On the formation of mixed vacancy-copper clusters in neutron-irradiated Fe-Cu alloys

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Abstract. Setting out from the results found in a set of small-angle neutron scattering (SANS) experiments for neutron-irradiated Fe-Cu model alloys, a rate theory model for the simulation of the irradiation-induced time-evolution of Cu-rich precipitates in these model alloys is presented which follows the idea that the precipitate clusters are mixed Cu-vacancy aggregates. This is done by explicitly allowing the defect clusters to absorb vacancies. The resulting Vacancy-Coupled Copper Clustering (V3C) model is calibrated by SANS experiments on two different Fe-Cu model alloys neutron-irradiated at four different doses. Quantitative agreement with the SANS experiments could be achieved by introducing a dependence of the Fe-Cu interface energy on the amount of vacancies in the mixed precipitate clusters. Phenomenologically, this energy can be seen as a function of the weight-percentage of Cu in the iron matrix. An empirical expression for this dependence is suggested. In addition, the new V3C model is used to gain some preliminary insight into the time-evolution of the chemical composition of the mixed Cu-vacancy clusters, confirming qualitatively the experimental findings. The relation of our ansatz to the heterogeneous Cu-precipitation mechanism proposed by others for neutron-irradiated Fe-Cu alloys of low Cu content is discussed.

1. Introduction

Rate theory (RT) modeling plays an important role in the field of neutron-irradiation induced damage of reactor pressure vessel (RPV) steels. In fact, regardless of the inherent limitations RT is one of the few methods which allows – in a multi-scale modeling framework – to close the gap between the processes happening on the atomic level and the properties accessible to experiments such as transmission electron microscopy (TEM) or small-angle neutron scattering (SANS). In particular RT is capable of modeling defect evolutions for periods of up to 40 years and more of reactor operation time. There is a continuing interest in the application of RT models to the Fe-Cu system under neutron irradiation [1-5]. To calibrate such models experimental data on both, reactor pressure vessel steels as well as especially designed Fe-based model alloys, are vital. As part of the experimental program related to the international REVE (reactor for virtual experiments) project a set of well-defined model alloys was fabricated and neutron-irradiated under several irradiation conditions [6]. Within the integrated project PERFECT (prediction of irradiation damage effects on reactor components) of the 6th European Framework program (FP6) these samples were investigated by a series of complementary experimental techniques, including TEM, SANS, PAS (positron annihilation spectroscopy) and TAP (tomographic atom probe). The details of the SANS experiments will be reported in a companion paper [7]. 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 with compositions quite close to real reactor pressure vessel (RPV) steels. In this investigation, we will focus on the two binary Fe-Cu model alloys Fe-0.3\%Cu and Fe-0.1\%Cu.

The aim of the present paper is to suggest modifications to the standard RT models for Cu-rich RPV steels which allow to reproduce the whole 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 each of the four irradiation conditions applied (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 sufficient to explain the observations. And in fact, as already reported by Radiguet et al. [8] it is impossible to parameterize a rate theory model for pure Cu precipitates which would be able to describe the experimental results even qualitatively. A heterogeneous nucleation process is thus suggested in Ref [8] with the Cu-containing precipitate clusters being formed in a second stage on top of the nanovoids primarily produced by the applied ion irradiation. The same result, namely the formation of mixed Cu-vacancy agglomerates, can also be obtained by successive vacancy absorption. Therefore, we investigated whether explicitly taking into account the absorption of iron vacancies by the copper-rich precipitates allows to set up a RT model which is able to reproduce the size distributions observed in the SANS experiments.

