NIPPON STEEL TECHNICAL REPORT No. 102 JANUARY 2013

Technical Report

UDC 620 . 186 . 4 : 539 . 4 . 072

Analysis of Hydrogen Trap States by Carbonate in Steel with *ab initio* Calculation

Kazuto KAWAKAMI*

Abstract

The analysis ab-initio calculations about the trap state of hydrogen atoms by the carbides in bcc-Fe were performed and showed following results. The main trap site of small TiC precipitate is coherent interface, that of the small VC precipitate is carbon vacancy and the strain fields around the precipitates have only small trap energy. The cementite has week trap sites on the inside. The diffusion paths between them are through some semi-stable sites and the minimum potential barrier from the stable trap to the semi-stable site correspond to the activation energy of de-trap from cementite.

1. Introduction

The first-principles (*ab initio*) calculation is a technique that permits the calculation of the structural formation energy, stable structure, etc. simply by inputting the type of an atom and its three-dimensional arrangement. Owing to the remarkable advances in computer performance and computing methods in recent years, it has come to be used as a powerful tool for atomic-level analysis, together with experimentation. This paper describes an example in which an *ab initio* calculation was applied to analyze the main hydrogen trap sites in carbides within steel and their trapping energy.

Hydrogen is an element that causes steel to become brittle. However, unlike other elements that can embrittle steel, hydrogen does not enter steel in the ordinary steel manufacturing process, and hence, it poses no serious problems. Even so, hydrogen can cause a delayed fracture of steel during the welding or embrittlement of steel in a corrosive atmosphere. In particular, high-strength steels of greater or equal to 980 MPa are highly susceptible to hydrogen embrittlement. Therefore, to use such high-strength steel safely, it is necessary to control the hydrogen in steel properly. For example, the hydrogen that has entered the steel during welding is released from the steel by post-weld heat treatment to prevent it from delayed fractures. However, since this incurs extra cost, attempts have been made to temporarily distribute the hydrogen that has unavoidably been introduced into steel to many hydrogen trap sites in the steel so as to prevent the hydrogen from concentrating at the grain boundaries and other weak points, thereby causing hydrogen embrittlement. To utilize hydrogen trap sites effectively, it is important to clarify where and how intensely the hydrogen is trapped.

However, it was difficult to experimentally determine where and in what state hydrogen exists in the steel, especially the bcc phase, since its diffusion rate is extremely high, its solute concentration is extremely low, and moisture in the experimental apparatus produces background noise. The technique to analyze the desorption behavior of occluded hydrogen obtained by measuring the amount of hydrogen emitted when a hydrogen-charged specimen is heated at a fixed rate is called thermal desorption spectroscopy (TDS) or thermal desorption analysis (TDA). It permits the measurement of the activation energy for hydrogen desorption and the amount of hydrogen trapped and is used to analyze the hydrogen trap states. However, it cannot be used to determine the correspondence between defects and trap sites.

It is already known that TiC and VC precipitates used for the precipitation strengthening of steel can trap hydrogen. Therefore, they are expected to help enhance both strength and resistance for the hydrogen embrittlement of steel. However, the exact locations of the trap sites in those precipitates—whether they are the surrounding strain fields, coherent interfaces, non-coherent interfaces, or car-

* Senior Researcher, Mathematical Science & Technology Research Lab., Advanced Technology Research Laboratories
20-1, Shintomi, Futtsu, Chiba 293-8511

bon vacancies—and the approximate depths of those trap sites are unclear. Some researchers say that cementite also has hydrogen trap sites at the interfaces and in the inside, although the details are unknown. Recently, *ab initio* calculations have made it possible to analyze the hydrogen trap states at complicated defects such as dislocations and grain boundaries. As a result, it has become possible to analyze the states of shallow traps using the low-temperature TDS developed by Takai et al.[1] and measure the hydrogen trap positions at an atomic level using the three-dimensional atom probe (3DAP) of Takahashi et al.[2] Therefore, we analyzed the hydrogen trap states at an atomic level by *ab initio* calculations and verified them with our experimental results.

