Size and Temperature Dependence of the Point Defect Binding Free Energy to Defect Clusters in bcc Fe

Yoshiyuki WATANABE, Kazunori MORISHITA[1)], Takashi NOZAWA and Hiroyasu TANIGAWA

National Institutes for Quantum Science and Technology (QST), Rokkasho, Aomori 039-3212, Japan

[1)]*Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan*

(Received 13 July 2022 / Accepted 30 September 2022)

Size and temperature dependence of the point defect binding free energy has numerically evaluated for self-interstitial atom (SIA) clusters and vacancy clusters in bcc Fe by using continuum models based on thermodynamics and linear elasticity. The estimated binding free energy of SIAs to SIA-clusters is much higher than that of vacancies to vacancy clusters, indicating that SIA-clusters are more thermally stable than vacancy clusters. For relatively small clusters, the estimated binding free energy at 0 K is comparably consistent with atomistic calculation data; and then, the SIA binding free energy at 850 K is averagely about 35% lower than that at 0 K, while the vacancy binding free energy is about 6% lower; which may remarkably affect the formation kinetics of those defect clusters under irradiation. These kinds of information will be one of the basic parameters for a theoretical model of the microstructural evolution of Fe-based materials in the nuclear fusion DEMO environment.

Keywords: structural material, irradiation damage, microstructural evolution, defect energetics, numerical analysis

DOI: 10.1585/pfr.17.1205105

F82H steel is expected as a blanket structural material in a tokamak-type nuclear fusion DEMO reactor. The material suffers from 14 MeV fusion neutron bombardments, which induces a huge production of irradiation defects such as vacancies, self-interstitial atoms (SIAs), helium atoms and those clusters, and then causes the microstructural change with the property degradation. For a realistic fusion DEMO design, it is necessary to develop a methodology that can mechanistically predict the material behavior under irradiation. The energetics of lattice defects, especially the binding free energy of point defects to defect clusters, is one of the key parameters to evaluate formation kinetics of defect clusters under irradiation because it is a factor that determines the thermal stability of defect clusters. In the previous theoretical studies [1–4] for bcc Fe that is the main component of F82H steel, the size dependence of the point defect binding free energy has been investigated, showing that the energy strongly depends on the size of the cluster; however, the temperature dependence of the binding free energy has not been well understood; therefore, the binding free energy at 0 K has been employed in numerical analysis of the formation kinetics of those defect clusters. Since the temperature condition of the fusion DEMO reactor in operation and maintenance is widely ranging from around 300 K up to 850 K, information on the thermal stability of defect clusters is required to develop a theoretical model of the microstructural evaluation of the blanket structural material in the fusion DEMO environment. In this work, the size and temperature dependence of the point defect binding free energy in bcc Fe was numerically evaluated for SIA-clusters and vacancy clusters of typical irradiation defects.

Before deriving the binding free energy, let us describe the formation free energy of defect clusters as below. The formation free energy of defect clusters is defined as the energy required for embedding a defect cluster into an otherwise perfect crystal. Assuming an SIA-cluster to be a circular prismatic dislocation loop in a continuum model based on thermodynamics and linear elasticity [5], the formation free energy of SIA-clusters is given by

$$F_{\mathrm{f}}^{\mathrm{Icl}}(n,T) = \frac{Gb^2R_{\mathrm{d}}}{2(1-\nu)}\left[\ln\frac{R_{\mathrm{d}}}{r_{\mathrm{c}}}+C\right]-\frac{2\pi R_{\mathrm{d}}}{b}\alpha k_{\mathrm{B}}T, \tag{1}$$

where n is the number of SIAs in an SIA-cluster, R_{d} is the radius of the cluster with a relationship with n as $R_{\mathrm{d}} = (\Omega n/\pi/b)^{1/2}$ in which Ω is the mean atomic volume as $\Omega = a_0^3/2$, $a_0 = 2.8665\times10^{-10}$ m [6] is the lattice constant of bcc Fe, b is the value of the Burgers vector of $(a_0/2)$ <111>. C is a number which takes into account the strain energy in the core of the dislocation. ν is the Poisson ratio, r_{c} is the radius of the dislocation core with $r_{\mathrm{c}} \approx b$, G is the rigidity modulus. Notice that in this work G and ν are described as a function of temperature by using the Voigt-Reuss-Hill approximation [7] with the experimental data [8, 9]: $G(T) = g_0 + g_1T + g_2T^2 + g_3T^3$, $(0\,\mathrm{K} \le T \le 900\,\mathrm{K})$, $g_0 = 86.05\times10^9$ Pa, $g_1 = -7.44242\times10^6$ Pa/K, $g_2 = -2.62880\times10^4$ Pa/K^2, $g_3 = 6.61478$ Pa/K^3; and $\nu(T) = e_0+e_1T+e_2T^2+e_3T^3$, $e_0 =$

