MINOS Centre of Excellence for Nuclear Materials

2nd **Int. Workshop** Irradiation of Nuclear Materials: Flux and Dose Effects
November 4-6, 2015, CEA – INSTN Cadarache, France

Atomistic Modelling of Segregation and Precipitation in Fe-Cr Alloys under Irradiation

Frédéric SOISSON[1], Chu Chun FU[1], Thomas JOURDAN[1], Maylise NASTAR[1],
Oriane SENNINGER[1], Enrique MARTINEZ[2], Yves BRÉCHET[3]

[1]CEA-DEN-DMN, Service de Recherches de Métallurgie Physique, SRMP (Saclay, France)
[2]Los Alamos National Laboratory, Materials Science in Radiation Dynamics Group (Los Alamos, USA)
SIMAP, INP Grenoble, CNRS UJF (Saint Martin d'Hères, France)

Iron-chromium alloys are the basis for ferritic and ferritic-martensitic steels that will be used in future fission (generation IV) and fusion nuclear reactors. With Cr content between typically 8 to 12% [1], or even 14% in the matrix of some oxide dispersion-strengthened steels [2], one can expect the precipitation of a Cr-rich α' phase that can be strongly accelerated under irradiation, due to point defect supersaturation. This precipitation can cause hardening and embrittlement. Radiation-induced segregation (RIS) is another important technological problem. It can lead to a Cr depletion at grain boundaries and therefore to a loss of corrosion resistance and again, to embrittlement. RIS in austenitic steels is well known and presents almost systematic trends: depletions of Cr and enrichments of Ni at grain boundaries. In ferritic steels, the experimental situation is far from being so clear: depletions and enrichments of Cr have been observed, without clear correlation with the irradiation conditions and the materials properties [3].

Segregation and precipitation occur by formation, migration and elimination of point defects (vacancies and self-interstitials). We present a model that includes these mechanisms, and combines ab initio and atomistic kinetic Monte Carlo (AKMC) simulations. Migration barriers and jump frequencies are computed by using effective pair interactions with concentration and temperature dependences. Thanks to these dependences, the simulations are able to well reproduce the thermodynamic [4] and diffusion [5] properties of dilute and concentrated alloys, including the effects of the magnetic configurations and magnetic transitions, which are especially important in Fe-Cr alloys. They also give kinetics pf precipitation during isothermal annealing in good agreement with experimental studies [5].

Simulations of α' precipitation under irradiation, predict that the kinetics can be considerably accelerated. For example, irradiations of alloys with 15 to 18%Cr at 290°C and a dose rate of 3.4×10^{-7} dpa.s^{-1} produce a point defect supersaturations and therefore, an acceleration, of approximately 6-7 orders of magnitudes. To get a more precise estimation of the evolution of sink densities and point defect concentrations, cluster dynamics [6] have been used: the physical time scale of the Monte Carlo simulations is rescaled accordingly and one gets precipitation kinetics in good agreement with the few available experimental results [7,8]. The possible effect of ballistic mixing occurring in displacement cascades and the role of carbon, which is known to strongly interact with the vacancies, will be discussed.

RIS results from the elimination of excess vacancies (V) and self-interstitials (I) on sinks such as dislocations, grain boundaries, or free surfaces. Permanent fluxes of point defects towards the sinks are then sustained, i.e. permanent fluxes of chemical species, leading to a modification of the local composition near the sinks. RIS can be analyzed properly in the framework of the thermodynamics of irreversible processes, that gives the flux of a specie α (atom or defect) as a function of the gradients of chemical potentials μ_β : $J_\alpha = -\sum L_{\alpha\beta} \nabla \mu_\beta$. The tendencies to solute enrichment or depletion near the sinks are controlled by the Onsager coefficients, $L_{\alpha\beta}$. In Fe-Cr alloys, one must observe a depletion of Cr near the sinks if $L_{CrV}/L_{FeV} > L_{CrI}/L_{FeI}$, an enrichment of Cr in the opposite case. Onsager coefficients can be directly estimated in Monte Carlo simulations (Fig. 1a). Simulations have been also performed to model directly the evolution of point defects and solute distributions near a grain boundary (Fig. 1b). As expected from the analysis of the Onsager coefficients, at 650 K the interstitial contribution dominates and one observes an enrichment of Cr. On the contrary at 950K vacancy contribution is

dominant and Cr depletion occur [9]. We will compare these trends with experimental observations of RIS. Finally, the AKMC enables to study the interaction between segregation and precipitation [9]: typical cases will be presented.

(a)   (b)
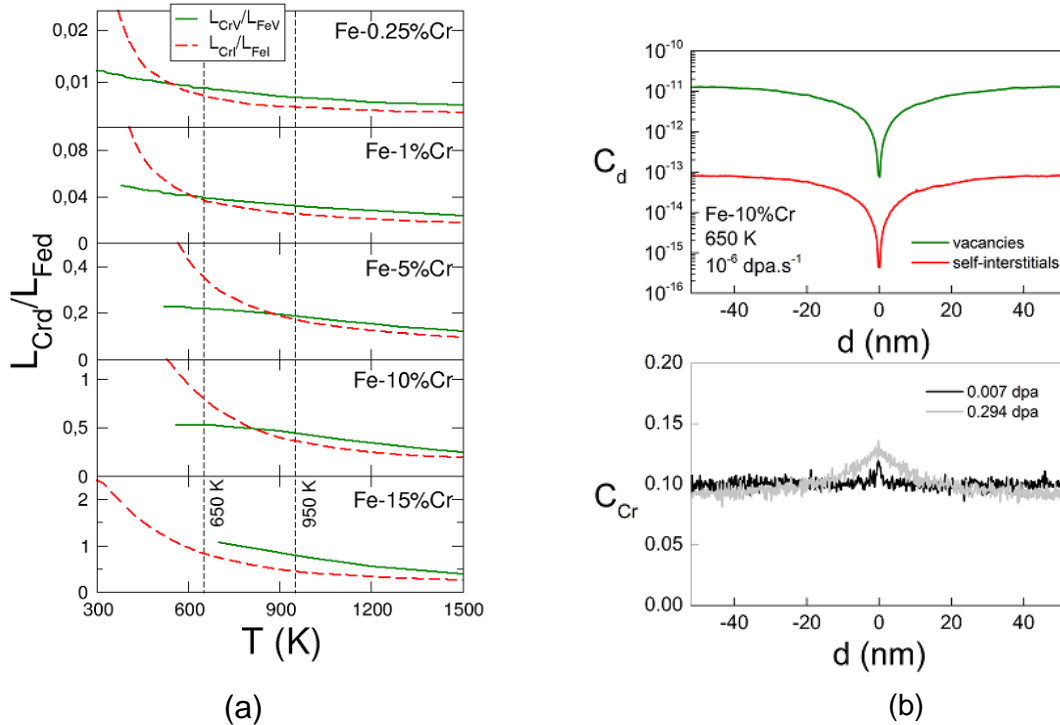
Fig. 1: (a) Evolution of the ratios of Onsager coefficients with the temperature, in Fe-Cr alloys of different compositions, estimated by Monte Carlo simulations, (b) Monte Carlo simulation of radiation induced segregation of Cr near a grain boundary (steady-state concentration profiles of point defects and concentration profiles of Cr at two successive doses).

