

Research synergies for development of high performance structural materials

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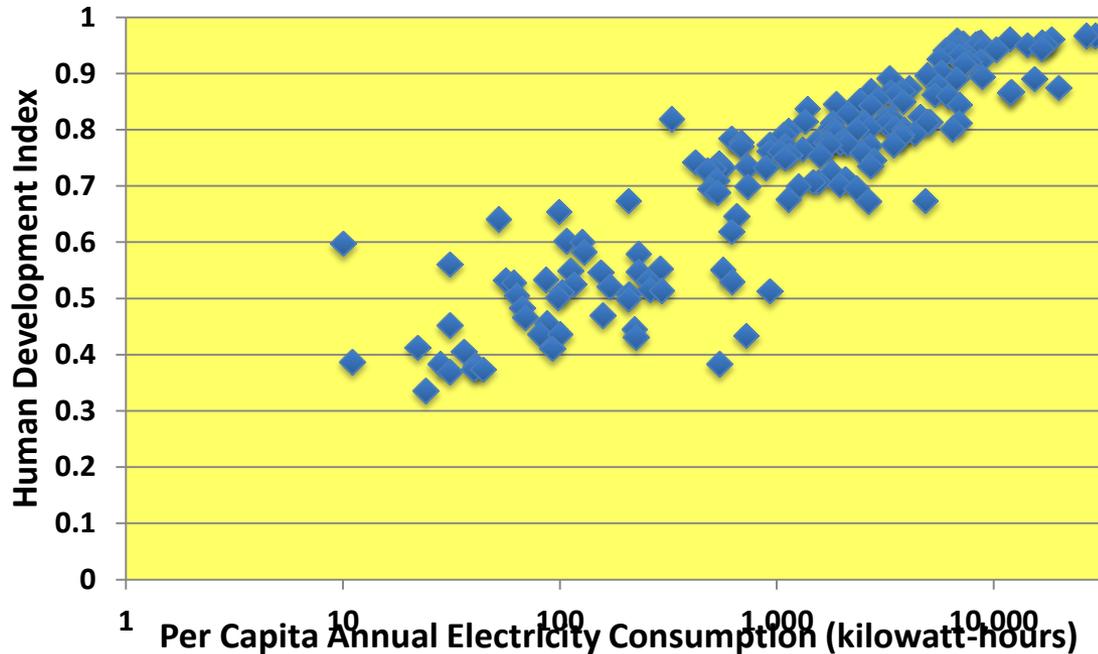
**MatISSE/JPNM workshop on cross-cutting issues in structural materials
R&D for future energy systems**