author's e-mail: watanabe.yoshiyuki@qst.go.jp

0.2838, $e_1 = 1.34091\times10^{-5}\,\mathrm{K}^{-1}$, $e_2 = 1.46282\times10^{-8}\,\mathrm{K}^{-2}$, $e_3 = 4.19036\times10^{-12}\,\mathrm{K}^{-3}$. The second term in Eq. (1) is for the entropy of vibration and configuration of atoms at the dislocation core with $a \approx 1.4$. Here, assuming that C is not sensitive to temperature, fitting Eq. (1) to the formation free energy of an isolated SIA at $T_0 = 0\,\mathrm{K}$, $F_\mathrm{f}^\mathrm{Icl}(1,T_0) = 3.94\,\mathrm{eV}$ obtained from DFT calculation [1], gives $C = 2.09076$.

In the same way, assuming a vacancy cluster to be a spherical void in a continuum model [10], the formation free energy of vacancy clusters is given by

$$F_\mathrm{f}^\mathrm{Vcl}(m,T) = \gamma S\left(1-\frac{q}{R_\mathrm{s}}\right), \tag{2}$$

where m is the number of vacancies in a vacancy cluster, R_s is the radius of the cluster with a relationship with m as $R_\mathrm{s} = (3\Omega m/4/\pi)^{1/3}$. $S = 4\pi R_\mathrm{s}^2$ is the surface area of the cluster. q is the curvature correction coefficient of the cluster surface. γ is the mean surface free energy of the flat surface. It is noted that in this work γ was formalized with the experimental data [11] as a function of temperature: $\gamma(T) = \gamma_0 + hT$, $(0\,\mathrm{K} \le T \le 1811\,\mathrm{K})$; $\gamma_0 = 2.41\,\mathrm{J/m^2}$ and $h = -1.62341\times10^{-4}\,\mathrm{J/m^2/K}$. Assuming that q is not sensitive to temperature, fitting Eq. (2) to the formation free energy of an isolated vacancy at 0 K, $F_\mathrm{f}^\mathrm{Vcl}(1,T_0) = 2.02\,\mathrm{eV}$ obtained from DFT calculation [1], gives $q = 6.54222\times10^{-11}\,\mathrm{m}$.

The binding free energy of point defects to a defect cluster is defined as the energy required to remove a point defect from a cluster. Using the formation free energies derived above, the binding free energy of SIAs to an SIA-cluster ($n \ge 2$) is described by

$$F_\mathrm{b}^\mathrm{I\_Icl}(n,T) = F_\mathrm{f}^\mathrm{Icl}(1,T) + F_\mathrm{f}^\mathrm{Icl}(n-1,T) - F_\mathrm{f}^\mathrm{Icl}(n,T), \tag{3}$$

and the binding free energy of vacancies to a vacancy cluster ($m \ge 2$) is described by

$$F_\mathrm{b}^\mathrm{V\_Vcl}(m,T) = F_\mathrm{f}^\mathrm{Vcl}(1,T) + F_\mathrm{f}^\mathrm{Vcl}(m-1,T) - F_\mathrm{f}^\mathrm{Vcl}(m,T). \tag{4}$$

Figure 1 shows the binding free energies estimated with Eq. (3) and (4) at 0 K as a function of size of defect clusters. Both the energy curves increase with the size, where the SIA binding free energy is much higher than the vacancy binding free energy, indicating that SIA-clusters are more thermally stable than vacancy clusters. Here, we focus on relatively small defect clusters with $2 \le x \le 20$, $(x = n,\ m)$ that are corresponding to the critical nucleus size of those clusters in nucleation process during irradiation. As shown in the figure, the trend of the energy curves with Eq. (3) and (4) is relatively consistent with the atomistic calculation data [2–4] obtained from DFT and MD methods. As to SIA-clusters, the energy value of the MD data is a little higher than the energy curve; it is because