References

[1] R.L. Klueh, A.T. Nelson, *Ferritic/martensitic steels for next-generation reactors*, J. Nucl. Mater. 371 (2007) 37.

[2] J.-L. Boutard et al, *Oxide dispersion strengthened ferritic steels: a basic research joint program in France*, J. Nucl. Mater. 455 (2014) 605.

[3] Z. Lu et al, *Irradiation-induced grain boundary chromium microchemistry in high alloy ferritic steels*, Scripta Mater. 58 (2008) 878

[4] M. Levesque, E. Martínez, C.-C. Fu, M. Nastar and F. Soisson, *Simple concentration-dependent pair interaction model for large-scale simulations of Fe-Cr alloys*, Phys. Rev. B 84, 184205 (2011)

[5] O. Senninger, E. Martinez, F. Soisson, M. Nastar and Y. Bréchet, *Atomistic simulations of decomposition kinetics in Fe-Cr alloys: influence of the magnetism*, Acta Mater. 73, 97–106 (2014).

[6] E. Meslin et al, *Cluster-dynamics modelling of defects in α-iron under cascade damage conditions*, J. Nucl. Mater. 382 (2008) 190.

[7] M. Bachhav, G. R. Odette, and E. A. Marquis, *α' precipitation in neutron-irradiated Fe‑Cr alloys*, Scripta Mater. 74 (2014) 48.

[8] V. Kuksenko, C. Pareige and P. Pareige, *Cr precipitation in neutron irradiated industrial purity Fe–Cr model alloys*, J. Nucl. Mater. 432 (2013) 160.

[9] O. Senninger et. al., *Modeling radiation induced segregation in Fe-Cr alloys*, submitted to Acta Mater.

Atomistic Modeling of Segregation and Precipitation in Fe-Cr Alloys under Irradiation

C.-C. Fu, T. Jourdan, M. Nastar, O. Senninger,
F. Soisson
SRMP, CEA Saclay

E. Martinez
Los Alamos National Laboratory

Y. Bréchet
SIMAP, Grenoble INP

www.cea.fr

MINOS

- **Fe-Cr alloys** : a model for ferritic and ferritic-martensitic steels (7-18%Cr)
  candidate materials for future nuclear reactors (Gen IV and fusion)

Potential problems under irradiation:
- α' precipitation → hardening and embrittlement
- Cr depletion at GBs → corrosion, embrittlement

Due to: point defect supersaturation
  Acceleration of precipitation
  Radiation Induced Segregation (RIS)
  Radiation Induced Precipitation (RIP)

- Main objectives:
  - quantify the acceleration of precipitation in supersaturated alloys
  - understand the mechanisms controlling RIS
  - study possible effects of equilibrium vs non-equilibrium segregation, ballistic mixing, carbon atoms,… on the precipitation and segregation kinetics

- Our approach : **Atomistic Kinetic Monte Carlo** (AKMC) simulations

MINOS
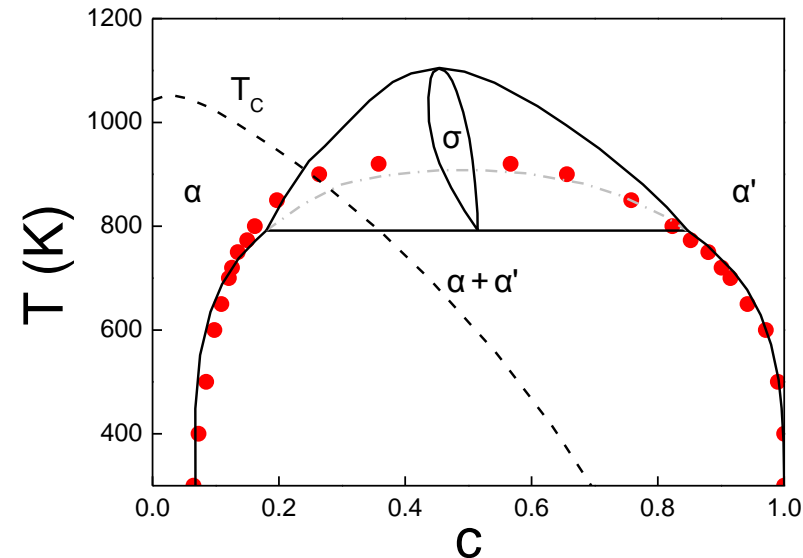
Pair interactions on stable (bcc) and saddle-point positions

- Diffusion by jumps of :
- Vacancies (V)
- Self-interstitial atoms (SIA) : <110> dumbbells
- Direct interstitials (C)

- The migration barriers are computed with a broken-bond model:
  - with composition and temperature dependent pair interactions
  - with saddle-point pair interactions
  - fitted on DFT calculations

- Formation of isolated Frenkel with replacement collision sequences or small replacement cascades

- Annihilation of V and SIA on a perfect sink

Γ_{AV}, Γ_{BV}, V, C, SIA

"grain boundary" = perfect pd sink

Sink strength

$$k_{tot}^2 = 12/L^2$$

L = 36 to 104 nm

MINOS
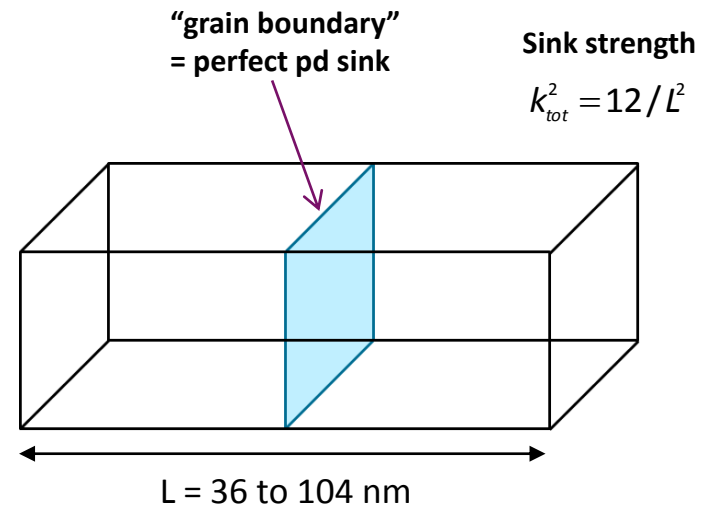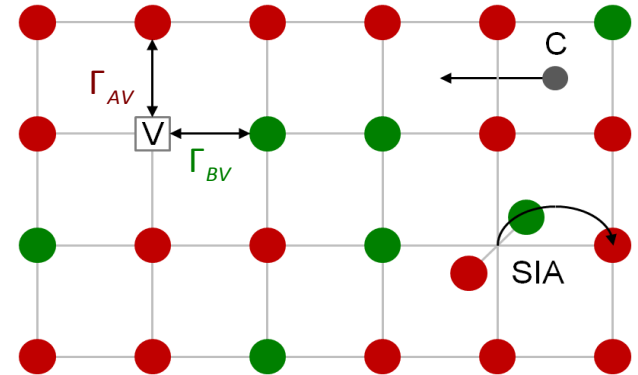
Concentration dependent pair interactions: $h_{FeFe}^{(n)}, h_{CrCr}^{(n)}, h_{FeCr}^{(n)}(x)$ fitted on DFT calculations of ΔH_{mix} at 0K