JRC-IET, Petten, The Netherlands

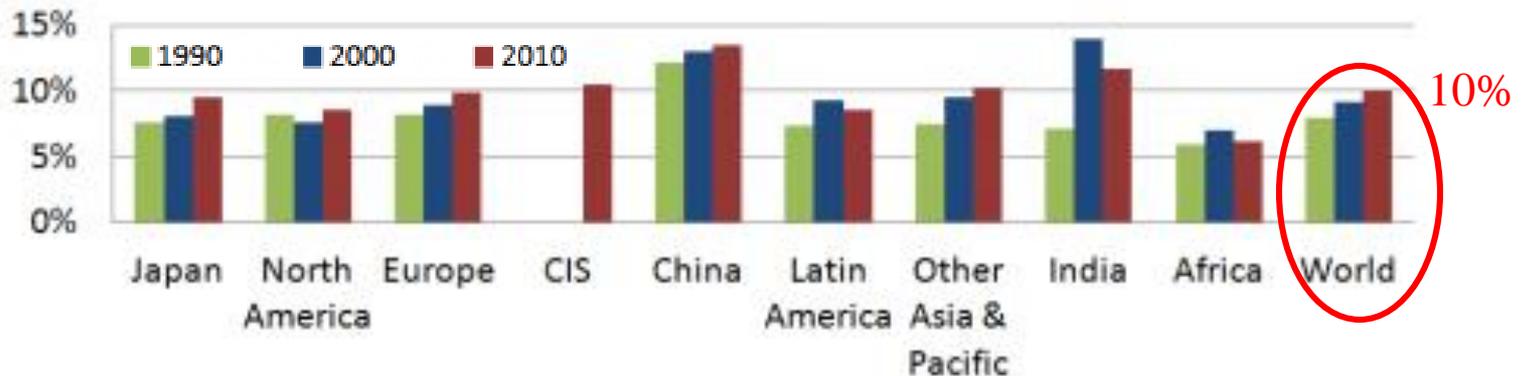
Nov. 25-26, 2015

Reliable and Stable Energy is of High Importance for Economic Development

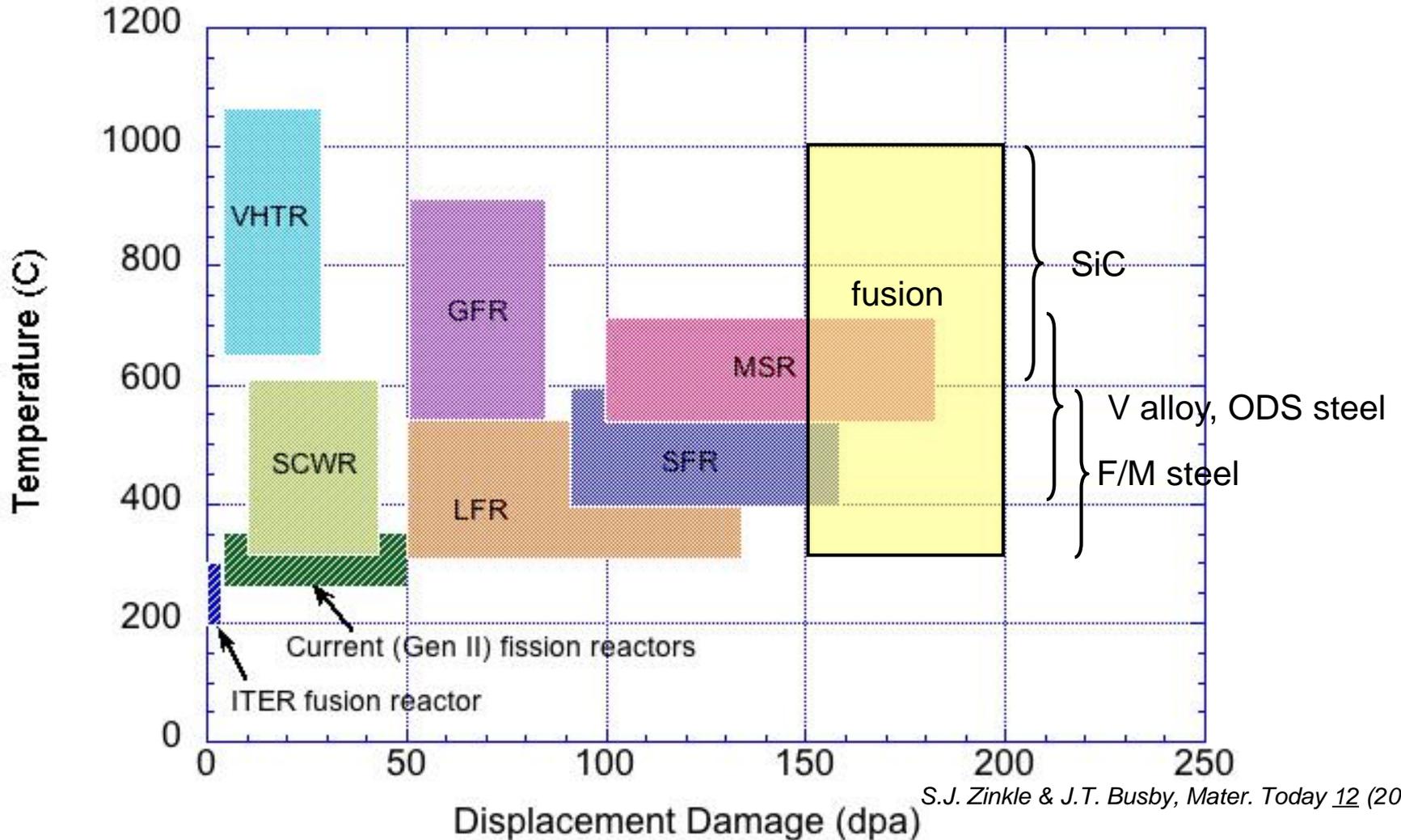
Quality of Life is Linked to Abundant Electricity



