Late Blooming Phases and Dose Rate Effects in RPV Steels: Integrated Experiments and Models

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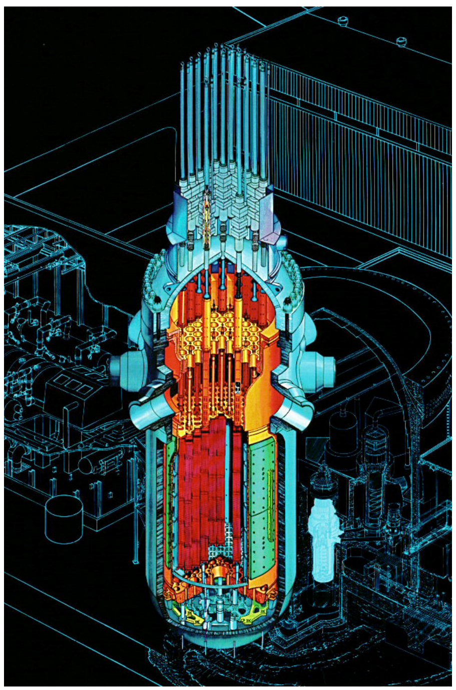
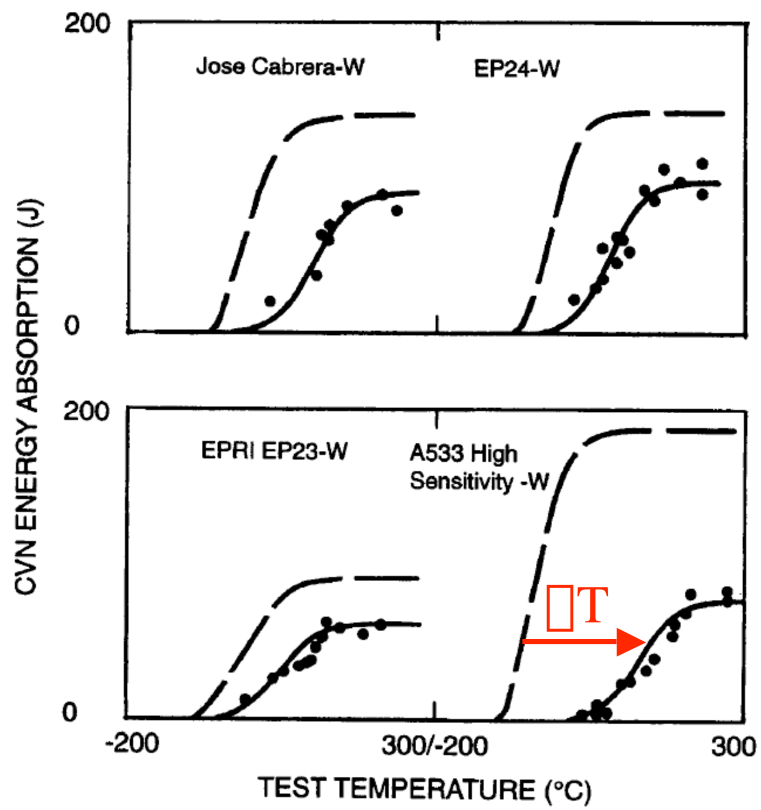
Outline

- Overview multiscale modeling of embrittlement (ΔT)
- Precipitate compositions in Cu-bearing alloys
- Late blooming phases in low Cu and Cu free alloys
- Summary and conclusions





Metallurgical

Cu, Ni, Mn, P, Si, heat treatment, ….

Environmental

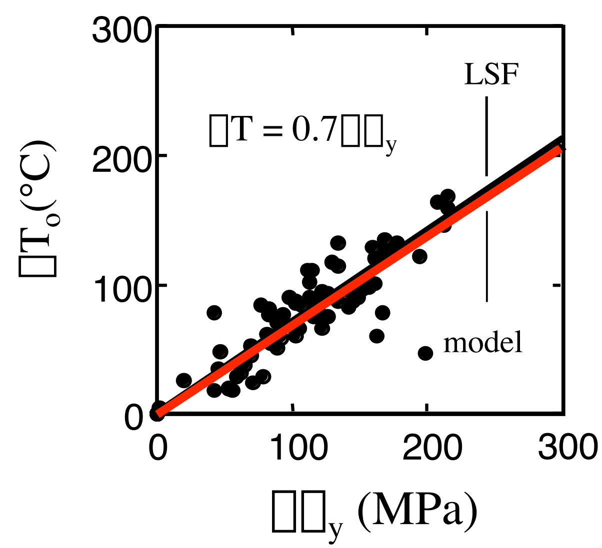
T, ϕ, $\phi(E)$, ϕt, history

Annealing

T_a, t_a

$$\Delta T = f(\text{synergistic combinations})$$

$$\Delta T \approx C(\ldots)\Delta\sigma_y$$
$$\Delta\sigma_y \approx \Delta\sigma_{ppt} + \Delta\sigma_{mf}$$
$$\Delta\sigma_{ppt} = \alpha(r)\sqrt{f_p} \ldots$$



Reliable predictions and extrapolations require models integrated with experiment