Magnetic and vibrational contributions: linear temperature dependence, fitted on $T_{\alpha-\alpha'}$ (exp)

M. Levesque et al, Phys. Rev. B 84, 184205 (2011)

$$g_{FeCr}^{(n)}(x,T) = h_{FeCr}^{(n)}(x) - Ts_{FeCr}^{(n)}(x) \text{ , with } n = 1,2$$

$$\Delta H_{mix} = \Omega(x)x(1-x)$$

$$\Omega(x) = \sum_n \frac{z_n}{2}\left[h_{FeFe}^{(n)} + h_{CrCr}^{(n)} - 2h_{FeCr}^{(n)}(x) \right]$$

PWSCF, GGA-PAW
- ● Special Quasi-random structures (SQS)
- ◇ Ordered structures
- —— Pair interaction model

MINOS
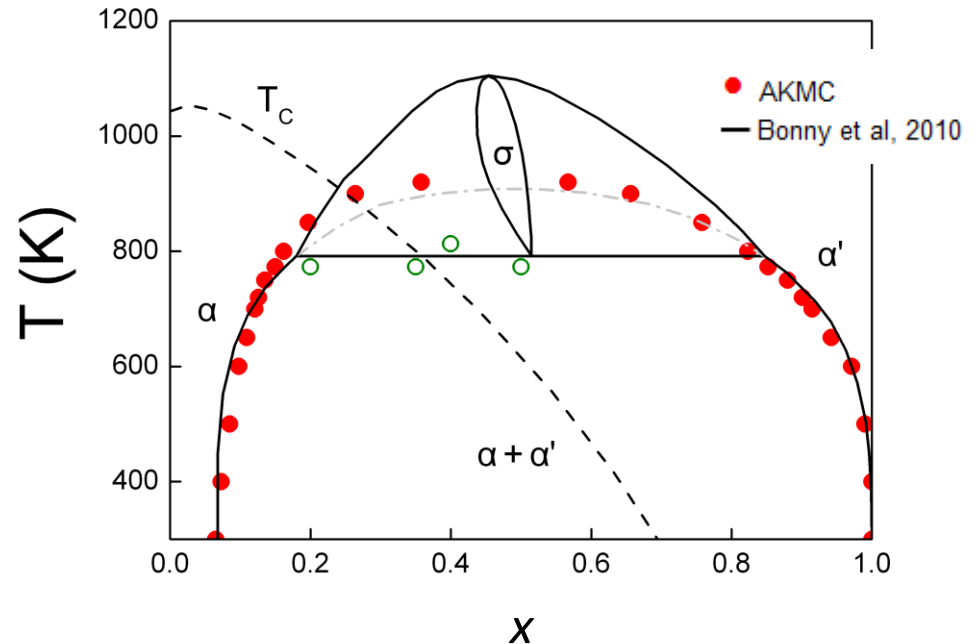
Tracer diffusion coefficients (pure iron)
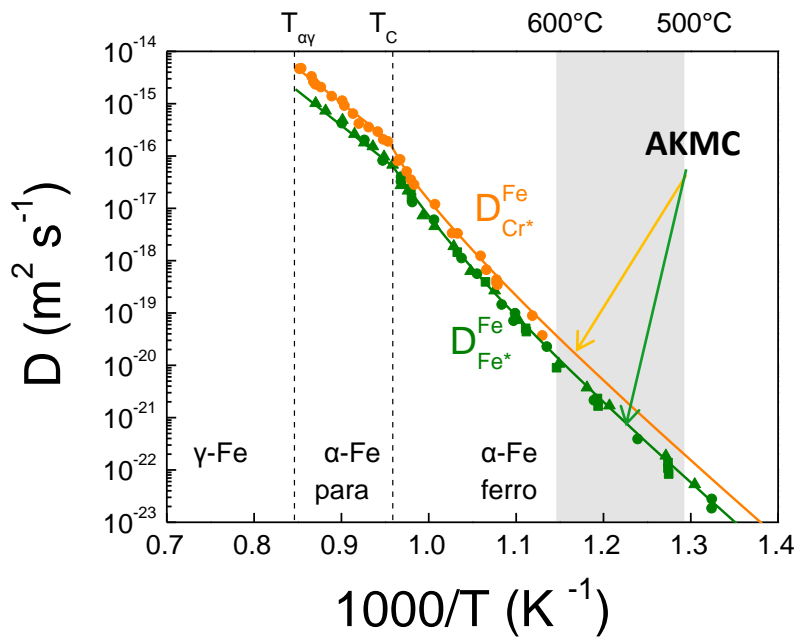
Interdiffusion coefficients in Fe-Cr alloys

[1] Braun & Feller-Kniepmeier, 1985
[2] Jönsson 1995
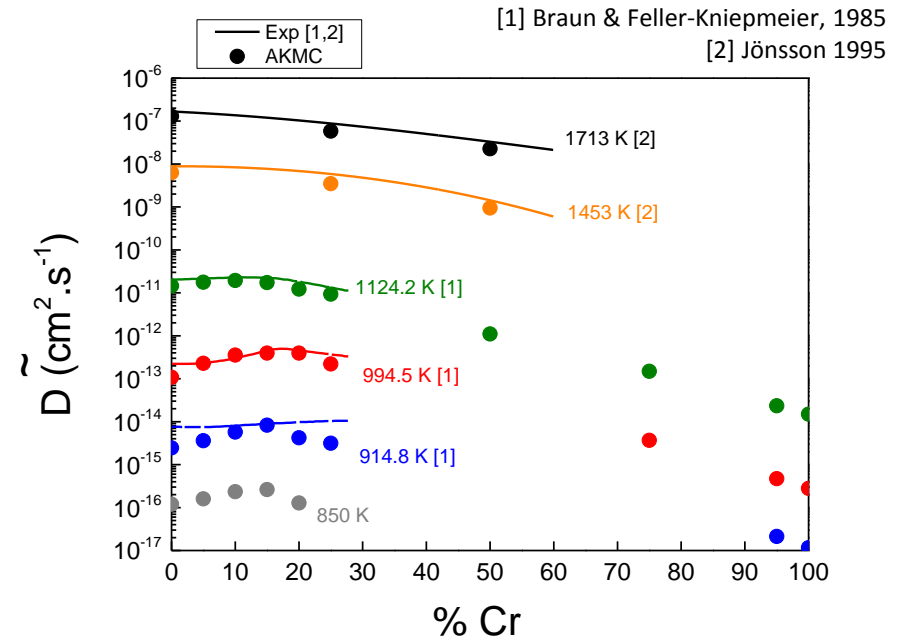
O. Senninger et al, Acta Mater. 73, 97–106 (2014)

