Development of Advanced Structural Materials

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Joint IAEA-ICTP Advanced Workshop on Development of Radiation Resistant Materials

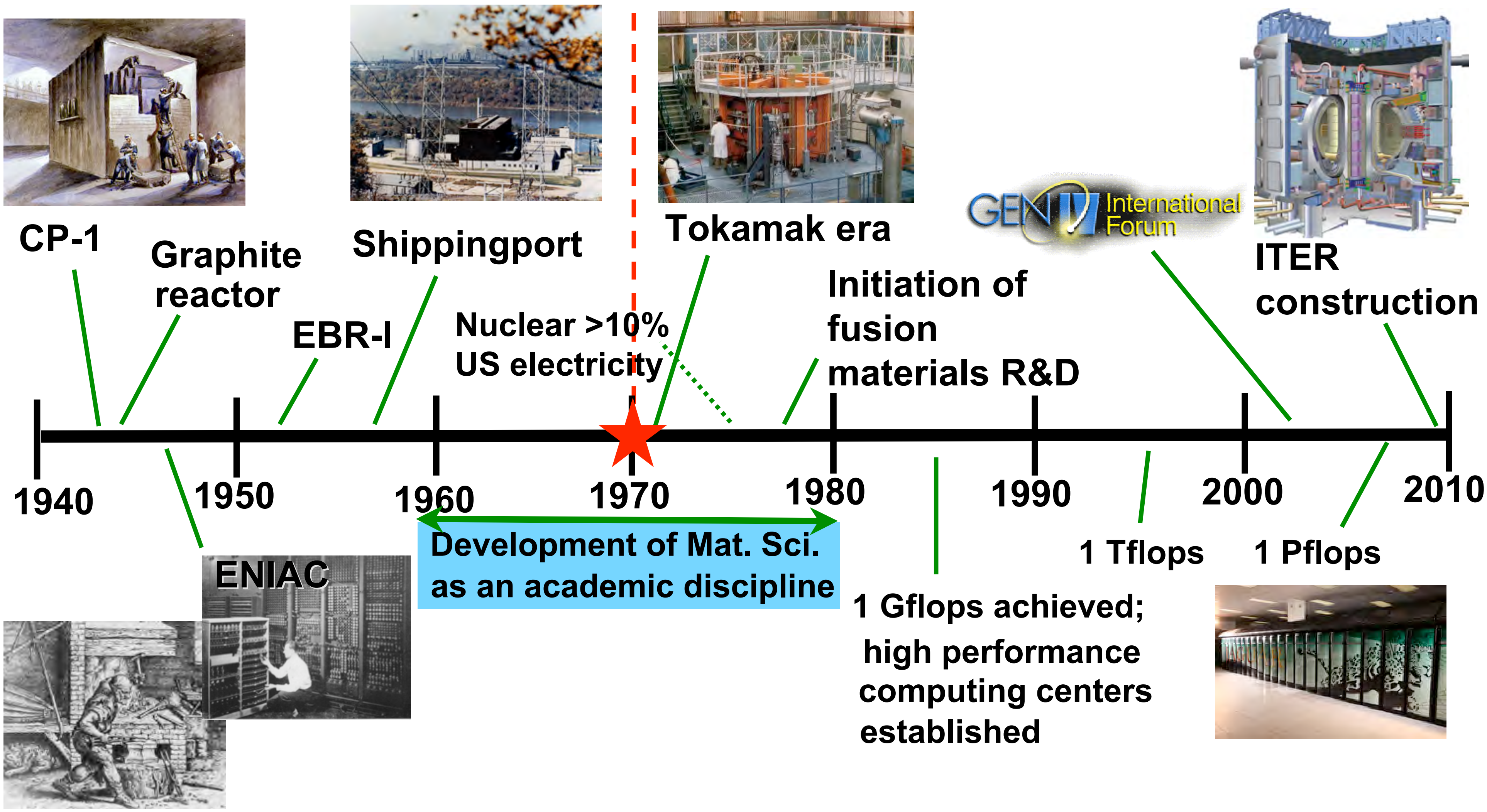
Miramare-Trieste, Italy, April 20-24, 2009

Outline

- **Brief history of nuclear power**
- **Effects of neutron bombardment on structural materials**
  - **"Five scourges" of radiation**
- **Prospects for development of high-performance radiation-resistant materials**
  - **Crucial role of nanoscale architectures**

Note: focus will be on steels; ceramic composites will be discussed in the talk this afternoon

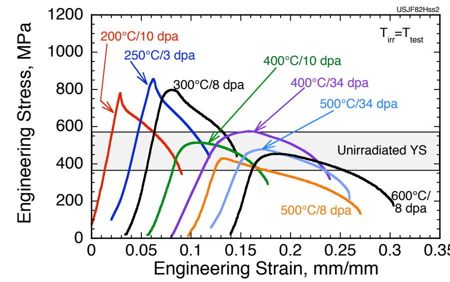
The Launching of Fission and Fusion Energy Bridges the Development of Modern Materials Science



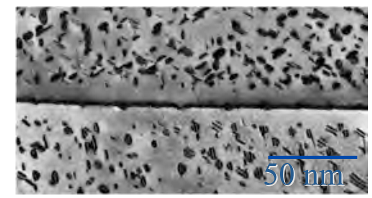
- **Fusion energy systems should take maximum advantage of current and emerging materials and computational science tools**

Radiation Damage can Produce Large Changes in Structural Materials

- **Radiation hardening and embrittlement (<0.4 T_M, >0.1 dpa)**

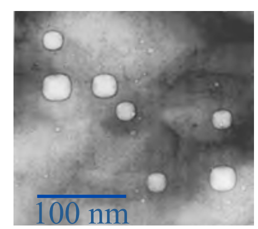


- **Phase instabilities from radiation-induced precipitation (0.3-0.6 T_M, >10 dpa)**

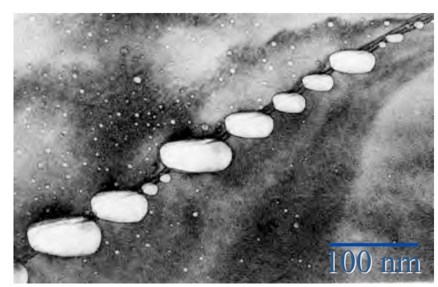


- **Irradiation creep (<0.45 T_M, >10 dpa)**

- **Volumetric swelling from void formation (0.3-0.6 T_M, >10 dpa)**

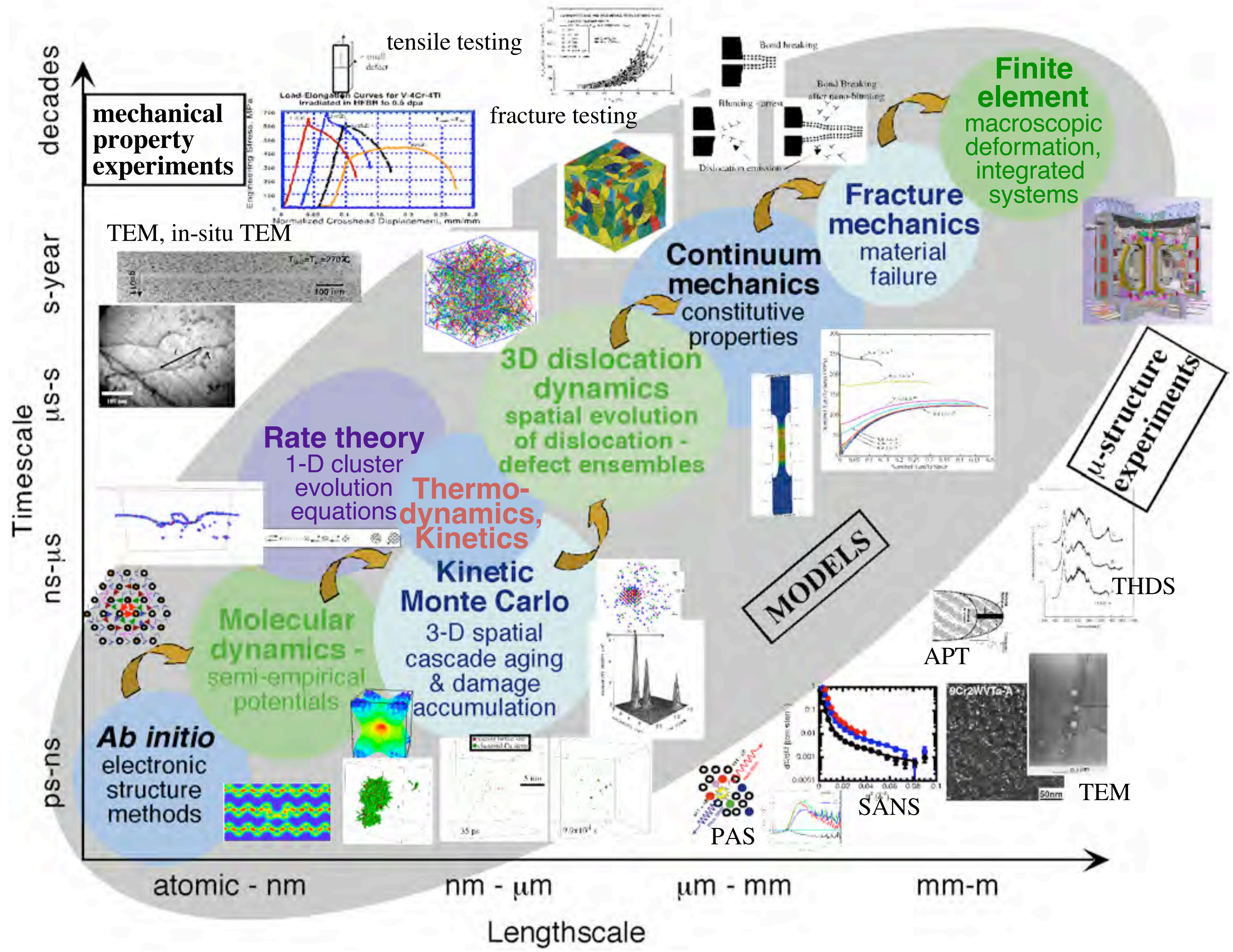


- **High temperature He embrittlement (>0.5 T_M, >10 dpa)**



after S.J. Zinkle, Phys. Plasmas 12 (2005) 058101

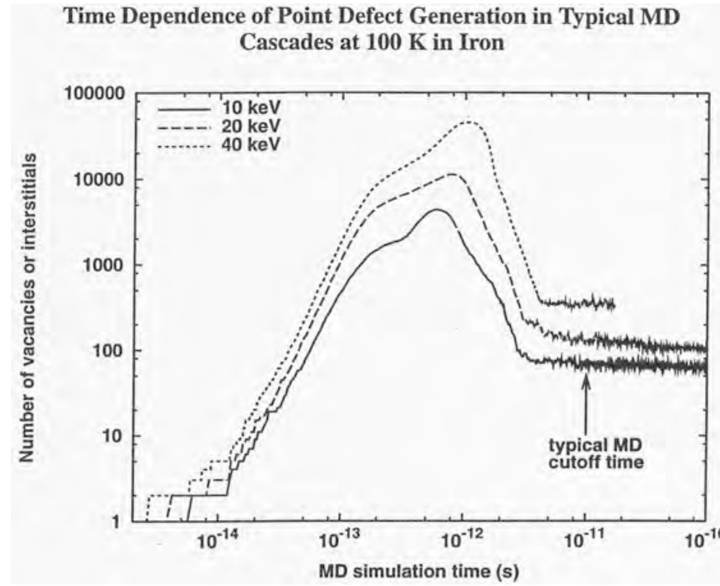
Radiation damage is inherently multiscale with interacting phenomena ranging from ps to decades and nm to m



B.D. Wirth, UC-Berkeley

Advanced nuclear energy systems impose harsh radiation damage conditions on structural materials

- 1 displacement per atom (dpa) corresponds to stable displacement from their lattice site of all atoms in the material during irradiation near absolute zero (no thermally-activated point defect diffusion)
  - Initial number of atoms knocked off their lattice site during fast reactor neutron irradiation is ~100 times the dpa value
    - Most of these originally displaced atoms hop onto another lattice site during "thermal spike" phase of the displacement cascade (~1 ps)



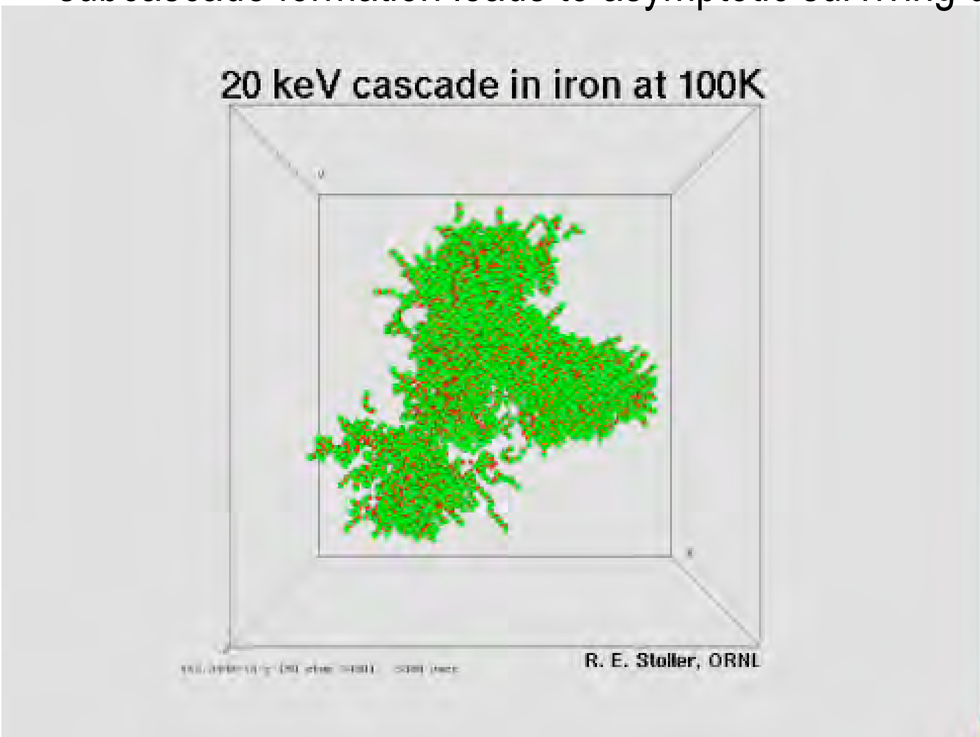
R.E. Stoller

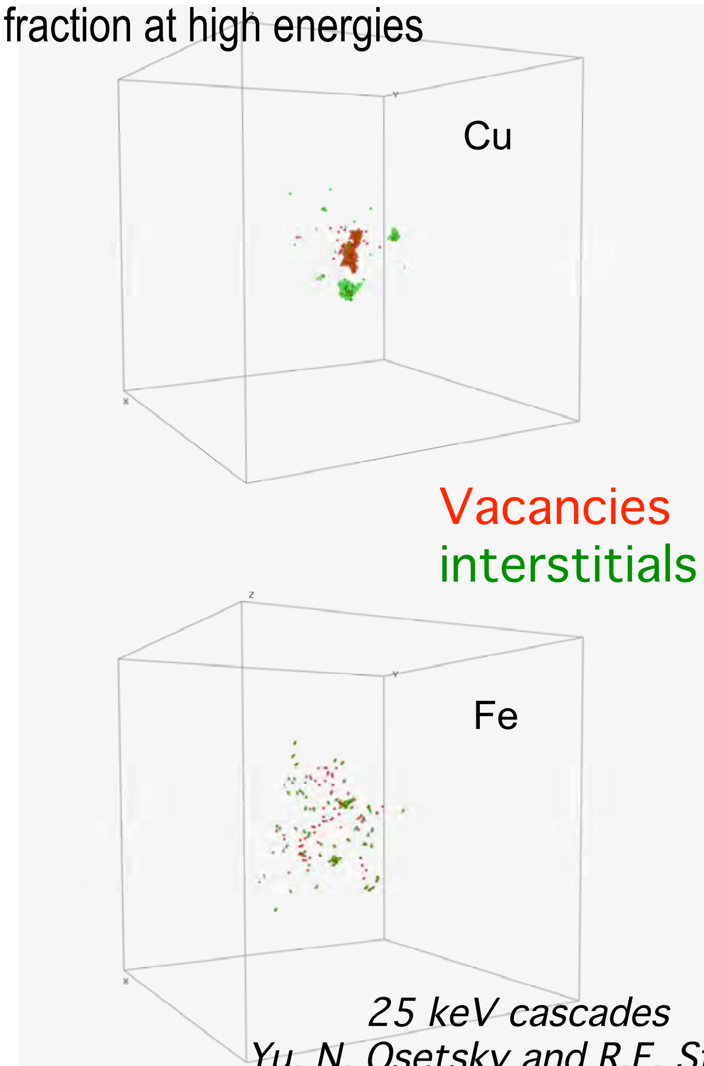
- Requirement for structural materials in advanced nuclear energy systems (~100 dpa exposure):
  - ~99.95% of "stable" displacement damage must recombine
    - ~99.9995% of initially dislodged atoms must recombine
- Two general strategies for radiation resistance can be envisioned:
  - Noncrystalline materials
  - Materials with a high density of nanoscale recombination centers

after S.J. Zinkle, Phys. Plasmas 12 (2005) 058101

Recent Molecular Dynamics simulations have provided key fundamental information on defect production

- Effect of knock-on atom energy and crystal structure on defect production
- subcascade formation leads to asymptotic surviving defect fraction at high energies