Consumer energy expenditures per share of GDP in different world regions

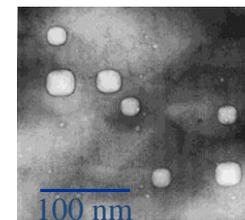
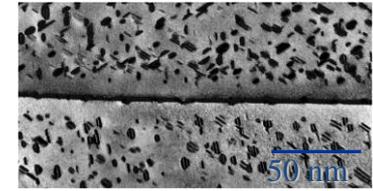
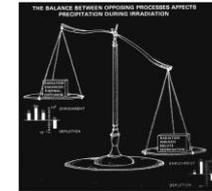
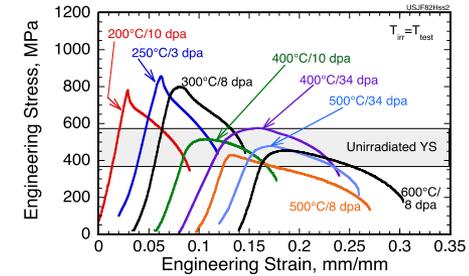


Comparison of Gen IV and Fusion Structural Materials Environments



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)**

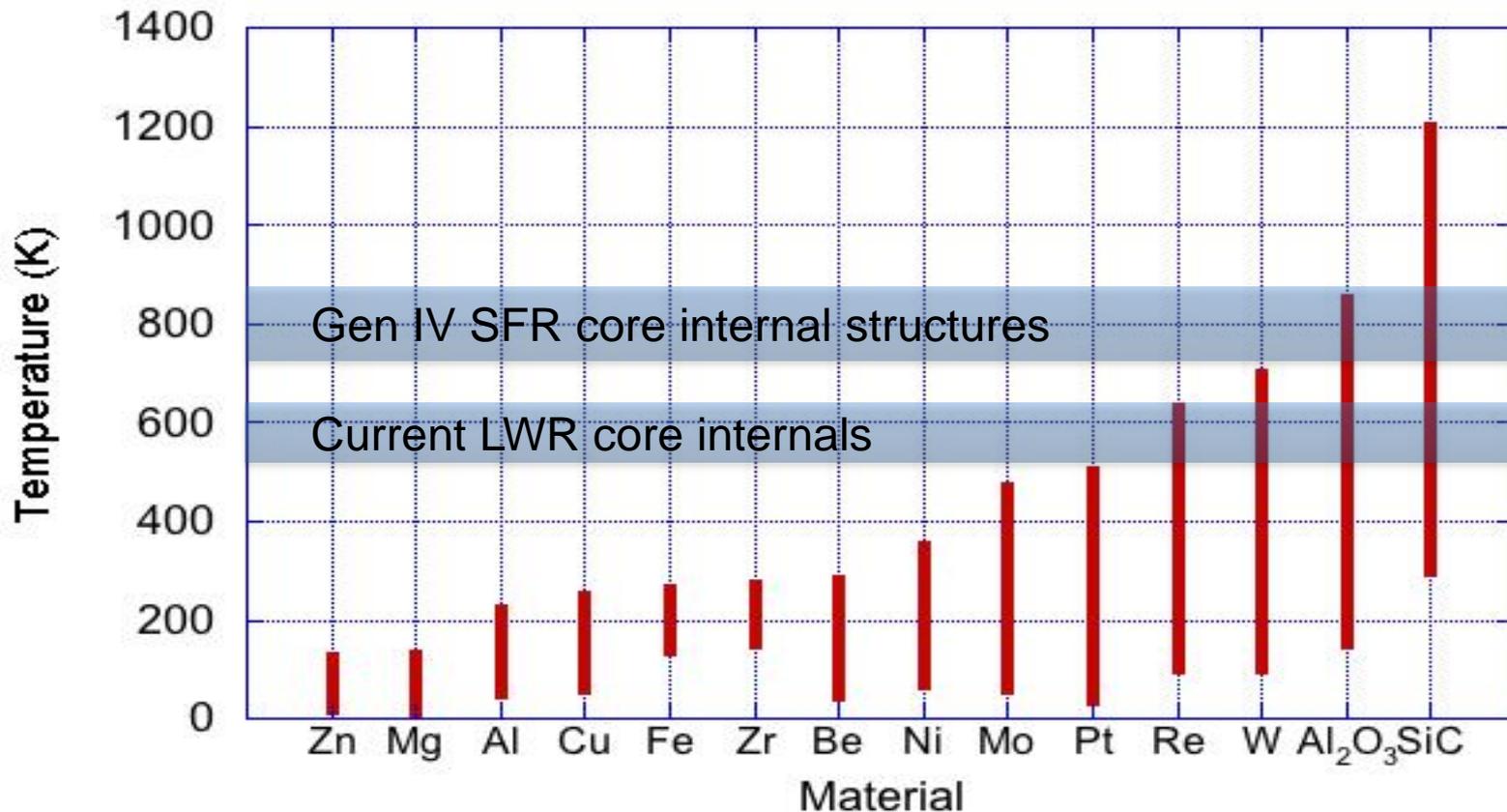


Options for designing radiation resistance

- Three general strategies for radiation resistance can be envisioned:
 - Utilize materials with negligible point defect mobility at desired operating temperatures
