Technical Report

Structure and Energy of Interface between Iron and Precipitate

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Abstract

The precipitates in steel play an important role to strengthen steel. One of the important factors of controlling growth of the precipitate is interface energy between precipitate and iron. It is necessary for the interface energy to calculate more than 1,000 atoms. The calculation is achieved by the use of O(N) method of large scale first-principles electronic structure calculation on TSUBAME 2.0. The interface energy of the semi-coherent interface is the value between the coherent interface energy where Fe atom is located next to Nb atom and that where Fe atom is located next to C atom.

1. Introduction

Precipitates in steel are very important because they help increase the strength of steel by their precipitation strengthening mechanism and permit the control of the steel grain size by preventing grain growth. Therefore, estimating the size and density of precipitates for a specific alloy composition and process conditions is important for predicting the properties of steel. As described in a separate technical report in this special issue, a property prediction model has been used to predict the microstructure and mechanical properties of steel. Concerning the precipitation and growth of precipitates in that property prediction model, the number of nucleation sites, diffusion coefficients of solute elements, and energy at the precipitate-iron interface were so fitted that they would correspond with the precipitate size and density that had been obtained in past experiments. Those parameters were used to estimate the precipitate size and density and obtain the grain size, etc. for a specific alloy composition and process conditions.

However, precisely analyzing experimental data (precipitate size and density) required for the above parameter fitting is difficult and involves considerable uncertainties. Besides, it is difficult to decide on those parameters across the board for a wide variety of alloy compositions and process conditions. Furthermore, since all the parameters need to be decided at a time, they may decrease in physical significance.

In the present study, we attempted to obtain the precipitate-iron

interface energy—a parameter that can hardly be decided directly by experiment—by first-principles calculation. The precipitates in steel first occur in a form coherent with the parent phase iron. As they grow, they become semi-coherent precipitates, since the strain accumulated in the parent phase disappears. When the precipitate-parent phase interfaces are coherent, the calculation of the interface properties and energy, important factors in the precipitation and growth of precipitates, is possible. However, for semi-coherent interfaces, the interface properties and energy had not been determined, since that would require extremely large-scale calculations. In the present study, we succeeded in determining the structure and energy of semi-coherent interfaces by using the order-N method, which permits large-scale first-principles calculations, with the TSUBAME 2.0 supercomputer at the Tokyo Institute of Technology.

2. Calculation Method

Various types of precipitates are formed in steel, of which the NaCl-type precipitate plays an important role in the enhancement of steel strength and the formation of steel microstructures. It is known that the NaCl-type precipitate has a Baker-Nutting orientation relationship—$(100)_{NbC}//(100)_{Fe}$, $[010]_{NbC}//[011]_{Fe}$, $[001]_{NbC}//[0\bar{1}1]_{Fe}$—with the bcc-Fe parent phase, and it is considered that extremely small precipitates of lesser or equal to 1 nm are coherent with the Fe parent phase. However, as the precipitates increase in size, the coherent precipitates become semi-coherent precipitates so as to reduce the strain accumulated in the parent phase. To calculate the interfacial

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energy of those semi-coherent precipitates, it is necessary to handle the number of atoms shown in **Table 1**. In the table, the number of layers indicates the sum of the number of Fe layers and the number of NbC layers in the c-axis direction in the coherent interface structure shown in **Fig. 1**. Thus, calculating the interfacial energy for 14 layers (7 Fe layers + 7 NbC layers) requires handling as many as 1,463 atoms even for NbC, which has a large lattice mismatch with the bcc-Fe parent phase.