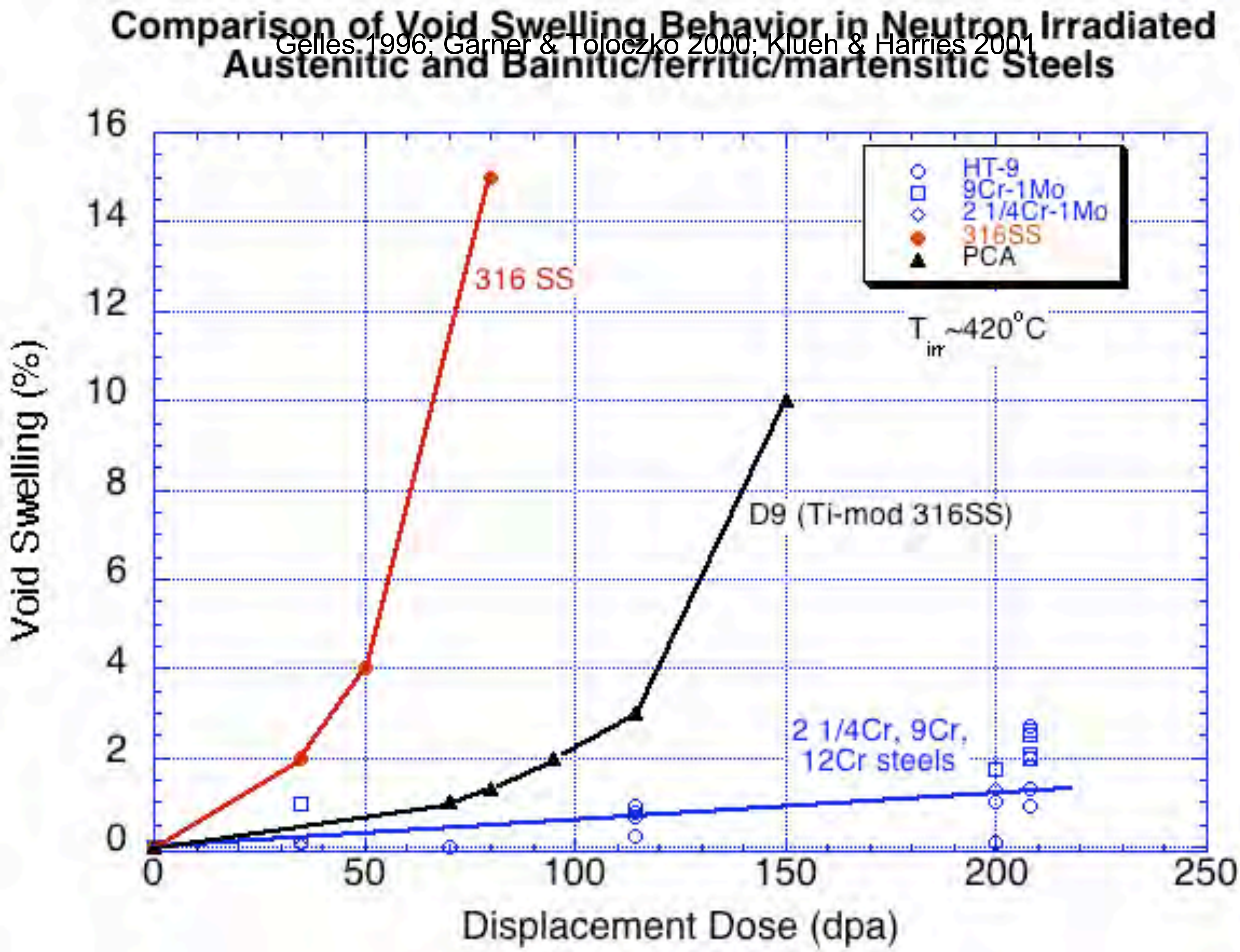




25 keV cascades
Yu. N. Osetsky and R.E. Stoller

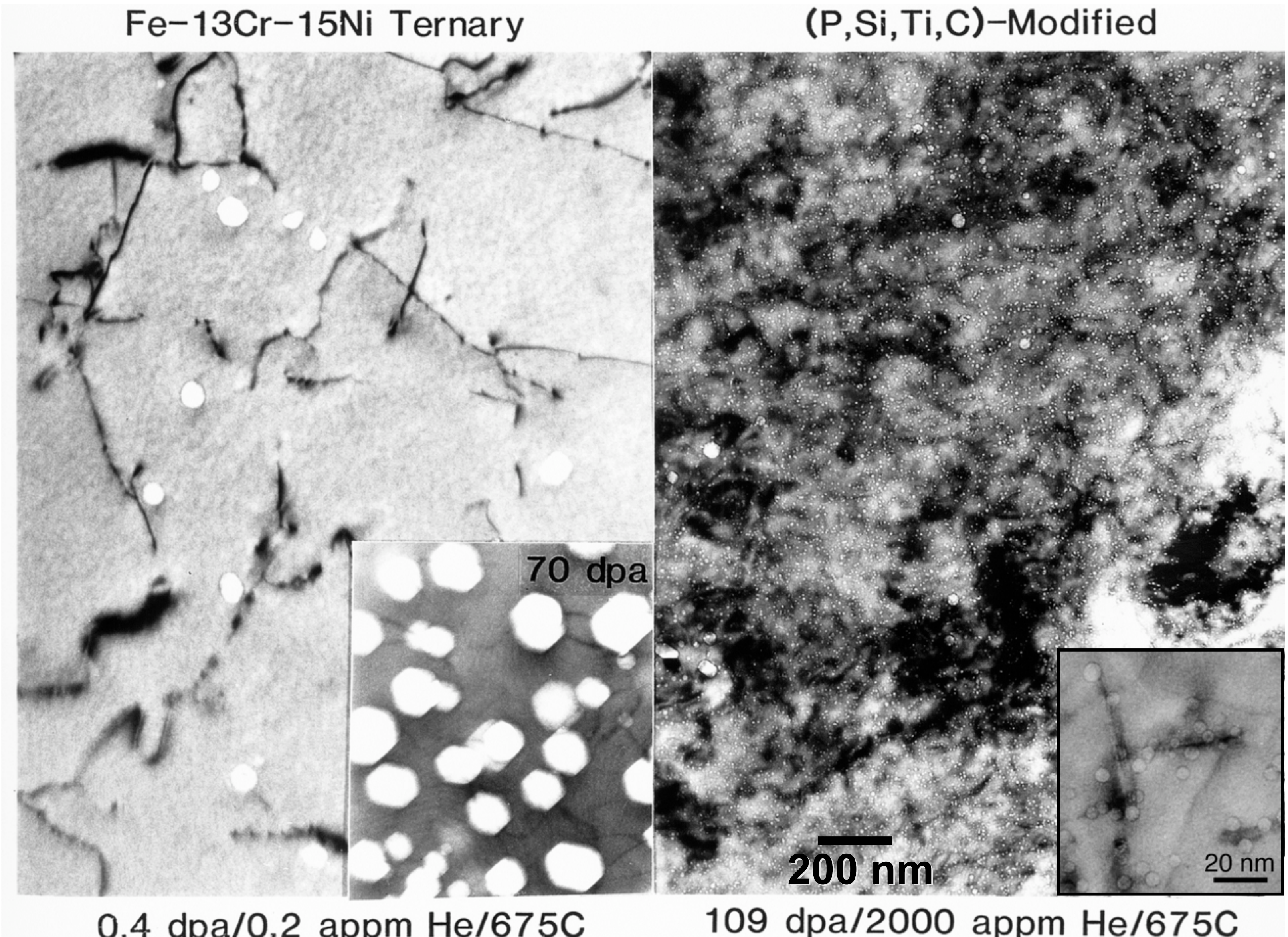
Large vacancy clusters are not directly formed in BCC metal displacement cascades

after S.J. Zinkle, Phys. Plasmas 12 (2005) 058101



Comparison of Void Swelling Behavior in Neutron Irradiated Austenitic and Bainitic/ferritic/martensitic Steels
Gelles 1996; Garner & Toloczko 2000; Klueh & Harries 2001
Void Swelling (%)
Displacement Dose (dpa)
HT-9
9Cr-1Mo
2 1/4Cr-1Mo
316SS
PCA
316 SS
T irr ~420°C
D9 (Ti-mod 316SS)
2 1/4Cr, 9Cr, 12Cr steels

Swelling Resistant Alloys can be developed by Controlling the He Cavity Trapping at Precipitates

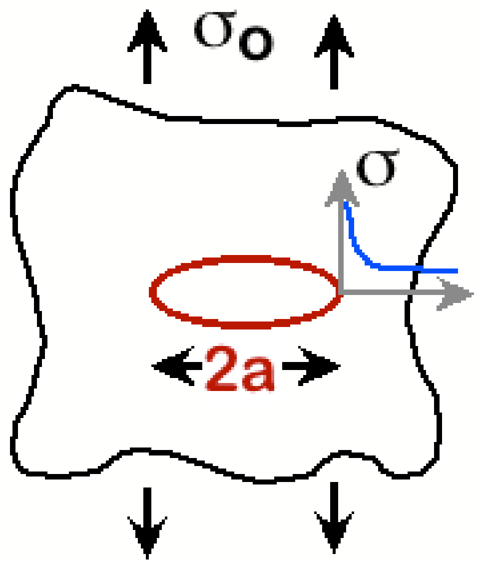


Mansur & Lee
J. Nucl. Mat.
<u>179-181</u>
(1991) 105

These nanoscale precipitates also typically provide improved thermal creep strength

FLAWS ARE STRESS CONCENTRATORS!

- Ellip
  a pl



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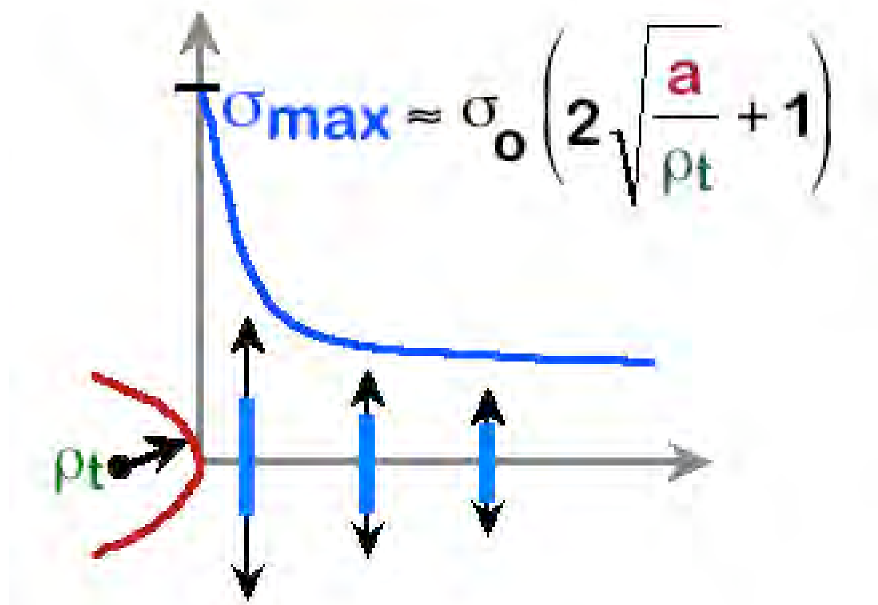
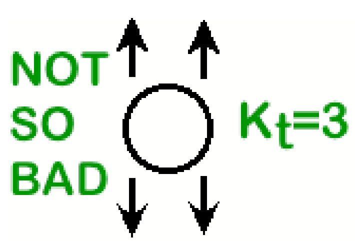
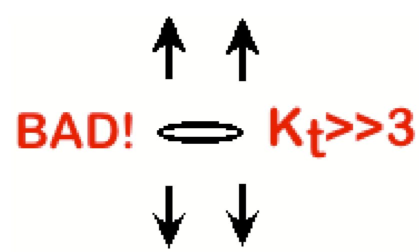


- Stress conc. factor: $K_t = \sigma_{max} / \sigma_o$

- Large K_t promotes failure:



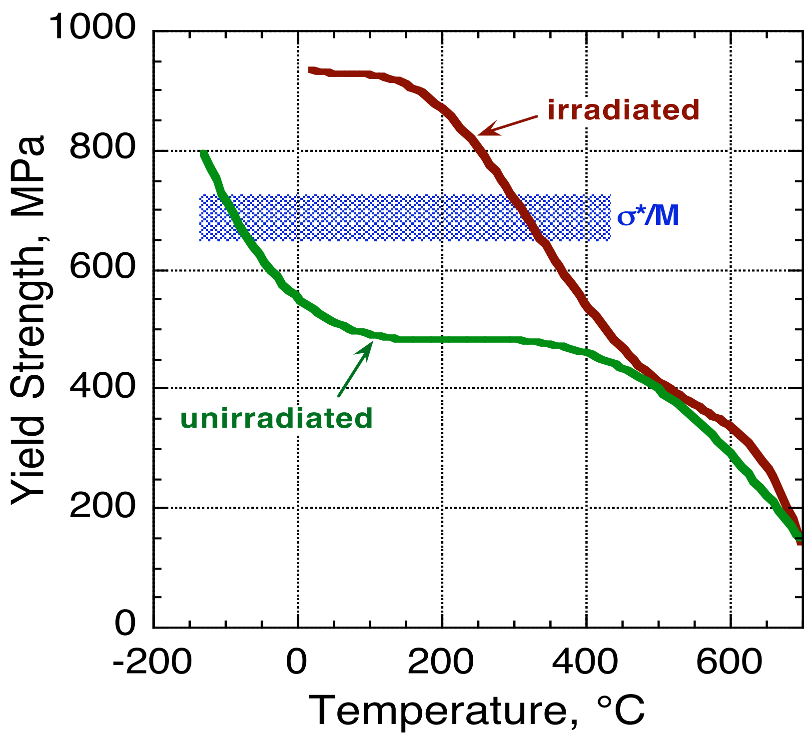


J. Hayton

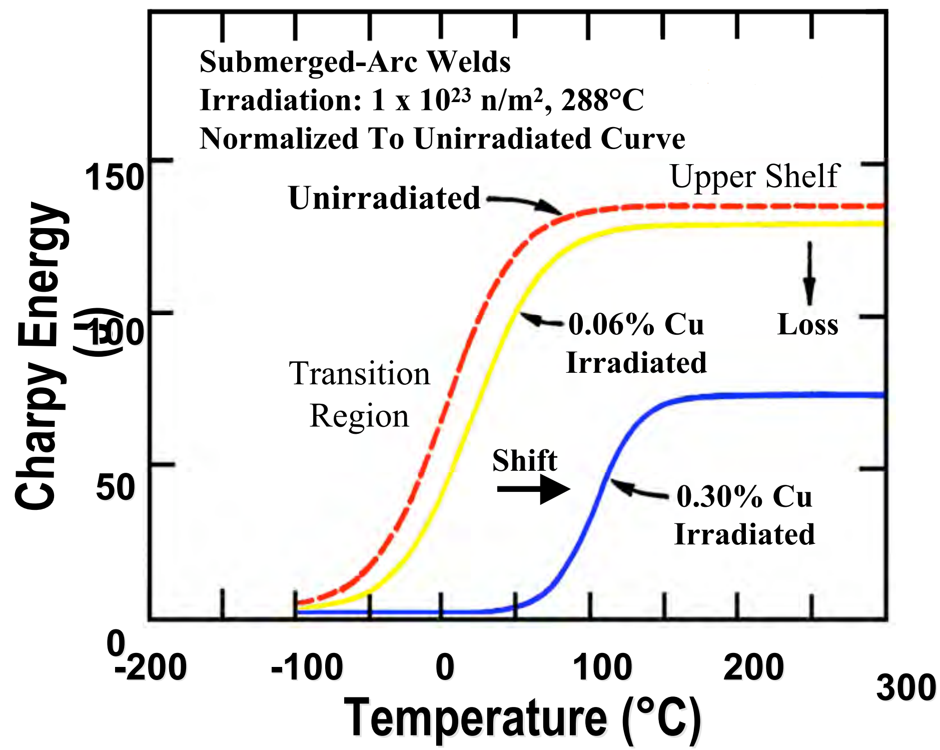
Fracture Toughness of Irradiated BCC Structural Alloys

- There are two general approaches to mitigate DBTT increases
  - Reduce radiation hardening by alloying modifications (e.g., low-Cu RPV steels)
  - Increase σ* (e.g., new ODS steels?)

- **Ludwig-Davidenkov relation provides a rough estimation of embrittlement due to radiation hardening**

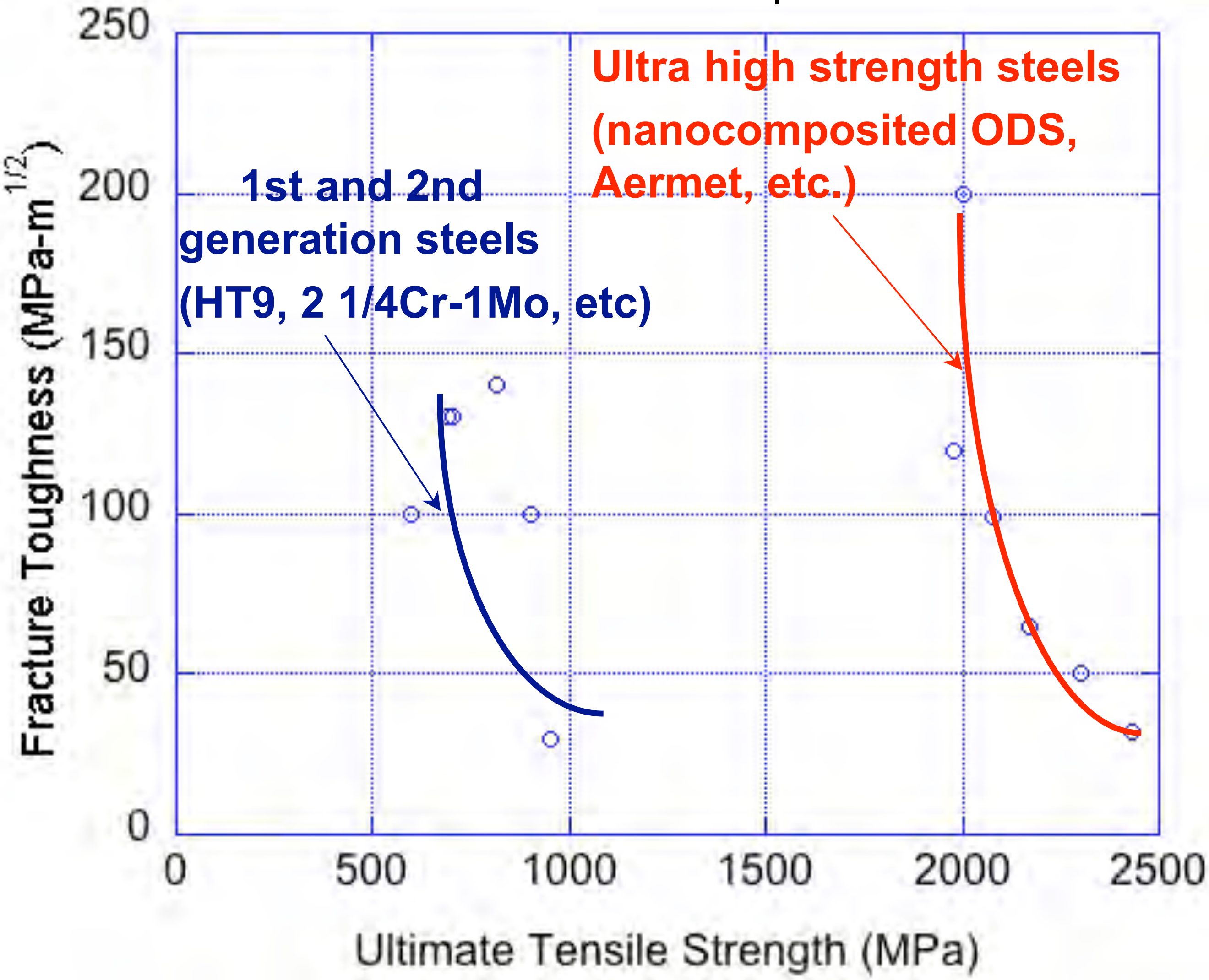


- **Significant improvements in resistance to low temperature radiation embrittlement can be achieved by selective alloying (e.g., reduced Cu in reactor pressure vessel steels)**



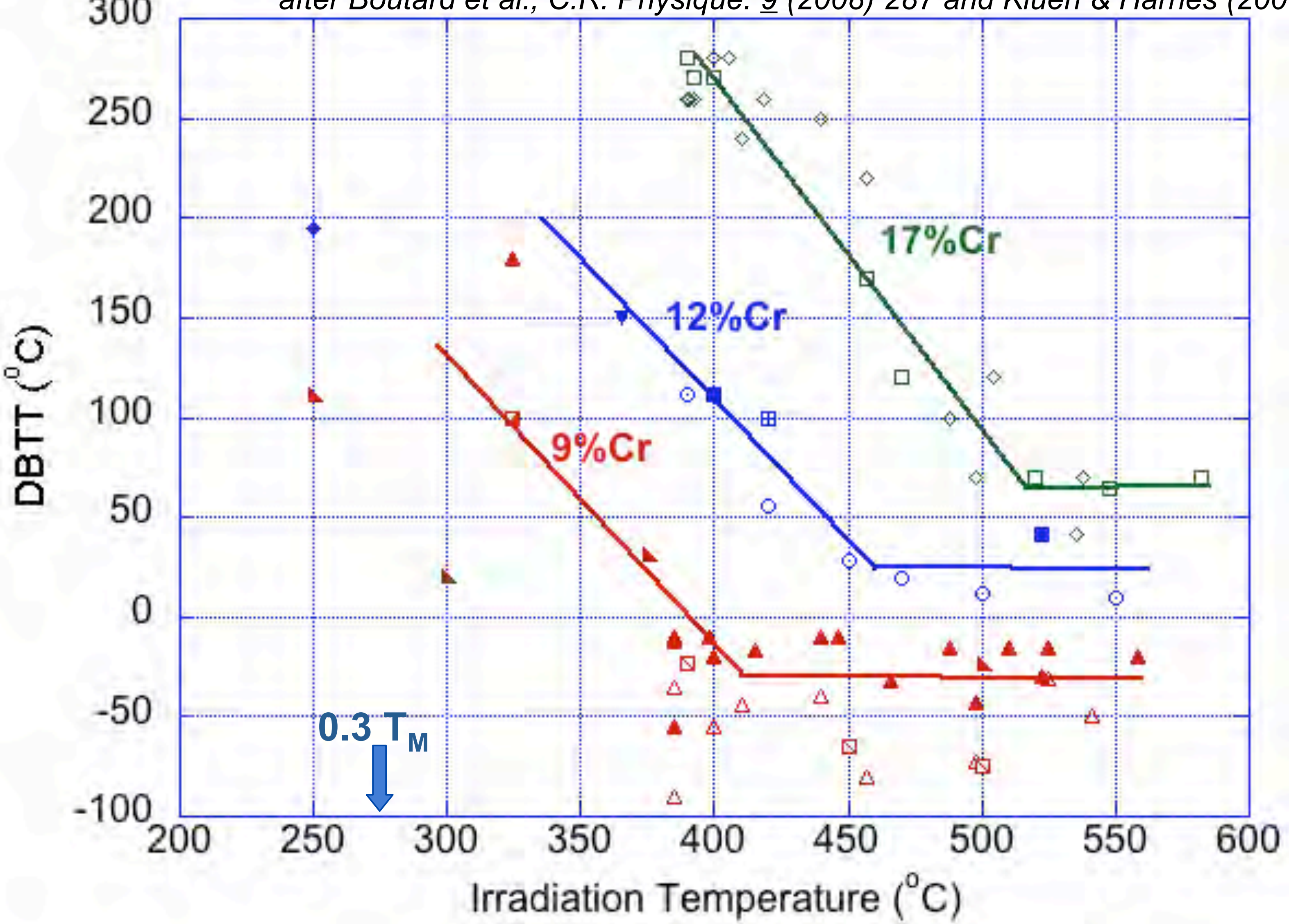
Recent progress in developing high-strength steels that retain high-toughness has been remarkable

