Atomistic modeling of segregation and precipitation in ferritic steels under irradiation

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Motivations

• Fe-Cr alloys : a model for ferritic and ferritic-martensitic steels (7-14%Cr), candidate materials for future nuclear reactors (Gen IV and fusion)
Potential problems :
  - α’ precipitation, strongly accelerated by irradiation → hardening and embrittlement
  - radiation induced segregation, e.g. Cr depletion at GBs → corrosion, embrittlement

A model system for spinodal decomposition (decomposition in unstable solid solution)

ASTRID
Sodium cooled fast reactor
Gen IV
(fuel cladding, wrapper tubes)

ITER
Fusion reactor (Test Blanket Modules)
Potential technological problems:

- Coherent $\alpha - \alpha'$ decomposition (accelerated by irradiation) in alloys with 9-14%Cr
  - hardening and embrittlement
- Cr depletion at grain boundaries (radiation induced segregation - RIS)
  - loss of corrosion resistance, embrittlement

- Special thermodynamic and diffusion properties $\leftrightarrow$ magnetic properties
The precipitation kinetic pathways depend on point defect diffusion properties. Key points: the dependence of the migration barriers and the defect concentrations with the local configuration.

A multiscale Approach

*Ab initio* calculations (thermodynamics and diffusion)

Diffusion model on a rigid lattice

Atomistic Kinetic Monte Carlo simulations (AKMC)

Applications to Fe-Cr alloys

decomposition during thermal ageing
decomposition under irradiation
radiation induced segregation
comparison with experiments (3D atom probe and SANS)
DFT calculations of point defect properties

- **Vacancies**
  - weak Cr-V interactions
  - a low $\Delta H_2$ migration barrier

- **Self-Interstitials (SIAs)**
  - Fe-Cr alloys: $<110>$ dumbbells
  - mixed dumbbell is stable ($E_b = +0.02$ eV)
  - With a low migration barrier
  - $\rightarrow$ A rapid diffusion of Cr, both by vacancies and SIAs

$D_{Cr}^* > D_{Fe}^*$

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Diffusion and interaction model

• **Pair interactions on a rigid BCC lattice:** free energy of one atomic configuration \( G_{\text{conf}} = \sum_{ij} g_{ij}^{(n)} \)
  FeCr alloys:
  - temperature dependent and composition dependent interactions
  \( \rightarrow \) effects of vibrational entropies and magnetic transitions.

• **Diffusion by thermally activated point defects jumps**
  - jump frequency: depend on the local environments

\[
\Gamma_{AV} = v_A \exp \left( -\frac{\Delta G_{AV}^{\text{mig}}}{k_B T} \right)
\]
  - migration barriers: broken-bond models

\[
\Delta G_{AV}^{\text{mig}} = G_{sys}(SP) - G_{sys}(ini) = \sum_i g_{Ai}^{SP} - \sum_{j,n} g_{Aj}^{(n)} - \sum_{k,n} g_{kV}^{(n)}
\]
  fitted on DFT calculations (0K)

• **AKMC: residence time algorithm**
  - thermal ageing: simulations with \( 10^6 - 10^7 \) atoms, PBC and 1 vacancy \( \rightarrow \) time scale: \( t_{MC} = \frac{1}{\sum_i \Gamma_i} \)

  physical time: \( t = t_{MC} \times (\overline{c}_V^{MC} / \overline{c}_V^{eq}) \)

  - under irradiation: point defect formation and elimination mechanisms \( \rightarrow \) real time scale
THERMODYNAMICS AND DIFFUSION
Thermodynamics: the Fe-Cr phase diagram

- **Short range ordering below approximately 10%Cr, unmixing tendency above**
  
  Pair interactions on a rigid BCC lattice: $V_i = g_{FeFe}^{(i)} + g_{CrCr}^{(i)} - g_{FeCr}^{(i)}$
  
