

Defect Sinks and Their Reactions

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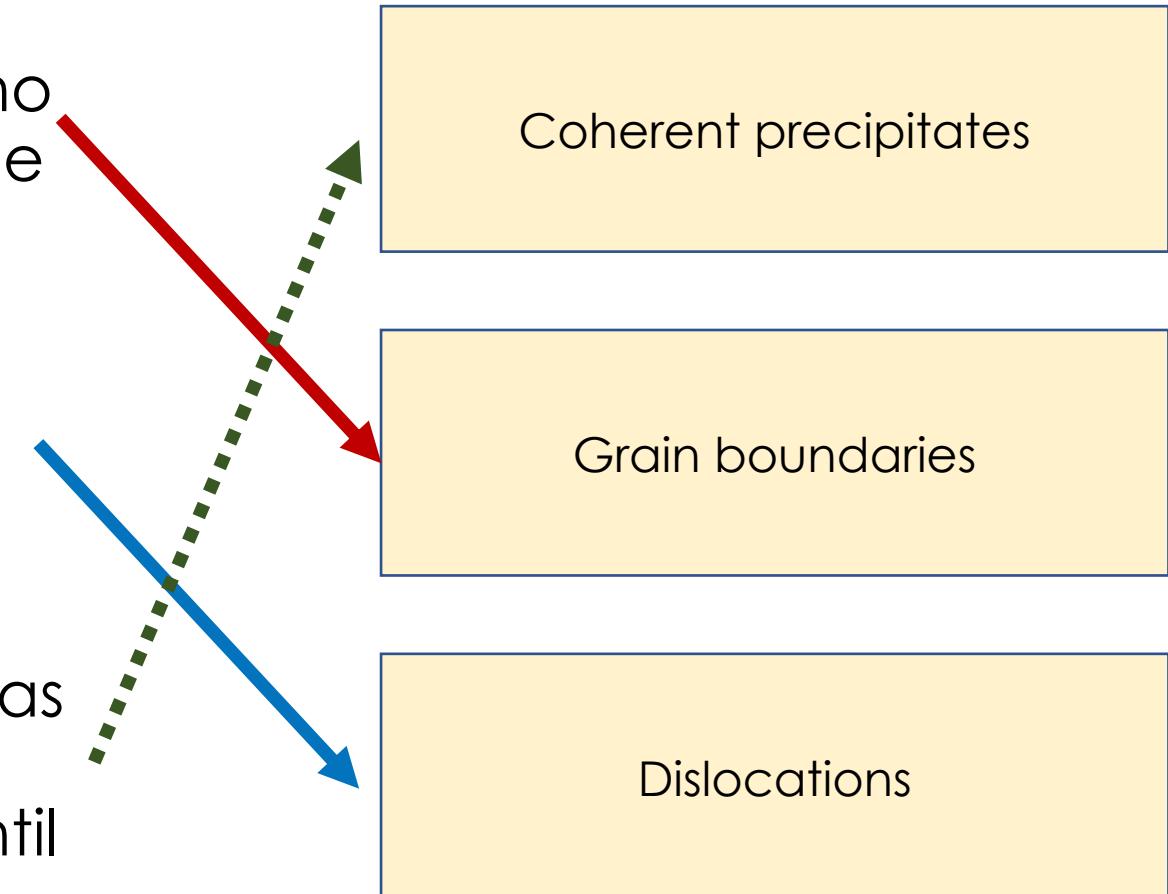
Sink types

- Sinks can behave differently:

- **Neutral sinks:** Neutral sinks show no preference for capturing one type of defect over another.

- **Biased sinks:** Biased sinks show a preferential attraction for one defect over another.

- **Variable sinks:** Variable sinks act as traps for defects which hold the defect but preserve its identity until annihilation or it is released.



Sink Type II - Cavities

The rate of absorption per cavity is then given as:

$$j_{i,v}^{Cavity} = 4\pi r_o D_{i,v} C_{i,v}^{bulk}$$

Considering all cavities using N_c (cavities per unit volume), we get:

$$J_v^C = 4\pi r_o N_c D_v C_v^{bulk}$$

$$J_i^C = 4\pi r_o N_c D_i C_i^{bulk}$$

Then:

Point Defect Kinetic Equations

- If we neglect clustering:

$$\frac{\partial C_v}{\partial t} = K_0 - K_{iv}C_iC_v - \sum_s K_{vs}C_vC_s + D_v\nabla^2C_v$$

$$\frac{\partial C_i}{\partial t} = K_0 - K_{iv}C_iC_v - \sum_s K_{is}C_vC_s + D_i\nabla^2C_i$$

- Example of defect absorption to cavities:

$$\frac{\partial C_v}{\partial t} = K_0 - K_{iv}C_iC_v - z_vp_dD_vC_v + 4\pi R_cN_cD_vC_v$$

$$\frac{\partial C_i}{\partial t} = K_0 - K_{iv}C_iC_v - z_ip_dD_iC_i + 4\pi R_cN_cD_iC_i$$

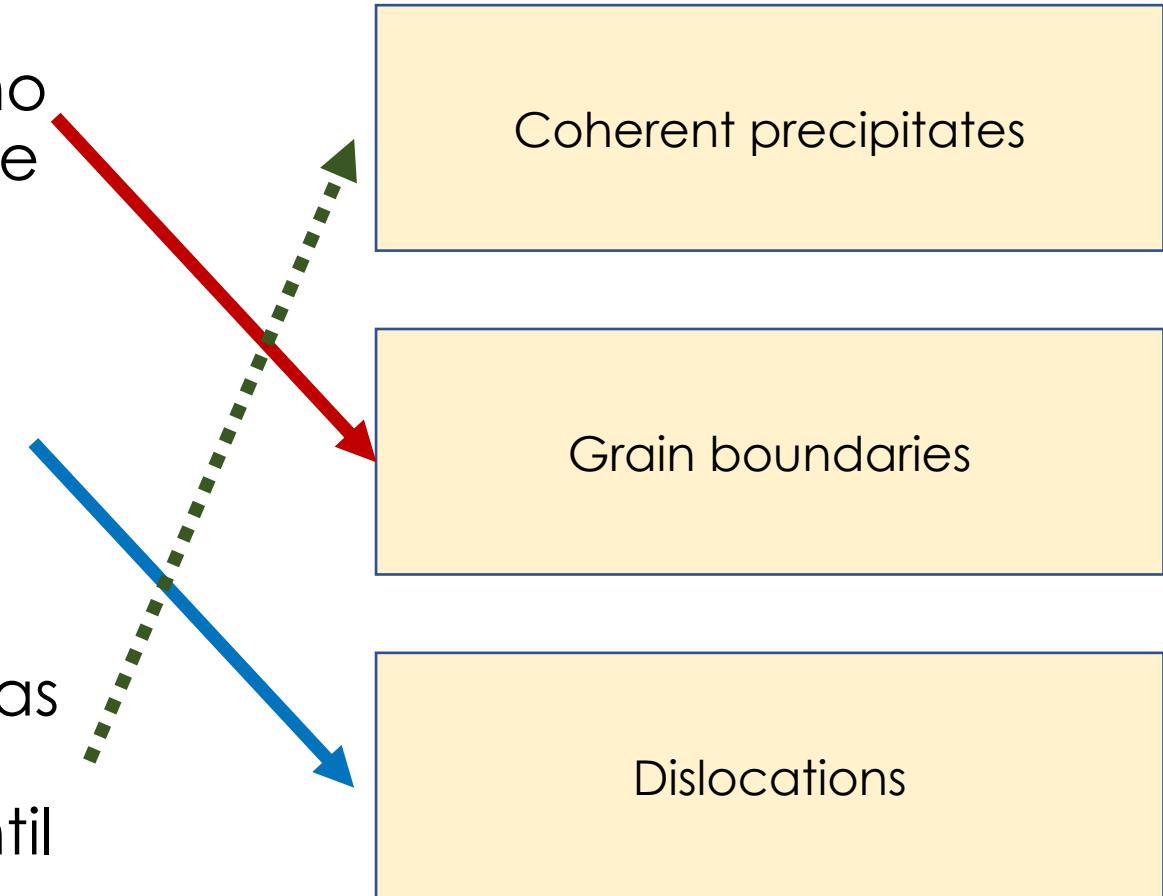
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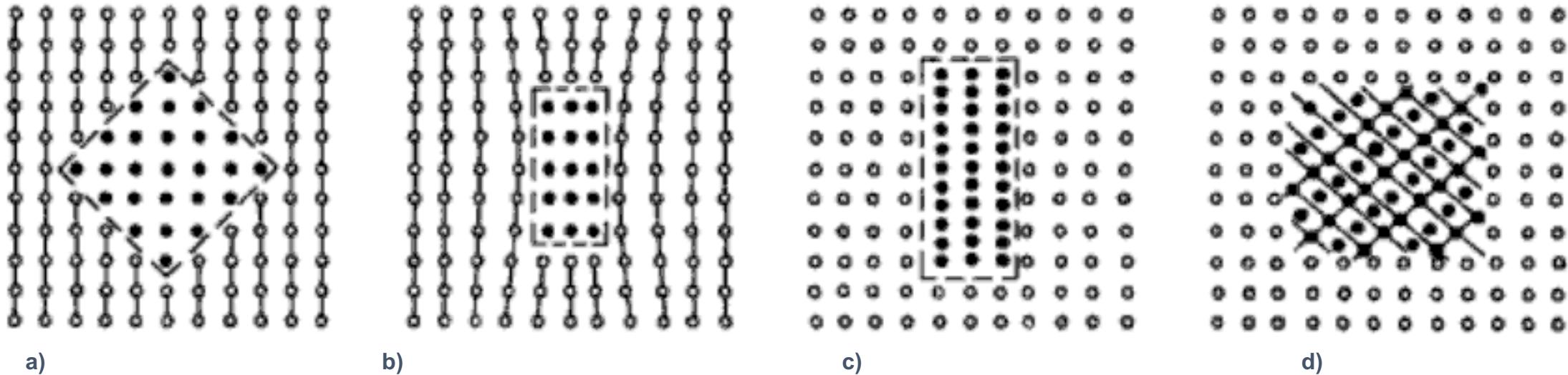
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Sink Type III – Coherent Precipitates (PPTs)



- Precipitates are the result of the local solubility limit being reached causing a new phase to form
- Precipitates can be either coherent, partially coherent or incoherent
 - Coherency: a perfect lattice match between the PPT and matrix
 - Coherency affects how dislocations interact with the PPT
 - Coherency can also affect diffusion in and around the PPT

Sink Type III – Coherent Precipitates (PPTs)



- Precipitates impede dislocation motion
- Inclusion of precipitates can strengthen a material

Sink Type III – Coherent Precipitates (PPTs)