Under those conditions, first-principles calculations that are required of iron or any other metallic system had not been applied to such large-scale calculations. This is because in conventional first-principles calculations, the computing time was proportional to the square to cube of the number of atoms involved in the calculation(**Fig. 2**). However, in recent years, a new first-principles calculation method (called the order-N method) has been developed in which the computing time is proportional to the number of atoms.[1-5] In the present
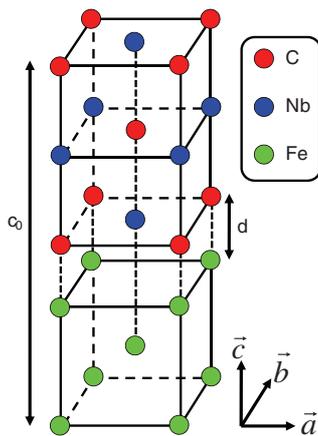
study, using the OpenMX program,[6] which can even be applied to metallic systems, we even enabled a first-principles calculation involving more than 1,000 atoms, which has been difficult to perform using the conventional method because it involved a long computational time.

In the OpenMX program, to render the computing time proportional to the number of atoms, the entire system to be calculated is first divided into regions, each surrounding a single atom, and then the solution for each of those regions is obtained, and finally they are integrated into the ultimate calculation result (**Fig. 3**). Therefore, the smaller the divided region, the shorter the computing time for each region, making it possible to increase the scale of calculation. On the other hand, to decrease the deviation of the calculation result from that obtained by the conventional method, it is necessary to increase the size of the divided region. Thus, it is important to decide on a size of divided region that permits a large-scale calculation without sacrificing the calculation accuracy. Each divided region used in the present study was a sphere with a radius of 6 Å with a single atom at the center. The fact that the conventional and order-N methods had a marginal influence on calculation results was confirmed as follows.

First, we calculated the lattice relaxation and vacancy formation energy during the vacancy formation in iron. **Fig. 4** shows the results of the measurement of deviation of atomic distance due to the formation of a vacancy in Fe_{127}. The unit cell of Fe_{127} is a lattice consisting of $4 \times 4 \times 4$ bcc unit lattices with two atoms, from which one atom is removed and a vacancy is introduced in that position. From Fig. 4, it can be seen that regardless of the distance from a vacancy, the conventional and order-N methods have marginal difference. Namely, it was confirmed that the order-N method permits the accu-

Table 1   Number of atoms to be treated for semi-coherent precipitate

| Number of layers	TiC	VC	NbC
6	2118	11238	627
10	3530	18730	1045
14	4942	26222	1463
Lattice mismatch	6.7%	2.8%	10.1%

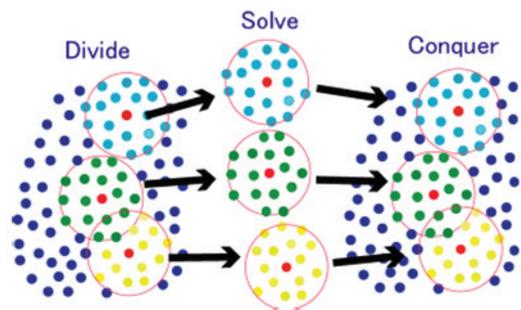**Fig. 1   Atomic structure of coherent interface (number of layers is 6)**

Fig. 2   Computational time of first-principles calculation

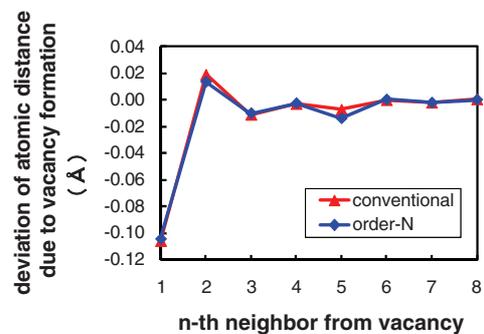**Fig. 3   Basic concept of order-N method**

Fig. 4   Difference between distance from vacancy and atomic distance without vacancy

rate calculation of the structure around a vacancy in iron.

Next, we analyzed the vacancy formation energies obtained by the above calculations (**Table 2**). The table shows the vacancy formation energy in each of four different cases: (1) both structural optimization and total energy calculation performed by the conventional method, (2) structural optimization performed by the conventional method and total energy for that structure estimated by the order-N method, (3) structural optimization performed by the order-N method and total energy for that structure estimated by the conventional method, and (4) both structural optimization and total energy calculation performed by the order-N method. It can be seen that the vacancy formation energies in all the cases are almost the same.