  - 1<sup>st</sup> and 2<sup>nd</sup> nn interactions, composition dependence fitted on DFT calculations of $\Delta H_{mix}$
  (SQS, PWSCF, GGA-PAW)
  
  - Temperature dependence fitted on the experimental $c_p$ and the $\alpha-\alpha'$ critical temperature

- **Phase diagram**: good agreement with the modified CALPHAD diagram (Bonny et al, 2010)
  
  \[ V_i = g_{FeFe}^{(i)} + g_{CrCr}^{(i)} - g_{FeCr}^{(i)} \]

\[ \Delta H_{mix} \] (meV)

\[ T (K) \]

- Asymmetrical miscibility gap, non-vanishing Cr solubility at low $T$
Fe-Cr alloys: Tracer Diffusion Coefficients

- at 0K: DFT calculations of vacancy migration barriers (10 for $D_{Fe*}^{Fe}$ and $D_{Cr*}^{Fe}$)

- Vibrational entropies (ferromagnetic iron): $\Delta S_{V}^{for}(Fe) = 4.1k_B$ and $\Delta S_{V}^{mig}(Fe) = 2.1k_B$

- Acceleration at the ferro-paramagnetic transition in the $\alpha$ phase → corrections of the migration barriers, fitted on experimental tracer and interdiffusion coefficients

tracer diffusion coefficients in iron

- $T_c$ rapidly decreases with the Cr concentration

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Fe-Cr alloys: Interdiffusion Coefficients

- No experimental data below 900K
- The interdiffusion coefficients strongly decrease with the Cr content
- It's important to take into account the evolution of the vacancy concentration

PRECIPITATION KINETICS: THERMAL AGEING (NO IRRADIATION)
Kinetics of α-α’ decomposition: AKMC vs 3DAP

Fe-20%Cr  T = 500°C

AKMC (E. Martinez, O. Senninger, CEA)  3D atom probe (Novy et al, GPM Rouen, 2009)
Kinetics of $\alpha-\alpha'$ decomposition: AKMC vs SANS

Small Angle Neutron Scattering experiments:
- 500°C: Bley (1992)
- 540°C: Furusaka et al. (1986)

- F/P transition: strong acceleration of the decomposition between above 35% Cr (lower $T_C$)
- Better agreement with experimental kinetics

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PRECIPITATION UNDER IRRADIATION
Irradiation damage: short term evolution

Ion and neutron irradiations: displacement cascades
Molecular dynamics in α-Fe ($E_{\text{PKA}} = 20$ keV, 20 ps)

- **Displacements:** creation of vacancies (V), self-interstitials (I) and point defect clusters
  radiation damage in dpa (displacement pet atom)
  dose rate in dpa.s$^{-1}$

- **Replacements:** change of the lattice sites → ballistic mixing

- **Long term evolution**
  - acceleration of diffusion → thermodynamic equilibrium
  - elimination of excess point defect → solute fluxes → radiation induced segregation
  - ballistic mixing (in alloys: homogenization, disordering)

E.A. Calder (2010)
EAM potential
Molecular Dynamics

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Cr precipitation in iron under irradiation:
Experimental Observations

Fe-Cr based alloys, with 9-20%Cr at ≈300°C
the precipitation α’ (Cr-rich) is too slow to be observed during isothermal annealing

α’ precipitates have been observed after:
- neutrons irradiation
  Fe-9% and 12%Cr at 300°C 7 x 10^{-7} dpa.s^{-1}, 0.6 dpa  V. Kuksenko et al, JNM 2013
  Fe-9 to 18% Cr 290°C 3.4 x 10^{-7} dpa.s^{-1}, 1.82 dpa  M. Bachhav et al, SM 2014
- electron irradiation
  Fe-15%Cr at 300°C 3.9 x 10^{-5} dpa.s^{-1}, 0.7 dpa  O. Tissot et al, SM 2016
- ion irradiation
  Fe-15%Cr at 300°C 5.2 x 10^{-5} dpa.s^{-1}, 0.7 dpa  O. Tissot et al, MRL 2016

