Training School, 3 - 7 September 2018 Polytechnic University of Valencia (Spain)



IRRADIATION EFFECTS ON RPV STEELS: MICROSTRUCTURE & MECHANICAL PROPERTIES

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Outline



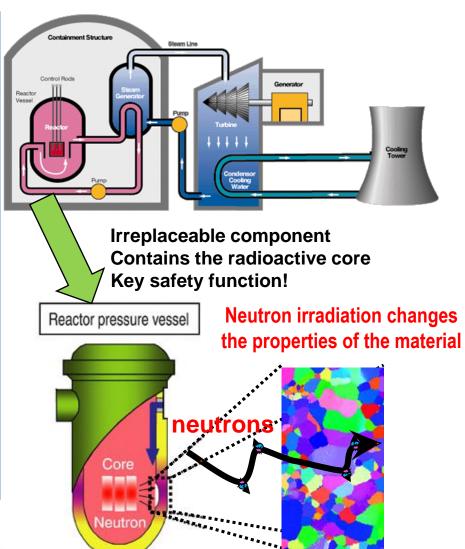
- Introduction to RPV steel embrittlement
- Main microstructural and microchemical changes under irradiation
 - Damage production in cascades
 - Point-defect driven microstructural changes (cavities, loops, ...)
 - Solute redistribution
- Origin of radiation hardening
 - Dislocation pinning
- Radiation hardening and embrittlement
 - Origin of the correlation between hardening and embrittlement
 - Embrittlement without hardening
- Origin of radiation embrittlement in RPV steels
 - Handbook mechanisms and three feature models (trend curves)
 - Current understanding in SOTERIA: paradigm shift



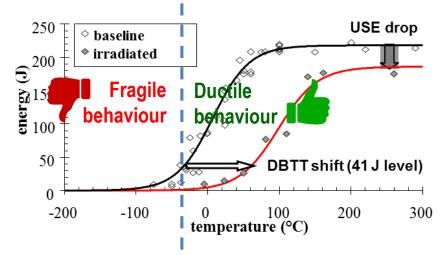
INTRODUCTION TO RPV STEEL EMBRITTLEMENT

Irradiation embrittlement of reactor pressure vessel steels

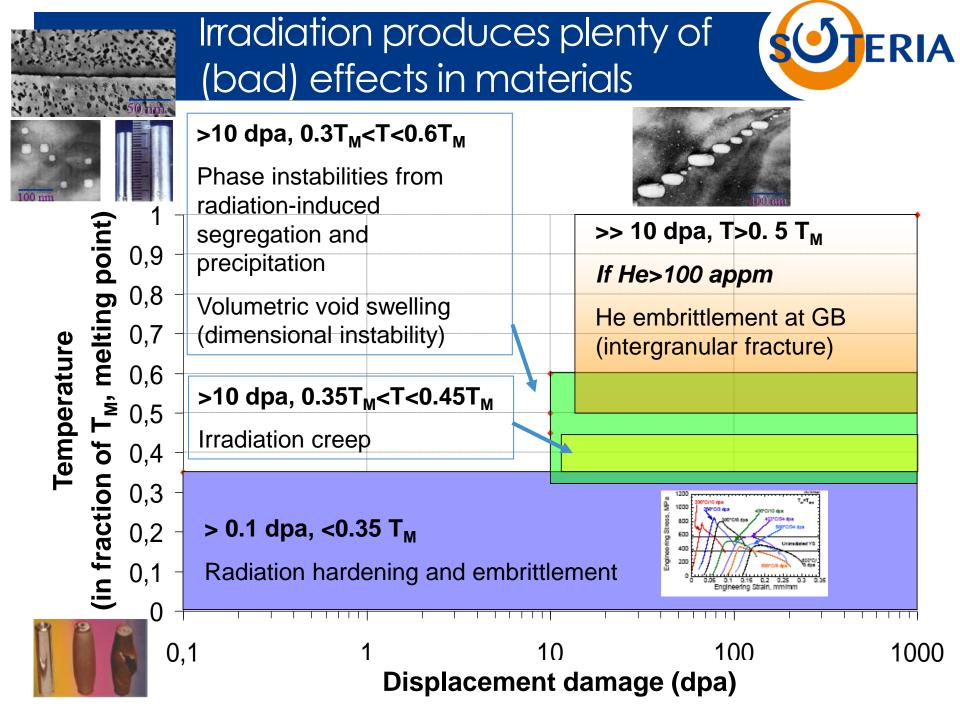








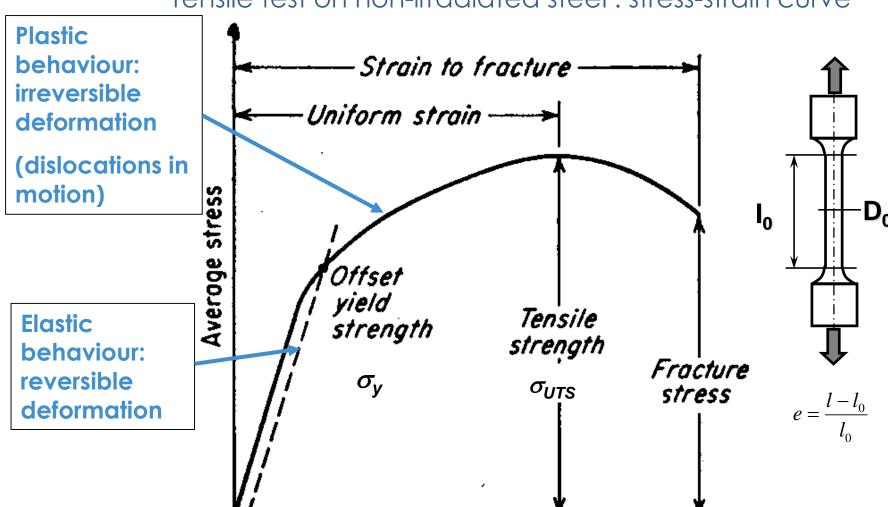




What is radiation hardening?



Tensile test on non-irradiated steel: stress-strain curve



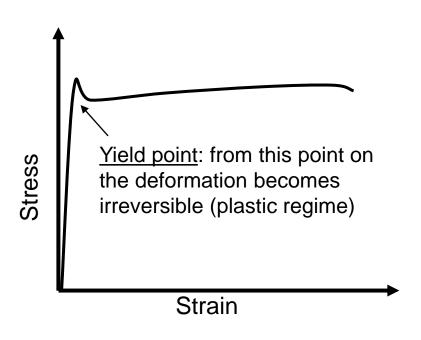
Conventional strain e

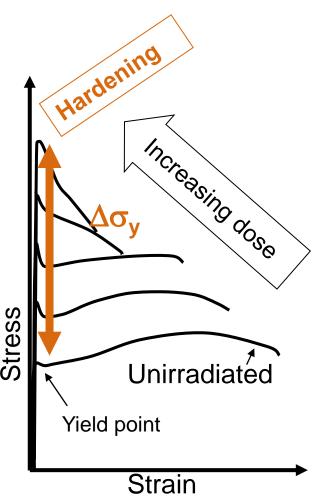


What is radiation hardening?



Hardening = Yield strength increase







What is radiation embrittlement?

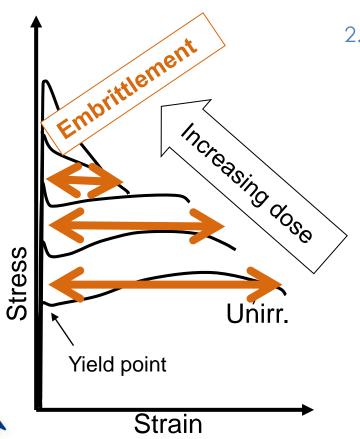


Brittle material = breaks without prior deformation

Embrittlement =



2. increase of temperature below which material is brittle



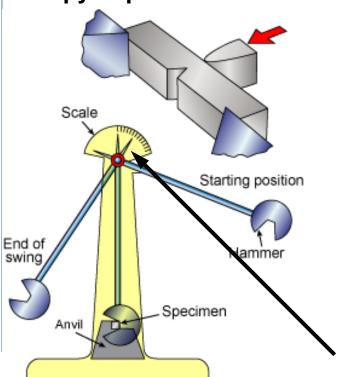


What is radiation embrittlement?

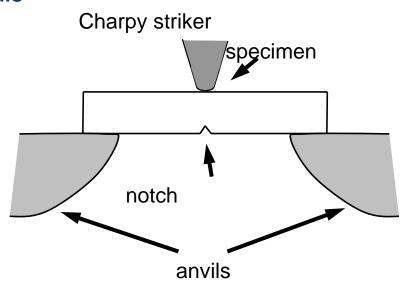


Brittle material = breaks without prior deformation Embrittlement =

Charpy impact test



- reduction of elongation (deformation) before fracture
- 2. increase of temperature below which material is brittle



Scale provides energy absorbed by specimen when breaking: the higher, the more ductile the material

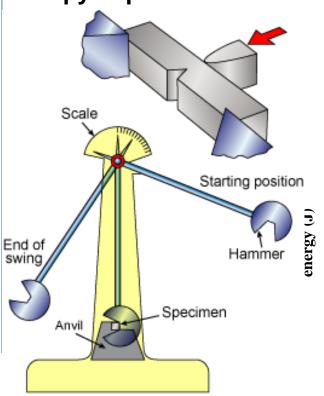


What is radiation embrittlement?

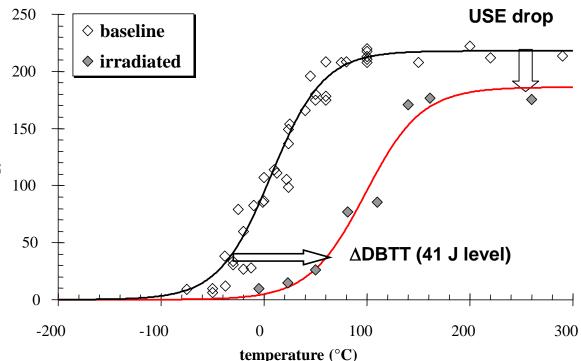


Brittle material = breaks without prior deformation Embrittlement =

Charpy impact test



- reduction of elongation (deformation) before fracture
- 2. increase of temperature below which material is brittle





$\Delta DBTT$ and $\Delta \sigma_{v}$ are (generally) linearly correlated ...



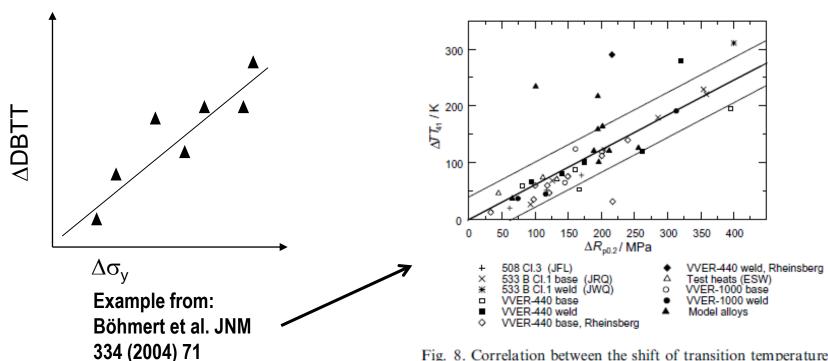


Fig. 8. Correlation between the shift of transition temperature ΔTT_{48} and the yield stress increase $\Delta R_{p0.2}$.

