MODELLING OF VACANCY CLUSTER EVOLUTION IN NEUTRON IRRADIATED IRON

Aleksandr Gokhman¹, Frank Bergner, and Andreas Ulbricht

1. Introduction

There is experimental evidence for the formation of stable nm-sized vacancy clusters (VC) in low-copper iron alloys irradiated with fast neutrons under in-service conditions of reactor pressure vessels (RPVs) [1,2]. Modelling of the evolution of VCs in pure iron under neutron irradiation is both of fundamental interest and of practical importance, because vacancies and VCs (even if not present after long-term irradiation) may play an intermediary role in the formation of Cu-rich clusters in RPV steels resulting in an irradiation-induced degradation of mechanical properties. In the present investigation we apply rate theory (RT) to simulate the evolution of VCs in pure bcc iron. Similar work was reported by Odette [3] and Hardouin Duparc et al. [4]. Odette directly solved the master equation with clustering of self-interstitial atoms (SIAs) neglected. Hardouin Duparc et al. considered both planar SIA clusters and planar VCs and transformed the master equation into a Fokker-Planck equation, which may be a problem at small cluster sizes. The objective of the present investigation is to introduce the effect of lattice relaxation into the framework of Odette’s approach.

2. Method

The cluster dynamics approach is based on the following assumptions:
• Generation rates of vacancy clusters (VCs) are adopted from molecular dynamics calculations quoted in [5].
• VCs are assumed to be spherical.
• Both agglomeration and direct generation of clusters of self-interstitial atoms (SIAs) are neglected as in [3].

The rate of change of the number density of VCs is specified by the following master equation:

\[
\frac{dC_n}{dt} = \beta_{n-1,v}C_{n-1} + (\alpha_{n+1,v} + \alpha_{n+1,i})C_{n+1} - (\beta_{n,v} + \beta_{n,i} + \alpha_{n,v})C_n + G_{n,v}
\]

(1)

\[C_n\] concentration of VCs consisting of \(n\) vacancies \((n > 1)\)
\[\alpha_{n,v}\] rate of emission of vacancies by VCs containing \(n\) vacancies
\[\beta_{k,k}\] rate of absorption of vacancies \((k = v)\) or SIAs \((k = i)\) by VCs containing \(n\) vacancies
\[G_{n,v}\] rate of direct generation of VCs containing \(n\) vacancies

In the diffusion-limited regime the rate, at which vacancies (SIAs) are absorbed for spherical VCs, is given by:

\[
\beta_{n,k} = \frac{4\pi R_n D_k C_k}{Q_u}
\]

(2)

¹ South Ukrainian Pedagogical University, Odessa, Ukraine
where $R_n$ is the radius of a spherical VC containing $n$ vacancies, $D_k$ is the diffusivity of vacancies ($k = v$) or SIAs ($k = i$), $\Omega_a$ is the atomic volume of iron, and $C_k$ is the number density of free vacancies ($k = v$) or SIAs ($k = i$). The evolution of $C_k$ with time is given by integration of the RT equations according to [3]:

$$\frac{dC_k}{dt} = G_k - \frac{4\pi r(D_v + D_i)C_v C_i}{\Omega_a} - D_k C_k S_k$$

(3)

Here $r$ is the recombination or trap radius, $G_k$ is the production rate of free vacancies ($k = v$) or SIAs ($k = i$), and $S_k$ is the sink strength for vacancies ($k = v$) or SIAs ($k = i$). Eq. (3) is the special form of Eq. (1) for $n = 1$. In Eq. (3) it is assumed that the rate of emission of vacancies from VCs is much less than the production rate. $S_k$ is taken to be proportional to the dislocation density, $\rho$ [3] with a factor of proportionality of 1 (1.2) for vacancies ($k = v$) or SIAs ($k = i$) [5]. $G_k$ is taken to be proportional to the neutron dose rate expressed in units of dpa/s (dpa = displacements per atom) with a factor of proportionality of 0.183 for both vacancies and SIAs. Taking into account that the recombination term in Eq. (3) for SIAs is much less than the sink term, Eq. (3) can be solved analytically [6]. Odette [3] used the stationary values of $C_v$ and $C_i$ obtained from the condition, $dC_{v(i)}/dt = 0$, instead of the time-dependent solution of Eq. (3).