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

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

2. The rate theory model

Standard rate theory models for the formation of copper-rich precipitates in irradiated reactor pressure vessel steels as described, for example, in Refs. [1-2,4,9-10] consist of the following three essentials: 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. Additionally, the conservation of the total number of Cu atoms is exploited. This model is denoted as CD-P model in Ref. [2]. A more realistic picture of the irradiation induced processes is obtained by taking into account the formation of voids and SIA loops as is done (for example) in the CD-P-VIC model described in Ref. [2]. Yet, the basic problems remain, since the Cu-containing precipitates are still described as if they were pure Cu clusters. Thus we will focus on the less complex CD-P model here. The balance equations in this model read

\[
\frac{dC_A}{dt} = G_A - k_i c_v c_i - k_A C_A , \quad A = v, i ,
\]

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, \( k_i c_v c_i \) 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 external sinks such as grain boundaries or dislocations in the iron matrix where the decay rates \( k_A \) are proportional to the dislocation density \( \rho \). The classical master equations for these clusters are of the general form (e.g. Refs. [1,4,9,11])

\[
\frac{dC_n}{dt} = J_{n-\frac{1}{2}} - J_{n+\frac{1}{2}} \quad \text{with} \quad J_{n+\frac{1}{2}} = k_n \cdot (C_{Cu} C_n - K_{n+1}(T) C_{n+1})
\]

where \( C_n \) is the concentration of the \( n \)-atomic defect clusters, measured in cluster per lattice site. Here, clusters containing two or more Cu atoms are assumed to be immobile. The velocity \( J_{n+\frac{1}{2}} \) for the
growth reaction $\text{Cu}_n + \text{Cu} \leftrightarrow \text{Cu}_{n+1}$ consists of an absorption part $k_n \text{Cu}_n \text{C}_n$ and an emission part $\alpha_{n+1} \text{C}_{n+1} = k_{n+1} K_{n+1}(T) \text{C}_{n+1}$ which is set up by the detailed balance principle. The equilibrium constants $K_n(T)$ do neither depend on the mobility of the solute monomers, nor on the concentrations of the involved species. They are solely determined by the thermodynamic of the cluster growth reactions at the given temperature $T$. In particular, none of the details of the more sophisticated CD-P-VIC model has any impact on these constants.

Besides the concentration $C_{\text{Cu}} = C_1$ 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 $\frac{d}{dt} C_n$ depends on a couple of material parameters $p_1, p_2, \ldots$, the most important ones being the coherent specific Fe-Cu interface energy $\gamma_{\text{Fe-Cu}}$ entering the equilibrium constants $K_n(T)$ and the irradiation enhanced Cu diffusion coefficient $D_{\text{Cu}}^*$ entering the reaction rate coefficients $k_n$. Assuming a vacancy assisted diffusion mechanism for the Cu atoms the irradiation enhancement of the Cu diffusivity can be modeled by

$$D_{\text{Cu}}^* = D_{\text{Cu}} \frac{C_v(t)}{C_{v}^{\text{eq}}} ,$$

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

Within the above framework the system of point defects and the copper subsystem are often treated independently [2,4,10] by replacing $C_v(t)$ with the steady-flux solutions $C_v^{\text{eq}}$ of the balance equations (1). 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 mentioned above, there are indications for the copper precipitates in Fe-Cu model alloys of moderate Cu content actually being mixed defect clusters which contain copper and vacancies together. These indications come from both, theoretical studies [13-15] and experimental data, e.g. based on the ratio of magnetic and nuclear contributions to SANS (the so-called A-ratio) [9,16]. Recent results of atom probe experiments on Cu containing Fe-based model alloys [17] support this view. They also found the precipitates not being pure Cu clusters.

The structural optimizations (based on empirical inter-atomic potentials) reported in Refs. [14] and [15] show that the uptake of solute Cu atoms and/or vacancies by mixed Cu-vacancy clusters is always energetically favored (positive binding energies throughout), as is the formation of such clusters from pure voids and pure Cu clusters. We repeated this kind of structural optimizations with the more recent inter-atomic Fe-Cu potential developed by Pasianot et al. [18] and found the same overall behavior of the energy potential surface of the Cu$_n$V$_m$ clusters as in the investigations before [14-15].