2. Main Subject

2.1 Analysis of hydrogen trap states by TiC/VC carbides[3]

TiC/VC carbides have an NaCl-type crystal structure and form fine planar coherent precipitates in bcc-Fe. Metal and carbon atoms are arranged as a square lattice on the (001) face of TiC/VC carbides. Since the arrangement of atoms is nearly similar to that of Fe atoms as a lattice on the (001) face of bcc-Fe, a wide coherent plane with the square lattices strained appears so as to make them coincide with each other. For a small precipitate, it takes the form of a plate, as shown in **Fig. 1**.

Fig. 2 shows the results of an *ab initio* calculation of the stability of the interface between TiC carbide and the Fe parent phase. The calculation was performed by assuming a periodic boundary condition of five Fe layers and five TiC layers. The figure plots the interface energies for the lattice constant when the size of the entire phase perpendicular to the interface was fixed so as to minimize the energy for the constant of the square lattice parallel with the interface. From the figure, it can be seen that the Fe atom at the parent phase interface is most stable when it is arranged directly above the C atom at the TiC interface. This result is in agreement with that of a calculation performed by Jung et al. using carbide.[4] It also matches the observation results of fine precipitates. Since the sides of a planar precipitate are not coherent in the thickness direction, its structure is complex and its details are unknown. However, it can be predicted that the carbon at the precipitate side tends to move toward the Fe atom in a manner similar to the movement of carbon at the carbide interface.

For estimating the hydrogen trap energy of a coherent strain, we performed an *ab initio* calculation of the lattice constant dependence of the bcc-Fe forming energy including hydrogen in the interstitial positions and observed that a 1% volume expansion gives an energy gain of 5 kJ/mol. Then, we estimated the strain around carbide in the form of a plate using an FEM calculation. The calculation was performed using a disk-shaped piece of carbide embedded in a small disk-shaped hole provided in the bcc-Fe parent phase. The round surface of the disk corresponds to a coherent interface, and the ratio of the hole diameter to the carbide diameter was that of one times $\sqrt{2}$ of bcc-Fe lattice constant to the carbide lattice constant.

On the other hand, the side ratio was assumed to be 1 from the result of a TEM observation of the number of matrix Fe layers corresponding to the number of carbide layers. This represents a phenomenon whereby the carbide grows while absorbing many vacancies. The distribution of volumetric strain around a TiC precipitate obtained by the above calculation is shown in **Fig. 3**. It can be seen that the volumetric strain is the largest in the neighborhood of the carbide coherent interface, that it is not more than approximately 3% though the TiC has a large lattice constant, and that the hydrogen trap energy by the coherent strain is lesser or equal to 0.25eV. When the TiC precipitate increases in size to a certain level, a misfit dislocation is introduced into it and the coherent strain is relieved. As a result, it is considered that the ability of the coherent strain to trap hydrogen is lost.

The hydrogen trap energy at the carbide/Fe interface and the carbide, respectively, was obtained by comparing the minimum trap energy obtained by an *ab initio* calculation for lattice relaxation be-