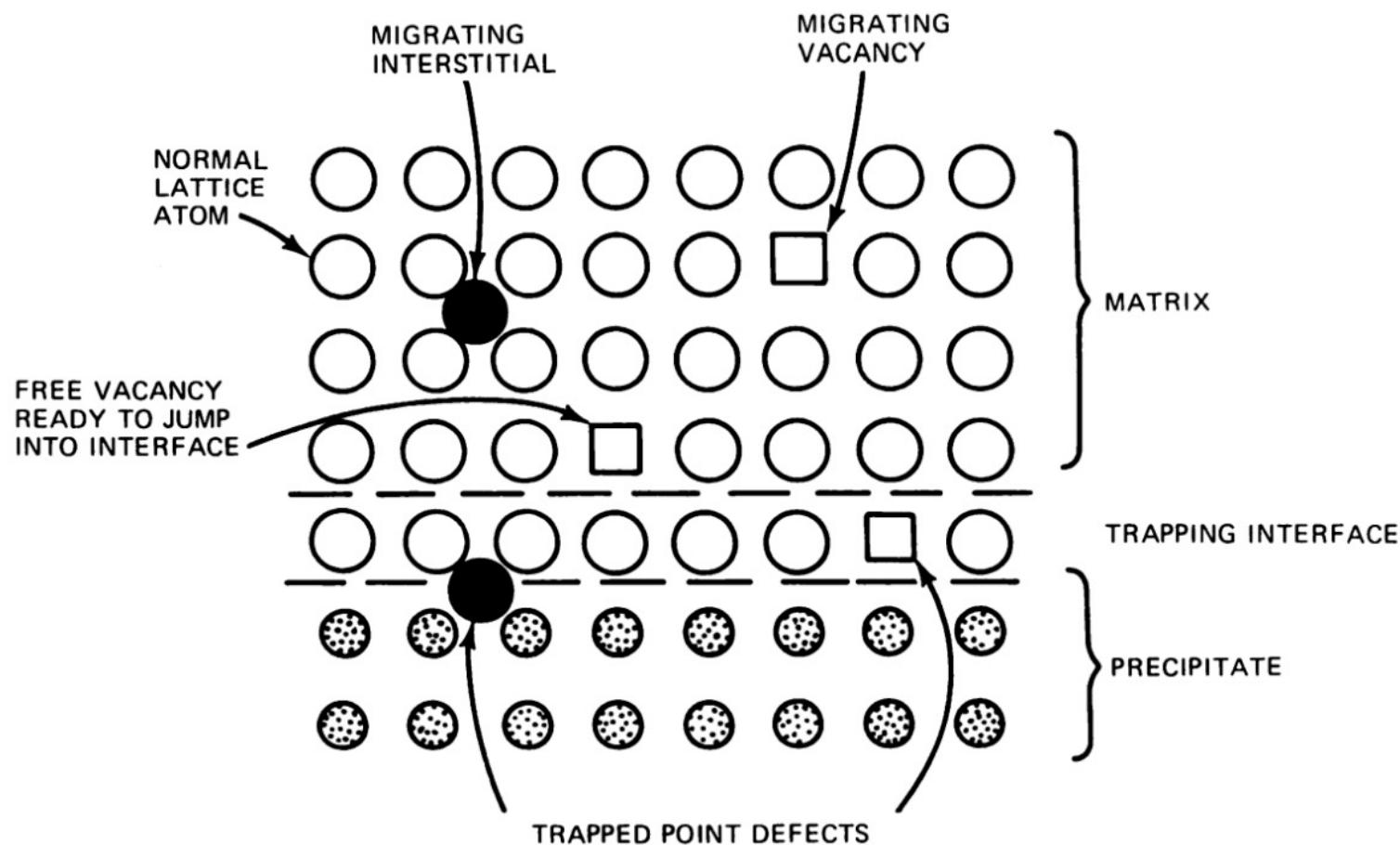


Fig. 19.14 Schematic diagram of the interface between a coherent precipitate particle and the host matrix. (After Ref. 23.)

Sink Type III – Coherent Precipitates (PPTs)

- Coherent precipitates act as traps
- Bias to interface depends on the other biased sinks present in the microstructure (such as dislocations!)
- Vacancies and interstitials reduce the strain field at the trap due to the lattice mismatch

Putting it together:

Table 5.2 Reaction rate constants for defect–sink reactions

Reaction	Rate constant	Sink strength	Eq. #
v + v	$K_{2v} = \frac{z_{2v}\Omega D_v}{a^2}$	—	Equation (5.58)
i + i	$K_{2i} = \frac{z_{2i}\Omega D_i}{a^2}$	—	Equation (5.58)
v + i	$K_{iv} = \frac{z_{iv}\Omega D_i}{a^2}$	—	Equation (5.61)
v, i + void			
Reaction rate control	$K_{vv} = \frac{4\pi R^2 D_v}{a} \quad K_{iv} = \frac{4\pi R^2 D_i}{a}$	$k_{vv}^2 = k_{iv}^2 = \frac{4\pi R^2 \rho_v}{a}$	Equation (5.65)
Diffusion control	$K_{vv} = 4\pi R D_v \quad K_{iv} = 4\pi R D_i$	$k_{vv}^2 = k_{iv}^2 = 4\pi R \rho_v$	Equation (5.84)
Mixed rate control	$K_{vv} = \frac{4\pi R D_v}{1 + \frac{a}{R}} \quad K_{iv} = \frac{4\pi R D_i}{1 + \frac{a}{R}}$	$k_{vv}^2 = k_{iv}^2 = \frac{4\pi R \rho_v}{1 + \frac{a}{R}}$	Equation (5.102)
v, i + dislocation			
Diffusion control	$K_{vd} = \frac{2\pi D_v}{\ln(\mathcal{R}/R_{vd})} \quad K_{id} = \frac{2\pi D_i}{\ln(\mathcal{R}/R_{id})}$	$k_{vd}^2 = \frac{2\pi \rho_d}{\ln(\mathcal{R}/R_{vd})} \quad k_{id}^2 = \frac{2\pi \rho_d}{\ln(\mathcal{R}/R_{id})}$	Equations (5.99, 5.100)
Reaction rate control	$K_{vd} = z_{vd} D_v \quad K_{id} = z_{id} D_i$	$k_{vd}^2 = z_{vd} \rho_d \quad k_{id}^2 = z_{id} \rho_d$	Equation (5.67)
Mixed rate control	$K_{vd} = \frac{D_v}{\frac{1}{z_{vd}} + \frac{\ln(\mathcal{R}/R_{vd})}{2\pi}} \quad K_{id} = \frac{D_i}{\frac{1}{z_{id}} + \frac{\ln(\mathcal{R}/R_{id})}{2\pi}}$	$k_{vd}^2 = \frac{\rho_d}{\frac{1}{z_{vd}} + \frac{\ln(\mathcal{R}/R_{vd})}{2\pi}} \quad k_{id}^2 = \frac{\rho_d}{\frac{1}{z_{id}} + \frac{\ln(\mathcal{R}/R_{id})}{2\pi}}$	Equation (5.104)
v, i + grain boundary			
Diffusion control	$K_{vgb} = 4\pi D_v d \quad K_{igb} = 4\pi D_i d$ $K_{vgb} = \pi k D_v d^2 \quad K_{igb} = \pi k D_i d^2$	$k_{gb}^2 = 24/d^2, \quad d < 10^{-3} \text{ cm}$ $k_{gb}^2 = 6k/d, \quad d > 10^{-3} \text{ cm}$	Equation (5.115) Equation (5.116)
v, i + coherent ppt	$K_{vCP} = 4\pi R_{CP} D_v Y_v, \quad K_{iCP} = 4\pi R_{CP} D_i Y_i$	$k_{vCP}^2 = 4\pi R_{CP} \rho_{CP} Y_v, \quad k_{iCP}^2 = 4\pi R_{CP} \rho_{CP} Y_i$	Equation (5.120)

Radiation Induced Segregation (RIS)

- RIS at grain boundaries
- Some “classic” examples
- Modeling RIS in binary alloys

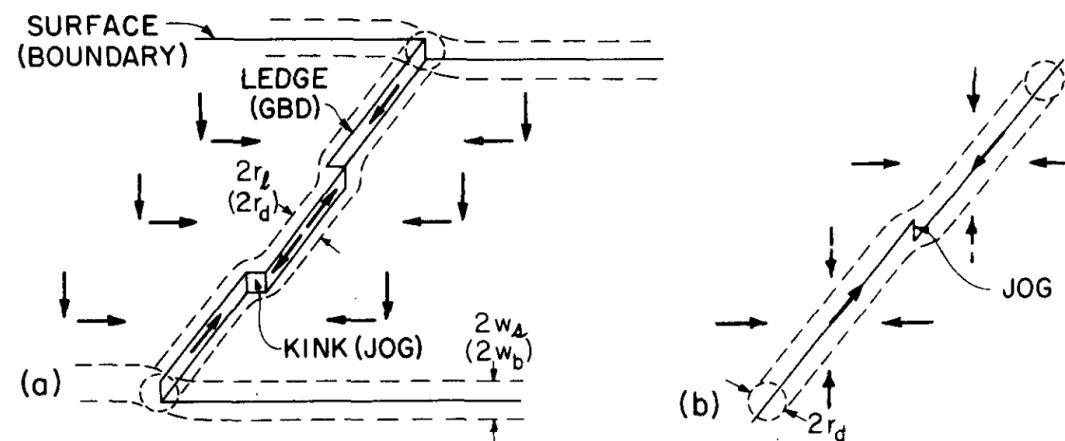


Fig. 4. Model for diffusion: (a) at void surface, or, alternatively, at grain boundary (parentheses); (b) at dislocation loop segment.

- **Goal:** Understand the role of diffusion imbalances on the occurrence of RIS in multi-component alloys



Danger!



This is the first meme that pops up when you google “danger meme”

Radiation Induced Segregation in High Chromium
Ferritic/Martensitic Steels

By

Kevin G. Field

A dissertation submitted in partial fulfilment of the requirements for the degree of

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(Materials Science)

at the

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2012

Date of final oral examination: 11/9/12

The dissertation is approved by the following members of the Final Oral Committee:

Todd Allen, Associate Professor, Engineering Physics

Jake Blanchard, Professor, Engineering Physics

Paul Voyles, Associate Professor, Materials Science and Engineering

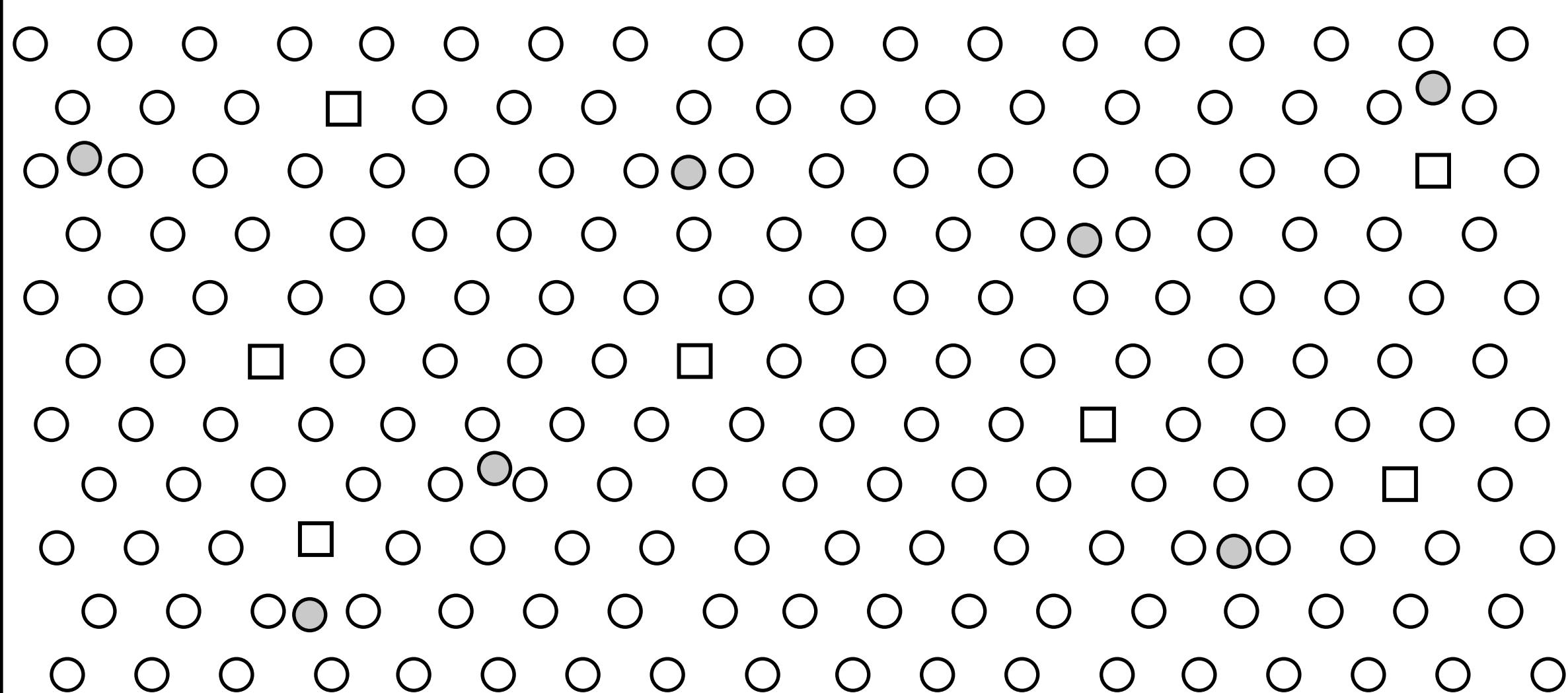
John Perepezko, Professor, Materials Science and Engineering

