# **Light Water Reactor Sustainability Program**

# Incorporation of copper-rich precipitation model into developed Ni-Mn-Si precipitate development models September 30, 2016 Milestone



September 30, 2016

U.S. Department of Energy Office of Nuclear Energy

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# Incorporation of copper-rich precipitation model into developed Ni-Mn-Si precipitate development models September 30, 2016 Milestone

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### SUMMARY

This report has been assembled to address a milestone to "Complete report on high fluence predictions of phase stability documenting current model predictions for hardening of reactor pressure vessel steels as a function of flux, fluence and composition" due September 30, 2016. The milestone includes a complete report detailing the both atomistic and continuum modeling of radiation-induced copper-rich precipitates and its coupling to Mn-Ni-Si precipitate formation kinetics against experimental irradiation and thermal annealing data.

This work was done in close collaboration with Professor G. R. Odette and his group at the University of California, Santa Barbara. The regular and strong interactions between all the participants in this collaboration has been critical to the development of this work and the content here represents intellectual contributions from the entire team.

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SU	MMAR	Y		iii
AC	KNOW	LEDGE	MENTS	iv
AC	RONY	MS AND	NOMENCLATURE	X
1.	INTRO	ODUCTI	ON	12
2.	EXEC	UTIVE	SUMMARY OF MAJOR RESULTS	13
3.	METH	IODS		14
	3.1	Kinetic	Monte Carlo Simulations	14
		3.1.1	The Kinetic Monte Carlo model	14
		3.1.2	Kinetic Monte Carlo Model Parameterization	15
	3.2	Cluster	Dynamics Simulations	16
		3.2.1	Simulation Models	16
		3.2.2	Parameters for the MNSP Cluster Dynamics model	20
		3.2.3	Coupling Cu to Mn-Ni-Si precipitation	22
4.	RESU	LTS		25
	4.1	Kinetic	Monte Carlo Simulation of Co-precipitation of Cu-MnNiSi Precipitates	25
		4.1.1	Morphological characteristics of Cu-MnNiSi precipitates	25
		4.1.2	KMC simulation of the nucleation and growth of the Cu-MnNiSi precipitates	26
	4.2	Cluster	Dynamics	29
		4.2.1	Update on Mn-Ni-Si precipitates under irradiation	29
		4.2.2	Update on Mn-Ni-Si precipitates under annealing	39
		4.2.3	Precipitation in Cu bearing alloys	42
5.	SUMN	MARY O	F MAJOR RESULTS	54
	5.1	Kinetic	Monte Carlo (KMC)	54
	5.2	Cluster	Dynamics	54
		5.2.1	Cu-free alloys	54
		5.2.2	Cu bearing alloys	55
6.	FUTU	RE WOI	RK	56
7.	REFE	RENCES	5	
		~	· · · · · · · · · · · · · · · · · · ·	/

# CONTENTS

# FIGURES

Figure 1. A flowchart of precipitate formation in RPVs in the presence of Cu.	. 24
<ul><li>Figure 2 (a) Atom maps for LD alloy irradiated in BR2 (the composition ) (b) Atom maps for LD alloy irradiated in ATR1 (c) APT map of a typical precipitate in the bulk, BR2 condition (d) APT map of a typical precipitate in the bulk, ATR1 condition, isoconcentration surface is added to guide the eye</li></ul>	25
Figure 3 (a) a snapshot of the KMC simulation, showing the microstructure of the simulated alloy (b) a magnified Cu-MnNiSi precipitate, with iso-concentration surfaces to clearer show the structure of the precipitate (c) a 1-D composition line scan of the precipitate.	27
Figure 4 Temporal evolution of the Cu-MnNiSi precipitate reproduced by KMC simulations: (a) Formation of a Cu precipitate coated by a layer of MnNiSi, (b) and (c) nucleation of MnNiSi ordered phase on the Cu precipitate, and (d) and (e) further growth of the MnNiSi ordered phase. Note that the Cu precipitate is always on the edge of the whole precipitate.	28
<ul><li>Figure 5 (a) movement of the center of mass (COM) of the whole precipitate compared to that of the Cu precipitate (b) distance between COMs as the precipitate grows.</li><li>The radius of the whole precipitate is also plotted to show that the distance between COMS is directly correlated to size of the Cu-MnNiSi precipitate</li></ul>	29
Figure 6. Comparison of number density, mean radius and volume fraction between simulation results calculated from local atom probe compositions and available experimental data.	34
Figure 7. Evolution of precipitates as a function of fluence for CM6 and LG at different conditions. Lines represent simulated data for single APT tip compositions. For cases with multiple APT tips and associated compositions, rather than plot multiple lines, a band showing the range of obtained values is given	35
Figure 8. Comparison between calculation results and experimental data for Ringhals and Ginna reactors.	36

Figure 9. Ratio of number density of precipitates created by heterogeneous and homogeneous nucleation mechanisms.	. 37
Figure 10. Effect of compositions on a) volume fraction and b) ductile-brittle-transition- temperature for low (0.7Mn0.85Ni0.25Si), medium (1.0Mn1.15Ni0.35Si), and high (1.3Mn1.75Ni0.65Si) solute (all values at. %) alloys. The low solute lines are difficult to observe as they are nearly zero.	. 39
Figure 11 Comparison between simulation results and annealing experimental data under 400°C and 425°C	. 41
Figure 12 Comparison of between simulation results and experimental data under annealed at different temperatures. a) CM6; b) LG.	. 41
Figure 13. Cu diffusion coefficient in the literature [32, 66-73] and the fitted value in this work.	. 44
Figure 14. Comparison between CD model and experimental results for evolution of precipitates in LC, LD, LH, and LI alloys as a function of fluence	. 47
Figure 15. Comparison between CD and experimental results for precipitates number density, radius, and volume fraction.	. 48
Figure 16. Comparison between CD model and experimental data [75] of Cu precipitation under aging at 500 °C. We note that the CD model parameters used here (Table 10) were obtained from fitting to irradiation data and not the data in this figure.	. 49
Figure 17. Comparison between CD model and experimental data [76-78] of Cu precipitation in pure Fe-1.34at.%Cu under aging at 500 °C. The CD parameters used here (Table 10) were obtained from fitting to irradiation data. Poor agreement between modeling and experimental data compared with good agreement in Figure 16 suggests the dramatic effects of other impurities (e.g.	
Mn, Ni, and Si) on the precipitation of Cu.	. 50

Figure 18. The minimum Cu (at.%) for formation CRP in RPV steels based on	
parameters in Table 10 (flux=1x10 <sup>16</sup> n/m <sup>2</sup> .s , T= 290 °C, 0.9Mn0.9Ni0.25Si	
(at.%))	. 51
Figure 19. The effect of Cu on precipitates volume fraction and ductile-to-brittle	
transition temperature under LWR conditions $(3x10^{14} \text{ n/m}^2\text{.s and } 290 ^\circ\text{C})$ .	52
Figure 20. Precipitates volume fraction and ductile-to-brittle transition temperature as a	
function of time for low (0.7Mn0.85Ni0.25Si0.1Cu), medium	
(1.0Mn1.15Ni0.35Si0.2Cu), and high (1.3Mn1.75Ni0.65Si0.3Cu) solute alloys	
(all values at. %) under LWR conditions $(3x10^{14} \text{ n/m}^2\text{.s and } 290 ^\circ\text{C})$ .	. 53
Figure 21. The effect of solute content on precipitate volume fraction and ductile to	
brittle transition temperature evolution in alloys with and without Cu under	
LWR conditions (3x10 <sup>14</sup> n/m <sup>2</sup> /s and 290 °C). Alloys compositions: low solute	
0.7Mn0.85Ni0.25Si(0.1Cu), medium solute 1.0Mn1.15Ni0.35Si(0.2Cu), and	

# TABLES

Table 1 The interaction parameters used in the simulation.	. 15
Table 2. Cohesive energy of primary RPVs elements	. 16
Table 3 Estimation of number density of nucleation sites on dislocations and grain boundaries. All values are approximate.	. 18
Table 4 Equilibrium solute product for each phase at different temperatures	. 21
Table 5 Diffusion coefficients under thermal condition.	. 21
Table 6 Parameters used in calculating radiation enhanced diffusion coefficient	. 21
Table 7. Composition of alloys used in CD modeling of MNSP in low Cu RPV steels	. 30
Table 8 Diffusion coefficients of Ni in alpha-Fe measured in paramagnetic and	
ferromagnetic state	. 33
Table 9. Alloys designation and corresponding bulk composition.	. 42
Table 10. Fitted parameters for Cu part of CD model	. 45

# ACRONYMS AND NOMENCLATURE

APT	Atom probe tomography
BCC	Body-centered cubic
CD	Cluster dynamics
CM6	Name of different alloy composition used by University of California, Santa Barbara, collaborators
CRP	Cu-rich precipitate
LC, LD, LH, LI, LG	Name of different alloy composition used by University of California, Santa Barbara, collaborators
LWR	Light water reactor
КМС	Kinetic Monte Carlo
MNSP	Mn-Ni-Si rich precipitate
PIA	Post-irradiation annealing
RIS	Radiation-induced segregation
RMSD	Root mean square difference
RPV	Reactor pressure vessel
UMD	Unstable matrix defects

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#### 1. INTRODUCTION

Reactor pressure vessels (RPVs) are permanent components in light water reactors (LWRs) and their irradiation embrittlement is one of the potential barriers to extending the lifetime of light water reactors. One of the main causes of embrittlement in RPVs is the formation of nanometer-scaled Cu-rich precipitates (CRPs) and Mn-Ni-Si-rich precipitates (MNSPs) [1]. Although the formation of nanoscale precipitates in RPV steels has been well established [2], we are not aware of any complete model (considering both CRPs and MNSPs) which addresses their impact on the RPVs embrittlement on a time-scale appropriate for life-extension (60-80 years)

In this report, we developed a multiscale model to address the process of formation and growth of CRPs and MNSPs in RPV steels under both irradiation and aging. We used the kinetic Monte Carlo technique for atomistic simulation, which gave us insight into early stages of Cu-Mn-Ni-Si precipitation and its morphological evolution. For continuum modeling, first we developed a Cluster Dynamics (CD) model for MNSPs which was capable of capturing the MNSPs evolution over the time scale of reactor lifetimes. Then we expanded the MNSPs CD model to include the effect of Cu. This model expansion is necessary as RPV steels essentially always have some potentially relevant level of Cu. The model of the coupling of Cu to MNSPs was informed by the kinetic Monte Carlo simulations. Both MNSPs and Cu+MNSPs CD models were benchmarked against high flux irradiation experimental data from the literature and UCSB and uncertain parameters (e.g. interfacial energy) were fitted to experimental data. Then the models were used to gain insight into embrittlement of RPVs under light water reactor (LWR) extended life conditions under which no experimental data is available. The CD models (with fitted parameters from irradiation experiments) were also validated against aging experimental studies at higher temperatures. The good agreement between modeling and experimental aging data supports the fidelity of fitted parameters for both irradiation and aging.