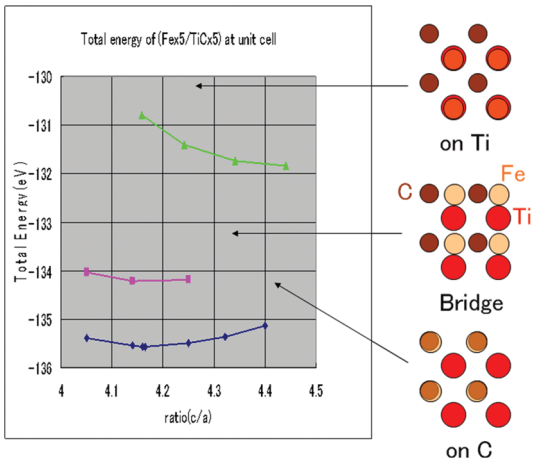

Fig. 2 Lattice constant dependency of relative interface energy of TiC

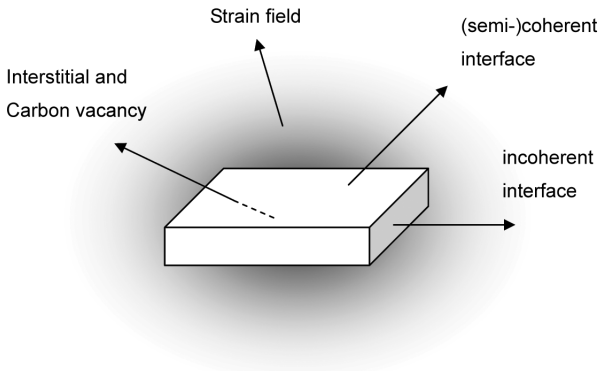

Fig. 1 Shape of fine MC carbide and the trap site of hydogen

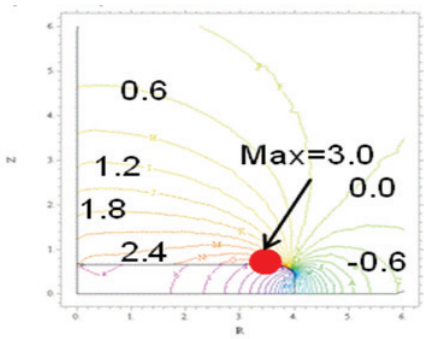

Fig. 3 Distribution of volumetric strain around TiC precipitate
Red circle is the position of maximum strain.

tween when hydrogen atoms were arranged at the carbide/Fe interface and within the carbide and when hydrogen atoms were arranged between the lattices. The results are summarized in **Table 1**. It can be seen that the carbon vacancies in both TiC and VC have a high amount of trap energy. However, since TiC has very few vacancies, the carbon vacancies in TiC are not effective trap sites. On the other hand, VC has many vacancies. However, the hydrogen in the bcc-Fe parent phase cannot reach the carbon vacancies in VC unless it moves through the interstitial site that serves as a diffusion barrier. Therefore, it is considered that the carbon vacancies that serve as effective trap sites are those that exist in the neighborhood of the VC interface.

At a coherent interface, hydrogen is positioned at the near center of a tetrahedron formed by three Fe atoms and one metallic atom, as shown in **Fig. 4**. The trap energy at the coherent interface differs between TiC and VC. From Fig. 4, it can be seen that the TiC coherent interface becomes a trap site, whereas the VC interface barely becomes a trap site. This is considered to reflect the fact that there is a difference in space between the interfaces and that metallic Ti occludes more hydrogen than metallic V; that is, the difference in affinity for hydrogen between them. At a semi-coherent interface, misfit dislocations occur periodically in the form of a square lattice. However, according to the results of an *ab initio* calculation of an NbC/Fe interface performed by Sawada et al.[5] on the misfit dislocations, the Fe atoms at the interface enter an anti-phase state in which they adjoin metallic atoms, not carbon atoms, in the carbide, thereby slightly increasing the interface space. A similar arrangement is considered to occur at the semi-coherent interfaces of TiC and VC. Namely, it is considered that the hydrogen at the interface combines with carbon atoms in a slightly wider dislocation space and becomes more stable.

Table 1 Trap energy of each site with VC, TiC precipitates (eV)

	VC	TiC
Coherent strain	< 0.15	< 0.3
Interstitial site	– 1.1	– 0.6
C vacancy	1.2	1.3
Coherent interface	– 0.06	0.5

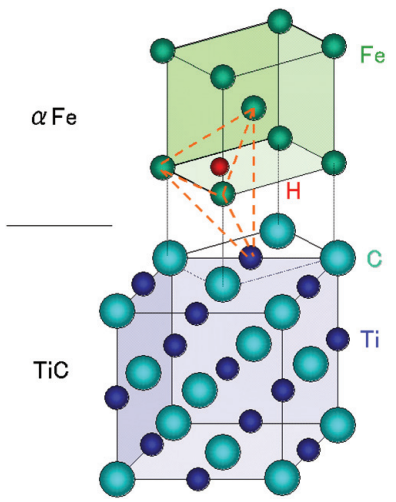

Fig. 4 Hydrogen trap site at commensurate interface of TiC/Fe

The above calculation results suggest that the main hydrogen trap sites of TiC are coherent and semi-coherent interfaces and those of VC are carbon vacancies in the neighborhood of coherent interfaces or semi-coherent interfaces. They agree well with the results of 3DAP measurement by Takahashi et al.[2] and the experimental results reported by Wei et al.[6]. The sides of the precipitates in the thickness direction become non-coherent interfaces. Details of the atomic arrangement there are still unknown, and the hydrogen trapping state in that location needs to be analyzed in the future.