To allow for such mixed Cu-vacancy clusters, 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 equation (1) is replaced by

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

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 an $n$-atomic defect cluster, and $V_{\text{Fe}}$ 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 (and describes diffusion limited vacancy absorption by spherical
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. Instead, the balance equations and the master equations have to be solved simultaneously. In a point defect system, the balance equations cannot be solved independently of the copper subsystem (defect clusters). Because the latter term imposes the time modulation of the copper subsystem onto the forward coupling which is mediated via the vacancy dependence of the diffusion coefficient $D^c_{Cu}$ 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 $S_j = k_i C_i$ to the sink term is considered, because the (oversized) Cu clusters are assumed not to be able to absorb SIAs in any 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 migration energy, $E_{m,i}$ | 0.4 eV | [19] |
| Interstitial pre-exponential factor, $D_{0,i}$ | $0.05 \times 10^4$ m²/s | [19] |
| Interstitial diffusion coefficient at 300 °C, $D_i$ | $1.52 \times 10^{-9}$ m²/s | [19] |
| Vacancy migration energy, $E_{m,v}$ | 1.3 eV | [19] |
| Vacancy pre-exponential factor, $D_{0,v}$ | $0.5 \times 10^{-4}$ m²/s | [19] |
| Vacancy diffusion coefficient at 300 °C, $D_v$ | $1.85 \times 10^{-16}$ m²/s | this work |
| Copper migration energy, $E_{m,Cu}$ | 2.29 eV | [2] |
| Copper pre-exponential factor, $D_{0,Cu}$ | $7.2 \times 10^{-6}$ m²/s | [2] |
| Copper diffusion coefficient at 300 °C, $D_{Cu}$ | $5.27 \times 10^{-26}$ m²/s | this work |
| Vacancy formation energy, $E_{i,v}$ | 1.64 eV | [2] |
| Non-configurational vacancy entropy, $\Delta S_v$ | 3 $k$ | a |
| Thermal vacancy concentration at 300 °C, $C_v^eq$ | $7.62 \times 10^{-14}$ | | |
| Copper demixing temperature, $\Omega$ | 6255 K | [2] |
| Non-configurational copper entropy, $\Delta S_{Cu}$ | 0.866 $k$ | [2] |
| Solubility limit of Copper at 300 °C, $C_{Cu}^{eq}$ | $4.33 \times 10^{-5}$ | [2] |
| Vacancy-interstitial recombination radius, $r_{rec}$ | 5.74 Å | [19] |
| Recombination rate constant at 300 °C, $k_{i,i}$ | $9.31 \times 10^{11}$ / s | [7] |
| Dislocation density, $\rho$ | $0.9 \times 10^{14}$ / m² | |
| Interstitial sink strength bias, $z_i$ | 1.2 | [2] |
| Interstitial decay rate at dislocations at 300 °C, $k_i$ | $1.64 \times 10^{5}$ / s | $k_i = z_i D_i \rho$ |
| Vacancy sink strength bias, $z_v$ | 1.0 | [2] |
| Vacancy decay rate at dislocations at 300 °C, $k_v$ | $1.67 \times 10^{2}$ / s | $k_v = z_v D_v \rho$ |
| Cascade efficiency factor, $\eta$ | 0.366 | [20] |
| Fraction of cascade point defect clusters, $f_{cl,A}$ | 0.5 | [21, 22] |
| Point defect production rate, $G_A$ | $2.56 \times 10^8$ / s | |

* For temperatures of 270-300 °C the listed parameters are essentially equivalent to the parameter pair $E_{i,v} = 1.6$ eV [2] and $\Delta S_v = 2.2 k$ [23].

Although the absorption of vacancies by Cu-rich precipitates is fully taken into account, the suggested V3C model contains some idealizations. The precipitate clusters are assumed to be perfect absorbers whose properties do not change when taking up vacancies. In particular, the Cu clusters do not grow upon vacancies absorption nor do they reemit any vacancies in our model. Both effects could have some impact on the cluster formation, but to include them in a rate theory model requires to describe the time-evolution of the chemical composition of each defect cluster. Work is in progress to setup such an extended rate theory. The aim of the present study is to demonstrate that already with the above idealizations the V3C model is able to reproduce the experimental observations reasonably.
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 for the RT simulation in table 2. The bcc lattice constant $a_{Fe}$ of Fe is chosen to 2.8665 Å, that of bcc Cu to $a_{Cu} = 2.9607$ Å [24]. The parameters listed here are essentially the same as those used in our previous studies on Cu precipitation in model alloys of about 0.4% Cu [10,25]. The thermodynamic data for the Cu precipitation is taken from Ref. [2]. However, the pre-exponential factor for Cu diffusion suggested therein ($0.63 \times 10^{14}$ m$^2$/s) had to be reduced by about one order of magnitude, in order to set the time-scale properly such that the Ostwald ripening stages of the defect clusters start at the experimentally observed doses (see below). The resulting value of $5.27 \times 10^{-26}$ m$^2$/s for the thermal copper diffusion coefficient $D_{Cu}$ at 300 °C is reasonably close to the values obtained from the Arrhenius parameters used in other simulation studies, but still noticeably larger than the extrapolations of the available experimental data down to 300 °C (see table 3 for details). In particular, our Cu diffusion parameter is very close to the one obtained from MD (molecular dynamics) simulations on vacancy assisted Cu diffusion in bcc iron based on the ACKLAND97 embedded atom potential for Fe-Cu [24].