### 2. EXECUTIVE SUMMARY OF MAJOR RESULTS

- Qualitative and semi-quantitative models for Cu+MNSP evolution were developed which allow understanding of key mechanisms governing precipitate evolution and prediction of behavior trends under life-extension conditions.
- Kinetic Monte Carlo (KMC) simulation established a novel mechanism for precipitate growth that can explain the appendage morphology of Cu+MNSPs and may play a role in other multicomponent precipitates (see Sec. 4.1.2).
- Cluster Dynamics (CD) modeling suggested that DBTT shifts of up to about 450 °C are possible under life-extension conditions associated with MSNPs in the high-solute (1.3Mn1.75Ni0.65Si, at.%) alloys (see Sec. 4.2.1.4).
- CD modeling suggested that DBTT shifts can be both significantly larger and happen significantly earlier in the presence of Cu, consistent with experimental results from UCSB. The Cu effects are due to both Cu precipitation and catalyzing MNSP formation. For medium to high solute concentrations the addition of Cu can increase the 80 year DBTT shift by up to ~120 °C, and the fraction of the 80 year DBTT shift occurring at 40 years increases from about 25-70 % (in Cu-free alloys) to 75-80 % (in Cu bearing alloys) (see Sec. 4.2.3.2).

#### **3. METHODS**

#### 3.1 Kinetic Monte Carlo Simulations

#### **3.1.1** The Kinetic Monte Carlo model

The KMC model is developed based on the framework of the model by Enrique and Bellon [3], and directly modified from the code developed by Shu et al. [4], adding multinary simulation capability and body-centered cubic (bcc) structural information.

A bcc rigid lattice is constructed from an N×N×N (N = 64 or 256) rhombohedral crystal with periodic boundary conditions. The faces of rhombohedron correspond to {110} planes of the bcc crystal. Atoms migrate by thermally activated jumps, assisted by nearest-neighbor atom-vacancy exchanges. A single vacancy is introduced into the system. Nearest-neighbor atomic pair interactions ( $\varepsilon_{XY}$ ) and atom-vacancy interactions ( $\varepsilon_{XY}$ ) are used to model cohesion and vacancy formation energies of the system, and their fitting will be discussed in detail in Sec. 3.1.2. Homoatomic pair interactions (i.e., interactions between atoms of the same chemistry) are estimated by assuming they are related to cohesive energies through  $E_{coh}^{X} = \frac{Z}{2} \varepsilon_{XX}$ , where Z is the nearest-neighbor site coordination number (Z = 8 for bcc structure). Hetero-atomic interactions (i.e., interactions between atoms with different chemistry) are defined through the ordering energy as  $\omega_{XY} = 2\varepsilon_{XY} - \varepsilon_{XX} - \varepsilon_{YY}$ . The value of  $\omega_{XY}$  determines the shape of the binary X-Y phase diagram. Effective atom-defect pair interactions are used to reproduce the values of vacancy defect formation energies, defined as  $E_{XY}^f = Z\varepsilon_{XY} - \frac{Z}{2}\varepsilon_{XX}$ [5].

The frequency of the thermal jumps is determined using standard rate theory. The attempt frequency is set to be a constant equal to  $6 \times 10^{12} s^{-1}$ , similar to the atomic vibration frequency. The activation energy is calculated using

$$E_a^X = E_0^{\text{mig}} + E_a^{\text{saddle}},\tag{1}$$

where  $E_a^{saddle}$  is the saddle-point energy.  $E_a^{saddle}$  is calculated using the final-initial-state energy (FISE) approximation,  $E_a^{saddle} = \frac{E_f - E_i}{2}$ , where  $E_i$  and  $E_f$  are the system total energies before and after the jump of the vacancy. The reference activation energy  $E_0^{mig}$  is assumed to be

dependent on the chemical species of the migrating atom, and the value of  $E_0^{\text{mig}}$  is taken from Ref. [6], by Messina et al.

During the simulation, time is incremented using a residence-time algorithm [7]. Since a single vacancy is introduced in the simulation cell, a fixed vacancy concentration is unphysically imposed. Thus, a rescaling of the KMC time  $t_{MC}$  is needed in order to obtain the physical time t that can be directly compared with the experiments. We follow the approach proposed by Nastar et al. [8] for the rescaling:

$$t = t_{MC} \frac{C_V^{KMC}(X)}{C_V^{irr}(X)},$$
(2)

where  $C_V^{KMC}(X)$  is the vacancy concentration in phase *X*, measured in KMC simulation, and  $C_V^{irr}(X)$  is the radiation enhanced vacancy concentration in *X* phase, calculated according to Ref. [9].

#### 3.1.2 Kinetic Monte Carlo Model Parameterization

The homo-atomic pair interactions  $\varepsilon_{XX}$  for determining  $E_i$  and  $E_f$  are determined from measured cohesive energies for bcc phase of the pure element. The hetero-atomic pair interactions  $\varepsilon_{XY}$  are obtained from molar excess free energies ( $G_{AB}^m$ ), calculated by the CALPHAD method. Specifically, assuming a regular solution model one can write

$$G_{AB}^{m} = x_{A}G_{0}^{A} + x_{B}G_{0}^{B} + RTx_{A}\ln x_{A} + RTx_{B}\ln x_{B} + x_{A}x_{B}\Omega_{AB}, \qquad (3)$$

where  $\Omega_{AB} = \frac{Z}{2} N_A \omega_{AB}$ .  $\Omega_{AB}$  is available or can be fit from the CALPHAD model for  $G_{AB}^m$  and connects the CALPHAD output to the KMC input.

In previous milestones, we have described the details of the parameterization involving Fe, Mn, Ni and Si. In this milestone, we add Cu in the interactions, which were obtained from Ref. [10]. The used interactions are listed in Table 1.

Table 1 The interaction parameters used in the simulation.

$\Omega_{ m AB}$	Cu	Mn	Ni	Si
Fe	0.458	0.094	0.007	-1.542
Cu		0.090	0.106	-0.344

Mn	-0.465	-0.907
Ni		-1.850

Table 2. Cohesive energy of primary RPVs elements

Element	Fe	Cu	Mn	Ni	Si
$E_{cho}^{X}(eV)$	-4.28	-3.49	-2.92	-4.34	-4.03

#### **3.2** Cluster Dynamics Simulations

#### **3.2.1** Simulation Models

#### **3.2.1.1** Basic Cluster Dynamics model

As described in previous milestones, the CD method [11-14] gives the size distribution of clusters by solving a series of ordinary differential equations as follows:

$$\frac{\partial f(n,t)}{\partial t} = \omega_{n-1,n}^{(+)} f(n-1,t) - \omega_{n,n-1}^{(-)} f(n,t) + \omega_{n+1,n}^{(-)} f(n+1,t) - \omega_{n,n+1}^{(+)} f(n,t)$$
(4)

where

f(n,t) = concentration of clusters containing *n* atoms at time *t*.

The coefficient  $w_{n,n+1}^{(+)}$  s are the rates at which clusters of size *n* absorb single atoms to grow to size n+1,  $w_{n,n-1}^{(-)}$  s are the rates at which clusters of size *n* emit single atoms to shrink to size *n*-1, and  $\Delta G(n)$  is the formation energy of clusters with *n* atoms. More details regarding this method can be found in Ref. [11-14].

For a system containing k precipitating components, the rates of absorption are given by:

$$\omega_{n,n+1}^{(+)} = \left[ \sum_{i=1}^{j} \left( \frac{v_{i\alpha}^2}{\omega_{n_i,n_i+1}^{(+)}} \right) \right]^{-1}$$
(5)

where

 $w_{n_i,n_i+1}^{(+)}$  = rate at which clusters of size *n* gain one atom of species *i*.

The parameter  $v_{i\alpha}$  accounts for the change in the composition of component *i* as the cluster grows from size *n* to *n*+1. It is defined by the following expression:

$$v_{i\alpha} = x_{i\alpha} + n \frac{dx_{i\alpha}}{dn}$$
(6)

where

 $x_{i\alpha}$  = atomic fraction of component *i* in clusters of size *n*.

Here it is assumed that  $x_{i\alpha}$  does not change with *n*, thus  $v_{i\alpha}$  equals  $x_{i\alpha}$ .

For diffusion-limited growth of the clusters, the absorption rate becomes:

$$\omega_{n,n+1}^{(+)} = 4\pi c_{\beta} a_{\alpha} D_{eff}^{d} n^{1/3}$$
(7)

$$\frac{1}{D_{eff}^d} = \sum_{i=1}^k \frac{v_{i\alpha}^2}{x_{i\beta} D_i}$$
(8)

where

 $C_{\beta}$  = total volume concentration of the particles of the different components in the ambient phase

 $x_{i\beta}$  = molar fraction of the different components in the ambient phase.

The emission rate is given by:

$$\omega_{n+1,n}^{(-)} = \omega_{n,n+1}^{(+)} \exp(\frac{\Delta G(n+1) - \Delta G(n)}{k_{R}T})$$
(9)

where

 $\Delta G(n) =$  formation energy of clusters with *n* atoms from the matrix, which can be written as:

$$\Delta G(n) = n(g_p - \sum_i x_i \mu_i) + \sigma(n)$$
<sup>(10)</sup>

where

 $g_p$  = free energy per atom of the precipitate phase

 $\mu_i$  = chemical potential of component I in the matrix

 $\sigma(n)$  = interfacial energy of a cluster of size *n*.

With this form, the difference  $\Delta G(n+1)$ - $\Delta G(n)$  reduces to:

$$\Delta G(n+1) - \Delta G(n) = g_p - \sum_i x_i \mu_i + [\sigma(n+1) - \sigma(n)]$$
(11)

In dilute alloys, the chemical potentials can be written as:

$$\mu_i = \mu_i^0 + kT[ln\gamma_i + lnc_i] \tag{12}$$

When the matrix phase is in equilibrium with the precipitate phase, it can be written as:

$$g_{p} - \sum_{i} x_{i} \mu_{i} = 0$$

$$g_{p} - \sum_{i} x_{i} [\mu_{i}^{0} + kT \ln \gamma_{i}] = kT \sum_{i} x_{i} \ln c_{i}$$
(13)

In dilute alloys, the emission rate can be written as:

$$\omega_{n+1,n}^{(-)} = \omega_{n,n+1}^{(+)} \frac{\overline{\prod_{i} c_{i}^{x_{i}}}}{\prod_{i} c_{i}^{x_{i}}} \exp\left(\frac{\sigma(n+1) - \sigma(n)}{k_{B}T}\right)$$
(14)

where  $\prod_i c_i^{x_i}$  and  $\overline{\prod_i c_i^{x_i}}$  are the solute product and solute product at equilibrium, respectively, and they are represented by  $K_{sp}$  and  $\overline{K_{sp}}$ , respectively.