Dane Morgan, Associate Professor, Materials Science and Engineering

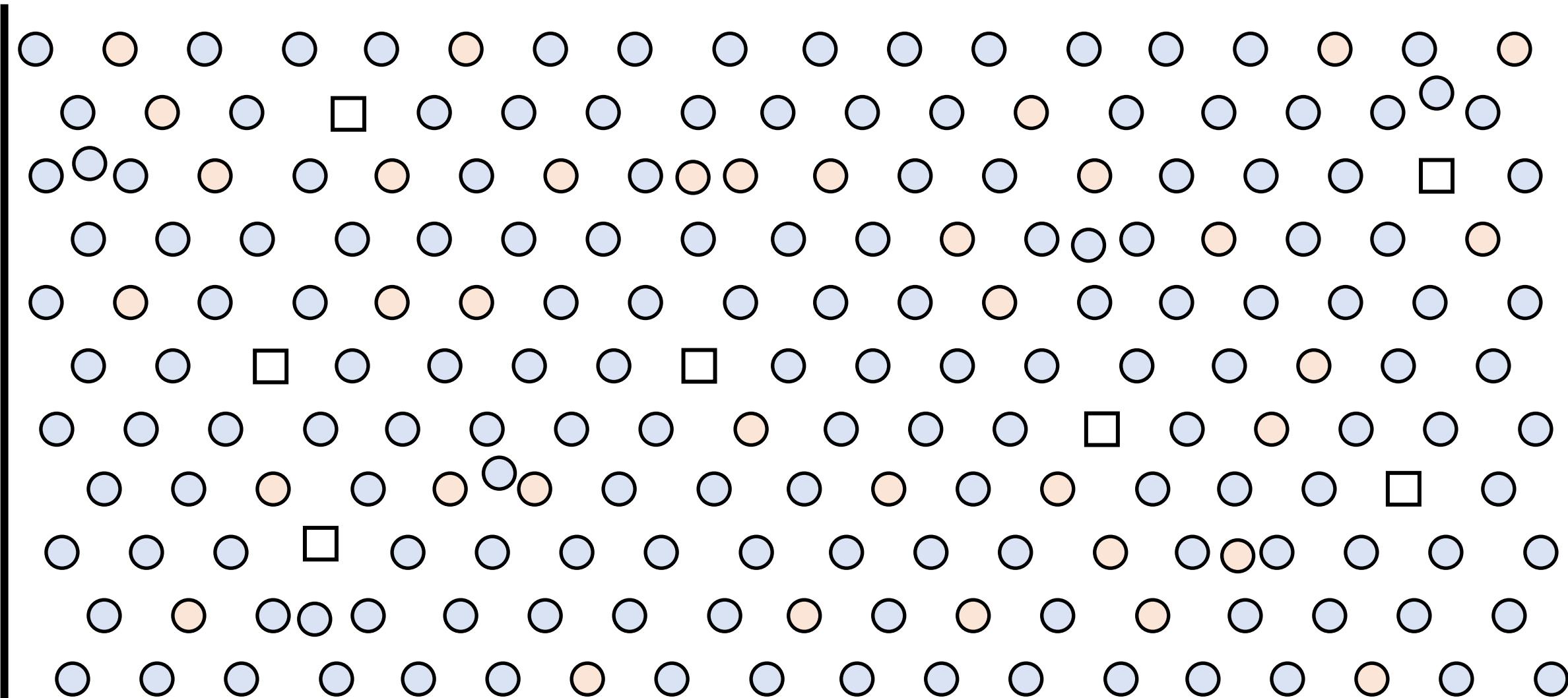
Radiation-induced segregation

The segregation-induced at defect sinks due to preferential association of defects with a particular alloying component and/or preferential participation of a component in defect diffusion.

Current vision of radiation damage



Closer to reality...



Sink (GB, loop, void, etc...)



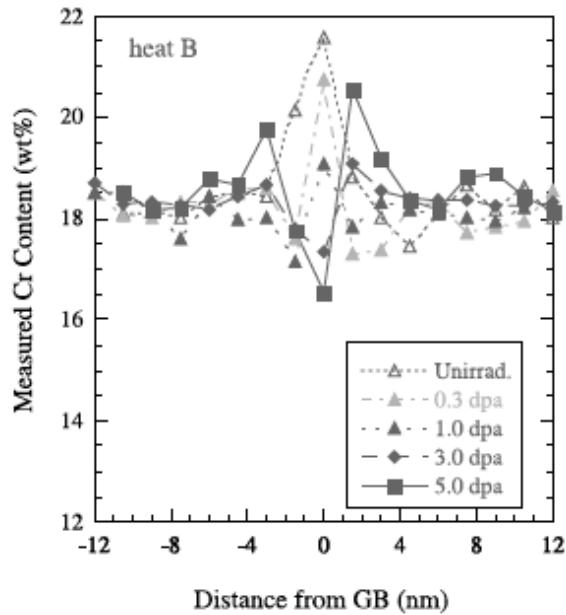
THE classic examples



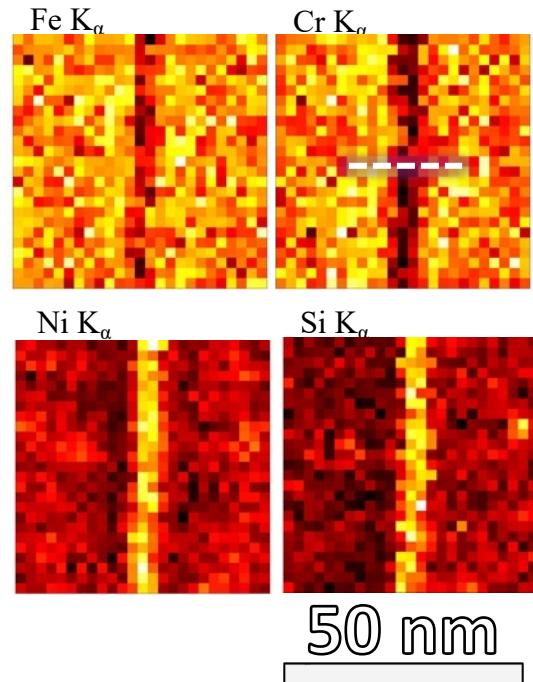
Formation of Ni_3Si precipitates in undersaturated solid solution under irradiation (left) in the bulk on preexisting dislocations and at interstitial dislocations, (center) at grain boundaries, and (right) at free surfaces. Reproduced from Holland, J. R.; Mansur, L. K.; Potter, D. I. Phase Stability During Radiation; TMS-AIME: Warrendale, PA, 1981.

Example of RIS in austenitic stainless steels

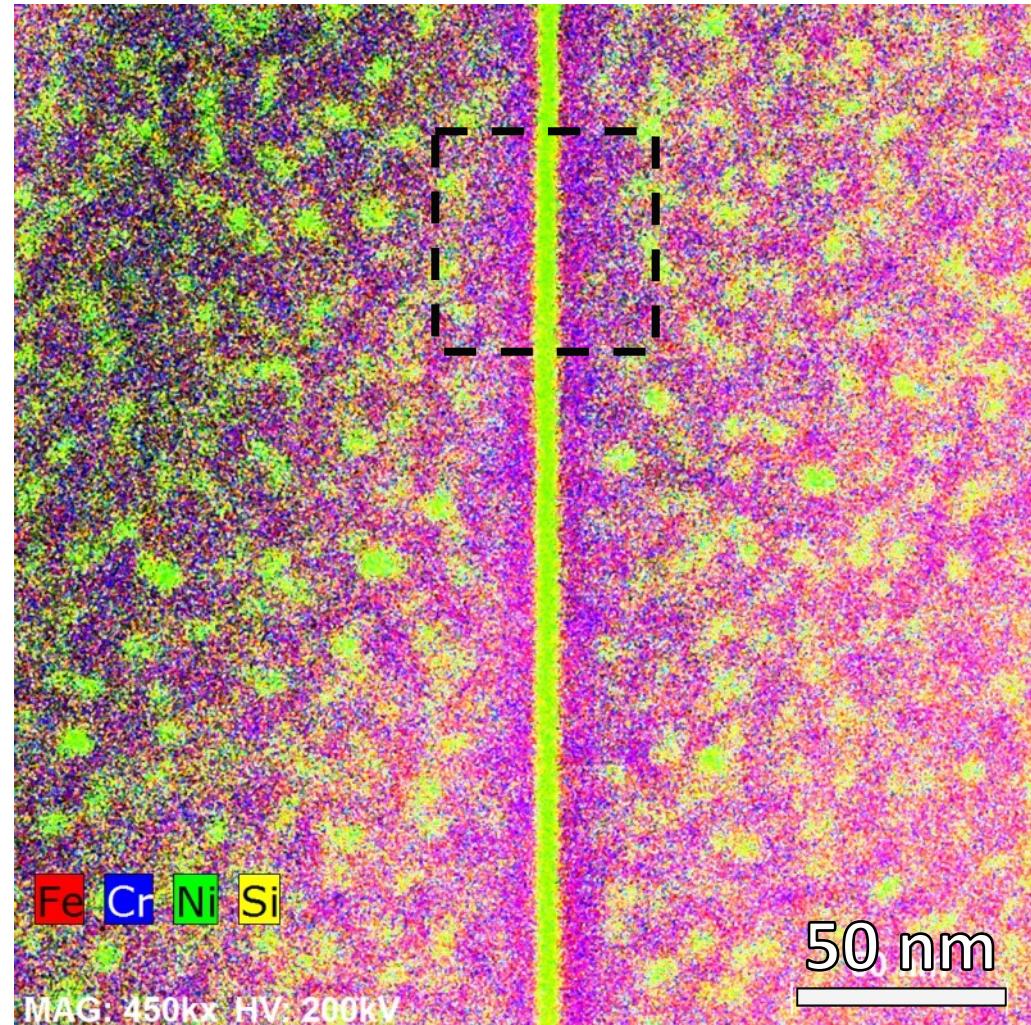
My thesis advisor's
data (2002)



My data (2013)