Framework

nm-scale features -> $\Delta\sigma_y$ -> ΔT

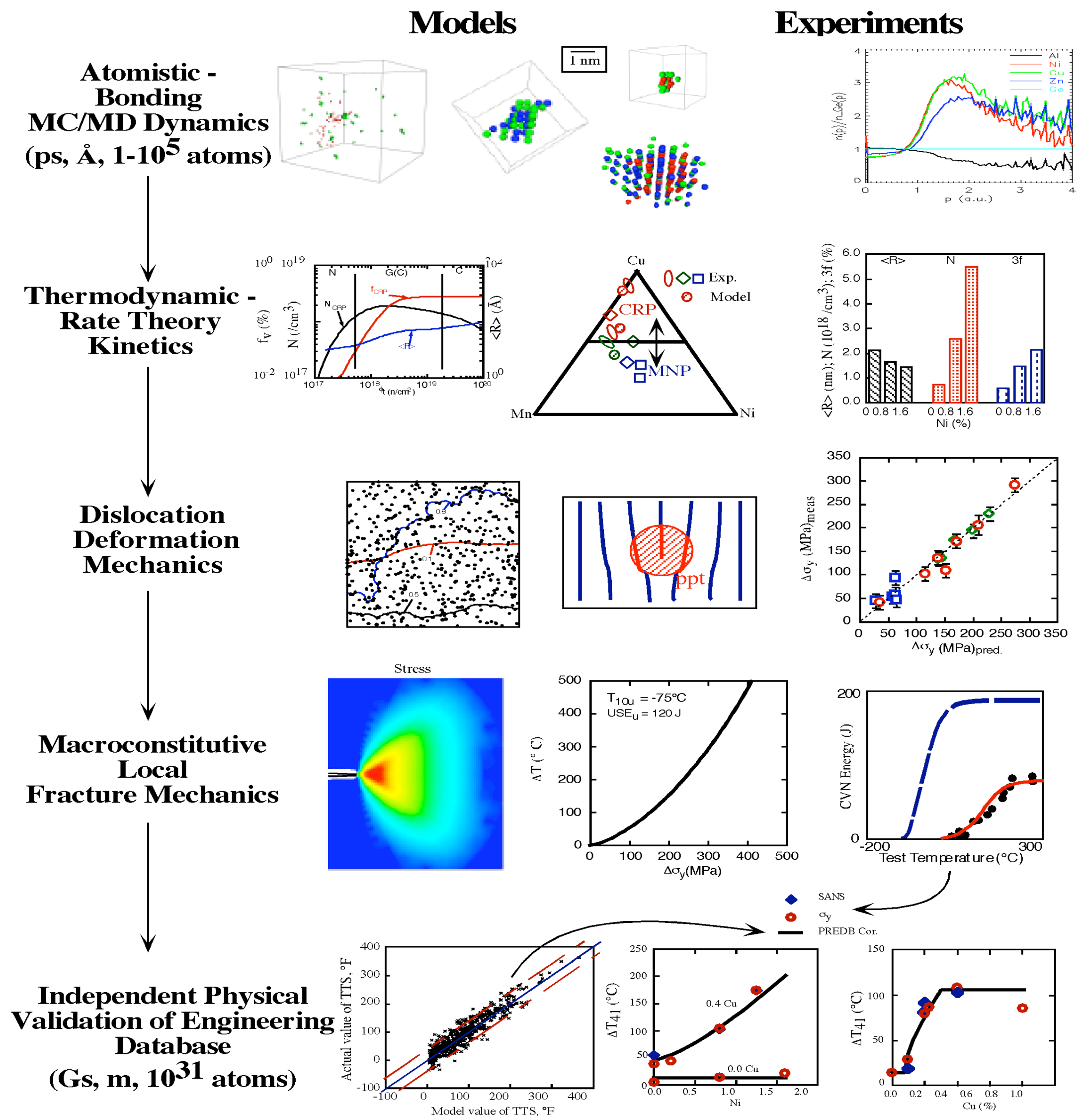
Examples of Models Leading Experiment

- Cascade vacancy solute cluster complexes (1980)
- Two-feature integrated multiscale model of □T by accelerated precipitation of Cu from supersaturated solution due to radiation enhanced diffusion (RED) to form copper rich precipitates (CRPs) (1983)
- Mn and Ni partitioning to CRPs responsible for strong Ni effects on $□□_y$ (1989)
- Mn-Ni rich precipitates (MNPs) and potential for severe □T in low Cu and Cu free steels due to late blooming Mn-Ni-Si phases (1992)
- Complex compositional structures of CRPs and MNPs (1995)
- Many others

MSMP Modeling of Embrittlement

Modeling Hierarchy

- Defect production in aged cascades
- Long-range diffusion of defects & solutes
- Defect & solute clustering
- Nanofeatures □> □□$_y$
- □□$_y$ □> □T
- REVE RPV-1

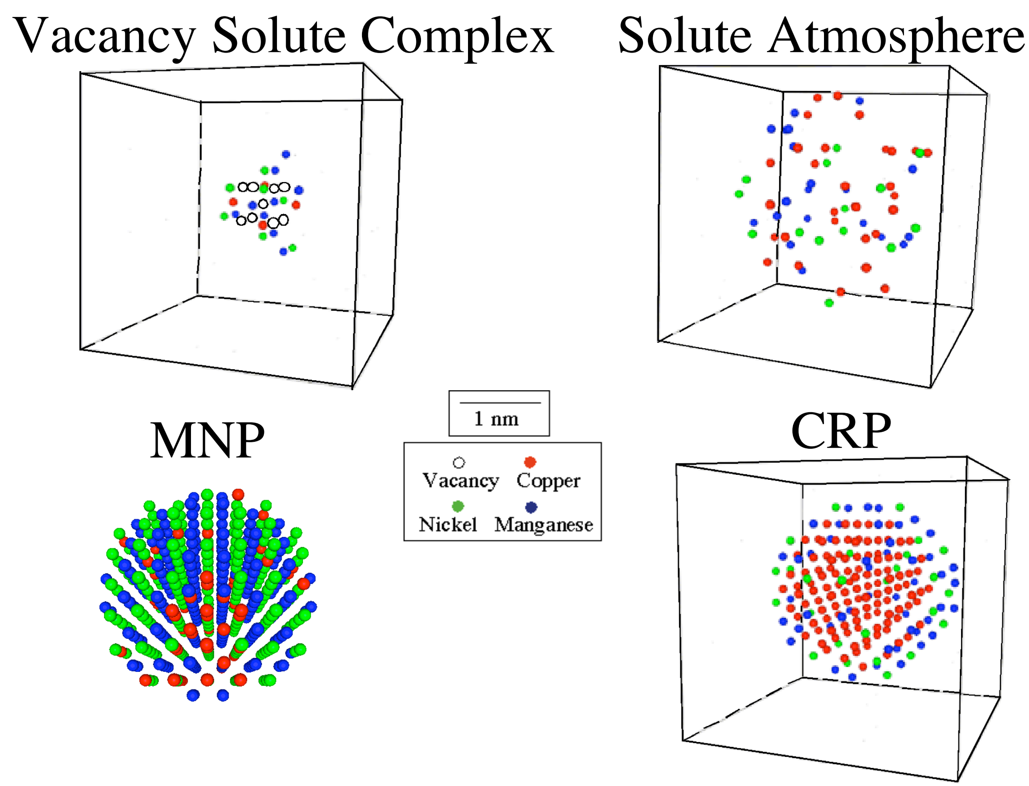


Multiscale Multiphysics Modeling of Irradiation Damaged Materials: Embrittlement of Pressure Vessel Steels, G. R. Odette, et al *MRS Bulletin*, March 2001

