



STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

Radiation effects in structural steels for nuclear applications: an atomistic study

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Thesis overview

Material	Application	Problems to study
<i>Austenitic stainless steels</i>	Internal components	hardening and dislocation channeling
<i>Ferritic-martensitic (FM) steels</i>	Fusion and GEN IV installations	hardening
<i>Reactor pressure vessel (RPV) steels</i>	Reactor pressure vessel of GEN II reactors	hardening

RPV steels and their exploitation conditions

Reactor pressure vessel (RPV) steels

Chemical composition (16MND5):

Cu: 0.05% Mn: 1.07%

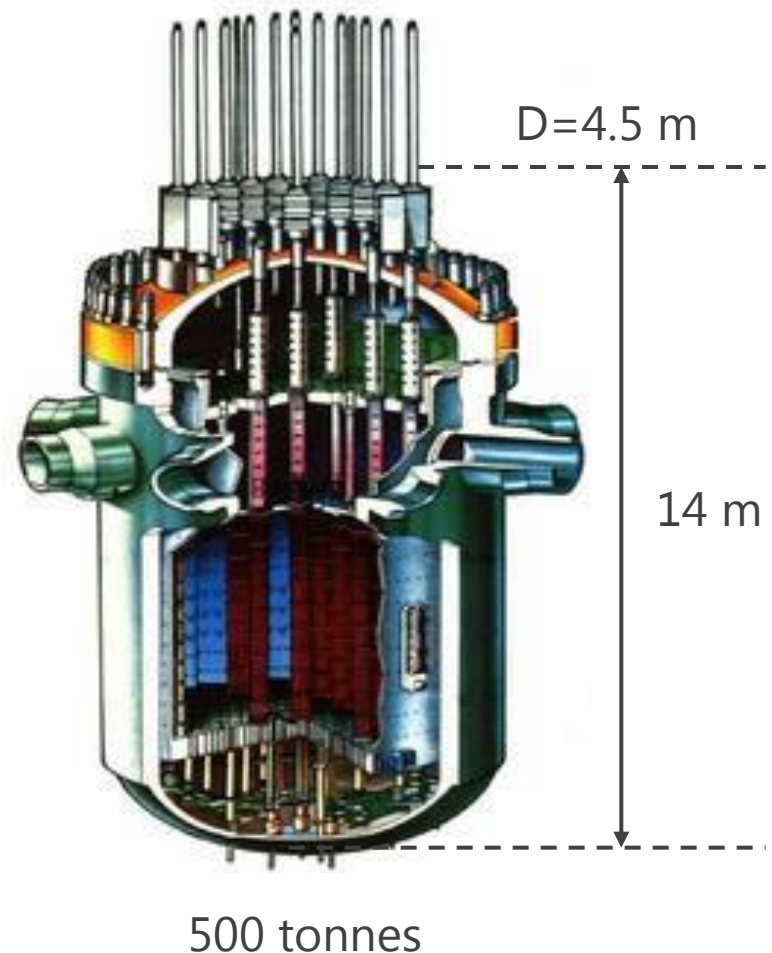
Ni: 0.60% C: 0.05%

P: 0.01% Si: 0.50%...

Exploitation conditions:

Temperature: 290 ± 30 °C

Dose: ~ 0.1 dpa during 40 years



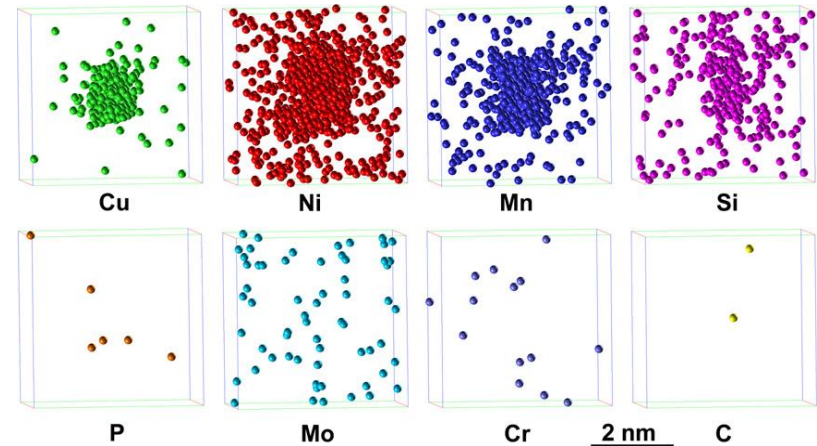
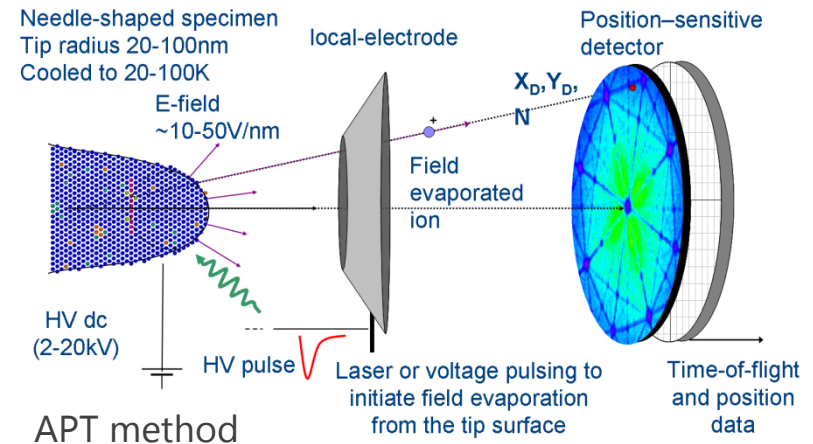
Radiation-induced degradation. Microstructure