The distribution function f(n=1,t) at n=1 is described as:

$$f(n=1,t) = c_{\beta} \prod_{i=1}^{k} x_{i\beta}^{x_{i\alpha}}$$
(15)

#### 3.2.1.2 Heterogeneous nucleation on Cascade Damage model

Dislocations and grain boundaries are usually considered as heterogeneous nucleation sites. There are also some experimental data showing the nucleation of MNSPs on these sinks [15, 16]. However, the available nucleation sites on dislocations and grain boundaries, as shown in Table 3, are too few to match the high concentrations seen in experimental data  $(10^{24} \text{m}^{-3})$  [17]. The number of heterogeneous nucleation sites on grain boundaries calculated here is the upper limit of available sites. Therefore, these sources of heterogeneous nucleation, while they may be present, cannot be playing a significant role in the typically observed precipitate density (although they may play a major role for very low solute alloys or under some conditions where only a low number of density of precipitates is observed). Heterogeneous nucleation on Cu precipitates has also been observed [17], and will be discussed further in Sec. 3.2.2.

Table 3 Estimation of number	density of nuc	eleation sites on	n dislocations and	l grain boundaries
All values are approximate.				

Nucleation types	Typical parameters				Nucleation sites (m <sup>-3</sup> )
Diclosofice	Densi	Density ρ Typical precipitate diameter of		Il precipitate diameter d	p/d
Dislocation	$(1-10) \times 10^{14} \mathrm{m}^2$			1-5nm	$\approx 10^{22} - 10^{23}$
Grain Boundary	Grain size (D)	bounda	Grain ry thickness δ	lattice sites C <sub>0</sub>	$C_0 \delta/D$ ≈10 <sup>23</sup>
	10 <sup>-5</sup> m		10 <sup>-9</sup> m	$10^{27} \text{m}^{-3}$	

However, heterogeneous nucleation on cascade damage is a possible mechanism for MNSP nucleation and thus we have developed an approach to include it in our model. According to Monte Carlo simulations [18-20] as well as indirect experimental measurements [21-25], there will be a high density of unstable matrix defects (UMDs) that form in cascades (the impact of these UMDs on radiation enhanced diffusion (RED) are discussed in Sec. 3.2.1.3). These UMDs, which are believed to be sub-nm vacancy clusters, complexed with solutes, can serve as nucleation sites for larger stable matrix features (SMF) such as loose aggregates of solutes [26].

Also nanometric dislocation loops have been observed by TEM in VVER steels [21-23] and PWR steels under high dose with ions or electrons [24, 25]. A recent Monte Carlo study showed that these small dislocation loops may act as locations for heterogeneous nucleation of solute precipitates [20].

Here we assumed that a certain size of clusters ( $n_h$ , which is fit to the experimental data, see Sec. 3.2.2) can be generated at a certain rate by direct or indirect effects of cascades. We therefore assumed that the rate of cluster production scales with number of cascades. We also assumed that the rate scales with the amount of solute available to form the precipitate, which we represented by the triple product  $K_{sp}$ . The heterogeneous nucleation generation rate r (n·m<sup>-3</sup>) as a function of time is then calculated as

$$r(n_h, t) = \alpha \cdot \sigma \theta / \Omega \cdot K_{sp}(t) / K_{sp}^0$$

$$r(n \neq n_h, t) = 0$$
(16)

where  $\sigma$  is the cross section of cascades,  $\theta$  is irradiation flux,  $\Omega$  is the atomic volume,  $\alpha$  (n/cascade) is generating rate coefficient,  $K_{sp}$  (t) is the solute product of system at time t, and  $K_{sp}^{0}$  is a reference solute product, chosen as 0.01, which is approximately the beginning solute product in RPV steels.

With the cascade induced nucleation the general equation for cluster dynamics becomes:

$$\frac{\partial f(n,t)}{\partial t} = r(n,t) + \omega_{n-1,n}^{(+)} f(n-1,t) - \omega_{n,n-1}^{(-)} f(n,t) + \omega_{n+1,n}^{(-)} f(n+1,t) - \omega_{n,n+1}^{(+)} f(n,t) (17)$$

#### 3.2.1.3 Radiation enhanced diffusion (RED) model

The radiation enhanced diffusion (RED) model used here is based on that developed by Odette et al. [9]. The radiation enhanced diffusion coefficients are expressed as

$$D^{irr} = D_{\nu} X_{\nu} \frac{D^{th}}{D^{sd}} + D^{th}$$
(18)

Where  $D^{irr}$  is the diffusion coefficient under irradiation,  $D_v$  is the diffusion coefficient of vacancies,  $X_v$  is the vacancy concentration under irradiation,  $D^{th}$  is the solute thermal diffusion coefficient of solute under thermal aging condition, and  $D^{sd}$  is the self-diffusion coefficient of Fe in the matrix.

Defect conservation balances, treating vacancy and SIA production, transport and fate, were used to establish the steady-state vacancy concentration  $(X_v)$  under irradiation, which can be expressed from rate theory models as a function of the fraction of vacancies and self-interstitials (SIA) that escape recombination and reach fixed dislocation sinks  $(g_s)$ , which is given as:

$$X_{\nu} = \frac{g_s \xi \sigma_{dpa} \phi}{D_{\nu} S_t} \tag{19}$$

Here,  $\phi$  is irradiation flux,  $\sigma_{dpa}$  is the displacement-per-atom (dpa) cross-section,  $\xi$  is the fraction of vacancies and SIA created per dpa. Assuming that defect recombination occurs as vacancies and SIA diffuse freely through the ferrite matrix it can be shown that

$$g_s = \frac{2}{\eta} \left[ (1+\eta)^{1/2} - 1 \right]$$
(20)

$$\eta = \frac{16\pi r_v \xi \sigma_{dpa} \phi}{\Omega_a D_v S_t^2} \tag{21}$$

Here,  $r_v$  is the SIA-vacancy recombination radius,  $\Omega_a$  is the atomic volume, and  $S_t$  is sink strength.

We will assume that the precipitate growth is dominated by vacancy mediated diffusion of solutes to the precipitates, so correct modeling of the vacancy concentrations and associated RED is critical. Vacancy fates include clustering, annihilation at sinks and recombination with SIA. The dominant fixed sinks for vacancies are typically dislocations in RPVs. However, UMDs also act as vacancy sinks and can be dominant at very high flux. Furthermore, recombination will be greatly enhanced if vacancies are strongly bound to these UMDs. Odette et al.[9] have built a model to include the effect of UMD in the recombination-dominated regime under very high irradiation flux. This irradiation flux effect can be simply described by adjusting  $g_s$  by a scaling law as

$$g_s(\phi) \approx g_s(\phi_r) (\frac{\phi_r}{\phi})^p$$
 (22)

Here,  $\phi_r$  is a reference flux and p is a scaling exponential factor. The effective p starts at 1 in the thermal diffusion dominated regime at very low flux; p is 0 in the sink-dominated regime and p=0.5 in the recombination-dominated regime. The p again approaches 1 at high flux in the UMD sink-dominated regime. We will use this scaling law expression in our model to effectively include the effects of UMDs on the vacancy concentrations.

#### **3.2.2** Parameters for the MNSP Cluster Dynamics model

All the parameters used in the cluster dynamics model for MNSPs are given in this section. Additional approaches for the Cu+MNSP model are described in the Methods Sec. 3.2.3 and the fitting process and obtained parameters for this model are described as part of the new work for this milestone in Sec. 4.2.3. The equilibrium solute products of the two phases studied at different temperatures are obtained from the TCAL2 database [27]. These equilibrium solute products at different temperatures are listed in Table 4. Note that the equilibrium solute product here for T6 are calculated with composition of 51.1%Ni-33.3%Mn-15.6%Si, since for the alloys studied here the predicted equilibrium compositions of T6 vary over a Ni composition of just 51%-52%.

Tomporatura (°C)	Equilibrium solute product (×10 <sup>-3</sup> )			
Temperature (°C)	Т3	T6		
280	1.96	2.33		
284	2.12	2.53		
290	2.21	2.56		
300	2.45	2.82		
400	6.26	6.57		
425	7.86	7.95		

Table 4 Equilibrium solute product for each phase at different temperatures

The thermal diffusion coefficients of Mn, Ni, Si and Fe in ferromagnetic Fe used in this paper are summarized in Table 5.

Element	$D_0 (cm^2/s)$	Q (kJ/mol)	Reference
Mn	1.49	234.0	[28]
Ni	1.4	245.6	[29]
Si	0.78	231.5	[30]
Fe	27.5	254.0	[31]

Table 5 Diffusion coefficients under thermal condition.

All other parameters are listed in Table 6. Most of them are obtained from two papers [9, 32]. Four of them, heterogeneous nucleation size and rate coefficient (see Sec. 3.2.1.2) and two interfacial energies are fitting parameters. These parameters were fitted to 28 experimental data points of precipitate number density, mean radius and volume fraction for alloys under different irradiation conditions by mapping a fine grid of the values of these parameters in reasonable range, and the optimal set of parameters were obtained for parameter values where the smallest root mean square difference (RMSD) between simulation results and experimental data was realized.

Table 6 Parameters used in calculating radiation enhanced diffusion coefficient.

SIA – vacancy recombination radius (r <sub>v</sub> , nm)	0.57 [9]
Fraction of vacancies and SIA created per dpa ( $\xi$ )	0.4 [9]
Displacement-per-atom (dpa) cross-section ( $\sigma_{dpa}$ , m <sup>2</sup> )	$1.5 \times 10^{-25}$ [9]
Atomic volume ( $\Omega_a$ , m <sup>3</sup> )	1.18×10 <sup>-29</sup>
Vacancy diffusion coefficient pre-exponential factor (D <sub>v</sub> , m <sup>2</sup> s <sup>-1</sup> )	1×10 <sup>-4</sup> [32]
Vacancy migration energy ( $E_v^m$ , eV)	1.3 [32]
Dislocation sink strength (dislocation density) ( $\rho$ , m <sup>-2</sup> )	$2 \times 10^{14}$ [9]

Flux effect scaling exponential factor (p)	0.2 [33]
Cascade cross section ( $\sigma_{Cascade}$ , m <sup>2</sup> )	$2 \times 10^{-28}$ [33]
Reference solute product $(K_{sp}^0)$	0.01
Heterogeneous nucleation size $(n_h)$	60
Heterogeneous nucleation generation rate coefficient ( $\alpha$ )	0.03
Interfacial energy of T3 phase ( $\sigma_{T3}$ , J/m <sup>2</sup> )	0.190
Interfacial energy of T6 phase ( $\sigma_{T6}$ , J/m <sup>2</sup> )	0.175

