MECHANISMS OF FORMATION OF NANO-FEATURES

Flux effects on radiation damage in ferritic Fe-Mn and Fe-Ni alloys

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Flux effects in binary Fe-3%Ni AND Fe-3%Mn ALLOYS

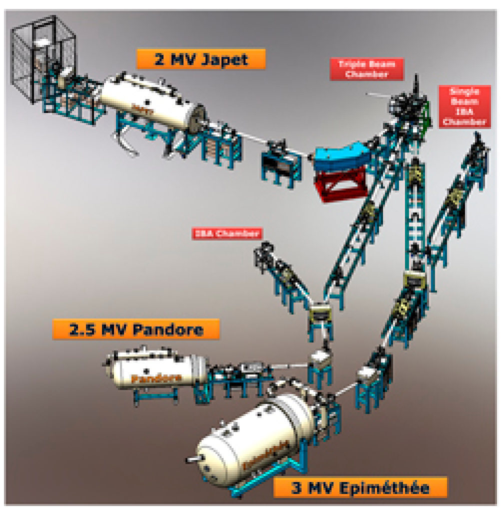
Experiments → **NPP**

Damage rate (Fe)	Ion accelerators	MTR	NPP
	10^{-5}-10^{-3} dpa/s	10^{-9}-10^{-7} dpa/s	10^{-10} dpa/s

Flux effects ?

Radiation damage using particle accelerators

JANNuS-Saclay platform, CEA Saclay



Ion irradiation conditions

- Fe ions
- 400°C
- 1.3 dpa
- Vacuum < 4 x 10^{-8} Torr
- 2 damage rates:
  - 27 MeV Fe^{9+}
  - 8 10^{-6} $dpa.s^{-1}$
  - 2 MeV Fe^{3+}
  - 5.4 10^{-4} $dpa.s^{-1}$

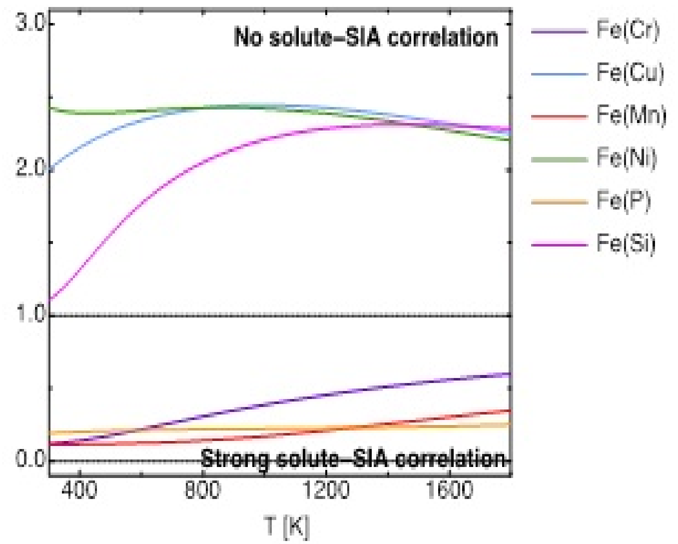
X 65

Mn and Ni drag by PDs

Ni

Ni-SIA: No correlation

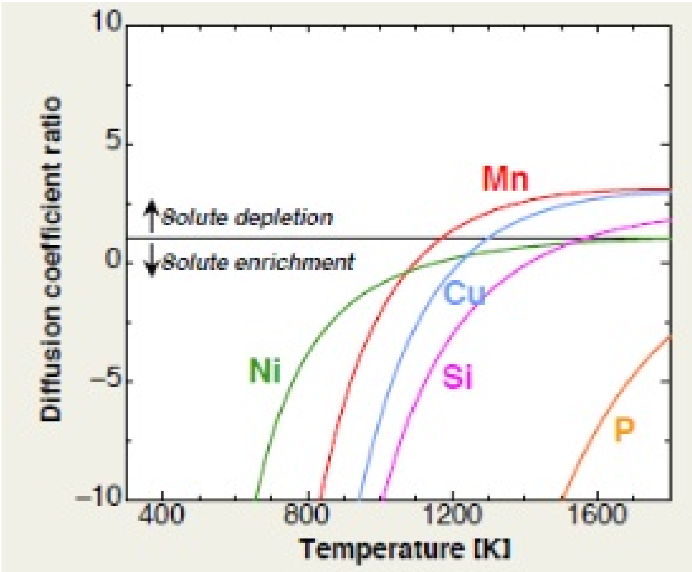
Ni: enrichment up to 1087 K (V)



Mn

Mn-SIA: High correlation

Mn: enrichment up to 1011 K (V and SIA)



L. Messina et al. Phys. Rev. B, 2016, 93
L. Messina et al. Phys. Rev. B 2014, 90

Flux effects on Fe-3%Ni microstructure

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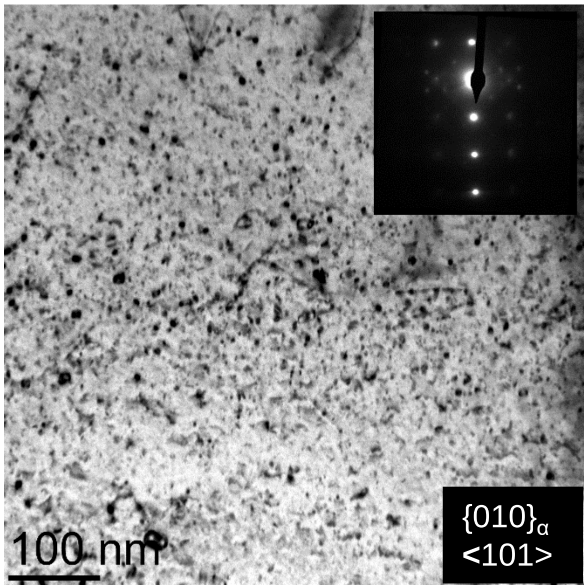
High flux

1.4 nm, 3.0 x 10^{22} m^{-3}



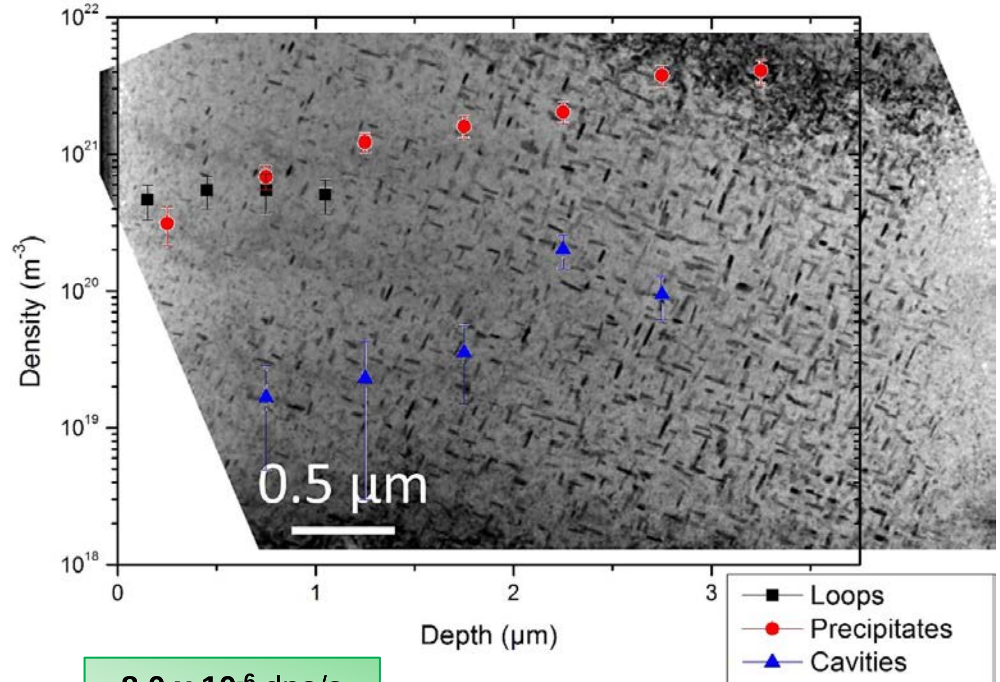
1.2 ± 0.4 nm
5.2 ± 1.2 x 10^{22} m^{-3}

5.4 x 10^{-4} dpa/s
1.7 dpa

60 x 60 x 250 nm^3

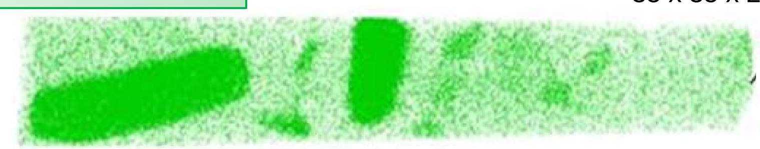
10.7 ± 0.6 %Ni : Radiation induced segregation