- Methods of analysis:**
- Microscopy: TEM
 - Chemical composition: APT
 - Presence of vacancies: PAS

Evolution of microstructure:

- Cu-rich solute clusters
 $D=0.5-1.5 \text{ nm}$ $\rho=(0.1-2.0) \times 10^{24} \text{ m}^{-3}$
- Mn-Ni-rich solute clusters
 $D=0.5-1.5 \text{ nm}$ $\rho=(0.1-2.0) \times 10^{24} \text{ m}^{-3}$
detected at sufficiently high neutron fluence
- Dislocation loops (invisible to TEM) ?

Thermodynamic mechanisms of their nucleation and growth are not fully understood



APT maps of solute-rich clusters in a RPV steel neutron irradiated to a fluence of $1.6 \cdot 10^{23} \text{ m}^{-2}$ ($E > 1 \text{ MeV}$)

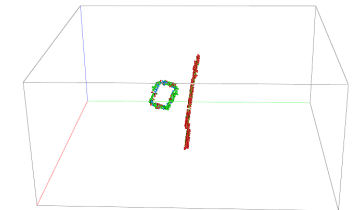
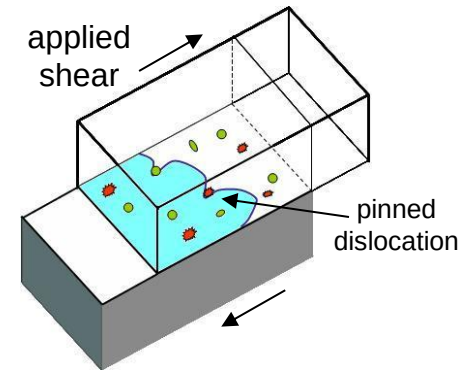
Radiation-induced degradation. Mechanical properties

Microfeatures

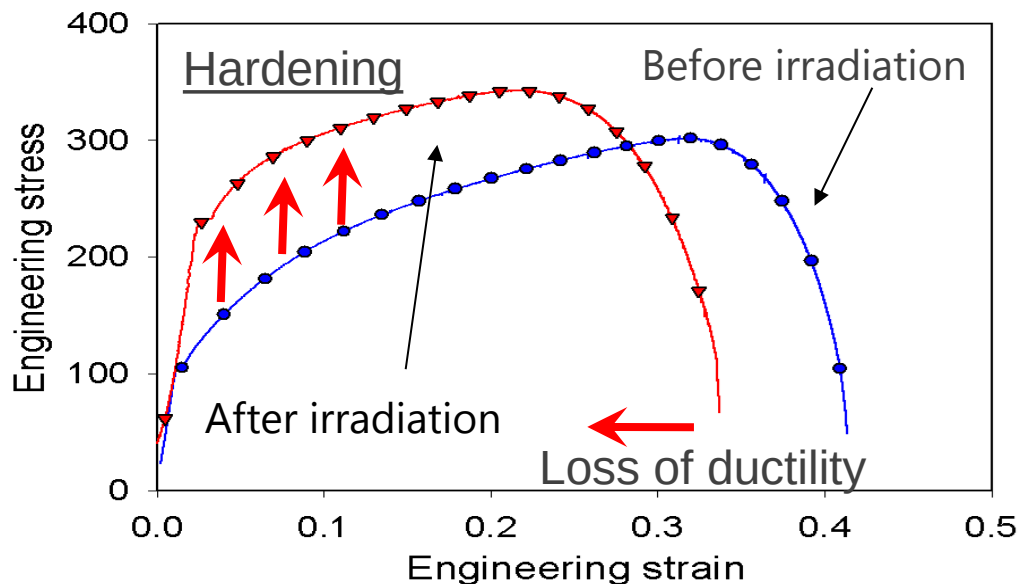
- dislocation loops, precipitates hinder the dislocation movement

are causing macroscopic effects:

- hardening and loss of ductility



Computer simulations



Tensile test experiment

Problem in mind

- How the Mn-Ni-rich solute clusters are formed?