The vacancy emission rates, $\alpha_{n,v}$, are related to the absorption rates, $\beta_{n,v}$, and the change of Gibbs free energy, $\Delta G$, in accordance with the detailed balance principle:

$$\alpha_{n,v} = \beta_{n,v} \exp \left[ \frac{\Delta G(n) - \Delta G(n-1)}{k_B T} \right]$$

(4)

Here $k_B$ is Boltzmann’s constant; $T$ is the temperature in K and $\Delta G(n)$ is the change of Gibbs free energy, when a VC of $n$ vacancies is formed. Ignoring any interaction between VCs and matrix except surface energy, $\Delta G(n)$ is given by:

$$\Delta G(n) = -n\Delta \mu + 4\pi R_n^2 \gamma$$

(5)

where $\Delta \mu$ is the change of chemical potential and $\gamma$ is the specific surface energy. In the case of an ideal solution [7]:

$$\Delta \mu = k_B T \ln \left( \frac{C_v}{C_{R,n}} \right)$$

(6a)

where the Thomson-Freundlich term, $C_{R,n}$, is given by:

$$C_{R,n} = \exp \left( -\frac{E_f}{k_B T} + \frac{2\gamma \Omega_a}{k_B T R_n} \right)$$

(6b)

and $E_f$ is the energy of formation of a single vacancy.

The maximum considered number of vacancies in a cluster corresponds to the number of equations in the system, Eq. (1). We have chosen $n_{max} = 9000$ in agreement with the
maximum VC radius of about 3 nm observed in SANS experiments on low-copper model alloy A [8]. The values of the material parameters used in the calculations are listed in Table 1. These values have been adopted from [3]. The direct generation rates of VCs listed in Table 2 have been adopted from molecular dynamics calculations quoted in [5].

For computational purposes the system of equations, Eqs. (1) to (6), was transformed into a dimensionless representation. The program D02EJF (NAG Fortran Library Manual) applied to solve the master equation integrates a stiff system of first order ordinary differential equations using a variable order, variable step method implementing the backward differential formulae.

We have observed that the mean radius of the calculated VC distribution strongly depends on the dislocation density, $\rho$. Furthermore, the total volume fraction of VCs turned out to depend strongly on the surface energy, $\gamma$. Therefore, these quantities have been taken as fitting parameters in order to reproduce the mean radii and volume fractions observed by means of SANS experiments for the irradiation conditions of the low-copper alloy A (Table 3).

**Table 1: Material parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Data taken from [3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancy migration energy</td>
<td>1.3 eV</td>
</tr>
<tr>
<td>Vacancy pre-exponential</td>
<td>$0.5 \times 10^{-4}$ m$^2$/s</td>
</tr>
<tr>
<td>Interstitial migration energy</td>
<td>0.4 eV</td>
</tr>
<tr>
<td>Interstitial pre-exponential</td>
<td>$5 \times 10^{-6}$ m$^2$/s</td>
</tr>
<tr>
<td>Vacancy formation energy, $E_f$</td>
<td>1.64 eV</td>
</tr>
<tr>
<td>Recombination radius, $r$</td>
<td>0.574 nm</td>
</tr>
<tr>
<td>Surface energy, $\gamma$</td>
<td>1-2 J/m$^2$</td>
</tr>
<tr>
<td>Dislocation density, $\rho$</td>
<td>$5 \times 10^{14}$ 1/m$^2$</td>
</tr>
<tr>
<td>Lattice parameter, $a_0$</td>
<td>0.2866 nm</td>
</tr>
</tbody>
</table>

**Table 2: Direct generation rate of cascade VC containing $n$ vacancies**

<table>
<thead>
<tr>
<th>$n$</th>
<th>$G_{n,v}$ in $10^{-9}$ dpa/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Data taken from Fig. 8 of Ref. [5]</td>
</tr>
<tr>
<td>1</td>
<td>17.5</td>
</tr>
<tr>
<td>2</td>
<td>0.26</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
</tr>
<tr>
<td>5</td>
<td>0.23</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>2.5</td>
</tr>
<tr>
<td>8</td>
<td>1.75</td>
</tr>
<tr>
<td>≥9</td>
<td>0</td>
</tr>
</tbody>
</table>
Relaxation of the lattice is considered by introducing an additional term, $W(n)$, into Eq. (5).

$$\Delta G(n) = -n\Delta \mu + 4\pi R_n^2 \gamma + W(n)$$

(7)

The binding energy of a vacancy in a cluster containing a number of $n$ vacancies,

$$E^V_b(n) = E_f + \Delta G(n-1) - \Delta G(n),$$

(8)

assumes the general form

$$E^V_b(n) = E_f - x \left[ n^{2/3} - (n-1)^{2/3} \right] + y$$

(9a)

$$x = 2.5 \left( \frac{8\pi}{3} \right)^{1/3} a_n^2 \gamma$$

(9b)

$$y = \left[ \ln(C_v) - 3 \right] k_B T - \left[ W(n) - W(n-1) \right]$$

(9c)

Table 3: Irradiation conditions and SANS results for the low-Cu model alloy A [8]