- Acceleration of the diffusion at the F/P transition
- The Curie temperature decreases with the Cr concentration
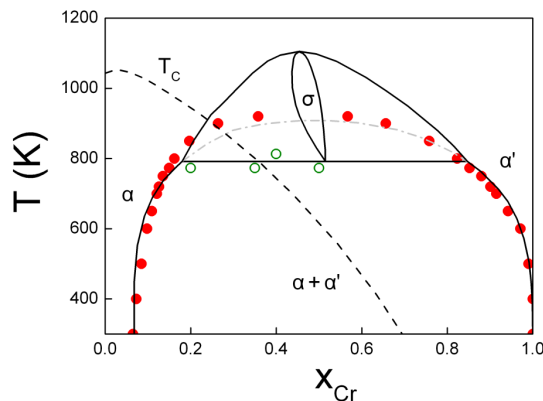
Fe-20%Cr   T = 500°C

AKMC (E. Martinez et al, 2012)   3DAP (Novy et al, 2009)
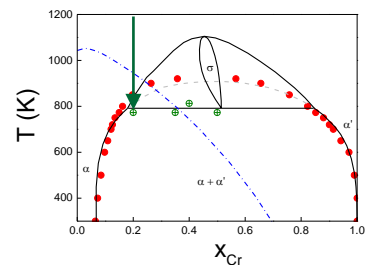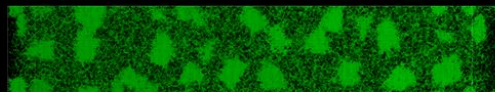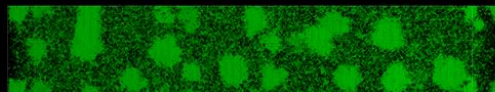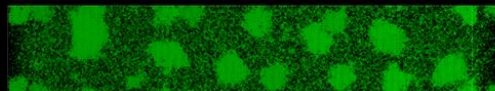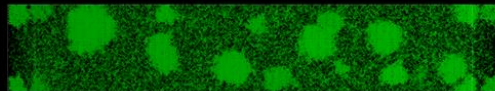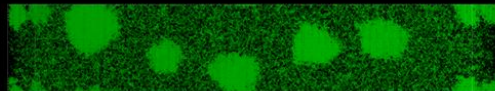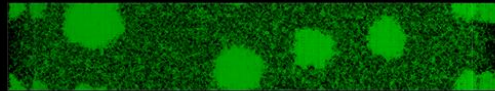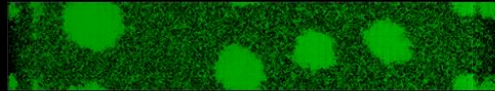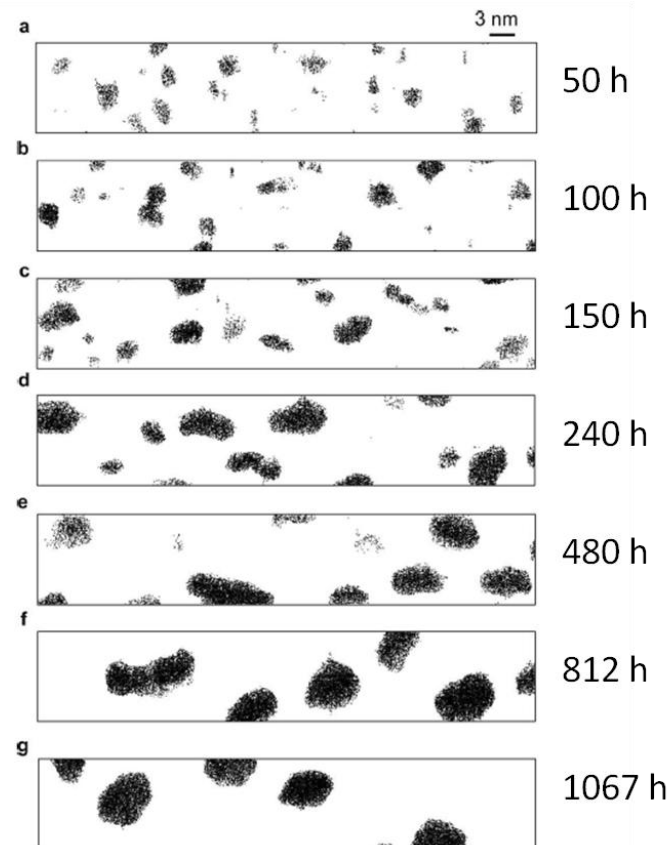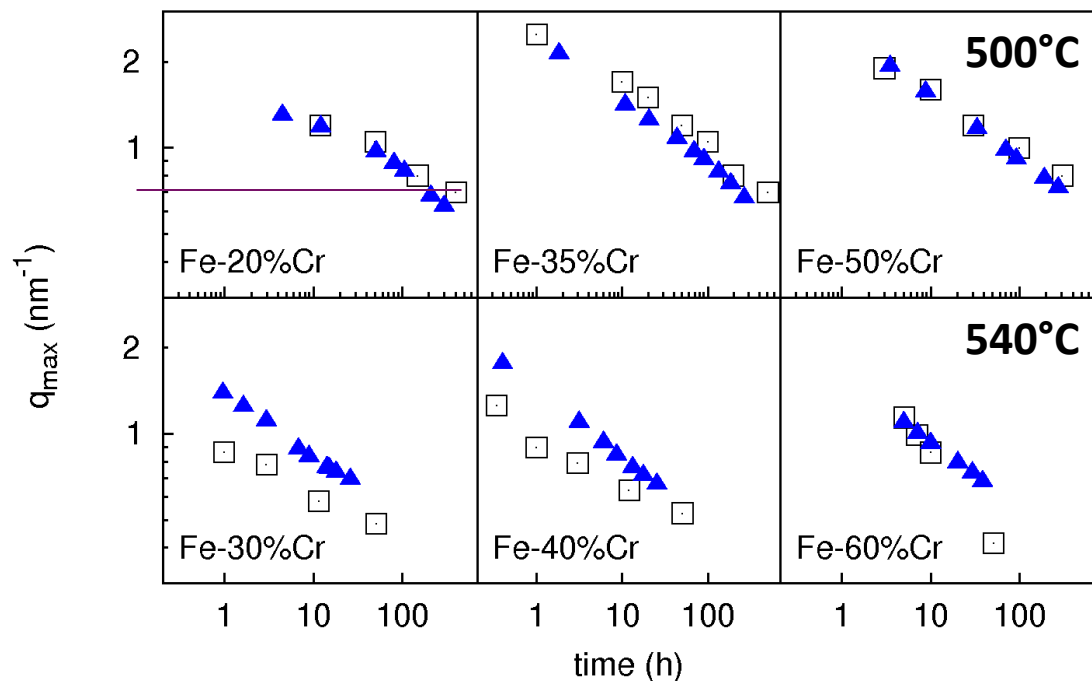