Radiation embrittlement with hardening disappears above ~400°C.

<u>Embrittlement without hardening</u> exists as well, e.g. in presence of He (He-embrittlement), or due to segregation of elements like P at GBs: this may occur at all temperatures

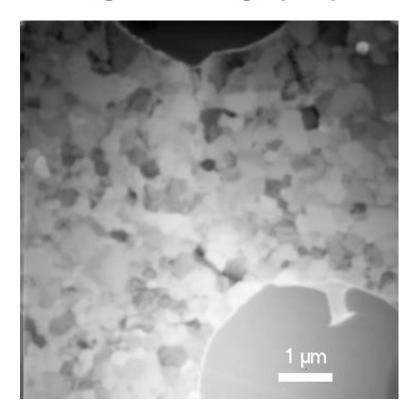


MAIN MICROSTRUCTURAL & MICROCHEMICAL CHANGES UNDER IRRADIATION

Under a microscope steels are aggregates of grains

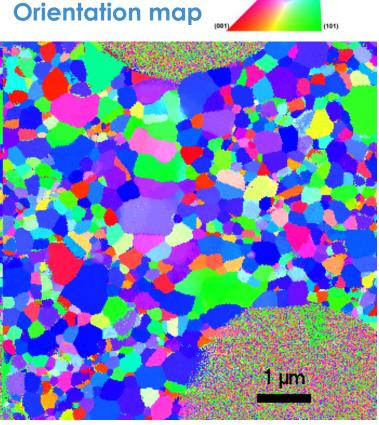


Brightfield image (TEM)



Metallographic examination of deformed specimen - grains are clearly visible



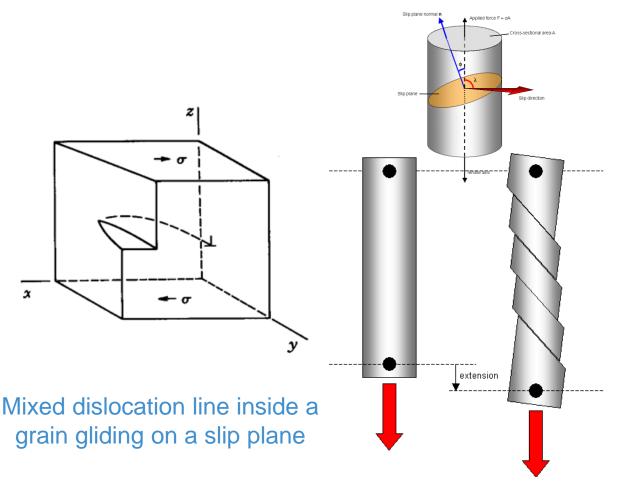


Electron back-scatter diffraction (EBSD) – each colour corresponds to a grain with different orientation

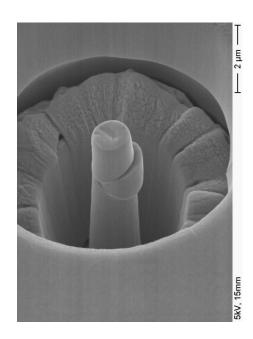


Inside grains, dislocations allow plastic deformation







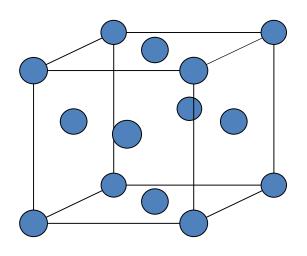


Compression test on nano-pillar in single grain



At the atomic scale a metal is a crystal lattice





Face centered cubic, fcc



Body centered cubic, bcc



[100] [110] [111]

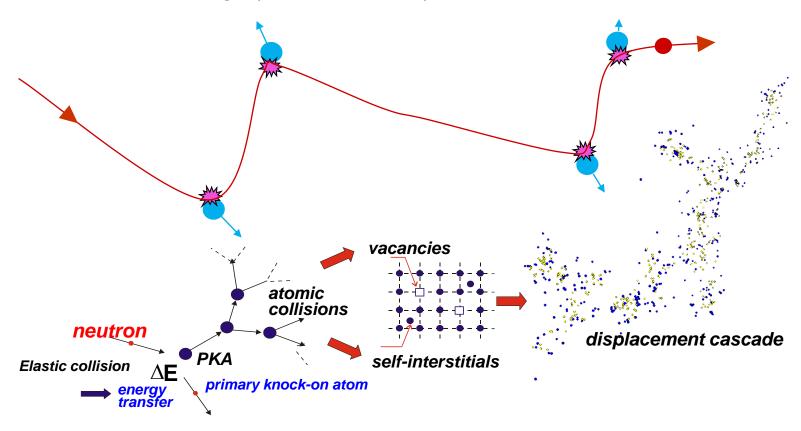


Radiation damage: It all starts with a neutron hitting an atom ...



Neutrons = uncharged particles ⇒ can travel long distances in matter When reacting with nuclei of atoms they can produce

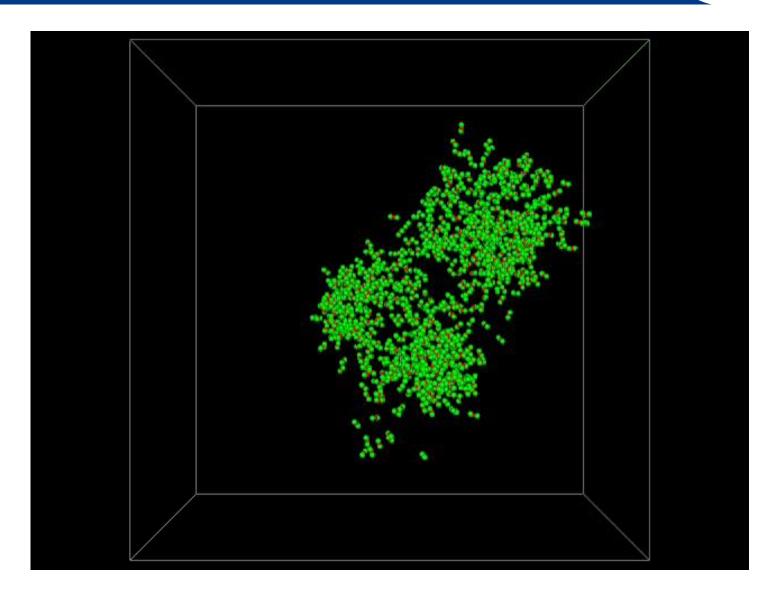
- Activation
- Transmutation (He, H)
- Displacement damage (elastic collisions)





Displacement cascade: the mother of all evils ... ERIA

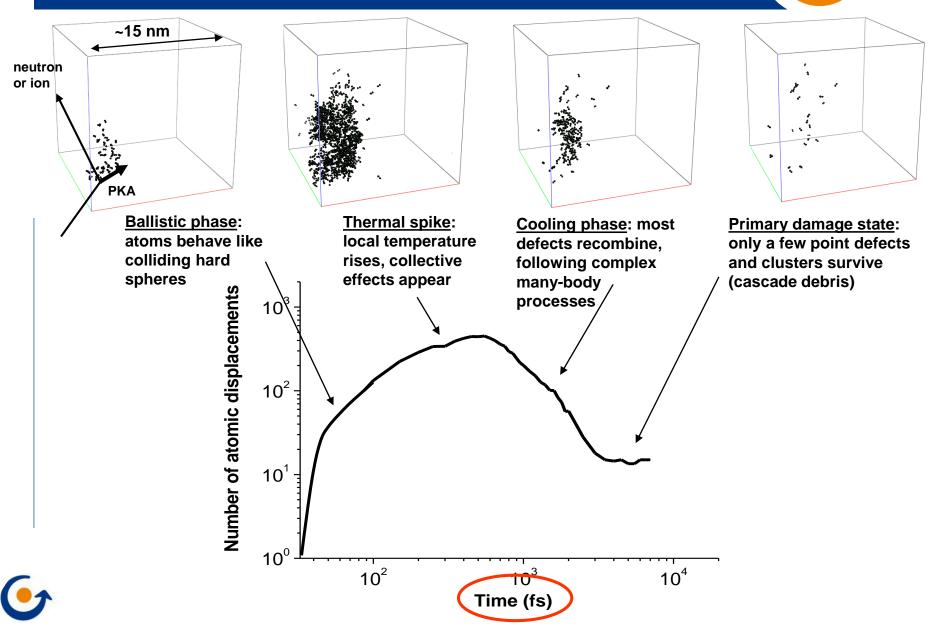






A closer look at the cascade phases **ERIA**

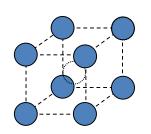




Clustering of vacancies

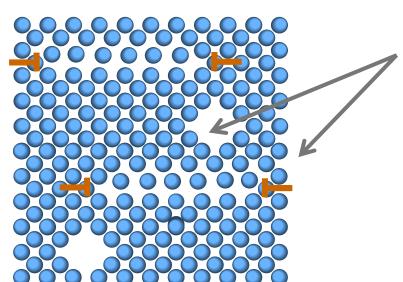


What's a vacancy and how does it migrate?



Vacancy and its migration mechanism in the bcc structure

When vacancies meet during migration they form stable clusters
How does a vacancy cluster look like?



nano-cavity vacancy dislocation loop

nano-cavities growing to voids are
typical of Fe alloys
vacancy dislocation loops are rarely
observed in Fe alloys
(only under heavy ion irradiation:
dense cascades)

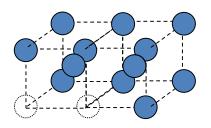


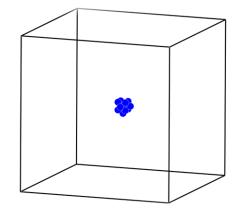
Vacancy cluster migration



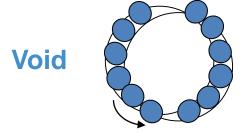
Can nano-cavities and voids migrate?

Di-vacancy





Small vacancy clusters can migrate (slowly) in 3D Voids may grow by coalescence



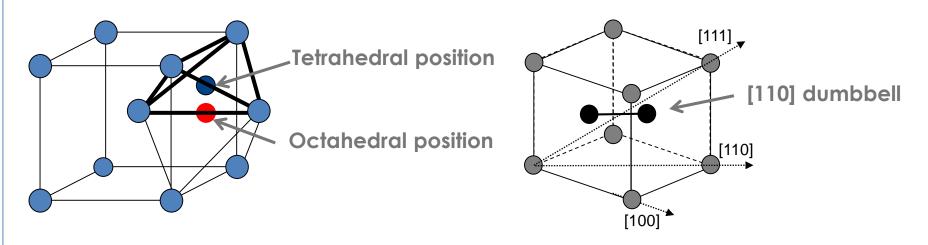
Even voids may migrate via surface vacancy rearrangement



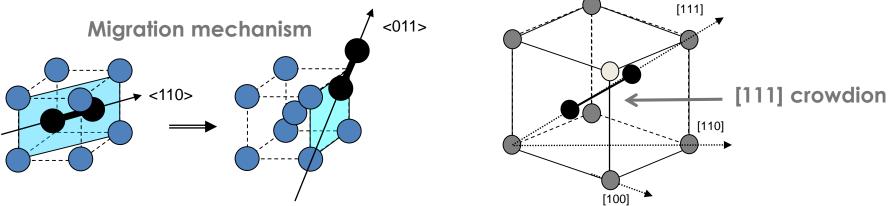
Self-interstitial atoms (SIA) in Fe alloys (SIA)



How does an SIA in Fe look like? How does it migrate?



