

APPLICATION OF RATE THEORY MODELING TO CLUSTER EVOLUTION IN BINARY FE-CU ALLOYS

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1. Introduction

The degradation of the mechanical properties of reactor pressure vessel steels caused by the irradiation with fast neutrons is a phenomenon, in which processes on a multitude of time and length scales are involved. It is not efficient and, in particular at the sub-nm and sub- μ s scales, not even possible to cover all the important constituents of the damage process by means of experiments. Therefore, a multi-scale modeling approach has been adopted in recent years. This kind of approach is based on an interplay of models on different time scales, scale-bridging concepts as well as modeling oriented experiments.

Within the integrated project PERFECT of the 6th European Framework program (FP6) a set of well-defined model alloys was fabricated and neutron-irradiated under different irradiation conditions [1]. These samples were investigated by a series of complementary experimental techniques, including TEM (transmission electron microscopy), PAS (positron annihilation spectroscopy) and SANS (small-angle neutron scattering). The latter experiments were carried out at the SCK-CEN in Mol and evaluated at the FZD in Rossendorf. Four different neutron fluences were investigated at one and the same neutron flux. The material matrix comprises pure iron and a set of binary, ternary and quaternary model alloys such as Fe-1.2%Mn-0.7%Ni-0.1%Cu with compositions already quite near to real reactor pressure vessel (RPV) steels. We will focus on the two binary Cu-Fe model alloys Fe-0.3%Cu and Fe-0.1%Cu here. The aim of the present paper is to present a rate theory (RT) model which is able to reproduce the complete set of SANS data, in particular the volume fraction of the defect clusters and the peak radius of the size distribution function (SDF), for both model alloys and all four irradiation conditions (see Table 1). The dependence of the SANS data on the neutron fluence was found to be quite complex, suggesting that a pure Cu precipitation model might not be enough to explain the observations. And in fact, we were not able to find a suitable parameter set for a rate theory model based on pure Cu precipitates which could reproduce the experimental results even qualitatively. Therefore, we explicitly take into account the absorption of iron vacancies by the copper-rich precipitates for the simulation of the defect cluster evolution in our new Vacancy-Coupled Copper Clustering (V3C) model.

Table 1: Irradiation conditions for the Fe-0.1%Cu and Fe-0.3%Cu model alloys.

Parameter	Value
Temperature, T	300 °C
Neutron flux, ϕ ($E > 1$ MeV)	0.95×10^{18} n/m ² s
Dose rate, G_{dpa} ($E > 1$ MeV)	1.40×10^{-7} dpa/s
Dose	0.026, 0.051, 0.10, 0.19 dpa

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2. The rate theory model

Standard rate theory models for the formation of copper-rich precipitates in irradiated reactor pressure vessel steels as describe, for example, in Ref. [2] consist of the following three essentials: a balance equations for the evolution of each of the mobile point defects, vacancies and self-interstitial atoms (SIAs), a set of master equations for the evolution of the immobile defect clusters up to a given maximum size, and a model for the irradiation enhancement of the Cu mobility in the iron matrix. The balance equations read

$$\frac{dC_A}{dt} = G_A - k_{vi} C_v C_i - k_A C_A, \quad A = v, i, \quad (1)$$

where C_v and C_i are the concentrations of the vacancies and SIAs, respectively, measured in point defect per lattice site. Here, G_A are the generation rates of the point defects due to irradiation, $k_{vi} C_v C_i$ is the recombination rate of the vacancies and self-interstitials, and $k_A C_A$ the loss rates of each type A of point defect at the dislocations in the iron matrix with the decay rates k_A being proportional to the dislocation density ρ . The classical master equations are of the general form (e.g. Refs. [2,3])

$$\frac{dC_n}{dt} = f(C_{n-1}, C_n, C_{n+1}, C_{Cu}; p_1 = \gamma_{Cu-Fe}, p_2 = D_{Cu}^*) \quad (2)$$