PAS method point to their association with vacancies. No strong hardening on solute-vacancy clusters.

Ab initio calculations suggest the thermal stability of a V-C pair. Nucleus for such clusters? → should be studied

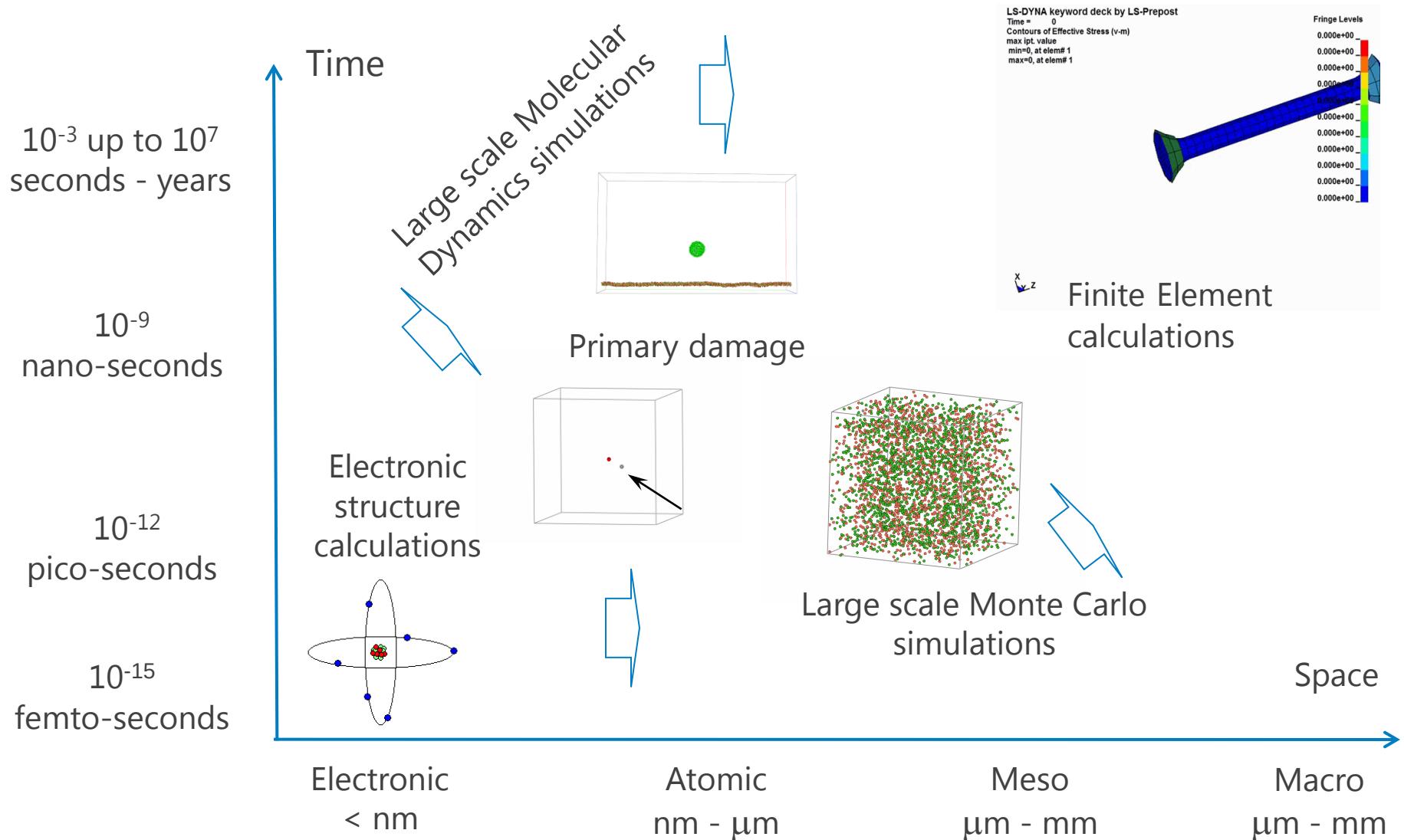
- Can Mn-Ni-rich clusters be associated to dislocation loops?