The vacancy formation energies that have been obtained experimentally range between 1.8 and 2.0 eV.[7, 8] The calculation results obtained in the present study agree well with those experimental values. Thus, concerning vacancies, which are one of the defects in iron, we could confirm that the order-N method permits the optimization of the structure around a vacancy and the calculation of the vacancy formation energy as accurately as the conventional method. This implies that with respect to lattice relaxation around precipitates in iron as well, it should be possible to calculate it accurately using the order-N method.

Next, concerning the bcc-Fe and NbC layer structures—the object of the present study, we confirmed that the electronic states and atomic structures calculated by the order-N method agree well with those calculated by the conventional method. **Fig. 5** compares the calculation results for the electronic density of states of the $Fe_5/(NbC)_5$ obtained by the Vienna ab initio simulation package (VASP)[9-12] program with those obtained by the OpenMX program. It can be seen that they agree very well. The distance between the Fe and NbC

Table 2 Vacancy formation energy

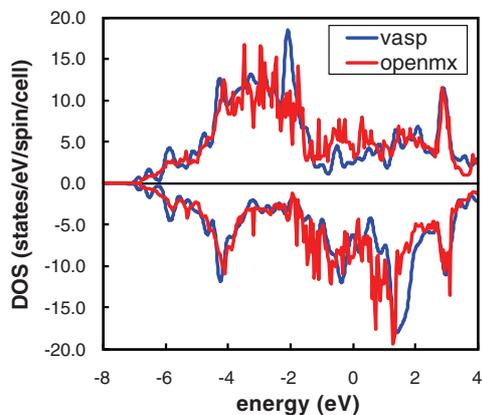| Structure optimization	Conventional	Conventional	Order-N	Order-N
Energy estimation	Conventional	Order-N	Conventional	Order-N
Vacancy formation energy (eV)	2.09	2.07	2.09	2.08

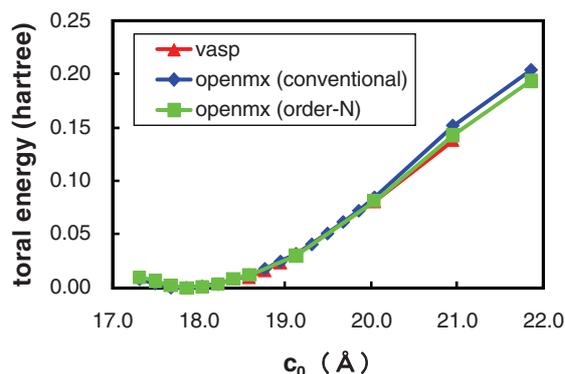**Fig. 5 Density of states of $Fe_5/(NbC)_5$**

Fig. 6 c_0 dependence of total energy of $Fe_5/(NbC)_5$

layers can be measured experimentally with significant difficulty. Therefore, it was optimized using the conventional and order-N methods, respectively. **Fig. 6** shows the total energy dependence of $Fe_5/(NbC)_5$ on the c-axis length—the parameter varied for the optimization of the distance between layers. It can be seen that with regard not only to the c-axis length, which minimizes the total energy, but also the manner in which the energy changes when the c-axis length is varied, the order-N method fairly accurately reproduces the results obtained with the conventional method.

3. Results and Considerations

At the coherent interface shown in Fig. 1, the atom that adjoins the Fe atom at the interface between the Fe and NbC layers was assumed to be a C atom. However, actually, it is possible to change the relative positions of the Fe atom in the Fe layer and the Nb and C atoms in the NbC layer. Therefore, we studied if the interfacial energy would vary according to whether the atom adjoining the Fe atom was a C atom or a Nb atom. **Fig. 7** plots energies at the above coherent interface. It can be seen that the interfacial energy is more stable when a C atom adjoins the Fe atom, that the change in energy gradually decreases as the distance between the Fe and NbC layers increases, and that the energy difference almost becomes zero when c_0 is greater or equal to 28 Å. These facts indicate that when the Fe and NbC layers are coherent with each other, a C atom exists next to the Fe atom at the Fe-NbC interface.