#### 3.2.3 Coupling Cu to Mn-Ni-Si precipitation

Formation of pure Mn-Ni-Si precipitates (MNSPs) in RPV steels is limited to Cu-free or very low Cu bearing (Cu<0.06at.%) alloys. However, there exist some level of Cu in major in-service RPV steels and its concentration can reach up to 0.25at.% [34]. In the presence of Cu, it is seen that MNSPs are usually spatially correlated with Cu-rich precipitates (CRPs) in RPV steels [24, 35-38]. Note that here we define a CRP as a primarily Cu containing precipitate, but one that also includes other solutes (e.g., a Cu core with Mn, Ni and Si atoms coating it). In section 3.2.1, we described the general cluster dynamics model for single and multicomponent precipitates formation and we parameterize it for MNSPs in Cu-free (Cu<0.06at.%) steels in section 3.2.2. In this section, we expand the CD model to treat the precipitation of Cu along with Mn-Ni-Si. The coupling of Cu and MNSPs is necessary to fully understand their combined impact on the embrittlement of RPV steels

Based on KMC results (sections 4.1) and test reactor data [39-41] we know that CRPs will form in alloys containing more than ~0.06at.% Cu. The mechanism for formation of CRPs in the presence of MNS is still being explored, but from atom probe observations [42] and our KMC simulations, we propose that the mechanism is as follows. In the early stages of irradiation, Cu clusters precipitate out, then the Mn, Ni, and Si move toward Cu precipitates and coat the Cu precipitates in just a monolayer or so of Mn, Ni, and Si, forming CRPs. The CRPs enrichment in these solutes can be understood and modeled within the framework of both classical thermodynamics [43] and atomistic simulations [44] (section 3.1). As the irradiation continues the Cu depletes in the matrix (due to its very low solubility limit) while Mn-Ni-Si are still supersaturated. During the Cu precipitation and after, Mn, Ni, and Si continue to precipitate out on the CRP, forming an appendage morphology of a well-developed MNSP, which is discussed in detail in section 4.1.

The above process of coupling Cu and Mn-Ni-Si precipitation is highly complex, and all the features could not be readily incorporated into a practical model. Instead, we took an approximate approach that built separate Cu and MNS precipitate models, and then coupled them in a simple manner that mimicked the essence of the above processes, while simultaneously requiring relatively few adjustable parameters (as illustrated schematically in Figure 1). The right branch of Figure 1 shows the MNSP model, uses the theoretical approach from Sec. 3.2.1 and whose parameters are given in Sec. 3.2.2. The left branch of Figure 1 shows the Cu precipitation model. This model uses the same theoretical approach as described in Sec. 3.2.1, although all of the formalism for multiple species is simplified to just Cu. The parameters for this model are given in Sec. 4.2.3.1 and are one of the major results of our work for this milestone. Finally, the coupling of Cu and MNS precipitation is shown schematically by the middle branch of Figure 1. This portion is quite new and we describe it in some detail here as well as Sec. 4.2.3.1.

We coupled the Cu and MNSP by assuming that a Cu precipitate which has 20 atoms (~Cu precipitate critical size) or more can nucleate a same sized MNSP (i.e. a Cu precipitate containing 50 atoms nucleate a MNSP with 50 atoms). While Cu precipitation is in the nucleation stage, this co-nucleation of Cu and MNSP is allowed to continue in the model. When the Cu nucleation stops, we decouple the co-nucleation and let the Cu and MNSP grow separately. The Cu growth after this stage is limited due to the significant Cu depletion in the matrix, but MNSPs continue to grow, which represents the appendage growth. This way of coupling Cu to MNSP is a quite severe approximation and leaves out many features of our understanding of the true mechanism of precipitation described above. Perhaps the most dramatic feature of the approximation is that we replace the complex process of Mn, Ni, and Si segregating to the Cu/Fe interface and then growing as an appendage with a single nucleation event of an MNSP separate from the Cu precipitate. This approximation still captures the key role of Cu catalyzing the nucleation and growth of MNSPs but greatly simplifies the process in ways that may impact the fidelity of the predicted MNSP evolution. In addition, the atom probe experiments and KMC simulations show that Cu precipitates are coated with Mn, Ni, and Si atoms, which means the Cu precipitate is really a CRP, and CRPs will have a different interfacial energy than pure Cu precipitates. However, our CD model treats the Cu precipitate as evolving entirely independent of the Mn, Ni, and Si, with a fixed Cu/Fe interface and interfacial energy. We are currently exploring adding the effect of segregation of Mn, Ni, and Si to the Cu/Fe

interface into the model and initial studies suggest that this will have a relatively small impact on the overall hardening and DBTT predictions. At this stage we assess the impact of the model approximations by determining to what extent we can model a large body of Cu+MNSP evolution data, and the relatively good success we have compared to the experimental data (see Sec. 4.2.3) supports that our approach has captured the essential elements of the Cu+MNSP coupling..



Figure 1. A flowchart of precipitate formation in RPVs in the presence of Cu.

#### 4. **RESULTS**

### 4.1 Kinetic Monte Carlo Simulation of Co-precipitation of Cu-MnNiSi Precipitates

#### 4.1.1 Morphological characteristics of Cu-MnNiSi precipitates

The high-Ni-Cu content steels code named LD (Cu-0.25 Ni-1.18 Mn-1.08 Si-0.54 at.%) were irradiated at ~ 290 °C to a high neutron fluence of  $1.3 \times 10^{20}$  n cm<sup>-2</sup> and a very high neutron fluence of  $1.1 \times 10^{21}$  n cm<sup>-2</sup> in the Belgian Reactor 2 (BR2) and the US Advanced Test Reactor (ATR), respectively. The samples were then characterized using 3D-APT. Typically, atom probe tips being analyzed have several million atoms, and contain several hundred precipitates. Cluster analysis is performed using maximum separation method to delineate the Cu-MnNiSi precipitates. Isoconcentration surfaces are also used, specifically to visualize more clearly the fine structure of the Cu-MnNiSi precipitates.



Figure 2 (a) Atom maps for LD alloy irradiated in BR2 (the composition ) (b) Atom maps for LD alloy irradiated in ATR1 (c) APT map of a typical precipitate in the bulk, BR2 condition (d) APT map of a typical precipitate in the bulk, ATR1 condition, isoconcentration surface is added to guide the eye.

We obtain two snapshots of the temporal evolution of the microstructure from the 3D APT observations. In the high fluence sample (BR2), as shown in Figure 1(a) and (b), the precipitates

are mostly Cu-rich precipitates, coated by a thin layer of Mn, Ni and Si atoms. As the microstructure further evolves, as shown in Figure 1(c) and (d), the Cu-MnNiSi precipitates grows mainly by the growth of the MnNiSi phase, as Cu is depleted in the matrix after early stage of precipitation. The striking feature is that, although the Cu precipitate is relatively small compared to the whole precipitate, it is not enveloped by the MnNiSi phase and does not form a core-shell structure, even at this very high fluence. Instead, the Cu precipitate is always on the edge of the whole precipitate, forming a microstructure that can be termed as eccentric-core-shell structure, or MnNiSi appendage on Cu precipitate. The origin of this special microstructure of the precipitate is not obvious and requires an atomistic explanation.

#### 4.1.2 KMC simulation of the nucleation and growth of the Cu-MnNiSi precipitates

In the KMC simulations, a five-component alloy, containing Fe, Cu, Mn, Ni and Si, was constructed on a rigid body-centered cubic lattice to represent the LD alloy. The parameterization of the KMC simulation has been partly validated by simulating post-irradiation annealing of the MnNiSi phase (described in previous milestones), and showed impressive agreement with the post-irradiation annealing results [45], reproducing the observed evolution of volume fraction,  $f_v$ , precipitate number density, N, and mean radius,  $\langle r \rangle$ .

In this study, we simulated the microstructural evolution of the alloy under neutron irradiation. The initial configuration of the alloy was a solid solution, which had the same composition as in the experiments. Remarkably, the KMC simulations reproduced the Cu-MnNiSi appendage morphologies observed with 3D APT. Figure 3(a) is a snapshot of the KMC simulation. The Cu precipitates and MnNiSi phase formed co-precipitates, with a Cu precipitate on the edge of the whole precipitate. A magnified precipitate is shown is Figure 3(b), in which two isoconcentration surfaces were constructed to show a clearer boundary of the Cu precipitate and the Cu-MnNiSi co-precipitate. Along the direction of the arrow, we performed a 1-D composition line scan across the precipitate, which is plotted in Figure 3(c). The peaks representing the Cu precipitate and the MnNiSi phase can be clearly distinguished, showing the asymmetric positioning of the Cu precipitate. In the simulation, the MnNiSi phase is a B2 ordered structure, in which Ni and Mn occupy the two sublattices, with Si atoms randomly replacing some Mn atoms. This ordering state is believed to be very probable at the early stage of the precipitate grow to larger sizes, the structure of MnNiSi phase is likely to transform to that of the G-phase, as characterized by

synchrotron-based x-ray diffraction [46]. Nevertheless, the precipitate structure predicted by our KMC simulation captures the fact that the ordered MnNiSi precipitate has a lower free energy level compared to the disordered counterpart.



Figure 3 (a) a snapshot of the KMC simulation, showing the microstructure of the simulated alloy (b) a magnified Cu-MnNiSi precipitate, with iso-concentration surfaces to clearer show the structure of the precipitate (c) a 1-D composition line scan of the precipitate.

A unique advantage of the KMC simulation over present experimental characterization methods is that it can track one particular precipitate and identify its detailed temporal evolution. Figure 4 is a sequence of snapshots of a typical Cu-MnNiSi co-precipitate, showing its temporal evolution. At the early stage of nucleation, Figure 4(a), the precipitate is what we call a Cu-rich precipitate (CRP), which in this case has a Cu core with Mn, Ni and Si atoms coating it, the latter of which are stabilized by their ability to lower the Cu-Fe interfacial energy. In the early stage of the growth regime, see Figure 4(b-c), more Cu, Mn, Ni and Si atoms diffuse to the precipitate. Interestingly, the MnNiSi phase preferentially grows on one side of the whole precipitate. At the later stages of growth, Figure 4(d-e), as the Cu atoms in the matrix deplete, the growth of the Cu-MnNiSi precipitate is mainly by incorporating Mn, Ni and Si atoms, forming the ordered B2 phase. Note that instead of growing a thick shell of MnNiSi phase around the Cu precipitate, forming a core-shell structure, the Mn, Ni and Si atoms continue the preferential growth on one side of the precipitate. Thus, the

simulations reproduce the interesting morphology of the Cu-core-MnNiSi-appendage observed in APT experiments.



Figure 4 Temporal evolution of the Cu-MnNiSi precipitate reproduced by KMC simulations: (a) Formation of a Cu precipitate coated by a layer of MnNiSi, (b) and (c) nucleation of MnNiSi ordered phase on the Cu precipitate, and (d) and (e) further growth of the MnNiSi ordered phase. Note that the Cu precipitate is always on the edge of the whole precipitate.