The [110] dumbbell is the most stable configuration for the single SIA in Fe

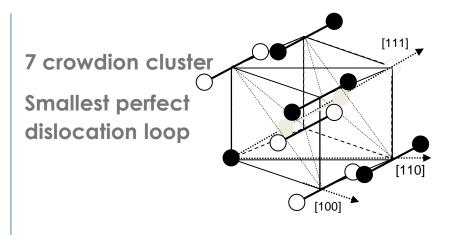


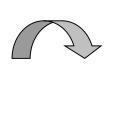


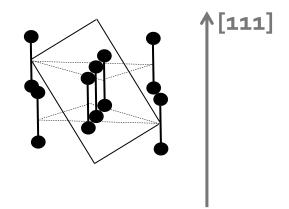
crowdion is stable in other bcc metals and is the unit for SIA clusters in Fe

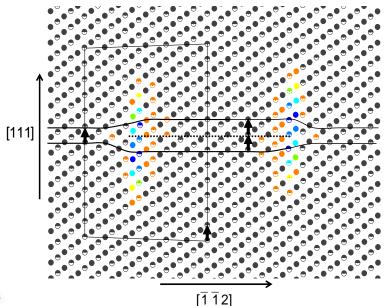
SIA clusters in Fe alloys: prismatic dislocation loops





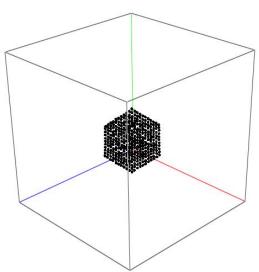






Dislocation loop with Burgers vector 1/2<111>

View normal to [111]



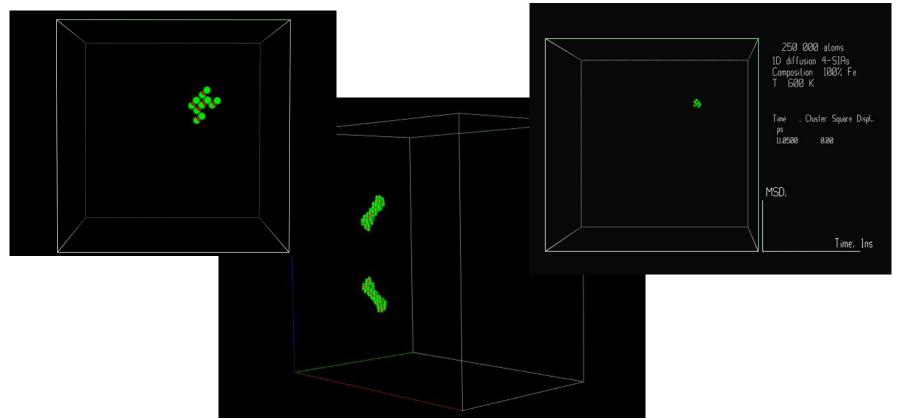


Migration of SIA loops = bunches of parallel crowdions



SIA clusters migrate fast in one-dimension

(at least in pure metals)

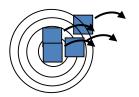




Cluster dissolution



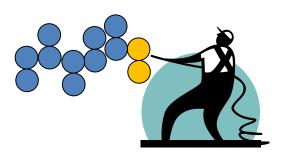
Emission of vacancies from small clusters and voids



At ~300°C small vacancy clusters dissolve easily unless stabilised by something else (eg He or solute atoms): the smaller, the easier the emission

Large voids, however, are stable up to ~500°C or higher and may grow at the expenses of small clusters that dissolve

Emission of SIA from loops



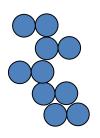
SIA clusters are highly stable and generally do not easily emit single SIAs spontaneously

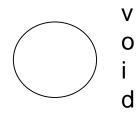


Defect recombination and disappearance at sinks

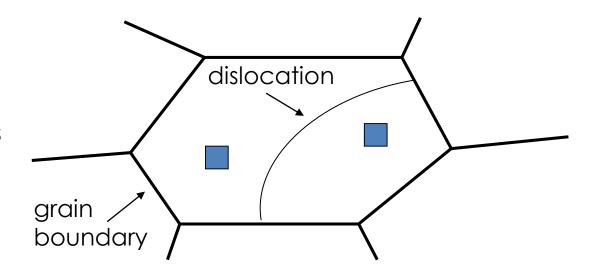


Recombination of SIA with Vacs





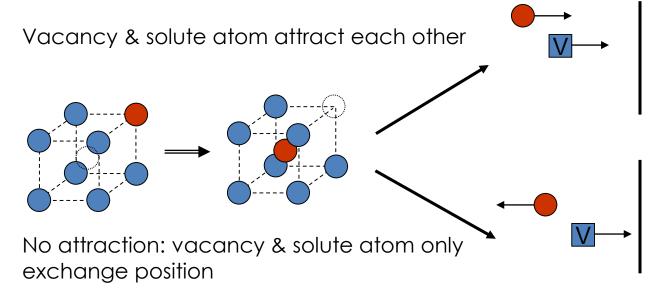
Disappearance at sinks





Transport of chemical species



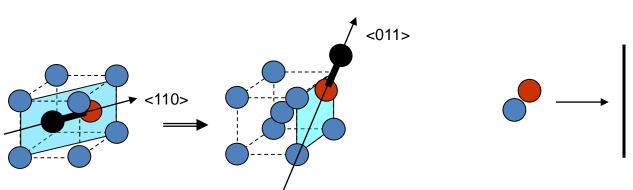


Sink for Vacs



Sink for SIAs



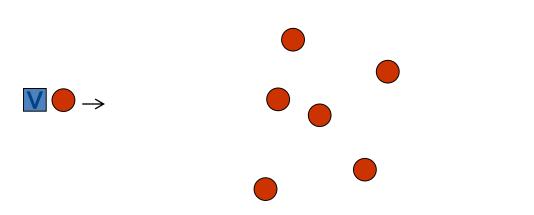




If stable, mixed dumbbell transports solutes to sinks

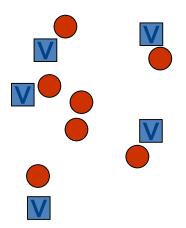
Formation of aggregates of solutes = radiation enhanced precipitation (if stable thermodynamic phase)







If solutes "like each other" (free energy decreases when they cluster > formation of new phase), precipitation occurs



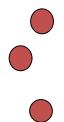
Under **irradiation** the presence of many point-defects **enhances precipitation**

If vacancies "like" the solutes, then complexes containing both may form (same can happen with SIAs)

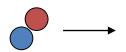


Segregation at sinks = accumulation/depletion of solutes = radiation induced segregation (RIS)

Under irradiation, massive solute transport by SIAs <u>induces</u> accumulation of solutes at sinks



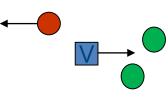


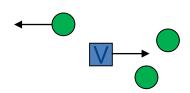


Different diffusivity via non attracted vacancies may lead to solute depletion at sinks





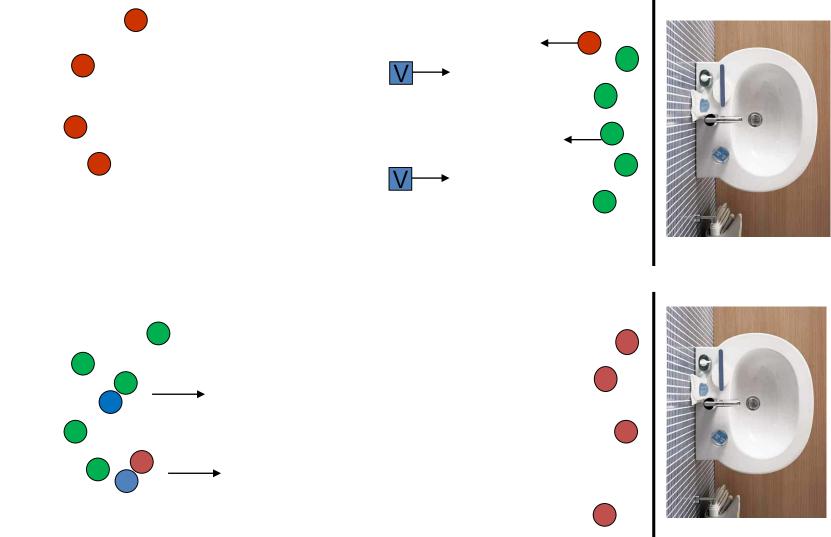








Competition between chemical species can produce solute separation

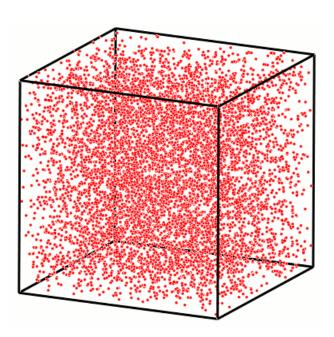




Radiation <u>enhanced</u> and radiation induced



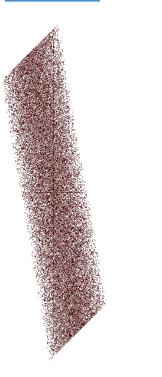
Enhanced



Precipitates form because higher number of point defects under irradiation <u>enhances</u> transport and <u>accelerates</u> their formation

They would form also under high T annealing

Induced



Courtesy F. Soisson

Precipitates form because continuous flux of point defects to sink increases local solute concentration, until solubility limit is locally exceeded

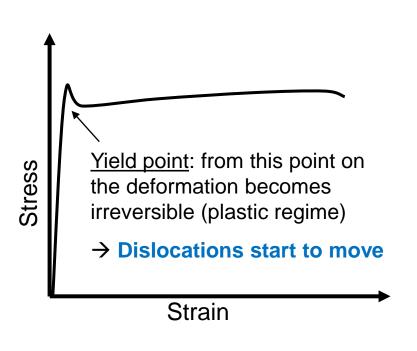
This would **NOT** happen without irradiation

