Numerical Analysis of Hydrogen Trap State by TiC and V₄C₃ in bcc-Fe

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(Received on December 26, 2011; accepted on April 5, 2012)

Hydrogen trap states by TiC and V₄C₃ precipitates in bcc-Fe are investigated by numerical calculations. The trap states at interstitial site and carbon vacancy in metal carbide and bcc-Fe/metal-carbide interface were studied by ab-initio calculation. The calculated trap energies of these sites for TiC compared with the energy at interstitial site in bcc-Fe were respectively –58 kJ/mol, 125 kJ/mol and 48 kJ/mol and those for V₄C₃ were respectively –106 kJ/mol, 116 kJ/mol and –6 kJ/mol. The activation energy of detrapping from an isolated carbon vacancy is estimated at 183 kJ/mol for TiC and at 222 kJ/mol for V₄C₃ from the difference of the calculated energy at carbon vacancy and that at interstitial site in metal carbide. Hydrogen trap energy in coherent strain field around of TiC and V₄C₃ coherent precipitates in bcc-Fe are also calculated by Finite Element Method (FEM). The calculated energies are respectively less than 29 kJ/mol and less than 15 kJ/mol. These results indicate the main trap site of TiC is TiC/bcc-Fe interface, because TiC contains few carbon vacancies and has large activation energy of detrapping at the sites. That of V₄C₃ is carbon vacancies because V₄C₃ contains abundant carbon vacancies and the activation energy of migration between the neighbored carbon vacancy sites is expected to be lower than the calculated value. The estimated main trap sites of TiC is in good agreement with 3 Dimensional Atom Prove (3D-AP) observation results which reported that hydrogen atoms observed at TiC/bcc-Fe interface of TiC precipitate in bcc-Fe.

KEY WORDS: transition metal carbide; bcc-Fe; hydrogen; trap energy; ab-initio calculation.

1. Introduction

Although high tensile steel over 1000 MPa has been already put to practical use, hydrogen embrittlement problem restricts its expansion. As the strength of steel increases, hydrogen embrittlement problem becomes more serious. Therefore, many researchers have been investigating hydrogen embrittlement to suppress it. Metal carbide precipitate in steel such as TiC and V₄C₃ is one of useful hydrogen trap sites and expected to mitigate hydrogen embrittlement.

Several researches have been reported about hydrogen trapping state by metal carbide precipitate. TiC and V₄C₃ precipitates in bcc-Fe have coherent, semi-coherent or incoherent interface in accordance with their sizes. Bernstein(1,2) concluded by hydrogen permeation experiment that incoherent interface and coherent interface were strong trap sites. On the other hand Lee(3) concluded from Thermal Desorption Analysis (TDA) that the activation energy of hydrogen detrapping from incoherent interface was larger than that of semi-coherent interface. Wei(4) reported that misfit dislocation on the coherent interface of small TiC precipitate was main trap sites and the activation energy of desorption was 46–59 kJ/mol. The hydrogen trapping states of V₄C₃ precipitate were also investigated mainly by TDA. Tsuchida(5) reported that coherent vanadium carbide precipitate has weaker activation energy of desorption than incoherent one. Asahi(6) reported that the activation energy for vanadium carbide was 33–35 kJ/mol. Since hydrogen in steel is very fast even in low temperature and its concentration is very low especially in bcc Fe, it is very difficult to study experimentally about the trap site of precipitate in atomic scale. Although the macro scale experiments make the macroscopic estimation of trap site possible, atomic scale information is lacked. For example, it is not clear that the trap site of coherent TiC precipitate is strain field around precipitate or interstitial sites in TiC. On the other hand, the atomic structures of the coherent metal/carbide interface were studied by ab-initio calculation,(7) but the precipitate with the coexistence of hydrogen has not been studied numerically in atomic scale yet. The hydrogen trapping state of metal carbide in steel is still ambiguous. Based on this situation, we performed numerical analysis to investigate the hydrogen trapping state by metal carbide.