- Generally obtained by producing high density of nanoscale precipitates and elimination of coarse particles that serve as stress concentrator points

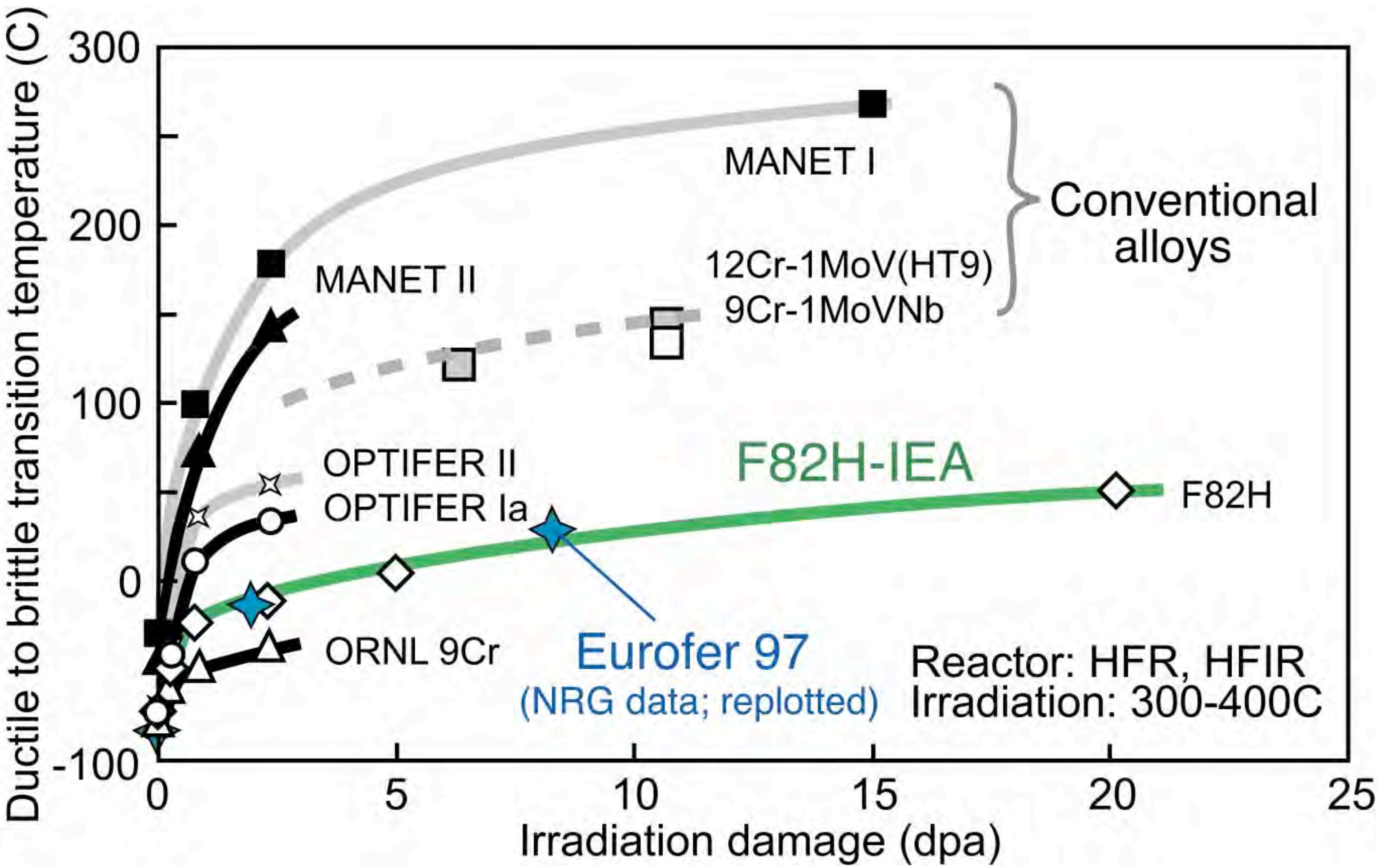


Effect of Neutron Irradiation on the Ductile to Brittle Transition Temperature in Ferritic/martensitic Steels

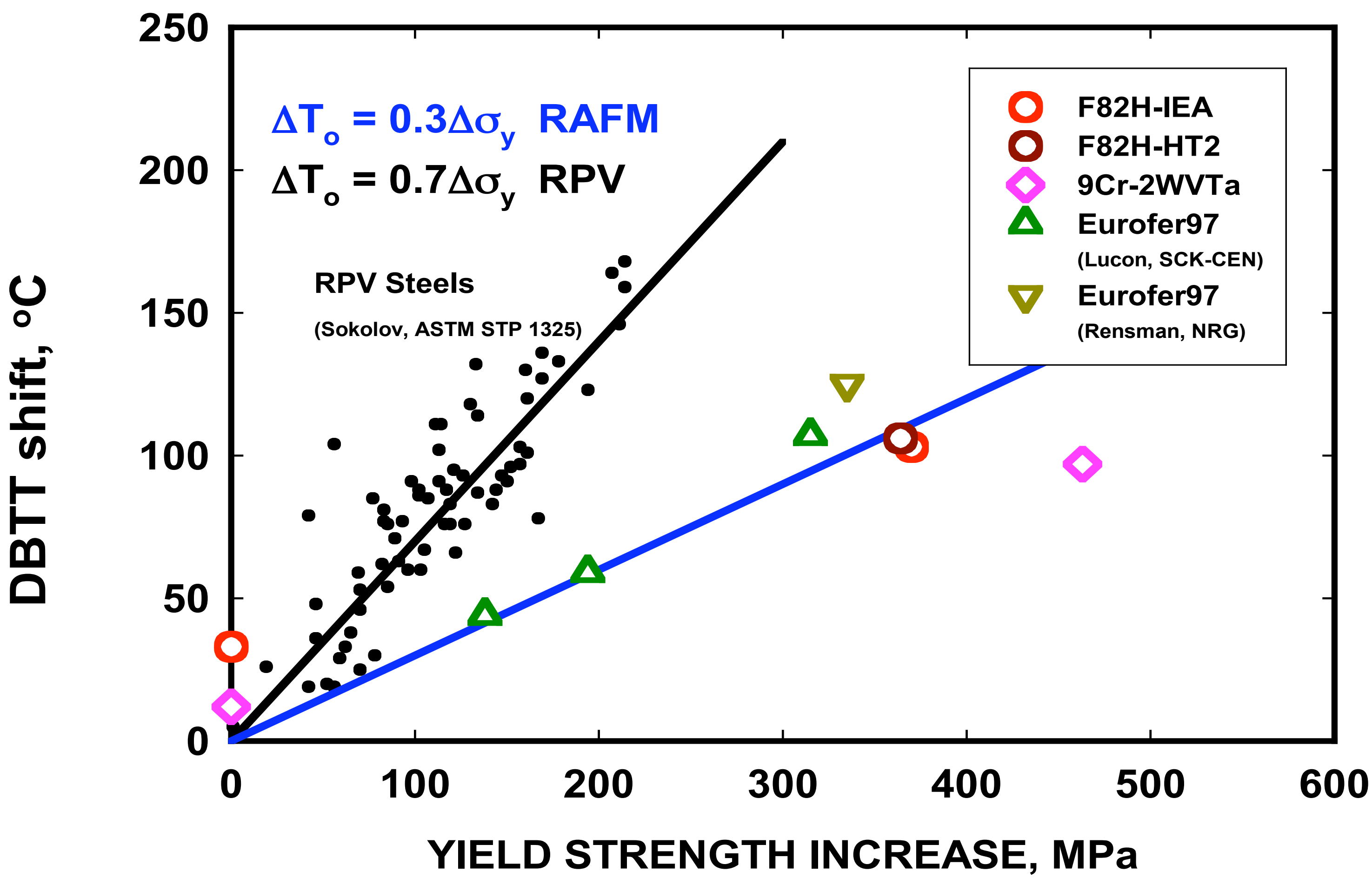
after Boutard et al., C.R. Physique. 9 (2008) 287 and Klueh & Harries (2001)



Effect on Neutron Irradiation on DBTT of Ferritic/martensitic Steels



8-9%Cr RAFM Steels Exhibit Less Embrittlement Per Unit of Hardening Than Low-Alloyed RPV Steels



M.A. Sokolov et al., ICFRM12, J. Nucl. Mater. 367-370 (2007) 68

High temperature He embrittlement in austenitic stainless steel: Effect of annealing time and applied stress at 750˚C on grain boundary cavities

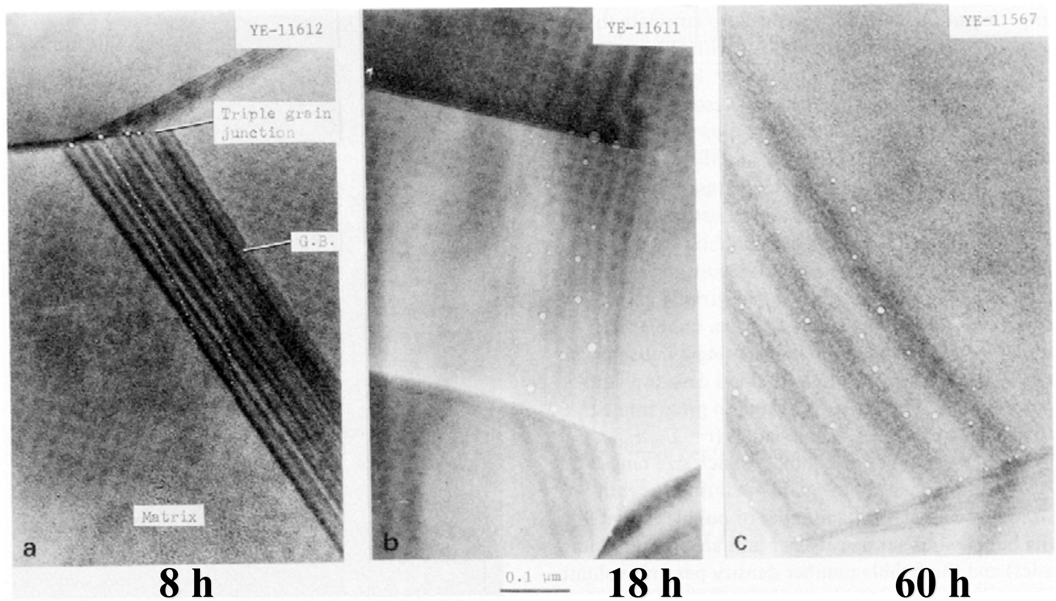
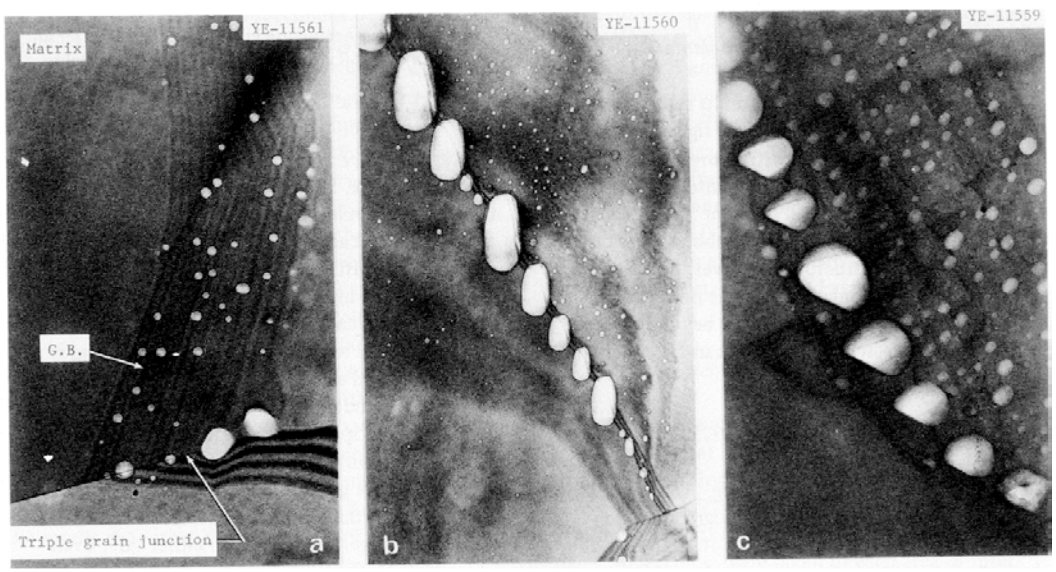


Fig. 2. Growth of helium bubbles in unstressed Fe–17 Cr–17 Ni specimens after annealing at 1023 K for (s) 2.88×10^4 s, (b) 6.48×10^4 s and (c) 21.60×10^4 s.

0 MPa

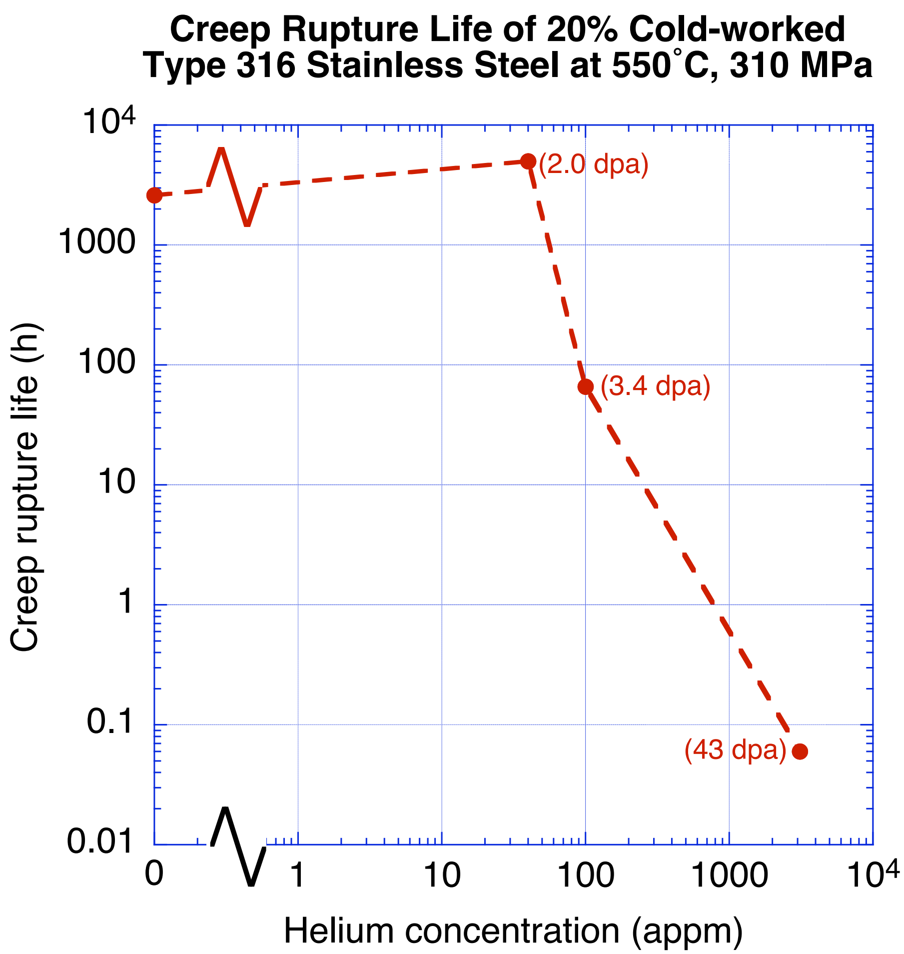


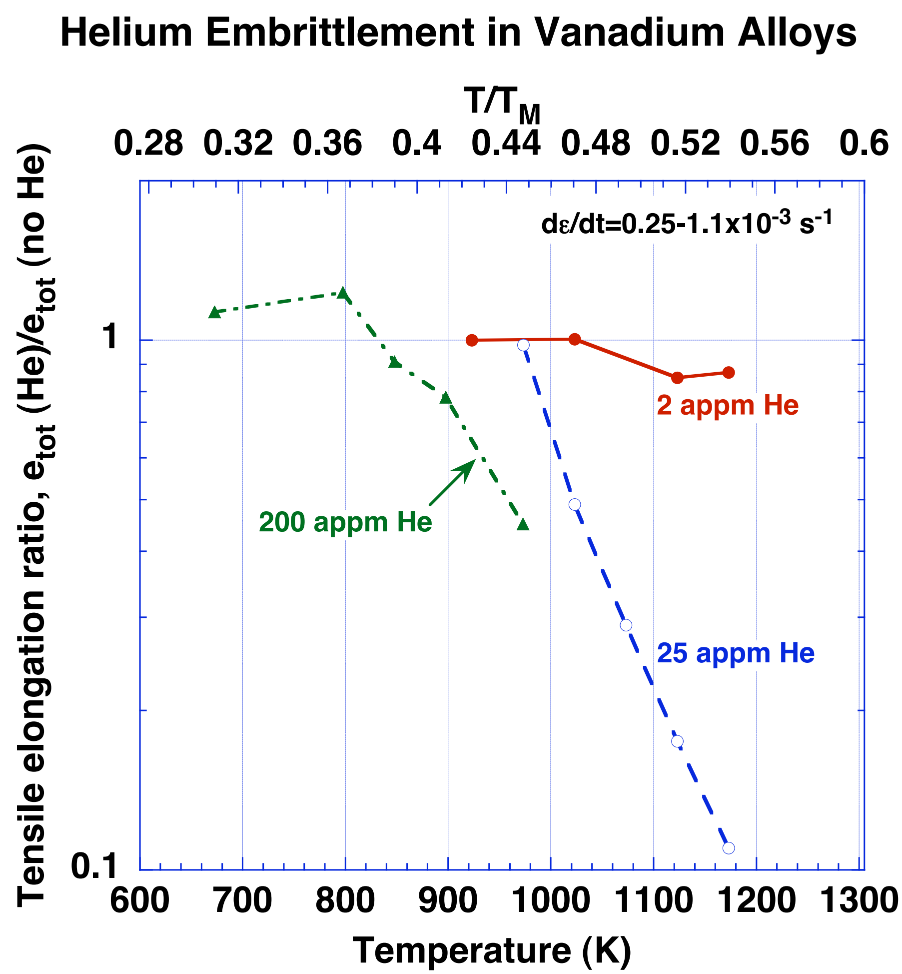
19.6 MPa

D.N. Braski et al.
J. Nucl. Mat. <u>83</u> (1979) 265

He Embrittlement of Grain Boundaries Occurs at High Temperatures

Mechanism based on critical number of gas atoms for unconstrained cavity growth



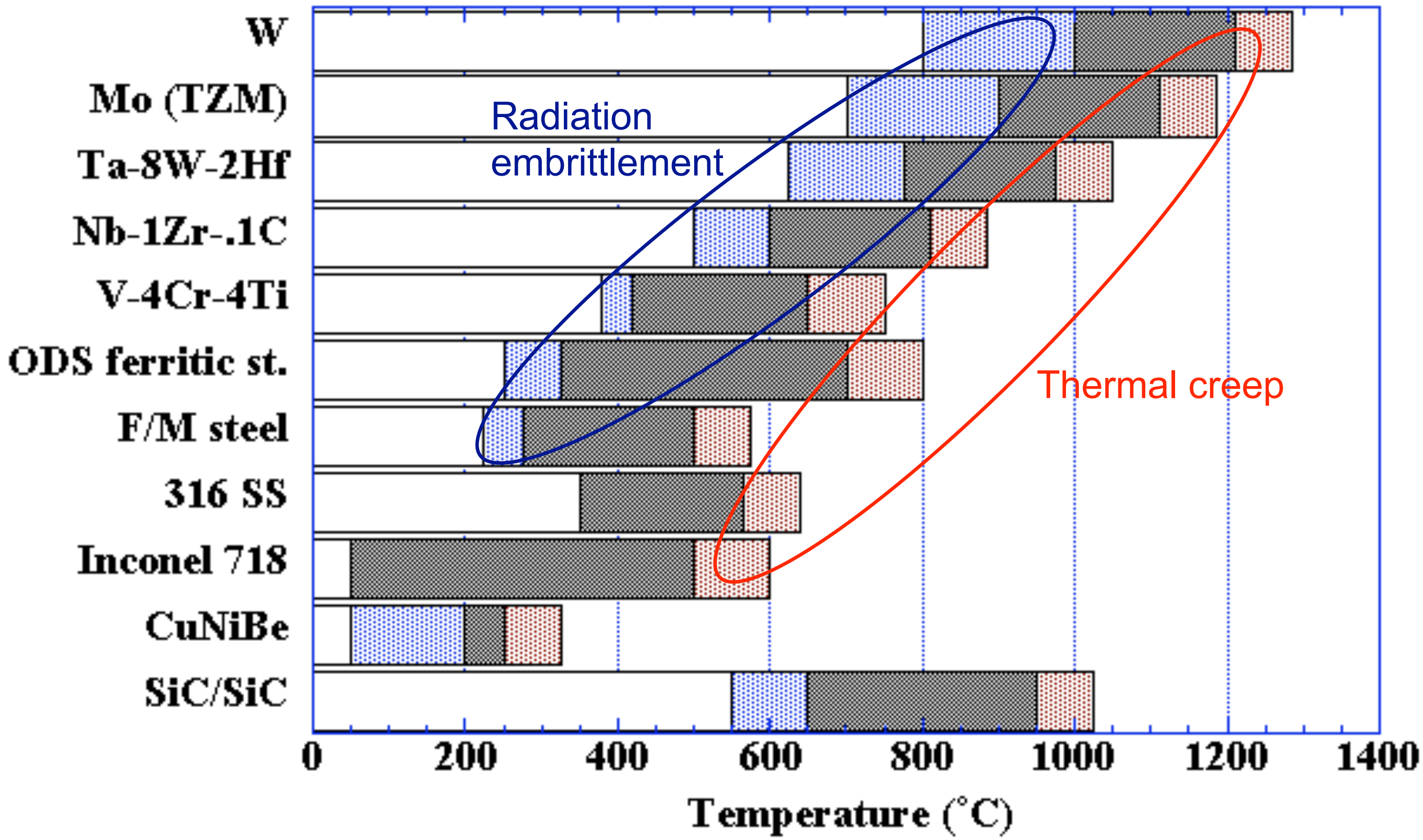


He trapping at nanoscale precipitates within grains is key for inhibiting He embrittlement

However…….. The formation and microstructural stability of these precipitates may be strongly affected by irradiation

Can we break the shackles that limit conventional structural materials to ~300^{o}C temperature window?