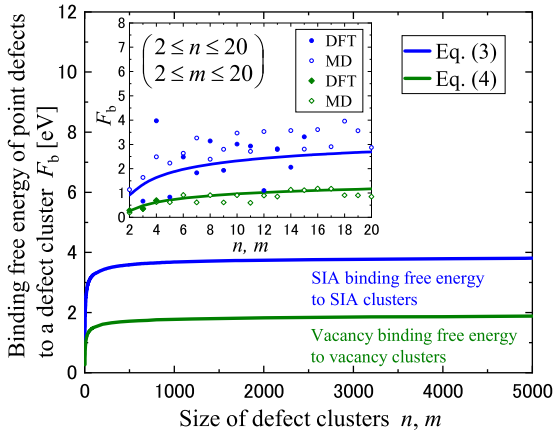

Fig. 1 Size dependence of the binding free energy of point defects to a defect cluster at 0 K in bcc Fe.

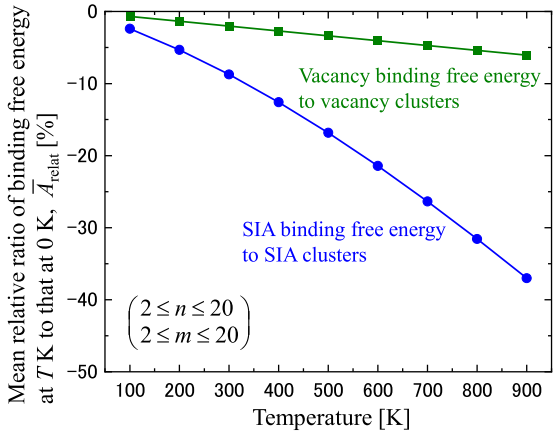

Fig. 2 Temperature dependence of the binding free energy of point defects to small defect clusters in bcc Fe.

there is a difference of about 1 eV in $F_\mathrm{f}^\mathrm{Icl}(1,T_0)$ between this work and the MD data.

Figure 2 represents the temperature dependence of the binding free energy for the small clusters estimated with Eq. (3) and (4), in which the mean relative ratio is defined in the following equation:

$$\bar{A}_\mathrm{relat} = \left\langle \frac{F_\mathrm{b}(x,T)}{F_\mathrm{b}(x,T_0)} - 1 \right\rangle \times 100\ \%, \quad (2 \le x \le 20). \tag{5}$$

Both the binding free energies considerably depend on temperature and decrease with temperature, in which the SIA binding free energy at 850 K is averagely about 35% lower than that at 0 K, while the vacancy binding free energy is about 6% lower; which may remarkably affect the nucleation process of those defect clusters during irradiation. These kinds of information will be one of the basic parameters to develop a theoretical model of the microstructural evolution of F82H steel in the fusion DEMO environment.

This work was supported by (i) BA project for fusion DEMO and (ii) the joint program of IAE, Kyoto University (ZE2020B-29).

[1] C. Domain and C.S. Becquart, Phys. Rev. B **65**, 024103 (2001).
[2] C.S. Becquart and C. Domain, Phys. Rev. B **202**, 44 (2003).
[3] R. Alexander *et al.*, Phys. Rev. B **94**, 024103 (2016).
[4] K. Morishita *et al.*, Nucl. Instrum. Methods Phys. Res. B **202**, 76 (2003).
[5] G.F. Bolling and D. Fainstein, Phil. Mag. **25**, 45 (1972).
[6] F.W. Von Batchelder and R.F. Raeuchle, Acta Cryst. **7**, 464 (1954).
[7] R. Hill, Proc. Phys. Soc. A **65**, 349 (1952).
[8] J.J. Adams *et al.*, J. Appl. Phys. **100**, 113530 (2006).
[9] D.J. Dever, J. Appl. Phys. **43**, 3293 (1972).
[10] K. Morishita and R. Sugano, J. Nucl. Mater. **353**, 52 (2006).
[11] W.R. Tyson and W.A. Miller, Surf. Sci. **62**, 267 (1977).