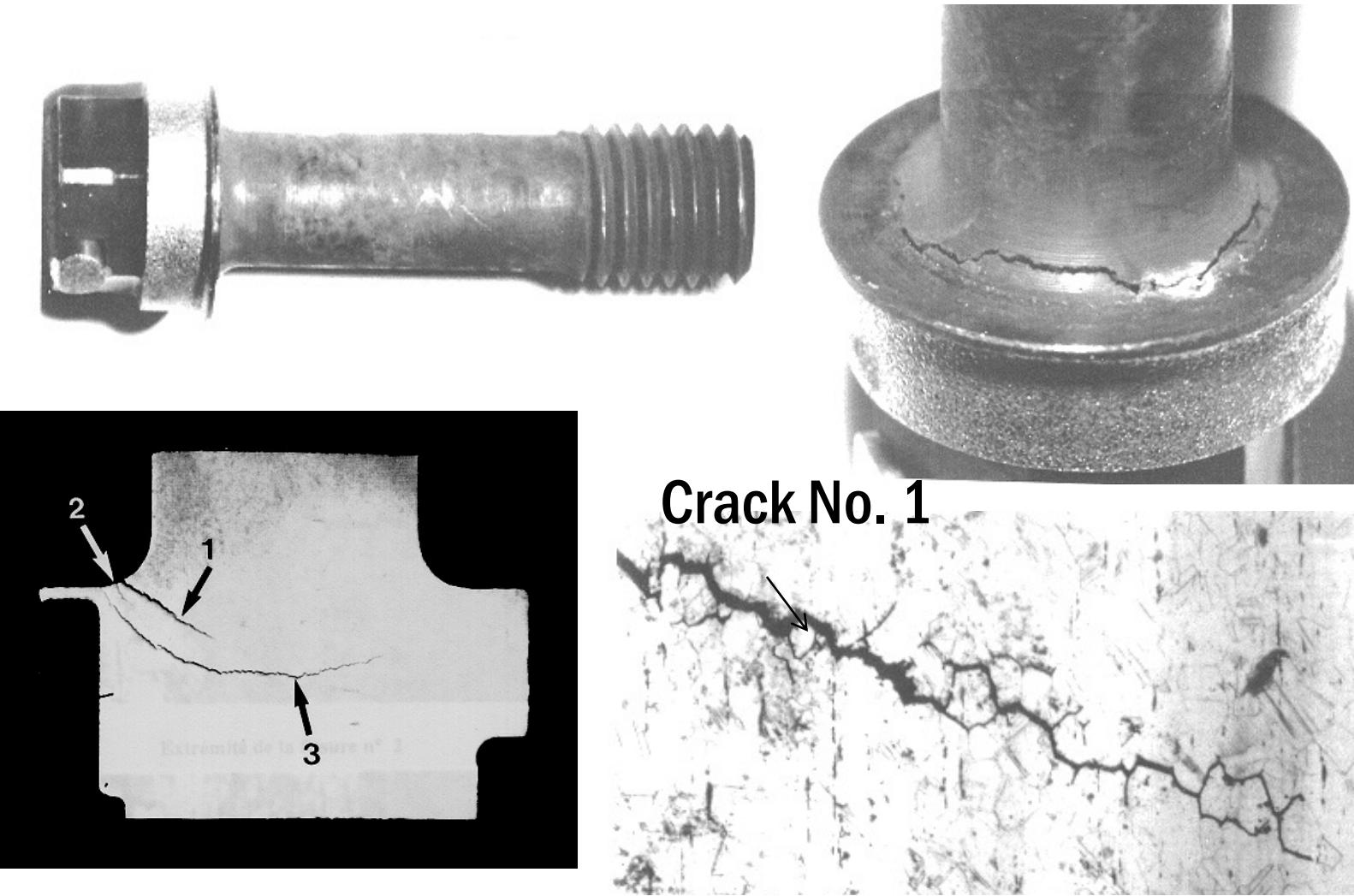


My post-docs data (2017)



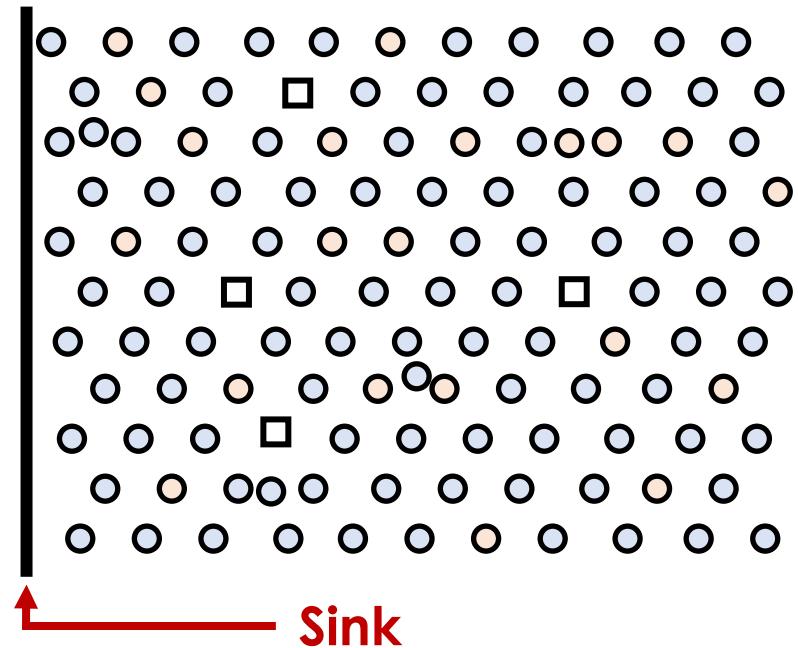
All are <1 hr scans on irradiated
(5.5-10.2 dpa) austenitic stainless steel!

Basis for looking at and understanding RIS:



Source: G.S. Was

RIS visual



- Motion of defects means motion of atoms

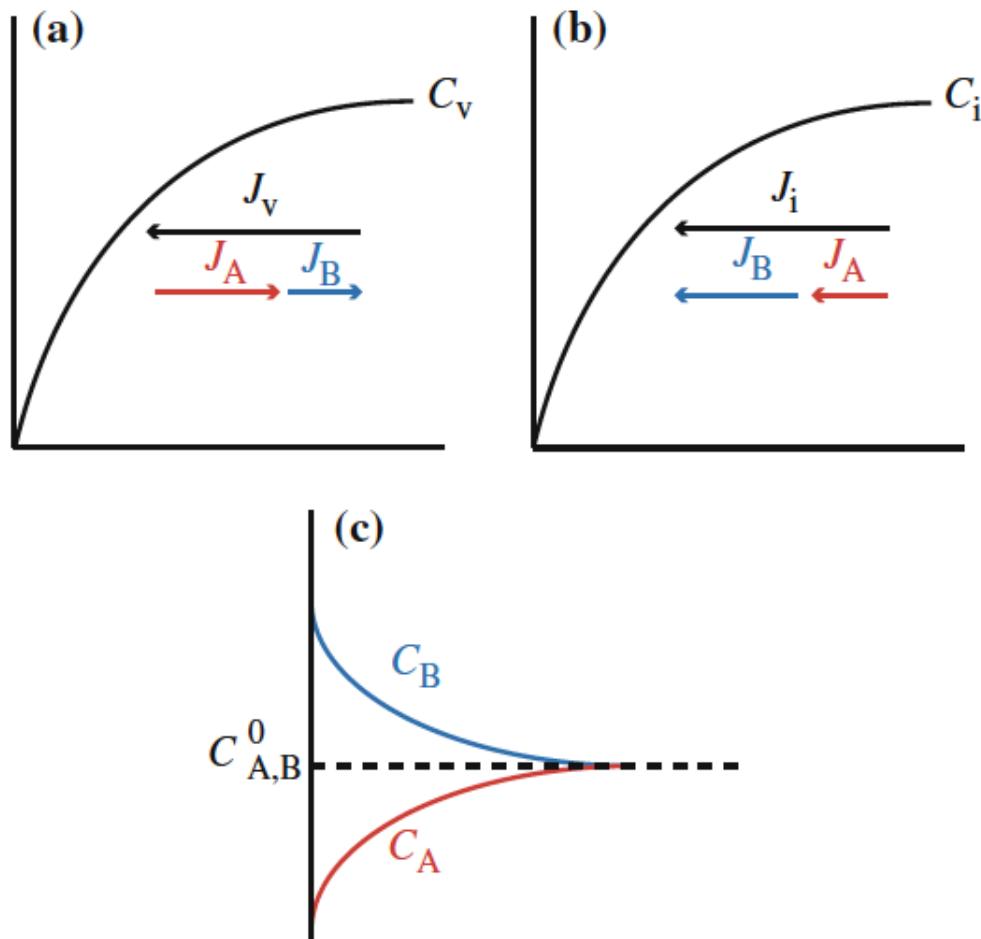
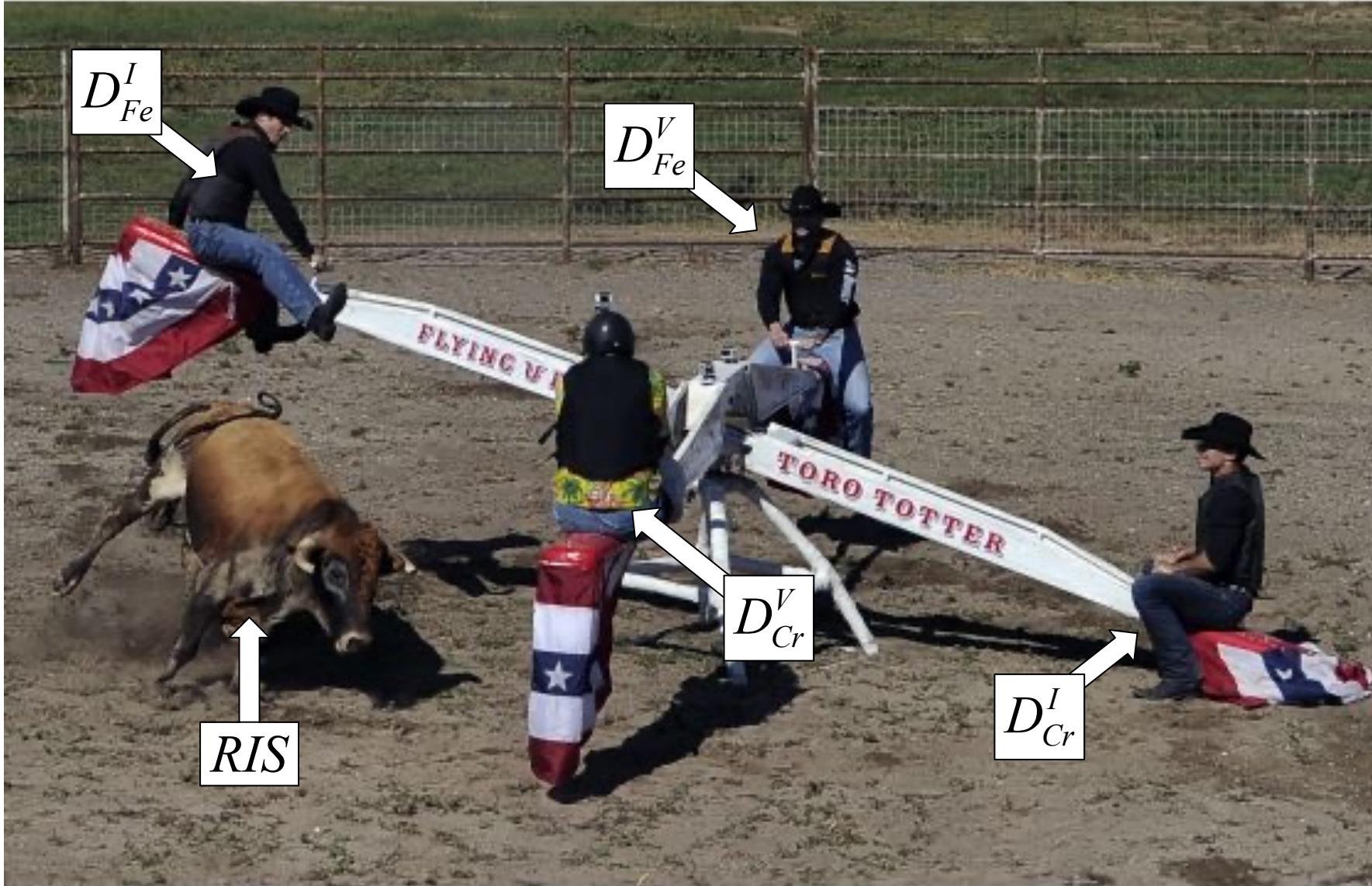


Fig. 6.2 Schematic of radiation-induced segregation in a binary, 50 % A–50 % B system showing (a) the development of the vacancy concentration profile by the flow of vacancies to the grain boundary balanced by an equal and opposite flow of A and B atoms, but not necessarily in equal numbers, (b) the development of the interstitial concentration profile by the flow of interstitials to the grain boundary balanced by an equal flow of A and B atoms migrating as interstitials, but not necessarily in equal numbers, (c) the resulting concentration profiles for A and B

RIS becomes a balancing act



Let's model a concentrated alloy of A & B atoms, e.g. A_xB_{x-1}

Assumptions:

- A & B atoms are distributed uniformly throughout (e.g. no long or short range ordering)
- Sink is acting in the perfect sink condition (black hole)