The formation of the Cu-core-MnNiSi-appendage structure is not expected. In particular, having the Cu precipitate on the edge of the whole precipitate and in contact with the Fe matrix is expected to be energetically unfavorable, considering the high Cu/Fe interfacial energy. Therefore, it is important to determine the thermodynamic and/or kinetic factors that lead to this morphology. To elucidate the mechanism that causes the Cu precipitate to be on the edge of the whole precipitate, we plot the typical movement of the center of mass (COM) of both the whole precipitate and the Cu precipitate alone, as shown in Figure 5(a). The black trajectory, which shows the movement of the COM of the whole precipitate, is very short during the growth of the precipitate, indicating an isotropic growth rate in all the radial directions. However, the blue trajectory, which tracks the movement of the COM of the Cu precipitate, shows a clear absolute displacement toward one direction. Given the fact that the lattice sites are conserved in the KMC simulations, an absolute movement of Cu precipitate toward one direction must be compensated by a net mass flux in the opposite direction, in this case, the flux of Mn, Ni and Si atoms. This observation suggests that during the process of the formation of Cu-MnNiSi precipitate, there is

a diffusion path for Mn, Ni and Si atoms through the Cu precipitate and the Cu precipitate does not block the Mn, Ni and Si diffusion. In Figure 5(b) we plot together the distance between COMs of Cu precipitate and the whole precipitate as well as the radius of the whole precipitate. We see that the larger the distance between the COMs, the larger the precipitate size. This measurement demonstrates that as the precipitate grows the COM of the Cu and whole precipitate are moving apart proportional to the precipitate size, which is what one expects for an appendage growth where Cu is always on the edge of the precipitate. Therefore, this result demonstrates that during the growth of the whole precipitate, the Cu precipitate is always on the edge.

In summary, these studies show that in this complex multi-component system, the coprecipitation process can lead to a counterintuitive appendage microstructure that can then be understood from the KMC simulations. Understanding the detailed kinetic pathway of the earlystage precipitation is essential to inform other higher-level modeling techniques, such as cluster dynamics.



Figure 5 (a) movement of the center of mass (COM) of the whole precipitate compared to that of the Cu precipitate (b) distance between COMs as the precipitate grows. The radius of the whole precipitate is also plotted to show that the distance between COMS is directly correlated to size of the Cu-MnNiSi precipitate.

#### 4.2 Cluster Dynamics

#### 4.2.1 Update on Mn-Ni-Si precipitates under irradiation

In the previous milestone we attempted to discover the source of significant disagreements between our CD model and some experimental data for samples with very-low-solutecomposition, very-high-flux and very-high-fluence from the ATR1 reactor.<sup>1</sup> We explored the effect of thermodynamic database and radiation induced segregation (RIS) on the evolution of Mn-Ni-Si precipitates. It was found that errors in the CALPHAD thermodynamics are not the main reason for the disagreement between calculation results and ATR1 experiments. It was also found that the simple RIS model that we implemented was not accurate enough to increase the accuracy of the model. Therefore, in this subsection we will update the cluster dynamics model by excluding the outlier experimental data at extreme conditions (very-low-solute-composition, very-high-flux and very-high-fluence) and provide a model that can predict the evolution of MNSPs in low-Cu RPV steels under both realistic power reactor and typical experimental high flux conditions. The composition of the studied alloys are given in Table 7.

Alloy Name	Cu (at.%)	Mn (at.%)	Ni (at.%)	Si (at.%)
Ringhals E	0.05	1.25	1.50	0.41
Ringhals N	0.03	1.14	1.68	0.28
Ginna Forging	0.07	0.57	0.92	0.67
BR2-TU LG	0.01	1.18	0.73	0.44
BR2-TU CM6	0.0	1.16	1.63	0.35
BR2-G2 CM6	0.0	0.94	1.61	0.35
BR2-G1 LG	0.01	1.09	0.86	0.49
BR2-G1 CM6	0.0	1.09	1.34	0.33
ATR1 CM6	0.0	1.42	1.69	0.39

Table 7. Composition of alloys used in CD modeling of MNSP in low Cu RPV steels

#### 4.2.1.1 Update on thermal diffusion coefficients

This subsection we will update how we obtained the thermal diffusion coefficients given the limited data of impurity diffusion coefficients in  $\alpha$ -Fe in literature. For the self and impurity

<sup>&</sup>lt;sup>1</sup> As this report was being completed we learned that due to a recalculation of the reactor properties the ATR1 irradiations were now believed to have been performed at 320°C, rather than the previously reported value of 290°C. There was no time to update the results in this work and thus all simulations in previous reports and the present report for ATR1 are at an incorrect temperature of 290°C. However, simple arguments suggest that correcting this temperature will not fix the discrepancies in the model but will in fact make them worse, so it is unlikely that the temperature reporting error is the source of the model discrepancy.

diffusion coefficients for an alloy in a ferromagnetic state, Ruch et al. [47] proposed a model for D(T) in which the temperature dependence is described assuming a constant value for the prefactor ( $D_0$ ) and a temperature dependence of activation energy originating from the effect of magnetic disorder. The ferromagnetic activation energy is a function of paramagnetic activation energy with the formula

$$Q^f = Q^p (1 + \alpha s^2) \tag{23}$$

where  $Q^{f}$  is the activation energy in the fully ordered ferromagnetic state at zero temperature,  $Q^{p}$  is the activation energy in disordered paramagnetic state, *s* is the reduced magnetization at any finite temperature, which is a function of temperature and was reported by Potter [48].

However, although self-diffusion coefficients of Fe have been studied by a number of researchers [31, 49-54], there is very limited experimental data on the thermal diffusion coefficients of Mn, Ni, and Si impurities in ferromagnetic Fe. Only one experiment has been done for Mn [28] and Ni [29], and no experiment has been done for Si to the author's knowledge. Therefore, we have developed a consistent approach to estimate the diffusion coefficient for Fe and all the impurities in a way that minimizes errors associated with limited data.

For Mn and Ni the available experimental results were fit to Arrhenius relations with constant activation energy as shown by the following equation.

$$D^{th} = D_0 \exp\left(-\frac{q_c^f}{kT}\right) \tag{24}$$

Where  $D_0$  is the pre-factor, and  $Q_c^f$  is the activation energy in ferromagnetic Fe, taken as a constant number. While this activation energy might actually have a significant temperature dependence, it cannot be determined reliably from the limited data. Therefore, for Mn and Ni we will use the constant activation energy fitted to the relatively high temperature (873-1000K, where *s* is about 0.5~0.7) experiments and extrapolate to low temperature.

Now we consider the Fe diffusion coefficient. While one might be tempted to use the most accurate temperature dependent form given in Eq. (23) we propose that a more accurate model can be constructed by treating the Fe diffusion consistently with how we treat Mn and Ni. The need for a consistent treatment of different species diffusivity values emerges from Eq. (18), which shows that the radiation enhanced diffusion coefficients are determined by the ratios of

 $D^{th}/D^{Fe}$ . Assuming Arrhenius expressions with temperature dependent activation energies for diffusion this ratio can be explicitly written in the following equation

$$\frac{D_{i}^{th}}{D_{Fe}} = \frac{D_{0i}^{th} exp\left(-\frac{Q_{i}^{p}(1+\alpha_{i}s^{2})}{RT}\right)}{D_{0Fe} exp\left(-\frac{Q_{Fe}^{p}(1+\alpha_{Fe}s^{2})}{RT}\right)} = \frac{D_{0i}^{th}}{D_{0Fe}} exp\left(-\frac{Q_{i}^{p}(1+\alpha_{i}s^{2}) - Q_{Fe}^{p}(1+\alpha_{Fe}s^{2})}{RT}\right) = \frac{D_{0i}^{th}}{D_{0Fe}} exp\left(-\frac{C}{RT}\right)$$
(25)

where  $C = Q_i(1 + \alpha_i s^2) - Q_{Fe}(1 + \alpha_{Fe} s^2)$ . From these equations we see that the best way to to obtain an accurate ration D<sup>th</sup>/D<sup>Fe</sup> (and therefore to best model radiation enhanced diffusion coefficients) is to use consistent approximations which yield the closest value to the correct value for the term *C*.

Now we can compare to possible approaches to obtaining the most accurate value for C in cases where we have only approximate and partial knowledge of the thermal diffusion coefficients. If we had all the temperature dependent activation energies and evaluated the C parameter at the RPV temperature  $T_2$  (with the magnetic moment at this temperature  $s_2(T_2)$ ) then we would get the correct true value of C, which we call  $C_{true} = -[Q_i(1 + \alpha_i s_2^2) - Q_{Fe}(1 + \alpha_i s_2^2)]$  $\alpha_{Fe}s_2^2$ ). Whatever approach we use should yield a C value as close to  $C_{true}$  as possible. As mentioned above, due to limited data we are using impurity *i* diffusion coefficient with a fixed activation energy, which is taken as some temperature  $T_1$  with magnetic moment  $s_1(T_1)$ . Now we consider two approaches, (a) where we use the temperature-dependent activation energy for Fe and (b) where we use a temperature-independent activation energy for Fe taken from data at approximately  $T_1$ . For case (a) we obtain a value of  $C_a = [Q_i(1 + \alpha_i s_1^2) - Q_{Fe}(1 + \alpha_{Fe} s_2^2)]$  and for case (b) we obtain a value of  $C_b = [Q_i(1 + \alpha_i s_1^2) - Q_{Fe}(1 + \alpha_{Fe} s_1^2)]$ . The changes in C from the ideal true value for the two cases are therefore  $C_a - C_{true} = Q_i \alpha_i (s_1^2 - s_2^2)$  and  $C_b - C_{true} =$  $(Q_i\alpha_i - Q_{Fe}\alpha_{Fe})(s_1^2 - s_2^2)$ . If we make the reasonable assumption that Fe and its impurity have somewhat similar values of activation energy and  $\alpha$  parameter then it is clear that  $(Q_i \alpha_i Q_{Fe}\alpha_{Fe}$ ) is likely to be much closer to zero then  $Q_i\alpha_i$ , and that therefore method (b) is likely to be significantly better than method (a). This argument can be summarized by noting that by treating the Fe activation energy as temperature independent, in a manner consistent with the approximate treatment of the impurity, we maximize cancellation of errors more that by using the more accurate temperature-dependent Fe activation energy model that is inconsistent with the approximate treatment of the impurity.

As for Si, since no experiments have been done for the diffusion of Si in ferromagnetic Fe, an estimation of the ferromagnetic activation energy is done by scaling the Si activation energy using the ratio between ferromagnetic energy  $(Q_c^f)$  and paramagnetic energy  $(Q^p)$  of Ni in Fe. In other words, we set  $Q_c^f(Si) = Q^p(Si) \frac{Q_c^f(Ni)}{Q^p(Ni)}$ . Ni is chosen here because both ferromagnetic and paramagnetic state diffusion are measured by the same researcher and the pre-factors given are very close to each other in these two states, as can be seen from Table 8. Thus, the activation energy of Si in ferromagnetic Fe will be calculated from the value measured at paramagnetic state and adjusted by the ratio 1.05 given in Table 8.