2.2 Analysis of hydrogen trap state by cementite[7]

Cementite is also one of the factors that govern the strength and ductility of steel, and the interaction between cementite and hydrogen has long been studied. By the TDA of pearlitic steel, which contains a large proportion of lamellar cementite, it is already known that steel showing only one hydrogen emission peak exhibits another emission peak on the high-temperature side when it is worked on.[8] Although the peak on the high-temperature side is considered to be caused by some defect in the cementite caused by the working, it was unclear whether the emission peak on the low-temperature side is due to the cementite interface or the cementite interior.

First, for analyzing the hydrogen trap state inside cementite, we performed an *ab initio* calculation on a system containing one hydrogen atom in a unit cell of the cementite and obtained the stable and metastable sites for hydrogen. As a result, it was found that all the sites around carbon atoms were unstable sites for hydrogen, whereas, as shown in **Fig. 5**, the O site where six Fe atoms adjoin was the most stable, and the T sites where four Fe atoms adjoin were metastable sites. The hydrogen in cementite moves between adjoining stable sites and metastable sites.

Fig. 6 shows those adjoining sites connected together by a white line. There are two different paths leading from a stable O site to an adjoining O site: O-T_1-T_2-O and O-T_1-T_3-T_1-O. The activation energy between those sites was obtained by an *ab initio* calculation using the nudged elastic band method,[9] which permits obtaining a hydrogen diffusion path passing through the saddle point by linking with virtual spring several systems with hydrogen atoms arranged between two adjoining sites on the path. Those diffusion paths and potential barriers are schematically shown in Fig. 6. The barrier to movement from the most stable O site to the adjoining site T_1 is 57 kJ/mol. Since the barriers to movement from one T site to another (e.g., $T_1 \rightarrow T_2$) and from the T site to the O site are less than half of

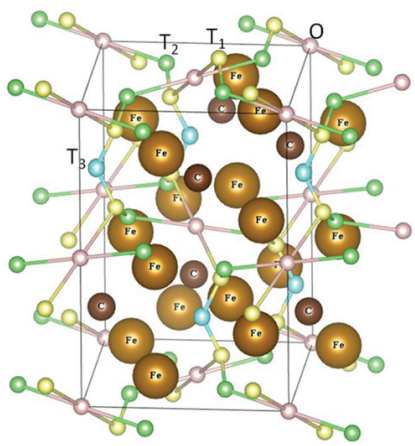

Fig. 5 Layout of the stable site O_1 and the semi-stable sites T_1,T_2,T_3 in cementite

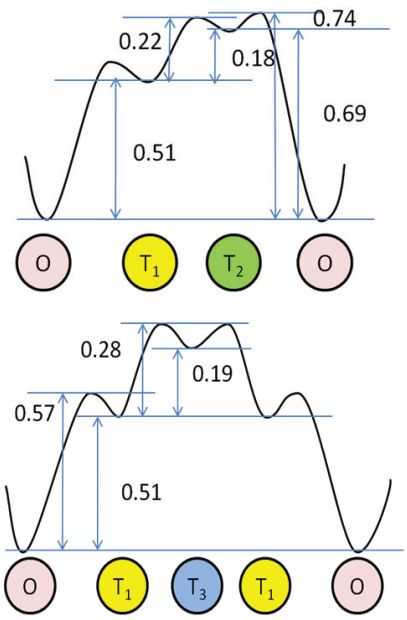

Fig. 6 Potential diagram of hydrogen along the diffusion paths
The energy unit is kJ/mol

the O → T_1 barrier, they can easily be cleared at temperatures at which the O → T_1 barrier can be cleared. Therefore, the activation energy for hydrogen diffusion in cementite is considered to correspond to the O → T_1 barrier.