Low flux



8.0 x 10^{-6} dpa/s
1.3 dpa

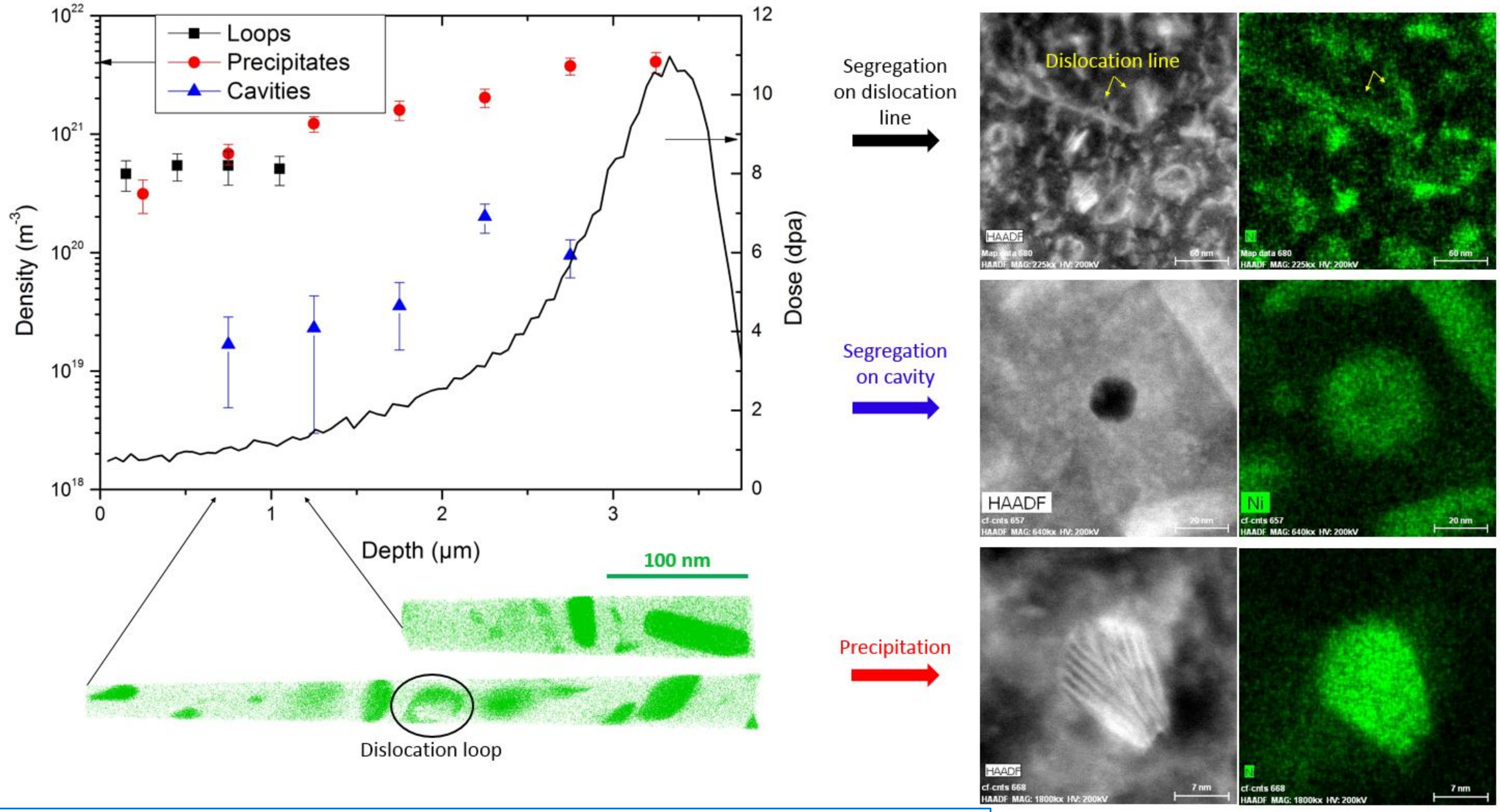
35 x 35 x 250 nm^3



Radiation induced precipitation of Fe-25%Ni (γ) or Fe_3Ni phase

Various microstructural features in the low flux irradiated Fe-3%Ni

Radiation induced segregation/precipitation in a BCC Fe-3at%Ni model alloy



FCC precipitate – BCC matrix interface = PD sink

ELECTRON IRRADIATIONS INDUCE Ni SEGREGATION

3.9 x 10^{-5} dpa/s
0.14 dpa
320°C

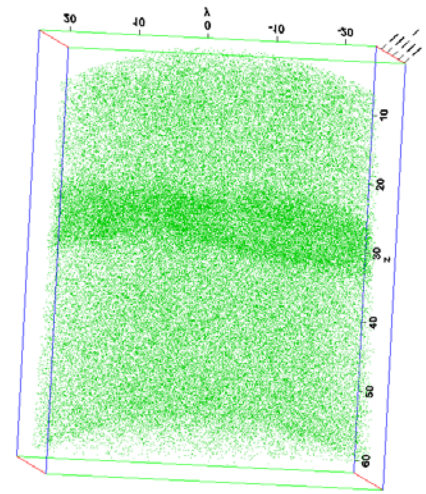
55 x 55 x 820 nm^3

Ni-enriched cluster **probably** on a dislocation line

Nuclei are needed for segregation

PD cluster density < 4.5 x 10^{20} m^{-3}

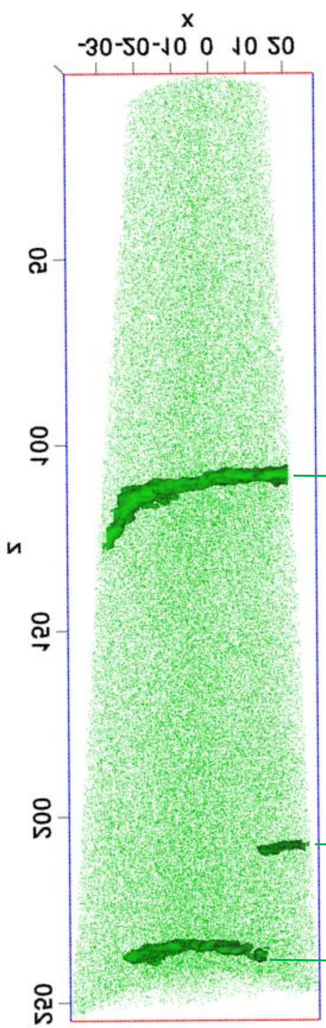
Radiation Induced Segregation of Ni by flux coupling (Ni-V)



23.6 ±0.3 at.%Ni

Intermetallic FCC Fe_3Ni phase formed in the BCC matrix ?