Possible explanation of experimental studies → should be investigated

- If yes, what is the effect of enriched dislocation loops on radiation-induced hardening?

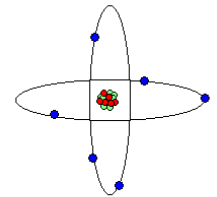
The interaction between dislocations and enriched dislocation loops should be addressed

Multiscale modelling approach



Ab initio calculations

- Quantum-mechanical approach to study electronic structure
- Electron density functional for many-electron systems



Advantages	Limitations
• Accuracy • Description of complex systems • Accumulated substantial database to compare with	• Small systems – up to 500 atoms • CPU time ☹ • 0 K calculations

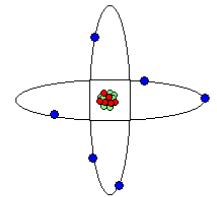
- VASP [1] 3rd-party *ab initio* code (license via UGent) optimized for computer clusters (up to 200 cpus)



Ab initio calculations

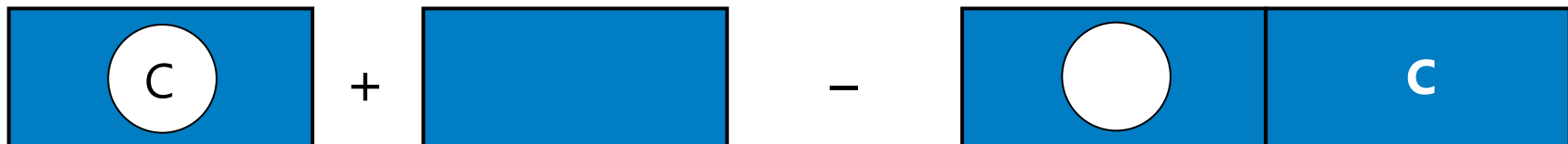
The main purposes of DFT calculations:

- Obtain relaxed configurations
- Select the lowest energy configuration out of similar ones
- Calculate binding energy between entities in a complex defect
- Provide additional parameters for development of interatomic potentials



The interaction energy of n defects $\{A_i\}$ is defined:

$$E_i(\{A_i\}) = [E(\{A_i\}) + (n-1)E_0] - \left[\sum_{i=1}^n E(A_i) \right]$$

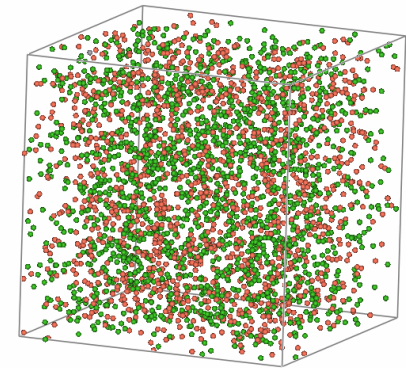


Metropolis Monte Carlo method

The method to study the kinetics of atoms ($\sim 100\,000$ in the system)
Requires interatomic potentials to calculate the total energy

General scheme:

1. Initialize from initial (random) configuration
2. Calculate the total energy
3. Give a displacement to a random atom
4. Calculate a random number $u=[0,1]$
5. Accept the move if energy decreases or if $u < \rho_{\text{new}}(E') / \rho_{\text{old}}(E)$, where
 $\rho(E) = \exp(-E/(kT))$
6. Go to 2

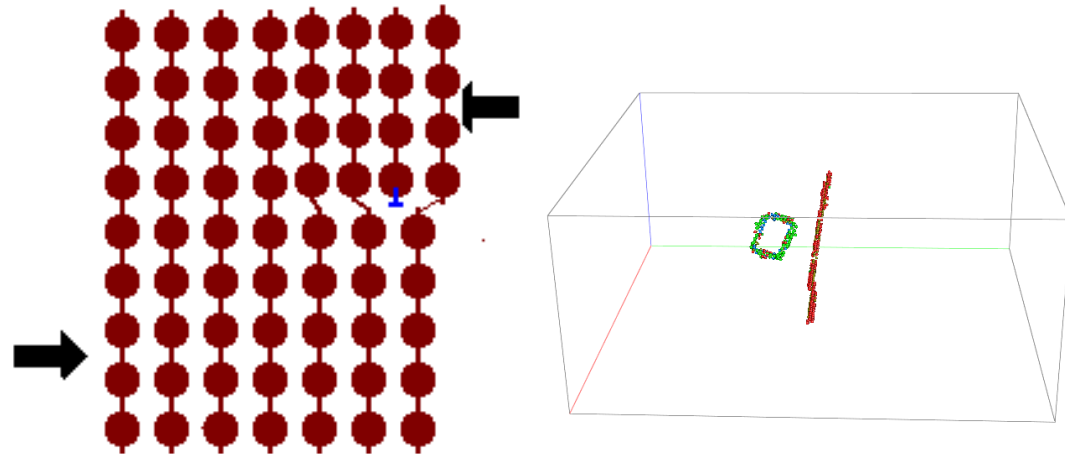


Our goal: get atomic configurations with segregation of Mn and Ni to dislocation loops