E. Martinez et al, Phys. Rev. B 86, 224109 (2012)
S. Novy et al, J. Nucl. Mater. 384 (2009) 96–102

MINOS

Small-angle neutron scattering experiments (SANS)
    500°C: Bley (1992)
    540°C: Furusaka et al. (1986)
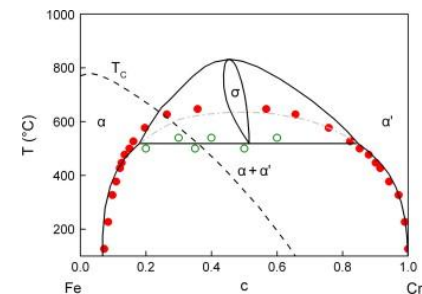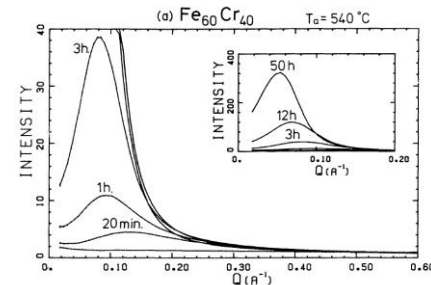
□ SANS experiments
▲ AKMC simulations
● AKMC simulations without magnetic acceleration

O. Senninger et al, Acta Mater. 73, 97–106 (2014)

Experimental evidences (3DAP)
in Fe-9% to 20%Cr alloys at 290-300°C
- **isothermal annealing**: α' precipitation is not observed
due to slow kinetics
- **neutron irradiation:** α' precipitation
Bachhav et al (Scripta Mater 2014)
Fe-3%Cr to 18%Cr, T= 290°C
3.4 x 10^{-7} dpa/s, 1.82 dpa

(a) 3%Cr (b) 6%Cr (c) 9%Cr (d) 12%Cr (e) 15%Cr (f) 18%Cr 25 nm

- P
- Si
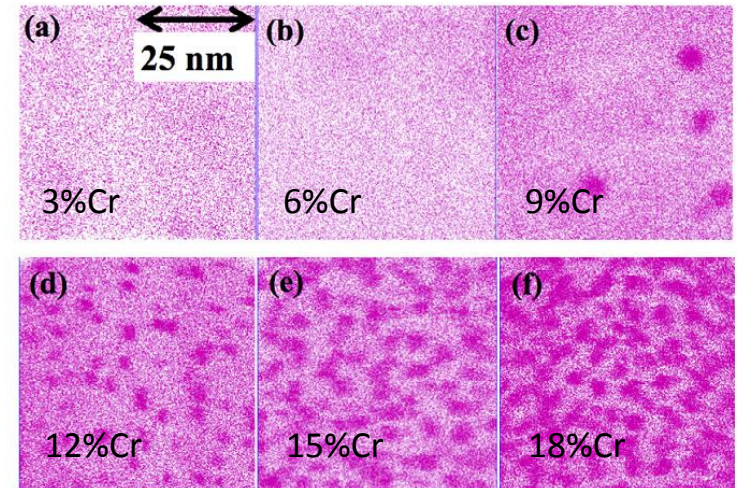
V. Kuksenko et al, JNM 432 (2013) 160
C. Pareige et al JNM 456 (2015) 471–476
Precipitation under neutron irradiation in Fe-9%Cr and
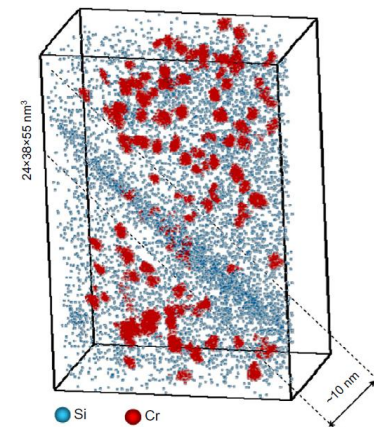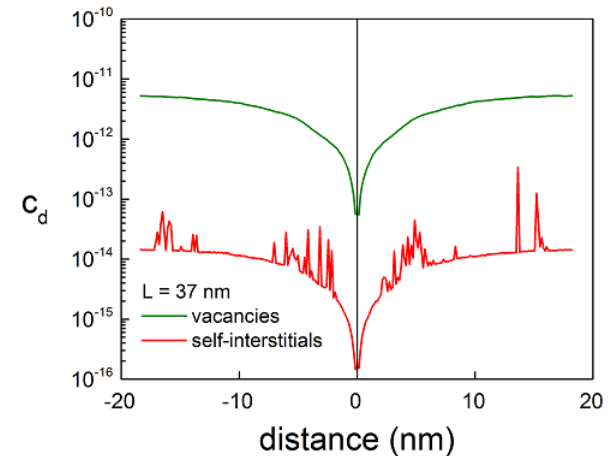Fe-12%Cr, but not under ion irradiation at higher flux

ions — neutrons — Cr rich clusters — V=46 x 46 x 115 nm³ — 300°C – 0.5 dpa — 300°C – 0.6 dpa

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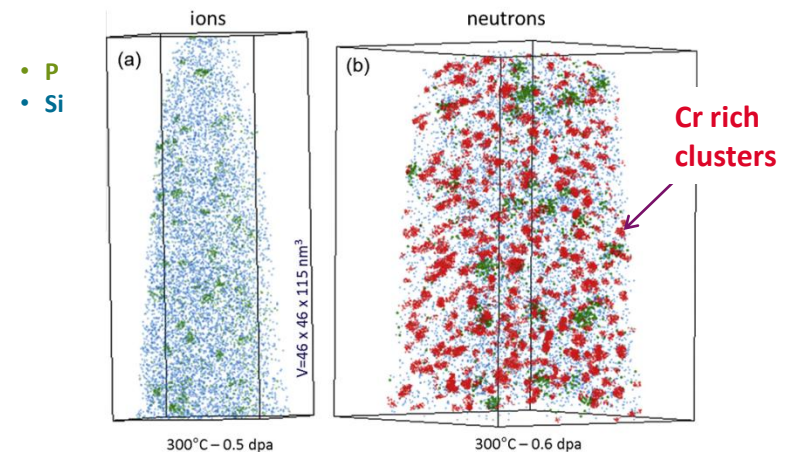
AKMC simulations
Fe-18%Cr @ 563 K, 3.4 x 10^{-7} dpa.s^{-1}