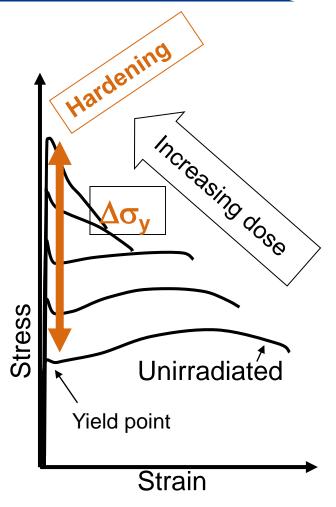


ORIGIN OF RADIATION HARDENING

Hardening = Yield strength increase



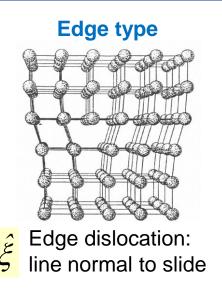


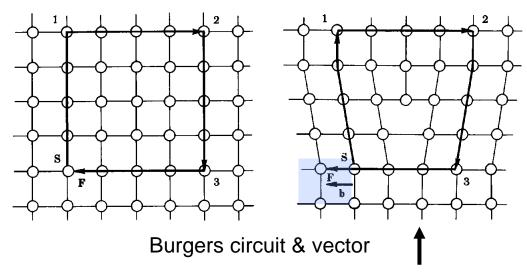


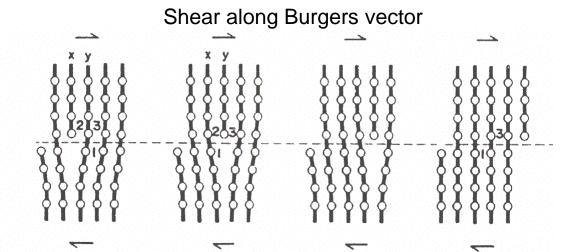


Dislocations







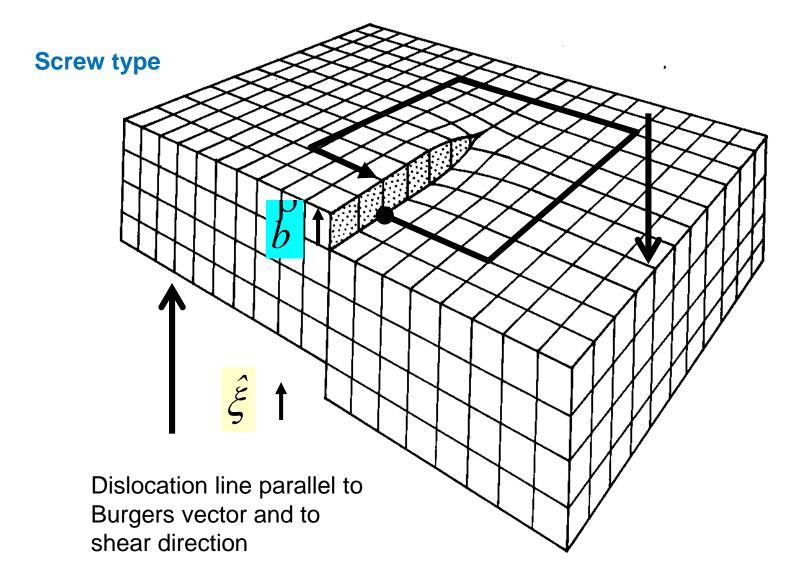




Dislocation glide under shear is the most frequent mechanism whereby metals are <u>irreversibly deformed</u> (<u>plastic deformation</u>)

Dislocations

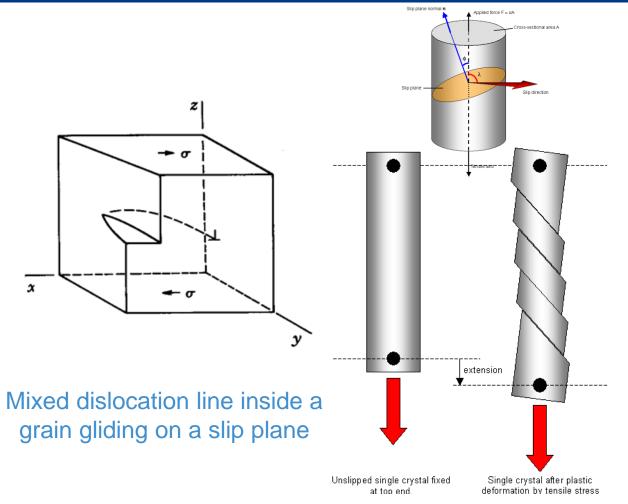


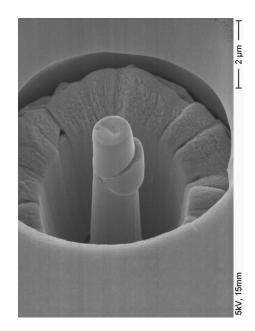




Metals deform plastically via dislocation motion







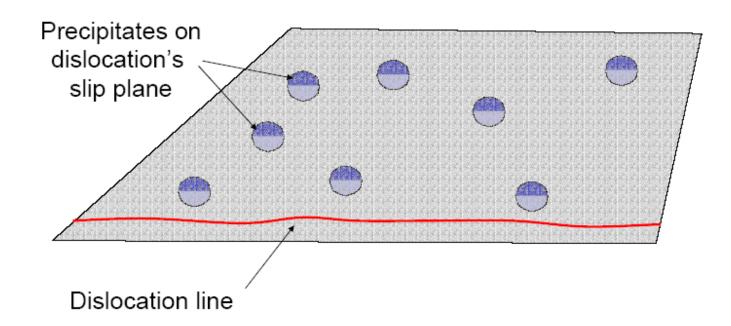
Compression test on nano-pillar in single grain

Deformation under tension of single crystal along slip planes



Shearable obstacles

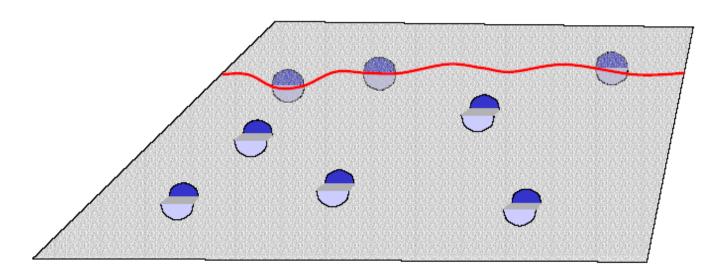






Shearable obstacles

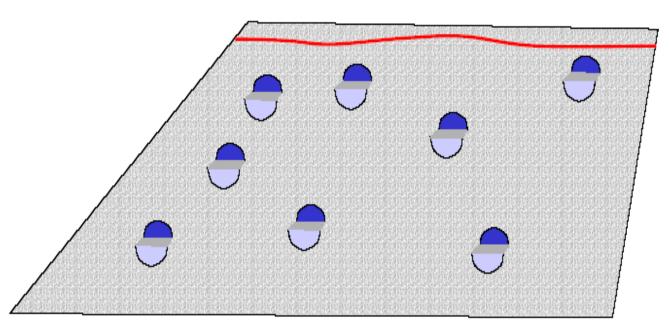




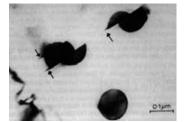


Shearable (weak) obstacles





Dislocations can cut through the obstacle: the bigger, the more difficult to cut it through Elastic, chemical, and phase stability effects also determine obstacle strength

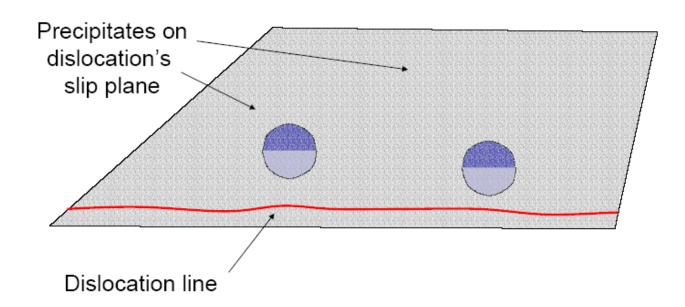


Increasing strain 'chops up' sheareable obstacles



Impenetrable obstacles

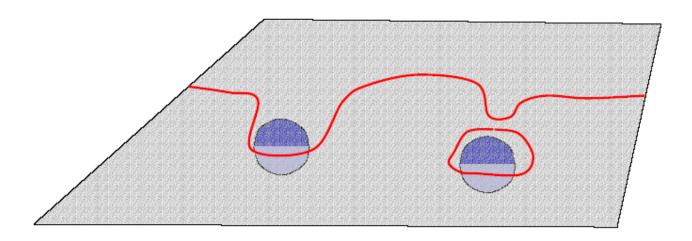






Impenetrable obstacles

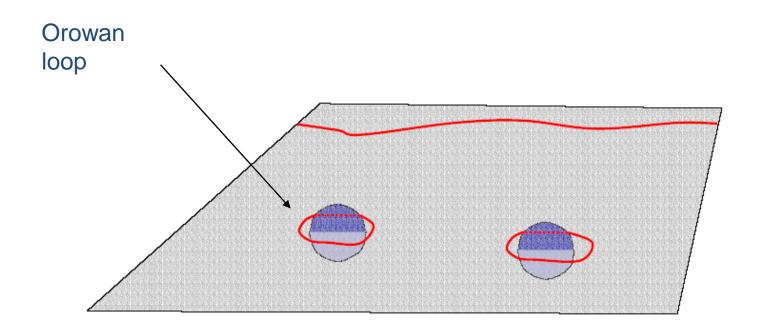






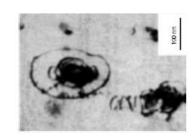
Impenetrable obstacles





The bigger the spacing between obstacles, the easier for the dislocation to squeeze through the gaps.

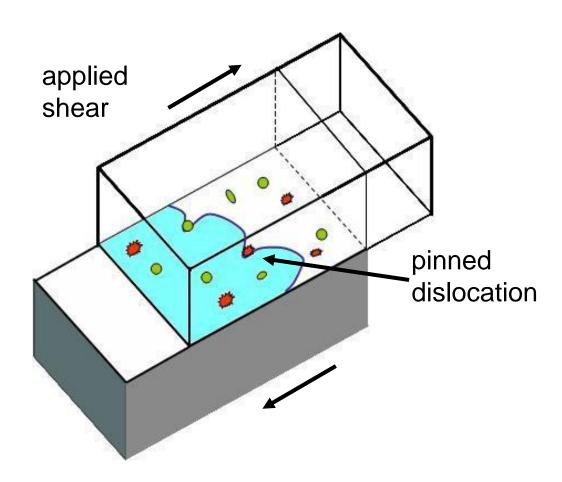
Each 'bypass' event leaves a dislocation loop behind, narrowing the gaps and increasing hardening.





So, why does the yield strength increase after irradiation?



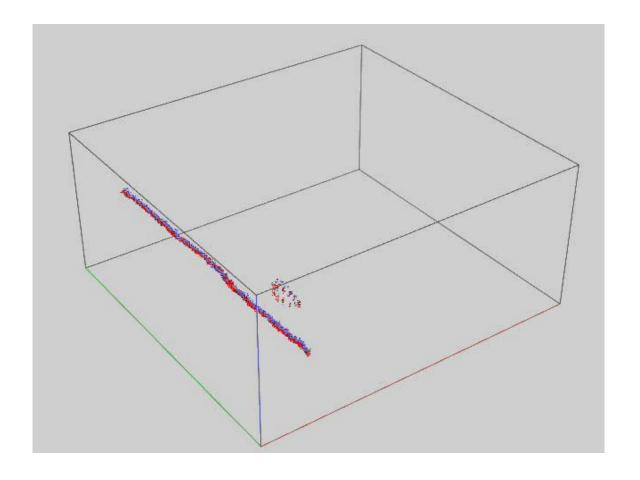


Radiation defect populations act as obstacles to dislocation motion



For example, what happens when a dislocation line meets a dislocation loop





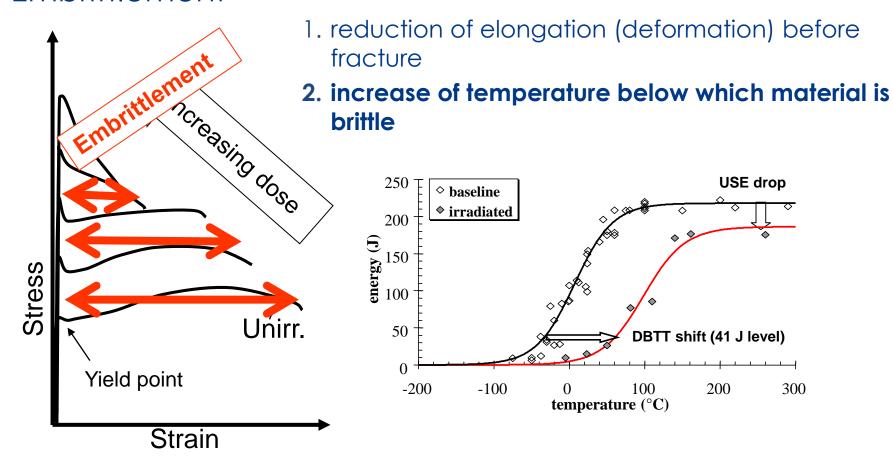


RADIATION HARDENING & EMBRITTLEMENT

Embrittlement = ?