PROTON IRRADIATIONS INDUCE Ni SEGREGATION



3.7 x 10^{-6} dpa/s
0.1 dpa
400°C

Core Ni content

9.9 ± 0.5 at.%

7.7 ± 1.6 at.%

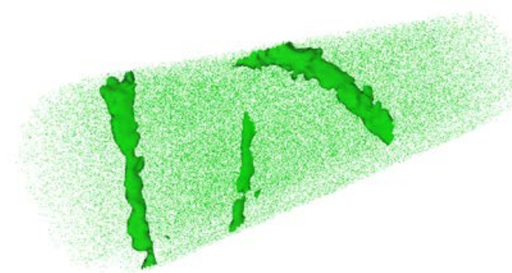
10.3 ± 0.8 at.%

Ni-enriched dislocation lines

Same as under electron irradiation :

Nuclei are needed for segregation

PD cluster density ~ 2.9 x 10^{21} m^{-3}

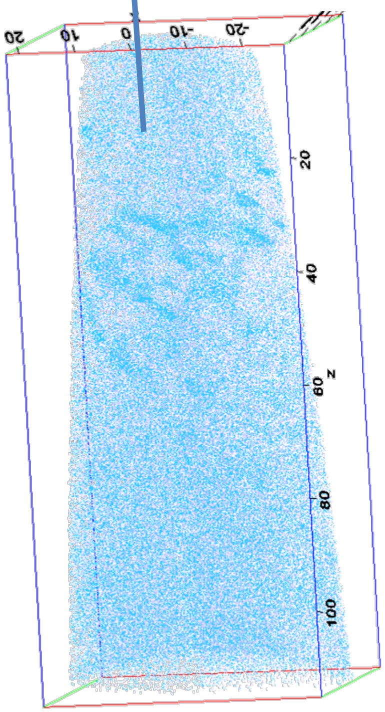


Radiation Induced Segregation of Ni by flux coupling (Ni-V)

High flux induces segregation in Fe-3%Mn

{110} type zone axis

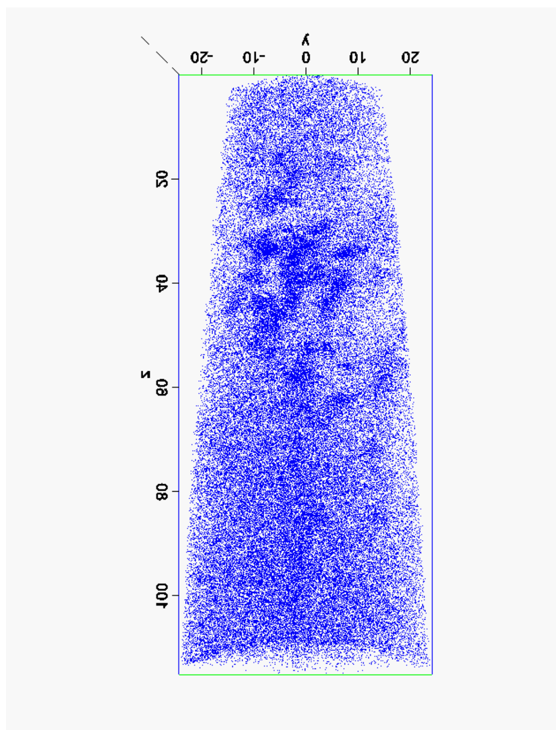
~ 45° between <110> type zone axis and planar Mn-enriched clusters



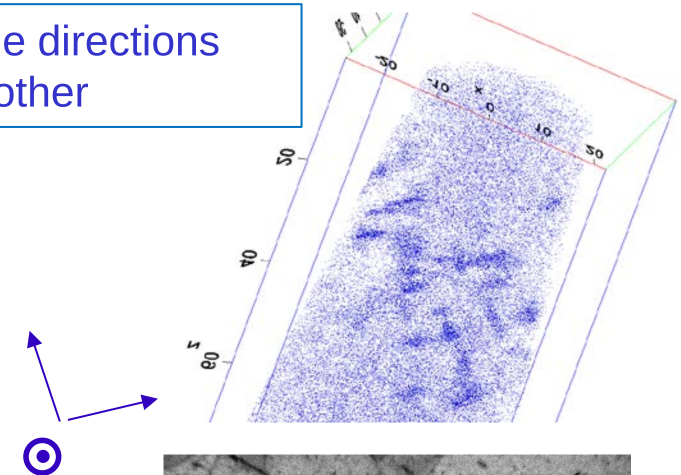
50 x 50 x 100 nm^3

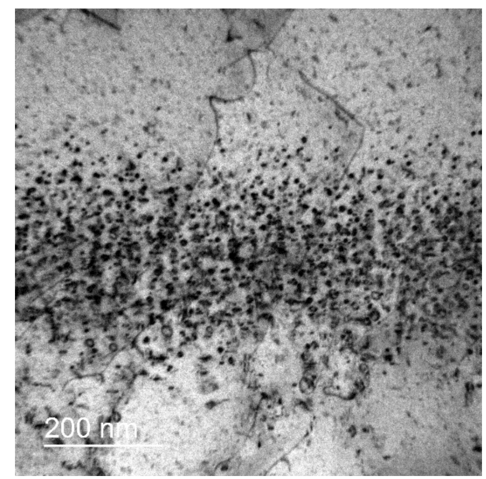
7.5 x 10^{-4} dpa/s
1.8 dpa

Planar objects : 3 visible directions
Perpendicular to each other



Core concentration : 38.5 ± 2.4 %
Mean radius : 1.4 ± 0.2 nm
Density : 2.9 ± 0.4 x 10^{23} m^{-3}





<100> type dislocation loops by TEM and APT

Radiation Induced Segregation

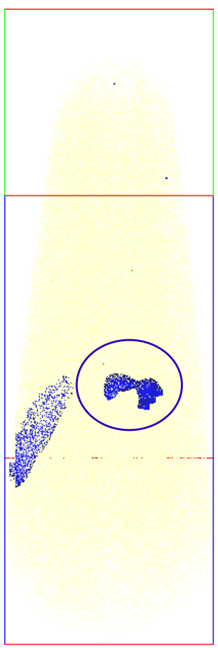
Low flux induces Mn decorated loops in Fe-3%Mn

8.0 x 10^{-6} dpa/s
1.3 dpa

Mn cluster density : 1.7 ± 1.2 x 10^{22} m^{-3}

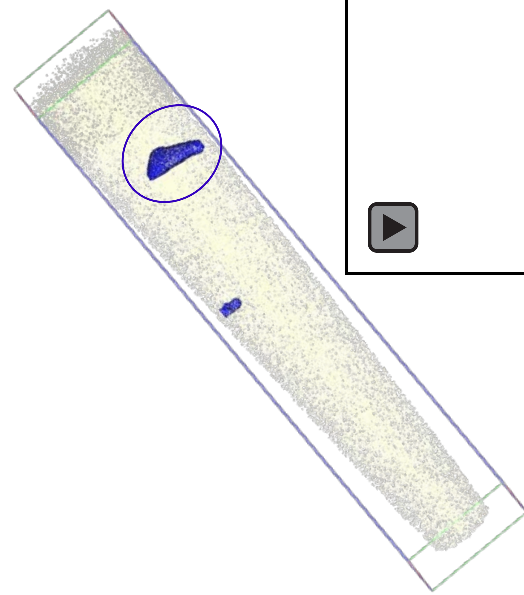
Small dislocation loop

Core concentration : 9.8 ± 0.1 %
Radius : ~ 1.35 nm



Large dislocation loop

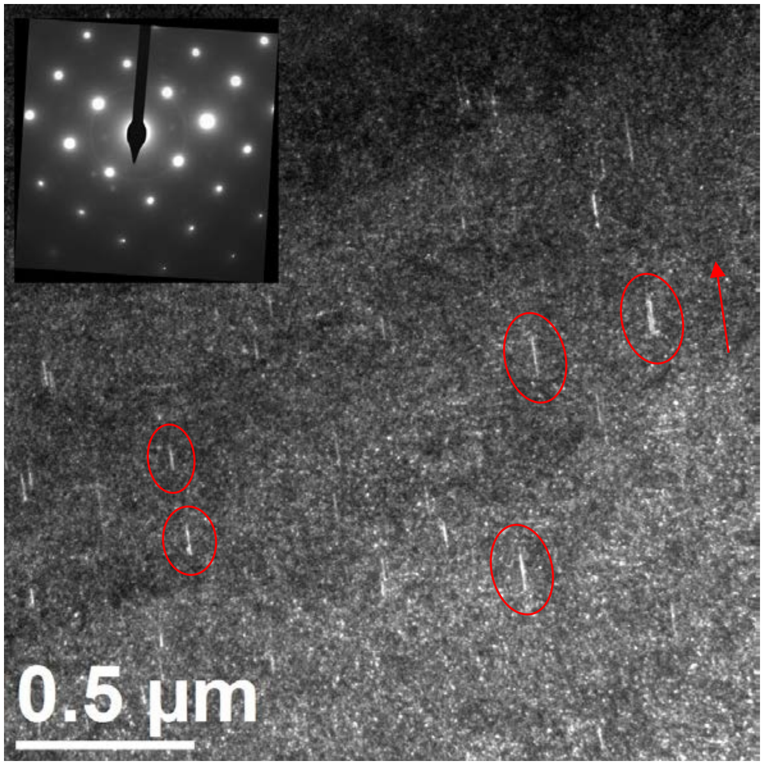
Core concentration : 56.8 ± 0.2 %
Radius : ~ 3.4 nm