Point defect concentration profiles

104 nm

GB
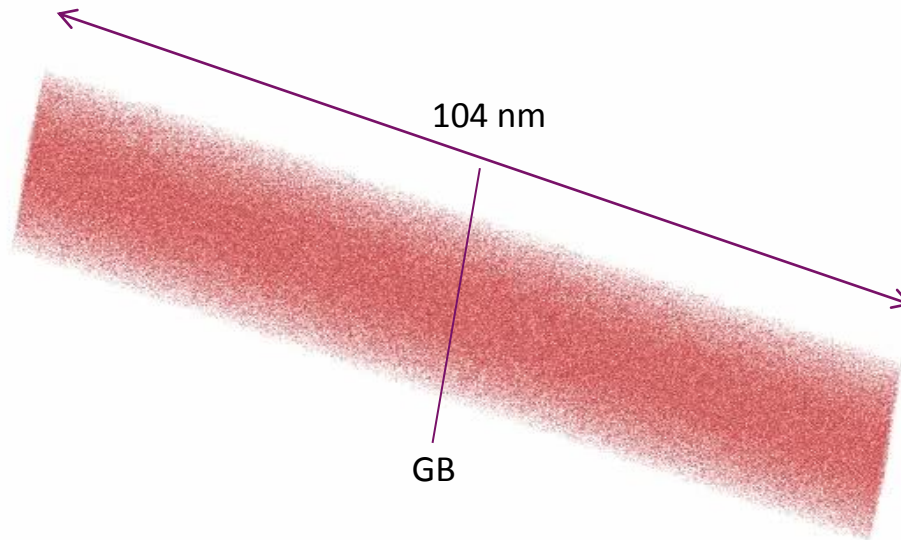
Precipitate free zones near the GBs

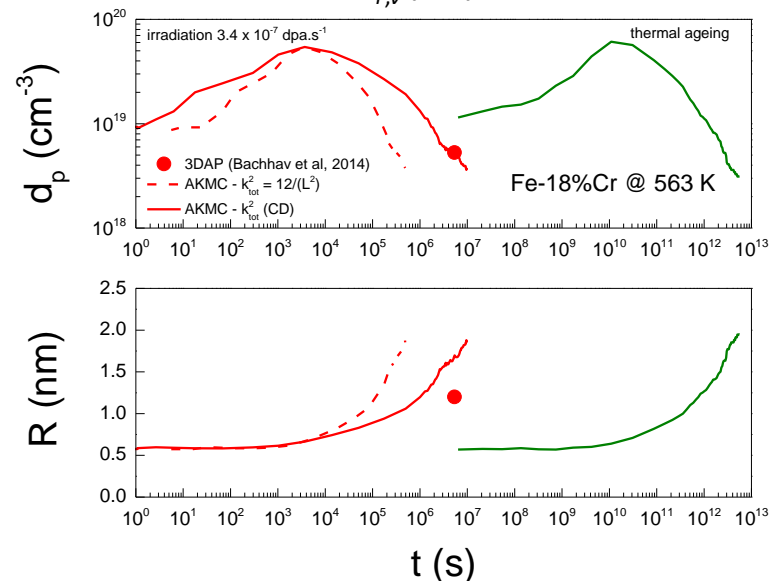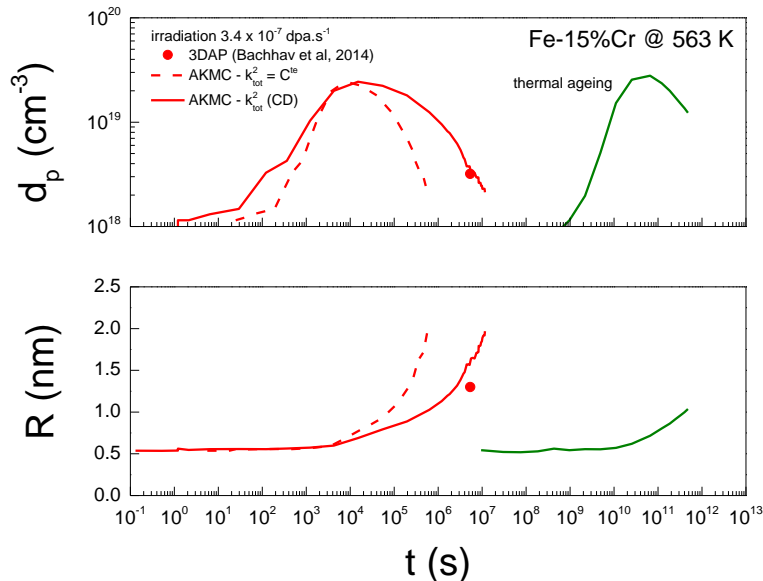3DAP
Kuksenko et al
(2012)
Fe-12%Cr
300°C – 0.6
dpa

MINOS

- **AKMC simulations:** one GB in the simulation box (constant sink strength: $k_{tot}^2 = 12/L^2$)
- **Cluster Dynamics:** evolution of the sink strength k_{tot}^2 (in pure iron)

  → better estimation of the point defect concentration $c_{i,v} = G/(k_{tot}^2 D_{i,v})$

  → rescaling of the Monte Carlo time scale

$$t = t_{MC} \times \frac{c_{i,v}(AKMC)}{c_{i,v}(CD)}$$

Strong acceleration by irradiation (x 10^6-10^7)

Good agreement with the experiments of neutron irradiation (Bachhav et al, 2014)

F. Soisson, T. Jourdan, Acta Mater 2016.

MINOS

- Experiments: Cr precipitation under neutron irradiation, but not under ion irradiation at higher flux
  A ballistic dissolution of α' precipitates, in displacement cascades ?

- AKMC simulations   - at different dose rates G (dpa.s^{-1})
                             - with different numbers of replacements/displacement

$N_{rep}/N_{dis} = 0$ (channeling)
$N_{rep}/N_{dis} = 10$ (replacement collision sequences)
$N_{rep}/N_{dis} = 100$ (cascades)

- **At 290°C** $\gamma = \dfrac{\Gamma_{bal}}{\langle \Gamma_{th} \rangle} \propto \dfrac{G}{c_v^{st} D_v} \square\ 10^{-3} - 10^{-4}$

- no dissolution of precipitates
- no effect of N_{rep}/N_{dis} on the precipitation kinetics
- dose rate effects: a simple acceleration
due to the point defect supersaturation

$$c_{i,v} = G / (k_{tot}^2 D_{i,v})$$

→ ballistic effects do not explain the difference
between ion and neutron irradiations