 - Amorphization with an accompanying volume change may occur if all point defects are immobile => select temperature range where vacancies are immobile but interstitials are mobile
 - Use materials with intrinsic resistance to radiation damage accumulation (e.g., BCC alloys, high entropy alloys?, noncrystalline materials?)
 - Materials with a high density of nanoscale recombination centers
 - Volumetrically-distributed precipitates or nanolayered structures
 - In many cases, there is an opportunity to use computational thermodynamics to purposefully design high performance radiation-resistant alloys

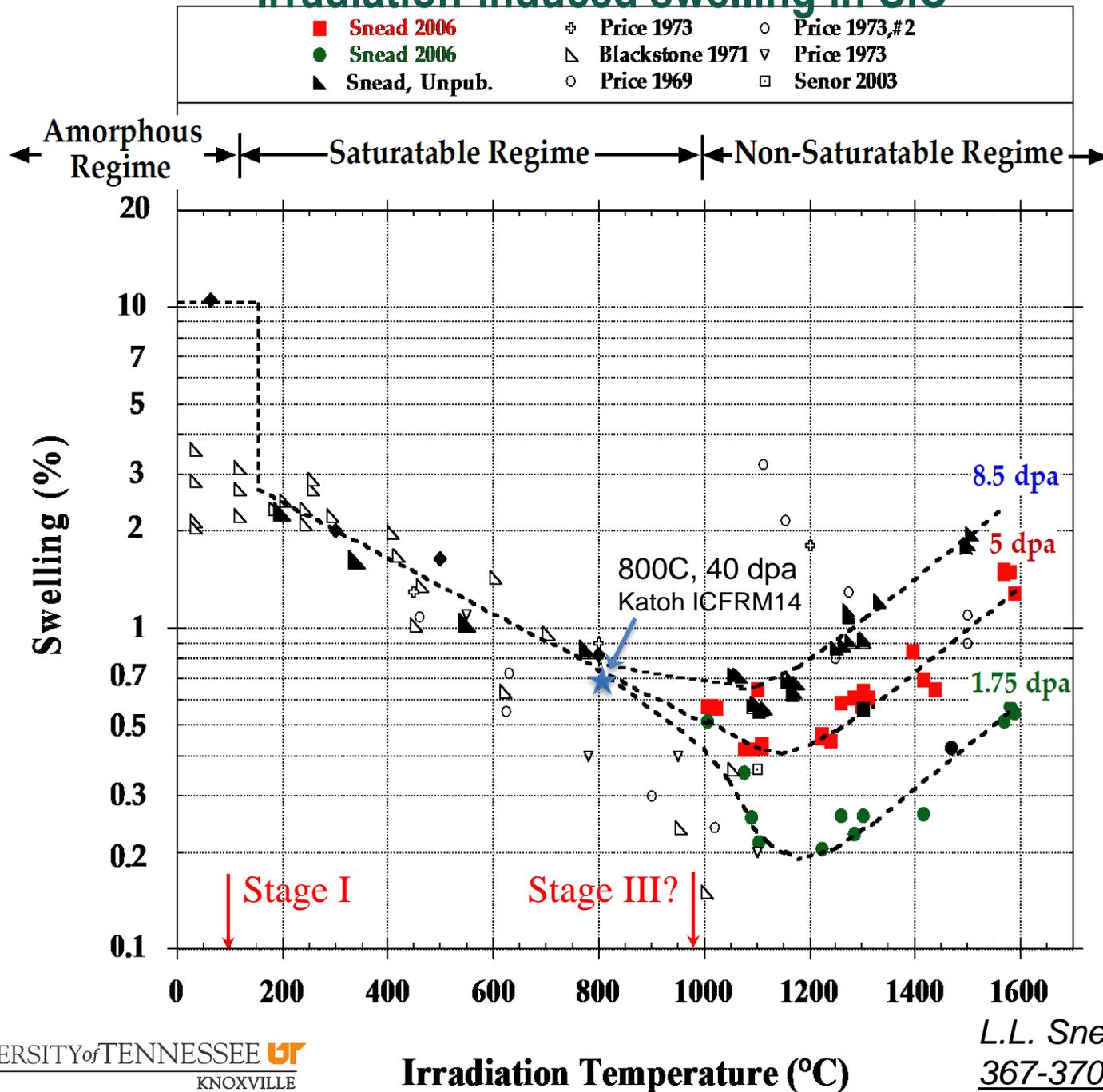
Approaches for radiation resistance 1: Immobile defects

