the following equation.

$$[E(Fe_{54}C_2)-\{54E(Fe)+2E(C)\}]/(54+2) \quad (1)$$

Here, E is the total energy obtained from the first-principles calculation. The total energy of graphite was calculated, 17 meV/atom was added to this value, and the result was used as the formation enthalpy for graphite, E(C)[14]. The formation enthalpy is quite high when the C-Fe-C structure is formed, or when the second carbon atom is in the first or second nearest neighboring positions of the first carbon atom. The formation enthalpy for the other positions is distributed within a rather small energy range. All the formation enthalpy values are positive, because the supercell contains 0.79 (mass%) C. This is much higher than the equilibrium solute carbon content in bcc-Fe. The solid circle in the far right

corresponds to the minimum energy position. A clear boundary can be seen between the open and solid circles. When the energy is over 18.3 meV/atom, the tetragonality is approximately 0.981 and, when it is less than this value, the tetragonality is approximately 1.036, which agrees well with the experimental data. In the $Fe_{54}C_2$ supercell, the formation enthalpy is relatively low when the calculated tetragonality is 1.036. The existence probability under the assumption of a Boltzmann distribution is calculated and is high in this case. In other cases, the formation enthalpy is relatively high and the existence probability is almost zero.

4. SUMMARY

The effects of carbon on the tetragonality have been evaluated using the first-principles calculation. Three kinds of supercell, $Fe_{54}C_1$, $Fe_{54}C_2$, and $Fe_{128}C_1$ (which correspond to Fe-0.40C, Fe-0.79C, and Fe-0.17C mass%, respectively) were used for the calculation of the tetragonality of the Fe-C system. The main obtained results are as follows:

(1) The tetragonality of the Fe-C system obtained from the first-principles calculation increases linearly with increasing carbon content and agrees well with experimental results.

(2) In the $Fe_{54}C_2$ supercell, the tetragonality of the Fe-C system change with the distance between two carbon atoms. The tetragonality value is either 0.981, 1.036, or 1.090 depending on the configuration of the two carbon atoms. When the Fe-C-Fe pair consisting of the first carbon atom and its two nearest neighbor Fe atoms is perpendicular to the second Fe-C-Fe pair, which is composed of the second carbon atom and its two nearest neighbor Fe atoms, the tetragonality is 0.981 and does not agree with experimental values. The mechanical energy is relatively large in this case. On the other hand, when the first Fe-C-Fe pair is parallel to the second pair, the tetragonality is 1.036, which agrees well with experimental data. Further, the mechanical energy is relatively small. When a straight C-Fe-C pair is formed, the tetragonality is 1.090 and both mechanical energy and formation enthalpy are high.

(3) In the $Fe_{54}C_2$ supercell, the formation enthalpy is relatively low when the calculated tetragonality is 1.036, and the existence probability under the assumption of a Boltzmann distribution is high. In other cases, the formation enthalpy is relatively high and the existence probability is almost zero.

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