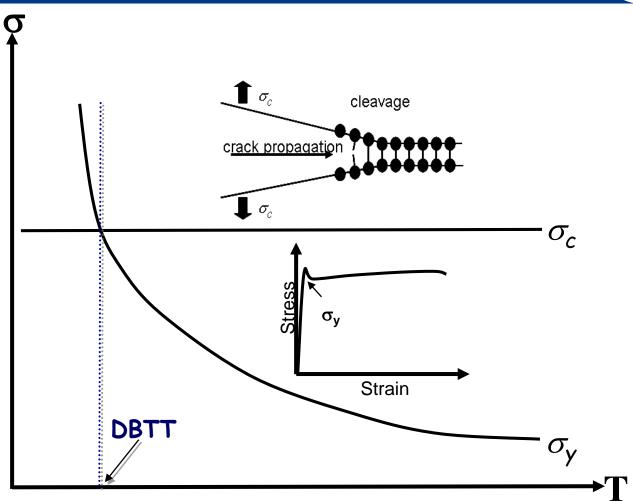
Brittle material = breaks without prior deformation Embrittlement =





What is the DBTT? The classical explanation





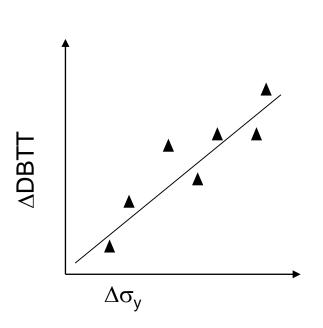
Ductile-brittle transition temperature (DBTT, or T_c) = temperature at which cleavage stress equals yield strength



However, the DBTT is <u>not</u> a material property: it depends also how the test is done

Δ DBTT and $\Delta\sigma_{y}$ are (generally) linearly correlated: why?





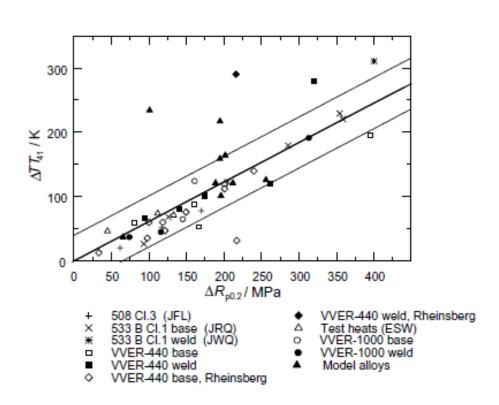


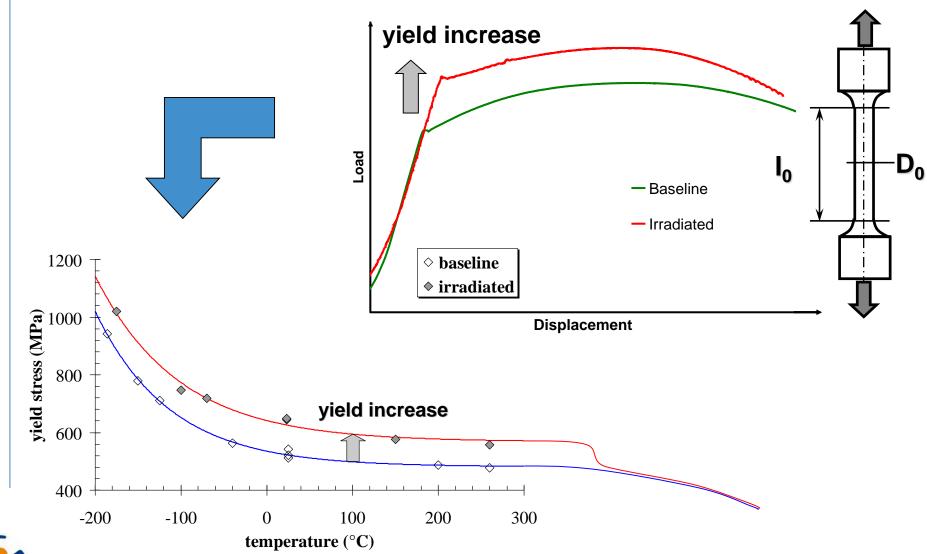
Fig. 8. Correlation between the shift of transition temperature ΔTT_{48} and the yield stress increase $\Delta R_{p0.2}$.

Example from: Böhmert et al. JNM 334 (2004) 71



Radiation hardening versus temperature (CO) ERIA

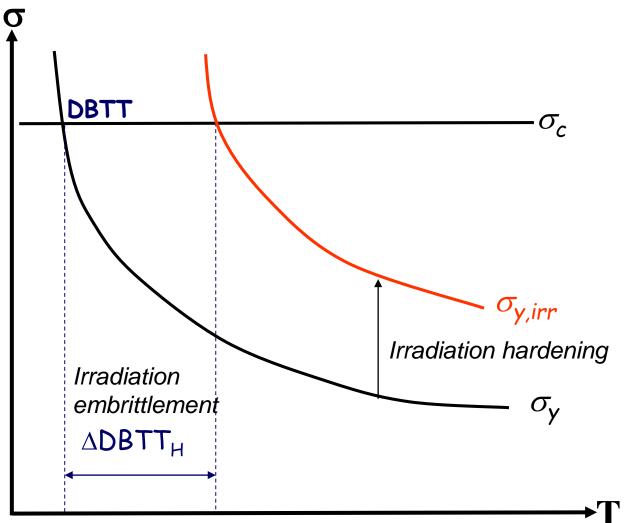






Effect of irradiation on σ_y and DBTT: The classical explanation:



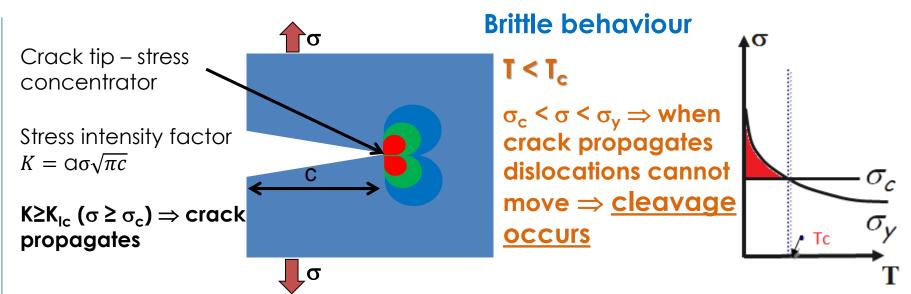




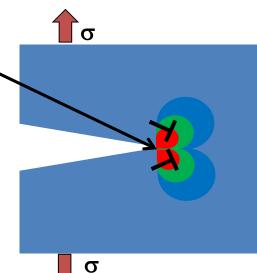
The linear relationship is valid so long as the curve $s_y(T)$ is rigidly shifted upward by irradiation for all temperatures

A closer look





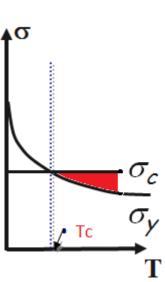
Crack tip – dislocation source



Ductile behaviour

 $T > T_c$

 $\sigma_y < \sigma < \sigma_c \rightarrow$ dislocations start to move before crack can propagate \Rightarrow deformation occurs
before fracture



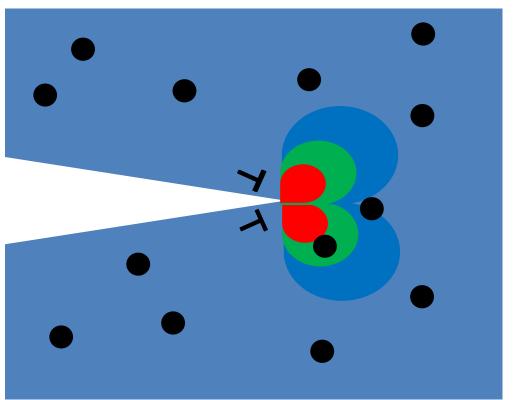


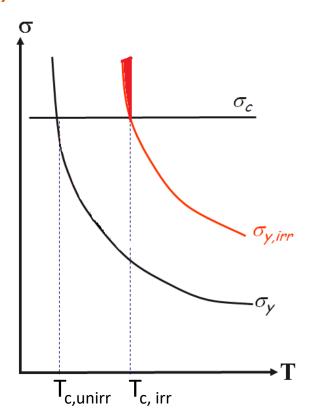
A closer look in presence of radiation defects





 $T > T_{c-unirr}$: Dislocation motion hampered by obstacles \Rightarrow even if dislocation are emitted, no (or little) deformation occurs



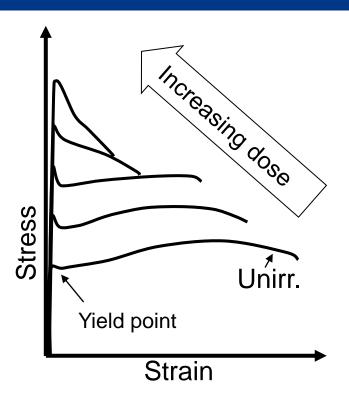




 σ_c is exceeded before dislocations set free \Rightarrow brittle behaviour Only if $\sigma_{y,irr}$ is exceeded dislocations become free and there is deformation, but cleavage already started \Rightarrow T_c effectively increased

Why is hardening accompanied by loss of elongation and does it correlate with embrittlement?





Because in general the origin of both hardening and embrittlement is the presence of obstacles to dislocation motion

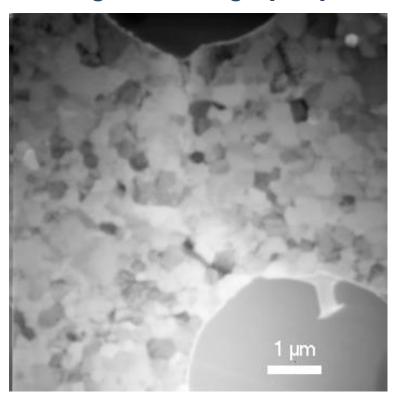
Key question to predict radiation hardening: which obstacles are responsible for dislocation pinning?