where C_n is the concentration of the n -atomic defect clusters, measured in cluster per lattice site. Besides the concentration C_{Cu} of the Cu atoms in the iron matrix and the number of clusters per lattice site of given size n and adjacent sizes $n \pm 1$, the reaction rate $\frac{d}{dt} C_n$ also depends on a couple of material parameters p_1, p_2, \dots , the most important ones being the coherent specific Cu-Fe interface energy γ_{Cu-Fe} and the irradiation enhanced Cu diffusion coefficient D_{Cu}^* . Assuming a vacancy assisted diffusion mechanism for the Cu atoms the irradiation enhancement of the Cu diffusivity can be modeled by [4]

$$D_{Cu}^* = D_{Cu} \cdot \frac{C_v(t)}{C_v^{eq}} \quad (3)$$

where C_v is the actual, irradiation-induced concentration of the vacancies in the iron matrix, while C_v^{eq} and D_{Cu} are the thermal vacancy concentration and the copper diffusion coefficient in the unirradiated material, respectively.

Often [4,5], the system of point defects and the copper subsystem can be treated independently, by replacing $C_v(t)$ by the steady-flux solutions C_v^{sf} of the balance equations (1) and (2). This is justified by the fact, that the typical time-scale of the point defect system is orders of magnitudes smaller than that of the copper system. Yet, as already mention above, there is quite some evidence for the copper precipitates in RPV steels and Cu-Fe model alloys of moderate Cu content actually being mixed defect clusters which contain both, Cu and vacancies (and other alloying elements). To allow for such mixed compositions, the defect clusters must be able to absorb vacancies. This is explicitly taken into account in our V3C (Vacancy-Coupled Cu-Clustering) model by letting the defect clusters act as additional vacancy sinks.

To this end, the simple decay rate k_v in Eq. (1) is replaced by

$$\begin{aligned} k_v(t) &= k_v^0 + \Delta k_v(t) \\ &= z_v D_v \rho + 4\pi D_v \sum_{n \geq 2} R_n C_n(t) / V_{\text{Fe}} \end{aligned} \quad (4)$$

Here, D_v is the diffusion coefficient of the vacancies in the iron matrix, z_v the dislocation sink strength bias for vacancies, R_n the radius of a defect cluster of size n , and V_{Fe} the atomic volume of bcc iron. The new sink term $S_v = k_v(t) C_v$ consists of a static contribution $S_v^0 = k_v^0 C_v$ due to the given dislocation network in the material, and a dynamic contribution $\Delta S_v = \Delta k_v(t) C_v$ which depends on the actual defect cluster distribution. Because the latter term imposes the time modulation of the copper subsystem onto the point defect system, the balance equations cannot be solved independently of the copper subsystem anymore. Actually, the balance equations can still be solved in an adiabatic fashion with a slowly varying quasi-steady-flux solution $C_v^{\text{q-sf}}(t)$ being used in Eq. (3). However, regardless of this detail, the new V3C model constitutes a two-fold coupling between the point defect and the copper subsystem, a forward coupling which is mediated via the vacancy-dependence of the diffusion coefficient D_{Cu}^* entering the master equations (2) and a backward coupling which is caused by the Cu-cluster-dependence of the vacancy decay rate $k_v(t)$ entering the balance equations (1). For the self-interstitial atoms only a static contribution term $S_i = k_i C_i$ to the sink term is considered, because the (oversized) Cu clusters are assumed not to be able to absorb SIAs to a relevant amount.

Table 2: Material parameters adopted for the rate theoretical simulation. Here k is the Boltzmann constant and T the irradiation temperature (in K).