2. Simulation Methods

2.1. Trap State at Interstitial Site, Carbon Vacancy and Interface

Ab-initio calculations were performed to study electronic and atomic structures and hydrogen trap energies of the carbon vacancy in NaCl type metal carbides and the coherent interfaces between them and the ferromagnetic bcc Fe. These calculations are performed by software Vienna Ab-initio...
Simulation Package ‘VASP’ which is based on Projector Augmented Wave (PAW) pseudo-potential, plane-wave and density functional theory (DFT). Generalized gradient approximation (GGA) was used for the exchange-correlation potential using the parameterization of Perdew. The Kohn–Sham equation was solved using plane wave expansions for the valence electron density and wave functions. Interactions between ions and electrons were described by the Vanderbilt ultrasoft pseudopotential. As the interface contains a ferromagnetic phase, bcc Fe, spin-polarized calculation was carried out. Jung reported the interface energies between metal carbides and bcc iron with ab-initio calculation, and we used the calculation parameters as follows based on Jung’s results. The unit cell of the bcc-Fe/carbide interface model consists of 5 Fe layers and 5 TiC or V₄C₃ layers, and the cell size parallel to the interface is the same as two times of (001) surface of the unit cell of TiC or V₄C₃ as shown Fig. 1. Their lattice constant parallel to the interface was set to that of carbides, because they are much harder than bcc-Fe. The cell size perpendicular to the interface was adapted to minimize its total formation energy. The set of wave number in the Brilloin zone (k-points) are $9 \times 9 \times 3$ and cut off energy is 200 Rydberg (Ryd). Since the number of k-points affects the accuracy of the trap energy, the total energy was calculated by using larger k-points $11 \times 11 \times 3$, and it was found that it was only 5 kJ/mol different from that calculated by using k-points $9 \times 9 \times 3$. Since the cell size also affects the accuracy of the trap energy through the long range interaction, we compared the trap energy calculated by using two times cell size parallel to the layers and found that the difference of the trap energy was less than 4 kJ/mol. These preliminary results support the appropriateness of the cell size and k-points used in the main calculations.

Although the composition of TiC is almost stoichiometric, a few carbon vacancies may be contained and work as strong trap sites. On the other hand V₄C₃ has almost 25% carbon vacancies based on the stoichiometric number. Figure 2 shows the schematic diagram of unit cell used in the carbon vacancy calculation.

The hydrogen trap energy at site n $E_n$ was estimated as follows to eliminate the error caused by calculation cell size difference and to cancel the influence of strained field.

$$ E_n = E_{tsn} - (E_{tsi} - E_{tmu}) $$

where $E_{tsn}$, $E_{tsi}$, $E_{tmu}$ are the total energy of the super lattice contained a hydrogen at n site, the super lattice contained a hydrogen at the interstitial site of the iron layer, that of the iron cell contained an interstitial hydrogen, whose lattice is strained as the same as that of super lattice, and that of the iron cell contained an interstitial hydrogen, which is unstrained. $3 \times 3 \times 3$ unit cell which contains 54 Fe atoms and one hydrogen atom, $7 \times 7 \times 7$ k-points and the same cut-off energy as above mentioned precipitate calculation were used in the calculation of the later two energies. The influence of strain field in Fe contained in $E_{tsi}$ was estimated by $E_{tmu} - E_{tmu}$.

The hydrogen trap energy of C vacancy $E_v$ was also estimated as follows.

$$ E_v = E_{tpv} - E_{tpi} + E_i $$

where $E_{tpv}$ is the total energy of carbide containing a hydrogen atom at C vacancy as shown in Fig. 2, $E_{tpi}$ is that of carbide containing a hydrogen at interstitial site of the carbide and $E_i$ is the interstitial trap energy of the carbide estimated under the condition that k-points are $9 \times 9 \times 9$ and cut off energy is 200 Ryd.