Grains and grain boundaries

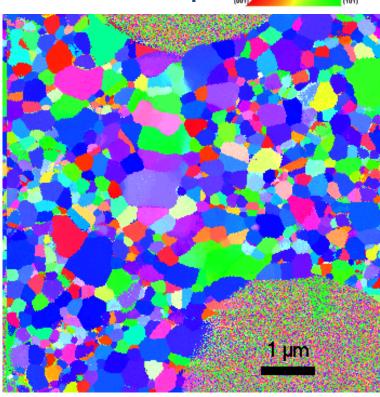


Brightfield image (TEM)



Metallographic examination of deformed specimen – grains are clearly visible

Orientation map

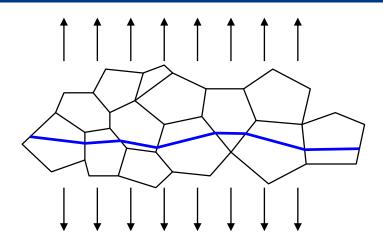


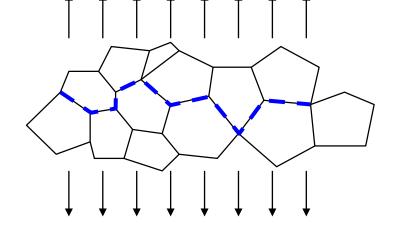
Electron back-scatter diffraction (EBSD) – each colour corresponds to a different crystallographic orientation



Transgranular and intergranular fracture







Cleavage fracture is <u>transgranular</u>

Embrittlement characterised by transgranular fracture is most often related to hardening (same fundamental mechanism)

ADBTT

Intergranular fracture may happen as a consequence of grain decohesion

Here fracture mechanism is <u>unrelated</u> to dislocations

- → no correlation with hardening
- → no previous deformation



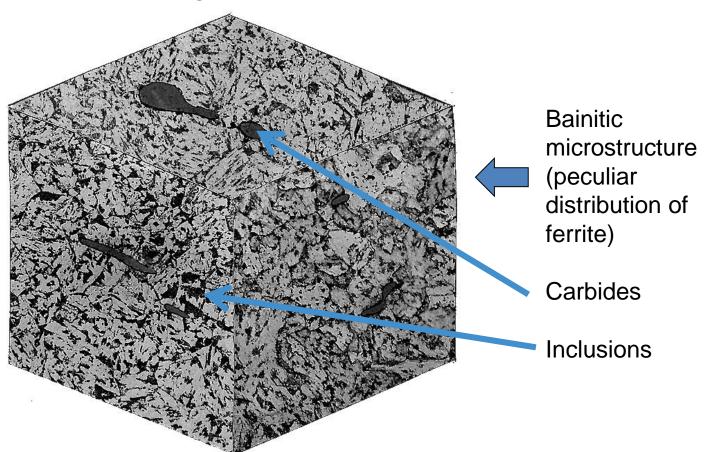
ORIGIN OF RADIATION EMBRITTLEMENT IN RPV STEELS

RPV Steels are Low Alloy Steels with Mn, Ni and Mo (Cr) addition



<u>A typical composition in a European PWR could be</u>: 0.1% C - <u>1.4% Mn</u> - <u>0.2% Si</u> - <u>0.7%</u> <u>Ni</u> - 0.5% Mo - 0.02% Al – <u>0.1% Cu</u> – <u>0.01% P</u> – (... Cr, Co, S) + Fe (balance)

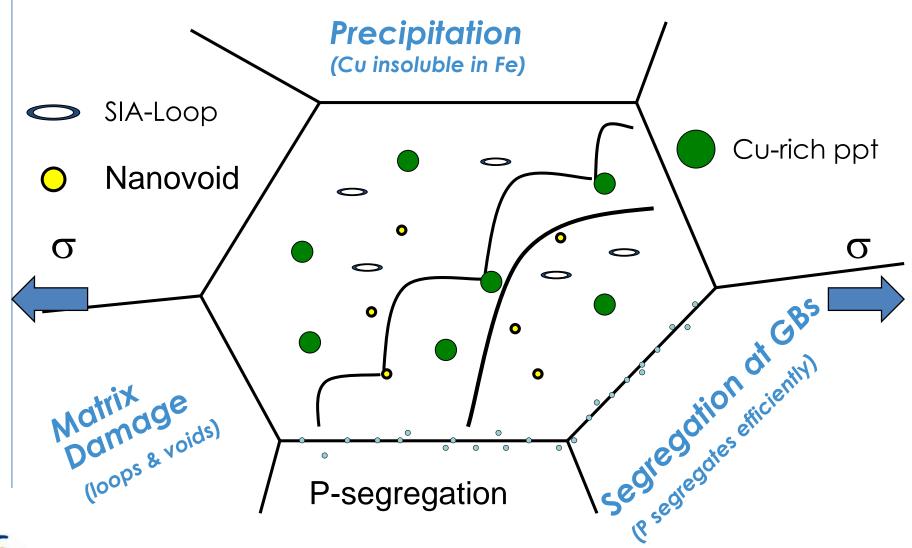
US RPV steels contain up to 0.3%Cu, some steels have high Ni&Mn content ~1.5%, VVER steels may have high Ni content (or none) and contain ~2%Cr, ...





Handbook mechanisms of RPV steel embrittlement under irradiation







Traditional mechanistic approach in the RPV steel world



- Radiation <u>enhanced</u>formation of Cu-rich ppts(with also Mn, Ni & Si)
- Radiation <u>produced</u> point defect clusters (nanovoids, loops)

Harden:

n

g

yield strength increase

$$\Delta \sigma_{y} \cong \Delta \sigma_{y}^{PPT} + \Delta \sigma_{y}^{MD}$$

 $\Delta {\sf DBTT}_{\sf H} \propto \Delta \sigma_{\sf y}$

 Radiation induced segregation at GB of embrittling elements (P)

promotion of intergranular fracture: \(\DBTT_{S} \)



 $DBTT \cong ADBTT_{H} + ADBTT_{S}$

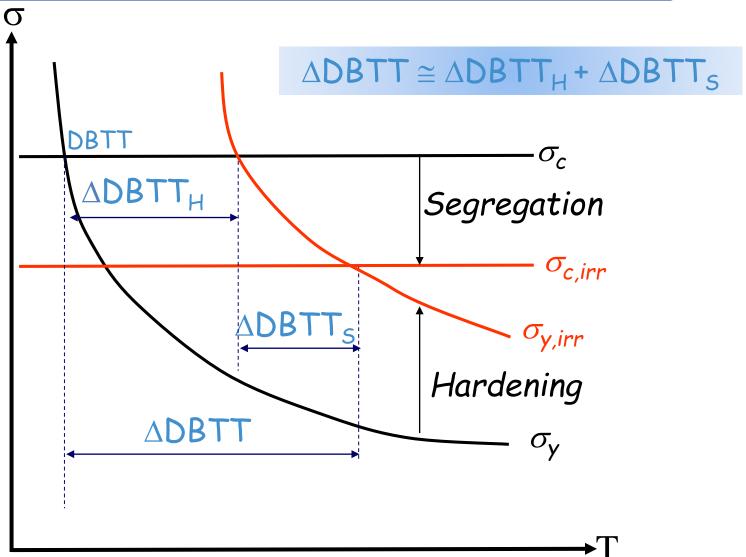
S

h



Graphical representation

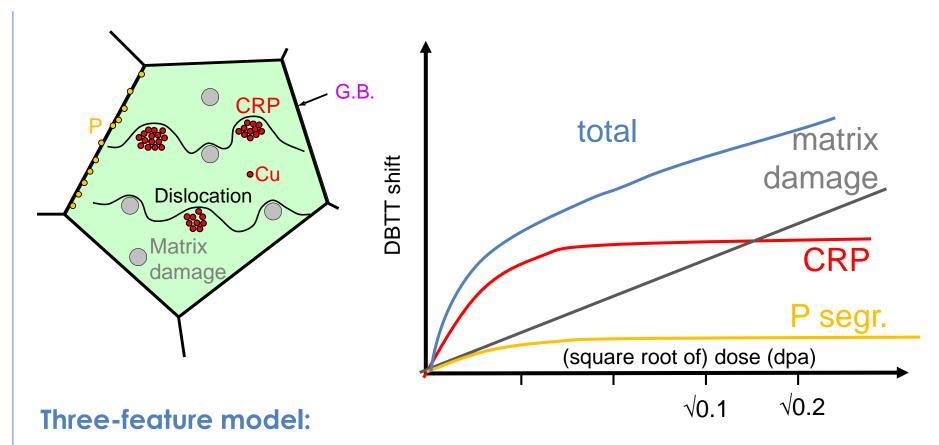






So, existing advanced mechanistic trend curves include up to three components





- Matrix damage = microvoids, dislocation loops, small solute/pointdefect clusters
- CRP = Cu-rich precipitates (Cu is virtually insoluble in Fe)
- P = radiation-induced segregation at grain boundaries GB



Examples of Mechanistic Correlations (trend curves)



■ Reg. Guide 1.99 – Rev. 2 (May 1988)*

$$\Delta T = CF \cdot f^{(0.28 - 0.10 \cdot \log(f))}$$

CF, chemistry factor is a function of Cu and Ni content and is given in tables for base and weld metals

f is the fast fluence (E > 1 MeV, 10^{19} n/cm²)



Examples of Mechanistic Correlations (trend curves)



■ ASTM E900-02*

$$\Delta T = SMD + CRP$$

SMD, stable matrix damage term, is given by:

$$SMD = A \cdot e^{\frac{20730}{T_c + 460}} \cdot \phi_t^{0.5076}$$

A = 6.70 × 10⁻¹⁸, T_c = irradiation temperature (°F), ϕ_t = fast fluence in n/cm² (E > 1 MeV)

CRP, copper-rich precipitation term (again Cu and Ni), is given by:

$$CRP = B \cdot \left(1 + 2.106 \cdot Ni^{1.173}\right) \cdot F(Cu) \cdot \left[\frac{1}{2} + \frac{1}{2} \cdot \tanh\left(\frac{\log(\phi) - 18.24}{1.052}\right)\right]$$

B = 234 for welds

B = 128 for forgings

B = 208 for Combusition Engineering plates

B = 156 for other plates

 $f(C_U) = 0 \text{ if } C_U \le 0.072\%$

 $f(Cu) = (Cu-0.072)^{0.577}$ if Cu > 0.072%



*Current version of ASTM E900 (E900-02, Standard Guide for Predicting Radiation-Induced Transition Temperature Shift in Reactor Vessel Materials)

Examples of Mechanistic Correlations (trend curves)



NRC model*

$$\Delta TT = SMD + CRP + bias$$

SMD, stable matrix damage term, is biased with P content (segregation):

SMD =
$$A \cdot e^{\frac{19310}{T_c + 460}} \cdot (1 + 110 \cdot P) \cdot \phi_t^{0.4601}$$

 $A = 8.86 \times 10^{-17}$ for welds

 $A = 9.30 \times 10^{-17}$ for forgings

 $A = 12.7 \times 10^{-17}$ for plates

P = phosphorus content

CRP, copper-rich precipitation term, again depends on Cu and Ni content:

$$CRP = B \cdot \left(1 + 2.40 \cdot Ni^{1.250}\right) \cdot F(Cu) \cdot \left[\frac{1}{2} + \frac{1}{2} \cdot \tanh\left(\frac{\log(\phi + 4.579 \times 10^{12} t_f) - 18.265}{0.713}\right)\right]$$