<u>Lower flux</u> : less numerous, larger and more enriched Mn features (decorated loops)

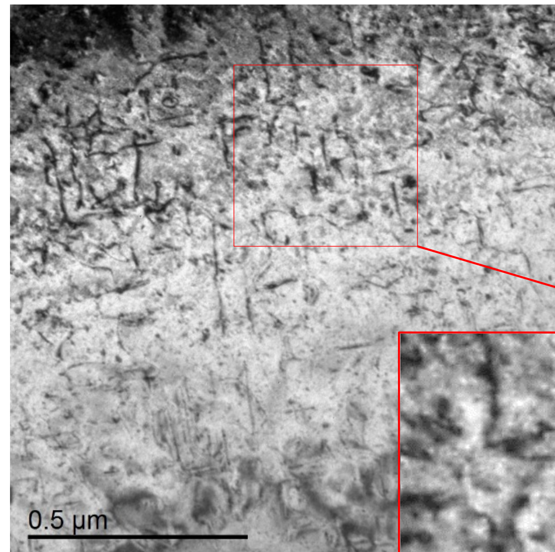
Mn segregation on large dislocation loops in Fe-3%Mn under low flux

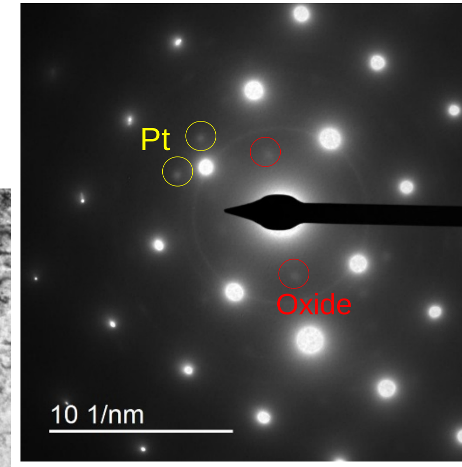
Presence of large <100> type dislocation loops in {100} zone axis visible by DF imaging …

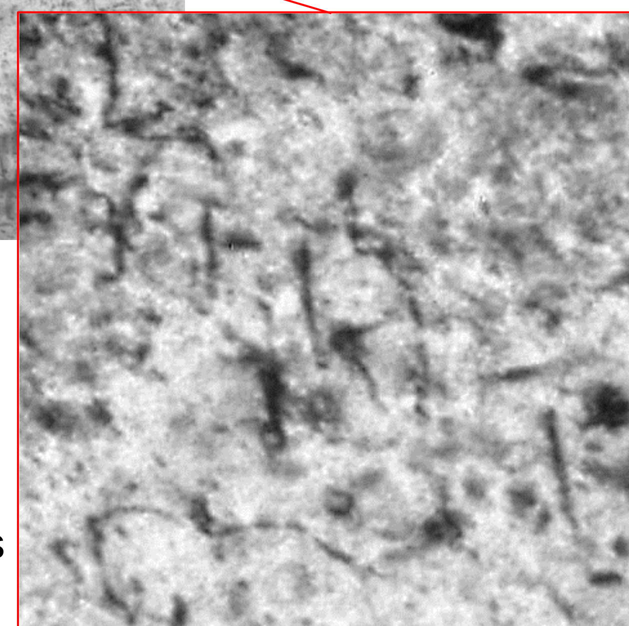


Large loops likely decorated by Mn

… and forming a dislocation network



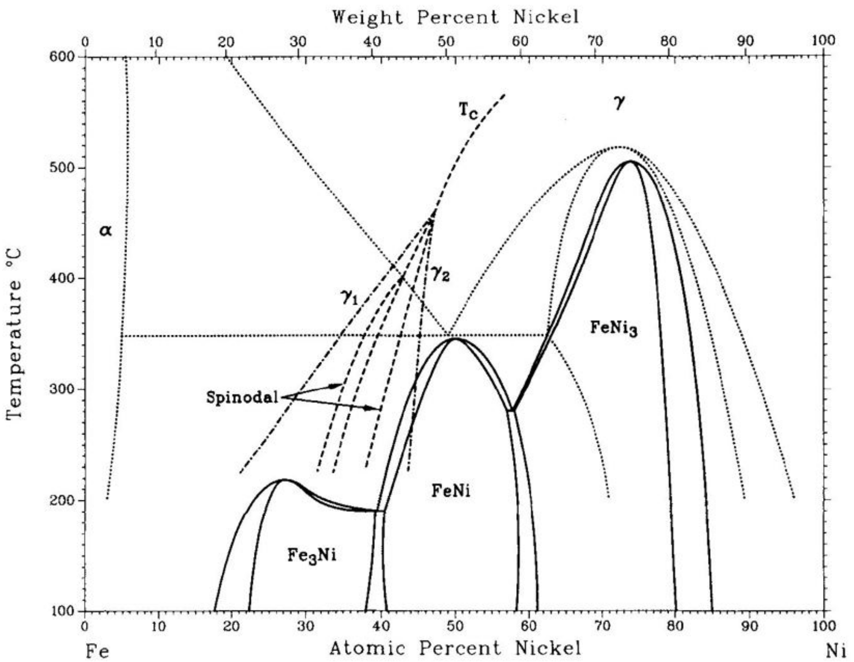




No precipitation

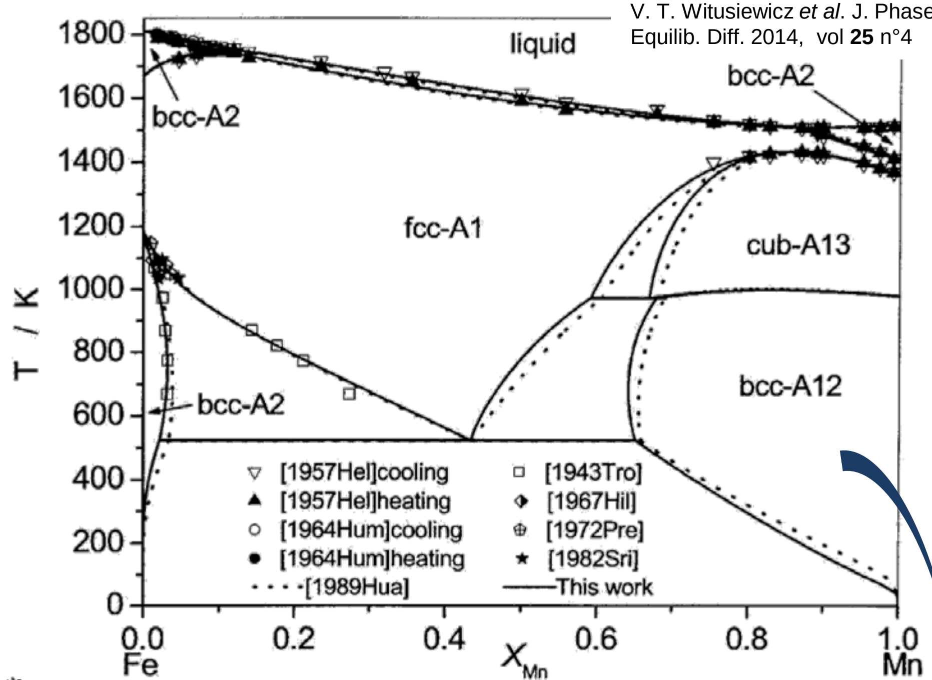
Large <100> and small <111> type dislocation loops in {100} zone axis visible by BF imaging …

Are these observations consistent with thermodynamics ?



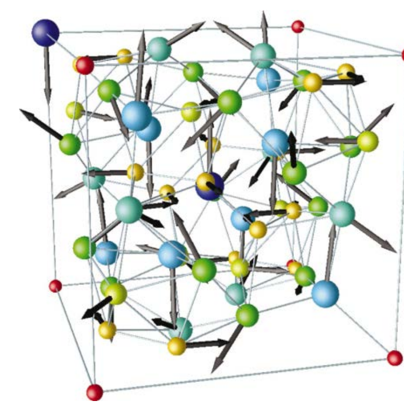
Swartzendruber, L.; Itkin, V.; Alcock, C., 1991, 12, 288–312

V. T. Witusiewicz *et al*. J. Phase Equilib. Diff. 2014, vol **25** n°4



Phase transformation → intermetallic Fe_3Ni phase, even outside of its known field of stability

No Fe-Mn intermetallic compound



D. Hobbs *et al*., PRB 68, 2003, 014407

- **HR-TEM**
- **Large scale facility : Synchrotron SOLEIL**

CONCLUSIONS

- Mn and Ni segregate on PD sinks thanks to PDs (flux coupling)

- For the same dose, lower flux irradiation promotes segregation/precipitation advancement

  → Fe_3Ni FCC phase precipitation in Fe-3%Ni formed outside of its stability field probably stabilised by radiation defects (to be investigated in more details)

- Mn and Ni have different behavior when taken separately, and this tendency to precipitate in case of Fe-Ni can be tentatively explained by the existence of intermetallics (Fe_3Ni, FeNi and $FeNi_3$), whereas no such phases appear in the Fe-Mn phase diagram

Same behavior in RPV steels ?