### 2.2. Trap State in Coherent Strain Field

The coherent NaCl type metal carbide precipitates have much coherent strain field, though larger precipitates are semi-coherent or incoherent. To estimate the trap energy of the coherent strain field, we simulated it with FEM calcula-

![Fig. 1. Unit cell for the calculation of hydrogen trap energy in superlattice consisting of perfect metal carbide films and bcc Fe films. Small black, gray and large white spheres are respectively C, Fe and Ti or V atoms. A hydrogen atom was located at the site where the hydrogen trap energy was calculated. The crystal directions of carbide and bcc-Fe are shown in right side. Fe/carbide interface are shown by broken line.](image-url)

![Fig. 2. Unit cell for the calculation of hydrogen trap energy in carbon vacancy in metal carbide. Gray and large white sphere are respectively Ti or V and C atoms, and small white sphere is H atom. H atom is located at the carbon vacancy site.](image-url)
The ratio of the radius of void and that of precipitate was almost the same as the ratio of thickness of void and precipitate on the coherent interface. The lattice constant of bcc-Fe parallel with (1,1,0) and (–1,1,0) axes of precipitate lattice and the boundary condition at the sphere surface was a pattern of Fe and TiC. The calculation space radius, which was set to 6 to avoid divergence at the corner, was approximated to a sphere whose radius was 20 times of the precipitate, keeping the almost rectangular shape. The calculation space was a sphere whose radius was 20 times of the precipitate, and the boundary condition at the sphere surface was no strain. It was inserted in a void in Fe matrix with almost same shape. (1,0,0) and (0,1,0) axes of bcc-Fe lattice are parallel with (1,1,0) and (–1,1,0) axes of precipitate lattice on the coherent interface. The lattice constant of bcc-Fe matrix is almost the same as \( \sqrt{3} \) times of that of precipitate. The ratio of the radius of void and that of precipitate was set to \( \frac{a_m}{a_p} \). The ratio of thickness of void and precipitate was set to both 1 and \( \frac{a_m}{a_p} \) to estimate its influence on the strain field, since the relationship between precipitate lattice and matrix one in the incoherent side interface is unknown, which is determined by the amount of absorbed vacancies during the growth of the precipitate. The elastic constants and Poisson’s ratio used are listed in Table 1. The aspect ratio of precipitate C/A was assumed 1/10 for all calculation.

Since the trap energy of elastic field is considered to be almost determined by volume change, the change of the formation energy of interstitial hydrogen in uniformly deformed bcc-Fe was estimated. The total energy change of the uniformly deformed bcc-Fe lattice was estimated by the same way as Etsi estimation. The increment of hydrogen trap energy by 1% increment in volume of bcc-Fe was estimated from these calculations.

3. Simulation Results

3.1. Trap State at Interstitial Site and Carbon Vacancy in TiC and Fe/TiC Interface

Figures 3(a), 3(b) and 3(c) shows the atomic structures of Fe/TiC superlattice with a hydrogen atom at interstitial site in bcc-Fe, at interstitial site in TiC and at Fe/TiC interface respectively. All atomic positions have been relaxed to minimize strain energy. The hydrogen at interstitial site in Fe was located on the center layer of 5 Fe layers and that at Fe/TiC interface was located on the interface shown as broken line in Fig. 3(c). The calculated energy of a hydrogen atom at interstitial site in TiC is 58 kJ/mol higher than that at interstitial site in bcc-Fe which is reference position. Therefore, the interstitial site is not stable but metastable. The metastable site is almost the center of a triangle whose vertexes are Ti atoms. The calculated energy of a hydrogen atom at Fe/TiC interface is 48 kJ/mol lower than that at the reference position. The stable position is not just on the interface line shown in Fig. 3(c) but near the line and almost center of tetrahedron consisting of 3 Fe atoms and a Ti atom. On the other hand, the calculated energy of a hydrogen atom at the center of a carbon vacancy shown in Fig. 2 is 125 kJ/mol.

3.2. Trap State at Interstitial Site and Carbon Vacancy in V_4C_3 and Fe/V_4C_3 Interface

The calculated atomic structures of Fe/V_4C_3 superlattice are almost same as the structure of TiC/Fe superlattice. However, the corresponding energies are quite different. The calculated energy of a hydrogen atom at interstitial site in V_4C_3 is 106 kJ/mol higher than that at the reference position. That is, the interstitial site in V_4C_3 is metastable. The calculated energy of a hydrogen atom at a carbon vacancy in V_4C_3 is 116 kJ/mol higher than that at the reference position. Although the activation energy of detrapping from an isolated carbon vacancy is estimated as higher than 222 kJ/mol from the difference of the energy at carbon vacancy and interstitial site in V_4C_3, a lot of carbon vacancies in V_4C_3 may result in lower activation energy of detrapping from one carbon vacancy to another neighboring

Table 1. Elastic constants used for FEM calculation.