The interface energy $\gamma_{Fe-Cu}$ of the defect clusters in the Cu-rich model alloy with 0.3wt% Cu are calculated using the entropy extension of the Cahn-Hilliard expression suggested by Mathon et al. [9],

$$\gamma_{Fe-Cu} = \gamma_{Cu} = 1.08k\left[\frac{1}{2}\Omega - T\left(1 + \frac{1}{3k}\Delta S_{Cu}\right)\right]/a_{Cu}^{2},$$

where $\Omega$ and $\Delta S_{Cu}$ are the demixing temperature and the non-configurational substitution entropy of Cu in Fe which are also used to calculated the solubility limit $C_{Cu}^{eq}$ of Cu (see table 2). With the parameters given in table 2 this results in $\gamma_{Fe-Cu}^{0.3\%} = 0.39$ J/m$^2$ at 300 °C. The interface energy of the Cu-poor model alloy had to be fitted (see next section).

4. Results and Discussion

The experimental data used to find a suitable parameter set for the rate theory model are shown in figures 1 and 2. While the simulated cluster size distribution functions of the Cu-rich model alloy Fe-0.3%Cu exhibit distinct maxima 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 for the Cu-poor model alloy Fe-0.1%Cu. 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. Precisely the same observations were made by Radiguet et al. [8] who report Cu cluster densities in the order of $10^{16}/m^3$.

### Table 3. Thermal diffusivity of Cu in $\alpha$-Fe extrapolated to 300 °C

(for the meaning of the symbols see table 2)

| Method       | $E_{in,Cu}$ [eV] | $D_{0,Cu}$ [m$^2$/s] | $D_{Cu}^{300°C}$ [m$^2$/s] | Reference |
|--------------|-----------------|----------------------|---------------------------|-----------|
| RT simulation| 2.29            | $0.63 \times 10^{-4}$ | $46.0 \times 10^{-26}$   | [2]       |
| RT simulation| 2.29            | $0.072 \times 10^{-4}$| $5.27 \times 10^{-26}$   | This work |
| RT simulation| 2.53            | $7.08 \times 10^{-4}$ | $4.01 \times 10^{-26}$   | [26]      |
| MD simulation| 2.31            | $0.052 \times 10^{-4}$| $2.54 \times 10^{-26}$   | [27]      |
| Exp., $\alpha$-Fe| 2.36        | $3.9 \times 10^{-4}$   | $1.20 \times 10^{-26}$   | [28]      |
| Exp., $\alpha$-Fe(ferro)| 2.53       | $0.47 \times 10^{-4}$   | $0.26 \times 10^{-26}$   | [29]      |
| Exp., $\alpha$-Fe(para)| 2.94        | $300 \times 10^{-4}$   | $0.04 \times 10^{-26}$   | [30]      |

* No Arrhenius-like behavior was observed for $\alpha$-Fe(ferro) in that study.

* The experimental data points reported in Ref. [31] are very close to the Arrhenius fits for $\gamma_{Cu}$ Fe and $\alpha$-Fe(ferro) given by Salje et al. [30].
when applying the CD-P-VIC rate theory model to irradiated Fe-0.1%Cu model alloys. They suggest a heterogeneous nucleation mechanism (see next section for a more detailed discussion on that issue).

