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Cluster dynamics simulation of reactor pressure vessel steels under irradiation

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Abstract. The coupling between copper rich precipitates (CRP) and point defects in neutron irradiated iron alloys and VVER steels was investigated by means of cluster dynamics (CD) simulations. The consideration of the strain energy effect on CRP kinetics as well as the application of the regular solution model for the case of different fixed copper contents of CRP provides a good agreement between the simulation results and experimental data for complex iron based alloys with small (0.015 wt%) and high (0.42 wt%) copper content. It was found that the CD simulation is applicable to irradiated VVER steel with 0.07 wt% of copper.

Introduction

Neutron irradiation results in essential changes with time of the microstructure of reactor materials. The distance between irradiated features (precipitates, clusters and atmospheres) exceeds significantly the size of them in neutron irradiated reactor pressure vessel, RPV, steels [1-8]. Therefore, the cluster dynamics (CD) approach originally suggested in [9] for small clusters and applicable to any ideal gas of clusters or spatially averaged system of clusters is found effective to investigate the long-term behavior of the neutron-stimulated microstructural changes of RPV steels [4, 10-13].

On the assumption that the motion of clusters consisting of two or more monomers is negligible, the evolution of the cluster population follows a master equation (Eq. 1):

$$\frac{dC_n}{dt} = C_{n-1}\beta_{n-1,n} + C_{n+1}\alpha_{n+1,n} - C_n(\beta_{n,n+1} + \alpha_{n,n-1}) \quad for \quad n \geq 2\,,$$
$$\frac{dC_1}{dt} = \sum_{n=2}^{\infty}\alpha_n C_n - \sum_{n=2}^{\infty}\beta_n C_n - 2\beta_1 C_1 + \alpha_2 C_2\,. \tag{1}$$

Here C_n is the spatially averaged concentration of clusters of size n; $\beta_{n,n+1}$ is the absorption coefficient, i.e. the probability density for the attachment per unit of time of one monomer to the cluster of size n; $\alpha_{n,n\text{-}1}$ is the emission coefficient, i.e. the probability density for the emission per unit of time of one monomer from the cluster of size n. The equation for copper monomers can also be derived on the basis of the conservation law for the number of monomers.

Copper diffusion, which is based on a vacancy mechanism, is enhanced due to the irradiation-induced increase of the vacancy concentration. Therefore, the copper diffusivity is given by Eq. (2):

$$D_{Cu}^{irr} = D_{Cu}^{th} C_{v1} / C_{v1}^{eq}\,. \tag{2}$$

Here D_{Cu}^{th} and C_{v1}^{eq} are the thermal Cu diffusivity and the vacancy concentration at equilibrium; D_{Cu}^{irr} and C_{v1} are the copper diffusivity and vacancy concentration under irradiation.

So far, our main focus of CD simulation has been the evolution of vacancies, interstitials and copper rich precipitates (CRP) for iron-based model alloys with composition closed to that of RPV steels under typical reactor conditions. The objective of the present paper is to consider the coupling of the copper-vacancy system by means of CD simulation for iron based model alloys as well as for irradiated VVER steels.

Coupled copper-vacancy model

In our paper the coupled copper-vacancy model is based on the following prerequisites:

- there is an influence of the copper subsystem on the vacancy subsystem due to the consideration of the CRPs as additional sinks (in addition to the dislocation network) for vacancy monomers;
- the content of the CRPs after the cascade stage does not change under subsequent neutron irradiation;
- the shape of the vacancy clusters and CRPs is assumed to be spherical;
- the diffusion-limited regime for Cu atoms, vacancies and interstitials is valid;
- the elastic interaction between CRPs and iron matrix is taken into account on the basis of continuum mechanics [14, 15].
- the ideal and regular solution models of the Cu-Fe system are applied.

