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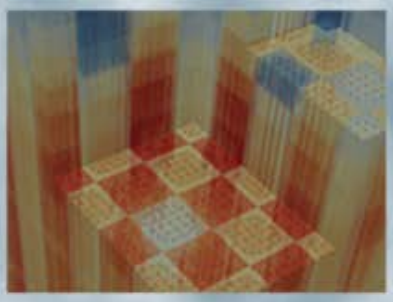
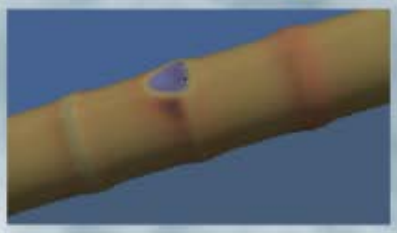
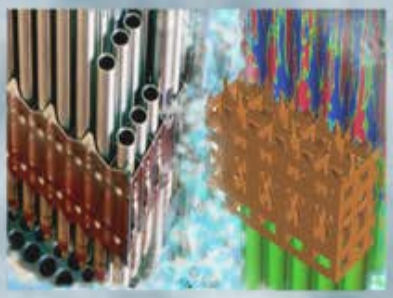
Materials Processing and Optimization (MPO) / Fuels, Materials and Chemistry (FMC)







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July 7, 2015

U.S. DEPARTMENT OF ENERGY | Nuclear Energy

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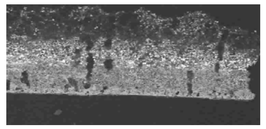
Consortium for Advanced Simulation of LWRs

Materials Processing and Optimization (MPO)

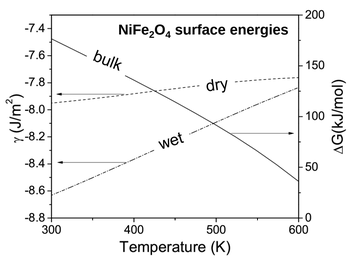
First-principles modeling of CRUD formation

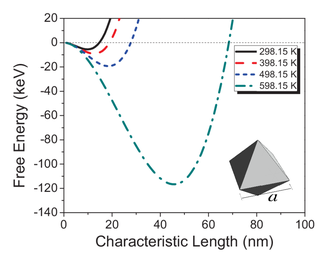


Zr Alloy Cladding

porous structure of agglomerated particulates; primarily $NiFe_2O_4$ and NiO

❑ First-principles calculations predict stable 50 nm nickel ferrite particles in PWR coolant

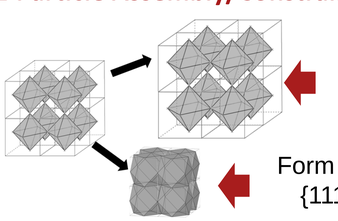




- Negative (111) surface energies
- Positive bulk formation energy

- 50 nm octahedral particles are stable in PWR coolant

❑ Particle Assembly/Constrained Expansion (PACE) Model

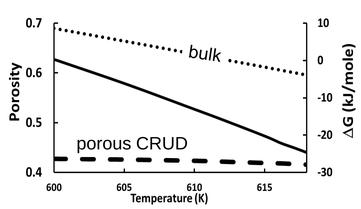


Thermodynamically driven to expand, the clusters can either grow

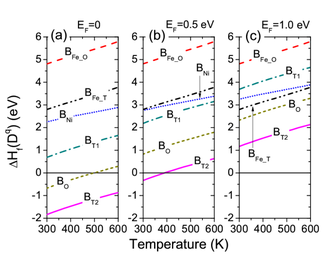
OR

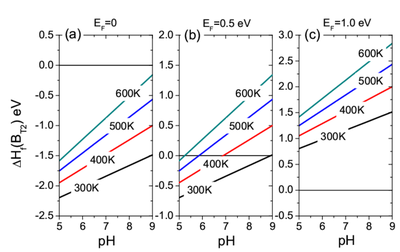
Form a connected porous structure with inner {111} surfaces – **constrained expansion**

- Porosity decreases with T



❑ Boron incorporation in $NiFe_2O_4$ under operating PWR conditions





- Under operating PWR conditions interstitial B can accumulate in the atomic structure of $NiFe_2O_4$
- Boron imputrties in $NiFe_2O_4$ can contribute to axial offset anomaly (AOA)

Fuels, Materials and Chemistry (FMC)

Surface stability of austenitic stainless steel alloys under PWR conditions

Materials used for **reactor vessel**, **primary piping**, and **steam generator tubing:**
Stainless steel alloys 304, 308, 309, and 316 and nickel-chromium superalloys 600, 690, and 800

GOAL:

- understanding the thermodynamic stability of stainless steel surfaces in contact with PWR coolant
- evaluate corrosion rates and corrosion product release rates
- equilibrium solublities and their relation to surface microstructures (e.g. surface composition and pitting) compared to bulk thermodynamics alone.

METHOD: semi-empirical thermodynamics based on the Density Functional Theory (DFT)

- chemical and magnetic disorder are modeled by six-component random alloys: $Fe^{\uparrow}_{(1-x-y)/2}Fe^{\downarrow}_{(1-x-y)/2}Cr^{\uparrow}_{x/2}Cr^{\downarrow}_{x/2}Ni^{\uparrow}_{y/2}Ni^{\downarrow}_{y/2}$
- formation energy of a vacancy in the surface layer under PWR coolant conditions :

$$\Delta H_f\left(V^q\right) = E^{DFT}_{slab}\left(V^q\right) - E^{DFT}_{slab} + \sum_i n_i \mu_{i^{z_i},aq} - \sum_i n_i z_i\left(\varepsilon_F + E^0_{VBM}\right) + q\left(\varepsilon_F + E^{def}_{VBM}\right)$$

$$\mu_{i^{z_i},aq} = \mu^0_{i^{z_i},aq} + k_B T \ln a_{i^{z_i}};$$ this term introduces **temperature** and **concentration** dependence

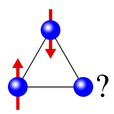
In the case of a metal ion:

$$\mu^0_{M^{z+},aq} = \Delta G^0_f\left(M^{z+},aq\right) + \mu_{M,solid} + z\left(\mu^0_{H^+,aq} - \frac{1}{2}\mu^0_{H_2,gas}\right)$$

from thermodynamic data — from DFT — this term introduces ***pH*** dependence

PRELIMINARY RESULTS:

- Local magnetic moments of Fe and Cr decrease with the distance from the surface
- Surface energies are extremely sensitive to the magnetic coupling between the surface atoms
  - this is especially important for the fcc(111) surface where the surface atoms are arranged in a triangular lattice
  - atoms tend to couple antiferromagnetically – geometrical frustration



- frustration is minimized when one corner of the triangle is occupied by Ni (small magnetic moment)
- frustration is higher when Cr is located in the surface layer (because its large magnetic moment)

probably Cr tends to segregate toward the bulk and Ni to the surface

- the order of the surface energy values for stainless steel and nickel-chromium superalloys is (111) < (100) < (110)

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