Table 8 Diffusion coefficients of Ni in alpha-Fe measured in paramagnetic and ferromagnetic state.

State	$D_0 (cm^2/s)$	$Q_c^f$ (kJ/mol)	Ratio $Q_c^f/Q^p$	Reference
Paramagnetic	1.3	234.3	1.05	[29]
Ferromagnetic	1.4	245.6		

According to discussion above, the final thermal diffusion coefficients of Mn, Ni, Si and Fe in ferromagnetic Fe used in this paper are summarized in Table 5.

#### 4.2.1.2 Comparison with experiments

Figure 6 shows the predicted cluster dynamics vs measured APT Mn-Ni-Si precipitate values (radius, number density, volume fraction) for our revised data set as predicted by a model fit to just this data. From the figure we can see that the calculation results show a very strong correlation with the experimental results, demonstrating qualitative and even semi-quantitative agreement across this large range of compositions and conditions. Figure 7 and Figure 8 show the evolution of precipitates as a function of fluence for all the alloys, where the conditions and experimental data are the same as shown in Figure 6. The results show that the model predicts all the alloys to be in the nucleation and growth stages of precipitates into the coarsening regime.



Figure 6. Comparison of number density, mean radius and volume fraction between simulation results calculated from local atom probe compositions and available experimental data.



Figure 7. Evolution of precipitates as a function of fluence for CM6 and LG at different conditions. Lines represent simulated data for single APT tip compositions. For cases with multiple APT tips and associated compositions, rather than plot multiple lines, a band showing the range of obtained values is given.



Figure 8. Comparison between calculation results and experimental data for Ringhals and Ginna reactors.

In summary, the present model gives predictions that agree semi-quantitatively with experimental APT values of MNS precipitate number density, radius, and volume fraction. Given the complexity of multicomponent radiation driven precipitation and the wide range of compositions and irradiation conditions represented, we believe that the level of agreement is a strong support that the model has captured the essential physics controlling the precipitation in most of these alloys and can be used to understand the role of different mechanisms, the influence of key controlling factors, and make qualitative predictions for MNS precipitate evolution in low Cu steels under both experimental and realistic LWR conditions. We note the success of the present model strongly suggests that vacancy enhanced diffusion dominates the

growth of these precipitates, and that interstitials do not play a significant role in bringing material to the precipitate, except perhaps in the initial nucleation stages.

#### 4.2.1.3 Heterogeneous nucleation mechanism

Figure 9 shows the ratio of number density of precipitates nucleated via the heterogeneous nucleation mechanism to that via the homogeneous nucleation mechanism. The figure shows that for 8 of the 10 alloys the ratio is well above 1, which means that heterogeneous nucleation mechanism dominates over homogeneous nucleation mechanism for these systems. Thus, it is necessary to consider the heterogeneous nucleation mechanism under irradiation to account for the observed behavior. We note that we are considering the heterogeneous nucleation mechanism described in Sec. 3.2.1.2, which is nucleation on radiation induced damage, and not nucleation on grain boundaries or dislocations. The latter mechanisms are typically unable to make significant contributions to MNS precipitates due to the low concentration of both grain boundary and dislocation defects in these alloys. Other mechanisms to facilitate MNS precipitate nucleation may dominate at other alloy compositions, e.g., in Cu containing steels Cu has been shown to play an important role in accelerating the growth of MNS precipitates, at least in part likely due to Cu catalyzing nucleation in some manner [17] (section 3.2.3).



Figure 9. Ratio of number density of precipitates created by heterogeneous and homogeneous nucleation mechanisms.

#### 4.2.1.4 Effect of precipitates on increase of ductile-to-brittle transition temperature ΔT

In this subsection, we explored the effect of MNS on hardening and  $\Delta T$  of RPV steels. As has been pointed out in Ref. [17], this hardening can be quite significant, and  $\Delta T$  shifts of 210°C are expected at high fluence in some systems. Thus, we calculated the effect of MNS precipitates on  $\Delta T$  with different alloy compositions. Three alloy compositions were chosen for this study, namely high solute (1.30at. %Mn-1.75%Ni-0.65%Si), medium solute (1.00 at. %Mn-1.15%Ni-0.35%Si) and low solute (0.70at. %Mn-0.85%Ni-0.25%Si).

The model used here to assess  $\Delta T$  in terms of precipitate volume fraction and fluence is an empirical model built by Odette et al [17, 55] by fitting to experimental data of MNS precipitates measured by APT and SANS. More detail about this model can be found in [17, 55]. Here we give just a short description.

The effect of precipitates on yield stress is given by the relation:

$$\sigma_p \approx C \alpha_p(r_p) G b \sqrt{f_p} / \langle r_p \rangle \tag{26}$$

Where  $C\approx 1.7$  is a constant that is determined by the Taylor factor (3.05) and obstacle planar spacing geometry,  $\alpha_p(r_p)$  is a size-dependent obstacle strength factor, *G* is the shear modulus, *b* is the Burgers vector, and  $f_p$  and  $\langle r_p \rangle$  are volume fraction and mean radius of precipitates, respectively. By fitting to APT or SANS measurement results, Wells et al. [17] obtained the result of  $\sigma_p/\sqrt{f_p}$  as a function of precipitates mean radius  $\langle r_p \rangle$ .

The precipitate hardening contribution is combined with contributions from any preexisting strong features  $\sigma_u$ , here taken as 200MPa, using an  $\alpha_p(\langle r_p \rangle)$ -dependent strength superposition model [55], yielding

$$\Delta \sigma_y = \sqrt{\sigma_p^2 + \sigma_u^2} - \sigma_u \tag{27}$$

Wells et al. [17] also fitted the relationship between change of  $\Delta T$  and the change of yield stress  $\Delta \sigma_y$ , which is given by

$$\Delta T = 0.68 \, \Delta \sigma_y \tag{28}$$

Based on this empirical model, the change of volume fraction of MNSPs and its effect on  $\Delta T$  as a function of fluence for different alloy compositions were calculated and are shown in Figure 10 a) and b), respectively. The flux used here is  $3 \times 10^{14} \text{m}^{-2} \text{s}^{-1}$ , which is a realistic LWR flux. Figure 10 a) shows that for the alloys studied, the evolution of MNSPs are predicted to still be at the nucleation and growth stage from 40 to 80 years, which suggests that there will be more precipitates observed in the future than what has been observed in current surveillance samples. The typical DBTT for RPV steels is usually around -100°C [36] and working temperature of these steels are about 290°C. For the alloys studied here, at 80-year extended life of reactors, the  $\Delta T$  cover a wide range, from several degrees up to more than 400°C. This latter shift would likely move the alloys DBTT to above their 290°C working temperature. These results further

support the point made by Wells, et al. [17] that MNS precipitates can potentially be a major cause of RPV embrittlement and must be understood and included in models as part of life extension considerations. We note that the effect of Cu precipitates must also be added to current RPV steels. The scale of this effect can vary but, e.g., the  $\Delta T$  in 0.04 at. %Cu is calculated to be around 60 °C [56], demonstrating that the Cu effects can add a significant shift to that seen from MNS. In addition, the Cu will accelerate the MSNP formation, as discussed in Sec. 3.2.3. The effect of Cu will be included and shown in Sec. 4.2.3.2.



Figure 10. Effect of compositions on a) volume fraction and b) ductile-brittle-transitiontemperature for low (0.7Mn0.85Ni0.25Si), medium (1.0Mn1.15Ni0.35Si), and high (1.3Mn1.75Ni0.65Si) solute (all values at. %) alloys. The low solute lines are difficult to observe as they are nearly zero.

#### 4.2.2 Update on Mn-Ni-Si precipitates under annealing

This subsection furthers validates the CD model of MNSPs by comparing number density, mean radius and volume fraction of precipitates as well as yield stress recovery from simulation and post-irradiation annealing (PIA). Two alloys, namely ATR1 CM6 and LG, were annealed in experiments after irradiated at flux 2x10<sup>18</sup>m<sup>-2</sup>s<sup>-1</sup> at 290°C to fluence 1.1x10<sup>25</sup>m<sup>-2</sup>. Experimental precipitate size distributions are determined by APT. Since almost all precipitates were dissolved in ATR1 LG alloy after being annealed for 1 week, only ATR1 CM6 alloy has been used for comparison to precipitate size distributions. However, both alloys were used to compare the yield stress recovery after 1 week annealing. For the simulations, the initial precipitate distribution is determined from APT measured precipitate size distributions after irradiation.

Figure 11 shows the comparison of precipitate number density, mean radius and volume fraction between simulation results and experimental data for ATR1 CM6 annealed at 400°C and 425°C, which generally shows good agreements between simulation results and experimental data for both number density and mean radius. The agreement for volume fraction appears less good, but all the values are less than 1%, meaning that just a few tenths of a percent error appears quite significant. Overall the agreement appears similar to that seen for the irradiated materials in Figure 6. One difference is that here the volume fractions all appear to overpredict those seen experimentally, with the errors usually arising from an overprediction of both number density and particle size. The exact origin of these errors is not quite clear. One possible source is in the experimental uncertainty induced by the fact that for some cases extensive annealing leaves just a few precipitates in the tips, which can lead to significant uncertainty in the true precipitate volume fraction. Perhaps the most likely model error is our use of a single constant composition and interfacial energy for the precipitate phases, which could couple strongly to the way the precipitates dissolve and/or coarsen. Figure 12 shows the comparison of yield stress changes due to irradiation between simulation results and experimental data after annealed for 1 week under different temperatures. Yield stress changes were calculated with the same formulas as described in Sec. 4.2.1.4. The large discrepancy between calculation results and experimental data at initial time for LG may either due to the uncertainty of the hardening model we used in Sec. 4.2.1.4 or due to the fact that there are other hardening mechanisms besides precipitates under irradiation which leads to higher yield stress compared to calculation results from precipitates only. As for the yield stress after annealed for 1 week, the figure shows that simulation results agree well with experimental data for higher annealing temperature (425°C and 450°C) but predicts higher yield stress (less recovery) compared to experimental data for lower annealing temperature (350°C, 375°C and 400°C). We believe that this quantitative discrepancy between simulation results and experimental data at lower temperature is due to the recovery of defects after annealing, which is not included in the model. This defect recovery is the dominant mechanism at lower temperature, and so there is a systematic error in the model vs. experiment. While this error is still present at higher temperature, the recovery of yield stress from defects is negligible compared to that from precipitate dissolution and so the systematic error is not readily apparent.



Figure 11 Comparison between simulation results and annealing experimental data under 400°C and 425°C



Figure 12 Comparison of between simulation results and experimental data under annealed at different temperatures. a) CM6; b) LG.

In summary, the semi-quantitative agreements between simulation results and annealing experimental data of both microstructure information measured by APT and mechanical yield stress further validated the cluster dynamics model built for evolution of MNSPs in low-Cu RPV steels.