Fine-Scale Hardening Features

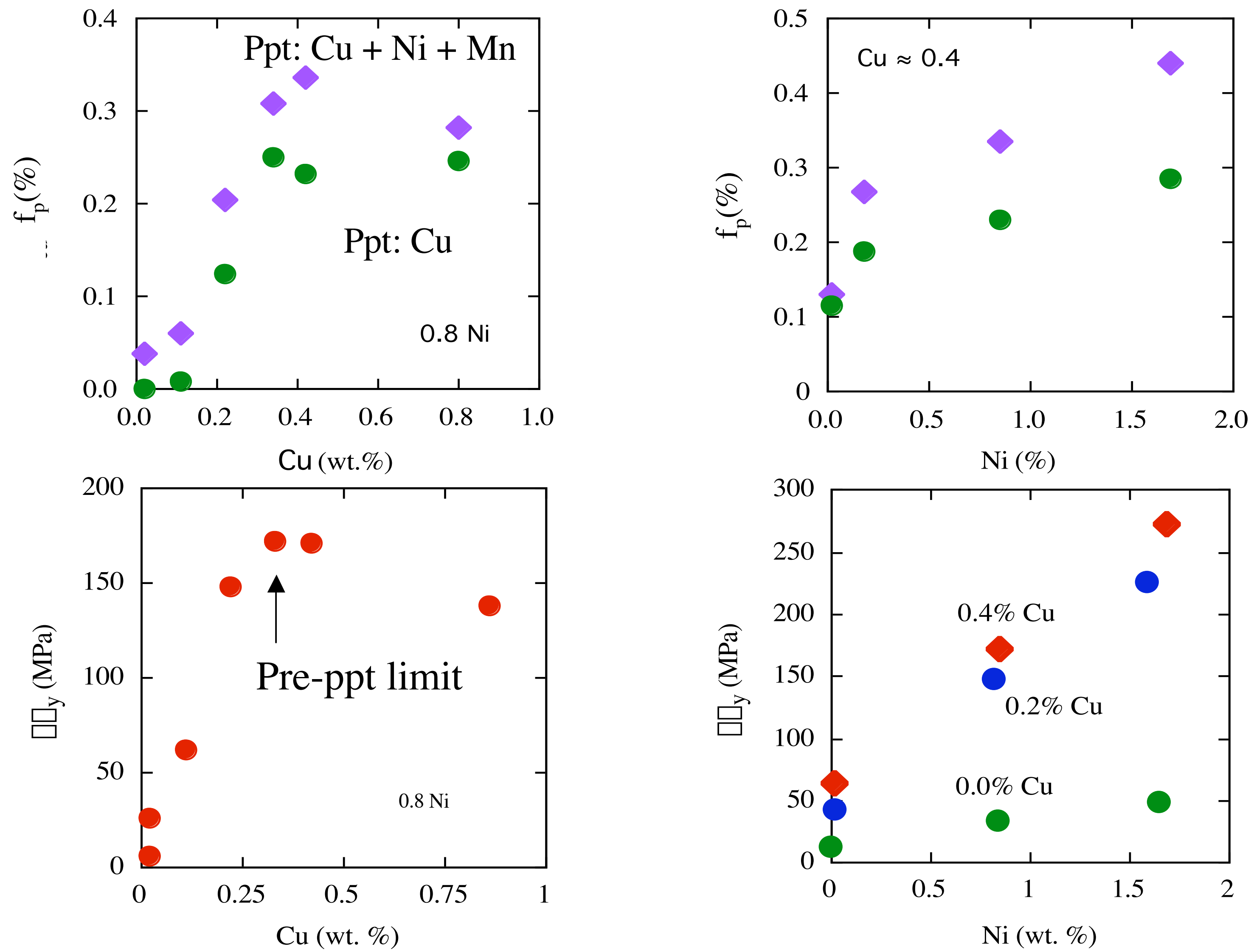
Hardening Features

- Cu rich precipitates
- Mn-Ni rich precipitates
- Matrix feature vacancy cluster solute complexes or remnants (Cu not required)



Focus on modeling precipitate composition and LBP in low/no Cu alloys

Alloy Ni-Cu-Mn Interactions

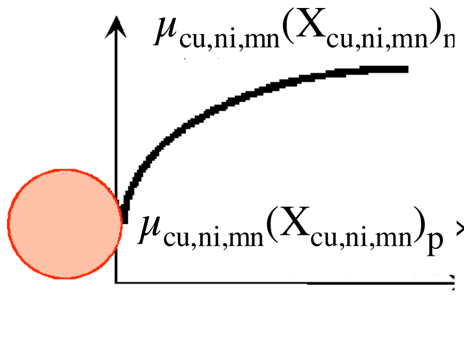


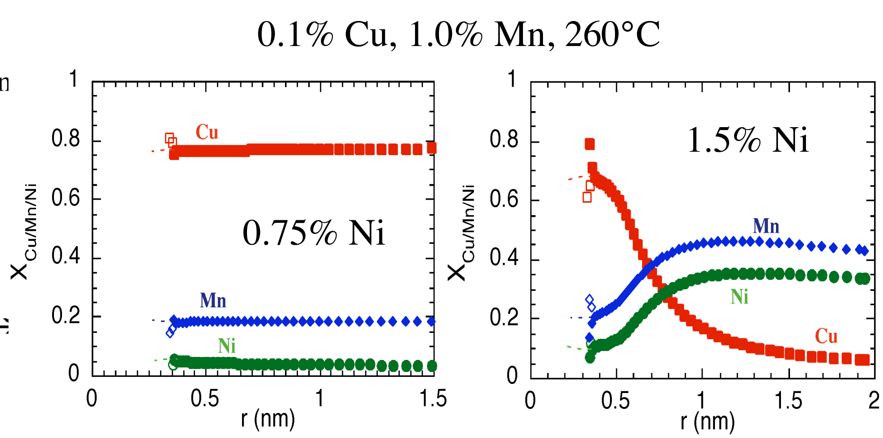
Thermodynamic Model

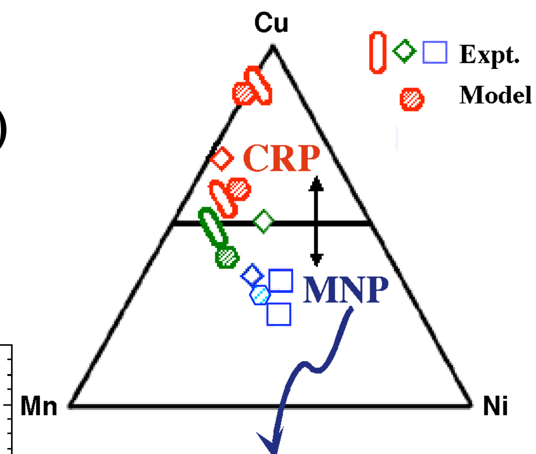
- Model Cu, Mn, Ni, .., Fe chemical potentials -

  $\mu_i = (\partial G/\partial n_i)_{T,nj,k}$ -

  in matrix (m) and precipitate (p) phases
- Flow i to ($\mu_{im} > \mu_{ip}$) or from ($\mu_{im} < \mu_{ip}$) precipitates until $\mu_{im} = \mu_{ip}$
- $G(X_{Cu}, X_{Ni}, X_{Mn}.., T)$ summed binary interaction contributions from CALPHAD extended-regular solution model parameters
- Composition and r_p-dependent □$_{pm}$ contribution
- Some approximations (e.g., no bcc Cu-Ni data) modest Mn-Ni parameter adjustments