The coefficients $\beta_{n,n+1}$ are determined for copper-vacancy clusters by:

$$\beta_{n,n+1} = 4\pi R_{nv} D_v C_{v1} / \Omega_{vac} + 4\pi R_{ncu} D_{Cu}^{irr} C_{Cu1} / \Omega_{Cu} . \tag{3}$$

where Ω_{vac} , Ω_{Cu} are the atomic volume of vacancy (iron) and copper, respectively; $R_{nv} / \Omega_{vac} = (3n_{vac}/\pi)^{1/3}/a_{Fe}^2$; $R_{nCu}/\Omega_{Cu} = (3n_{Cu}/\pi)^{1/3}/a_{Cu}^2$; $n_{vac} = (1-x_{\alpha Cu})\cdot n$ and $n_{Cu} = x_{\alpha Cu}\cdot n$ are the number of vacancies and copper atoms, respectively, in cluster with the given copper content ($x_{\alpha Cu}$); a_{Fe} and a_{Cu} are the lattice parameters of iron and copper. The coefficients $\alpha_{n,n-1}$ are determined by applying the detailed balance principle in terms of the change of the Gibbs free energy, $\Delta G(n)$, due to cluster formation [12]:

$$\alpha_{n,\,n+1} = \beta_{n-1,\,n} \cdot \exp \frac{\Delta G(n) - \Delta G(n-1)}{k_B T} . \tag{4}$$

The change of the Gibbs free energy, $\Delta G(n)$, due to cluster formation is given by:

$$\Delta G(n) = -n[(1 - x_{\alpha Cu})\Delta\mu_{nv} + x_{\alpha Cu}\,\Delta\mu_{nCu}] + 4\pi R_n^2 \gamma_{Cu-vac} + W_{el}(n) . \tag{5}$$

Here γ_{Cu-vac} is the surface tension of the boundary between iron matrix and cluster. γ_{Cu-vac} depends on both $x_{\alpha Cu}$ and dose but does not depend on cluster size (capillary approximation for binary system). $\Delta\mu_{nv}$ is the difference in the chemical potential between vacancy (copper) monomer attached to a cluster with n_v (n_{Cu}) monomers and in the matrix. $\Delta\mu$ is given by [16]:

$$\Delta\mu = \Delta\mu_{id} + \omega\,[(1 - C_{x1})^2 - (1 - C_{xeq})^2] , \tag{6}$$

where $\Delta\mu_{id}$ is the change of the chemical potential on the assumption of an ideal solution,

$$\Delta\mu_{id} = k_B T \cdot \ln(C_{x1} / C_{Rn}) \qquad and \quad C_{Rn} = C_{xeq} \cdot \exp\left(\frac{2\gamma\Omega}{k_B T R_n}\right) . \tag{7}$$

Here k_B is the Boltzmann's constant, T is the absolute temperature and ω is the demixing energy. The elastic interaction between iron matrix and CRP containing n monomers can be described by the strain energy that is produced by misfit in lattice parameters and elastic properties of cluster and iron matrix. To simplify the problem only the misfit in lattice parameters has been considered. In addition, the assumption on isotropy of elastic properties of iron matrix and CRP has been taken. CRP of radius less than 3 nm (maximum size of CRP observed in neutron irradiated steels) are coherent to the iron matrix and hence have the same bcc structure as iron [17]. For this case the strain elastic energy per 1 m^3 is given by Eshelby's formula [14, 15].

The long-term behavior of the quantities C_{v1} and C_{i1} is determined by equations (8-11):

$$\frac{dC_{v1}}{dt} = G_v - 4\pi r_{rec}(D_v + D_i)C_{v1}C_{i1}/\Omega_{vac} - D_v C_{v1} S_v^T , \tag{8}$$

$$\frac{dC_{i1}}{dt} = G_i - 4\pi r_{rec}(D_v + D_i)C_{v1}C_{i1}/\Omega_{vac} - D_v C_{i1} S_i^T . \tag{9}$$