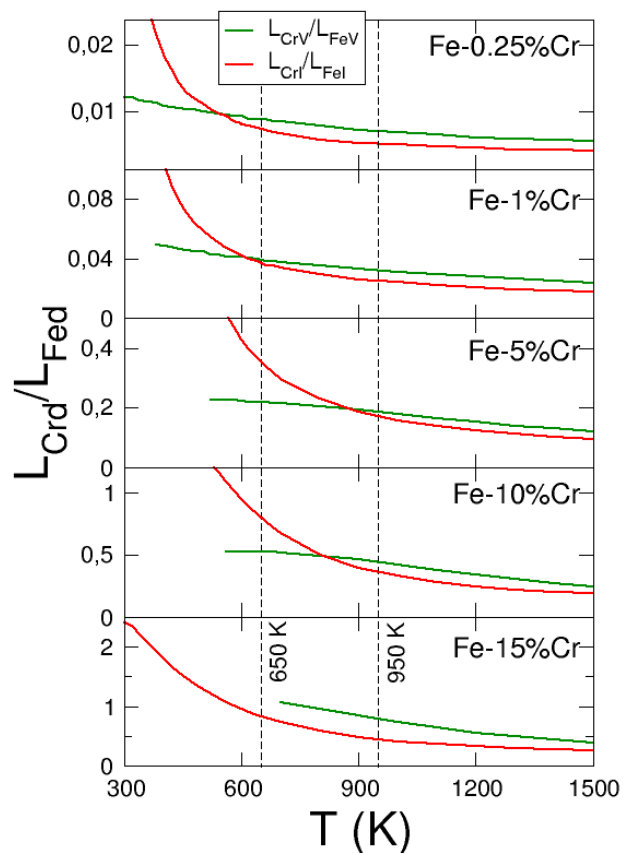- Possible ballistic effects **at lower temperatures** (below 100°C)
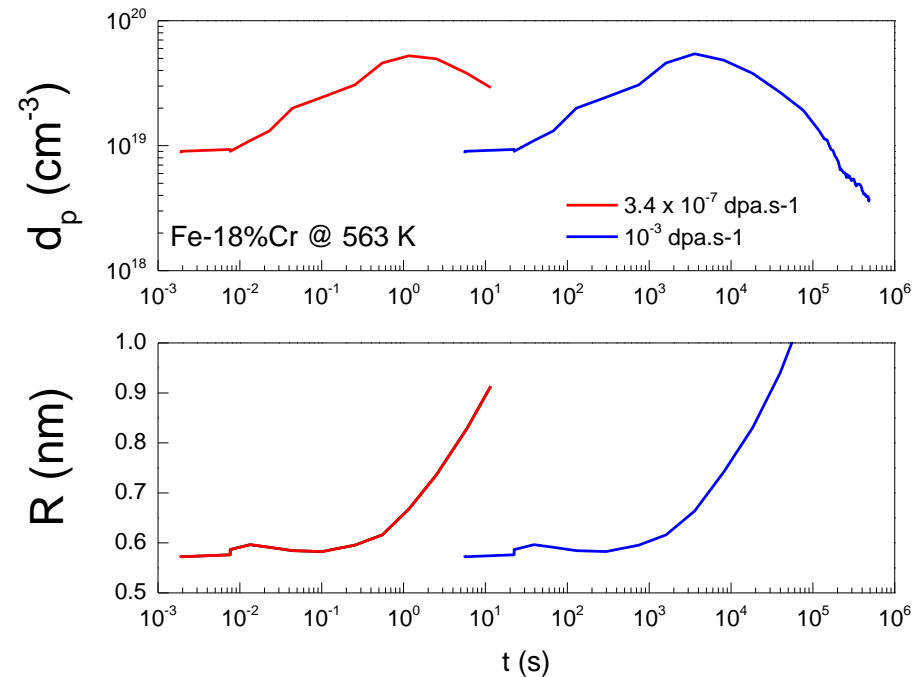
MINOS

$$J_i = -\sum_j L_{ij} \nabla \mu_j$$

J_V/J_{Cr} : negative coupling → Cr depletion at sinks, dominant at high T

J_{SIA}/J_{Cr} : positive coupling → Cr enrichment at sinks, dominant at low T

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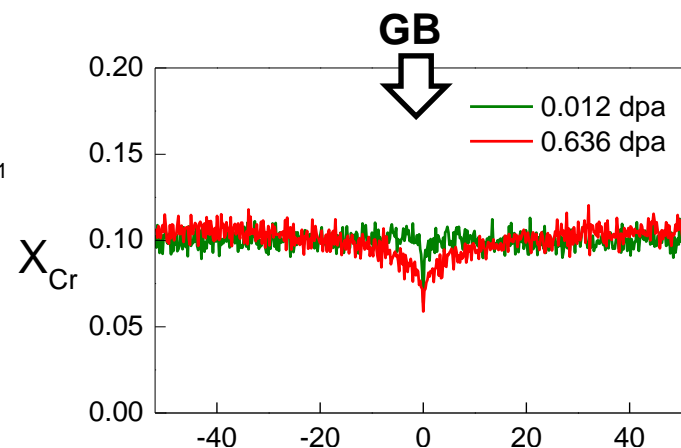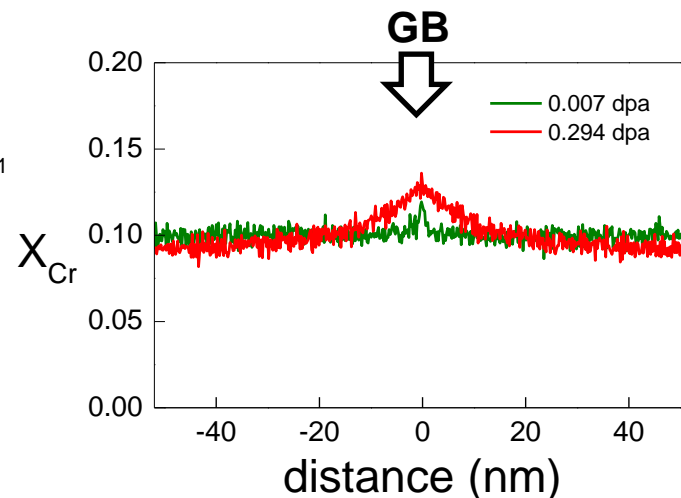T = 650 K, 10^{-6} dpa.s^{-1}

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

Steady-state profile:

$$\nabla C_{Cr} \propto -\left(\frac{L_{CrV}}{L_{FeV}} - \frac{L_{CrI}}{L_{FeI}} \right) \nabla C_V$$
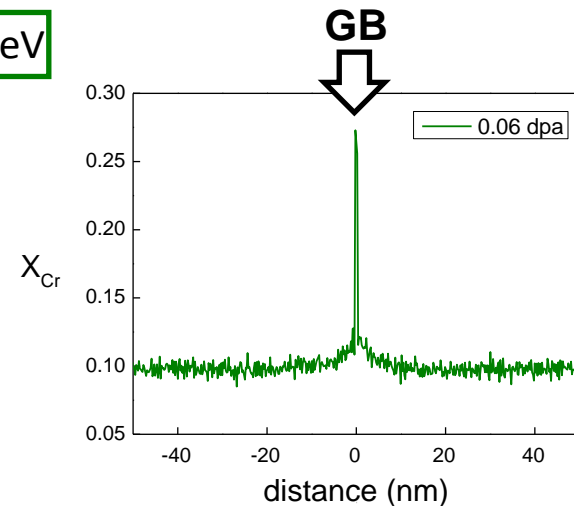
O. Senninger et al
Acta Materialia 103, 1–11 (2016)