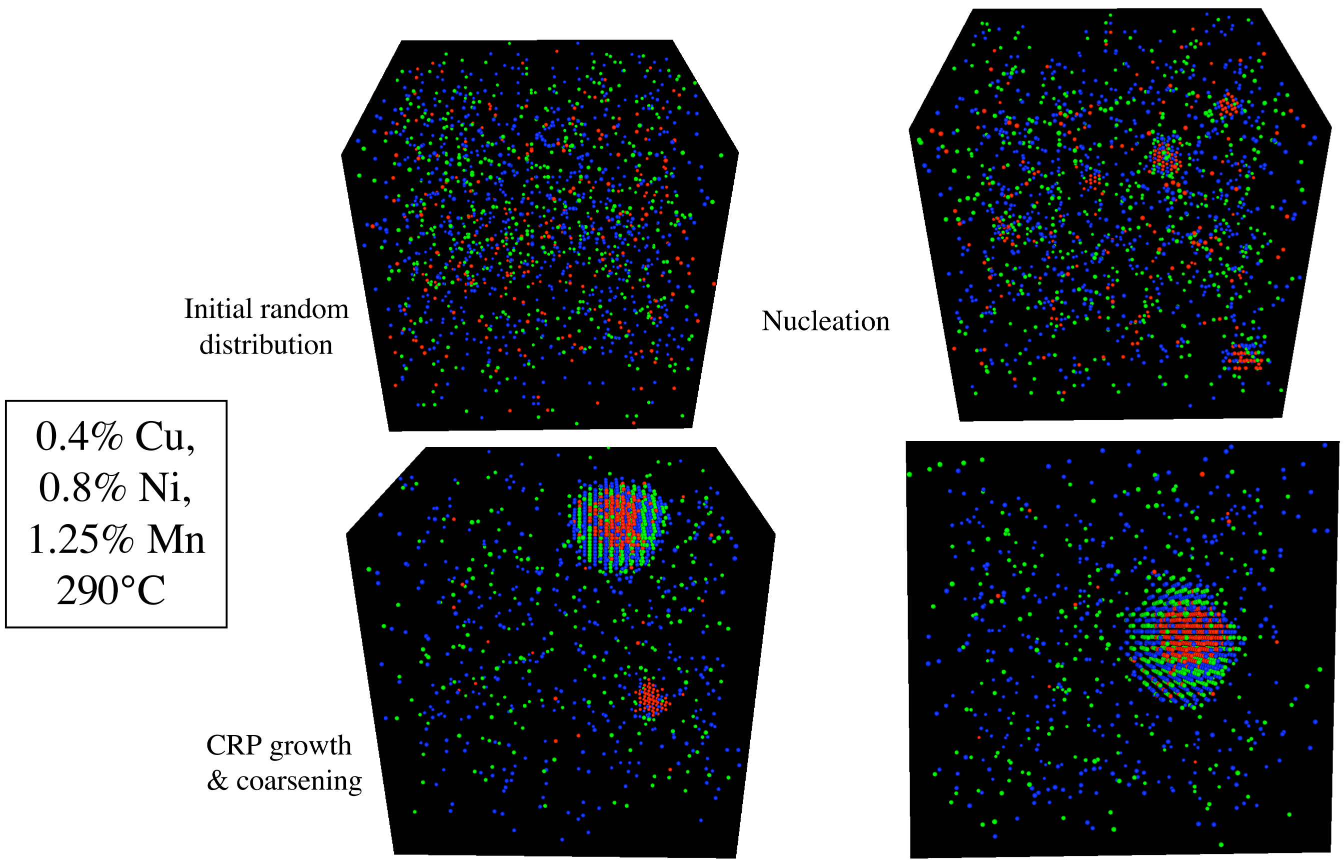




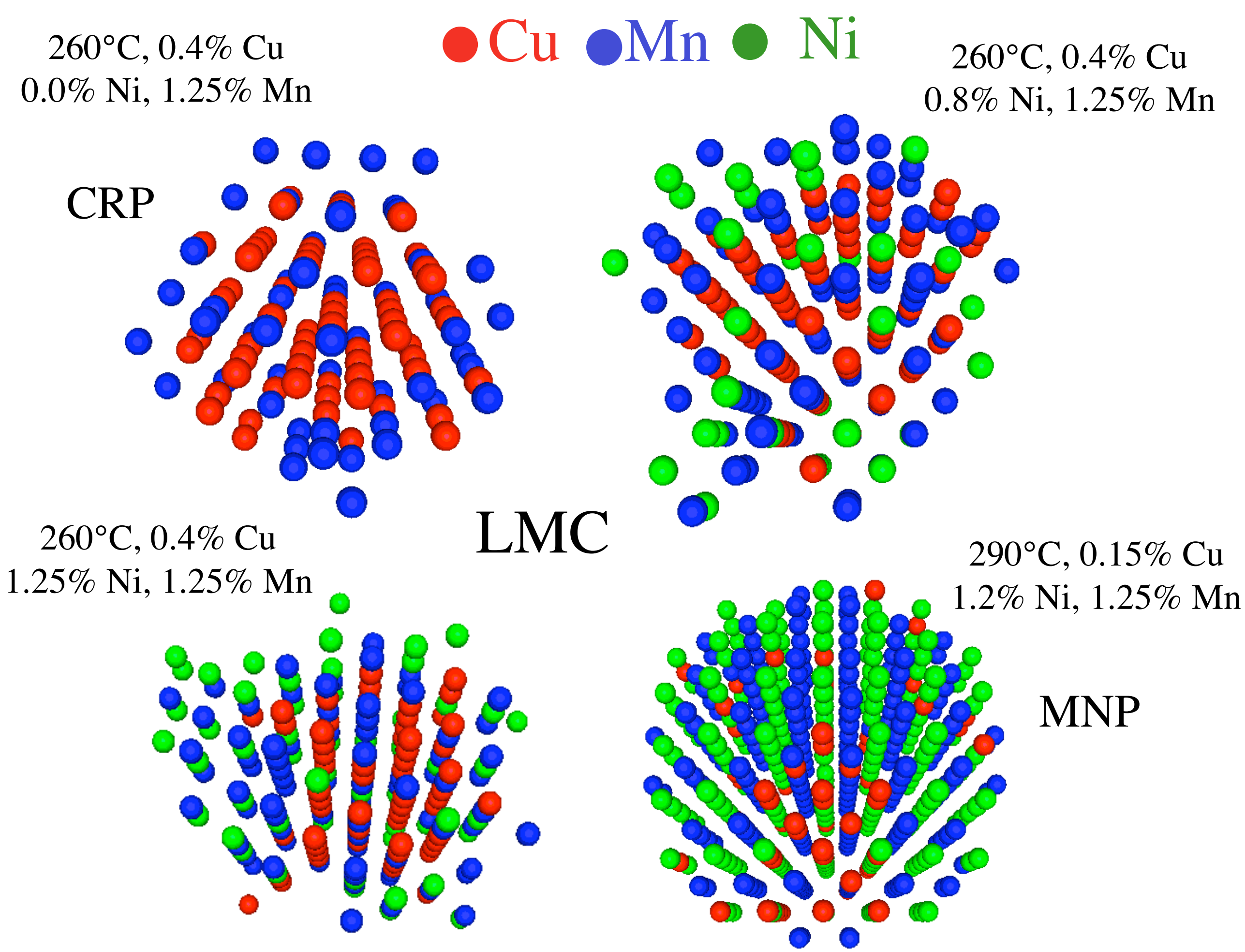
Promoted by low T_i, Cu and high Mn/Ni

LMC Simulations

- Extract regular solution pair bond energies (ϵ_{ij}) from $G(X_{Cu},X_{Ni}, X_{Mn}..,T)$ at the 'average phase' composition
- Kawasaki LMC free energy minimization
- Provides insight on the complex compositional structures

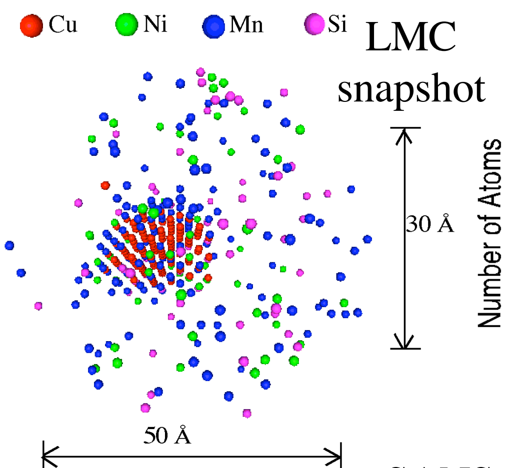


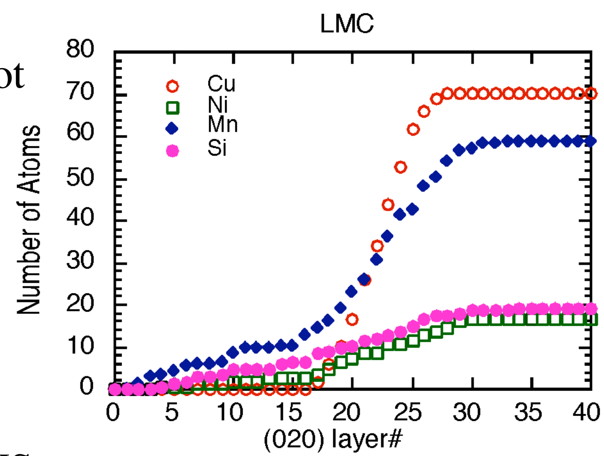
Nano-Precipitates

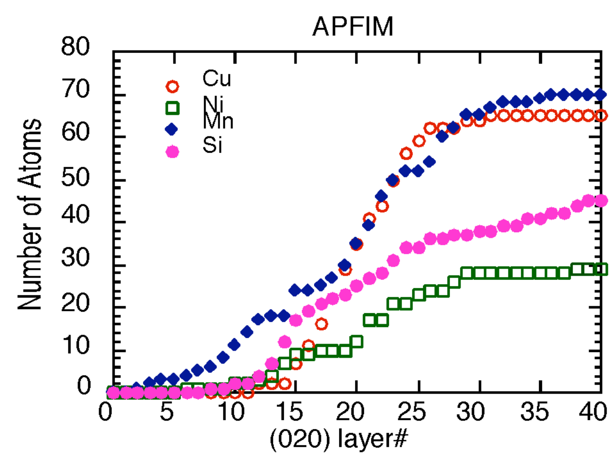


Characterization of CRPs/MNPs

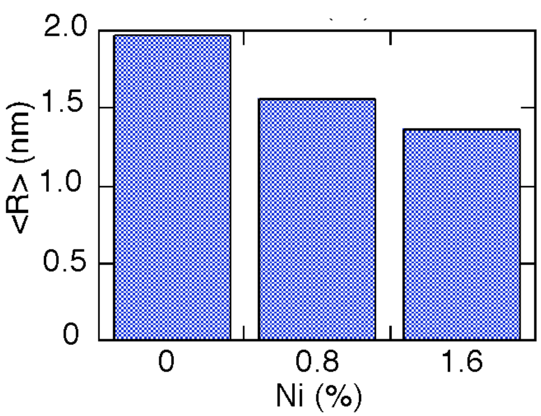
- TD model predictions for *Cu-bearing alloys* are consistent with observations from SANS, APT (minus Fe), AEM, combined resistivity-Seebeck coefficient (RSC) and CDB PAS