Here $G_v = G_{dpa}\eta(1-f_{vcl})$ and $G_i = G_{dpa}\eta(1-f_{icl})$ are the production rates of vacancies and interstitials, respectively, due to irradiation with neutron dose rate G_{dpa}; η is the efficiency coefficient; f_{vcl} (f_{vcl}) is the fraction of vacancies (interstitials) that form clusters already in the cascade stage; S_v^T (S_i^T) is the sink strength for vacancies (interstitials). The main sink for vacancies and interstitials is the dislocation net [4]:

$$S_i^T = z_i\rho \quad \text{and} \quad S_v^T = z_v\rho , \tag{10}$$

where ρ is the dislocation density and z_v=1; z_i =1.2 [4]. The copper-vacancy clusters are considered as additional sinks with the sink strength, $S_{Cu/vac}^T$, in our model:

$$S_v^T = z_v\rho + S_{Cu-vac}^T . \tag{11}$$

On the assumption of diffusion-limited regime for the kinetics of transport of free vacancies to the copper-vacancy clusters, the quantity S_v^T changes with irradiation time according to:

$$S_v^T = z_v\rho + 4\pi R_{mean} N_p , \tag{12}$$

where N_p and R_{mean} are the number density and mean radius of copper-vacancy clusters, respectively. They are found by means of an averaging procedure based on the size distribution determined from Eq. 1.

Computations

The master equation (Eq. 1) is a stiff system of ordinary differential equations. The lsoda code [18, 19] was checked to be a suitable solver. The data on energy of formation and energy of migration, pre-exponential factor, capture efficiency by dislocation net for vacancies and interstitials are taken from [4]. Other parameters, γ, ρ and D_{Cu}^{th}, are considered as fitting parameters due the wide range of their experimental values.

CD simulation for $x_{\alpha Cu} = 0$. For this case only the vacancy subsystem without coupling with the copper subsystem is considered and the values of γ_v and ρ are determined in CD investigations of the low-copper alloy *A* (0.015 wt% of copper) under VVER-reactor type conditions [12, 20]. The

ideal solution model of vacancy-iron system is taken according to [4]. The distribution of vacancy clusters, VC, after the cascade stage is taken from Fig. 8 of [13] with accounting for a difference of the G_{dpa} values in [12] and [13]. The time dependence of the vacancy concentration in iron has been taken from [12, 20]. It was found that the calculated mean radius and volume content of VC depend on the values of ρ and γ_v, respectively, and the best fit to the data from SANS for irradiation conditions *A2* [12, 20, 21] is obtained for $\rho = 1.84 \cdot 10^{-14}$ m^{-2} and $\gamma_v = 1.8779$ J/m^2.

CD simulation for $x_{\alpha Cu} = 1$. In CD simulations the values of D_{Cu}^{th} and γ_{Cu} are determined from the condition of the best fit to the R_{mean} and C_v for irradiation condition *B1, B2* of the high-copper content alloy *B* (0.42 wt % copper) under VVER-reactor type conditions [12, 20, 21]. For the regular solution model with accounting for the strain energy, the best fit is obtained for $D_{Cu}^{th} = 1.2218 \cdot 10^{-26}$m^2/s and $\gamma_{Cu} = 0.2706$ J/m^2.

CD simulation for $x_{\alpha Cu}$ determined from SANS measurements of irradiated alloy B. To estimate the value of $x_{\alpha cu}$ in clusters of irradiated alloy *B* the ratio of scattered intensities, $I = d\Sigma/d\Omega$, perpendicular and parallel to the magnetic field direction at SANS measurements is considered. This so-called A-ratio is found to be 5.0 and 5.3 for irradiation conditions *B1* and *B2*, respectively [20, 21], and the corresponding $x_{\alpha cu} = 0.835$ and 0.850 in assumption of copper-vacancy model of CRP. The best fit to SANS data [20, 21] is obtained for $\gamma_{cu-vac} = 0.3150$ J/m^2 (condition *B1*) and 0.3154 J/m^2 (condition *B2*) and $D_{Cu}^{th} = 5.5560 \cdot 10^{-26}$m^2/s for both conditions. The obtained values of γ_{cu-vac} can be interpreted as the linear combination with coefficients 0.972 and 0.028 of the surface tension values determined before for pure copper cluster in iron ($\gamma_{cu} = 0.2706$ J/m^2) and pure vacancy cluster in iron ($\gamma_v = 1.8779$ J/m^2), respectively. It supports the approach on the shell structure of copper - vacancy cluster in neutron irradiated steel, where the boundary between cluster and iron matrix contains preferentially copper atoms.