MINOS

$$J_i = -\sum_j L_{ij}\nabla\mu_j$$

J_V/J_{Cr} : negative coupling → Cr depletion at sinks, dominant at high T
J_{SIA}/J_{Cr} : positive coupling → Cr depletion at sinks, dominant at low T
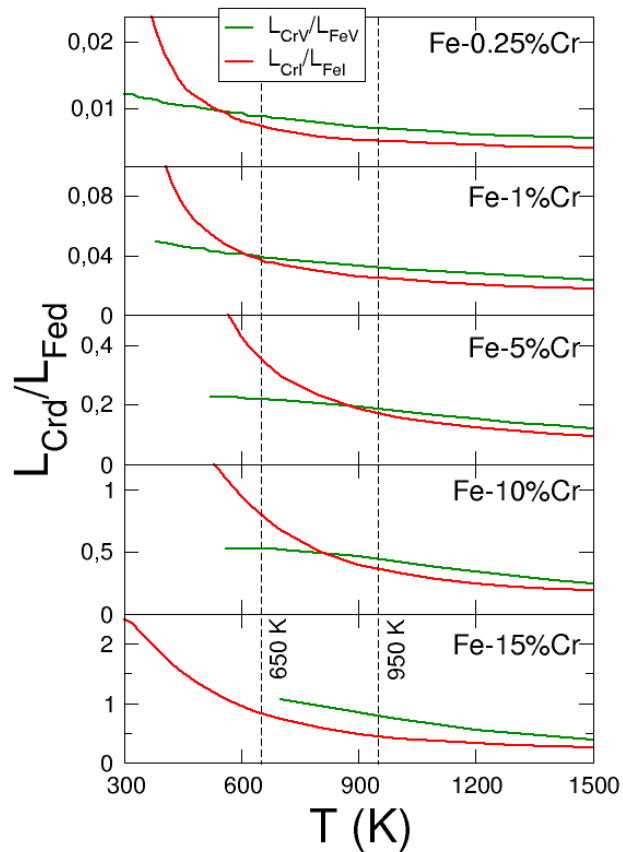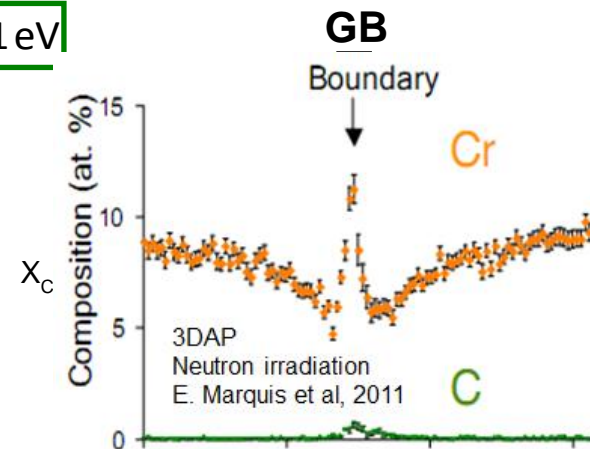
$$e_{Cr}^{seg} = -0.1\,\text{eV}$$

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

GB

$$e_{Cr}^{seg} = -0.1\,\text{eV}$$

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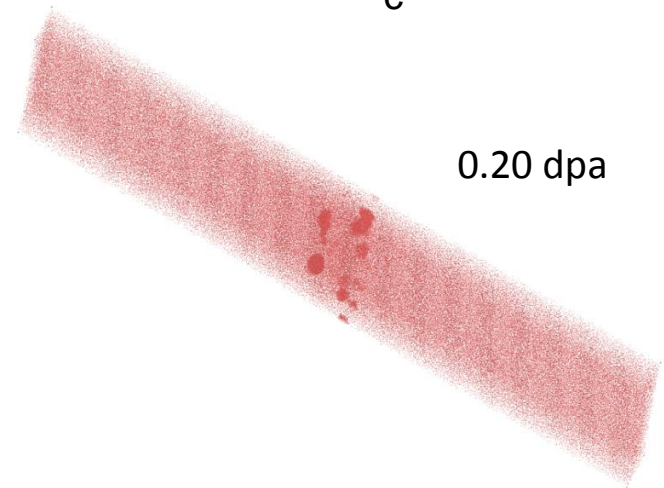
GB

W-shape profile

Steady-state profile:
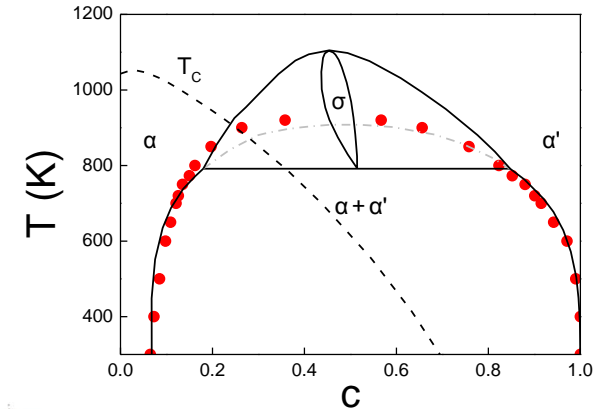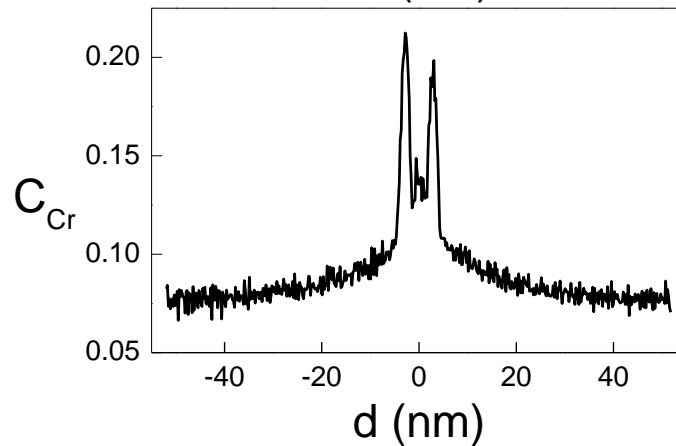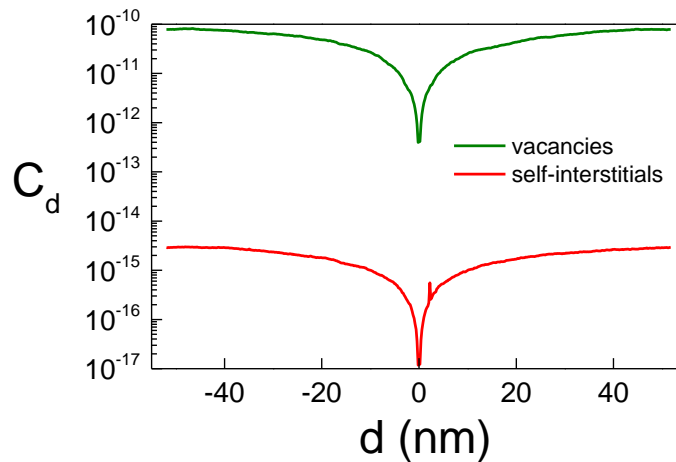
$$\nabla C_{Cr} \propto -\left(\frac{L_{CrV}}{L_{FeV}} - \frac{L_{CrI}}{L_{FeI}}\right)\nabla C_V$$

MINOS

Undersaturated alloys, at low T: strong Cr enrichment on sinks → RIS → radiation induced precipitation

T = 563 K
Fe-9%Cr
10^{-6} dpa.s^{-1}

0.20 dpa

MINOS

AKMC simulations with thermodynamic and point defect parameters fitted on DFT calculations

Good description of driving forces, diffusion properties and nucleation

In Fe-Cr alloys

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

- **Radiation Induced Segregation** is controlled by a balance between opposite effects of V and SIA
  the L_{ij} are very dependent of the details of migration barriers
  → may explain the variability of experimental studies (≠ RIS in austenitic steels)

- **Radiation accelerated precipitation**
  - a good agreement with neutron irradiations (with rescaling of the sink strength using CD)
  - no effect ballistic mixing in the experimental conditions (relatively high temperatures, high sink densities) → does
    not explain the difference between neutron an on irradiation
  - precipitation kinetics is less sensitive than Radiation Induced Segregation to the details of migration barriers

- **Related work, perspectives**
  - Phase-Field model for RIS (J.B. Piochaud, L. Thunier, A. Legris – UMET, Lille)
  - Precipitation under electron irradiation (O. Tissot, et al)
  - Effects of C (or O, N) on the kinetics of precipitation and segregation