B = 230 for welds

B = 132 for forgings B = 206 for Combusition Engineering plates

B = 156 for other plates

f(CU) = 0 if $CU \le 0.072\%$ $f(CU) = (CU-0.072)^{0.659}$ if CU > 0.072%

Subject to $Cu_{max} = 0.25$ (for welds with Linde 80 or Linde 0091 flux) or 0.305 (other welds), and $t_f = irradiation$ time, in hours

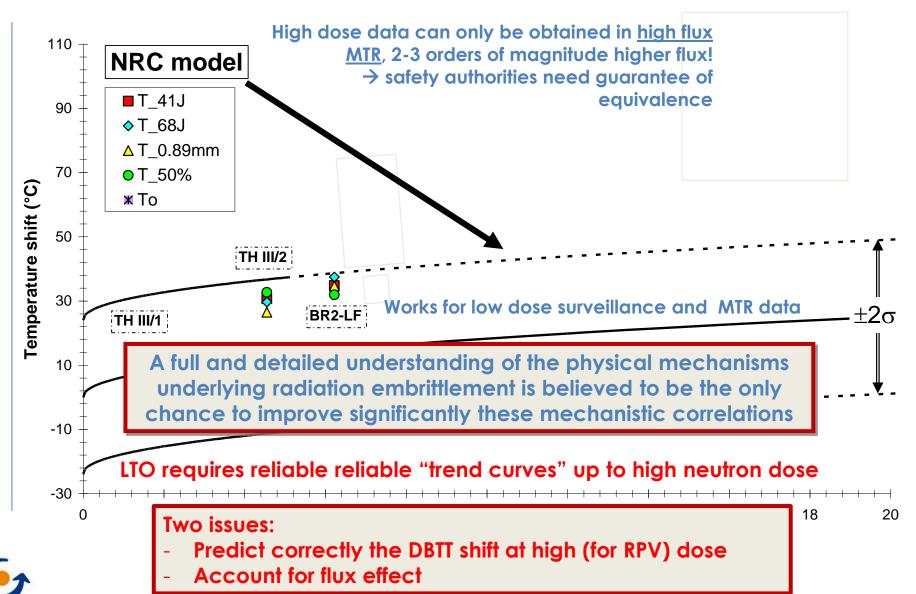
Bias term is equal to 0 if $t_f < 97,000 \text{ h}$ or 9.4 °F if $t_f \ge 97,000 \text{ h}$



^{*}Charpy Embrittlement Correlations – Status of Combined Mechanistic and Statistical Bases for U.S. RPV Steels (MRP-45): PWR Materials Reliability Program (PWRMRP). EPRI, Palo Alto, CA: 2001, 1000705

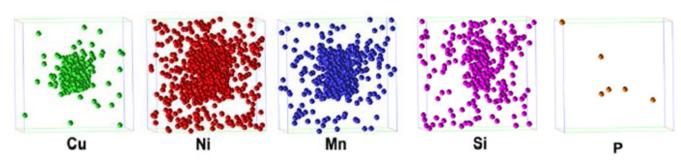
... but do they really work?





Search for mechanisms made the RPV jargon more and more complicated





Miller & Russel, JNM 371 (2007) 145

- Plenty of atom probe studies show that CRP contain also Ni, Mn, Si & P
- In low or no Cu steels "precipitates" that contain only Ni, Mn & Si are observed (even if none of these elements is above the solubility limit of the corresponding binary ...)

MD = matrix damage

SMD = Stable matrix damage (loops, voids)

Recently evolved into SMF=stable matrix features (defect-solute clusters)

UMD = Unstable matrix damage (would exist only if flux = dose-rate is high)

P = precipitates/phases

CRP = copper-rich precipitates (more Cu than other solutes: Mn, Ni, P, Si)

MNP = manganese-nickel-rich precipitates (more Mn-Ni than Cu)

LBPs = "late blooming" phases

Phases that give rise to <u>sudden (and unexpected) increase in embrittlement</u>, because they

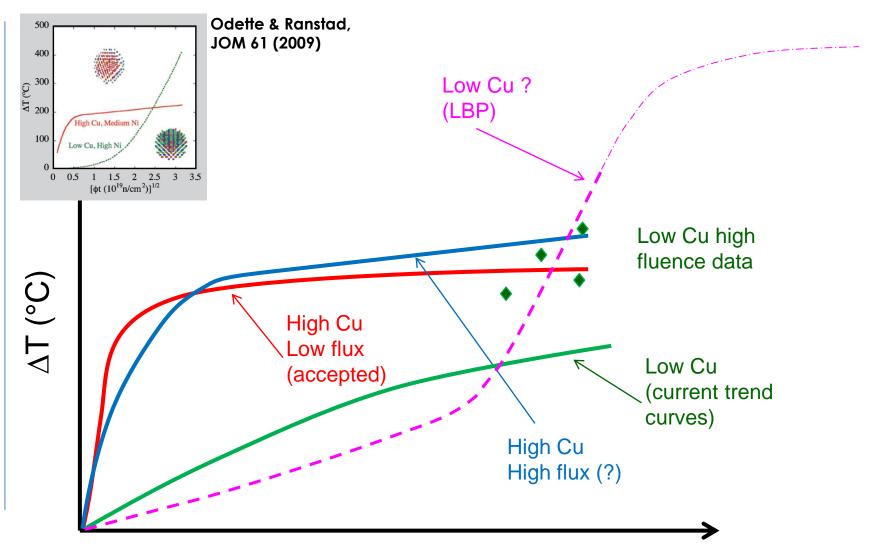
- have a long incubation period
- II. have rapid growth thereafter
- III. will be present in large volume fractions at equilibrium





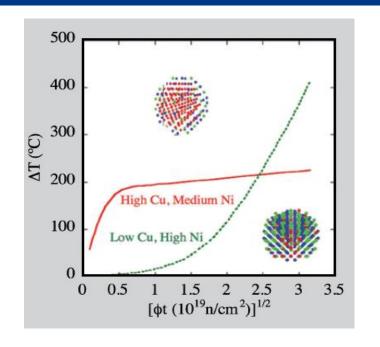
Late blooming phases: The great fear





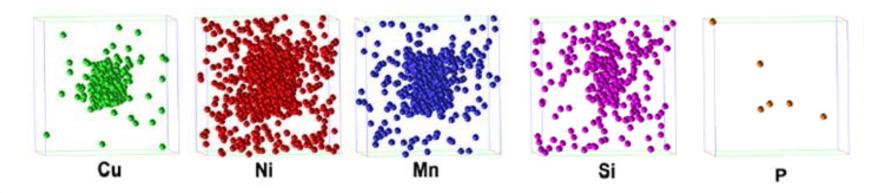






Is this prediction real?

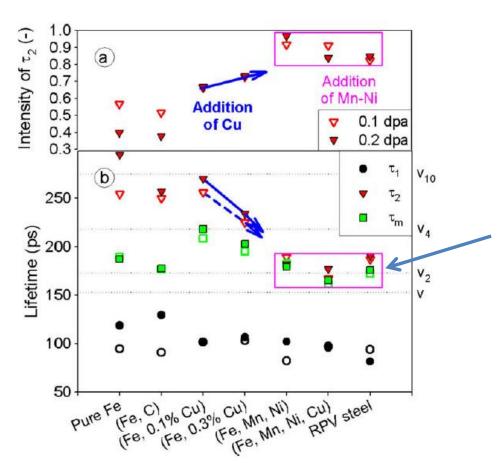
Attention needs to be focused on the physics of the <u>USUAL SUSPECTS</u>:





Voids are not observed in RPV steels irradiated to doses of relevance for extended lifetime of NPP





Positron Annihilation Spectroscopy (PAS)

reveals that only single- & di-vacancies form in alloys containing Mn&Ni, including RPV steels

M. Lambrecht, A. Almazouzi, Journal of Nuclear Materials 385 (2009) 334



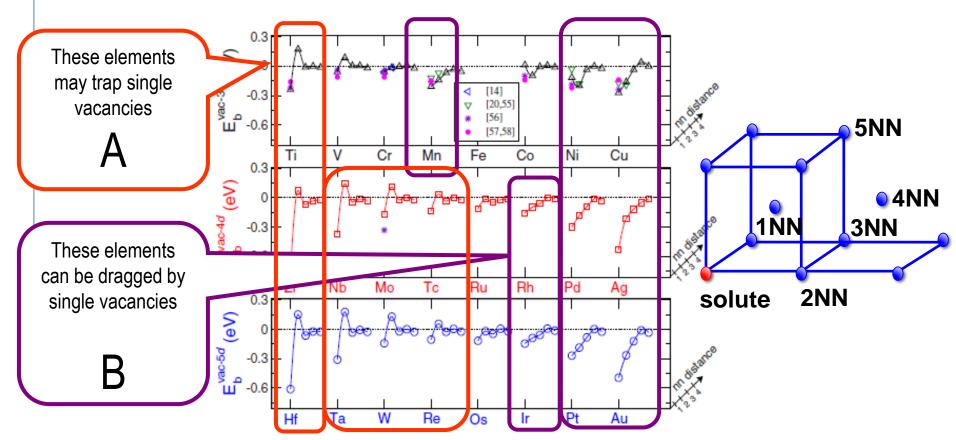
What is special about Cu, Ni, Mn, Si, P, ...? ERIA



PHYSICAL REVIEW B 81, 054102 (2010)

Ab initio study of solute transition-metal interactions with point defects in bcc Fe

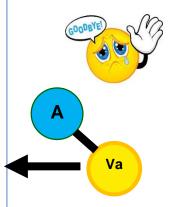
P. Olsson, T. P. C. Klaver, and C. Domain 1



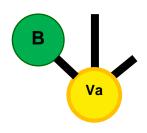


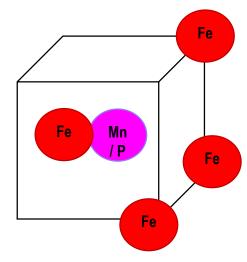
Key atomistic mechanism: solute dragging by point defects

Most solute atoms, for example Mo and Cr, will move via vacancy in the opposite direction to the vacancy



Instead, Mn and Ni, but also Cu, Si, and P, follow the vacancy during its migration

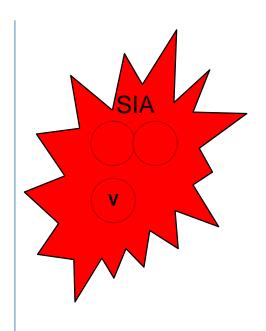


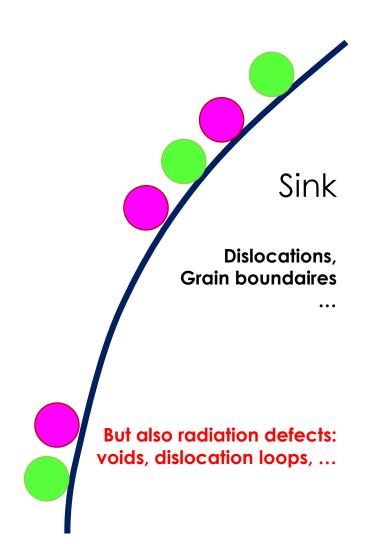




Consequence: all "usual suspects" in Fe will segregate at sinks!