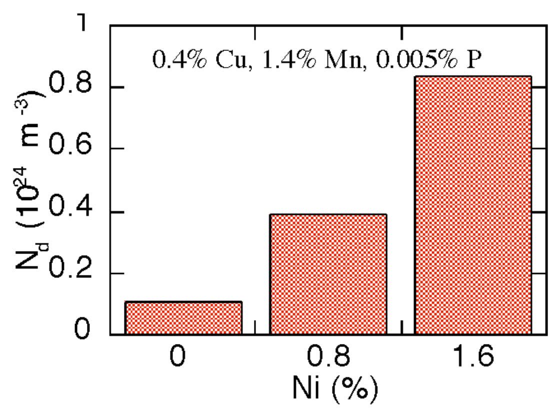


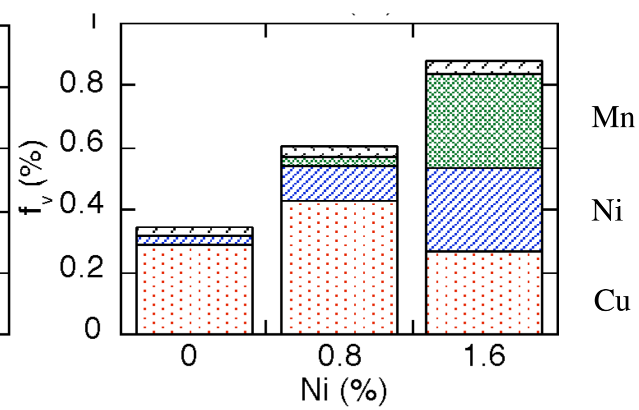




SANS







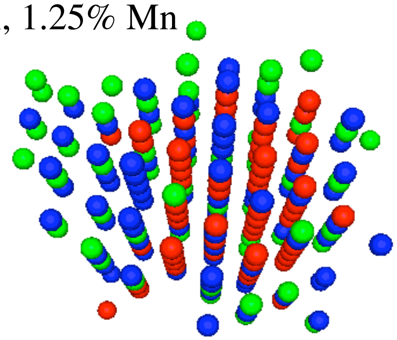
Nano-Precipitates

Not color change

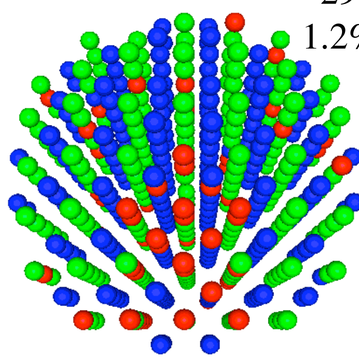
● Cu ● Mn ● Ni

LMC

260°C, 0.4% Cu
1.25% Ni, 1.25% Mn

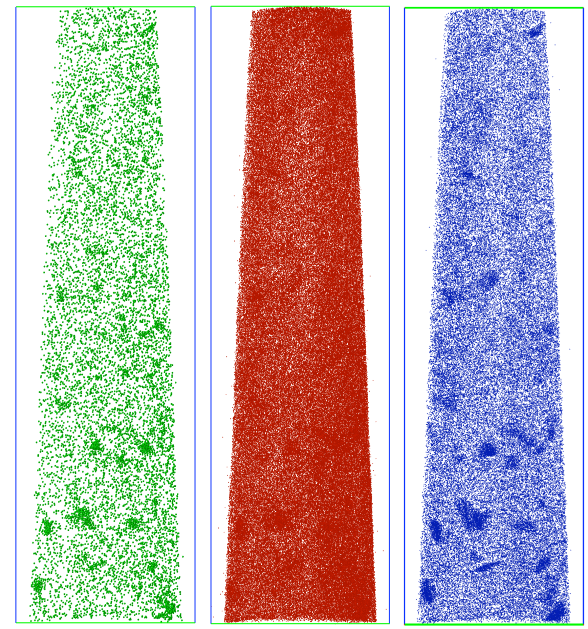


290°C, 0.15% Cu
1.2% Ni, 1.25% Mn



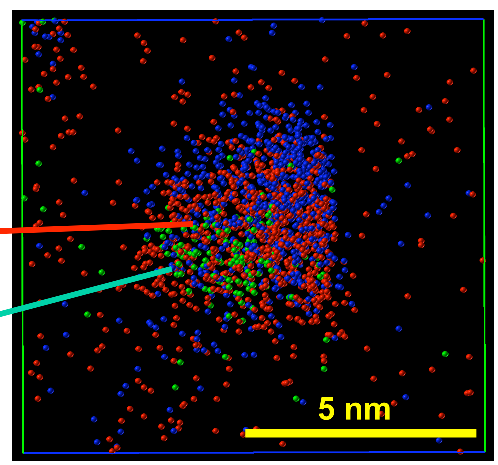
MNP

Cu Ni Mn



Ni + Mn

Cu

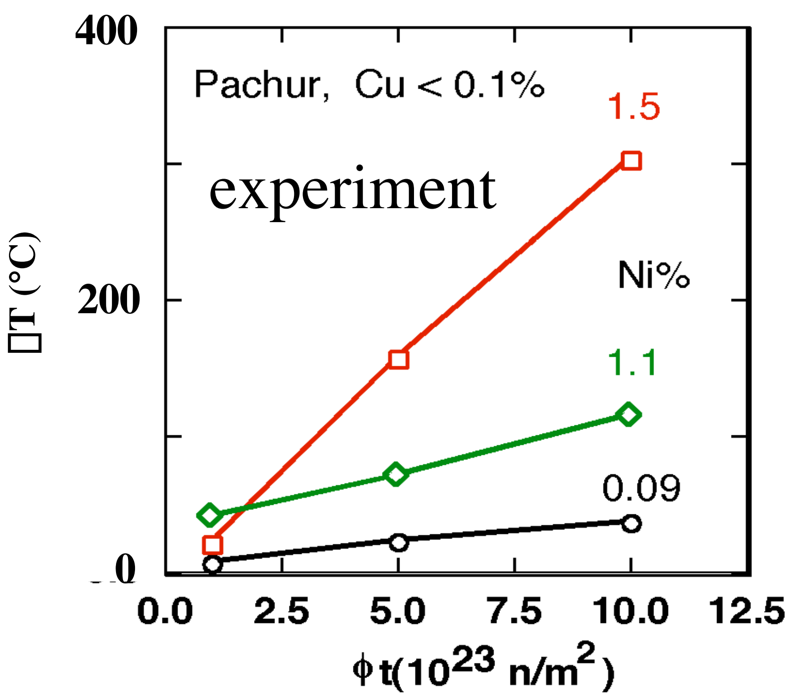


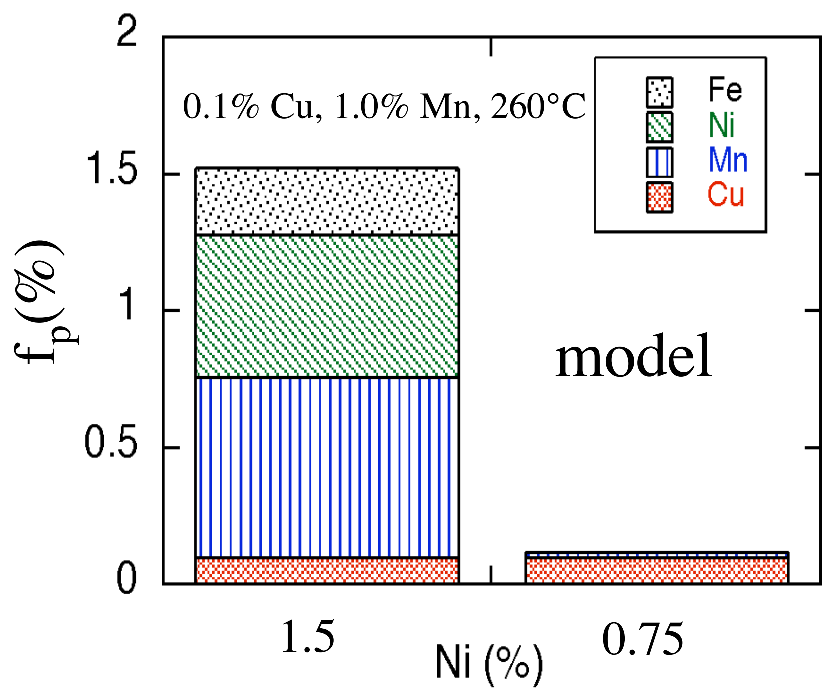
APT

Fe-0.2%Cu-1.6%Ni-1.6%Mn