α’ precipitates have not been observed after:
- ion irradiation
  Fe-12%Cr at 300°C 2 x 10^{-4} dpa.s^{-1}, 0.5 dpa  C. Pareige et al, JNM 2015
- ion irradiation
  Fe-15%Cr at 300°C 2.8 x 10^{-3} dpa.s^{-1}, 120 dpa  O. Tissot et al. 2016
- electron irradiation
  Fe-15%Cr at 300°C and 40°C 2.5 x 10^{-10} dpa.s^{-1}, 10^{-4} dpa  O. Tissot et al. 2016

General trend: strong acceleration of the precipitation at low/moderate dose rates
no precipitation at high dose rates
Point defect concentrations under irradiation

**Rate theory**

\[
\frac{dc_i}{dt} = G - R_c c_v - k_{tot}^2 D_i c_i \\
\frac{dc_v}{dt} = G - R_c c_v - k_{tot}^2 D_v c_v
\]

\[c_{v,i} >> c_{v,i}^{eq}\]

\[G = \sigma \Phi \ \text{creation} \ \propto \ \text{dose rate (dpa.s-1)}\]

\[R = 4\pi d_{rec} \left( D_i + D_v \right) / V_{at} \ \text{recombination I-V}\]

\[k_{tot}^2 : \text{total sink strength, elimination at sinks}\]

(grain boundaries, dislocations, point defect clusters,...)

**Cluster Dynamics**: evolution of point defect clusters

\[w^+(nv,v) \quad w^- (nv,v) \quad w^- (nv,i) \]

\[mi \quad w^- (nv,i) \quad i \]

Depending on the irradiation conditions, sink strengths vary between \(k_{tot}^2 = 10^8\) to \(10^{15} \text{ cm}^{-2}\)

Small vacancy clusters are usually the dominant sink, except at very low doses and under e- irradiations
Irradiation mechanisms in AKMC simulations

• **Formation of Frenkel pairs**
  
  Replacement collision
  
  Sequences (electron irradiation)
  
  1st nn replacements in 111 directions
  
  $n_{\text{rep}} = 10$
  
  **Displacement cascades** (ion and neutron irradiation)
  
  random 1\textsuperscript{st} and 2\textsuperscript{nd} nn replacements
  
  $n_{\text{rep}} = 100$
  
  within a sphere $R = 5 \text{ n}$

• **SIA-V recombination** ($d_{\text{rec}} = 3a$)

• **Point defect eliminations on perfect sinks**
  
  Clusters dynamics
  
  $k_{\text{tot}}^2(t)$
  
  AKMC simulations with random
distribution of individual pd sinks
  
  with the same strength

\[ k_{\text{tot}}^2(t) \]

\[ k_{\text{tot}}^2(t) \] increases
\Rightarrow $c_i$ and $c_v$ decrease
favors ballistic mixing

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Electron Irradiations

Experiments
O. Tissot et al
Scripta Materialia 122, 31-35 (2016)
Fe-Cr alloys – electron irradiations
300 and 400°C, $3.9 \times 10^{-5}$ dpa.s$^{-1}$
One dose: 1.82 dpa

AKMC simulations
good agreement with experiments
coarsening regime
No significant effect of ballistic mixing
($k_{tot}^2 < 10^{12}$ cm$^{-2}$)

Fe-15%Cr
300°C
$3.9 \times 10^{-5}$ dpa.s$^{-1}$

Fe-15%Cr
400°C
$3.9 \times 10^{-5}$ dpa.s$^{-1}$
Experiments
O. Tissot et al
Materials Research Letters, 1-7 (2016)
Fe-15%Cr alloys – ion irradiations
300°C, 2.8 \times 10^{-3} \text{ dpa.s}^{-1}
One dose: 120 dpa, no precipitate