Because the equilibrium constants \( K_n(T) \) determine the critical cluster size and the concentration of the critical clusters for a given Cu content, there is little choice in adopting a RT model based on the master equations (2), as does our V3C model and also the CD-P-VIC model used by Radiguet et al. The thermodynamics of the cluster formation must be different. One way to solve the problem is to let the interface energy depend on the composition of the defect clusters which in turn depends on the amount of Cu in the model alloy. Alternatively, one could also modify the solubility limit Cu in the Fe matrix, as a function of the defect cluster composition. Yet, since the equilibrium constants are much more sensitive to the interface energy than to the solubility limit, we decided for the interface energy.

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 °C, we were able 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 figures. 1 and 2). 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 \( D_{\text{Cu}} \) for the thermal Cu diffusivity in both alloys. A total of sixteen independent experimental data points could be reproduced this way (see figures. 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. [9] for the temperature dependence but adopting a simple linear dependence on the weight percentage \( w \) of Cu in the material:

\[
\gamma_{\text{Fe-Cu}}(T) = \gamma_{\text{CH}}(T) \times (1.35w + 0.595) \text{ for } 0.1 \leq w \leq 0.3
\]

with \( \gamma_{\text{CH}} \) as defined in equation (5).

Taking into account that both model alloys were subject to the same irradiation-induced vacancy production rate it is likely that on average the defect clusters of the Cu-poor model alloy take up more vacancies than the defect clusters in the Cu-rich material (simply because the term \( D_{\text{Cu}}^{\text{V}}C_{\text{Cu}} \) is about three times lower in Fe-0.1%Cu than in Fe-0.3%Cu while \( D_{\text{C}}^{\text{C}} \) is roughly the same in both samples). 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. On the other hand, at 300 °C, interface energies in the order of 0.4 J/m\(^2\) are reported for bare Cu clusters [2,9] while for bare voids (vacancy clusters) the interface energies lay in the range of 1-2 J/m\(^2\) [19]. The Cahn-Hilliard expression from equation (5), for example, applied to an iron-void
interface (using $E_{\text{v}} = 1.64 \text{ eV}$ and $\Delta S_\text{v} = 3 \text{ k}$ from table 2) yields a value of $1.47 \text{ J/m}^2$. Thus, a first guess for the interface energy of a mixed cluster would be some value in between these two limiting cases, but a thorough analysis of the underlying thermodynamics actually reveals that in the present case, the really relevant quantity, the effective interface energy for Cu exchange between mixed defect clusters and the iron matrix which is defined via the Gibbs-Thomson relation

$$\frac{d}{dn} \left[ \gamma_{\text{Fe-Cu}}(x) A(Cu_n V_m) \right] = \frac{2 \mu_{\text{Cu}}(x)V_{\text{Fe}}}{R(Cu_n V_m)}$$

with $x = \frac{n}{n + m}$ (7)

where $A(Cu_n V_m)$ is the surface area of a (spherical) mixed Cu$_n$V$_m$ cluster, $R(Cu_n V_m)$ its radius and $x$ the chemical composition of the cluster (measured as the fraction of Cu atoms here). It is sort of a chemical potential, rather than an energy, and can exhibit a quite different $x$-dependence than the interface energy $\gamma_{\text{Fe-Cu}}(x)$ itself. In particular, $\mu_{\text{Fe-Cu}}^\text{Cu}(x > 0)$ can be lower than the value $\mu_{\text{Fe-Cu}}^\text{Cu}(x = 0)$ for bare Cu clusters even if $\gamma_{\text{Fe-Cu}}(x)$ behaves the opposite.

4.1. **On the composition of the defect clusters**

The V3C model enables us to monitor the total amount of vacancies and Cu atoms taken up by all defect clusters. Based on this information a rough estimate on the average chemical composition of the precipitates can be given, as done in figure. 3 where the average atom (or mole) fraction $x_{\text{Cu}}$ of Cu in the defect clusters is shown as a function of the neutron damage. It is computed as the ratio between the total vacancy and solute Cu atom losses

$$L_{\text{v}}^\text{Cu}(t) = \int_0^t \Delta k_i(t') C_i(t') \, dt' \quad \text{and} \quad L_{\text{v}}^\text{Cu}(t) = \sum_{n > 2} n C_{n}(t) = C_{\text{Cu}}(0) - C_{\text{Cu}}(t)$$

respectively. Interestingly, a clear maximum in the Cu fraction is found for both model alloys, Fe-0.1%Cu and Fe-0.3%Cu, at about 20-30 mdpa, in nice qualitative agreement with the compositions extracted from the measured A-ratios of the SANS data using the relation [16]

$$A_{\text{SANS}} = \left( \frac{6}{9.5 - 7.7 x_{\text{Cu}}} \right)^2 + 1$$

(9)