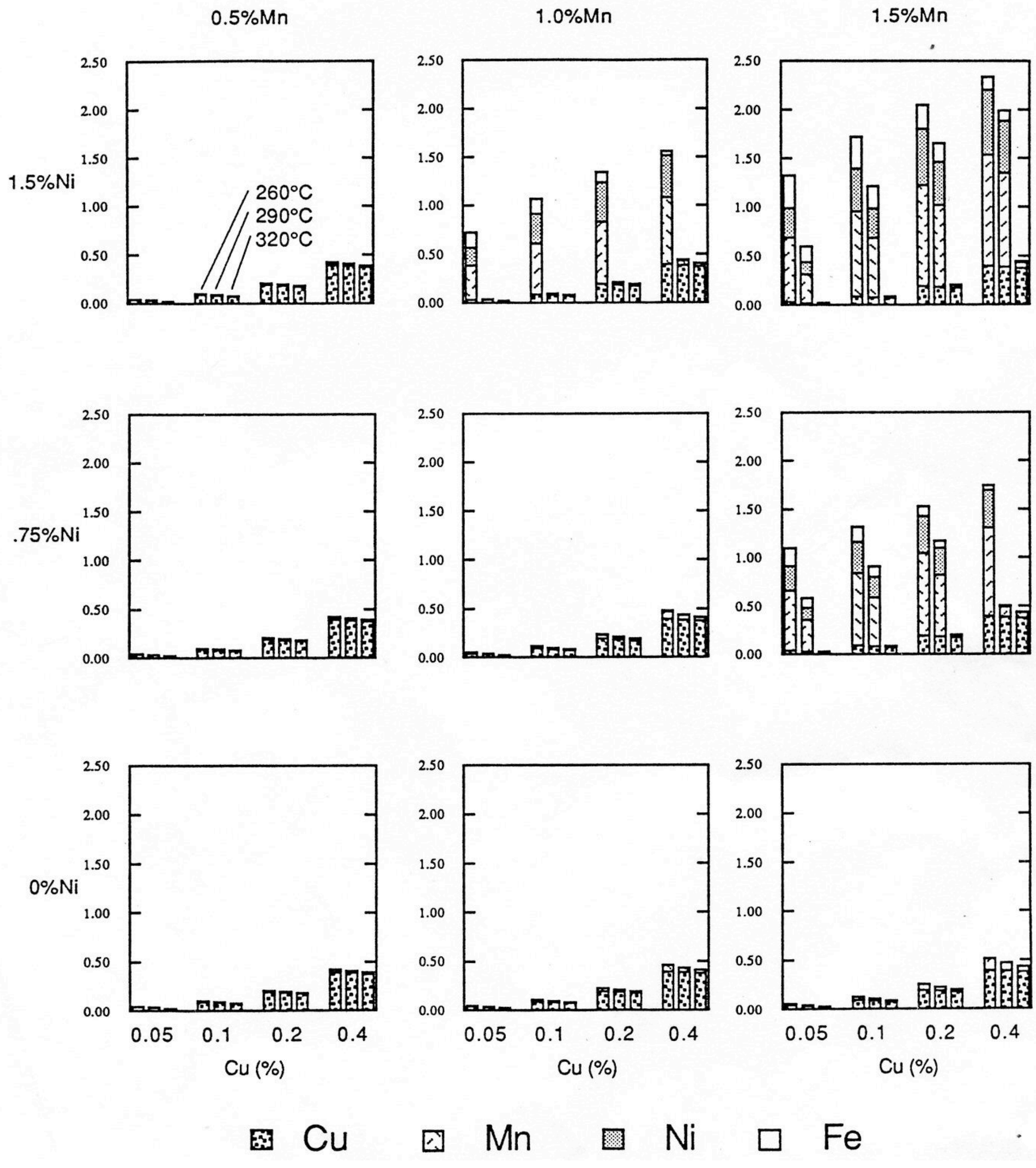
Late Blooming Phases?

- Model predicts *large f_p of Mn-Ni(-Si-P) phases at low/no Cu*
- *Lead to large □T* due to Mn-Ni rich phases???
- Steady-state cluster dynamics show slow nucleation rates at low Cu - some Cu is a good catalyst - how much needed???
- *Late blooming phases (LBP*) grow rapidly at high □t ???





Mn-Ni-Cu-T

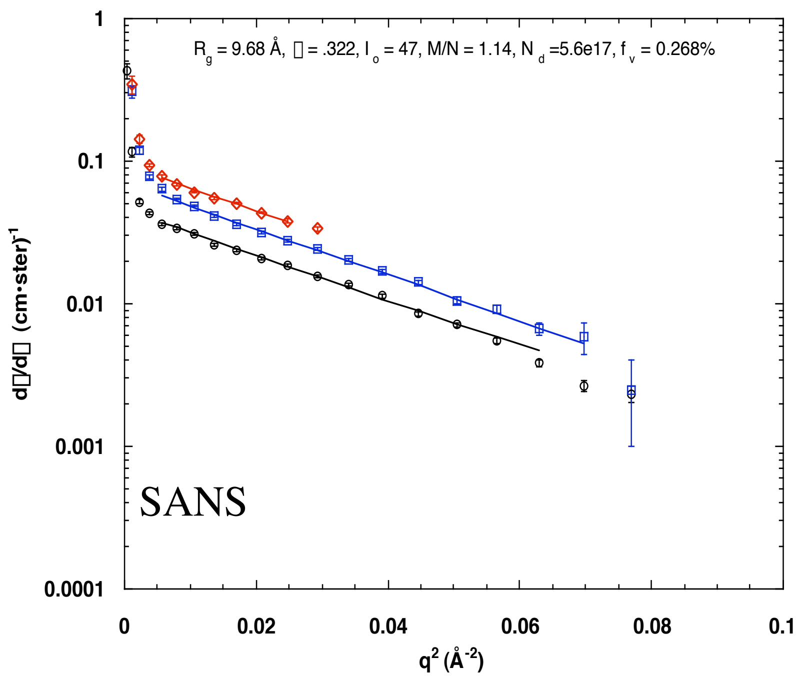


0.5%Mn
1.0%Mn
1.5%Mn
1.5%Ni
.75%Ni
0%Ni
260°C
290°C
320°C
0.00
0.50
1.00
1.50
2.00
2.50
0.05
0.1
0.2
0.4
Cu (%)
Cu
Mn
Ni
Fe