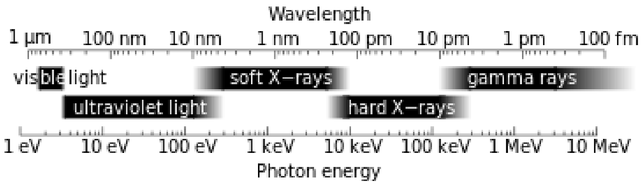
- Formation of solute clusters as a consequence of flux coupling between solutes and PDs & subsequent segregation on PD sinks
- Possible stabilisation of intermetallic phases (even if metastable) by radiation defects (PD clusters)

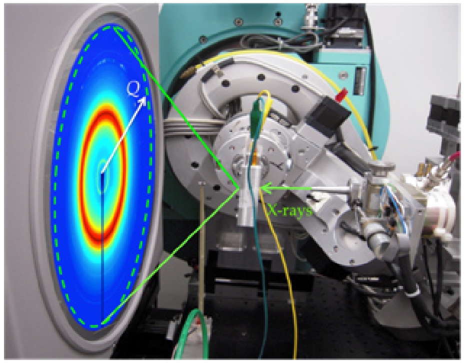
THANK YOU FOR YOUR ATTENTION

TOWARDS HIGHER RESOLUTION

Large scale facility : Synchrotron SOLEIL
MARS beam line

Saclay, France





<u>2 questions :</u>

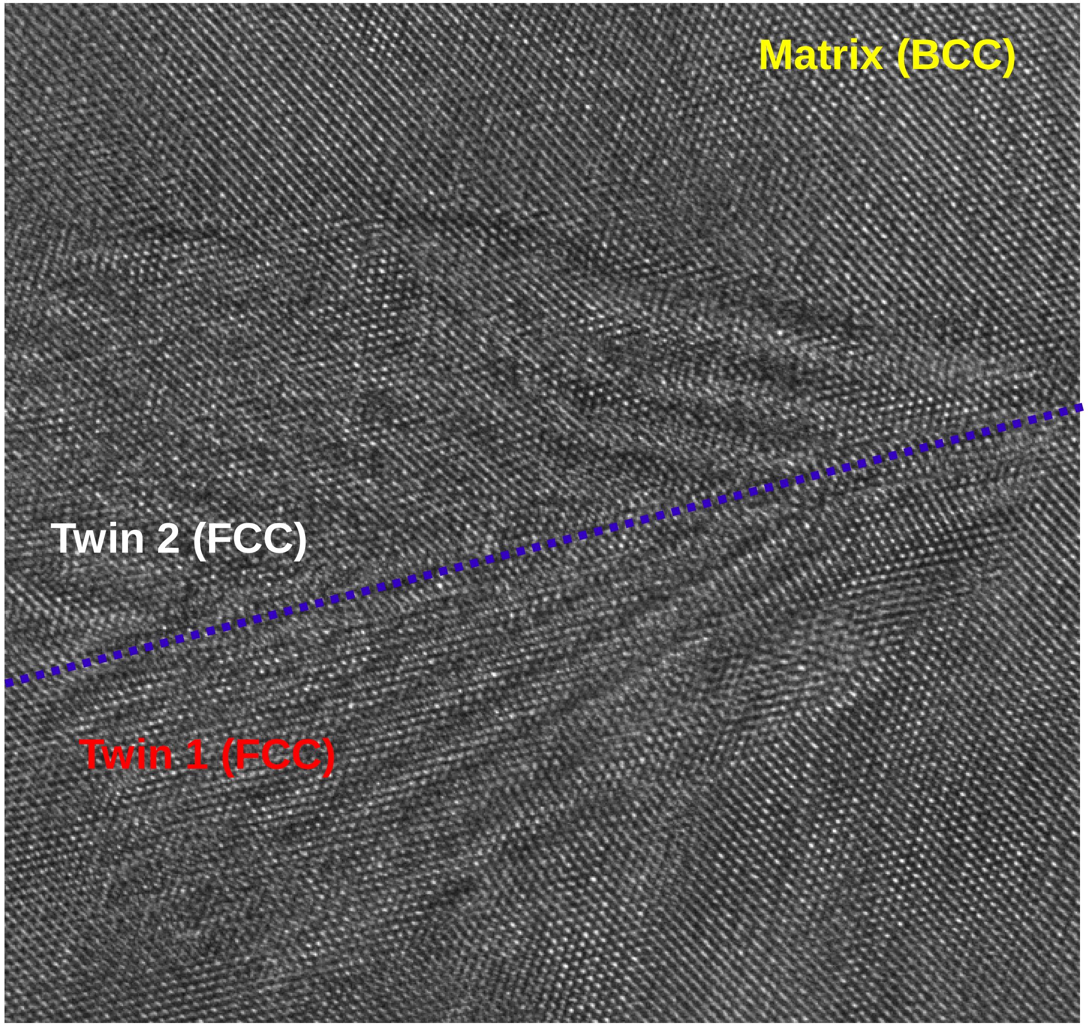
Fe-3%Ni : Is the Fe_3Ni phase ordered or not ? (low flux)

Fe-3%Mn : Did a second phase form ? (high and low fluxes)

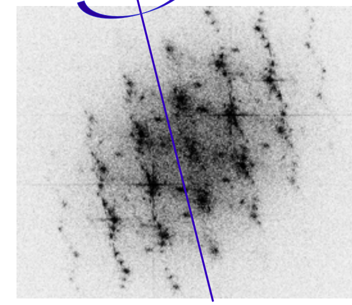
→ XRD (diffraction) for structural analysis (atomic structure)

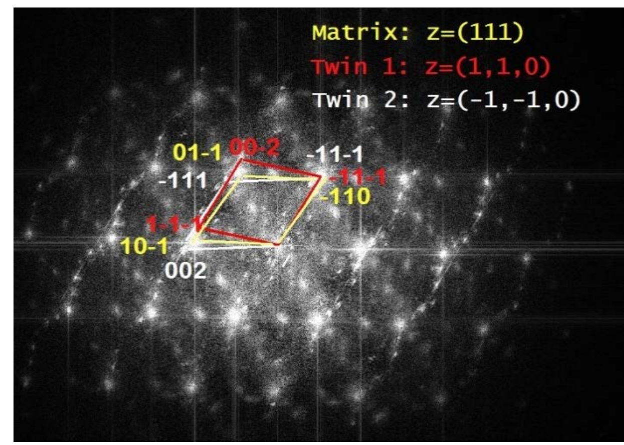
*Acknowledgments : Jean-Luc Béchade, Raphaelle Guillou and Denis Menut

REMINDER: Low flux irradiated Fe-3%Ni



Mirror symmetry between the 2 variants along the (111) planes : ~ 60°





Common direction: $[-11-1]_{fcc}$ //$[-110]_{bcc}$

KS (Kurjumov/Sachs relationship)

G.Kurdjumov and G. Sachs, Zeitschrift für Physik, 1930, 64, 325

The SOTERIA Consortium

SOTERIA

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IRSN
INSTITUT
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Electron irradiations: CD simulations

Hypothesis:

PD = dominant sinks [1]
Mobile vacancies (T > stage III)
Steady state reached (DiCi = DvCv)