Classical molecular dynamics

Molecular dynamics simulates the motions of atoms according to the forces between them

1. Initialize positions of atoms
2. Calculate forces between them
3. Solve Newton's equations of motion
4. Move atoms
5. Go to 1



$$F_i = m_i \ddot{r}_i = -\nabla U(r_{ij})$$

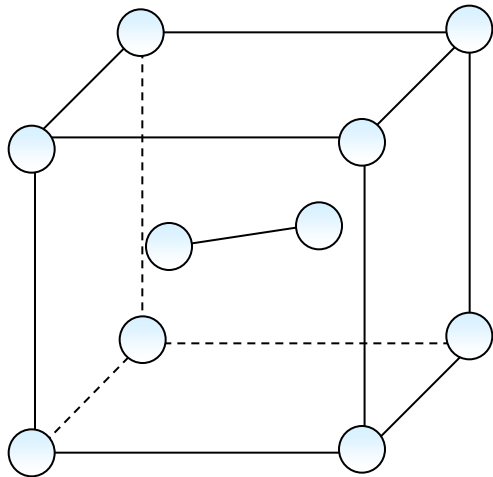
Interatomic potential – the only approximation

Limitation: up to 2 mln atoms.

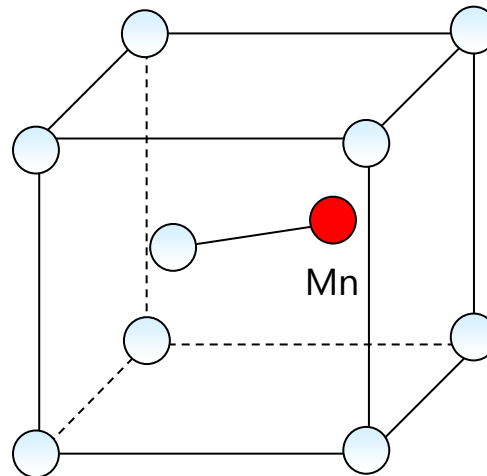
We apply the method to study plastic behaviour by means of dislocation-defect interaction

Results. Nucleation of Mn-Ni clusters

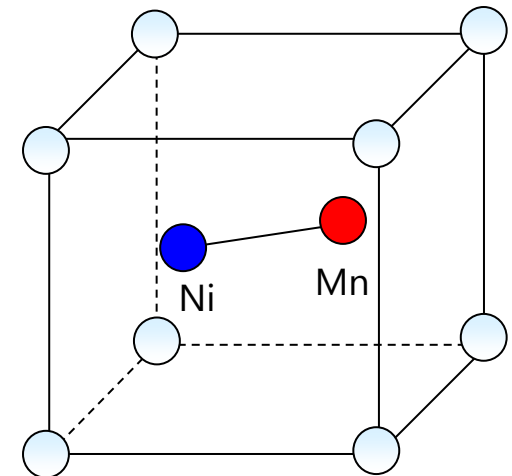
Mechanism #1. Self-interstitial atoms glue Mn and Ni atoms together