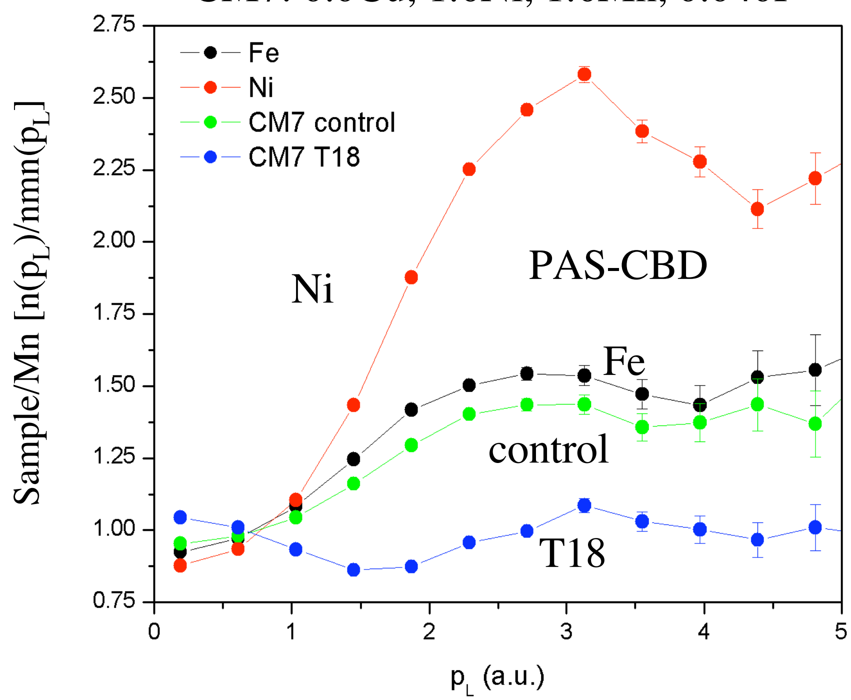
LBPs Found!

- Mn-Ni(-Si-P) LBPs - APT, SANS, RSC, PAS-CBD in no/low Cu special model alloys and Cu free RPV steels
- LBPs and □□$_y$ ≈ 160 to 190 MPa in RPV steels where expected - lower T ≈ 270°C and □ ≈ 3x10^{11} n/cm^2-s, high Ni = Mn = 1.6% - but only a moderate □t ≈ 1.8x10^{23} n/m^2

