# Hydrogen Behavior in Primary Precipitate of F82H Steel: Atomistic Calculation Based on the Density Functional Theory

Yoshiyuki WATANABE, Hirotomo IWAKIRI[1], Norihiko MURAYOSHI[1],
Daiji KATO[2] and Hiroyasu TANIGAWA

*Japan Atomic Energy Agency (JAEA), Rokkasho, Aomori 039-3212, Japan*
[1]*University of the Ryukyus, Okinawa 903-0213, Japan*
[2]*National Institute for Fusion Science (NIFS), Toki, Gifu 509-5292, Japan*

(Received 15 September 2015 / Accepted 2 October 2015)

Formation energy of an isolated hydrogen atom in $Cr_{23}C_6$ has been investigated using atomisitic calculation based on the density functional theory. The lowest calculated formation energy is −0.48 eV, where a hydrogen atom is located at a trigonal bipyramidal site surrounded by five Cr lattice atoms, due to electric charge of atoms. Although it is a rough estimate, a comparison with the formation energy in Fe may imply that hydrogen retention in F82H steel can be much higher in $Cr_{23}C_6$-based precipitate than in Fe-based matrix.

Keywords: hydrogen, F82H, carbide precipitate, density functional theory

DOI: 10.1585/pfr.10.1205086

F82H steel is proposed as a candidate of blanket structural materials in a nuclear fusion reactor. In the blanket structural materials, the trapping and release characteristics of hydrogen isotopes will influence material degradation, deformation, tritium inventory and tritium permeation to the coolant. Therefore, hydrogen behavior in a material during irradiation should be theoretically understood for a practical fusion reactor design. Energetics of lattice defects in a material is one of the important parameters required to evaluate the kinetics of defect behavior during irradiation. However, the defect energetics in F82H steel is not understood enough; especially, the energetics for hydrogen is not investigated for tricosachromium hexacarbide ($Cr_{23}C_6$) which is the main component of the precipitate on grain boundaries in F82H steel. In the present study, formation energy of an isolated hydrogen atom in $Cr_{23}C_6$ was investigated with atomistic calculation based on the density functional theory (DFT).

$Cr_{23}C_6$ crystal has a face-centered cubic structure with the space group 225 ($Fm3m$) containing 92 Cr atoms and 24 C atoms in a unit cell, as represented in Fig. 1. The present DFT calculations were performed with SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code [1]. The electron exchange and correlation are treated within the generalized gradient approximation (GGA) of the Wu-Cohen modification of Perdew-Burke-Ernzerhof (PBE) function [2]. The electron-ion interactions were described by normconserving Troullier Martins pseudopotentials factorized in the Kleinman-Bylander form. The valence wave functions were expanded in a basis set of localized atomic orbitals. We used double-$\zeta$ bases with polarization orbitals in Cr 4s, 4p, 3d, 4f, C 2s, 2p, 3d, 4f, and H 1s, 2p, 3d, 4f channels. In the present work, the super-cell containing 92 Cr atoms and 24 C atoms is used at 0 K under the periodic boundary condition with the lattice constant of 1.075 nm which is comparable to the experimental value of 1.066 nm [3]. Notice that the value (1.075 nm) is corresponding to the minimum point on the total lattice energy curve as a function of lattice volume in our preliminary calculations. $2 \times 2 \times 2$ $k$-point grids and a 200 Ry cutoff for the real space mesh were chosen.

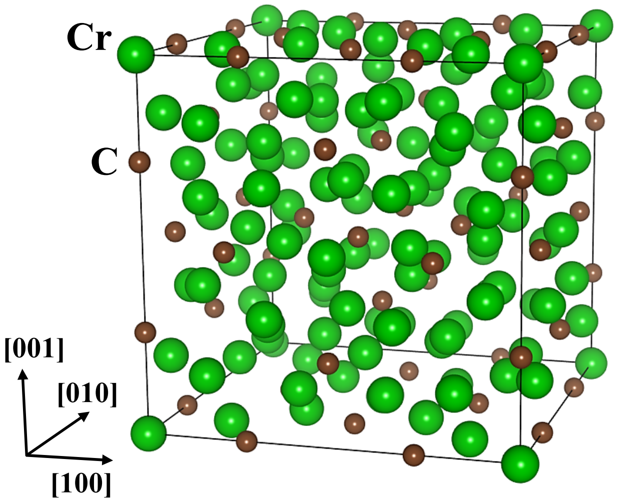

Fig. 1 A unit cell of perfect $Cr_{23}C_6$ crystal consisted of 92 Cr atoms and 24 C atoms.