CD simulations for irradiated VVER steels. The composition, irradiation conditions and SANS results of investigated VVER-1000 steels (codes *D*, *R16* and *R17*) are presented in Table 1 in accordance with [22-24]. Because of the small Cu-content in the CD simulation for steel *D* the assumption on the vacancy nature of irradiation-induced clusters (case $x_{\alpha c} = 0$) has been used. It was found that the experimental value of the volume content for irradiation conditions *D1* and *D2* can be fitted by CD simulations using the values $\gamma = 0.7$ J/m^2, $\rho = 7.00 \cdot 10^{-14}$ m^{-2} (*D1*) and $\rho = 3.56 \cdot 10^{-14}$ m^{-2} (*D2*). But for given values of γ and ρ, the calculated mean radius was found to be 0.24 nm smaller than the experimental one for both irradiation conditions. Moreover, for the unirradiated condition of the considered VVER steels the experimental value of ρ is about $3 \cdot 10^{-14}$ m^{-2} [24]. Hence the assumption on the presence of pure VC in the irradiated steel *D* is not justified at least for irradiated condition *D1*.

For steels *R16* and *R17* the presence of CRP has been assumed. For irradiated steel *R16* the experimental volume content and mean radius have been obtained in CD simulations for $\rho = 3 \cdot 10^{-14}$ m^{-2}, $D_{Cu}^{th} = 1.5875 \cdot 10^{-27}$ m^2/s and $\gamma_{cu-vac} = 0.1650$ J/m^2. These fitting parameters also reproduce the experimental value of the mean radius for irradiated steel *R17* but the calculated value of volume content was found to be less than the experimental one of 0.02%.

Table 1 Composition, irradiation conditions and SANS results for investigated VVER steels

Composition [wt %]	Dose [dpa]	Dose rate [10^{-7} dpa/s]	Irradiation temperature [K]	Mean radius [nm]	Volume content [%]
0.03Cu-1.2Ni -0.59Mn-0.26Si -2.2Cr-0.63Mo(*D*)	0.029 (D1)	0.295	563	0.90	0.02
0.03Cu-1.2Ni -0.59Mn-0.26Si -2.2Cr-0.63Mo(*D*)	0.097 (D2)	0.340	563	0.90	0.12
0.07Cu-1.1Ni -0.48Mn-0.31Si -2.2Cr-0.57Mo(*R16*)	0.046	0.028	528	1.00	0.06
0.13Cu-1.3Ni -0.47Mn-0.27Si -2.1Cr-0.57Mo(*R17*)	0.073	0.044	528	1.00	0.12

Summary

The coupling between CRP and point defects in neutron irradiated iron based alloys has been investigated by CD simulations using the LSODA code as a solver of the stiff system of ordinary differential equations. The approach was found to be successful for the special case of pure vacancy clusters applied to the low-copper alloy *A* under irradiation condition *A2*. Using reasonable values of thermal copper diffusivity in iron and surface tension provides noticeable agreement between calculations and SANS data for the Cu-enriched alloy *B* under irradiation conditions *B1* and *B2* as well as for irradiated steel *R16*. The additional consideration of the strain energy effect on CRP kinetics and application of the regular solution model for the case of different fixed copper contents of CRP improves quantitatively the results of the model calculations. For the case of irradiated steels *D* and *R17* the suggested approach requires further developments.