Next, for calculating the hydrogen trap state at the bcc-Fe and cementite interface, the grain orientation in the unit cell for calculation was set so as to meet the Bagaryatsky orientation relationship,[8] which is often observed in pearlite. Since bcc-Fe and cementite differ markedly in their lattice constants, their interface becomes non-coherent, unlike the carbide interface mentioned above. The *ab initio* calculation of ordinary solids using periodic boundary conditions cannot be performed for a coherent interface. Therefore, a unit cell in which one layer of a cementite unit cell is overlapped by six layers of Fe was adopted with the lattice constant parallel to the bcc-Fe interface rendered the same as that of cementite, and the length of the cell perpendicular to the interface was adjusted so as to minimize the trap energy. The trap energy was calculated with lattice relaxation by arranging hydrogen atoms at O sites in cementite, interface, and Fe interstitial sites.

The electron density distribution obtained is shown in **Fig. 7**. From the difference in the trap energy of those structures, the difference in energy between hydrogen at the interstitial site in Fe and hydrogen at the O site and interface in cementite is estimated. However, since the Fe lattice had become very strained, the influence of the strain was corrected. As a result, it was observed that the trap energy was 29 kJ/mol for the O site and 35 kJ/mol for the interface.

From the above analysis results, both the cementite interior and interfaces are trap sites and the desorption energy of 60 kJ/mol obtained by a TDS analysis is considered to be caused by the diffusion barrier in cementite.[1] Since the trap energy of the interface is nearly the same as that of the dislocation and grain boundary, it is considered difficult to distinguish between them experimentally. In addition, since a non-coherent interface can take on various structures, it requires a more detailed analysis in the future.

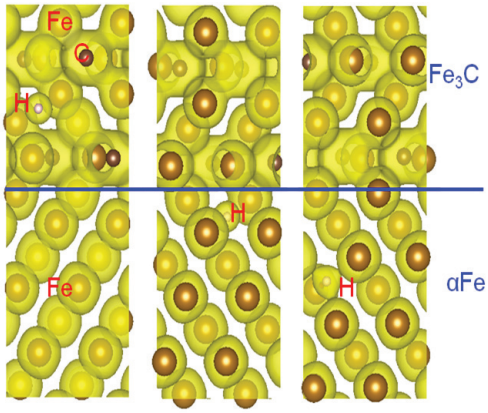

Fig. 7 Position of hydrogen trap site
Left : in cementite, center : at interface, left : in ferrite

3. Conclusion

Through an *ab initio* calculation of the hydrogen trap states in carbides, we obtained results compatible with our experimental results and clarified the main trap sites in them. Calculating the trap energy at semi-coherent and non-coherent interfaces is more complex. In addition, to evaluate the quantum effect of the hydrogen nucleus, which was not considered in the present study, it is necessary to calculate the potential between alloying elements and employ a more sophisticated technique, such as the molecular dynamics method that considers the quantum effect. With further advances in both computer hardware and software in the future, together with the progress of atomic-scale experimental analysis technology, computational science and analytical science will be applied as important tools for clarifying nanoscale phenomena in the field of steels as well.

References

1) Takai, K.: SCAS News. 2009-II, 3 (2009)
2) Takahashi, J., Kawakami, K., Kobayashi, Y., Tarui, T.: Scripta Mater. 63, 261 (2011)
3) Kawakami, K., Matsumiya, T.: Submitted to ISIJ Int.
4) Jung, W. S., Chung, S. H.: Modeling and Simulation in Material Science and Engineering. 18, 075008 (2010)
5) Sawada, H.: Report on Results of Joint Use of TSUBAME. 2009
6) Wei, F. G., Tsuzaki, K.: Metall. Mater. Trans. 37A, 331 (2006)
7) Kawakami, K., Matsumiya, T.: Submitted to ISIJ Int.
8) Hong, G. W., Lee, J. Y.: Journal of Material Science. 18, 271 (1983)
9) Zhou, D. S., Shiflet, G. J.: Metall. Mater. Trans. 23A, 1259 (1992)

Kazuto KAWAKAMI
Senior Researcher,
Mathematical Science & Technology Research Lab.
Advanced Technology Research Laboratories
20-1, Shintomi, Futtsu, Chiba 293-8511