Fe-Fe dumbbell



$E_I(\text{Fe-Mn}) = -0.6 \text{ eV}$

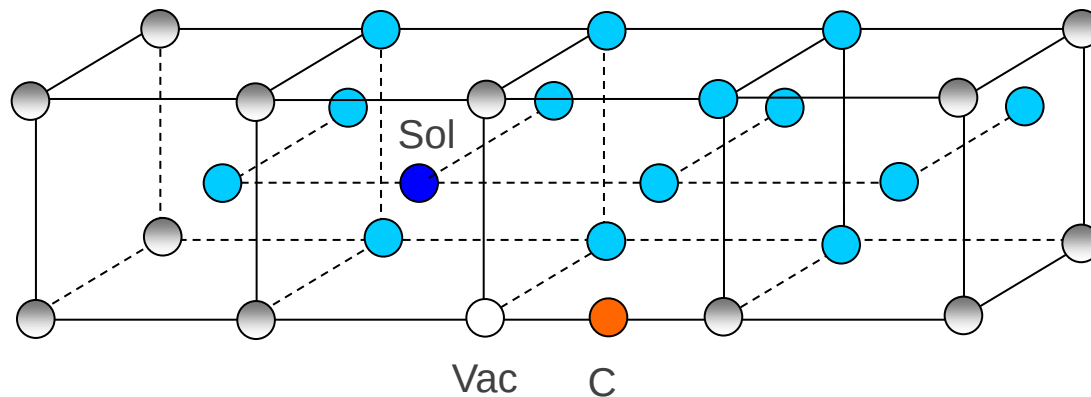


$E_I(\text{Ni-Mn}) = -0.1 \text{ eV}$

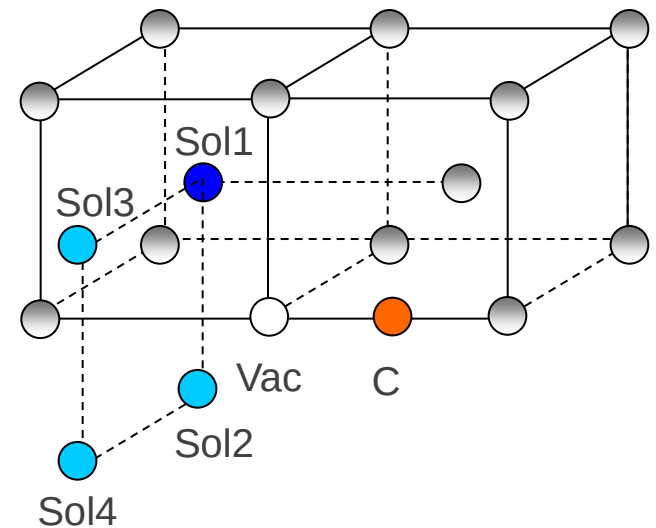
$\langle 110 \rangle$ dumbbells

Results. Nucleation of Mn-Ni clusters

Mechanism #2. Mn-Ni clusters can nucleate and grow at a V-C pair



Solute-vacancy-carbon complexes



Solute_N-vacancy-carbon complexes

Main results:

- Addition of Mn or Ni increases the total interaction energy by -0.2 eV up to -1.0 eV
- The dissociation energy of Mn-V-C and Ni-V-C complex is higher by 0.1-0.2 eV than $E_d(V-C)$
- Mn-V-C and Ni-V-C will dissociate via emission of a vacancy ($E_m=0.65$ eV)
- The further growth can be via addition of 3-Ni atoms or 1 Mn atom or by Ni-Mn-Ni-Ni chain

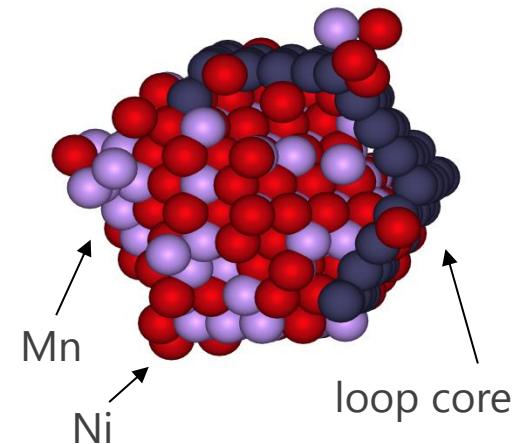
Results. Segregation of Mn and Ni to dislocation loops

The Fe-Mn-Ni interatomic potential has been developed on the basis of experimental & DFT data

MMC calculations of kinetics of Mn and Ni solutes around dislocation loops

It was established:

- No segregation in defect-free alloys at reactor operational temperature
- Strong segregation to dislocation lines
- As compared to Ni, the enrichment by Mn is by a factor of 3 higher