(see figure. 3). Growing initially essentially as voids, the defect clusters smoothly transform into Cu clusters with increasing neutron dose until the copper in the iron matrix is subsumed and the Ostwald ripening stage starts where only vacancies can still be taken up in total by the precipitates.

![Figure 3](image-url)

**Figure 3** Calculated average atom fraction $x_{\text{Cu}}$ of Cu in the mixed Cu-vacancy clusters as a function of dose and comparison with experimental results derived from the A-ratio of SANS data for both model alloys. Here, $x_{\text{Cu}} = 0$ means pure voids and $x_{\text{Cu}} = 1$ pure Cu clusters.

It is worth mentioning that the cluster compositions shown in figure. 3 are *predictions* of our V3C model, since the A-ratios were not used for the RT calibration. Understanding why quantitative
agreement could not be achieved is subject of further investigations. It might be related to the ability of the mixed Cu-vacancy clusters to also emit vacancies in a substantial amount. However, it is known that such mixed clusters tend to be copper coated voids [14-15], which might partly suppress vacancy emission.

As already mentioned, Radiguet et al. [8] suggest a “heterogeneous” nucleation process for Fe-0.1%Cu where Cu-containing precipitate clusters only form on top of already existing nano-voids. In principle, this type of heterogeneous nucleation is included in a rate theory model which allows for the formation of mixed Cu-vacancy clusters. And indeed, we find preferentially void formation at the beginning and increasing Cu absorption later on, which is in line with the heterogeneous processes put forward in Ref. [8]. Yet, since our V3C model was initially designed for small admixtures of vacancies to Cu-rich precipitates we assumed the defect clusters to be perfect vacancy absorbers while keeping the properties of pure Cu clusters. Therefore, the formation of pure voids is not possible in the V3C model. Clearly this limitation has to be removed in future applications.

Also it should be mentioned that when using the mixed Cu-vacancy formation energies from our structural optimization in a rate theory model for small two component clusters, there is no indication for Cu-precipitation (pure or mixed) to start only after some nanovoids have already been formed. More detailed rate theory models are required to clarify that issue.

5. Summary

Based on the experience that rate theory models for Cu-precipitation which treat the precipitate clusters as pure Cu clusters are not able to reproduce the experimentally observed behavior of Fe-Cu model alloys under neutron-(or ion) irradiation for Cu contents well below 0.3%, a rate theory model is set up which allows to take explicitly into account the absorption of iron vacancies by Cu-rich precipitate clusters. This way, mixed Cu-vacancy agglomerates can be formed as indicated by SANS and TAP measurements. The idea of switching to multi-component precipitates is not unique. It is also followed in the heterogeneous nucleation mechanism suggested by Radiguet et al. [8] for Fe-based model alloys of low Cu content.

In our Vacancy-Coupled Copper Clustering (V3C) model 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 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 on the cluster distribution obtained by means of SANS measurements on two neutron-irradiated Fe-Cu model alloys at four different doses.

An analytical expression for the interface energy of Cu-rich precipitates in Fe as a function of temperature and the Cu content of the iron matrix is given. It shows a reduction of the interface energy with increasing amount of vacancy in the defect cluster, a somewhat surprising result, at first glance, since voids exhibit significantly larger interface energies than bare Cu clusters, but which can be rationalized by a more sound thermodynamic analysis of the underlying copper exchange processes.

Some rough, but promising estimates on the evolution of the overall chemical composition of the defect clusters could be given as well, corroborating qualitatively the changes in compositions with increasing neutron damage found in recent SANS experiments. The main trend: high vacancy contents first, increasing Cu absorption later is in line with the heterogeneous nucleation process suggested for the Fe-0.1%Cu model alloy by Radiguet et al. [8].

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