<table>
<thead>
<tr>
<th>Irradiation condition</th>
<th>A1</th>
<th>A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutron dose rate, $10^{-9}$ dpa/s</td>
<td>0.4</td>
<td>3</td>
</tr>
<tr>
<td>Mean radius of VCs, nm</td>
<td>1.0 ± 0.1</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>Volume fraction of VCs, %</td>
<td>0.02 ± 0.005</td>
<td>0.10 ± 0.01</td>
</tr>
</tbody>
</table>

Fitting results of molecular dynamics calculations reported in [9] with Eq. (10), we obtained $x = 2.79$ eV and $y = 0.11$ eV. This fit is as least as good as the one-parameter fit (Eq. (9a) with $y$ set to 0) performed in [9], which gave $x = 2.59$ eV. The term $W(n)-W(n-1)$ to be introduced into Eq. (4) was calculated from Eq. (9c) using the value obtained for $y$. The remaining procedure corresponds to the one described above.

3. Results

In a sensitivity study the effect of several material parameters on the size distribution function (SDF) of VCs has been investigated for the case of lattice relaxation neglected. Depending on the value of the dimensionless quantity $c$, $c = C_i D_i / C_v D_v$, the shape of the SDF varies essentially. If $c > 1$, the calculated SDF has only one peak at a radius of about 0.3 nm. This peak corresponds to the direct generation of VCs as a result of the cascade stage (Table 2). If $c < 1$, a second peak appears at a radius greater than 0.3 nm. The radius of the second peak is an increasing function of irradiation time. The SDF calculated for the same set of material parameters and several irradiation times is shown in Fig. 1. After one year of irradiation, the volume fraction that corresponds to the second peak is much larger than the volume fraction covered by the first peak. We have also observed that, after a certain irradiation interval, the mean radius of VCs is mainly determined by the dislocation density, whereas the volume fraction of VCs is most sensitive to the surface energy.
Fig. 1: Calculated (relaxation of the adjacent lattice neglected) evolution of volume related cluster size distribution for a dose rate of $3 \times 10^3$ dpa/s after irradiation intervals as indicated. SANS-based experimental results for irradiation condition A2 of model alloy A (Tab. 3) are shown for comparison.

The experimental values of the mean radius (Table 3) are reproduced best, if a dislocation density, $\rho = 1.84 \times 10^{14} \text{ m}^{-2}$, is assumed. For irradiation conditions A1 and A2 (Table 3), best fit with respect to the volume fraction is obtained for values of the surface energy, $\gamma = 0.67 \text{ J/m}^2$ and $\gamma = 0.82 \text{ J/m}^2$, respectively.

The behaviour of the model with lattice relaxation taken into account is similar as described above. In this case, however, best fit with respect to the volume fraction is obtained for values of the surface energy, $\gamma = 1.94 \text{ J/m}^2$ (condition A1) and $\gamma = 2.02 \text{ J/m}^2$ (condition A2).

4. Discussion

The first peak of the calculated SDF of VCs (at about 0.3 nm) cannot be resolved by means of small-angle neutron scattering (SANS), because measuring errors strongly increase for radii below 0.5 nm. Experimental evidence is, however, available from positron annihilation measurements reported in [2] for the same alloy. The second peak of the calculated SDF corresponds to the experimental results obtained from SANS measurements. As variation of the irradiation interval in model calculations shows, the mean radius of VCs increases according to a $t^{1/5}$-law, which is slower than $\sim t^{1/3}$ predicted by the Lifshitz-Slyozov theory.

The values of the dislocation density and the surface energy obtained by adjustment of the model with experimental data are reasonable estimates (compare Table 1). The closer agreement of the surface energies obtained in the second set of calculations indicates both that consideration of cluster-matrix interaction is important and that the method is appropriate. Therefore, the corresponding estimation of the surface energy, $\gamma \approx 2.0 \text{ J/m}^2$, is more reliable than a value at or below 1 J/m$^2$ obtained without consideration of cluster-matrix interaction.

The shape of the size distribution function has not been considered so far. The experimentally obtained distribution is observed to be wider than the calculated ones (Fig. 1). However, prior to comparison a more detailed analysis has to be performed with respect to both estimation of
experimental errors including error propagation due to Fourier transformation and identification of model parameters influencing shape.

5. Conclusion

The present model of vacancy cluster evolution in bcc iron under neutron irradiation, which is based on rate theory according to [3], can be adjusted in such a way that both volume fraction and mean size of irradiation-induced vacancy clusters measured by means of SANS are reproduced. The values of the specific surface energy of clusters and the dislocation density needed to adjust the model are reasonable estimates for the alloy under investigation. The expectation that the surface energies for the two dose rates considered should agree is fulfilled more closely, if in addition to surface energy the relaxation of the lattice is taken into account by introducing an additional term, $W(n)$, into cluster-matrix interaction.

References


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