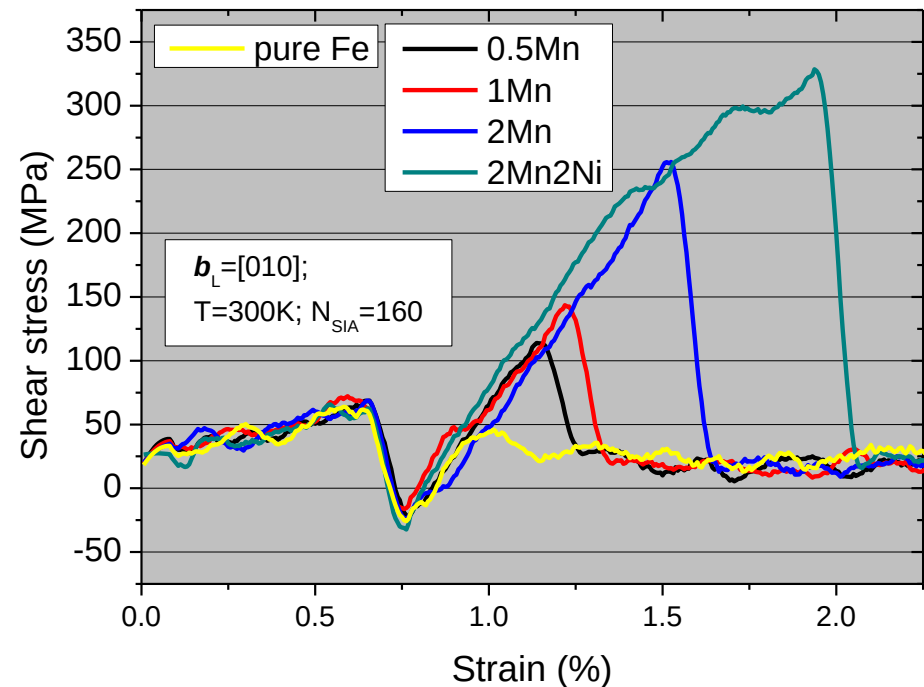
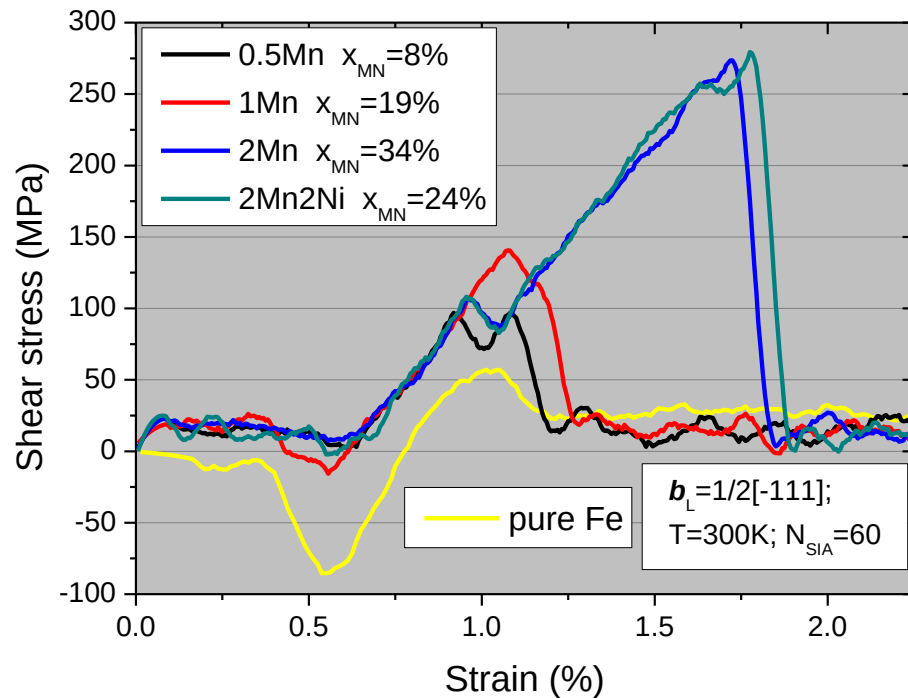


The Mn-Ni decoration of dislocation loop $\frac{1}{2}\langle 111 \rangle$ in the Fe-1%Mn-1%Ni alloy at $T=600\text{K}$

Results. Effect of the enrichment of the loops

Small dislocation loops of 1.5 nm (invisible to TEM)

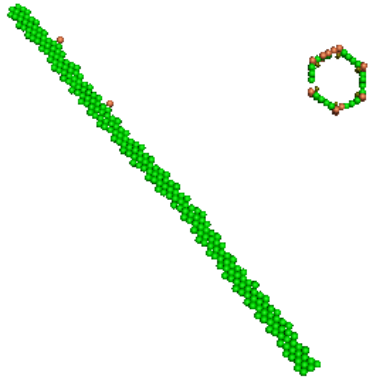
Large dislocation loops of 3.5 and 5.0 nm



Unpinning stress increases significantly
Higher Mn concentration enhances the unpinning stress