First, let's define the general kinetics equations

Since we now have A & B atoms:

$$\frac{\partial C_\nu}{\partial t} = -\nabla J_\nu + K_0 - K_{i\nu} C_i C_\nu$$

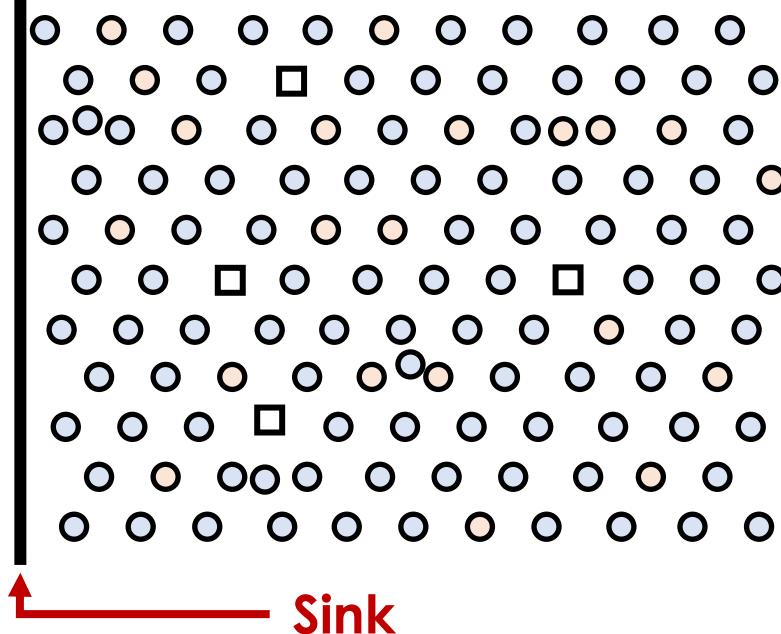
$$\frac{\partial C_A}{\partial t} = -\nabla J_A$$

$$\frac{\partial C_i}{\partial t} = -\nabla J_i + K_0 - K_{i\nu} C_i C_\nu$$

$$\frac{\partial C_B}{\partial t} = -\nabla J_B$$

Let's model a concentrated alloy of A & B atoms, e.g. A_xB_{x-1}

Now, let's write the flux in terms of i , v , A & B



The flux of interstitials will be the combined flux of A and B atoms via interstitial hopping:

The flux of vacancies will be the combined flux of A and B atoms via vacancy hopping:

Let's model a concentrated alloy of A & B atoms, e.g. A_xB_{x-1}

We now need to define the partial diffusion coefficients, since the flux (e.g., J_x) is proportional to the partial diffusion coefficients:

Let's model a concentrated alloy of **A** & **B** atoms, e.g. A_xB_{x-1}

Writing out all the diffusion coefficients in terms of partial diffusion coefficients:

$$D_A^v = d_{Av} N_v \quad D_v^A = d_{Av} N_A \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{Vacancies}$$

$$D_B^v = d_{Bv} N_v \quad D_v^B = d_{Bv} N_B \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{Vacancies}$$

$$D_A^i = d_{Ai} N_i \quad D_i^A = d_{Ai} N_A \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{Interstitials}$$

$$D_B^i = d_{Bi} N_i \quad D_i^B = d_{Bi} N_B \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{Interstitials}$$



Let's model a concentrated alloy of **A** & **B** atoms, e.g. A_xB_{x-1}

The total diffusion coefficients are::

$$D_v = D_v^A + D_v^B = d_{Av} N_A + d_{Bv} N_B \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{Defects}$$
$$D_i = D_i^A + D_i^B = d_{Ai} N_A + d_{Bi} N_B \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{Atoms}$$
$$D_A = D_A^v + D_A^i = d_{Av} N_v + d_{Ai} N_i \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{Atoms}$$
$$D_B = D_B^v + D_B^i = d_{Bv} N_v + d_{Bi} N_i \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{Atoms}$$

Let's model a concentrated alloy of A & B atoms, e.g. A_xB_{x-1}

$$J_A = -D_A \alpha \nabla C_A + d_{Av} N_A \nabla C_v - d_{Ai} N_A \nabla C_i$$

$$J_B = -D_B \alpha \nabla C_B + d_{Bv} N_B \nabla C_v - d_{Bi} N_B \nabla C_i$$

$$J_v = d_{Av} N_v \alpha \nabla C_A + d_{Bv} N_v \alpha \nabla C_B - D_v \nabla C_v = (d_{Av} - d_{Bv}) N_v \alpha \nabla C_A - D_v \nabla C_v$$

$$J_i = -d_{Ai} N_i \alpha \nabla C_A - d_{Bi} N_i \alpha \nabla C_B - D_i \nabla C_i = -(d_{Ai} - d_{Bi}) N_i \alpha \nabla C_A - D_i \nabla C_i$$

Let's model a concentrated alloy of A & B atoms, e.g. A_xB_{x-1}

$$\frac{\partial C_v}{\partial t} = \nabla [- (d_{Av} - d_{Bv}) \alpha \Omega C_v \nabla C_A + D_v \nabla C_v] + K_o - K_{iv} C_i C_v$$

$$\frac{\partial C_i}{\partial t} = \nabla [(d_{Ai} - d_{Bi}) \alpha \Omega C_i \nabla C_A + D_i \nabla C_i] + K_o - K_{iv} C_i C_v$$

$$\frac{\partial C_A}{\partial t} = \nabla [D_A \alpha \nabla C_A + \Omega C_A (d_{Ai} \nabla C_i - d_{Av} \nabla C_v)]$$

Let's model a concentrated alloy of A & B atoms, e.g. A_xB_{x-1}

$$\nabla C_A = \frac{N_A N_B d_{Bi} d_{Ai}}{\alpha(d_{Bi} N_B D_A + d_{Ai} N_A D_B)} \times \left(\frac{d_{Av}}{d_{Bv}} - \frac{d_{Ai}}{d_{Bi}} \right) \nabla C_v$$

If $\frac{d_{Ai}}{d_{Bi}} > \frac{d_{Av}}{d_{Bv}}$ →

Example Alloy B_{0.75}A_{0.25}

Given: $E_m^{Av} \sim 0.8 \text{ eV}$ $E_m^{Ai} \sim 0.10 \text{ eV}$

$E_m^{Bv} \sim 1.28 \text{ eV}$ $E_m^{Bi} \sim 0.15 \text{ eV}$

Will A or B atoms enrich at the sinks?

Interstitial Binding

Solutes can tightly bind to interstitials forming interstitial solute complexes, this can be accounted for by,

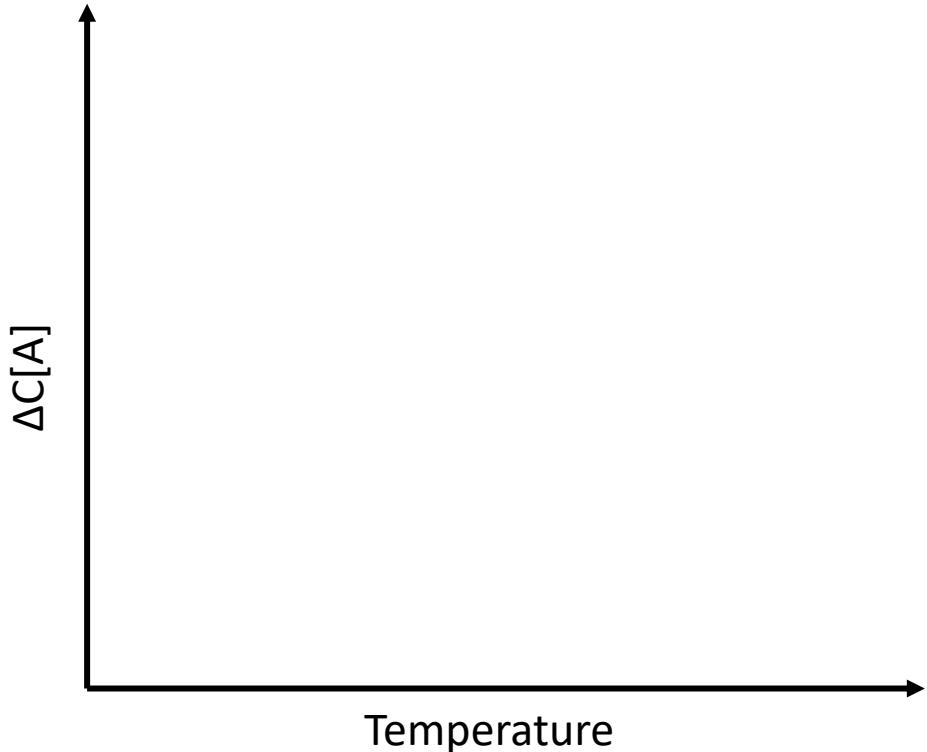
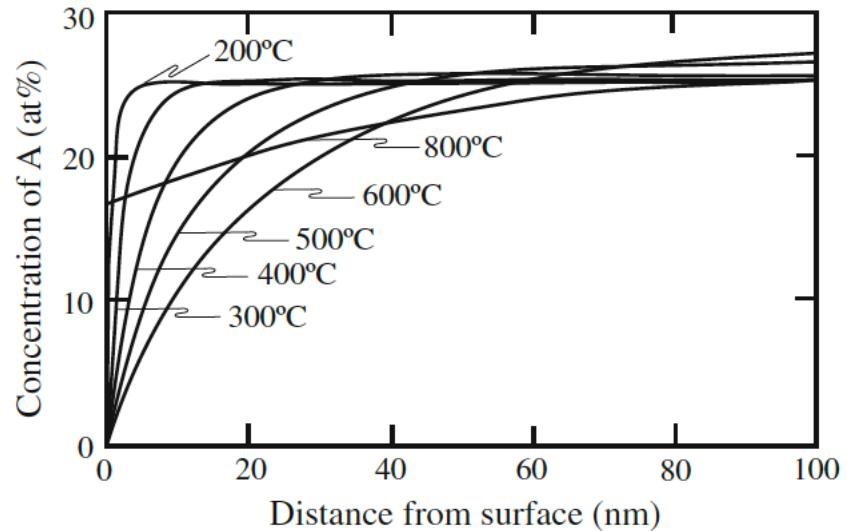
$$C_{Ai} = C_i \frac{C_A \exp\left(\frac{E_b^{Ai}}{k_B T}\right)}{C_A \exp\left(\frac{E_b^{Ai}}{k_B T}\right) + C_B}$$

Or simply,

$$\frac{d_{Ai}}{d_{Bi}} \approx \exp\left(\frac{E_m^{Bi} - E_m^{Ai} + E_b^{Ai}}{k_B T}\right)$$

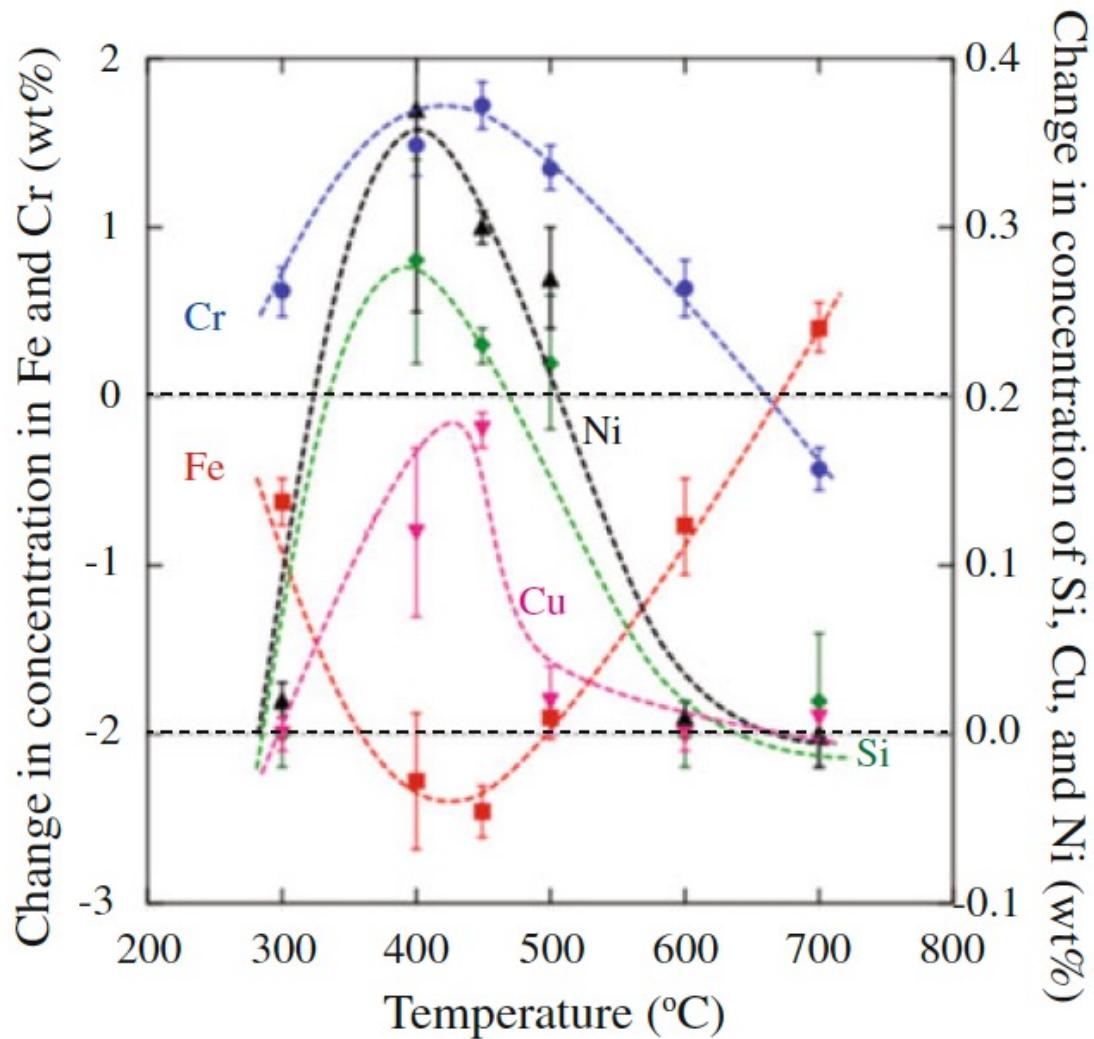
Temperature Dependence

Fig. 6.7 Steady-state concentration profiles of element A as a function of temperature for the same alloy and irradiation conditions as shown in Fig. 6.3 (after [4])



