§15. Interstitial Diffusion of C Interacting with Ambient H in Tungsten Crystals

Kato, D., Muroga, T.,
Iwakiri, H. (Univ. Ryukyus),
Morishita, K. (IAE, Kyoto Univ.)

In the present work [1], the H effects on the migration of an interstitial C in a W crystal (bcc) were investigated theoretically. To this end, the interaction of an interstitial C-H pair in the W crystal was evaluated by means of the first-principle method (density functional theory). With the first-principle method, the inter-atomic interactions in condensed matters can be calculated without recourse to model (semi-empirical) interaction potentials. Then, interstitial diffusion of C interacting with ambient H atoms was studied in the transition state theory.

Fig. 1 shows binding energies of three configurations of interstitial C-H pairs. In this calculation, a reference super-cell containing 128 W atoms is used. The present calculation gives negative binding energies for the all configurations, indicating inherently repulsive interaction in the interstitial pair. This contrasts to the attractive interaction in the isolated C-H pair in the gas-phase. Comparing with results of interstitial H-H pairs [2], the C-H repulsion appears much stronger. The nearest-neighbor interstitial pair of Fig. 1(a) is not in equilibrium. The C-H pair repels each other, relaxing to the equilibrium (meta-stable) configurations of (b) and (c). The present result suggests that the interstitial C cannot be a trap of H in the bulk W crystal.

In the transition state theory, transition between an initial and a final configuration of the interstitial C-H pair with C jumping into the adjacent site is studied. The jumping rate at which the transition between the initial and the final configuration takes place is given in terms of an activation free-energy and a hopping frequency to an intermediate (transition state) configuration. Four equivalent configurations of the interstitial C-H pair [(b) in Fig. 1] are possible per interstitial H. Since there are three octahedral-sites per W in the bcc crystal, a statistical probability of the C-H pair formation is $4N_H/3N_W$, where N_H and N_W are the numbers of H and W in the crystal, respectively. Here, it is assumed $N_H/N_W = x \ll 1$. In the ergodic assumption, a time-averaged jumping rate under the influence of the ambient H atoms is give by

$$\langle \Gamma \rangle = \Gamma_0 \left(1 - \frac{4}{3}x \right) + \Gamma_H \frac{4}{3}x, \qquad (1)$$

where Γ_0 and Γ_H are the jumping rates of the isolated C and the C-H pair, respectively. The reduced interstitial diffusion coefficient is multiplied by a site-blocking factor in the mean field approximation,

$$D^* = D \left(1 - \frac{2}{3}x \right). \qquad (2)$$

For 5 at% concentration of H, i.e. $x = 0.05$, influences on the diffusion length are illustrated in Fig. 2. Except for extremely high temperatures, the diffusion length is increased under the influence of the ambient H. It contrasts to trapping effects, e.g. vacancy, which would impede the migration of C. The present results indicate that enhancement of the jumping rate due to the repulsive interaction with the ambient H, Eq. (1), dominates over interference due to the site-blocking, Eq. (2).
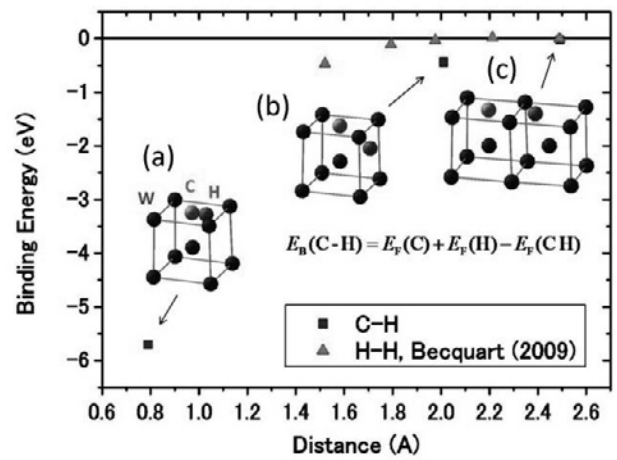
Fig. 1. Binding energies of interstitial C-H pairs in a W crystal. The binding energies of interstitial H-H pairs are also plotted for comparison.
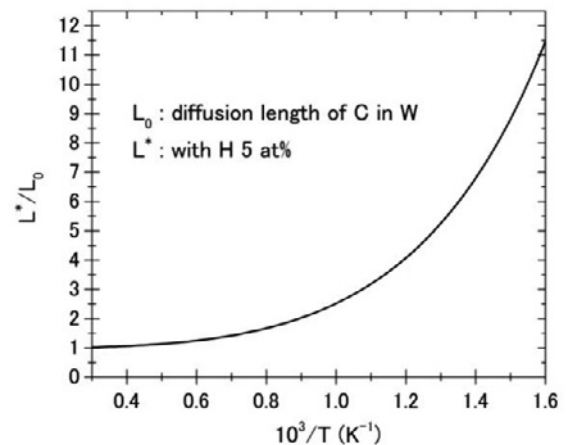

Fig. 2. Diffusion length ratio, $L^*/L_0 = (D^*/D_0)^{1/2}$, of an interstitial C in W crystal. L_0 is the diffusion length of an isolated C, L^* with 5 at% ambient H concentration.

1) Kato, D. et al., PFR: Regular Article, in press.
2) Becquart, C.S., Domain, C., JNM *386-388* (2009) 109.