CM6: 0.0Cu, 1.6Ni, 1.6Mn, 0.005P



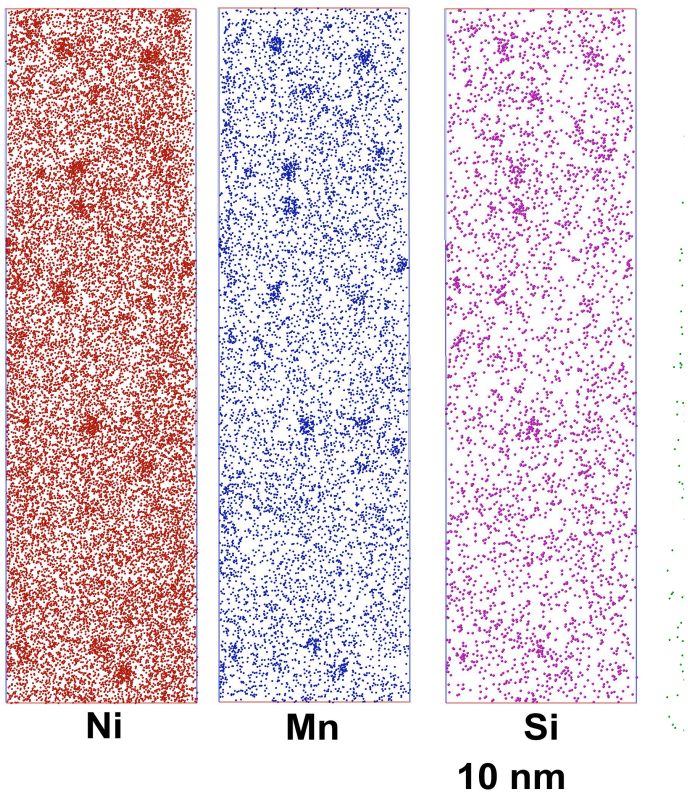
CM7: 0.0Cu, 1.6Ni, 1.6Mn, 0.040P



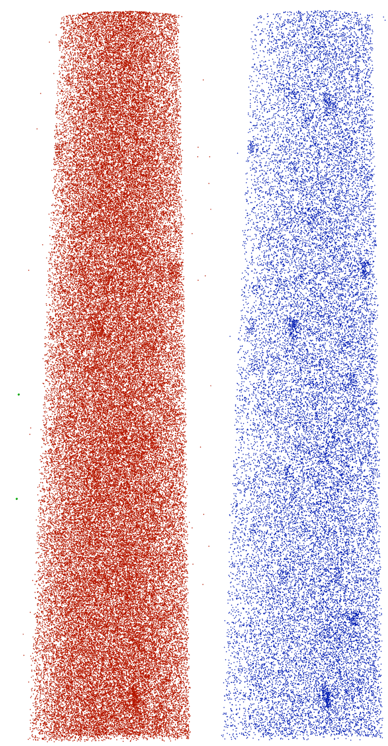
APT-LEAP

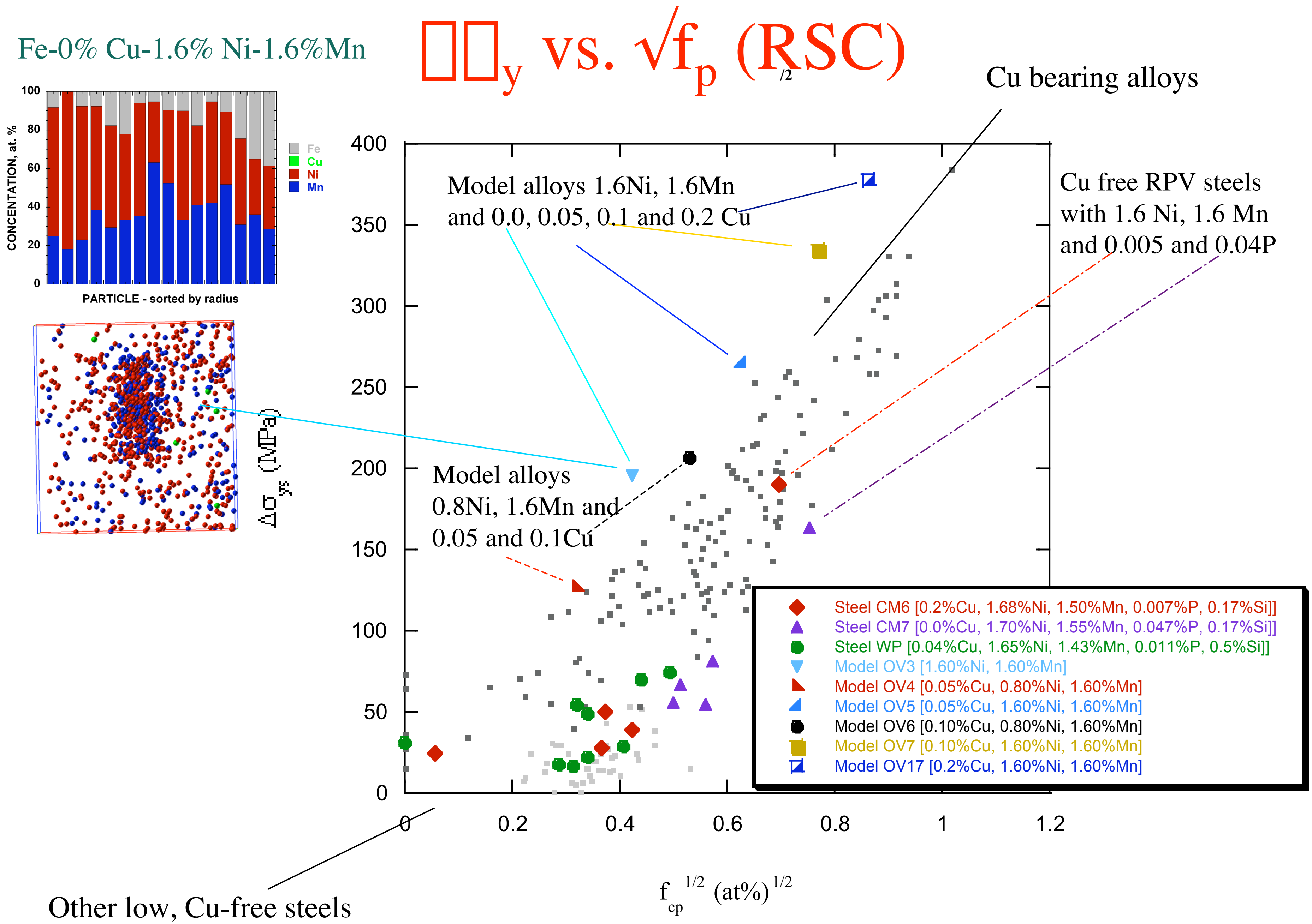
- CM6 Steel: 0.0Cu, 1.6Ni, 1.6Mn, 0.25Si, 0.005P, T ≈ 270°C, φ ≈ $3x10^{11}$ n/cm^2-s, φt ≈ $1.8x10^{19}$ n/cm^2
- OV3 Model Alloy; : 0.0Cu, 1.6Ni, 1.6Mn, T ≈ 290°C, φ ≈ $8x10^{11}$ n/cm^2-s, φt ≈ $1.3x10^{19}$ n/cm^2

CM6



OV3



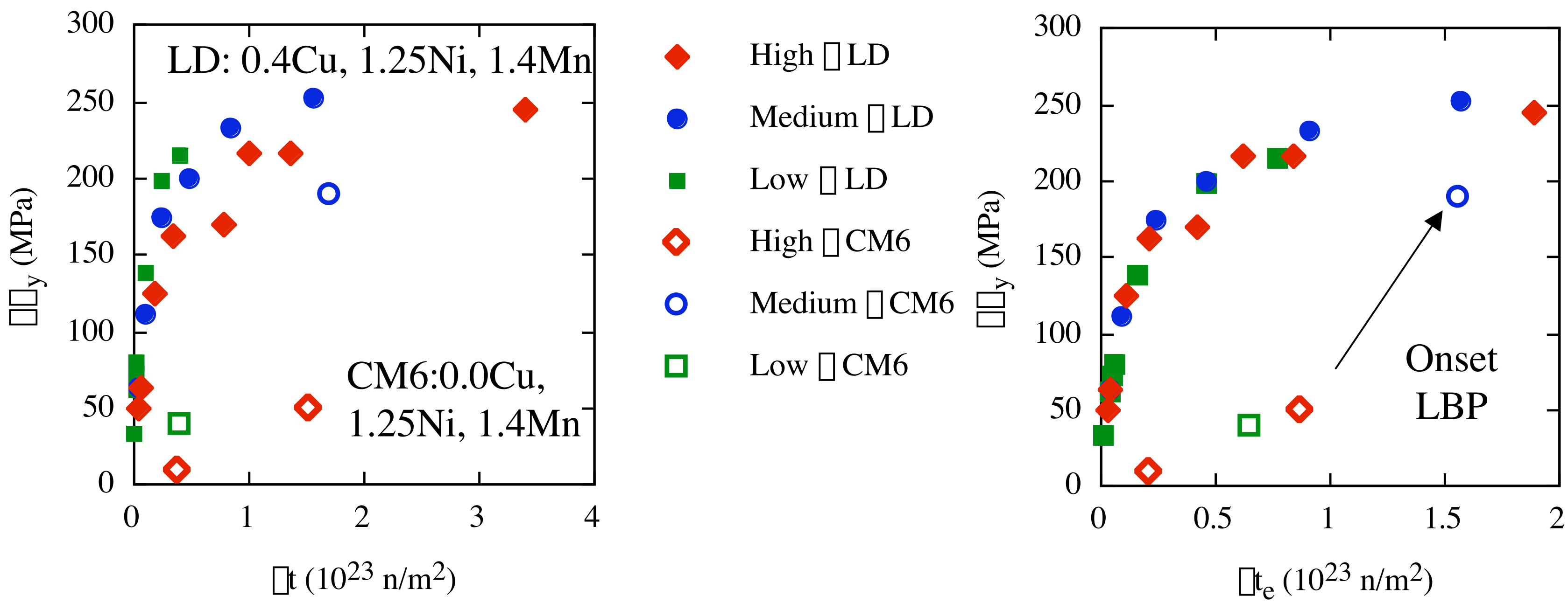


□□y vs. √fp (RSC)
Fe-0% Cu-1.6% Ni-1.6%Mn
CONCENTATION, at. %
PARTICLE - sorted by radius
Fe
Cu
Ni
Mn
Cu bearing alloys
Model alloys 1.6Ni, 1.6Mn and 0.0, 0.05, 0.1 and 0.2 Cu
Cu free RPV steels with 1.6 Ni, 1.6 Mn and 0.005 and 0.04P
Model alloys 0.8Ni, 1.6Mn and 0.05 and 0.1Cu
Δσys (MPa)
f cp 1/2 (at%) 1/2
Other low, Cu-free steels
Steel CM6 [0.2%Cu, 1.68%Ni, 1.50%Mn, 0.007%P, 0.17%Si]]
Steel CM7 [0.0%Cu, 1.70%Ni, 1.55%Mn, 0.047%P, 0.17%Si]]
Steel WP [0.04%Cu, 1.65%Ni, 1.43%Mn, 0.011%P, 0.5%Si]]
Model OV3 [1.60%Ni, 1.60%Mn]
Model OV4 [0.05%Cu, 0.80%Ni, 1.60%Mn]
Model OV5 [0.05%Cu, 1.60%Ni, 1.60%Mn]
Model OV6 [0.10%Cu, 0.80%Ni, 1.60%Mn]
Model OV7 [0.10%Cu, 1.60%Ni, 1.60%Mn]
Model OV17 [0.2%Cu, 1.60%Ni, 1.60%Mn]

Dose Rate Effects

- Strong ϕ-effect on CRP (all these alloys in the IVAR database*) and LBP hardening due to solute-vacancy trap recombination - for high Ni-Mn an effective fluence ϕt_e collapses the data at a reference flux $\phi_r = 3\text{x}10^{11}$ n/cm^2-s

$$\phi t_e = \phi t(\phi_r/\phi)^{1/2}$$



* _ 1500 datapoints

Summary and Conclusions

- Models have provided enormous insight on many complex embrittlement mechanisms and phenomena that simply could not be understood from experiment alone and vice versa
- Models have often led and guided experiment - e.g. the early prediction and recent successful search for LBPs
- A marriage of modeling to basic experiments (mechanism, single variable property and microstructure) has enabled robust predictive correlations of messy surveillance data and perhaps avoiding nasty surprises like LBP
- But models are certainly neither perfect nor complete and there remain a many open questions and opportunities