<table>
<thead>
<tr>
<th></th>
<th>TiC</th>
<th>VC</th>
<th>bccFe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus (GPa)</td>
<td>457</td>
<td>415</td>
<td>211</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.183</td>
<td>0.190</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Fig. 3. Relaxed structures of (a) hydrogen at interstitial site in Fe, (b) hydrogen at interstitial site in TiC and (c) hydrogen at Fe/TiC interface. Small black, gray, large white and small-est white spheres are C, Fe, Ti and H atoms. The interfaces are shown by broken lines.

Fig. 4. Calculated trapped energy of hydrogen as a function of number of hydrogen at V_4C_3 vacancy. The horizontal axis is number of hydrogen trapped by a carbon vacancy in V_4C_3. The vertical axis is energy difference of total energy between interstitial site in bcc Fe and carbon vacancy site in V_4C_3. Two broken lines show the energy level at interstitial sites in bcc Fe and V_4C_3.
carbon vacancy. In comparison with that, TiC contain few carbon vacancies\(^{11}\) and almost of all carbon vacancies are expected to be isolated with high activation energy of de-trapping. It suggests that carbon vacancies in V\(_4\)C\(_3\) are possibly effective trapping sites but carbon vacancies in TiC are not effective trapping sites. Therefore, the trap energies by carbon vacancy in V\(_4\)C\(_3\) with multi hydrogen atoms were calculated to estimate the capacity of a carbon vacancy. Figure 4 shows the calculation result which indicates that a vacancy can trap two hydrogen atoms, whose 1st and 2nd trap energy are 116 J/mol and 68 J/mol, respectively. On the other hand, the interface isn’t stable site. Although the calculated atomic position of the metastable site is almost the same as that of TiC case but the energy of a hydrogen atom at the interface is 6 J/mol higher than that of iron interstitial site.

3.3. Trap State in Coherent Strain Field of TiC

Figures 5(a) and 5(b) show calculation results of contour map of volumetric strain around TiC whose thickness is \(a_m/\sqrt{2}a_p\) times of and the same as that of a void, respectively. In the former case, where TiC precipitate thickness is larger than that of bcc-Fe matrix void, the most expanded trap site is the center of the coherent surface and its energy is estimated as 12 kJ/mol in assuming that the trap energy per 1% lattice expansion is 5 kJ/mol, which is derived from ab-initio calculation results about uniformly deformed lattice shown as Fig. 6. In the later case, the most expanded position is near corner and the trap energy is estimated as 29 kJ/mol the same way.

3.4. Trap State in Coherent Strain Field of V\(_4\)C\(_3\)

V\(_4\)C\(_3\) has smaller lattice mismatch to bcc-Fe than TiC but the relative strain distribution is resemble. The maximum expanded volume strain is also smaller, and there trap energy is estimated as 15 kJ/mol in the case of the void thickness is same as that of V\(_4\)C\(_3\). When the void thickness is smaller than precipitate’s, the maximum trap energy is estimated as 2 kJ/mol

4. Discussion

The summary of hydrogen trap energy by TiC and V\(_4\)C\(_3\) is shown at Table 2 and Fig. 7. The strain field around TiC and V\(_4\)C\(_3\) precipitate is not as large as acting strong hydrogen trap site. When the precipitate grows larger, misfit dislocations are introduced to relax stress. After further growth, the precipitate interface becomes incoherent. The misfit dislocations or incoherent interface may be another hydrogen trap sites, but calculation analysis has not been performed yet because of difficulty of ab-initio calculation. Therefore, we discuss only about the trap site of TiC or V\(_4\)C\(_3\) precipitate which have coherent interface.