Structural Material Operating Temperature Windows: 10-50 dpa

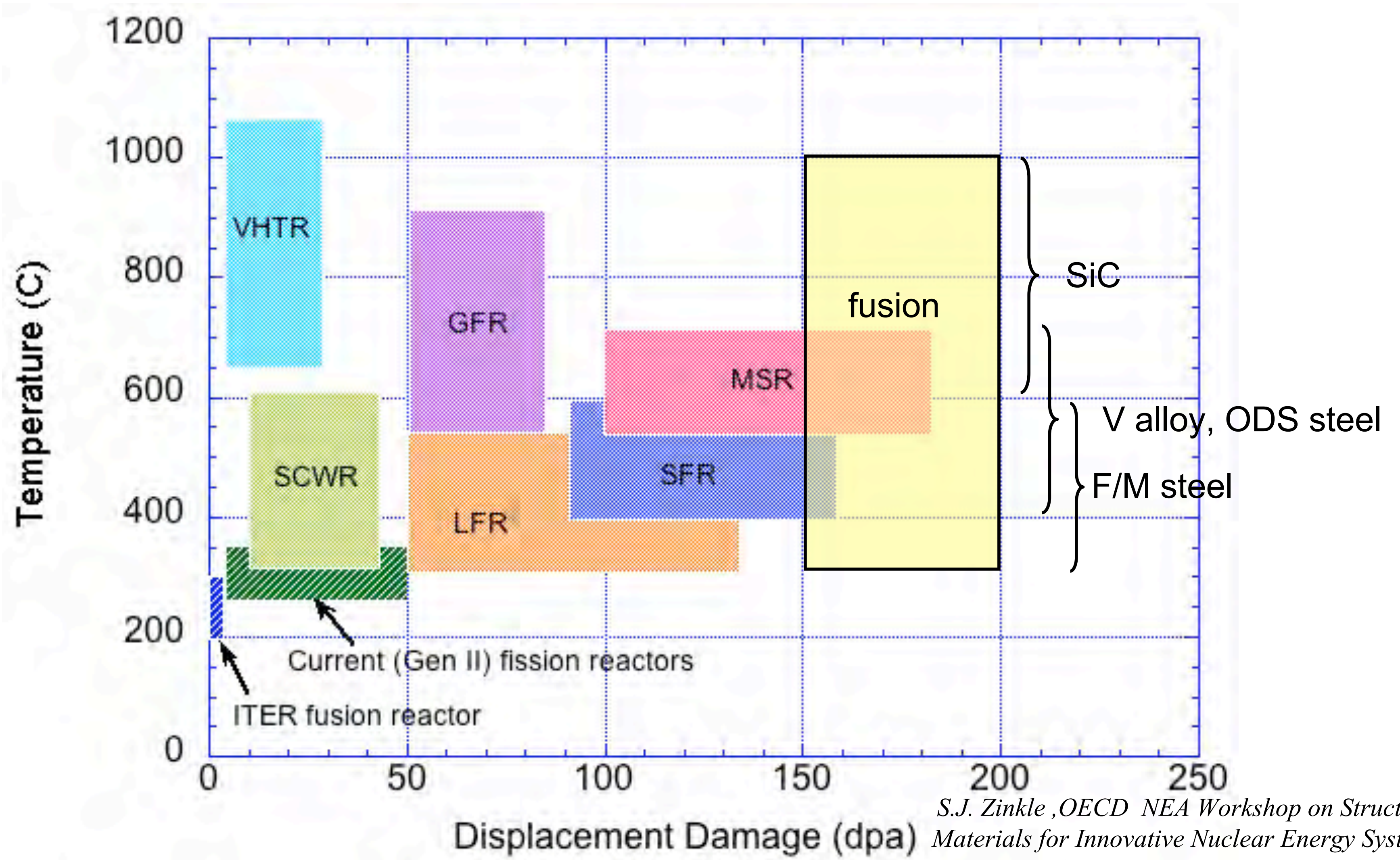


$\eta_{Carnot}=1-T_{reject}/T_{high}$

Additional considerations such as He embrittlement and chemical compatibility may impose further restrictions on operating window

Zinkle and Ghoniem, Fusion Engr. Des. *49-50 (2000) 709*

Comparison of Gen IV and Fusion Structural Materials Environments

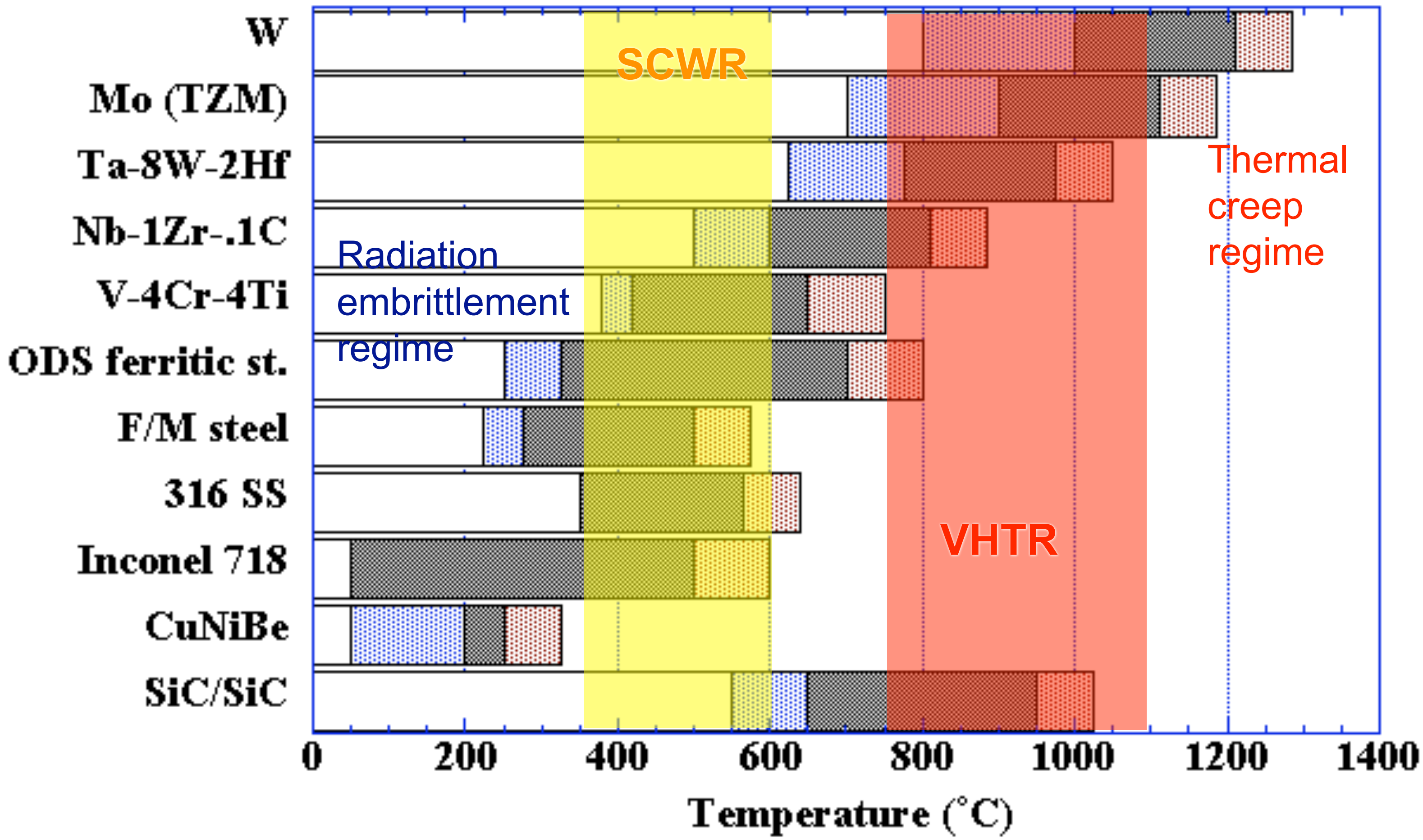


S.J. Zinkle ,OECD NEA Workshop on Structural Materials for Innovative Nuclear Energy Systems, Karlsruhe, Germany, June 2007, in press

All Gen IV and Fusion concepts pose severe materials challenges

New structural materials with temperature windows >300°C are needed for efficient development of Gen IV concepts

Structural Material Operating Temperature Windows: 10-50 dpa

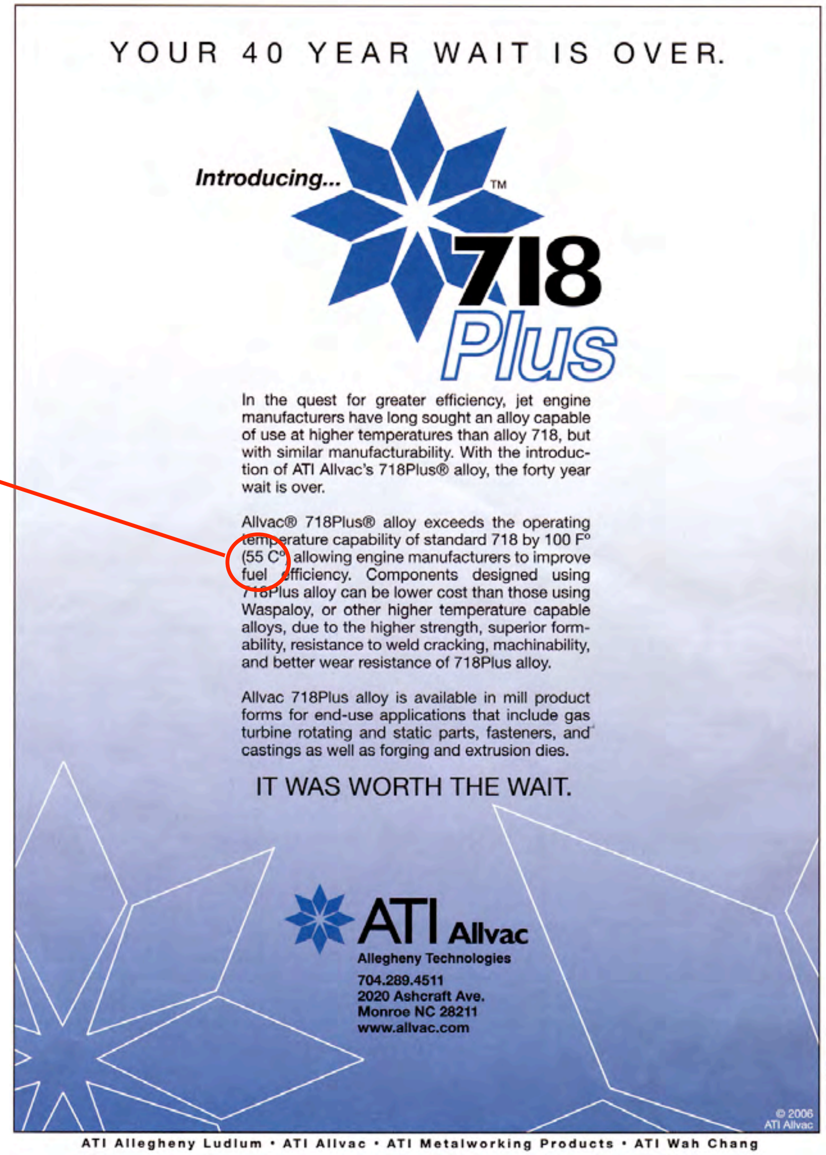


S.J. Zinkle ,OECD NEA Workshop on Structural Materials for Innovative Nuclear Energy Systems, Karlsruhe, Germany, June 2007, in press

Conventional Alloy Development is a Slow and Expensive Endeavor

- 55°C improvement in upper operating temperature limit after 40 years development!!

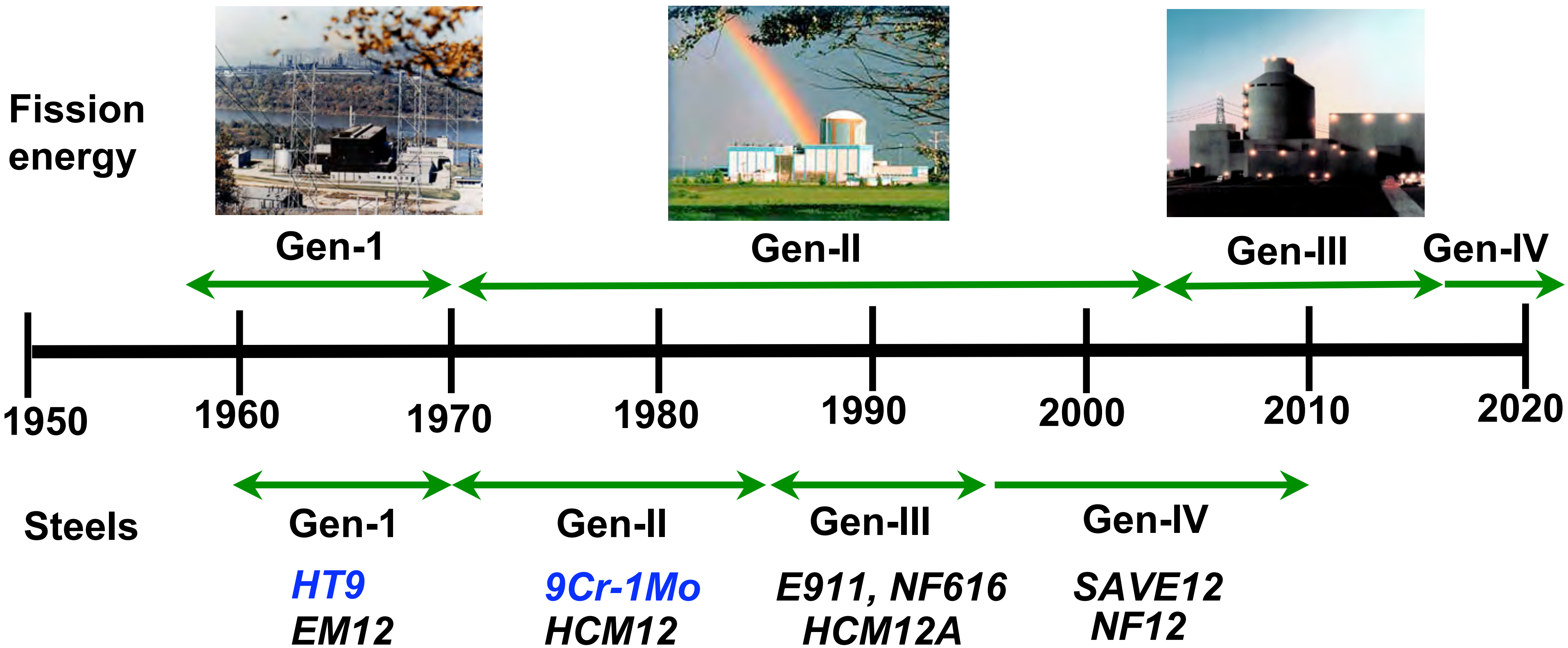
- Improvement in computational thermodynamics could accelerate development of new materials



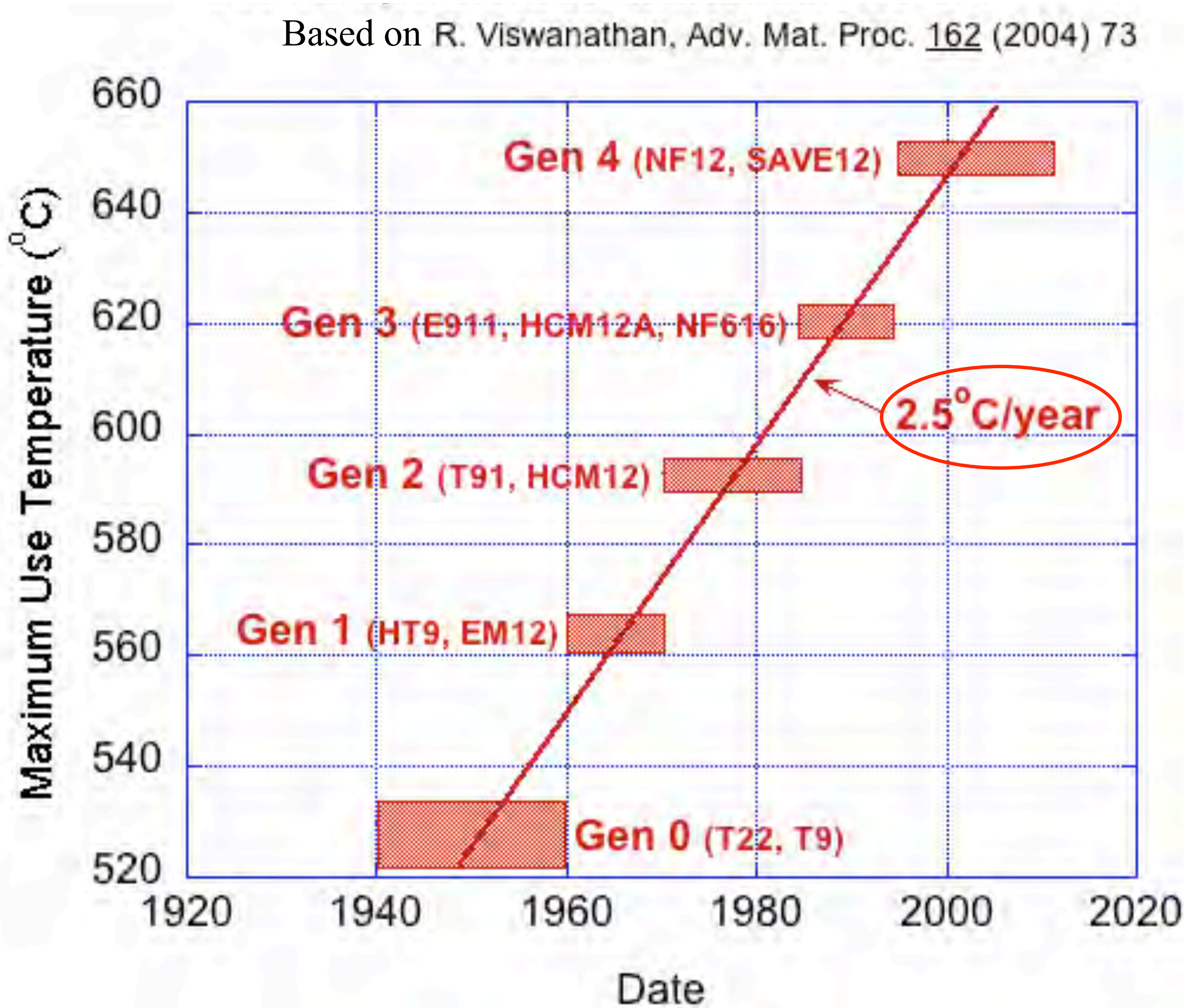
Advanced Materials & Processes (2006)