Parameter	Value	Reference
Interstitial diffusion coefficient at 300 °C, D_i	$1.52 \times 10^{-9} \text{ m}^2/\text{s}$	[9]
Vacancy diffusion coefficient at 300 °C, D_v	$1.85 \times 10^{-16} \text{ m}^2/\text{s}$	[9]
Copper migration energy, $E_{\text{m,Cu}}$	2.29 eV	[4]
Copper pre-exponential factor, $D_{0,\text{Cu}}$	$7.2 \times 10^{-6} \text{ m}^2/\text{s}$	this work
Copper diffusion coefficient at 300 °C, D_{Cu}	$5.27 \times 10^{-26} \text{ m}^2/\text{s}$	$D_{0,\text{Cu}} \exp(-E_{\text{m,Cu}}/kT)$
Vacancy formation energy, $E_{\text{f,v}}$	1.64 eV	^a
Non-configurational vacancy entropy, ΔS_v	$3 k$	^a
Thermal vacancy concentration at 300 °C, C_v^{eq}	7.62×10^{-14}	$\exp(\Delta S_v/k - E_{\text{f,v}}/kT)$
Copper demixing temperature, Ω	6255 K	[4]
Non-configurational copper entropy, ΔS_{Cu}	$0.866 k$	[4]
Recombination rate constant, k_{vi}	$9.31 \times 10^{11} / \text{s}$	[9]
Dislocation density, ρ	$0.9 \times 10^{14} / \text{m}^2$	[10]
Interstitial sink strength bias, z_i	1.2	[4]
Vacancy sink strength bias, z_v	1.0	[4]
Point defect production rate, G_A	$2.56 \times 10^{-8} / \text{s}$	[11,12,13]

^a For T around 300 °C essentially equivalent to $E_{\text{f,v}} = 1.6 \text{ eV}$ [4] and $\Delta S_v = 2.2 k$ [14].

3. Computations

The irradiation conditions of the investigated model alloys Fe-0.1%Cu and Fe-0.3%Cu are summarized in Table 1, the material parameters adopted for the RT simulation in Table 2. The bcc lattice constant a_{Fe} of Fe is chosen to 2.8665 Å, that of Cu to $a_{\text{Cu}} = 2.9607$ Å [6]. The parameters listed here are essentially the same as those used in our previous studies on Cu precipitation [7,8].

The thermodynamic data for the Cu precipitation is taken from Ref. [4]. However, the pre-exponential factor for Cu diffusion suggested therein (0.63×10^{-4} m²/s) had to be reduced by about one order of magnitude, in order to find the Ostwald ripening stage of the defect clusters to start at the experimentally observed cluster radii. The resulting value of 5.27×10^{-26} m²/s for the irradiation enhance copper diffusion coefficient D_{Cu}^* is reasonably close to the values obtained from the Arrhenius parameters used in other simulation studies, but still consistently larger than the extrapolations of the available experimental data down to 300 °C (see Table 3 for details). In particular, our Cu diffusion parameters are very close to ones obtained from MD (molecular dynamics) simulations on the vacancies assisted Cu diffusion in bcc iron based on the ACKLAND97 embedded atom potential for Fe-Cu [6].

The interface energy $\gamma_{\text{Cu-Fe}}$ of the defect clusters in the Cu-rich model alloy with 0.3wt% Cu are calculated using the entropy extended version of the Cahn-Hilliard expression suggested by Mathon *et al.* [2],

$$\gamma_{\text{Fe-Cu}}^{0.3\%} = \gamma_{\text{CH}} := 1.08k[\Omega - T(1 + \frac{1}{2k} \Delta S_{\text{Cu}})] / a_{\text{Cu}}^2, \quad (5)$$

where Ω and ΔS_{Cu} are the demixing temperature and the non-configurational substitution entropy of Cu in Fe which are also used to calculated the solubility limit

$$C_{\text{Cu}}^{\text{eq}} = \exp(\Delta S_{\text{Cu}}/k - \Omega/T) \quad (6)$$

of Cu in iron. With the parameters given in Table 2 this results in $\gamma_{\text{Fe-Cu}}^{0.3\%} = 0.39$ J/m² and $C_{\text{Cu}}^{\text{eq}} = 4.33 \times 10^{-5}$ at 300 °C. The interface energy of the Cu-poor model had to be fitted.

Table 3: Thermal diffusivity of Cu in α -Fe extrapolated to 300 °C (for the meaning of the symbols see Table 2).

