RADIATION-INDUCED FORMATION OF HARDENING SOLUTE CLUSTERS IN FERRITIC/MARTENSITIC ALLOYS: AN OBJECT KINETIC MONTE CARLO MODEL

N. Castin\textsuperscript{1}, M. Chiapetto\textsuperscript{1,2}, C. Becquart\textsuperscript{2} and L. Malerba\textsuperscript{1}

\textsuperscript{1}NMS Unit, SMA group

\textsuperscript{2}UMET

lmalerba@sckcen.be
Operating temperature window of nuclear materials

- Lower bound:
  - Radiation induced embrittlement (Low T)

- Upper bound
  - Thermal creep

- ... although in reality environment effects are generally the real limiting factor

Fig. 5 Estimated operating temperature windows (dark shaded region) for structural materials in nuclear energy systems for damage levels of 10 to 50 dpa. The light blue and red regions represent lower and upper temperature uncertainty bands.

Low temperature radiation embrittlement in F/M alloys

When irradiated below 400°C the yield strength increases significantly. This leads to shifts of the DBTT of up to 120°C.

Radiation hardening & embrittlement are caused by microstructural and microchemical changes.
F/M model alloys neutron/ion irradiated to different dpa to correlate microstructural changes to radiation hardening

### Composition in at.%

<table>
<thead>
<tr>
<th>Materials</th>
<th>Cr</th>
<th>Si</th>
<th>P</th>
<th>Ni</th>
<th>C</th>
<th>Al</th>
<th>S</th>
<th>Ti</th>
<th>V</th>
<th>N</th>
<th>Mn</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-2.5% Cr</td>
<td>2.6</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
<td>0.05</td>
<td>0.006</td>
<td>0.004</td>
<td>0.005</td>
<td>0.001</td>
<td>0.05</td>
<td>0.01</td>
<td>0.14</td>
</tr>
<tr>
<td>Fe-5% Cr</td>
<td>4.9</td>
<td>0.08</td>
<td>0.02</td>
<td>0.06</td>
<td>0.09</td>
<td>0.001</td>
<td>0.01</td>
<td>0.003</td>
<td>0.001</td>
<td>0.05</td>
<td>0.02</td>
<td>0.21</td>
</tr>
<tr>
<td>Fe-9% Cr</td>
<td>8.9</td>
<td>0.18</td>
<td>0.02</td>
<td>0.07</td>
<td>0.09</td>
<td>0.014</td>
<td>0.001</td>
<td>0.004</td>
<td>0.002</td>
<td>0.06</td>
<td>0.03</td>
<td>0.23</td>
</tr>
<tr>
<td>Fe-12% Cr</td>
<td>12.3</td>
<td>0.22</td>
<td>0.09</td>
<td>0.09</td>
<td>0.13</td>
<td>0.006</td>
<td>0.012</td>
<td>0.004</td>
<td>0.002</td>
<td>0.09</td>
<td>0.03</td>
<td>0.22</td>
</tr>
</tbody>
</table>
PIE identified several interesting microstructural features


2.5%Cr

9%Cr

M. Hernández Mayoral et al., J. Nucl. Mater. 474 (2016) 88

Objective: develop microstructure evolution models capable of describing this whole complexity
Object kinetic Monte Carlo method

Simulation box

Probability

\[ \Gamma_i = \nu_i \exp \left( -\frac{E_{a,i}}{kT} \right) \]

Time

\[ t \propto \frac{1}{\sum_i \Gamma_i} \]

Random number extraction, \( R_n \in [0,1] \)
Grey alloy – **key assumption**: slowing down of SIA clusters

- Interaction with Cr reduces SIA defect mobility

\[ D_{n}^{FeCr} = D_{n}^{Fe} \exp(\Delta F/k_{B}T) \]

\[ \frac{D_{n}^{FeCr}}{D_{n}^{Fe}} \]

\[ \Gamma_{X,V} = \nu \exp \left( -\frac{E_{a}}{k_{B}T} \right) \]
Cr addition suppresses formation of vacancy clusters

Slow SIA clusters are “easier” sinks for V

Enhanced recombinations

Reduced V concentration

Reduced swelling

Invisible loops associated with CrSiNiP clusters

METROPOLIS MONTE CARLO
T = 600-1200K, Fe10-12%Cr

APT: CrNiSiP clusters

OKMC: SIA clusters < 1.3 nm

M. Chiapetto et al., JNM 465 (2015) 326–336

Probably there are also solute clusters not associated with loops, but the model gives a reasonable order of magnitude

Further step: Introduce explicitly the transport of solutes to describe loop enrichment/solute cluster formation
Key atomistic mechanism: solute dragging by point defects

In general, one may expect that a solute atom will move via vacancy in the opposite direction to the vacancy.

Instead, Ni, Si, and P, follow the vacancy during its migration.

Finally, any solute forming a mixed dumbbell (Cr & P) will be dragged by it.
Dragging has solid physical basis rooted in DFT

L. Messina, P. Olsson, M. Nastar, T. Garnier, C. Domain, PRB 90, 104203 (2014)

VACANCY DRAG

• Vacancy can carry solute atoms along.
• Occurring for manganese, nickel, copper, phosphorus, silicon.

INTERSTITIAL TRANSPORT

• Interstitial atoms can couple with solute atoms and move together.
• Occurring for manganese, phosphorus, chromium.

NB: Cr atoms are essentially the only ones NOT dragged by vacancies (though dragged by SIA)
Solutes will segregate at dislocation loops!

APT results - Courtesy of Radiguet, Huang, Cammelli & Pareige, GPM – FP7/Longlife
Atomistic models provided diffusion data for Va-X pairs
Most parameters are the same as in the “grey alloy” model

- In particular SIA clusters are slowed down by Cr

- C atoms are simulated as traps

- Each time a point-defect finds a (dilute) solute, a new object (solute-Va pair, mixed dumbbell, …) is created
  - The binding energy defines for how long the point-defect drags the solute, i.e. until dissociation
  - Correlation effects with surrounding solutes are disregarded

Only single defects transport solutes:
- SIA transport P, Va transport Si, P & Ni

Ingredient to be further studied: loops can be also trapped by (dilute) solutes: Ni, Si, P
First results: Fe-2.5%Cr-0.1%Si-0.02%P

After processing the simulation box with a procedure that emulates the APT:

- The density of solutes-rich clusters compares well with experimental values.
- The radius is underestimated: explained by the absence of Cr.
First results: Fe-9%Cr-0.06%Ni-0.07%Si-0.01%P

After processing the simulation box with a procedure that emulates the APT:

- The Density of solutes-rich clusters compares well with experimental values.
- The radius is underestimated: explained by the absence of Cr.

![Graph showing density and average radius over dose](image-url)
First results: Chemical composition

The chemical composition of the solute-rich clusters, however, is not in agreement with APT:

- Absence of Cr by construction of the model
- Minor solutes in different proportion:
  - Revise compositions?
  - Inaccurate description of solute transport?
- Needs for accurate description of cluster free energy and cluster dissolution mechanisms?
Summary and Outlook

Model of microstructural evolution under irradiation of F/M steels

• Grey alloy model:
  • Cr affects mainly mobility of SIA clusters
  • Correct trends reproduced / solute clusters assessed as invisible loops

• Introduction of (dilute) solute transport:
  • Ni, Si, P dragged by point defects, accumulate on point-def clusters
  • Quantitative assessment of (dilute) solute enrichment is possible

• Future perspectives
  • Introduce cellular model for Cr precipitation and redistribution