Evolution of Improved Steels has Paralleled Improvements in Nuclear Reactor Designs

- **Gen-IV reactors should not be based on Gen-I structural materials!**



Historical development of improved high-temperature steels has exhibited slow and steady progress



Underlying alloy development philosophy for radiation environments

- **Produce high density of uniformly distributed nanoscale particles that are highly stable (thermal and neutron exposures)**
  - Avoid solutes and precipitate phases that are known to be susceptible to radiation induced dissolution or coarsening effects
  - Avoid phases that are known to cause embrittlement (e.g., δ-ferrite, chi and $M_{23}C_6$ phases in ferritic/martensitic steels)
- **Employ a suite of computational tools to guide experimental studies**
  - Thermodynamic codes for identifying intrinsic equilibrium structures in the absence of irradiation
  - Multiscale codes (atomistic, molecular dynamics, kinetic/lattice Monte Carlo, chemical rate theory, etc.) to probe radiation effects behavior
- **Use targeted experiments to validate computational results and to probe conditions unsuitable for quantitative computational analysis**
  - experiments use model alloy systems as well as complex engineering alloys

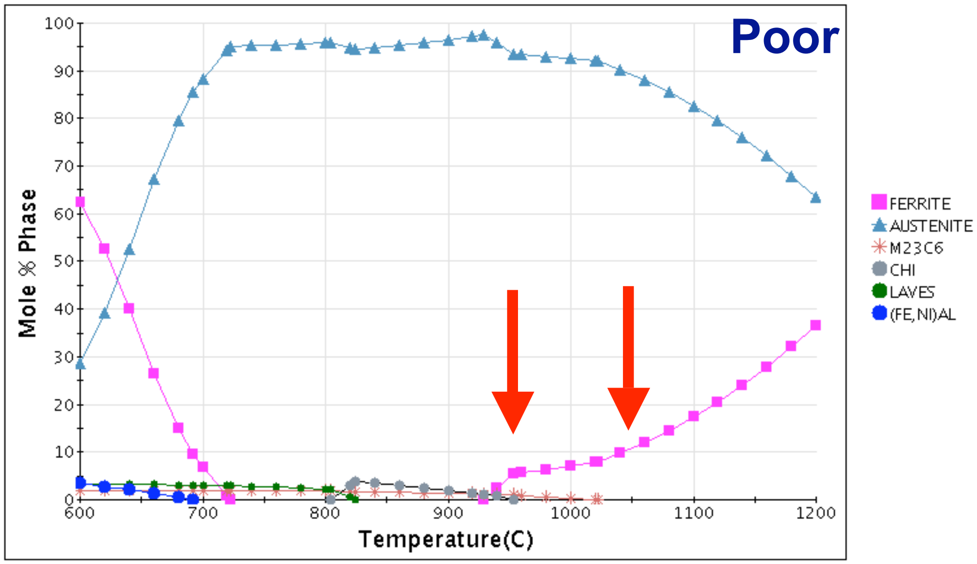
Options for Development of Improved Steels

- Steels can exhibit a wide range of properties depending on detailed composition and thermomechanical treatment
- Evolutionary approach
  - Ingot metallurgy/ classical precipitation strengthening
    - Computational thermodynamics to guide development
- Revolutionary approaches
  - Nanoscale dispersion strengthening
    - Use vacancies as an additional lever to create stable dispersoids
  - Engineered laminate architectures (nano- and micro-)
  - Potential for near net shape fabrication

Modern computational thermodynamics reveals pathway to improve precipitation hardened stainless steels

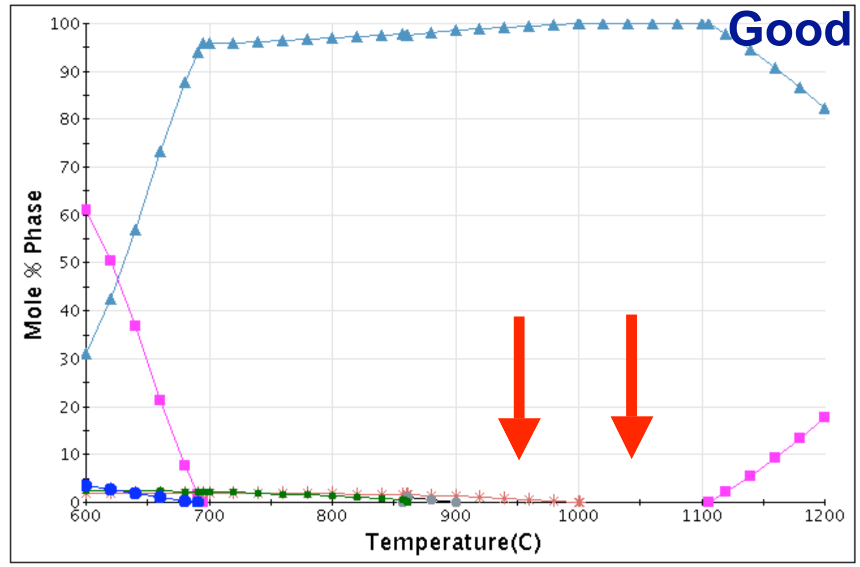
Both 15%Cr-7%Ni alloys are within allowable chemical composition for PH15-7 Mo precipitation hardened stainless steel (UNS S15700)

Fe-1.0Al-0.09C-15.0Cr-1.0Mn-2.5Mo-7.25Ni-1.0Si wt(%)



"average" Cr, Mo, Ni

Fe-1.0Al-0.09C-14.0Cr-1.0Mn-2.0Mo-7.5Ni-1.0Si wt(%)



"low" Cr, Mo and "high" Ni

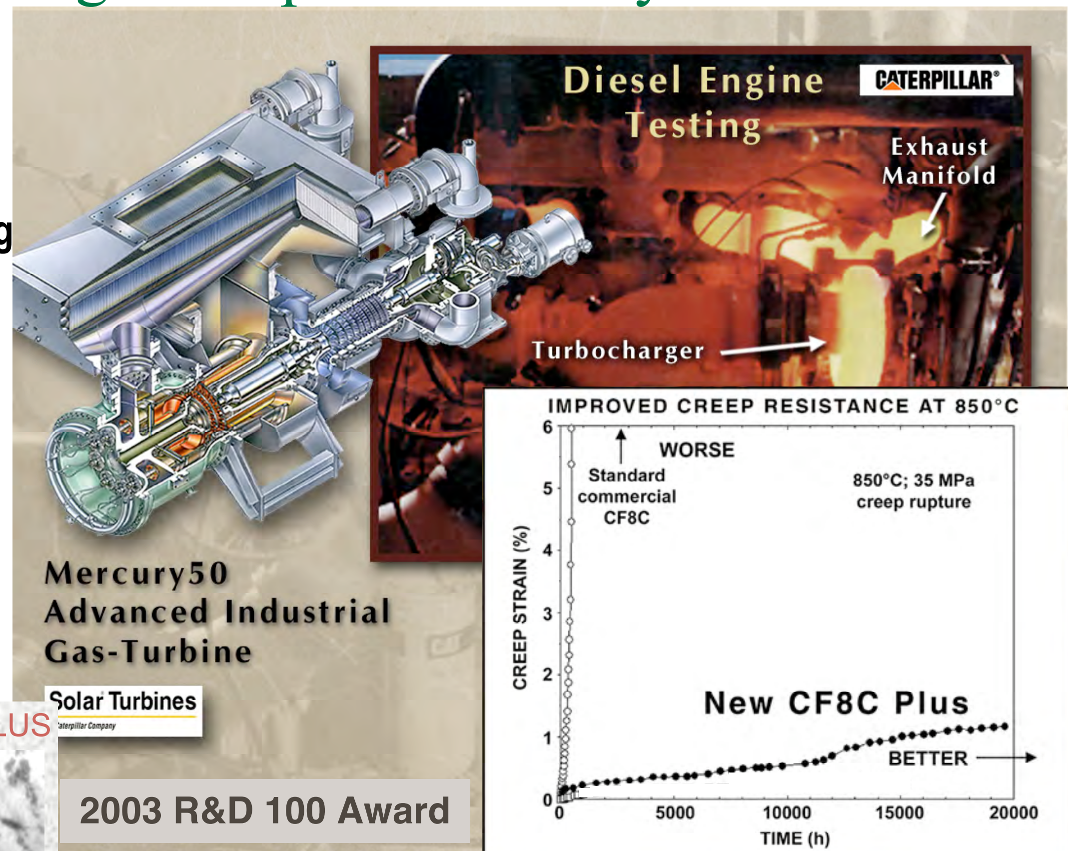
UNS S15700: 14.0-16.0 Cr, 6.50-7.75 Ni, 2.0-3.0 Mo

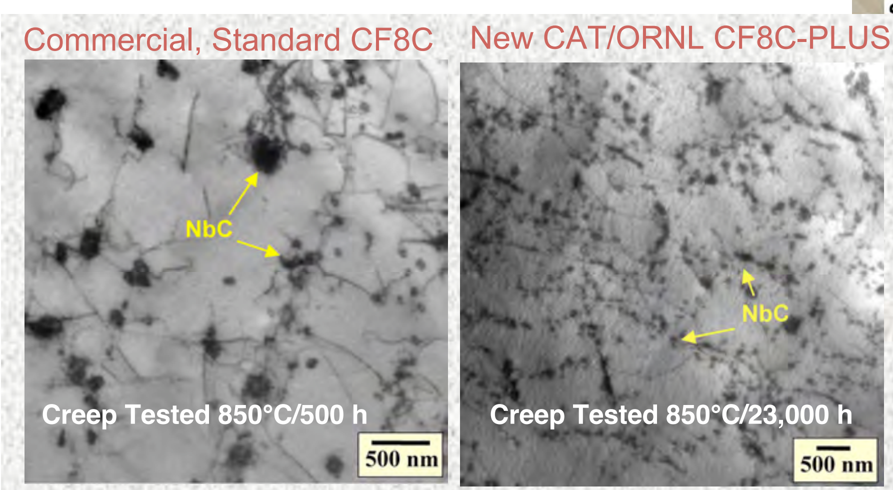
- **Within alloy specifications, large differences can be expected with standard heat treatment**
- **Computational thermodynamics calculations can lead to composition and heat treatment optimization**

J.M. Vitek

Microstructural Evolution In Irradiated Stainless Steels Provided the Key for Developing Improved High Temperature Alloys

- *Reactant Effects* **(ie. Ti, V+Nb enhance MC formation)**
- *Catalytic Effects* **(ie. Si enhances Fe_2Mo or M_6C)**
- *Inhibitor Effects* **(ie. C, P or B retard the formation of Fe_2Mo or FeCr sigma phase during aging, G-phase during irradiation)**
- *Interference Effects* **(ie. N forms TiN instead of TiC; N does not form NbN instead of NbC; therefore C and N can be added with Nb, but not Ti)**





(TEM, As Cast)

Result of microstructural modification:

- **Formation of stable nanoscale MC carbide dispersions to pin dislocations**
- **Resistance to creep cavitation and embrittling grain boundary phases (ie. sigma, Laves)**
- **Resistance to dislocation recovery/ recrystallization**

FreedomCAR and Vehicle Technologies and Distributed Energy and Electricity Reliability Programs of DOE-EERE

P.J. Maziasz

Technology Transfer of CF8C-Plus Cast Stainless Steel

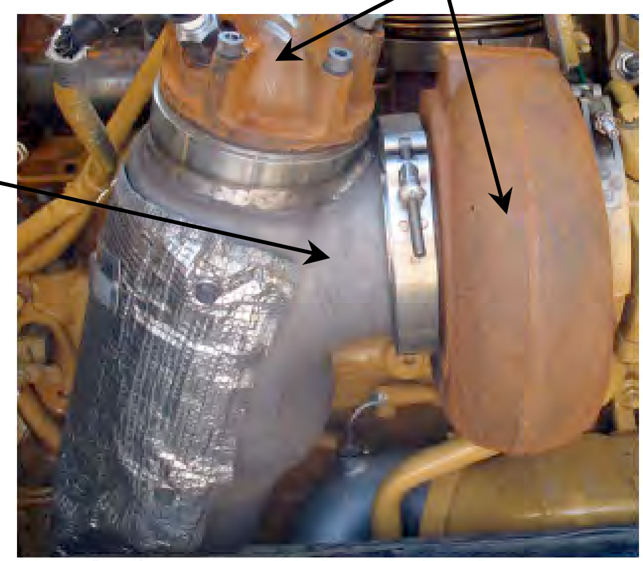
6,700 lb **CF8C-Plus** end-cover cast by MetalTek for Solar Turbines Mercury 50 gas turbine

- **MetalTek International, Stainless Foundry & Engineering, and Wollaston Alloys received trial licenses in 2005 (18 months after project start)**
- **Over 350,000 lb of CF8C-Plus steel have been successfully cast to date**
  - **Now used on all heavy-duty truck diesel engines made by Caterpillar (since Jan. 2007)**
  - **Solar Turbines (end-cover, casings), Siemens-Westinghouse (large section tests for turbine casings), ORNL, and a global petrochemical company (tubes/piping).**
  - **Stainless Foundry has cast CF8C-Plus exhaust components for Waukesha Engine Dresser NG engines**

80 lb **CF8C-Plus** exhaust component cast by Stainless Foundry for Waukesha NG reciprocating engine

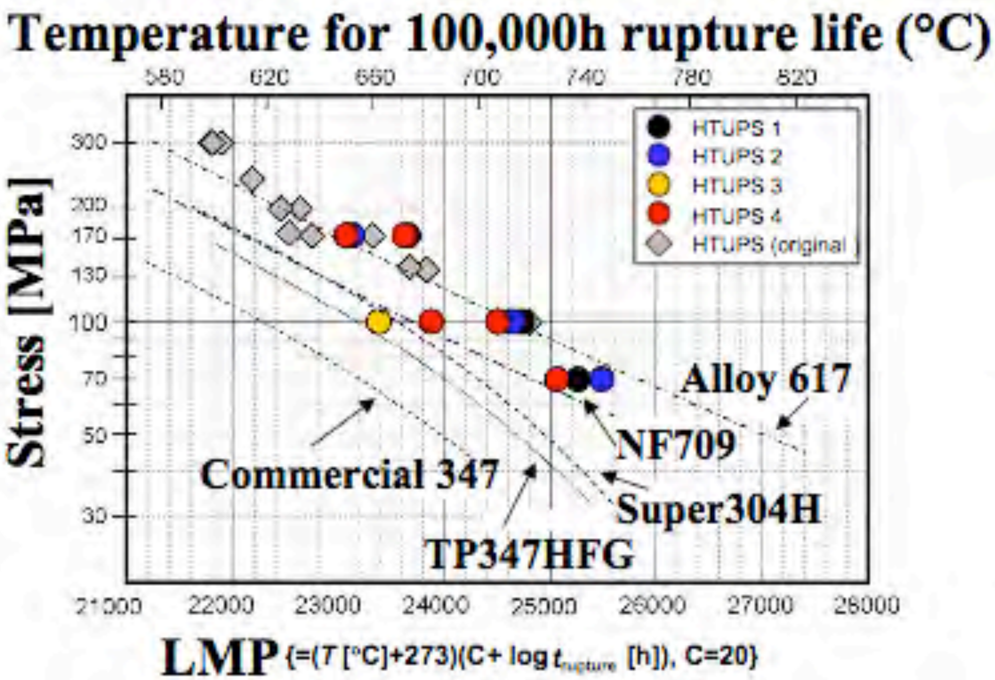
SiMo cast iron

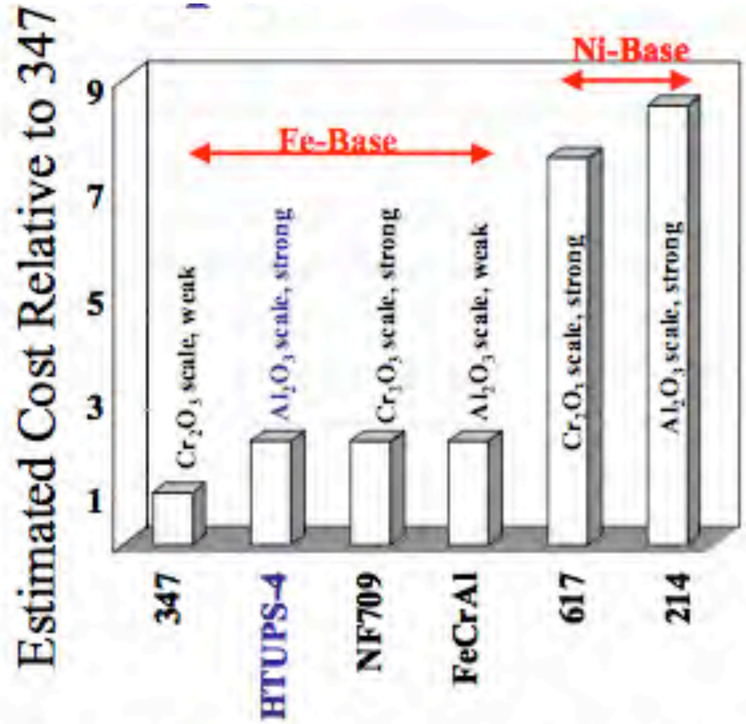
CF8C-Plus steel

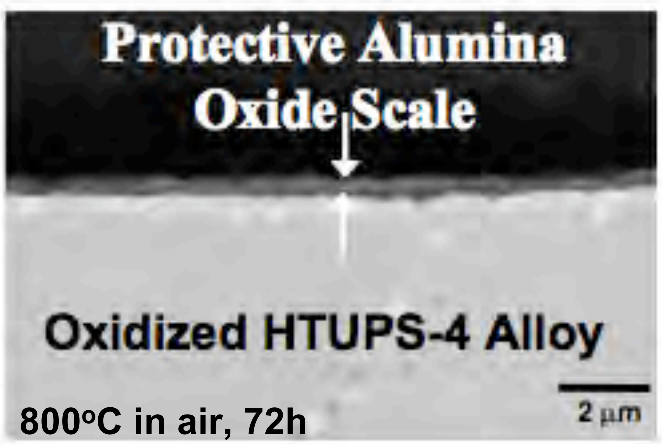


Caterpillar Regeneration System (CRS) Housing

Development of New Alumina-Forming, Creep Resistant Austenitic Stainless Steel





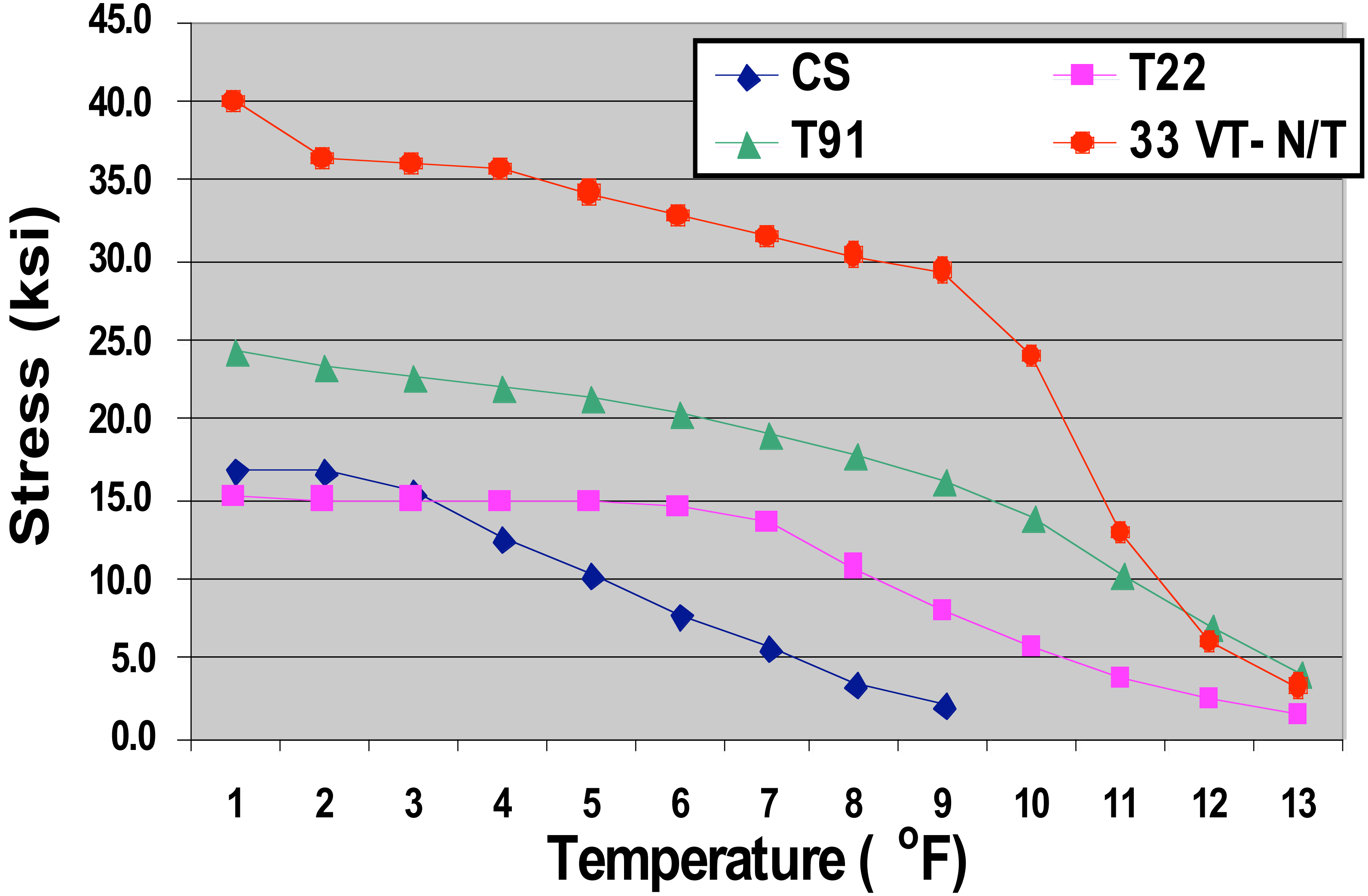


- Designed for 600-800°C structural use under aggressive oxidizing conditions
  - -superior oxidation resistance to conventional chromia-forming alloys
- Comparable cost to current heat-resistant austenitic stainless steels