Thus, to investigate the cause thereof, we measured the local electronic density of the states of the C atom when a C atom adjoined the Fe atom and when a Nb atom adjoined the Fe atom (**Fig. 8**). In the figure, the blue line indicates the electronic density of states of C at the center of the NbC layer, and the red line indicates the electronic density of states of C at the interface with the Fe layer. When a C atom adjoins the Fe atom at the interface between the Fe and NbC layers, there is no significant difference in the electronic density of the states between C at the center of the NbC layer and C at the interface with the Fe layer (Fig. 8(a)). On the other hand, when a Nb atom adjoins the Fe atom at the interface between the Fe and NbC layers, the electronic density of the states of C at the interface with the Fe layer is higher than that of C at the center of the NbC layer (Fig. 8(b)). This is considered to account for why a C atom tends to easily adjoin the Fe atom at the Fe-NbC interface. It is also considered to explain the fact that only when a Nb atom adjoins the Fe atom, the number of Fe or Nb atoms located nearest to the C atom decreases from 6 to 5.
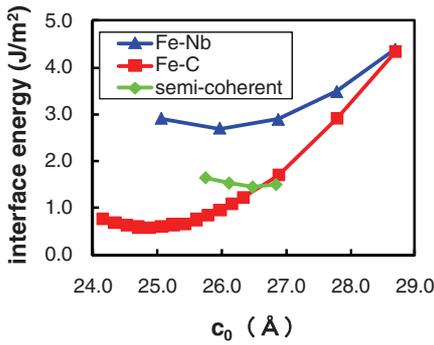
Fig. 7 c_0 dependence of interface energy (number of layers is 14)
Fe-C: Fe is located near C at the coherent interface. Fe-Nb: Fe is located near Nb at the coherent interface. Semi-coherent: semi-coherent interface.
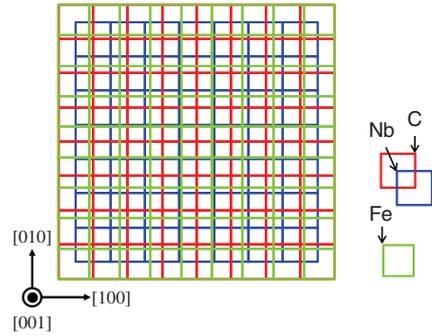

Fig. 9 Semi-coherent interface of Fe/NbC (interface of 9 × 9 units of bcc-Fe and 8 × 8 units of NbC)
Fe, Nb and C atoms are located at the corner of green, blue and red squares, respectively.
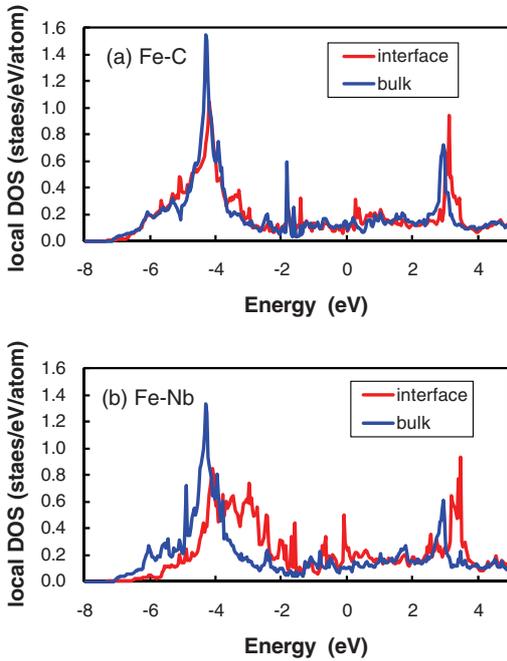

Fig. 8 Local density of states of C
(a) Fe is located near C at the coherent interface, (b) Fe is located near Nb at the coherent interface.

