§42-24 Ab Initio Study of the Solubility and Kinetics of Hydrogen in F82H Steel

Iwakiri, H., Murayoshi, N. (Univ. Ryukyus), Watanabe, Y., Tanigawa, H. (JAEA), Kato, D.

In a nuclear fusion reactor, blanket structural materials suffer from bombardment of high-energy neutrons, in which a variety of point defects are produced by atomic displacement and nuclear transformation. Hydrogen and helium play a particularly important role, when produced at the various species, causing drastic changes in materials structural properties, even at low concentrations. In this work, hydrogen behavior in primary precipitate of $Cr_{23}C_6$ in F82H steel was numerically investigated, based on density functional theory (ab-initio).

All the calculations were perfored using the density functional theory (DFT) method as implemented in the SIESTA 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 norm-conserving 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- ζ bases with polarization orbitals in Cr 4s, 4p, 3d, 4f, C 2s, 2p, 3d, 4f, and H 1s, 2p, 3d, 4f channels. The calculations were carried out in a supercell containing 116 atoms. The convergence of the calculations has been tested, and we found a $2 \times 2 \times 2$ k point grid and a 200 Ry cutoff for the real space mesh can give well converged results. Relaxation is performed until all the Hellmann-Feynman forces are converged to 0.01eV/Å. Electronic convergence is achieved when the difference between the total energies of the last two consecutive steps is less than 10^{-4} eV.

Fig. 1 shows the lattice energy curve of $Cr_{23}C_6$ as a function of the lattice volume, in which the local minimal value corresponds to the most energetically favorable lattice parameter for the enthalpy. The calculated lattice parameter a = 10.753 Å were found to be in good agreement with the experimental values of 10.66 Å in the framework of the density functional theory.

The solution energy ΔE_s of a hydrogen atom (H) was then calculated as follows:

$$\Delta E_{\rm S} = E_{\rm tot} ({\rm Cr}_{23}{\rm C}_6 {\rm -H}) - E_{\rm tot} ({\rm Cr}_{23}{\rm C}_6) - \frac{1}{2} E_{\rm tot} ({\rm H}_2)$$

where $E_{tot}(Cr_{23}C_6-H)$ is the total energy of the $Cr_{23}C_6$ supercell with a hydrogen atom, is that of $Cr_{23}C_6$ perfect crystal, and $E_{tot}(H_2)$ is that of an H_2 molecule. Hydrogen atoms accommodated with in twenty different sets of lattice site, we found the two energetically favorable positions of a hydrogen atom: (i) trigonal-bipyramid (TB)-site (surrounded by five Cr lattice atoms); (ii) tetrahedral (T)-site (surrounded by four Cr lattice atoms). These positions and crystal structure of $Cr_{23}C_6$ are shown in Fig. 2. The type of uptake for hydrogen has long been known as occlusion, in which there are two types of materials: (i) endothermic storage materials and (ii) exothermic storage materials. Since the exothermic alloys have "negative" solution energy, which take up hydrogen to very much greater extent. In this study, the solution energy at the TB-site is -0.48 eV and that of T-site is -0.44eV. These results indicate that $Cr_{23}C_6$ alloy is exothermic hydrogen occluding alloy. Considering about the solution energy of hydrogen in interstitial site in α -Fe is about +0.21 eV, hydrogen can be relatively stable in $Cr_{23}C_6$ precipitates in a wide range of temperature.



Fig. 1. Cell volume dependence of total energy for $Cr_{23}C_6$ perfect crystal.



Fig. 2. Energetically favorable positions of a hydrogen atom in $Cr_{23}C_6$: trigonal ipyramid (TB)-site and tetrahedral (T)-site.

- [1] E. Artacho, Phys. Status Solidi B 215 (1999) 809
- [2] Z. Wu and R.E. Cohen, PRB 73 (2006) 235116