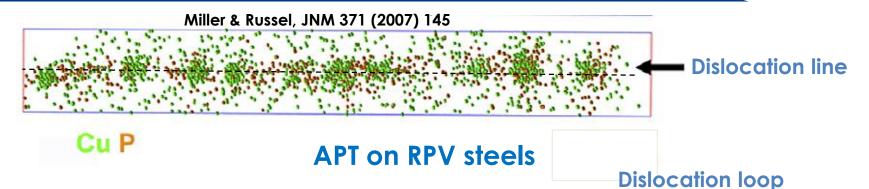




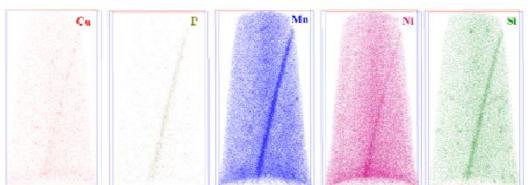


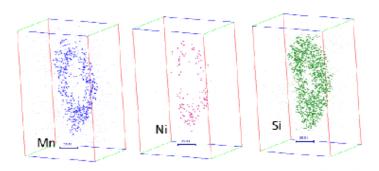


And atom probe shows that indeed they do!



Radiguet, Huang, Cammelli & Pareige, GPM – FP7/Longlife



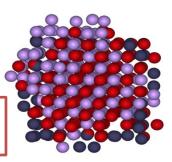


Grain boundary Grain Boundary Profile

G. Bonny et al., J. Nucl. Mater. 452 (2014) 486

Atomistic simulations tell that loops make Mn-Ni ppts stable even outside thermodynamic field of stability:

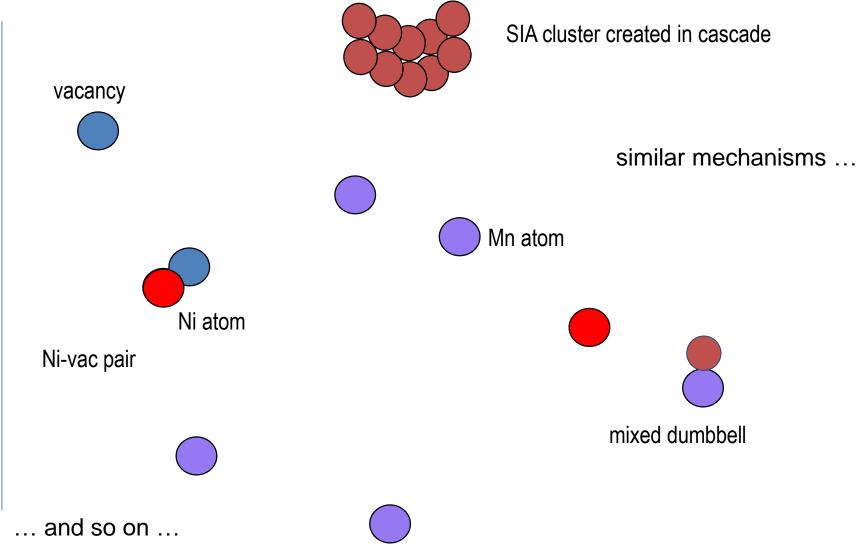
Point-defect clusters catalyse the formation of precipitates!





So, how could solute-rich clusters be formed?







Composition of steels & irradiation conditions that have been simulated



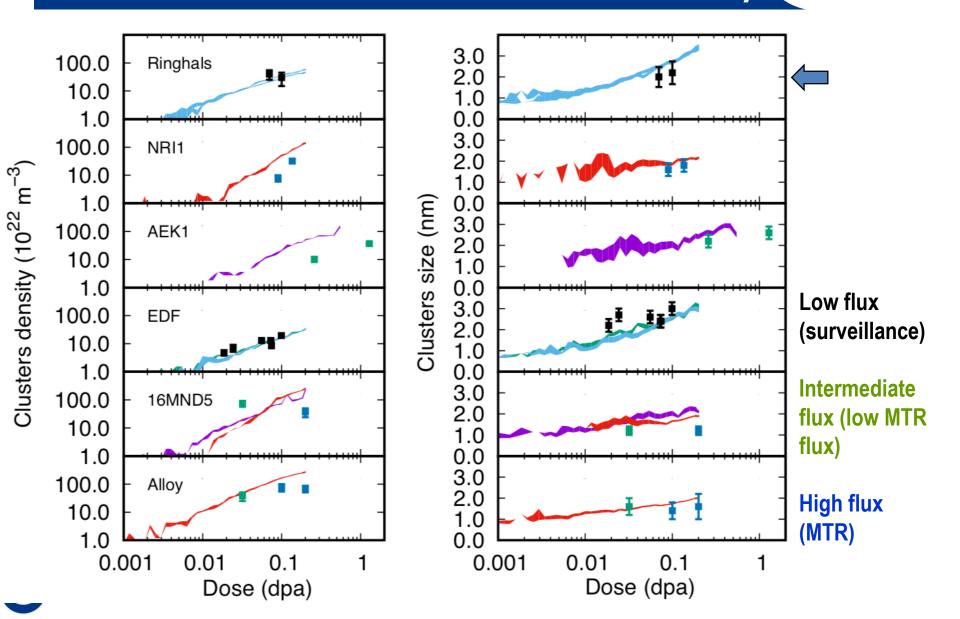
	С	Р	Si	Mn	Ni	Cu	Cr	Mo	V
Ringhals	s 0.24	0.016	0.42	1.48	1.50	0.07	0.07	0.31	0.002
NRI 1	0.32	0.011	0.73	0.75	1.59	0.035	1.99	0.40	-
AEK 1	0.74	0.032	0.57	0.54	0.066	0.078	2.82	0.39	0.30
EDF 1	0.78	0.018	0.61	1.28	0.61	0.078	0.16	0.23	0.022
EDF 3	0.25	0.016	0.69	1.43	0.61	0.029	0.021	0.33	0.004
16MND	5 0.65	0.013	0.39	1.32	0.71	< 0.005	0.21	0.33	-
Alloy	< 0.01	0.009	< 0.01	1.11	0.71	0.056	-	-	-

at% - Fe balance

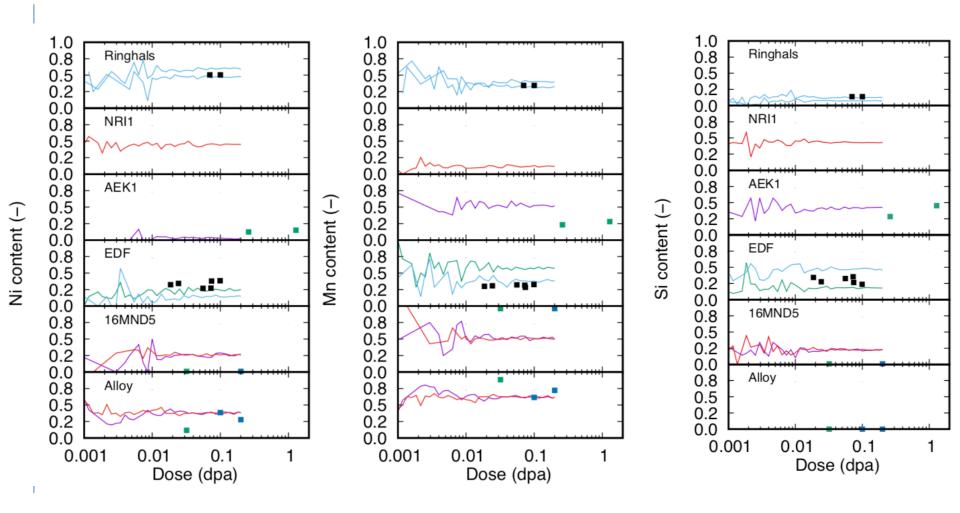
- All of them low Cu steels
- Ringhals: very high Ni+Mn
- □ NRI1 & AEK1: VVER type (2-3% Cr), one high Ni, one no Ni
- EDF1, EDF3, 16MND5: typical French RPV steels
- Alloy: FeMnNi model alloy
- □ Irradiation conditions: surveillance, MTR (different fluxes), T~300°C



Preliminary predictions for several RPV steels irradiated under different conditions: size & density



Predictions for several RPV steels irradiated under different conditions: composition

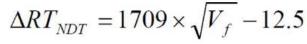


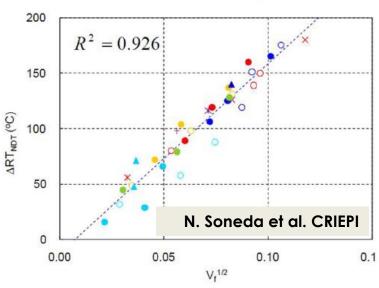


This model suggests that the distinction between matrix damage and precipitation is not real



- Solutes segregate at point-defect clusters, thereby creating complexes that contain both
- ☐ These complexes are the **main cause** of **dislocation motion obstruction**
- This is indirectly confirmed by the empirical linear correlation between (square root of) solute cluster volume fraction and DBTT (T_{NDT}) shift



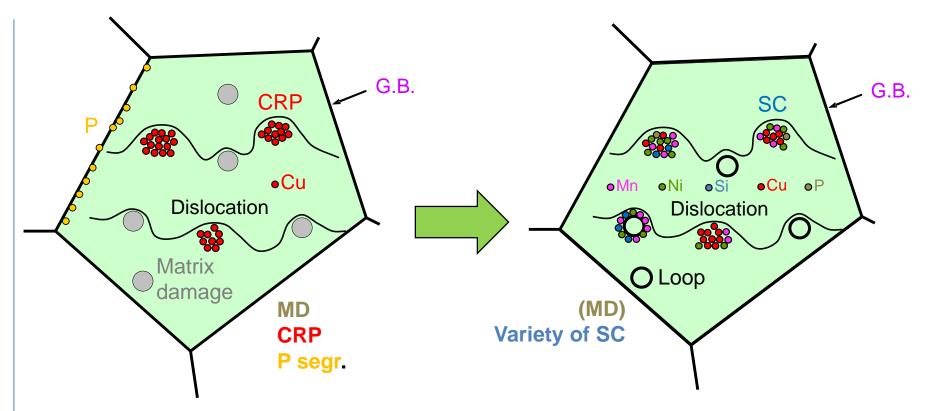


- □ This mechanism will determine the **kinetics of formation** of obstacles under irradiation
- The **solute clusters** that form **may eventually evolve into** defined **phases**, either stabilized by point-defects or thermodynamically foreseen, or both (**catalysis**)
- ☐ The formation of phases, however, is not governed by a classical nucleation and growth process, so **most likely there will be no "late blooming"** because phases are forming in a continuous way, since the beginning, while the irradiation proceeds



Conclusion: paradigm change for RPV embrittlement origin is in course





Combining microstructural examination with advanced atomistic modelling changed the understanding of the origin of RPV embrittlement from matrix damage & precipitates to solute/point-defect nanoclusters, potentially leading to improved engineering correlations and physics-based multiscale models applicable to steels



Acknowledgments



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- □ Part of the research leading to these results was funded by the European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement Ni. 604862 (MatISSE Project) and contributes to the Joint Programme on Nuclear Materials of the European Energy Research Alliance (EERA-JPNM)