#### 4.2.3 **Precipitation in Cu bearing alloys**

In this section, we parameterize the CD model of Cu bearing RPVs, proposed in section 3.2.3, and compare the modeling results with experimental data obtained from Odette group at UC-Santa Barbara. Table 9 shows the alloys designation and their corresponding bulk composition.

Alloy	Cu (at.%)	Mn (at.%)	Ni (at.%)	Si (at.%)
LC	0.21	0.97	0.91	0.53
LD	0.21	1.08	1.00	0.52
LH	0.08	0.97	0.72	0.45
LI	0.15	1.21	0.72	0.43

Table 9. Alloys designation and corresponding bulk composition.

Based on the described methodology in section 3.2.3, in copper bearing alloys we have nucleation of both pure Cu and MNSPs. While the Cu is in the nucleation stage we simultaneously nucleate a partner MNSP for each Cu precipitate that appears or grows in the simulation with a size larger than 20 atoms. Each Cu precipitate has one partner MNSP. The partner MSNP is then constrained to grow at the same rate as the Cu during the Cu nucleation phase, and do not grow by the normal mechanisms of MNSP evolution. In this way, we approximate the complex co-formation of Cu and MNSPs in our CD model. When the Cu nucleation stops we decouple the growth of Cu and Mn-Ni-Si and let them grow separately according to their individual thermodynamics and kinetics. We note that the Cu content in all alloys listed in Table 9 is high enough to form Cu-rich precipitates. However, even if Cu is lower than 0.06at.% (the onset of Cu-rich precipitation formation in RPVs [34]), experimental results [57] suggest it can still enhance the nucleation of MNSPs. The effect of very low Cu (Cu<0.06at.%) on MNSP nucleation needs further investigation and has not yet been treated in detail in the model.

#### 4.2.3.1 Parameters for Cu model

The precipitation of Cu in Fe was the subject of several modeling studies [58-64]. However, most of the previous models were for aging, and therefore they did not have the effect of irradiation on Cu precipitate evolution. Furthermore, previous models were generally compared to fairly limited experimental data points (e.g. aging at one single temperature for a fixed composition), which made them inapplicable across the many systems we are studying here. Therefore, we have developed our own model for Cu precipitation under irradiation. However, many necessary terms are available from previous models and we used these to guide the present model. Important parameters in modeling Cu precipitation are Cu solubility, diffusion coefficient, and interfacial energy. We obtain the Cu solubility from Soisson and Fu [64], which they determined by a combination of *ab initio* calculation and fitting to solubility data obtained from Fe-Cu aging at 550 and 450 °C [64]. We note that in RPV steels under irradiation the Cu precipitates sizes are smaller than 5-6 nm which is the onset of Cu structural transformation from BCC to R9 [65]. Therefore, it is important to have the Cu solubility when the equilibrium is between BCC Cu and Fe. The solubility in Ref. [64] was obtained by fitting to experimental data on the BCC Cu and Fe equilibrium. The solubility of Cu is modeled by the equation

$$C_{Cu}^{sol}(Fe) = \exp(\frac{\Delta S_{nc}}{k_B})\exp(-\frac{E_{Cu}^{sol}(Fe)}{k_B T})$$
(29)

where  $\Delta S_{nc}$  is the nonconfigurational entropy,  $E_{Cu}^{sol}(Fe)$  is the formation energy (mixing energy) of a substitutional impurity Cu in Fe matrix,  $k_B$  is Boltzmann constant, and T is the temperature. Soisson and Fu [64] found the  $E_{Cu}^{sol}(Fe) = 0.545 \ eV$  based on *ab initio* calculations and  $\Delta S_{nc} = 1k_B$  by fitting to experimental data.

Another important parameter is the Cu diffusion coefficient. The Cu diffusion coefficient in Fe has a wide range of values in the literature, as shown in Figure 13. Due to this uncertainty, we fit the Cu diffusion coefficient in order to match with the experimentally measured precipitation incubation fluence shown in Figure 14. The last key parameter is the Cu/Fe interfacial energy, which in general depends on the precipitate degree of coherency, crystallographic misorientation, elastic misfit strains, and solute segregation. Because of this complexity, interfacial energy generally cannot be determined reliably from direct experiment or atomistic calculations and it is usually treated as a fitting parameter in precipitation modeling. We fit the interfacial energy of Cu in order to get minimum average absolute value error (compared to experimental data) for

precipitates volume fraction, radius, and number density (shown in Figure 15). Note that the radiation enhanced diffusion necessary to model Cu precipitate evolution is treated exactly as for the rest of the CD model, as described in Sec. 3.2.1.3.



Figure 13. Cu diffusion coefficient in the literature [32, 66-73] and the fitted value in this work.

By using only homogeneous Cu nucleation, we were not able to get enough Cu precipitate nucleation to match the experiments. Specifically, for low Cu alloys like LI and LH which contain 0.15 and 0.08 at.% Cu, we do not see Cu precipitate formation in the fluence ranges for which it is seen experimentally. These inconsistencies indicate that Cu should also nucleate heterogeneously (similar to MNSPs). We note that the phenomenon of heterogeneous Cu nucleation in-cascade has already been reported by KMC modeling [74]. To incorporate the Cu in-cascade heterogeneous nucleation in CD, we use the similar formulation as we used for MNSPs (sections 3.2.1.2), except we modify the thermodynamic driving force to be that of Cu. This approach yields the equation

$$r_{Cu}(t) = \alpha \cdot \sigma \theta / \Omega \cdot \frac{Sol_{Cu}(t)}{Sol_{Cu}^{0}}$$
(30)

where  $\sigma$  is the cross section of cascades,  $\theta$  is irradiation flux,  $\Omega$  is the atomic volume,  $\alpha$  (n/cascade) is generating rate coefficient (which is fitting parameter),  $Sol_{Cu}(t)$  is the Cu concentration in matrix at time t, and  $Sol_{Cu}^0$  is Cu solubility limit. The other fitting parameter (rather than  $\alpha$ ) in heterogeneous Cu nucleation is the precipitate size that is created during a cascade. Odette and Wirth's [74] KMC simulation showed that under irradiation Cu precipitates of size 5 to 20 atoms can form in cascades. Therefore, we fit the Cu precipitate size in the range of 5 to 20 atoms, again fitting to best match the data in Figure 14. Table 10 shows all the fitting parameters for the Cu part of CD model.

Param	eter	Value
1.	$D_{Cu}(m^2/s)$	$1.43 \times 10^{-7} \exp(-\frac{1.91}{k_B T})$
2.	Interfacial energy (Cu-Fe) $(J/m^2)$	0.4
3.	$\alpha$ (#/cascade)	0.2
4.	Heterogeneous Cu precipitate size (# of atoms)	12
5.	Cu precipitate size above which create partner MNSP (# of atoms)	20 and larger
6.	The ratio of the number of atoms in MNSP to the number of atoms in Cu precipitate	1

Table 10. Fitted parameters for Cu part of CD model

In summary, we fit the following parameters 1-6 in the Cu model (following the order of Table 10): (1) Cu Diffusion coefficient, (2) Cu-Fe interfacial energy, (3) number of nucleated Cu precipitates per cascade, (4) number of Cu atoms nucleated in each precipitate when nucleated in a cascade, (5) the size above which Cu precipitates create partner MNSP, and (6) the ratio of MNSP to Cu in the partner MSNP growing with the Cu during Cu nucleation. Although we mentioned the fitting methods above, here we give a compact summary of the fitting order and data used in the fitting.

The ratio of the number of created atoms in MNSP to the number of atoms in Cu precipitates (6) was fit directly by the experimental data of LC and LD alloys in Figure 14, independent of any other parameters. In the plateau part of the experimental data (which corresponds to Cu depletion) in Figure 14 we see the volume fractions of precipitates is about two times of initial Cu (0.2at%). This indicates that we approximately have the same amount of Mn, Ni, and Si as Cu in the precipitates, which implies that the each Cu atom should correspond to one partner MNSP atom.

Also independent of the other parameters we set the minimum number of atoms in Cu precipitates which create the same sized MNSPs (5) to be 20 atoms as that is was close to Cu precipitates critical size. The results turn out to be quite insensitive to this value and we tested numbers between 10 to 100 and the results did not change significantly.

We fit the Cu diffusion coefficient (1) in order to match with the experimentally measured precipitation incubation fluence (the fluence before which significant precipitates appear) shown in Figure 14. This fit is done first with a reasonable guess for values for the parameters (2-4), and then redone again after parameters (2-4) were fit as below, although it is not very sensitive to the values of parameters (2-4). The other remaining parameters (2-4) (interfacial energy (2), Cu precipitate heterogeneous size (4), and  $\alpha$  (3)) were then fit simultaneously in order to get minimum sum of absolute value errors of model vs. experimental values for volume fraction, radius, and number density (data given in Figure 15). The fitting ranges considered were as follows: for interfacial energy we explored 0.370 to 0.420 mJ/m<sup>2</sup> (0.4 is the value used in [34]) with mesh size of 0.01; for the cascade induced Cu precipitate size we explored the range of 5 to 20 atoms (based on KMC simulation in [74]) with an initial coarse mesh size of 5 atoms and then finer mesh of 2 atoms in range of 10 to 15 atoms; for  $\alpha$  we initially considered the range 0.1 to 1.0 with coarse mesh (0.1, 0.5, and 1.0) then the most promising region was explored with a mesh of 0.1.

In Figure 14 we compare the CD model results and experimental data for evolution of precipitates in LC, LD, LH, and LI alloys as a function of fluence.



Figure 14. Comparison between CD model and experimental results for evolution of precipitates in LC, LD, LH, and LI alloys as a function of fluence.

We note that each experimental datum in Figure 14 has its own specific neutron flux (from  $7x10^{14}$  to  $1x10^{18}$  n/m<sup>2</sup>/s) and temperature (from 270 to 310 °C) and these are the ones used in the CD model. To compare the CD and experimental results more quantitatively, we plotted the CD predicted vs. actual values of precipitate radius, number density, and volume fraction in Figure 15.



Figure 15. Comparison between CD and experimental results for precipitates number density, radius, and volume fraction.

From Figure 14 and Figure 15 we can see that, except for the highest fluence data point (which corresponds to ATR1), the calculation results show a good agreement with the experimental results for a wide range of neutron flux (from  $7x10^{14}$  to  $1x10^{18}$  n/m<sup>2</sup>/s), temperature (from 270 to 310 °C), fluence and composition. While we do not know exactly the cause of the CD predicted low number density (and consequently low volume fraction) for ATR1 data,<sup>1</sup> we note that these data points have the highest neutron flux in data set, which could cause some radiation induced precipitation due to radiation induced segregation, which currently is not in the model. Similar problems were noted in the model predictions vs. other ATR1 data, as discussed in the previous report and in Sec. 4.2.1.