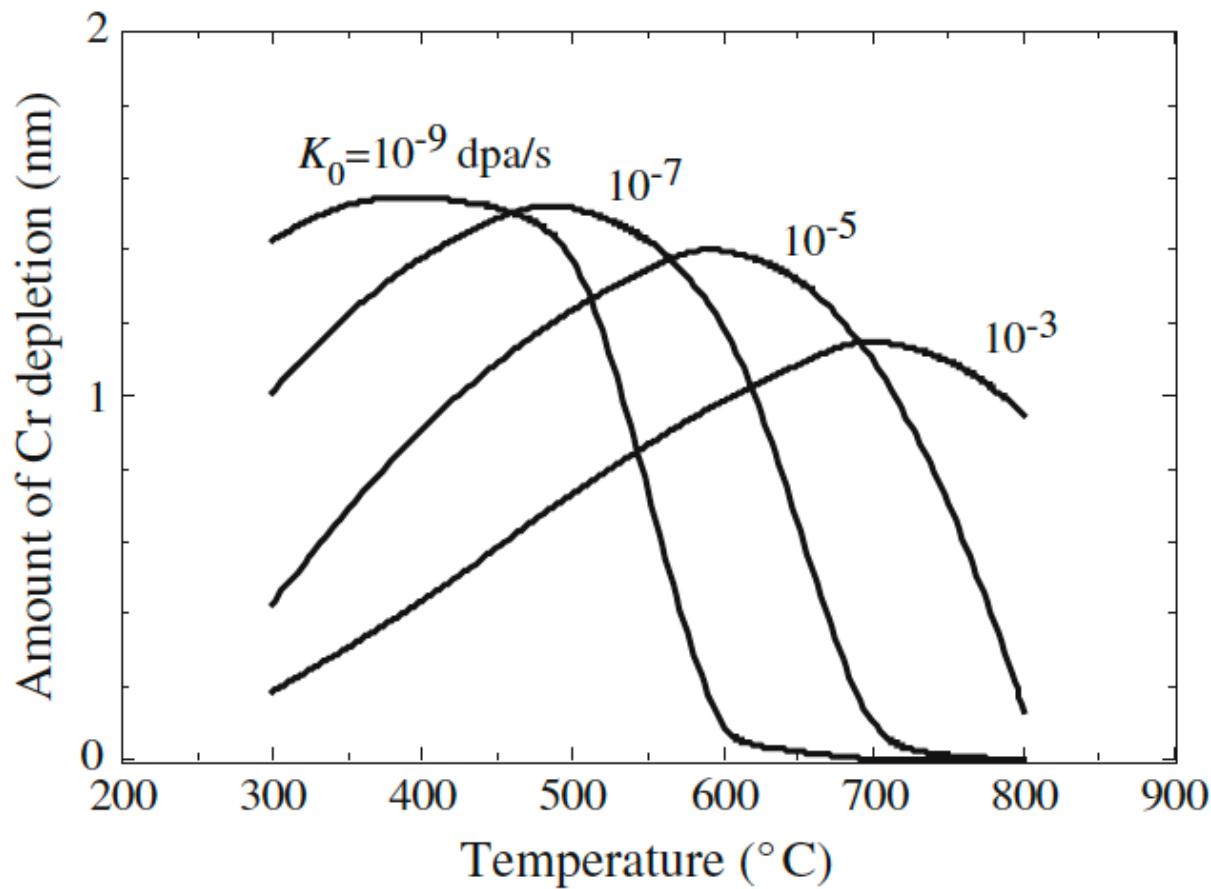
Temperature Dependence

Fig. 6.23 Grain boundary composition as a function of temperature in alloy T91 irradiated to 3 dpa with 2.0 MeV protons (after [26])

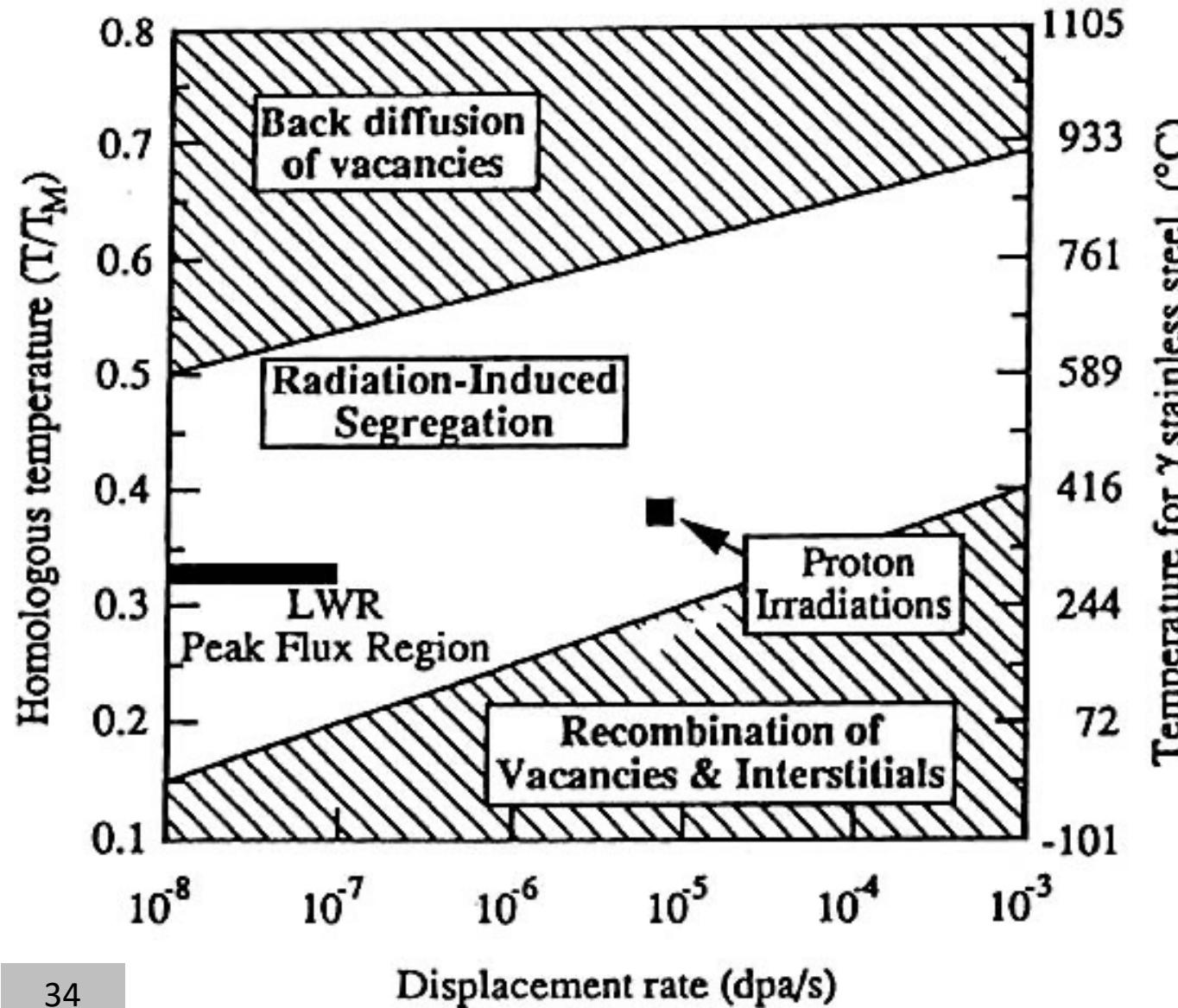


Dose Rate Dependence

Fig. 6.9 Dose rate dependence of grain boundary chromium depletion calculated using the MIK model for RIS (after [13, 14])