Method	$E_{\text{m,Cu}}$ [eV]	$D_{0,\text{Cu}}$ [m ² /s]	$D_{\text{Cu}}^{300^\circ\text{C}}$ [m ² /s]	Reference
RT simulation	2.29	0.63×10^{-4}	46.0×10^{-26}	[4]
RT simulation	2.29	0.072×10^{-4}	5.27×10^{-26}	this work
RT simulation	2.53	7.08×10^{-4}	4.01×10^{-26}	[15]
MD simulation	2.31	0.052×10^{-4}	2.54×10^{-26}	[16]
Exp., α -Fe(ferro)	2.53	0.47×10^{-4}	0.26×10^{-26}	[17]
Exp., α -Fe(para)	2.94	300×10^{-4}	0.04×10^{-26}	[18] ^a

^a No Arrhenius-like behavior was observed for α -Fe(ferro) in that study.

4. Results

While distinct maxima showed up in the simulated cluster size distribution functions of the Cu-rich model alloy Fe-0.3%Cu at all four neutron fluences, with peak radii and volume fractions quite close to the experimental values, no copper precipitation could be observed with the Cahn-Hilliard interface energy γ_{CH} for the Cu-poor model alloy Fe-0.1%Cu model alloy. Instead, the concentration of the Cu clusters at the critical nucleation size of about 25 Cu atoms turned out to be seven orders of magnitude smaller than for Fe-0.3%Cu (with a critical nucleation size of about 10 atoms), in total agreement with classical nucleation theory, and the simulated system remained in the deterministic growth stage until cluster sizes far larger than the experimentally observed ones were reached. The only way to overcome this discrepancy within our vacancy-coupled Cu clustering model was to let the interface energy depend on the composition of the model alloy.

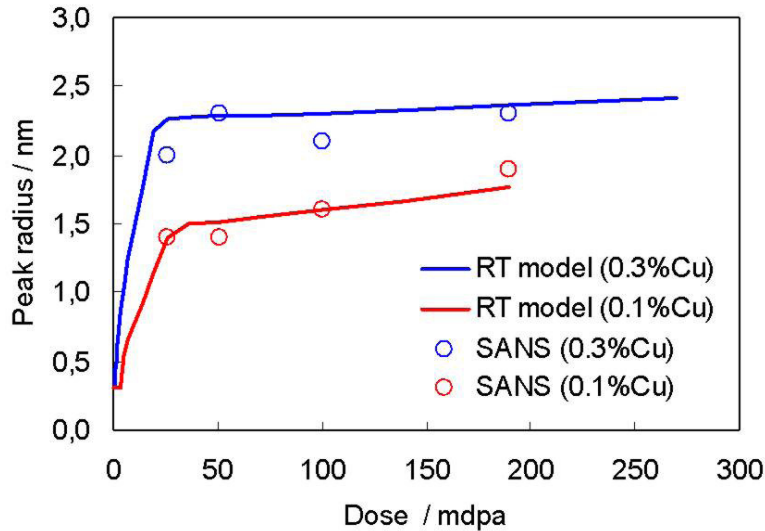


Fig. 1: Calculated peak radius of the Cu cluster distribution as a function of dose and comparison with experimental results obtained by SANS for both model alloys

By reducing the Fe-Cu interface energy for Fe-0.1%Cu to 73% of the Cahn-Hilliard value, i.e. to 0.29 J/m^2 at $300 \text{ }^\circ\text{C}$, it is possible to reproduce the experimentally observed peak radii and volume fractions at all four neutron fluences for the Fe-0.1%Cu system as well (see Figs. 1 and 2).