Y. Yamamoto, M.P. Brady et al., Science 316 (2007) 433

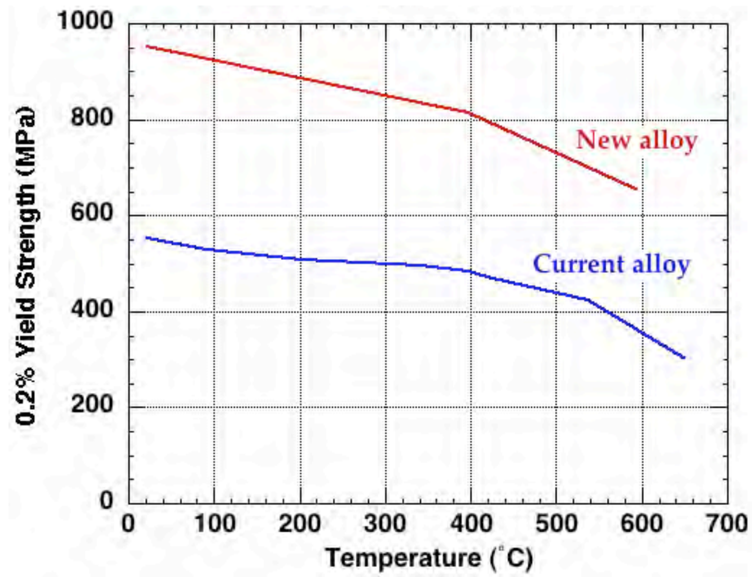
Presently, Vessels Operating at Temperatures Above 900F are Made of 2.25Cr-1Mo Steels. These Vessels Tend to be Large in Diameter

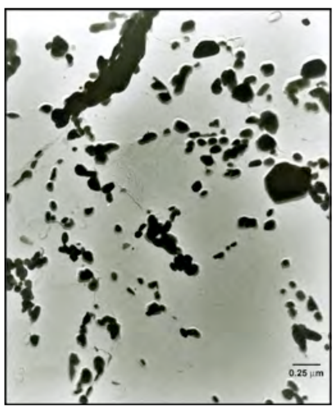
Allowable Design Stress Values for Several Steels



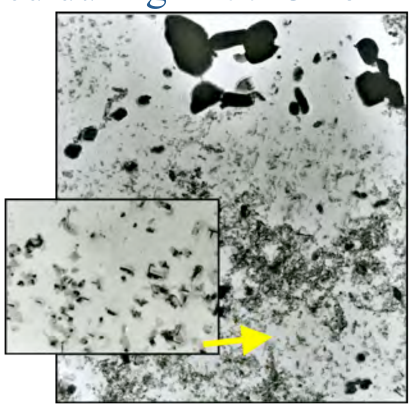
Creep Properties of New 3 Cr Steels have Advantages Over Existing 2 1/4Cr and 9-12Cr Steels

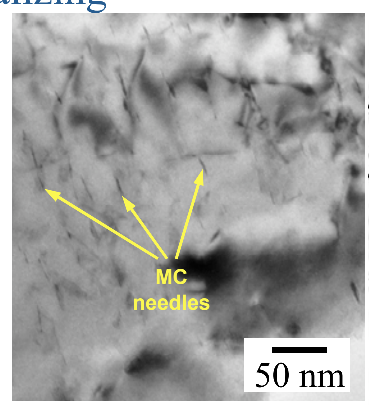
- Creep resistance improved over Japanese 2.25Cr (T23,T24) steels
- May not need to be tempered for high thermal creep strength; no postweld heat treatment?
- Properties better than HT9 and as good or better than modified 9Cr-1Mo steel
  - Long-term creep behavior (>5000 h) still needs to be determined
  - Two 50 ton heats procured by industry are being tested to obtain ASME code approval
  - Improved creep resistance is due to fine V-rich MC needles formed during 1100˚C normalizing



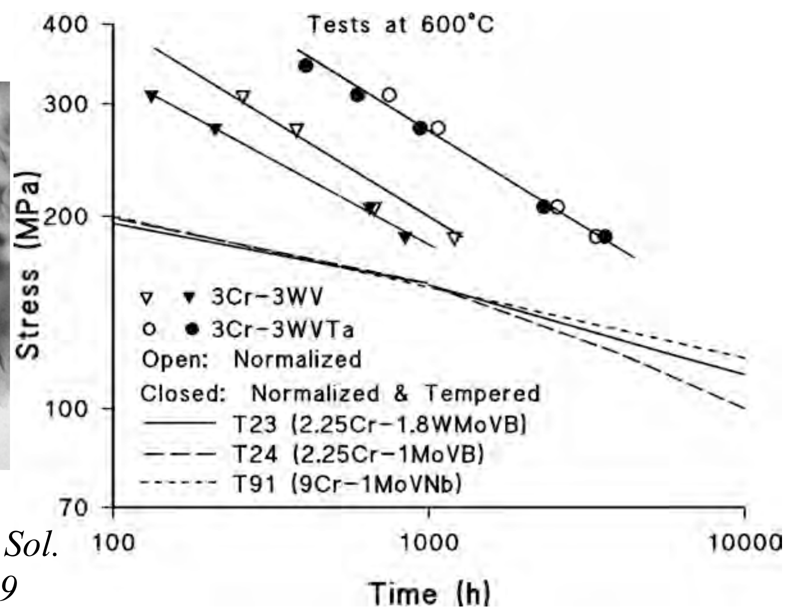


2 1/4 Cr-1Mo


New 2 1/4 Cr-2WV

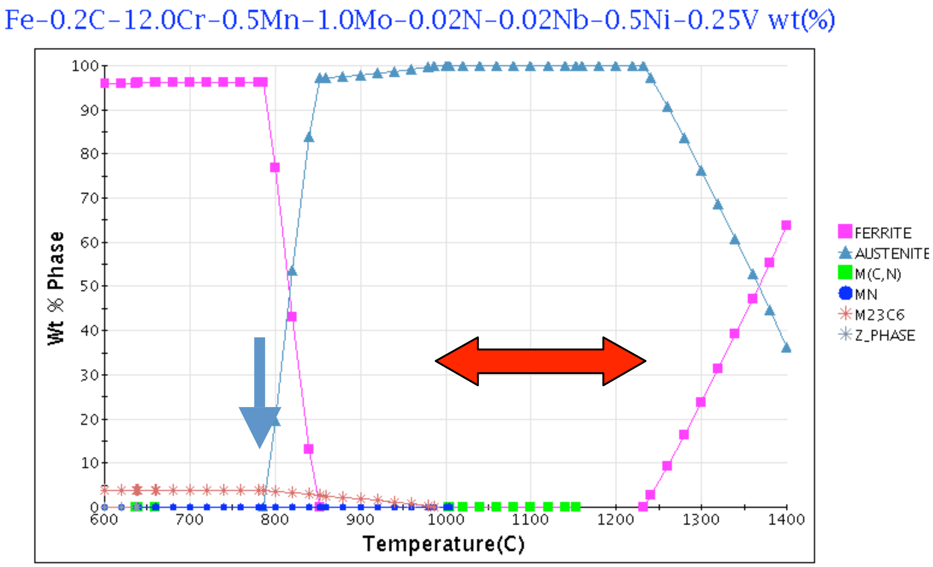


New 3 Cr-3WV

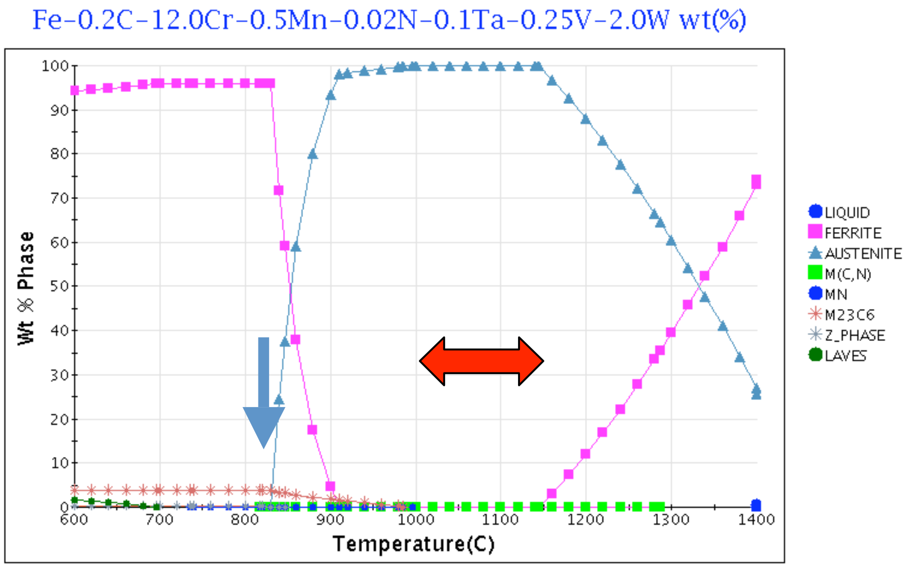


R. Klueh, Current Opin. Sol. St. Mat. Sci. 8 (2004) 239

Computational thermodynamics can be used to identify new heat treatment conditions for modified Cr-Mo steels



Standard 12Cr-1MoVNb

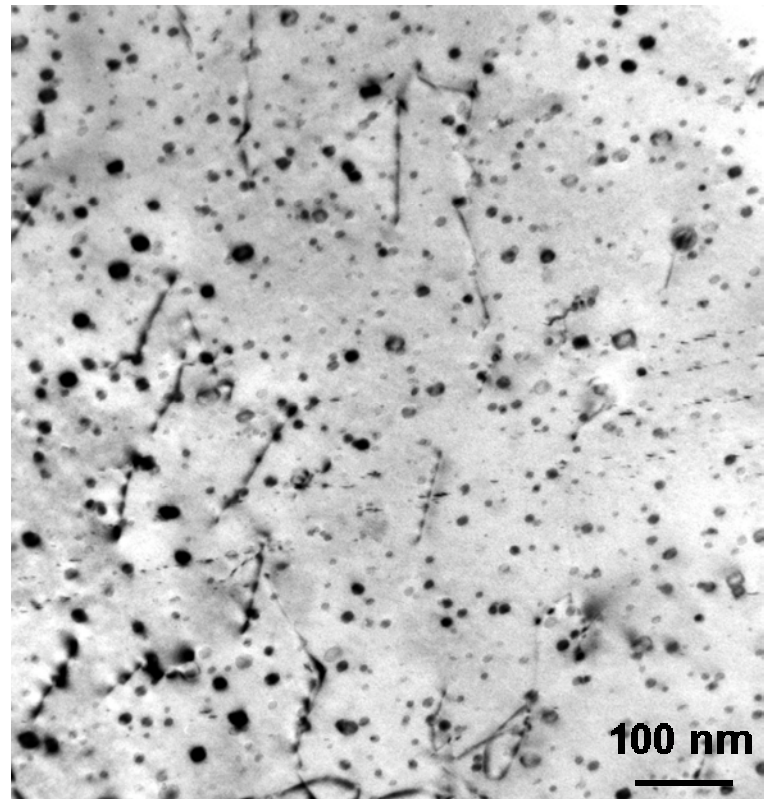


Modified 12Cr-V WTa

J.M. Vitek

New Thermomechanical treatment (TMT) Process Applied to Commercial 9-12%Cr Steels Yields Improved Microstructure

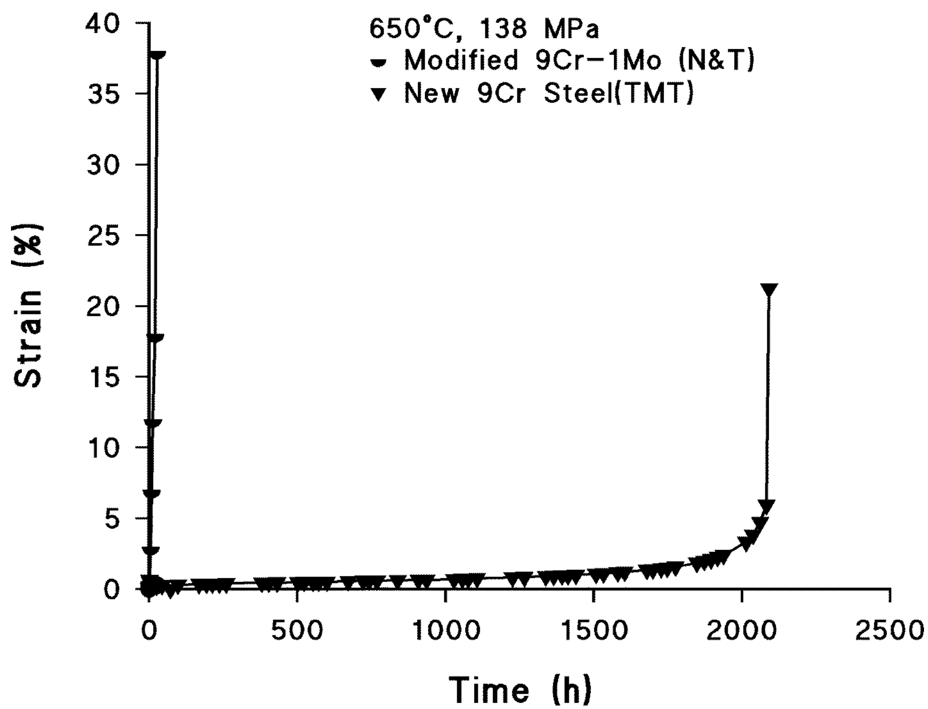
- **Commercial 9Cr-1Mo and 12 Cr steels were processed**
- **TMT (hot rolling) on 25.4–mm plates**
  - **Several TMT conditions were investigated**
- **Precipitates formed on dislocations introduced by hot rolling**
- **Precipitate dispersion is much finer than observed in conventionally processed 9-12Cr steel**

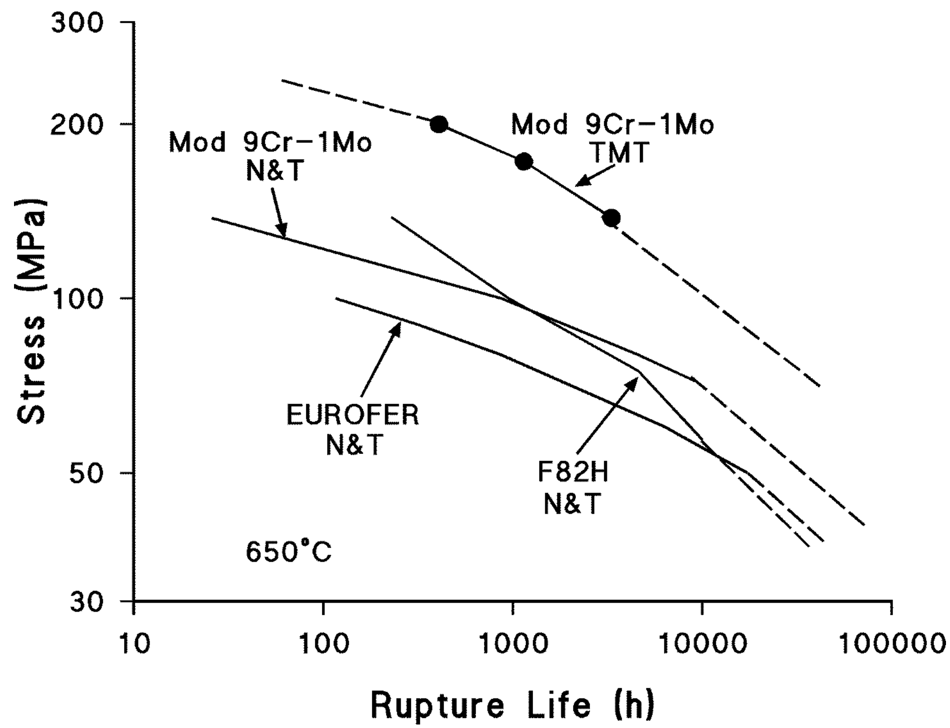


Modified 9Cr-1Mo—New TMT

R.L. Klueh et al., J. Nucl. Mat. 367-370 (2007) 48; Scripta Mat. 53 (2005) 275

Large Increase in Rupture Life of Modified 9Cr-1Mo at 650°C





- **Thermo-mechanical treatment (TMT) of modified 9Cr-1Mo produced steel with over an order-of-magnitude increase in rupture life**

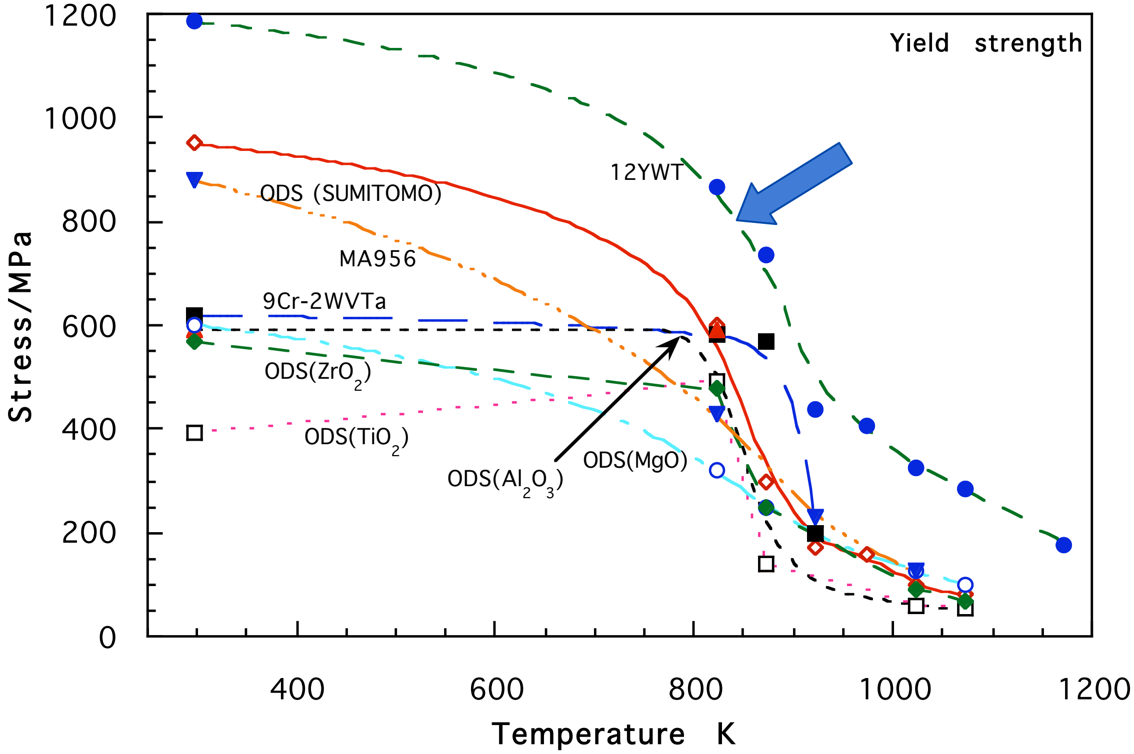
R.L. Klueh et al., J. Nucl. Mat. 367-370 (2007) 48; Scripta Mat. 53 (2005) 275