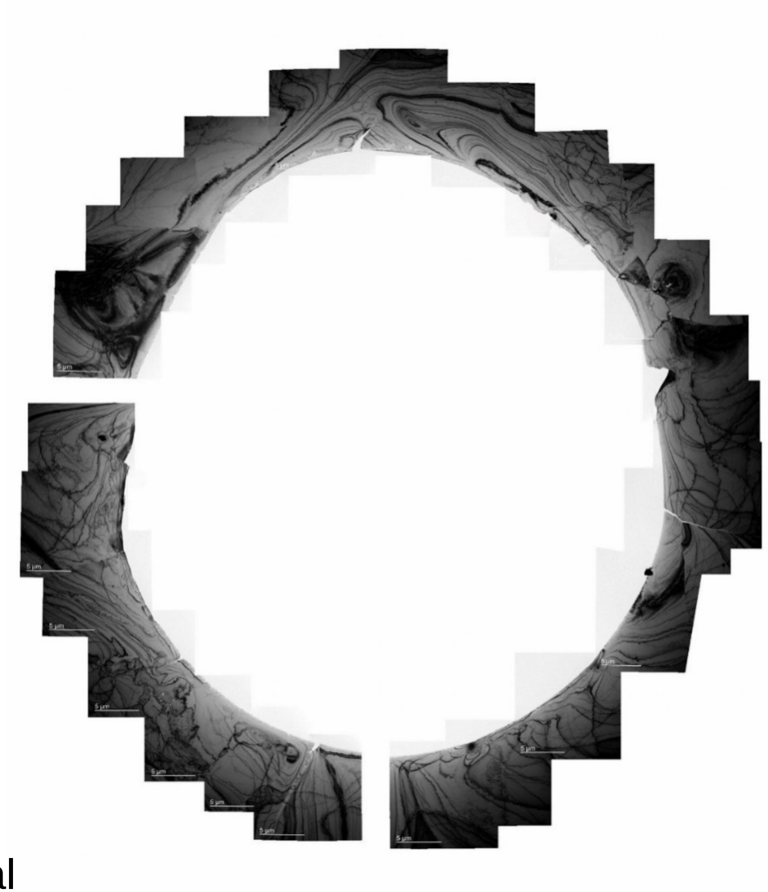
[1] Kiritani et al., J.Phys. Soc.Jpn., 38, 6 (1975)

Dislocation loop growth rate determined at several temperatures in a Fe-3%Ni thin lamella

→ Vacancy migration energy

Dislocation loop saturation density determined at several temperatures in a Fe-3%Ni thin lamella

→ SIA migration energy



20 µm

Electron irradiations: CD simulations

Dislocation loop growth rate determined at several temperatures in a Fe-3%Ni thin lamella

$$V = \frac{dr}{dt} = \frac{2}{b}(Z_i - Z_l)\left(\frac{GV_{at}D_{ol}}{R_{il}}\right)^{\frac{1}{2}} \exp(-\frac{E_m^l}{2k_BT})$$

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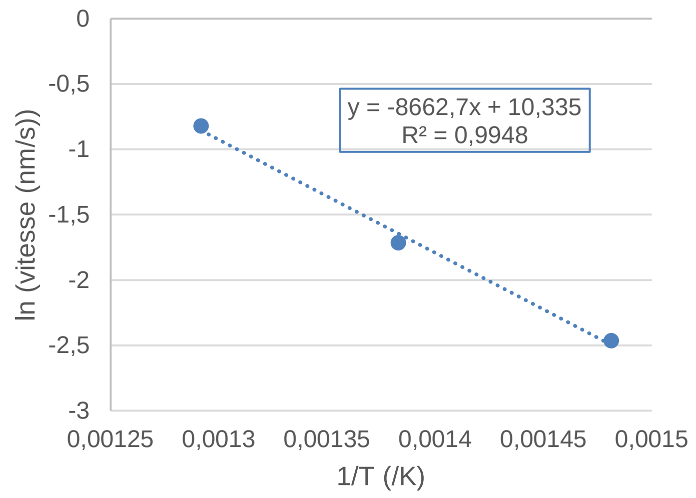


$$D_{ol} = 0.79\ cm^2.s^{-1}$$

$$E_m^l = 1.49\ eV$$

[1] Kiritani et al., J.Phys. Soc.Jpn., 38, 6 (1975)

Electron irradiations: CD simulations

Luca Messina : $E_l^m = 0.63\ eV$

Chu-Chun Fu [2]: $E_b^{(V-C)} \approx 0.45\ eV$ and $E_b^{(V_2-C)} \approx E_b^{(V_3-C)} \approx E_b^{(V_4-C)} \approx 0.7\ eV$

In our case : $1.49\ eV \approx E_m^l + E_b^{(V_n-C)} = E_m^{(V_n-C)}$ (= 0.63 + 0.7 = 1.33 eV)

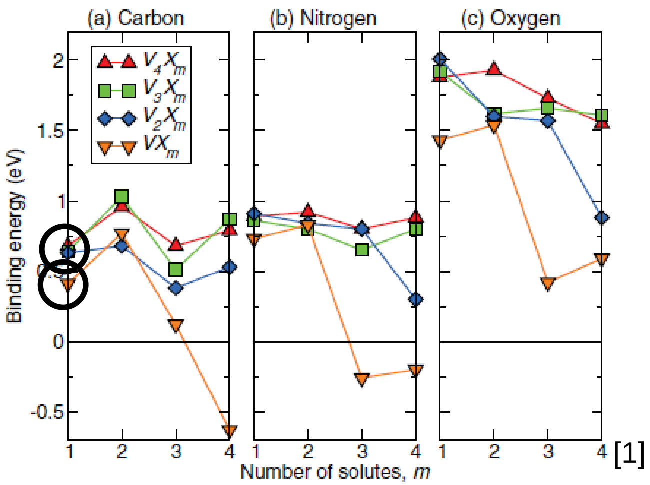


FIG. 9. (Color online) Binding energies of the clustering reactions $V_nX_{m-1} + X \rightarrow V_nX_m$ for $X = $ C, N, and O and for n and m up to four. Positive values indicate exothermic reactions.

Nitrogen and Oxygen can contribute even more in case of contamination

[1] Barouh, Fu et al, Phys Rev B, 90,054112 (2014)

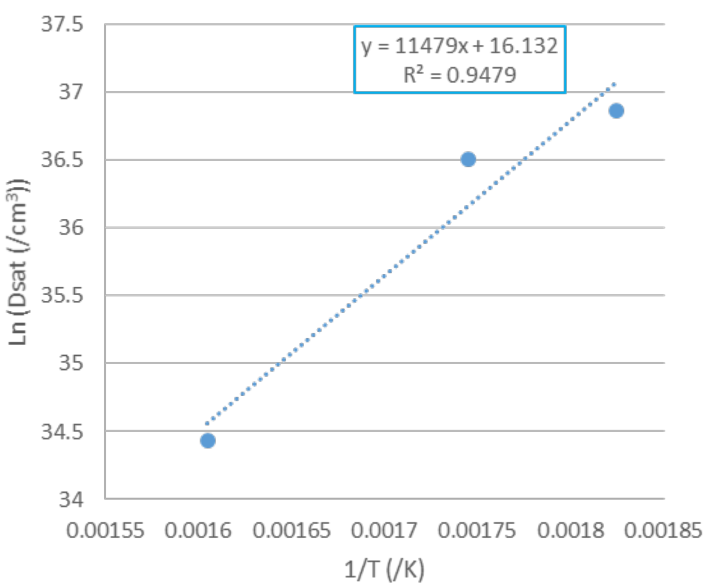
Electron irradiations: CD simulations

Dislocation loop saturation density determined at several temperatures in a Fe-3%Ni thin lamella

$$D_{sat} = \left(\frac{G}{(3R_{il} + 2\beta^{i}_{i,1}).V_{at}.D_{oi}}\right)^{\frac{1}{2}} \exp\left(\frac{E^{i}_{m}}{2k_B T}\right)$$

$$D_{ol} = 6.16\ cm^2.s^{-1}$$

$$E^{i}_{m} = 1.98\ eV$$



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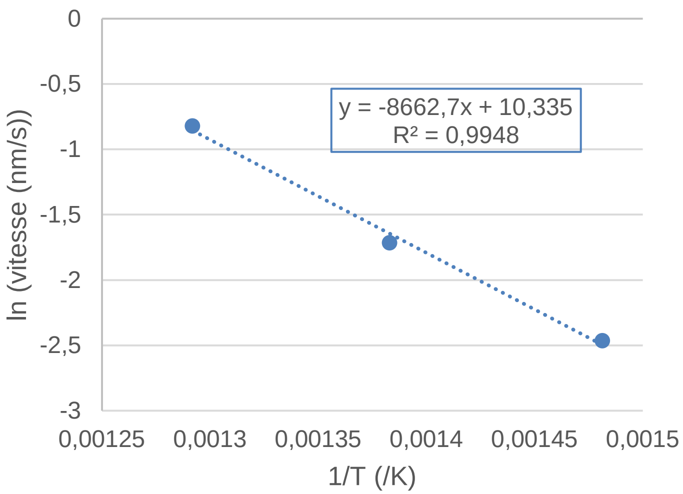
Z_n=efficacité de capture des dislocations pour le défaut n
r : rayon des boucles interstitielles, = d/2,
b : module du vecteur de Burgers,
G: taux de création de défauts ponctuels,
D_{ol} : facteur pré-exponentiel du coefficient de diffusion des lacunes,
R_{il} : coefficient de recombinaison,
E_m^l : énergie de migration des lacunes,
k_B : constante de Boltzmann,
T : température.