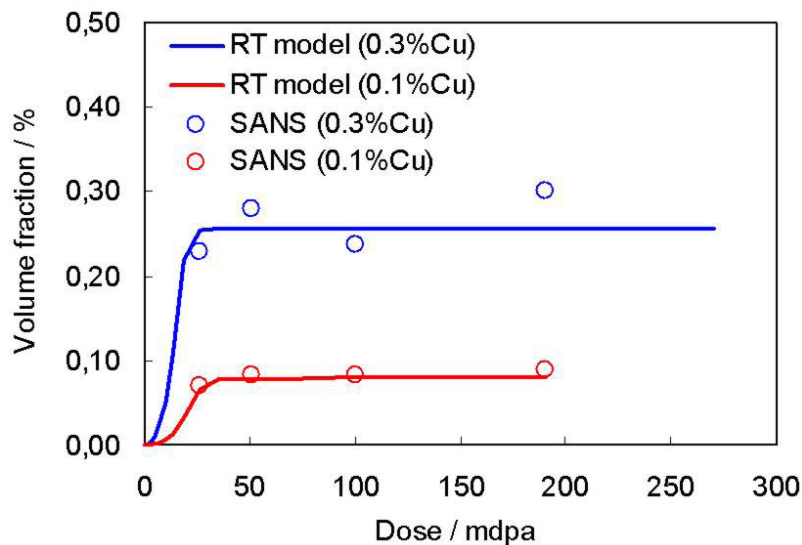


Fig. 2: Calculated volume fraction the Cu clusters as a function of dose and comparison with experimental results obtained by SANS for both model alloys.

atoms turned out to be seven orders of magnitude smaller than for Fe-0.3%Cu (with a critical nucleation size of about 10 atoms), in total agreement with classical nucleation theory, and the simulated system remained in the deterministic growth stage until cluster sizes far larger than the experimentally observed ones were reached. The only way to overcome this discrepancy within our vacancy-coupled Cu clustering model was to let the interface energy depend on the composition of the model alloy.

All other parameters are the same as for Fe-0.3%Cu. In particular, there is only one further adjusted parameter beside the interface energy reduction for Fe-0.1%Cu, the common pre-factor factor $D_{0,Cu}$ for the thermal Cu diffusivity in both alloys. A total of sixteen independent experimental data points could be reproduced this way (see Figs. 1 and 2) giving confidence that the chosen parameterization is reasonable. Based on the above observations we suggest, to model the temperature and

composition dependence of the Fe-Cu interface energy in a multiplicative way, by following Mathon *et al.* [2] for the temperature dependence but adopting a linear dependence on the weight percentage w of Cu in the material:

$$\gamma_{\text{Fe-Cu}}^{w\%}(T) = \gamma_{\text{CH}}(T) \times (1.35w + 0.595) \quad (7)$$

with γ_{CH} as defined in Eq. (5).

Taking into account that both model alloys were subject to the same irradiation-induced vacancy production rate it is likely that in average the defect clusters of the Cu-poor model alloy take up more vacancies than the defect clusters in the Cu-rich material. Thus, in view of the quite substantial oversize of copper compared to iron the suggested reduction of the repulsive interface energy with increasing amount of vacancies in the defect clusters seems reasonable.

5. Conclusions and Discussion

A vacancy-coupled rate theory model (RT) for Cu clustering (V3C) was established which explicitly takes into account the absorption of vacancies by Cu-rich precipitate clusters. Only two parameters, the Cu thermal diffusivity in iron and the reduction of the coherent interface energy in Fe-0.1%Cu compared to Fe-0.3%Cu were used in order to adjust the new RT model. Since the obtained value for the thermal Cu diffusion coefficient is the same for both materials and lies well in the range of reported diffusivities, effectively only one parameter was required, to reasonably reproduce the entire set of experimental data obtained by means of SANS for two neutron-irradiated Fe-Cu model alloys at four different doses. An analytical expression for the interface energy as a function of temperature and Cu content of the iron matrix is given. The suggested reduction of the interface energy between iron and mixed defect clusters of increasing vacancy content can easily be rationalized by the oversize of bcc copper compared to bcc Fe and is also corroborated by a more sound thermodynamic analysis of the underlying copper exchange processes.