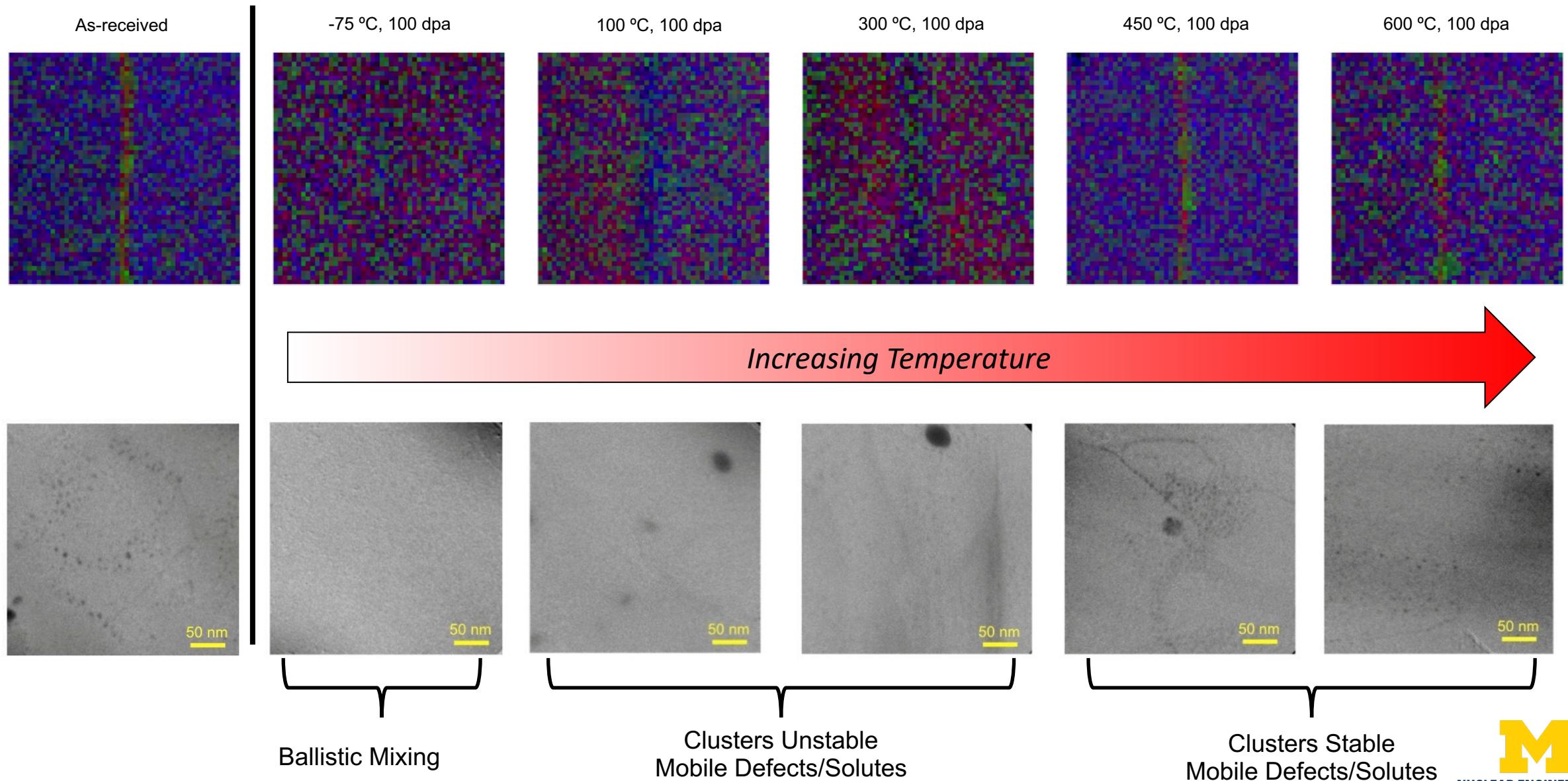


Temperature and Dose Rate Dependence

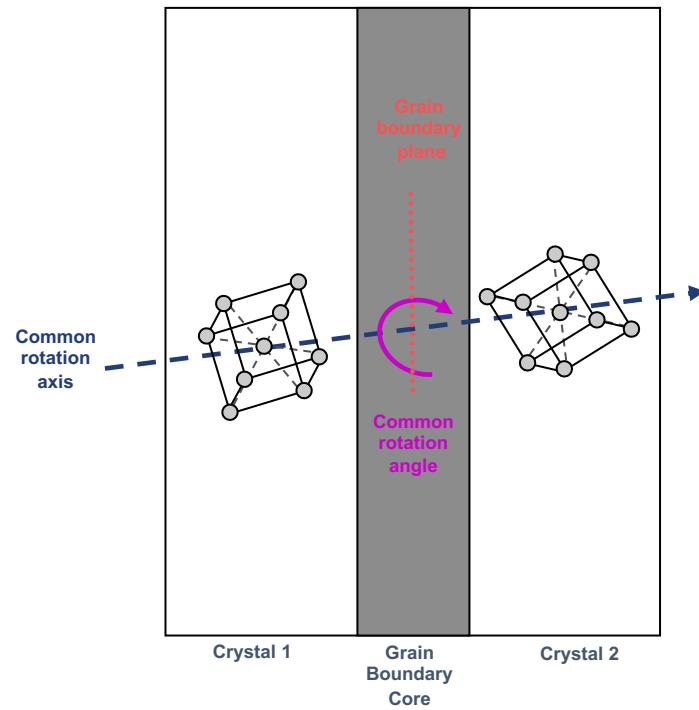


- The degree of segregation under irradiation will vary with temperature and dose rate.
- At low temperatures where defect mobility is limited, defect recombination dominates and RIS is minimal.
- At high temperatures where defect mobility and thermally induced defect populations are high, diffusion works to prevent or remove any composition gradients.
- At intermediate temperatures, however, RIS will occur.

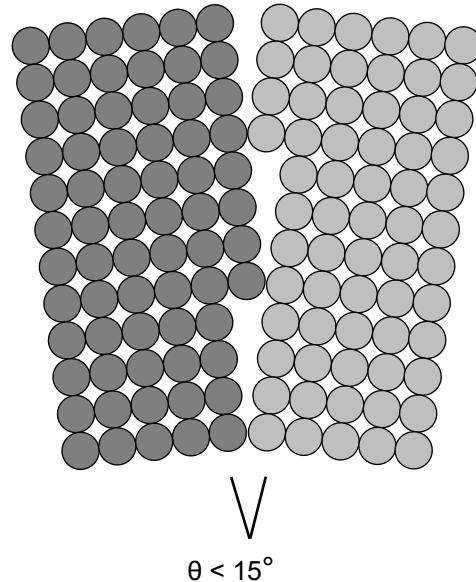
RIS is a “finger print” for defect mobility and loss



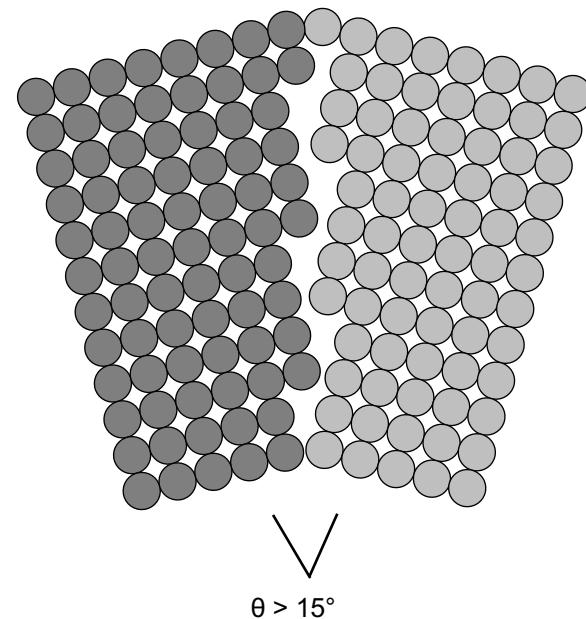
Grain Boundary Interfacial Structure Overview



Low Angle Grain Boundary

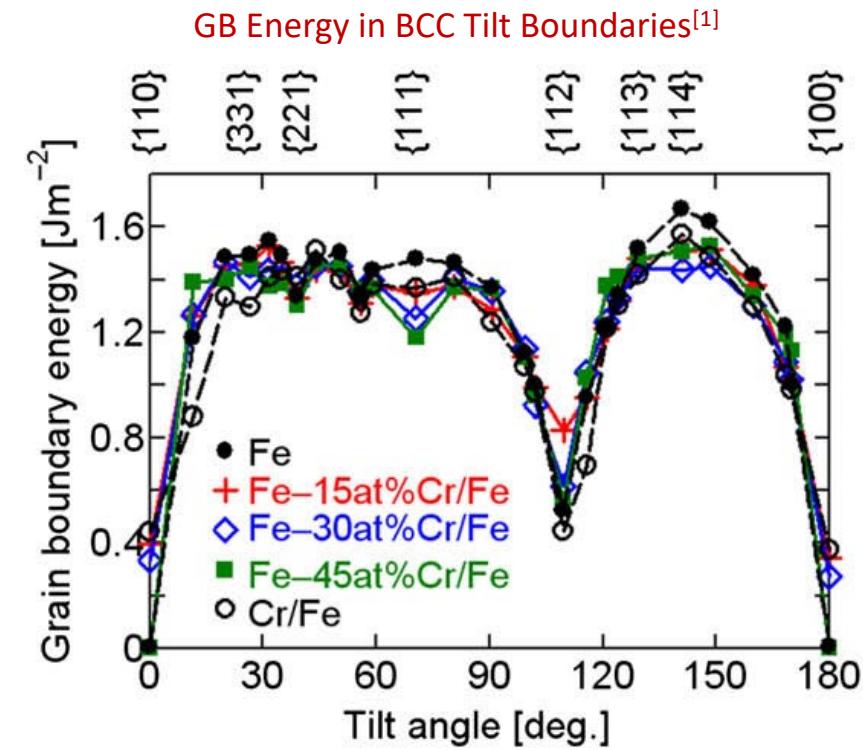
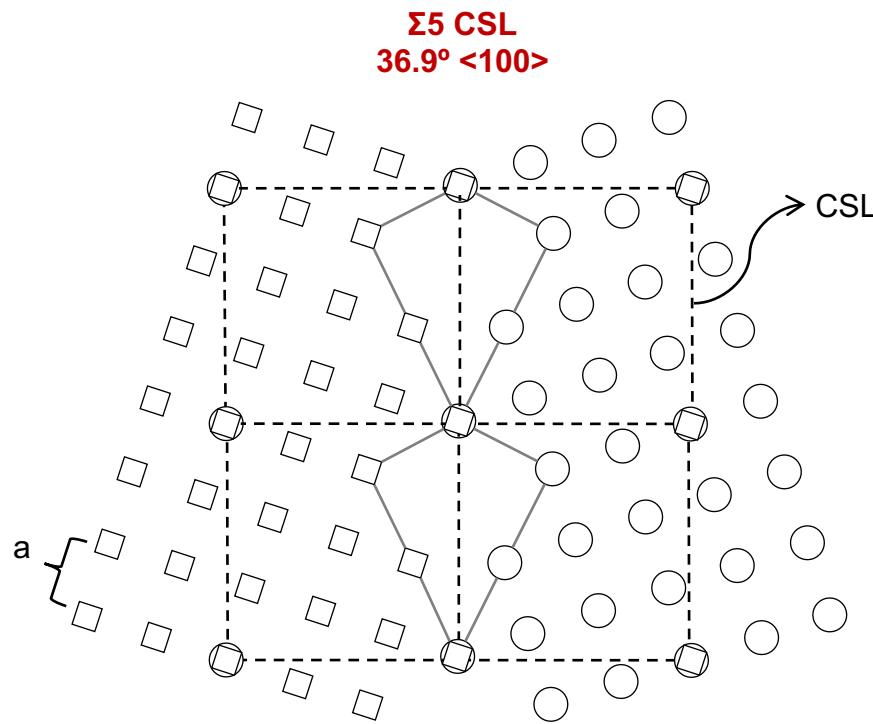


High Angle Grain Boundary



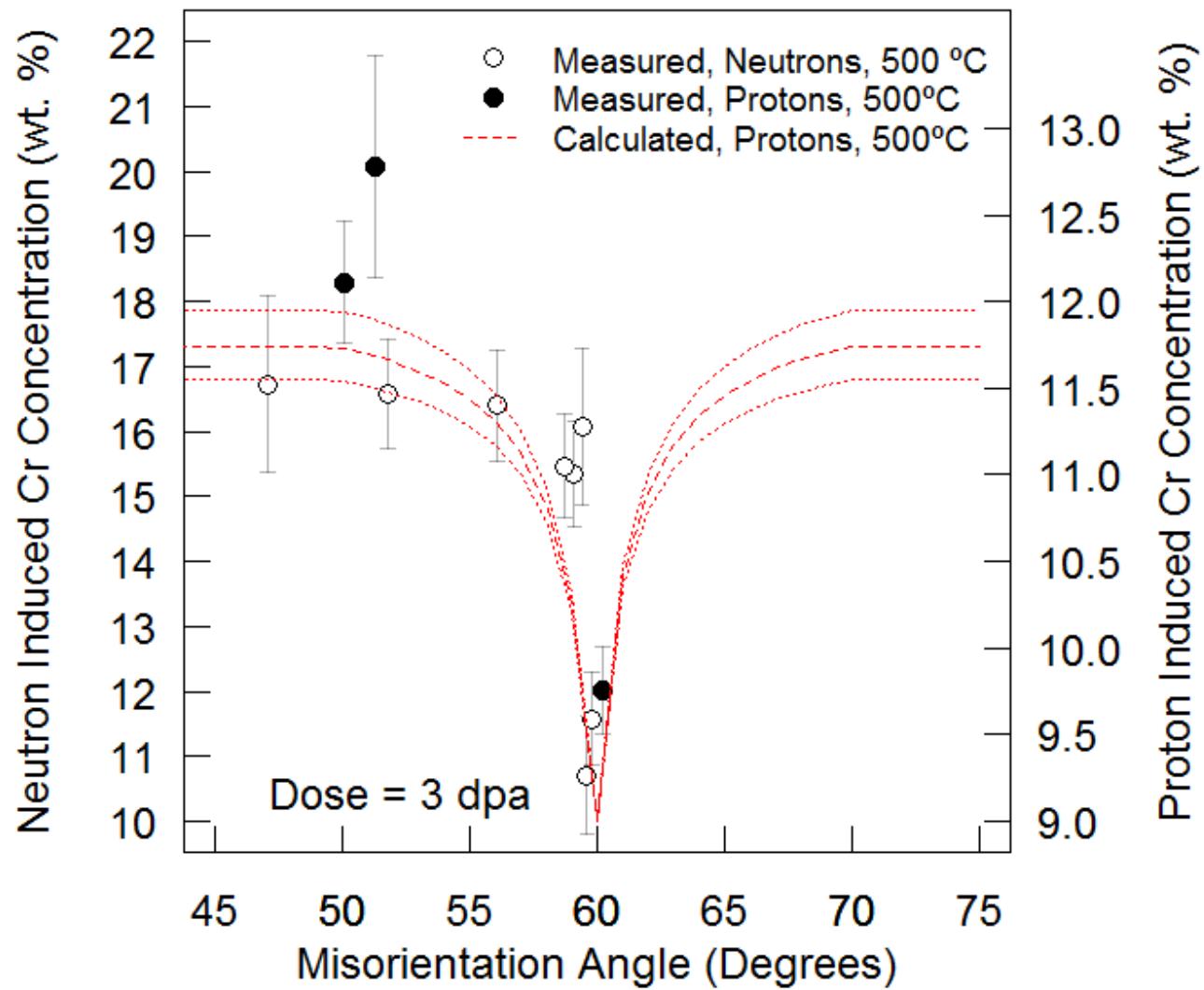
- Axis-angle representation for cubic materials helps describe GB structure:
 - **Axis:** The common crystallographic axis which comprises the boundary
 - **Angle (θ):** The degree of rotation between the two crystals along the axis
 - Axis-angle pairs describe GB: **low angle**, **high angle** or **special (low- Σ) GB**