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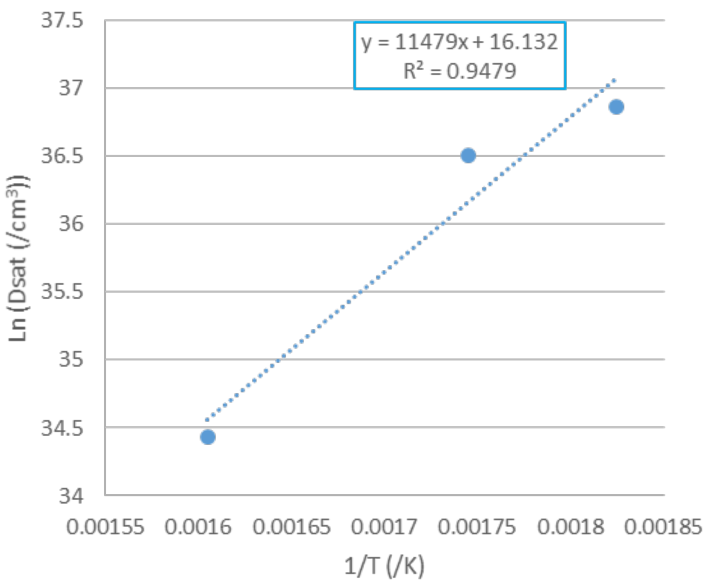
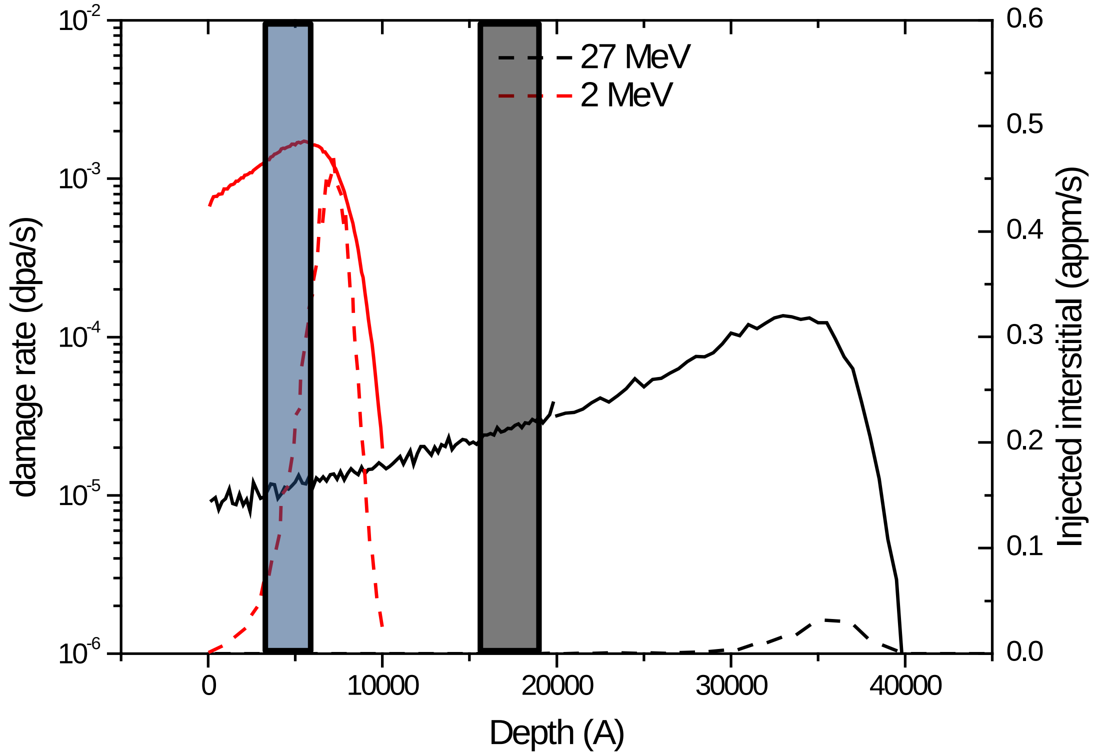
$\beta^i_{i,1}$: coefficient d'absorption d'un interstitiel par un autre interstitiel donné par la relation $\beta^i_{i,1} = Z_i\sqrt{\frac{4\pi V_{at}}{b}}$ où b est égal à 0,2 nm et Z_i est égal à 1,1
D_{oi} : facteur pré-exponentiel du coefficient de diffusion des interstitiels,
E^i_m : énergie de migration des interstitiels
R_{il} : coefficient de recombinaison,
k_B : constante de Boltzmann,
T : température.



$$D_{ol} = 6.16\ cm^2.s^{-1}$$

$$E^i_m = 1.98\ eV$$

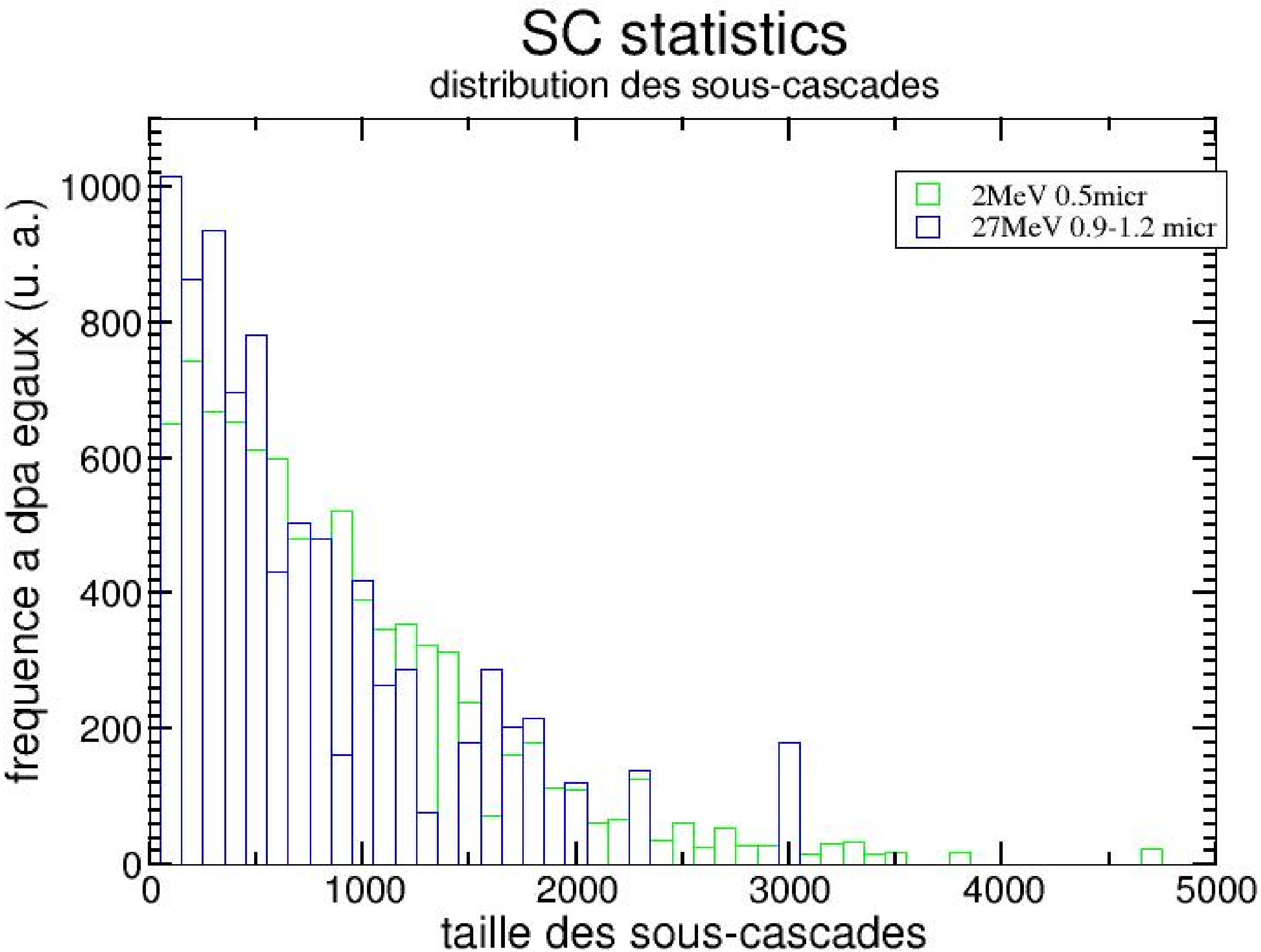
DAMAGES AND DAMAGE RATES



Irradiation aux auto-ions

Pour une même dose de 4 dpa+/-10 %, la différence en termes de taux de dommage est de **65**.