AKMC simulations
No precipitates at 120 dpa \left( k_t^{2} \approx 5 \times 10^{13} \text{ cm}^{-2} \right)
Suggest precipitates at low doses
(R > 1nm between approx. 0.1 and 10 dpa)
Precipitation under irradiation

- 3D Atom Probe of $\alpha'$ precipitation, neutron irradiation in supersaturated alloys
  Bachhav et al Scripta Mater. 74 (2014) 48
  V. Kuksenko et al, JNM 432 (2013) 160

AKMC simulations
Fe-18%Cr @ 563 K, $3.4 \times 10^{-7}$ dpa.s$^{-1}$

Kuksenko et al (2012)
3DAP
Fe-12%Cr
300°C – 0.6 dpa
Conclusions on ballistic mixing

G. Martin, P. Bellon (e.g. Driven alloys, Solid State Physics, Vol. 50, pp. 189-331, 1997)

Ballistic mixing effects $\rightarrow$ inverse coarsening, dissolution of precipitates, disordering
Thermally activated diffusion $\rightarrow$ accelerated precipitation (in a supersaturated alloy)

Ballistic mixing is dominant at high irradiation intensity: $\gamma = \frac{D_{bal}}{D_{th}} > 1$

high sink strength $\rightarrow$ low point defect concentration $\rightarrow$ ballistic dissolution

$D_{bal} = a^2 \Gamma_{bal} = a^2 n_{rep} G$

$D_{th}^{irr} = 2 c_v^{irr} D_v$ with $c_v^{irr} \approx \frac{G}{D_v k_{tot}^2}$ when elimination at sinks is dominant

- for a given sink density (or sink strength), the irradiation intensity is independent of the dose rate $G$
- $k_{tot}^2$ depends on the dose rates

The ballistic mixing effects are mainly controlled by the sink density
RADIATION INDUCED SEGREGATION
• A-B alloy under irradiation: annihilation of excess point defects at GBs, dislocations, surfaces, etc...

• Onsager equations: \( J_i = -\sum_j L_{ij} \nabla \mu_j \)

For example: if \( L_{BV}/L_{BB} > 0 \) fluxes of V and B in the same direction
otherwise in opposite directions

Fe-Cr alloys (E. Marquis, Oxford)
ODS steel - 12% Cr – after thermal ageing

under irradiation (Fe ions)
500°C

Compared to...
300°C

Boundary

Cr

C

20 nm
AKMC: Radiation Induced vs equilibrium Segregation

Steady-state profiles:

\[ \nabla C_{Cr} \propto -\left( \frac{L_{CrV}}{L_{FeV}} - \frac{L_{CrI}}{L_{FeI}} \right) \nabla C_{V} \]

one expects an enrichment of Cr at sinks at low T, a depletion at high T

Fe-10%Cr
T = 650 K, 10^{-6} dpa.s^{-1}

Fe-10%Cr
T = 950 K, 10^{-3} dpa.s^{-1}

\[ e_{Cr}^{seg} = -0.1 \text{ eV} \]

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Conclusions

- AKMC simulations with effective interactions fitted on DFT calculation
  **advantages:** good description of driving forces, diffusion properties (correlations) and nucleation
  **drawbacks:** rigid lattice approximation, time consuming (→ coupling with cluster dynamics, phase field)

In Fe-Cr alloys

- Magnetic effects are important (impact on thermodynamic and diffusion properties)

- **Radiation accelerated precipitation**
  ballistic disordering at high dose rates, controlled by the evolution of the sink density
  important for the comparison between ion and neutron irradiation

- **Radiation Induced Segregation** is controlled by a balance between opposite effects of V and SIA
  → may explain the variability of experimental studies (≠ RIS in austenitic steels)

- **Related work, perspectives**
  - large scale models
  - evolution of the mechanical properties
  - Austenitic steels (Fe-Ni-Cr, γ-CFC): paramagnetic → a challenge for DFT calculations
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