Fig. 10 Number of layers dependence of interface energy

In the case of a semi-coherent interface, not only are there points where Fe and C atoms adjoin, but also points where Fe and Nb atoms adjoin, as shown in **Fig. 9**, and neither the distance between the Fe and Nb layers nor the interfacial energy had been studied. Therefore, we calculated them with the semi-coherent interface of Fe/NbC shown in Fig. 9. The calculation involved 1,463 atoms, as shown in Table 1. This was made possible using the order-N method and TSUBAME 2.0—the supercomputer at the Tokyo Institute of Technology. Incidentally, optimizing the atomic structure for a single interlayer distance required approximately 360 parallel runs over two weeks.

In Fig. 7, in addition to the coherent interface energies, energies at a semi-coherent interface between 7 Fe layers and 7 NbC layers are plotted. From the figure, it can be seen that the semi-coherent interface energy approximately falls between the coherent interface
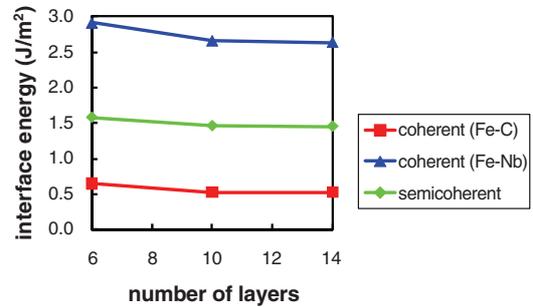
energy when Fe and C atoms adjoin and the coherent interface energy when Fe and Nb atoms adjoin, and that the c_0 value of the c-axis, or the distance between the Fe and NbC layers (d in Fig. 1), is similar to the value of a coherent interface when the Fe and Nb atoms adjoin.

Fig. 10 shows the dependence of coherent interface/semi-coherent interface energy on the number of Fe and NbC layers in the c-axis direction. Concerning the coherent interface, from Fig. 10, it can be seen that there is no significant difference between the interfacial energy for 10 layers and that for 14 layers. With respect to the d-value as well, it is already known that it does not differ much whether the number of layers is 10 or 14. Concerning the semi-coherent interface, it is already known that the interlayer distance within the Fe and NbC layers differs from the bulk when the number of layers is 6; however, we confirmed that the above difference disappeared when the number of layers was increased to 10. We also confirmed that there was not much difference between the calculated interfacial energy for 14 layers and that for 10 layers.