References

- [1] K. Verheyen, M. Jardin, A. Almazouzi, Coincidence Doppler broadening spectroscopy in Fe, Fe-C and Fe-Cu after neutron irradiation, *Journal of Nuclear Materials* 351 (2006) 209-215.
- [2] M. H. Mathon, A. Barbu, F. Dunstetter, N. Lorenzelli, and C. H. de Novion (1997), Experimental study and modeling of copper precipitation under electron irradiation in dilute Fe-Cu binary alloys, *Journal of Nuclear Materials* 245, 224-237.
- [3] J. Schmelzer Jr., U. Lembke, and R. Kranold (2000), Nucleation and growth of AgCl clusters in a sodium borates glass: Numerical analysis and SAXS results, *Journal of Chemical Physics* 113, 1268-1275.
- [4] F. Christien and A. Barbu (2004), Modelling of copper precipitation in iron during thermal aging and irradiation, *Journal of Nuclear Materials* 324, 90-96.
- [5] A. Gokhman, J. Boehmert, and A. Ulbricht (2003), Kinetic study of copper precipitates under VVER-type reactor conditions, *Radiation Effects & Defects in Solids* 158, 783-792.
- [6] G. J. Ackland, D. J. Bacon, A. F. Calder, and T. Harry (1997), Computer simulation of point defect properties in dilute Fe-Cu alloy using a many-body interatomic potential, *Philosophical Magazine A* 75, 713-732.

- [7] A. Gokhman and J. Boehmert (2003), A kinetic study of vacancy cluster evolution under VVER-type reactor conditions, *Radiation Effects & Defects in Solids* 158, 499-511.
- [8] A. Gokhman, F. Bergner, A. Ulbricht, and U. Birkenheuer (2008), Cluster dynamics simulation of reactor pressure vessel steels under irradiation, *Defect and Diffusion Forum* 277, 75-80.
- [9] G. R Odette (1998), in: M. Davies (Ed.), *Neutron Irradiation Effect in Reactor Pressure Vessel Steels and Weldments*, Vienna, p.438-504.
- [10] A. Almazouzi, M. Jardin, M. Lambrecht, L. Malerba, M. Hernández-Mayoral, D. Gómez-Briceño, Ph. Pareige, E. Muslin, and B. Radiguet (2005), Characterization of neutron irradiated samples (REVE matrix), deliverable P26, work-package II-3, integrated project PERFECT, 6th European Framework program EURATOM.
- [11] C. H. M. Broeders and A. Yu. Konobeyev (2004), *Journal of Nuclear Materials* 328, 197-214.
- [12] R. E. Stoller (2000), The role of cascade energy and temperature in primary defect formation in iron, *Journal of Nuclear Materials* 276, 22-32.
- [13] A. F. Calder and D. J. Bacon (1993), A molecular dynamics study of displacement cascades in α -iron, *Journal of Nuclear Materials* 207, 25-45.
- [14] J. J. Burton (1972), Vacancy-formation entropy in cubic metals, *Physical Review B* 5, 2948-2957.
- [15] S. I. Golubov, A. Serra, Yu. N. Osetsky, and A. V. Barashev (2000), On the validity of the cluster model to describe the evolution of Cu precipitates in Fe-Cu alloys, *Journal of Nuclear Materials* 277, 113-115.
- [16] J. Marian, B. D. Wirth, G. R. Odette, and J. M. Perlado (2004), Cu diffusion in α -Fe: determination of solute diffusivities using atomic-scale simulations, *Computational Materials Science* 31, 347-367.
- [17] M. S. Anand and R. P. Agarwala (1966), Diffusion of Copper in Iron, *Journal of Applied Physics* 37, 4248-4251.
- [18] G. Salje and M. Feller-Kniepmeier (1977), The diffusion and solubility of copper in iron, *Journal of Applied Physics* 48, 1833-1839.

Acknowledgements

This work was partly supported within the European Integrated Project PERFECT under Contract No. F6O-CT-2003-508840 and by the Bundesministerium für Wirtschaft under Contract No. 150 1315.