Although the strain field around TiC and V\(_4\)C\(_3\) precipitate is considered to be trap sites for coherent precipitate, it is found that they are not effective sites, because of their low trap energy less than 29 kJ/mol as calculated.
TiC and V$_4$C$_3$ precipitate are so small that the flat interfaces trapped by TiC with 3D-AP for the first time. The sizes of need to migrate short distance, about lattice parameter, TiC and V$_4$C$_3$, and the interstitial sites in carbides are meta- 

ture. Takahashi$^{12}$ has observed directly hydrogen atoms trap sites and those in TiC are not especially at low temper-

Wei.$^4$ 

precipitate is almost the same as the experimental results by Asahi.$^5$ The trap sites obtained experimentally by them were considered to be not carbon vacancies but other sites which had not been studied here. The further analysis of atomic scale will need to investigate those sites.

5. Conclusions

The trap states of hydrogen atom by coherent TiC and V$_4$C$_3$ precipitate in bcc-Fe were analyzed by ab-initio calculation and FEM calculation, and following results were obtained.

(1) The calculated trap energy by coherent strain filed is less than 15 kJ/mol for V$_4$C$_3$ and less than 29 kJ/mol for TiC.
(2) The calculated trap energy of interstitial site in TiC and in V$_4$C$_3$ is respectively −58 kJ/mol and −106 kJ/mol.
(3) The calculated trap energy of carbon vacancy is 125 kJ/mol for TiC and 116 kJ/mol for V$_4$C$_3$.
(4) The activation energy of hydrogen migration from vacancy to vacancy is estimated as 183 kJ/mol in TiC and 222 kJ/mol in V$_4$C$_3$ from the difference of the calculated energy at carbon vacancy and that at interstitial site in metal carbide. However, the abundant carbon vacancies may reduce the activation energy very much in the case of V$_4$C$_3$.
(5) The calculated trap energy of Fe/carbide interface is 48 kJ/mol for TiC and −6 kJ/mol for V$_4$C$_3$.

Based on the above mentioned results, it is concluded that the main trap site for coherent TiC precipitate is Fe/TiC interface. The calculated trap energy gives good agreement with TDS result, and the observed hydrogen site trapped in TiC by 3D-AP is in good agreement, too.

It is also concluded that the main trap site for V$_4$C$_3$ coherent may be carbon vacancy. The calculated detrapping energy does not agree with desorption energy by TDS. This difference indicates that the trap site observed for V$_4$C$_3$ is another trap site. The migration state of hydrogen in V$_4$C$_3$ and the trapped state at semi-coherent interface and incoherent interface should be investigated to recognize the trap state by carbide.

Acknowledgement

The authors wish to Dr. Takahashi for his useful discussion about 3D-AP observation results.

REFERENCES


| Table 2. The summary of the calculated trap energy of a hydrogen atom by TiC and V$_4$C$_3$ in bcc-Fe. The energy unit is kJ/mol. |
|-----------------|-----------------|
|                 | VC              | TiC             |
| Coherent strain | < 15            | < 29            |
| Interstitial site | −106           | −58             |
| C vacancy       | 116             | 125             |
| Coherent interface | −6            | 48              |

The carbon vacancies have the largest trap energy in both TiC and V$_4$C$_3$, and the interstitial sites in carbides are metastable and have higher energy than that of bcc-Fe. Although these results indicate that carbon vacancies are strong trap site, they are not effective in the case of the high diffusion barrier. The presence of the number of carbon vacancies contained is considered to affect the trapping effectiveness of the vacancies. Since the carbon vacancies in TiC is very low, hydrogen atoms have to migrate far to vacancies. On the other hand, in the case of V$_4$C$_3$ hydrogen atoms only need to migrate short distance, about lattice parameter, because the quarter of carbon sites is vacant. Based on these, it is considered that the carbon vacancies in V$_4$C$_3$ are active trap sites and those in TiC are not especially at low temperature. Takahashi$^{12}$ has observed directly hydrogen atoms trapped by TiC with 3D-AP for the first time. The sizes of TiC and V$_4$C$_3$ precipitate are so small that the flat interfaces are coherent or semi-coherent. The hydrogen atoms around TiC were observed at flat interface. Our results of calculation analysis are in good agreement with observed results and denote that the main trap sites of TiC are coherent interface trap site and not carbon vacancy. In addition, the calculated trap energy of the main trap site of coherent TiC precipitate is almost the same as the experimental results by Wei.$^4$

On the other hand, that of coherent V$_4$C$_3$ precipitate is larger than that of the experimental results by Asahi.$^5$