Fig. 11 shows the shift in the position of atoms due to structural optimization of a semi-coherent interface (a: shift of atoms located at the diagonal line within the (110) plane in Fig. 9, b: shift of Fe, Nb, and C atoms within the (001) plane next to the interface). It should be noted that at the initial position of each atom, an arrow having a length two times the shift distance of the atom is shown. It can be seen from the figure that Fe atoms move more than Nb/C atoms and that Fe, which is softer than NbC, relaxes and removes the strain. It can also be seen that the Fe atoms move toward the C atoms. This attests to the fact that at the coherent interface between
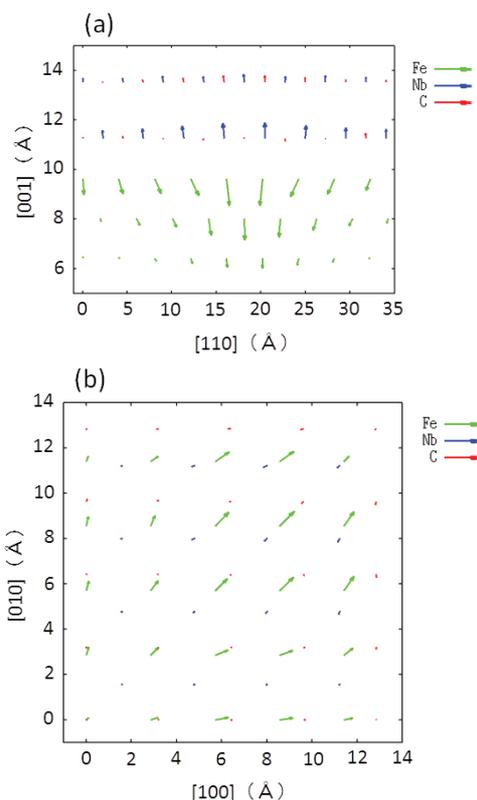
Fig. 11 Movement of atoms due to structure optimization of semi-coherent interface
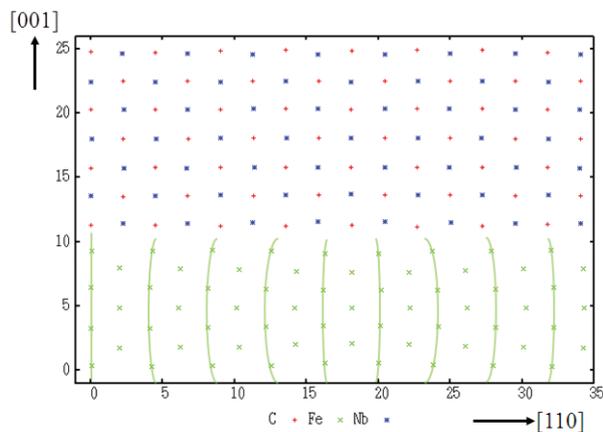**(a) (110) surface   (b) (001) surface next to the interface**

Fig. 12 Atomic structure of semi-coherent interface
Unit of vertical and longitudinal axes is Å.

Fe and NbC, the Fe atom adjoins the C atom rather than the Nb atom.

Fig. 12 shows the positions of atoms within the (110) plane of a semi-coherent interface subjected to structural optimization. It can be seen that the Fe atoms in the neighborhood of the interface have moved toward the C atoms and that the row of Fe atoms has curved. At the interface near both ends in the [110] direction, one Fe atom is located close to one C atom. On the other hand, there is a combina-

tion of one C atom and two Fe atoms near the center of the interface, indicating the presence of a dislocation.

4. Conclusion

We succeeded in calculating the energy at the iron-precipitate interface, which is an important factor in the precipitation and growth of precipitates that play an important role in the control of steel strength. For a semi-coherent interface between the precipitate and iron, it is necessary to calculate unit cells including more than 1,000 atoms. Such a calculation was enabled by the order-N method for first-principles calculations and the TSUBAME 2.0 supercomputer at the Tokyo Institute of Technology.

In future, we intend to calculate the strain energy to estimate the transition size from a coherent precipitate to a semi-coherent one and compare the calculation results with the experimental results. Because of the difficulty involved in directly estimating the interfacial energy experimentally, it is not easy to compare the calculated value with the experimental value. However, it has become possible to judge whether a specific precipitate is coherent or semi-coherent by using an aberration-corrected transmission electron microscope. We consider that it is also possible to determine the transition size from a coherent precipitate to a semi-coherent one by comparing the dependence of resistance per precipitate on precipitate size,[13] as obtained by a comparison between precipitate size measurement using a 3D atom probe and 0.2% proof stress measurement using a tensile test. The present study calculates the interfacial energy of known physical origin by the above comparisons.

In addition, we plan to calculate the change in the interfacial energy due to the difference in the precipitate or parent phase on the basis of calculated interfacial energies for various types of precipitates and parent phases. Furthermore, we intend to tackle tasks requiring large-scale calculations (e.g., calculation of the interaction between dislocation and point defect).

The order-N method has so far been applied mainly to studies of covalent compounds, such as biological macromolecules. However, it has seldom been applied to the field of metallic systems. We hope that the present study will help promote the application of this method to clarify various phenomena.

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