To further benchmark our Cu precipitation model for a different range of temperatures and compositions, we used the Cu parameters found for irradiated data to predict the Cu precipitation in Fe1.82at.%Cu0.2C1.38Al2.67Ni1.0Si0.5Mn under aging at 500 °C [75]. The comparison to these aging data is relevant as the alloy contains some amount of Mn, Ni, and Si, similar to the irradiated alloys being studied here. These elements can form a coating layer around Cu precipitates and mimic the similar morphology as we see in our KMC simulations and APT experiments of the RPV model alloys. Figure 16 shows the predicted Cu precipitates size and number density against experimental data [75]. The very good agreement between CD model (based on fitting parameters in Table 10) and experimental data strongly supports the validity of the Cu model. We also note that our model for Cu, which was fit to irradiation data on alloys with significant concentrations of other impurities, is only valid for other alloys with significant impurities. Tests for alloys without impurities (pure Fe-Cu) show significant discrepancies with our model predictions (Figure 17). This result is important as it shows that Cu models which do not explicitly treat interfacial segregation to the Cu/Fe interface must be used only in the domain of alloys with similar impurity content as the interfacial segregation effects have been renormalized into effective parameters in the model, e.g., the interfacial energy.



Figure 16. Comparison between CD model and experimental data [75] of Cu precipitation under aging at 500 °C. We note that the CD model parameters used here (Table 10) were obtained from fitting to irradiation data and not the data in this figure.



Figure 17. Comparison between CD model and experimental data [76-78] of Cu precipitation in pure Fe-1.34at.%Cu under aging at 500 °C. The CD parameters used here (Table 10) were obtained from fitting to irradiation data. Poor agreement between modeling and experimental data compared with good agreement in Figure 16 suggests the dramatic effects of other impurities (e.g. Mn, Ni, and Si) on the precipitation of Cu.

Another benchmark to show that the selected parameters (specifically interfacial energy) in Table 10 are in agreement with other experimental observations is to compare our prediction to experimental data on the minimum Cu for formation of Cu precipitates. The residual Cu in the RPV matrix is higher than equilibrium solubility limit due to excess free energy of precipitatematrix interface, which is important for nanometer-size scales (the Gibbs Thompson effect). Based on test reactor data the minimum Cu threshold for forming Cu precipitates (these precipitates are likely decorated at the interface with other impurities, so we will refer to them as Cu-rich precipitates, or CRPs) is between ~ 0.05 and 0.08at.% Cu [39-41], and the EONY model uses 0.06at.% Cu as the minimum Cu for formation of CRPs [34]. In Figure 18 we plot the Cu fraction in the matrix verses fluence (flux=1x10<sup>16</sup> n/m<sup>2</sup>/s and T= 290 °C) for different Cu levels (other elements are set at at.% 0.97Mn0.91Ni0.53Si). Figure 18 shows that for Cu lower than 0.06at.% the Cu fraction remains constant in the matrix which indicate that no Cu precipitation forms for Cu lower than 0.06at.% which is in good agreement with test reactor data and ENOY model. Again, we note that this agreement is for alloys with significant concentrations of impurities that segregate to the Cu/Fe interface.



Figure 18. The minimum Cu (at.%) for formation CRP in RPV steels based on parameters in Table 10 (flux= $1 \times 10^{16} \text{ n/m}^2$ .s , T= 290 °C, 0.9Mn0.9Ni0.25Si (at.%)).

#### 4.2.3.2 The effects of Cu on ductile-to-brittle transition temperature

As already discussed, Cu has very low solubility limit and high diffusion coefficient (compared with Mn, Ni, and Si) in Fe, which leads to very fast precipitation of supersaturated Cu. On the other hand, atomic interactions between solutes drag Mn-Ni-Si toward Cu precipitates. Therefore, Cu works as a catalyst in the formation of MNSPs. Figure 19 shows the predicted effect of Cu in formation of second phase precipitates and ductile-to-brittle transition temperature (DBTT) for an alloy with medium solute content (1.0Mn1.0Ni0.2Si0.2Cu, at.%) under LWR conditions (3x10<sup>14</sup> n/m<sup>2</sup>.s and 290 °C). Figure 19 shows that at the absence of Cu there is no DBTT up 60 years operation while, at the presence of just 0.2at.% Cu, the alloy will experience up to 250 °C in DBTT at 60 years operation. Figure 19 also shows that at the presence of Cu DBTT, which is due to co-precipitation of Cu and Mn-Ni-Si (CRPs). In the second regime, the embrittlement slope is lower than the first regime, and this regime corresponds to Cu depletion in the matrix and slow growth of MNSPs. Finally, the third regime is a plateau with no further embrittlement in RPV. This regime corresponds to complete depletion of Mn-Ni-Si in the matrix and MNSPs coarsening.

In Figure 20 we plot the evolution of precipitate volume fraction and DBTT for a low solute 0.7Mn0.85Ni0.25Si0.1Cu, medium solute 1.0Mn1.15Ni0.35Si0.2Cu, and high solute 1.3Mn1.75Ni0.65Si0.3Cu alloy under LWR conditions  $(3x10^{14} \text{ n/m}^2\text{.s} \text{ and } 290 \text{ °C})$ . This plot is similar to Figure 10 except it has Cu included in the alloys. One key result that we can get from Figure 19 and Figure 20 is a qualitative understanding of the status of current RPVs in present reactors. The oldest operating reactor in the USA is less than 50 years old (Oyster Creek, Operating since 1969). Therefore, majority of current RPVs are still in the precipitation growth regime, which indicates that the embrittlement data that we have from surveillance are lower than what the RPV steels will likely experience under life extension. This result is similar to that found in Sec. 4.2.1.4 from the model without Cu, although the inclusion of Cu in the model accelerates the amount of precipitation predicted at earlier times and suggests we may be able to observe most of the precipitate hardening already after ~40-50 years in the highest solute containing steels.

In Figure 21 we include similated volume fraction and DBTT values for range of alloys both without and with Cu (this figure simply combines results from Figure 10 and Figure 20) to show the effect of Cu at different solute level. As the Figure 21 shows, the model predicts that in the presence of Cu, even as low as 0.1at.%, there is a dramatic enhancement in precipitation formation in RPVs.



Figure 19. The effect of Cu on precipitates volume fraction and ductile-to-brittle transition temperature under LWR conditions ( $3x10^{14}$  n/m<sup>2</sup>.s and 290 °C).



Figure 20. Precipitates volume fraction and ductile-to-brittle transition temperature as a function of time for low (0.7Mn0.85Ni0.25Si0.1Cu), medium (1.0Mn1.15Ni0.35Si0.2Cu), and high (1.3Mn1.75Ni0.65Si0.3Cu) solute alloys (all values at. %) under LWR conditions ( $3x10^{14}$  n/m<sup>2</sup>.s and 290 °C).



Figure 21. The effect of solute content on precipitate volume fraction and ductile to brittle transition temperature evolution in alloys with and without Cu under LWR conditions  $(3x10^{14} n/m^2/s and 290 \text{ °C})$ . Alloys compositions: low solute 0.7Mn0.85Ni0.25Si(0.1Cu), medium solute 1.0Mn1.15Ni0.35Si(0.2Cu), and high solute 1.3Mn1.75Ni0.65Si(0.3Cu) (all values at. %).

### 5. SUMMARY OF MAJOR RESULTS

### 5.1 Kinetic Monte Carlo (KMC)

- KMC simulations were used to reproduce the formation of the Cu-MnNiSi appendage microstructure during co-precipitation. The KMC models also provided insights on Cu+ Mn-Ni-Si precipitates (MNSPs) growth to help model the coupled evolution with cluster dynamics.
- Detailed analysis indicates that there exists a diffusion path for MnNiSi atoms through the Cu core, pushing the Cu core to the edge of the Cu-MnNiSi precipitate and creating Cu-core-MnNiSi-appendage structure.
- This diffusion path is a novel growth mechanism that may occur in other multicomponent co-precipitation systems.

### 5.2 Cluster Dynamics

### 5.2.1 Cu-free alloys

- A heterogeneous nucleation mechanism of nucleating on damage caused by cascades plays a critical role in the nucleation of MNSPs in RPV steels, although the specific form of the nucleation rate needs to be further validated and potentially revised, perhaps by more detailed molecular modeling and fitting to experimental data.
- Semi-quantitative agreement between simulation results and annealing experiments further validated the cluster dynamics model for evolution of MNS precipitates in low-Cu steels.
- RPV alloys with similar compositions to the model alloys studied here are predicted be at the growth stage of the evolution of MNS precipitates under present reactor conditions, which suggests that significantly more precipitates will be observed than what has been observed to date in current surveillance samples. Predictions of volume fraction of precipitates as a function of fluence for a range of compositions is given under realistic reactor conditions to allow quick estimation of the volume fraction of MNS precipitates at a specific time.
- At LWR end of extended life fluence, there can be as large as 400°C ductile-brittletransition-temperature (DBTT) increase caused by MNSPs for very high Ni (1.75at.%)

and Mn (1.30at .%) alloy, which suggests that MNS precipitates must be understood and included in models as part of life extension considerations.

#### 5.2.2 Cu bearing alloys

- Even a small amount of Cu (e.g. 0.08at.%) can dramatically enhance the speed of RPV steel embrittlement by catalyzing the formation of MNSPs.
- We have developed a semi-quantitative model for Cu precipitation on irradiation and ageing in alloys with significant impurities that segregate to the Cu/Fe interface. The model predictions showed very good agreement with Cu aging experimental data at 500 °C and Cu solubility limits even though neither data set was used in fitting the model.
- The Cu DBTT curve is predicted to have three different regimes, in agreement with APT observations of precipitates from UCSB. The first regime has a very sharp DBTT growth due to fast Cu precipitation (along with its attached "partner" MNSP). The second regime has slow DBTT growth due to slow growth of MNSPs, and the third regime is a near plateau in DBTT that corresponds to Mn-Ni-Si depletion in the matrix and MNSP coarsening.
- For LWR conditions (3x10<sup>14</sup> n/m<sup>2</sup>/s and 290 °C), unlike Cu-free RPV steels, where their major embrittlement starts around 50 years of operation (for medium solute containing alloys, i.e. 1.0at.%Mn1.0Ni0.4Si), Cu bearing alloys (Cu>0.1at.%) experience embrittlement from very beginning of operation.

#### 6. FUTURE WORK

The main focus of additional work in the KMC modeling will be on completing the understanding of the appendage growth with a few additional tests to confirm the mechanistic understanding we have developed. The main focus of additional CD work will be extending the Cu+MNSP model to lower Cu-bearing alloy (lower than 0.06at.% when the CRP will not form), identifying an improved RIS model to treat high-flux conditions like ATR1, enhancing the model beyond simple p-scaling for treating radiation enhanced diffusion, and refining the model by fitting to the complete IVAR hardening database through empirical mechanical property models. Additional work beyond the KMC and CD models described here is focused on exploring new atom probe experiments on Cu precipitation to better understand flux effects and applying machine learning to predicting mechanical property changes in RPVs.

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