Coincident Site Lattice (CSL) Convention

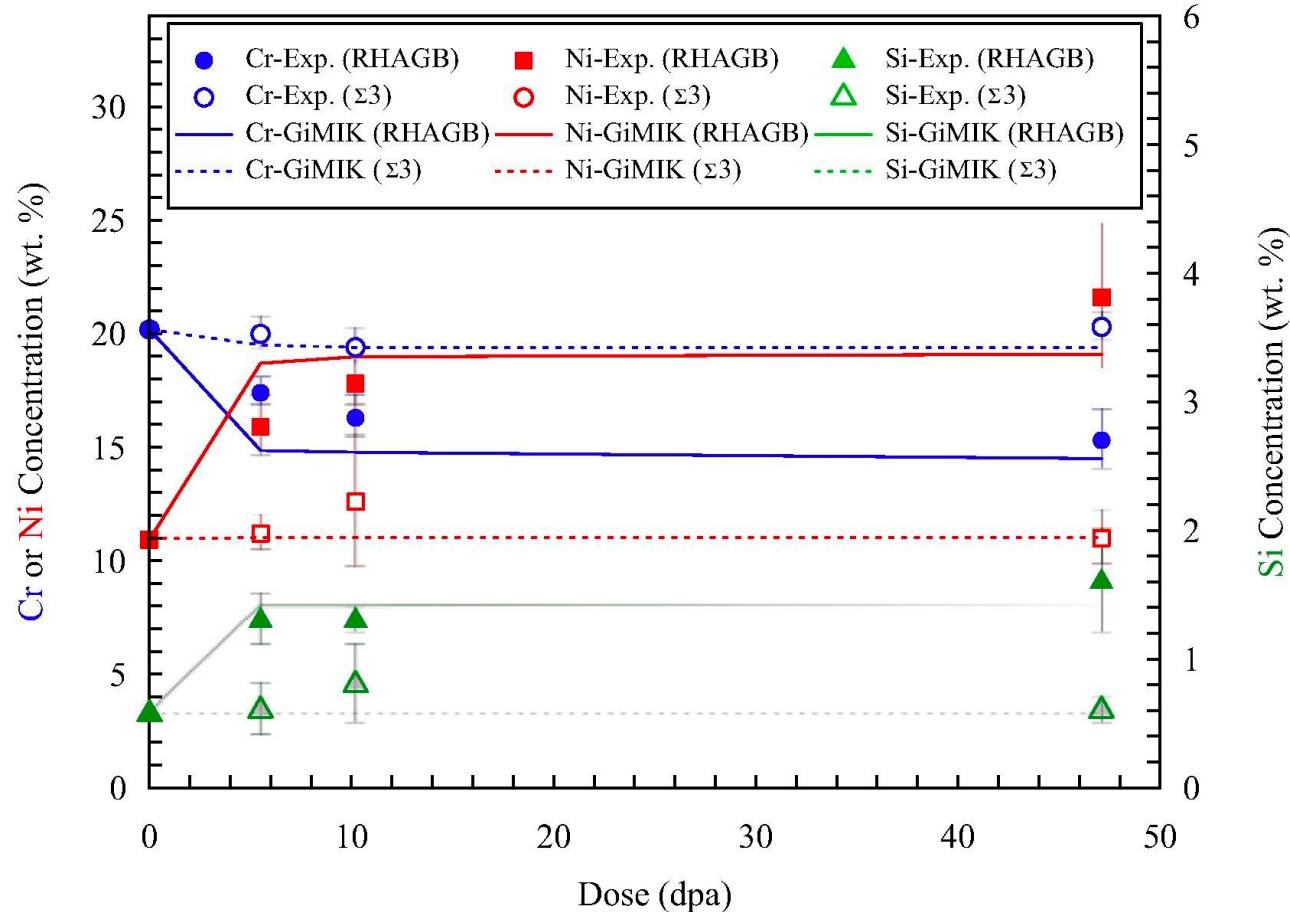
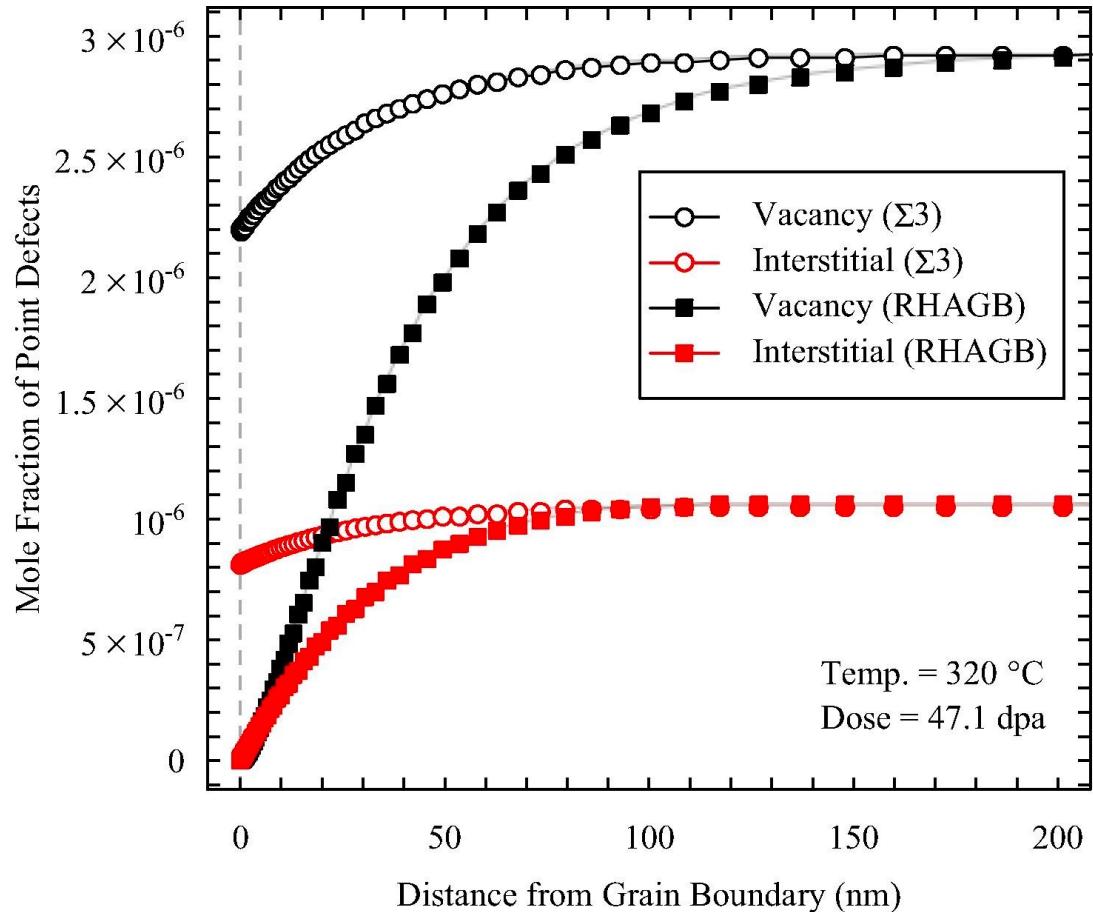


- CSL is a geometrical construction based on the geometry of the lattice
- Σ is the ratio between the area enclosed by a unit cell of coincidence sites and the standard unit cell
- Low Σ CSL boundaries have higher coherency compared to general HAGBs

Example model and experimental data for BCC steels



Example model and experimental data for FCC steels



Segregation to grain boundary dislocations

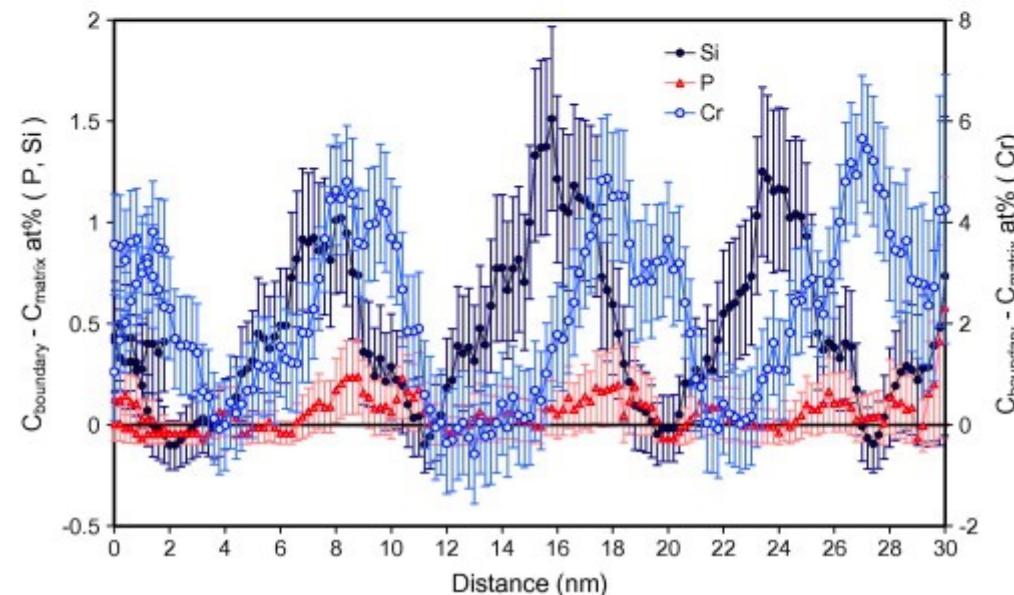
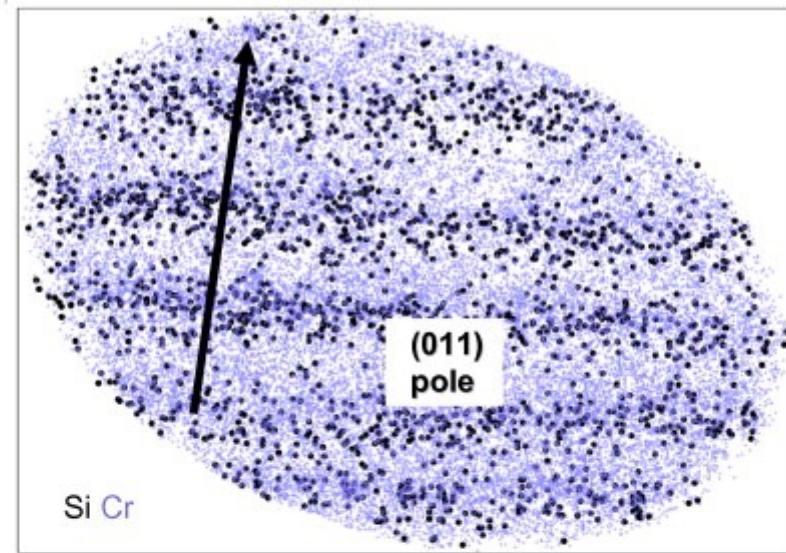


Image Stitching

100 nm



Questions?