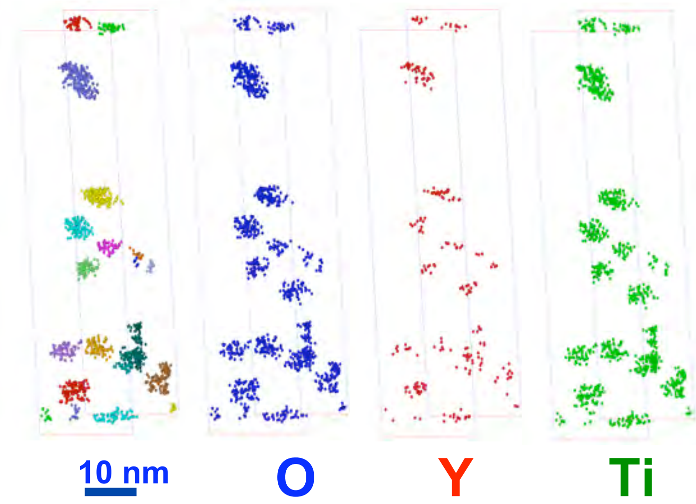
Oxide dispersion strengthened Steels

- There are two main options for ODS steels, based on pioneering work by Ukai and coworkers
  - Ferritic ODS steel (typically 12-16%Cr)
  - Ferritic/martensitic ODS steel (typically ~9%Cr)

Steel	Advantages	Disadvantages
12-16% Cr ODS ferritic steel	Higher temperature capability Better oxidation resistance	Anisotropic mechanical properties Lower fracture toughness
9% Cr ODS ferritic/martensitic steel	Nearly isotropic properties after heat treatment Better fracture toughness	Limited to temperature below ~700 C Marginal oxidation resistance at high temperatures

New 12YWT Nanocomposited Ferritic Steel has Superior Strength compared to conventional ODS steels



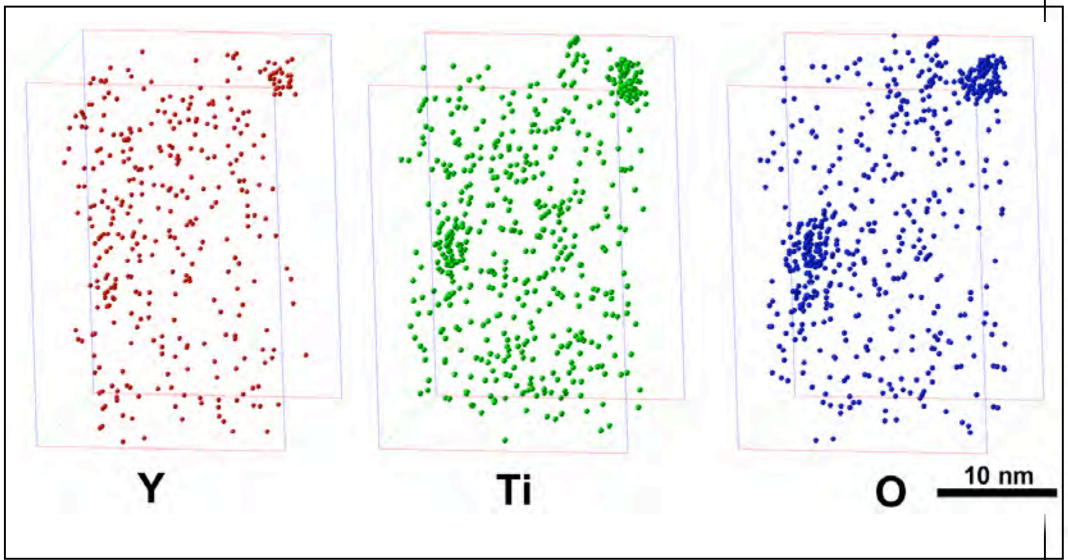


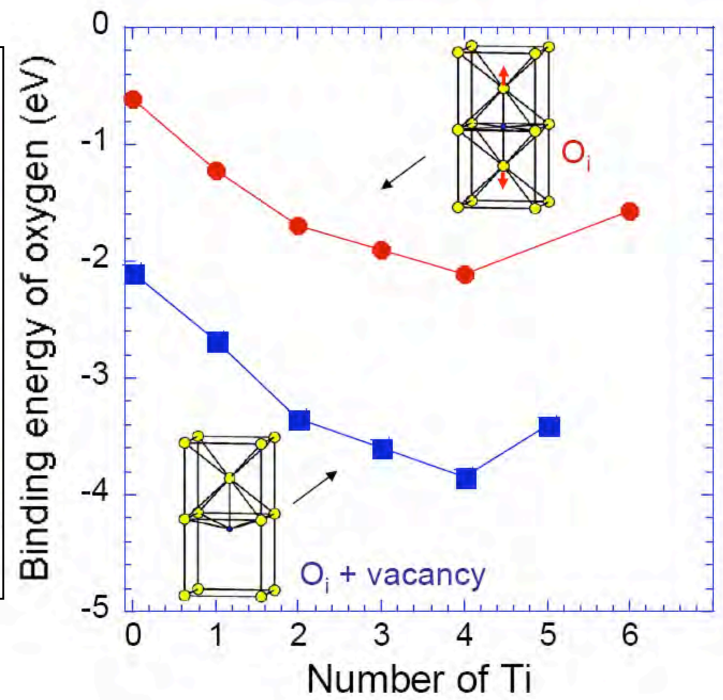
- Thermal creep time to failure is increased by several orders of magnitude at 800˚C compared to ferritic/martensitic steels
  – 2% deformation after ~2 years at 800°C, 140MPa
- Potential for increasing the upper operating temperature of iron based alloys by ~200°C
- Acceptable fracture toughness near room temperature

- Atom Probe reveals nanoscale clusters to be source of superior strength
  – Enriched in O(24 at%), Ti(20%), Y (9%)
  – Size : r_g = 2.0 ± 0.8 nm
  – Number Density : $n_v = 1.4 \times 10^{24}/m^3$
- Original Y_2O_3 particles convert to thermally stable nanoscale (Ti,Y,Cr,O) particles during processing
- Nanoclusters not present in ODS Fe-13Cr + $0.25Y_2O_3$ alloy

D.T. Hoelzer, M.K. Miller, et al.

Theory Has Shown That Vacancies Play a Pivotal Role in the Formation and Stability of Nanoclusters in ODS steel



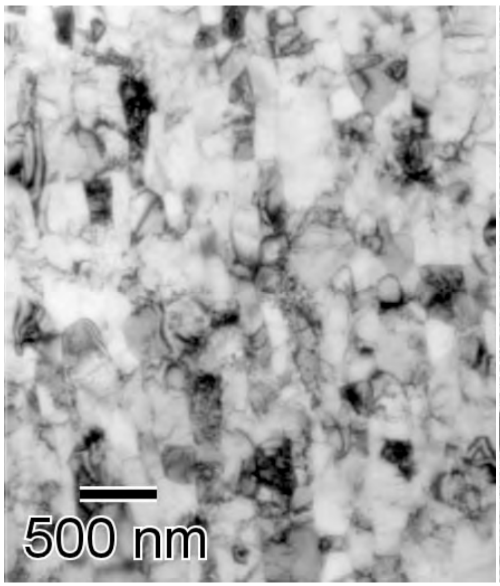


The presence of Ti and vacancy has a drastic effect in lowering the binding energy of oxygen in Fe *(C. L. Fu and M. Krcmar).*

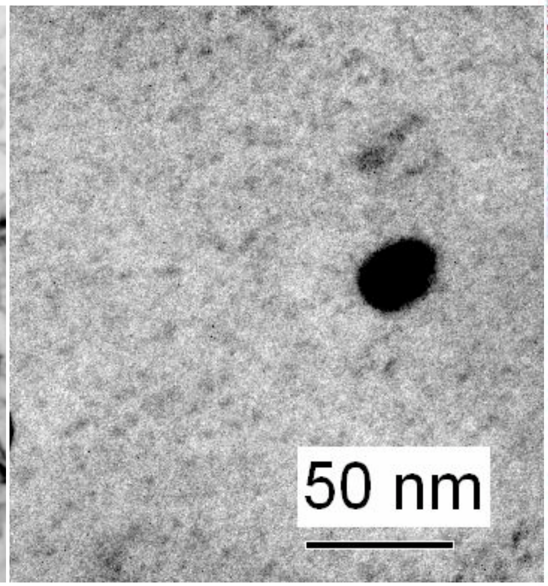
Nanostructuring Achieves Good Fracture Toughness and High-Strength Properties

NFA 14YWT Developed at ORNL

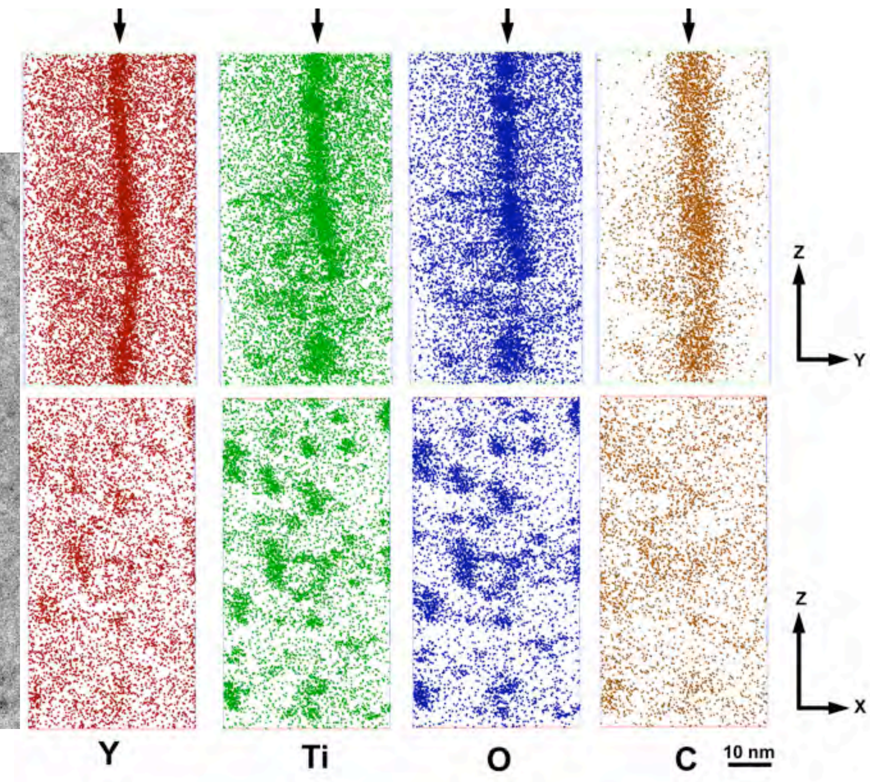
BF TEM



Fe M Jump Ratio

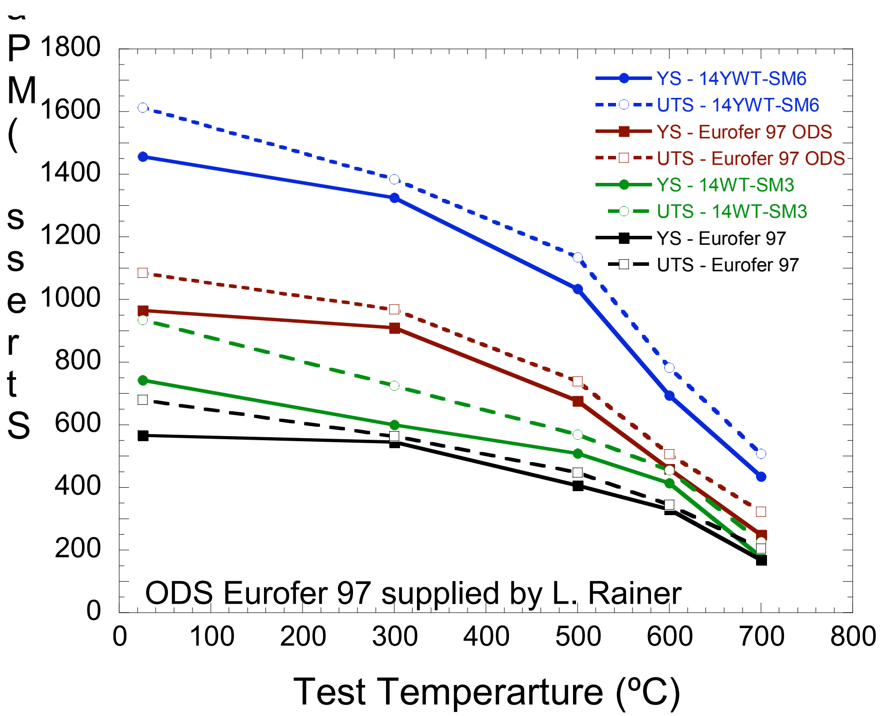


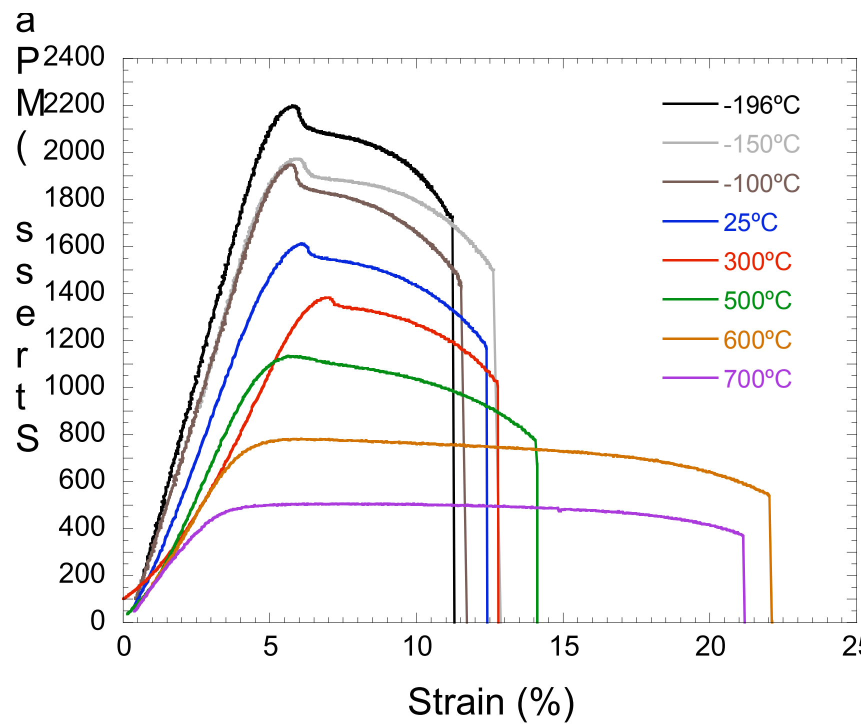
Grain boundary nucleation of NC



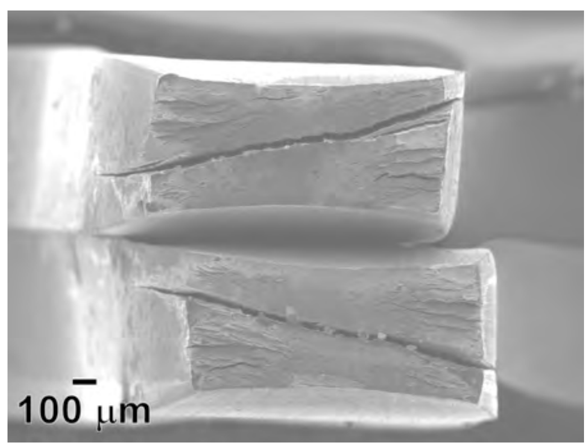
- Nano-size grain size with very high grain boundary interfacial area
- High number density of NC in-matrix with λ = 10-15 nm
- High number density of NC decorating grain boundaries

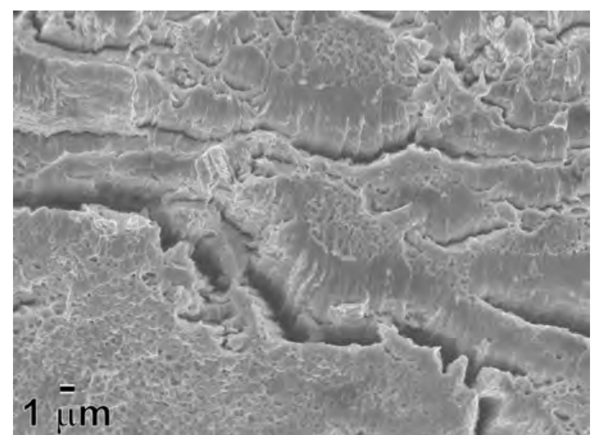
14YWT Shows High Strength and Some Ductility to -196ºC





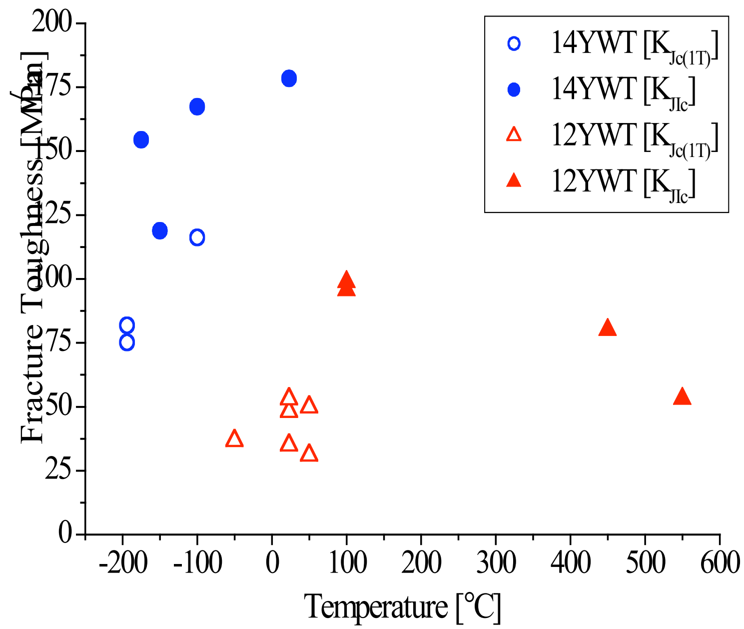
- At -196ºC ($\dot{\varepsilon} = 10^{-3}s^{-1}$)
  - mixed mode dimple rupture-cleavage failure
  - reduction in area = 43%
  - σ_f = 3.0 GPa
  - T.E. = ~7%

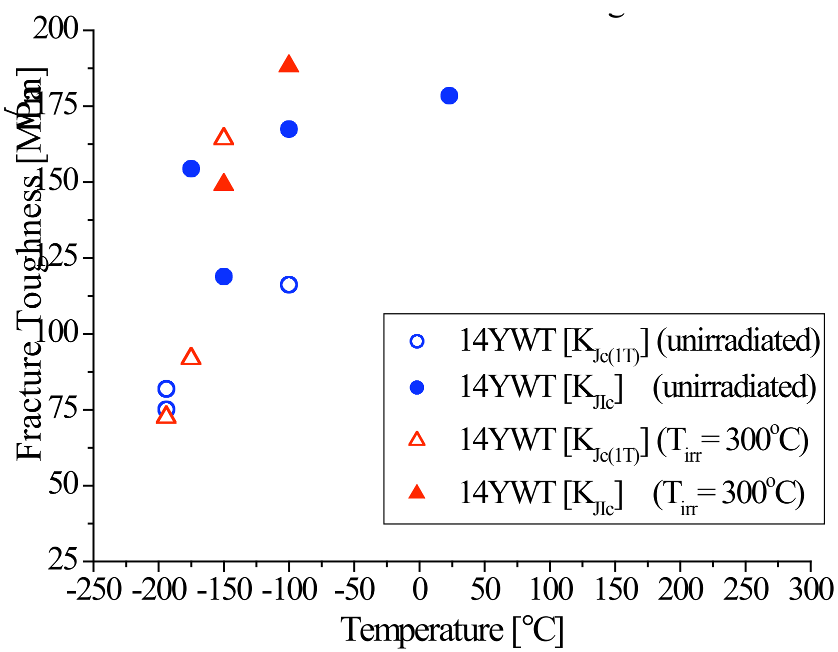




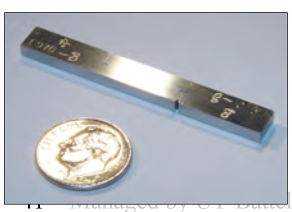
High Fracture Toughness Achieved in 14YWT

- The fracture toughness of 14YWT is much better than that of 12YWT
- The DBTT is shifted from ~75 ºC for 12YWT to -150 ºC for 14YWT