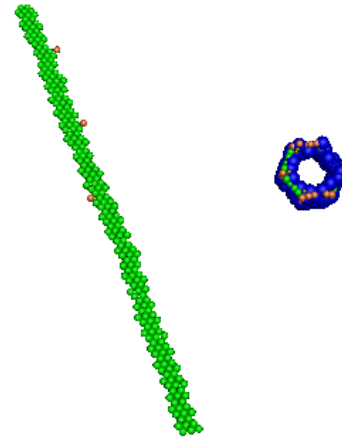
Results. Effect of the enrichment of the small loops

The undecorated loops are fully absorbed:



Pure Fe

The enriched loops are partially absorbed:

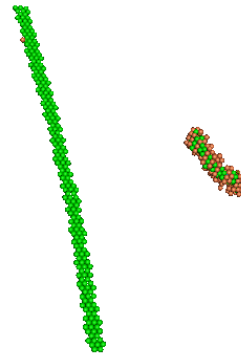


Fe-2%Mn-2%Ni alloy

Results. Effect of the enrichment of the large loops

The undecorated loops

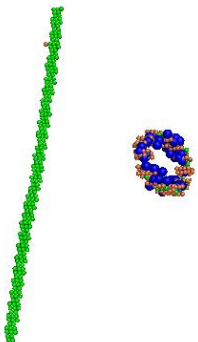
Pure Fe



Full absorption

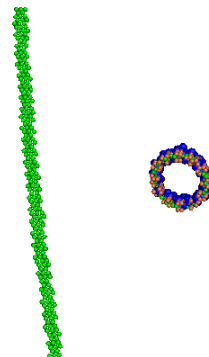
The enriched loops

Fe-0.5%Mn alloy



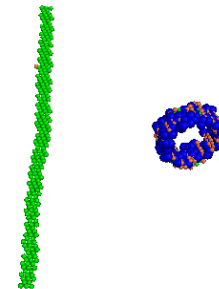
Drag

Fe-1%Mn-1%Ni alloy



Orowan type

Fe-2%Mn alloy



Shear

Conclusions

- How the Mn-Ni-rich solute clusters are formed?

Self-interstitial atoms can glue Mn and Ni atoms together

Formation of SIA-clusters is delayed up to a certain dose → explains the Mn-Ni delay

Mn- and Ni-rich clusters can nucleate and grow at a stable V-C pair

- Can Mn-Ni-rich clusters be associated to dislocation loops?

Yes, the enrichment is thermodynamically favourable

- If yes, what is the effect of enriched dislocation loops on radiation-induced hardening?

Segregation of Mn-Ni atoms increases significantly the strength of dislocation loops

The Mn-Ni atoms change the interaction mechanism from full to partial absorption

Now we understand better the radiation-induced degradation of RPV steels

Dissemination of the results

Main papers:

1. **A. Bakaev**, D. Terentyev, G. Bonny, T.P.C. Klaver, P. Olsson and D. Van Neck. Basic Properties of Minor Alloying Elements in High-Cr Ferritic Steels: An Ab Initio Study. *Journal of Nuclear Materials*, 444 (2014) 237
2. **A. Bakaev**, D. Terentyev, X. He, D. Van Neck. Synergetic Effects of Mn and Si in the Interaction with Point Defects in bcc Fe. *Journal of Nuclear Materials*, 455 (2014) 5
3. **A. Bakaev**, D. Terentyev, X. He, E.E. Zhurkin and D. Van Neck. Interaction of carbon-vacancy complex with minor alloying elements of ferritic steels. *Journal of Nuclear Materials*, 451 (2014) 82
4. G. Bonny, D. Terentyev, **A. Bakaev**, E.E. Zhurkin et al. On the thermal stability of late blooming phases in reactor pressure vessel steels: An atomistic study, *Journal of Nuclear Materials*, 442 (2013) 282
5. G. Bonny, D. Terentyev, L. Malerba, E.E. Zhurkin, Monte Carlo study of decorated dislocation loops in FeNiMnCu model alloys, *Journal of Nuclear Materials*, (2014), in press
6. D. Terentyev, X. He, G. Bonny, **A. Bakaev**, E. Zhurkin, L. Malerba Hardening due to dislocation loop damage in RPV model alloys: role of Mn segregation, *Journal of Nuclear Materials*, (2014), in press.



Journals: 6 papers + 2 in preparation
Conferences: 5 oral talks + 3 posters

- ***Ab initio* calculations**

Evaluate the possibility of nucleation and growth of Mn-Ni-rich clusters at a V-C₂ complex

- **Molecular dynamics & Metropolis Monte Carlo**

Consider interaction of screw dislocation and $\langle 100 \rangle$ dislocation loops

- **Going up-scale**

Use the dislocation-defect interaction database for parameterization of dislocation dynamics method to study the plasticity at micrometer scale

Questions?

Thank you for your attention

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