CASCADES AND SUB-CASCADES DISTRIBUTION

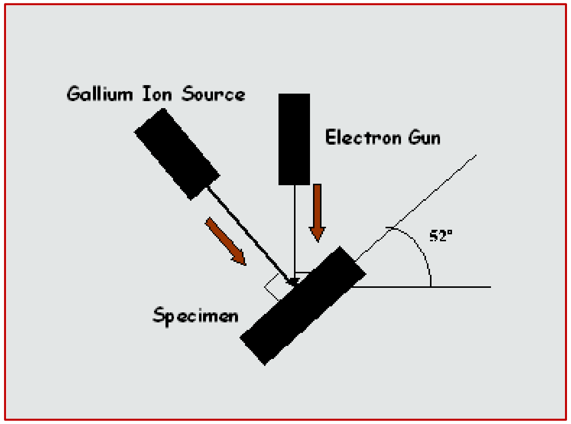


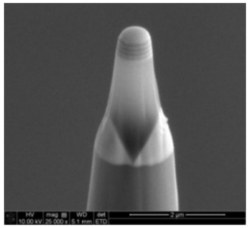
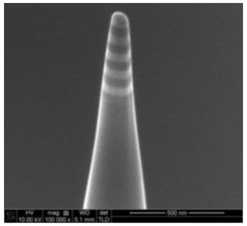
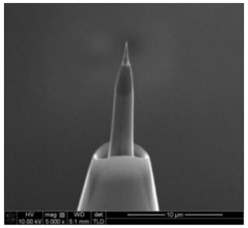
FIB LIFT-OUT

Tips

FIB : Ga^{+}, 30 - 2 - 1 kV

→ APT analysis

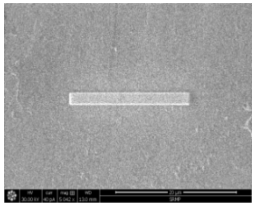
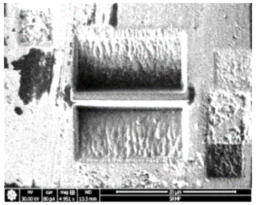
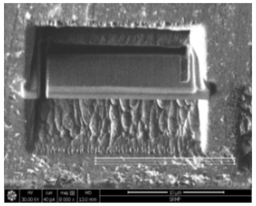
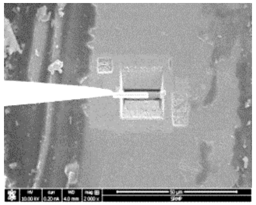
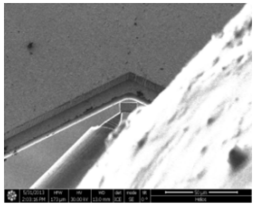
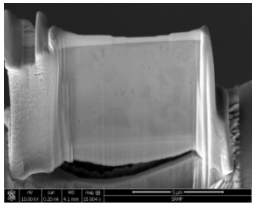


Lamellas

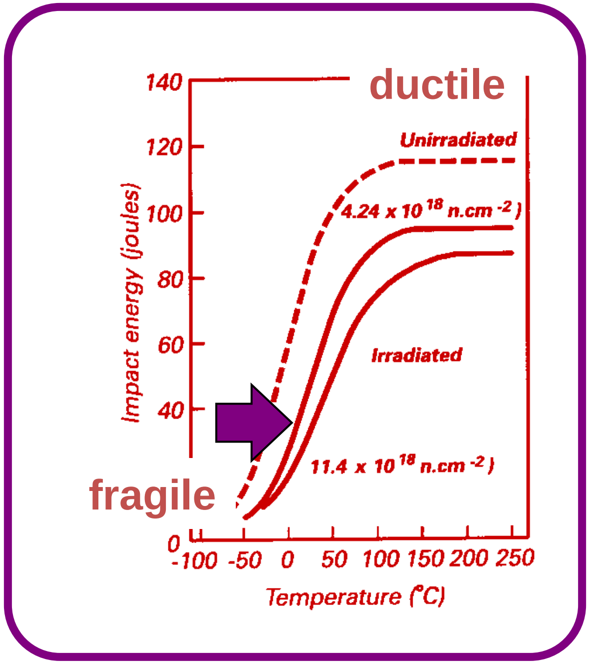
FIB : Ga^{+}, 30 - 2 - 1 kV

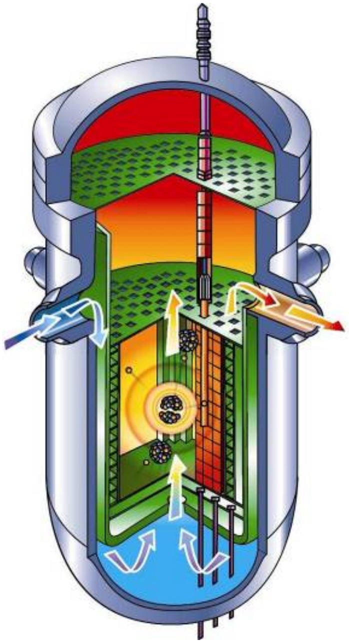
→ TEM observation and analysis

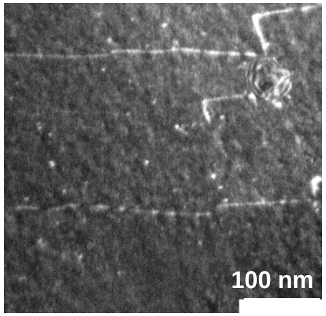







CONCLUSIONS

RPV steel (PWR): Fe – Cu, Mn, Ni, C, P, N, S, Si, Mo, Al, Cr

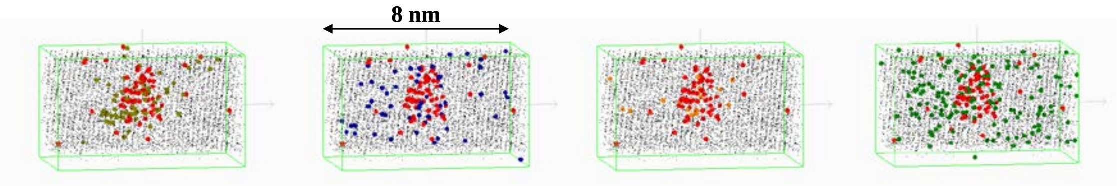






WBDF TEM image, Longlife european project,16MND5,
Neutrons, 0.18 dpa – 2.5 10^{-10} dpa/s

[WWER440, Pareige et al., (2004)]



CONCLUSIONS

1/65 ? Low flux

5.4×10^{-4} dpa/s → 8×10^{-6} dpa/s → 10^{-9} - 10^{-10} dpa/s

↘ flux = ↘ density and ↗ Ni content in clusters : APT

Tendency when decreasing damage rate = promote precipitation advancement

Fe-3%Ni (low flux)

Radiation Induced **Precipitation** of the metastable Fe_3Ni phase (ordered or disordered)

→ Synchrotron

Fe-3%Mn (high and low fluxes)

Radiation Induced Segregation or Precipitation → Synchrotron

Cluster Dynamics

V and SIA migration energies determined experimentally by means of electron irradiations (input parameters)