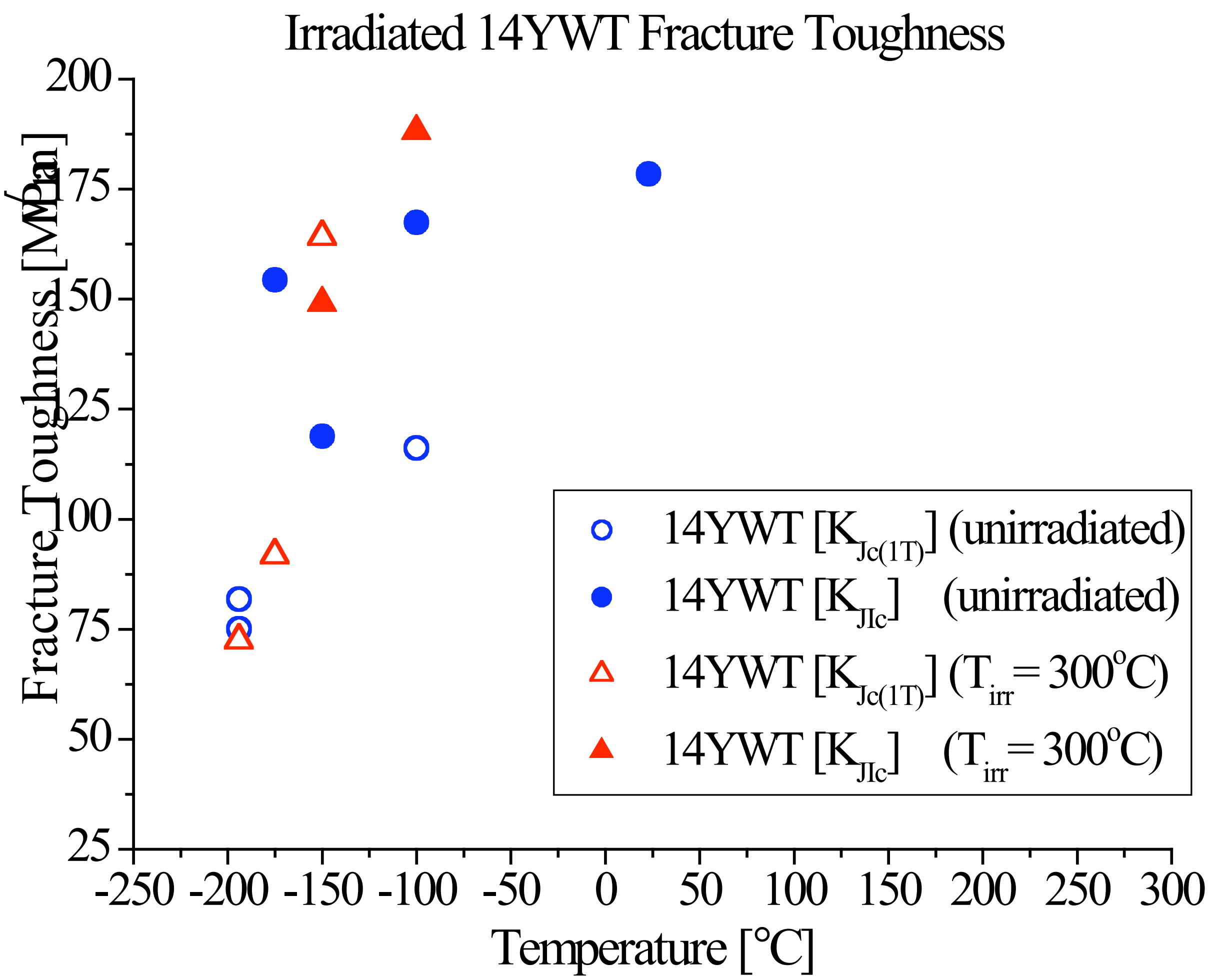


- Neutron irradiation to 1.5 dpa at 300ºC appears to slightly improve the fracture toughness above -150ºC
- More testing is required though…



- L-T Orientation
- Pre-cracked: crack length to width (a/w) ratio of 0.5
- Tested using the unloading compliance method (ASTM 1820-06)
- K_{Jc} for brittle cleavage calculated from critical J-integral at fracture, adjusted to 1-T reference specimen $K_{Jc(1T)}$
- K_{JIc} for ductile deformation behavior calculated from critical J-integral at onset of stable crack growth

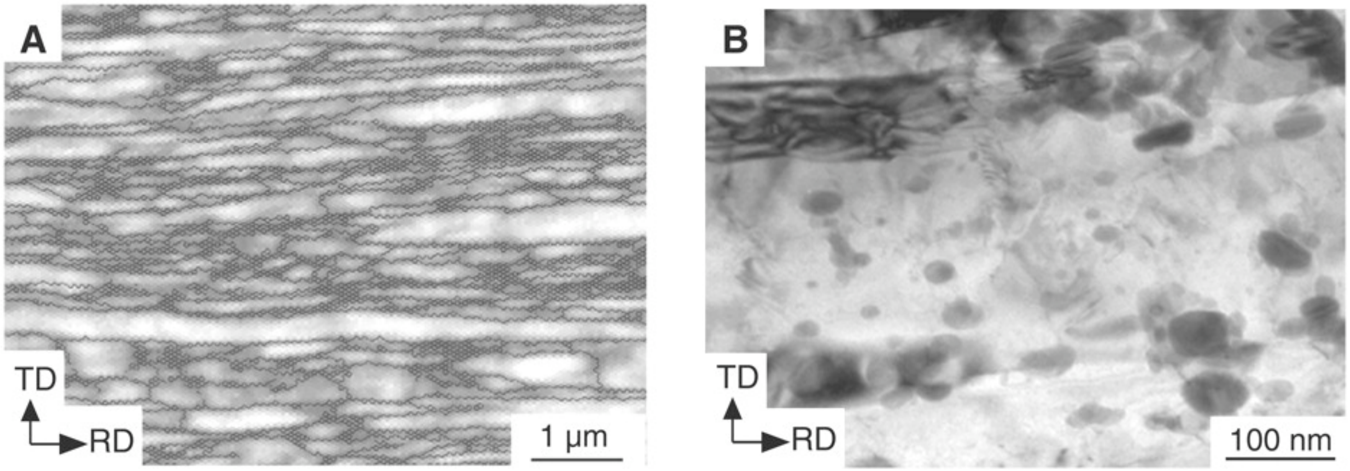
No DBTT shift was observed in 14YWT after irradiation at 300^{o}C to ~ 1.5 dpa

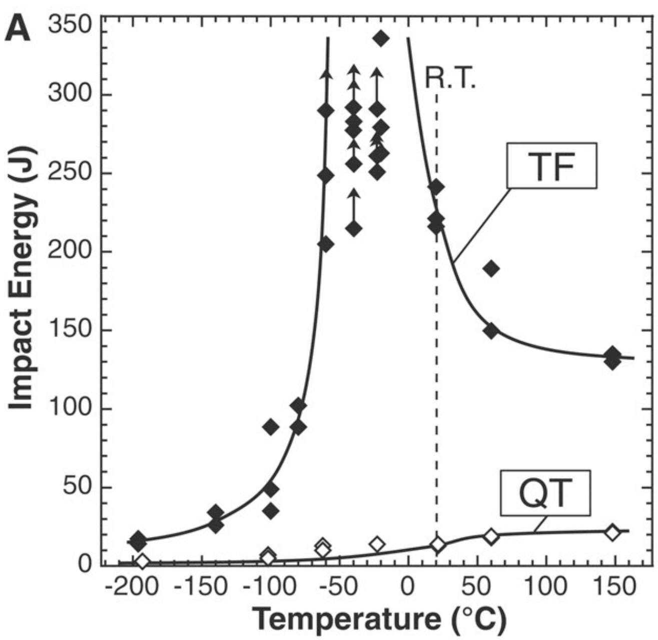


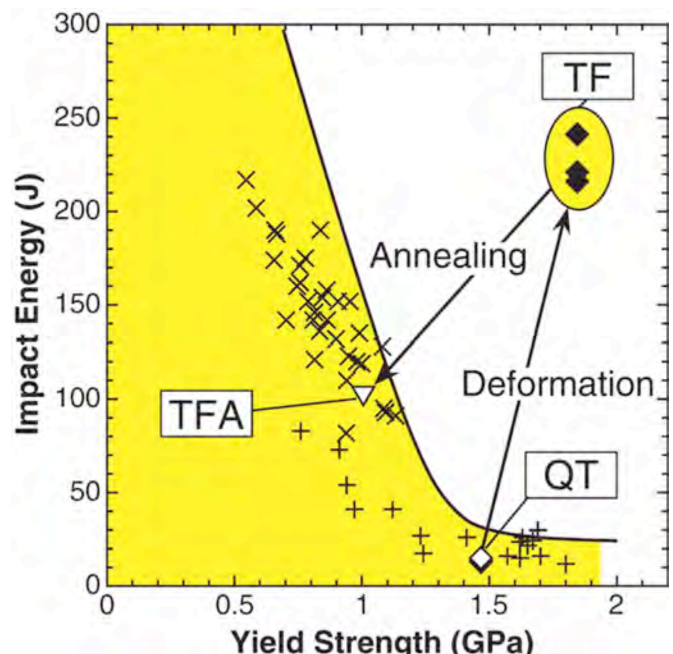
See M.A. Sokolov et al., poster R7.21

D.A. McClintock et al., ICFRM-13, to be published

Engineered laminate structure for ultra-strong, high toughness steels







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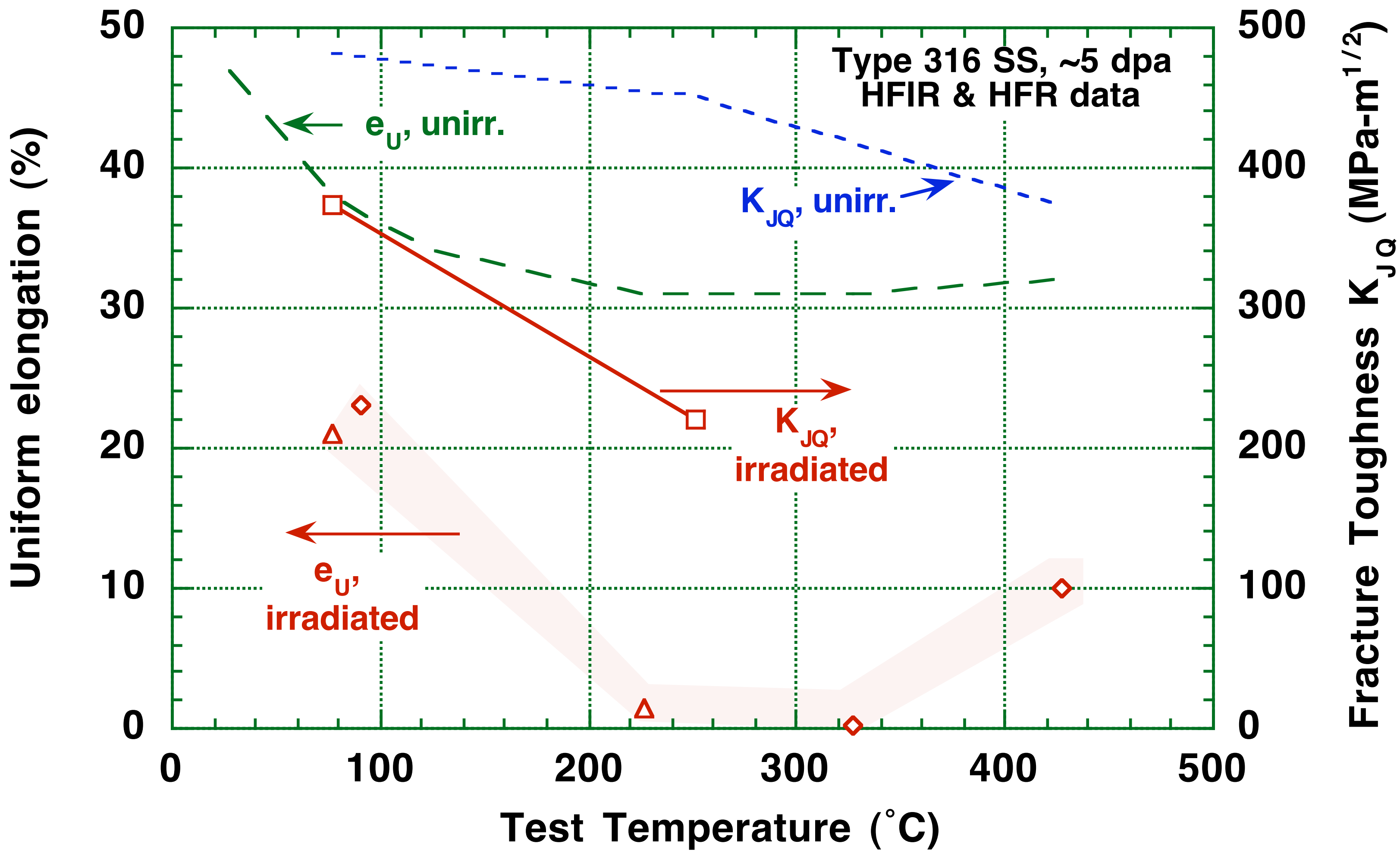
A. Kimura et al., Science 320 (2008) 1057

OAK RIDGE National Laboratory

Conclusions

- Existing structural materials are not ideal for advanced nuclear energy systems due to limited operating temperature windows
  - May produce technically viable design, but not with desired optimal economic attractiveness
- Substantial improvement in the performance of structural materials can be achieved in a timely manner with a science-based approach
- Design of nanoscale features in structural materials confers improved mechanical strength and radiation resistance
  - Such nanoscale alloy tailoring is vital for development of radiation-resistant structural materials for advanced fission reactors

Irradiation of Austenitic Stainless Steel in Mixed Spectrum Reactors causes Pronounced Loss in Elongation and Significant Reduction in Fracture Toughness

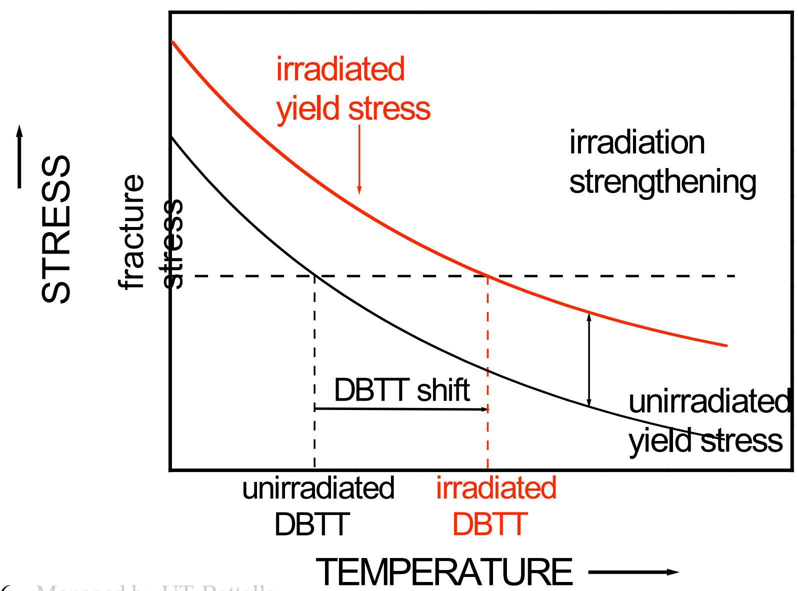


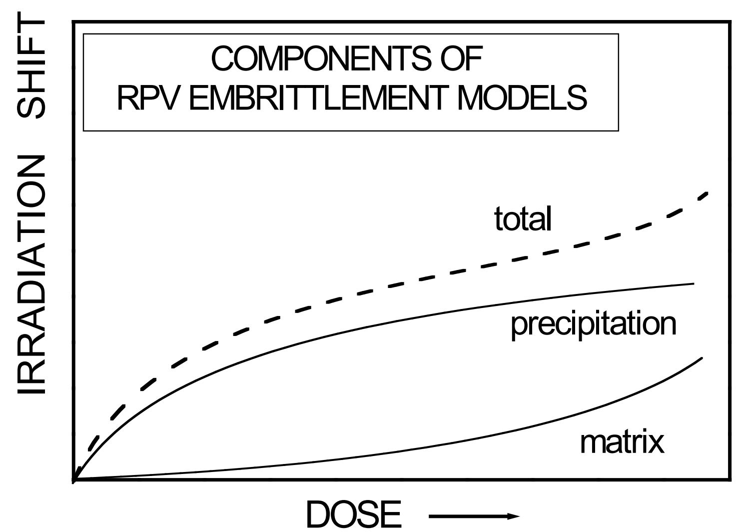
Fracture toughness embrittlement in irradiated metals

- **Ferritic steels** e.g. reactor pressure vessels (RPV)

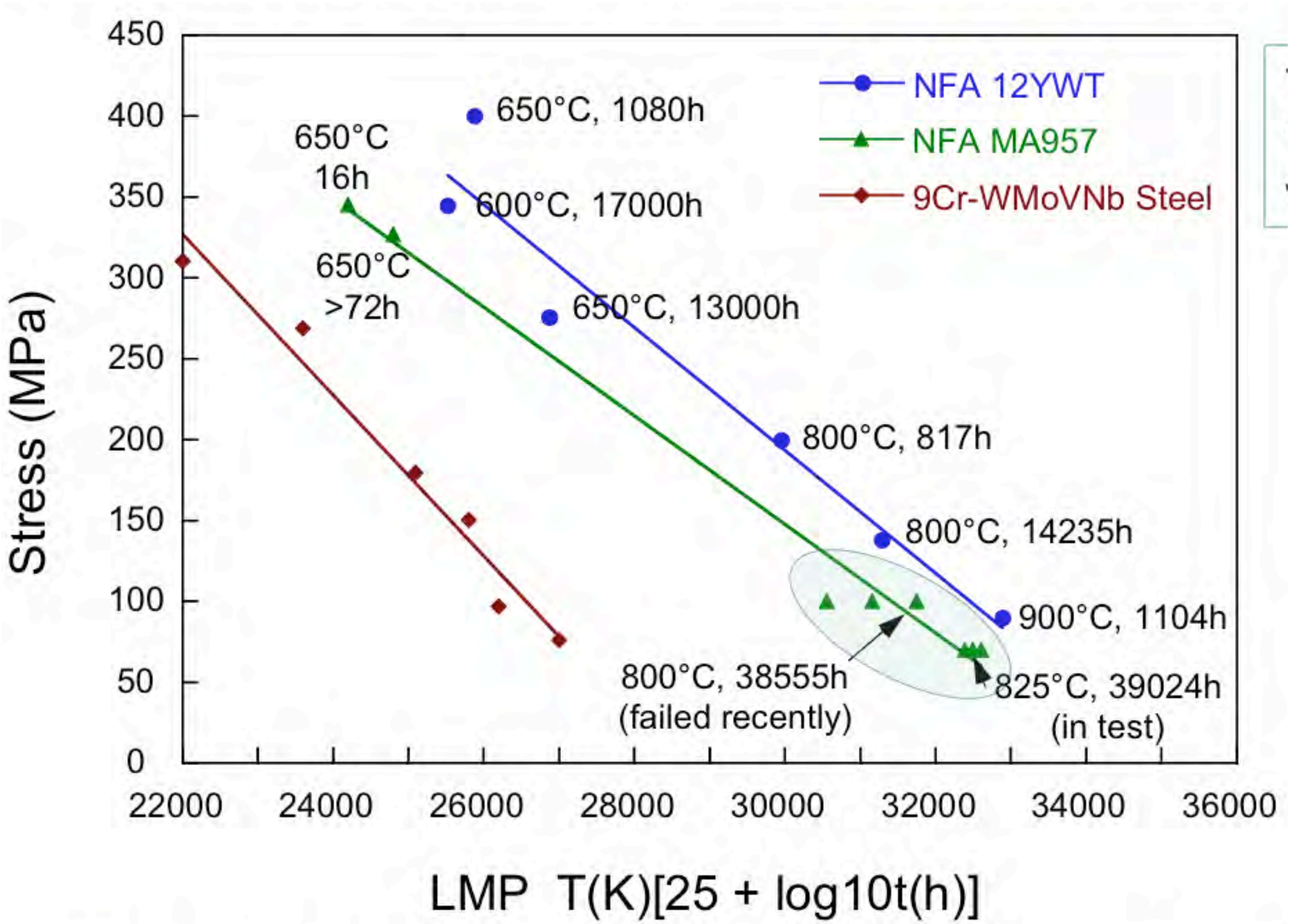
- low dose ($<10^{19}$ n cm^{-2}) and T ($\leq 300^oC$)
- DBTT increases and fracture toughness K_c decreases
- there is an additional component of hardening due to Cu-precipitates when small amounts of copper are present, e.g. in weld metal

⇒ important area of current research and long-term surveillance of existing fleet of fission reactor pressure vessels





NFA Show Significant Improvement in Creep Properties



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