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References

[1] G.R. Odette, Scr. Metall. **17** (1983) 1183.

[2] G.R. Odette, MRS Symposium Proceedings **373**, Pittsburgh, 1995, p.137.

[3] G.R. Odette, G.E. Lucas, Radiat. Eff. Def. Solids **144** (1998) 189.

[4] G.R Odette, in: M. Davies (Ed.), Neutron Irradiation Effect in Reactor Pressure Vessel Steels and Weldments, Vienna, 1998, p.438-504.

[5] J.T. Buswell, W.J. Phytian, R.J. Mc Elroy, S. Dumbill, P.H.N. Ray, J. Mace, R.N. Sinclair, J. Nucl. Mater. **225** (1995) 196.

[6] S.B. Fisher, J.T. Buswell, Int. J. Pressure Vessel Piping **27** (1987) 91.

[7] G.E. Lucas, G.R. Odette, P.M. Lombrozo, J.W. Sheckehard, in: F.A. Garner, J.S. Perrin (Eds.), Effects of Radiation on Materials: Twelfth International Symposium, ASTM STP 870, Philadelphia, 1985, p.900.

[8] S.C. Glade, B.D. Wirth, G.R. Odette, P. Asoka-Kumar, J. Nucl. Mater. **351** (2006) 197-208.

[9] K.Binder, Phys. Rev. B **15** (1977) 4425.

[10] S.J. Golubov, Yu.N. Osetsky, A. Serra, A.V. Barashev, J. Nucl. Mater. **226** (1995) 252.

[11] S.J. Golubov, Yu.N. Osetsky, A.Serra, A.V. Barashev, J. Nucl. Mater. **277** (2000) 113-115.

[12] A.Gokhman, J.Boehmert, A.Ulbricht, Radiat. Eff. Def. Solids **158** (2003) 783-792.

[13] F. Christien, A. Barbu, J. Nucl. Mater. **324** (2004) 90-96.

[14] J.D. Eshelby, Proc. Roy. Soc. **A 241** (1957) 376.

[15] T. Mura, Micromechanics of defects in solids, Kluwer Academic Publishers, Dordrecht, 1991.

[16] J. Schmelzer, Jr., U. Lembke, R. Kranold, J. Chem. Phys. **113** (2000) 1268-1275.

[17] G. J. Ackland, D.J. Bacon, A.F. Calder and T. Harry, Phil. Mag. A **75** (1997) 713-732.

[18] A. C. Hindmarsh, Odepack, a systematized collection of ode solvers, in scientific computing, R. S. Stepleman et al. (eds.), North-Holland, Amsterdam, 1983, pp. 55-64.

[19] L. R. Petzold, Automatic selection of methods for solving stiff and nonstiff systems of ordinary differential equations, siam j. sci. stat. comput. 4 (1983) 136-148.

[20] A. Gokhman, J. Boehmert, Radiat. Eff. Def. Solids **158** (2003) 498-511.

[21] F. Bergner, A. Ulbricht, A. Gokhman, D. Erak, Nature of defect clusters in neutron-irradiated iron-based alloys deduced from small-angle neutron scattering, J. Nucl. Mater. 2007, DOI: 10.1016/j.jnucmat.2007.05.044 (in print).

[22] A. Ulbricht, J.Boehmert, P.Strunz, C. Dewhurst, M.-H. Mathon, Microstructural investigations on Russian reactor pressure vessel steels by small-angle neutron scattering, Appl. Phys. A **74** (2002) S1128–S1130.

[23] A. Ulbricht, F. Bergner, P.K. Pranzas, SANS investigation of neutron-irradiated RPV steels with special emphasis on Ni effect, in: GeNF Experimental Report 2005, A. Schreyer, J. Vollbrandt, R. Willumeit (Eds.), GKSS Geesthacht, 2006, pp. 107-108.

[24] J. Kocik, E. Keilova, J. Cizak, I. Prohazka, J. Nucl. Mater. **303** (2002) 52-64.