Firstly, a hydrogen atom was embedded into a super-

---

*author's e-mail: watanabe.yoshiyuki32@jaea.go.jp*

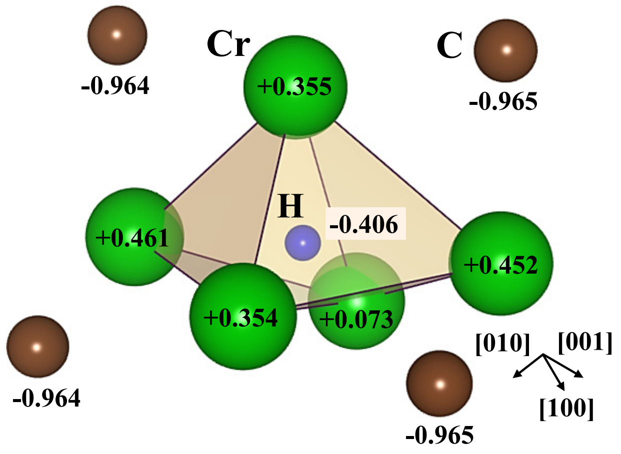

Fig. 2 The most relaxed configuration of a hydrogen (H) atom in $Cr_{23}C_6$ crystal, where H atom is located at a trigonal bipyramidal (TBP)-site surrounded by five Cr lattice atoms. H is negatively charged, whereas Cr and C maintain positively- and negatively-charged, respectively.

cell, where 14 different types of locations were chosen for the initial position of a hydrogen atom. The computational system was then fully relaxed until all the Hellmann-Feynman forces are converged to 0.01 eV/Å. Electronic convergence is achieved when the difference between the total energies of the last two consecutive steps is less than $10^{-4}$eV. After the relaxation, the converged value of total potential energy of the system was obtained.

Formation energy of a hydrogen (H) atom is defined as energy required for embedding a hydrogen atom into an otherwise perfect crystal in the following equation:

$$E_{\mathrm{F}}(\mathrm{H}) = E(92\mathrm{Cr}, 24\mathrm{C}, \mathrm{H}) - E(92\mathrm{Cr}, 24\mathrm{C}) - \frac{1}{2}E(\mathrm{H}_2),$$

where $E$(92Cr, 24C) is the total energy of the perfect $Cr_{23}C_6$ crystal, $E$(92Cr, 24C, H) is that of the super-cell containing a hydrogen atom, and $E(H_2)$ is that of the hydrogen molecule.

From the DFT calculations, we found the two energetically favorable sites of a hydrogen atom in $Cr_{23}C_6$: (i) trigonal bipyramidal (TBP)-site surrounded by five Cr lattice atoms, as shown in Fig. 2, with the formation energy of −0.48 eV; (ii) tetrahedral (T)-site surrounded by four Cr lattice atoms with the formation energy of −0.44 eV.

For the two energetically favorable sites, a more detailed investigation was done by means of the Mulliken's population analysis [4] that can simply estimate effective charge of atoms. Firstly, the effective charges of atoms in the perfect $Cr_{23}C_6$ crystal were estimated to be +0.219 for Cr atoms and −0.965 for C atoms. Those for the TBP-site were then estimated to be −0.406 for H, +0.073 to +0.461 for Cr and −0.965 to −0.964 for C, as written in Fig. 2. In the same way, those for the T-site were also estimated to be −0.353 for H, +0.052 to +0.308 for Cr and −0.956 for C. In both the two sites, H is negatively charged, while Cr and C maintain positively- and negatively-charged, respectively; this is the reason that a hydrogen atom surrounded by Cr atoms is energetically favorable in $Cr_{23}C_6$. Here, there is no significant difference, for the effective charges of atoms, between the TBP- and T-sites. It can be seen from that their formation energies are relatively close to the same.

As to the formation energy, the formation energy of a hydrogen atom in $Cr_{23}C_6$ is negative (−0.48 eV), which means that this solution reaction for hydrogen is exothermic. In contrast, the formation energy of a hydrogen atom in bcc-iron (Fe) is positive (+0.25 eV [5]), where this solution reaction for hydrogen is endothermic. Assuming that effects of the additives and impurities are not dominant for simplicity, those arguments described above lead to the following implication: Hydrogen atoms in F82H steel can be much more energetically favorable in $Cr_{23}C_6$-based precipitate than in Fe-based matrix, resulting in a drastic increase of hydrogen retention in the precipitate. This kind of information will be a basic to theoretically understand the diffusion and dissociation kinetics of hydrogen isotopes in F82H steel under irradiation.

This work was carried out using the HELIOS supercomputer system at Computational Simulation Centre of International Fusion Energy Research Centre (IFERC-CSC), Aomori, Japan, under the Broader Approach collaboration between Euratom and Japan, implemented by Fusion for Energy and JAEA.

[1] E. Artacho *et al.*, Phys. Status Solidi B **215**, 809 (1999).
[2] Z. Wu and R.E. Cohen, Phys. Rev. B **73**, 235116 (2006).
[3] H.L. Yakel, Acta Cryst. B **43**, 230 (1987).
[4] R.S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).
[5] E. Fromm and G. Horz, Int. Mater. Rev. **25**, 269 (1980).