- Defect accumulation is limited if one or more defect types are immobile
 - Utilize materials with negligible point defect mobility at desired operating temperatures
 - A key potential consequence (particularly in ordered alloys and ceramics) is amorphization, with accompanying significant volumetric and property changes



- Regime with intrinsically high point defect recombination typically occurs at too low of temperatures for power generation applications (except SiC and possibly Al₂O₃, W, Re)

Irradiation-induced swelling in SiC



SiC/SiC composites are now being qualified for jet turbines



Turbine shrouds using SiC/SiC

- Joint venture by GE and Snecma
 - 1st deployments on Airbus 320neo (2016) and Boeing 737 MAX (2017)
- Two new SiC fiber and CMC fabrication plants to be built in USA
- Higher temperature and lower weight will produce ~15% fuel savings
 - Should spur development of improved SiC fibers and lower cost composites for other applications

GE Successfully Tests World's First Rotating Ceramic Matrix Composite Material for Next-Gen Combat Engine

F414 low-pressure turbine blades prove silicon carbide CMC material for unprecedented deployment in GE's adaptive cycle combat engine

February 10, 2015

CINCINNATI, OH - February 10, 2015 - GE Aviation successfully tested the world's first non-static set of light-weight, ceramic matrix composite (CMC) parts by running rotating low-pressure turbine blades in a F414 turbofan demonstrator engine designed to further validate the heat-resistant material for high-stress operation in GE's next-generation Adaptive Engine Technology Demonstrator (AETD) program currently in deve

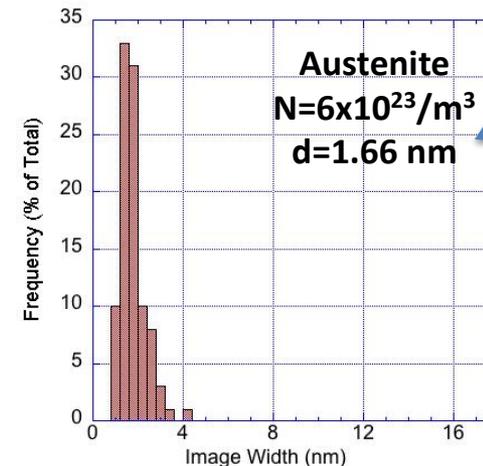
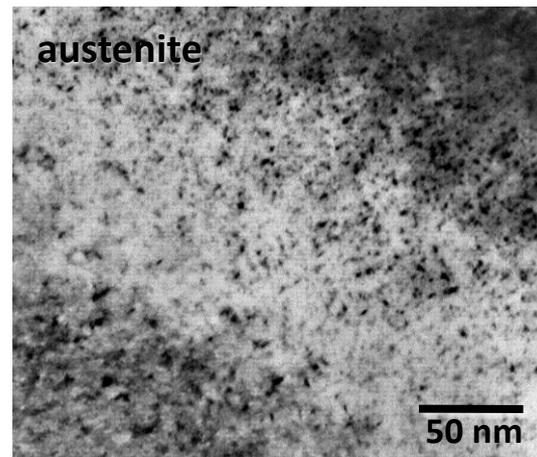
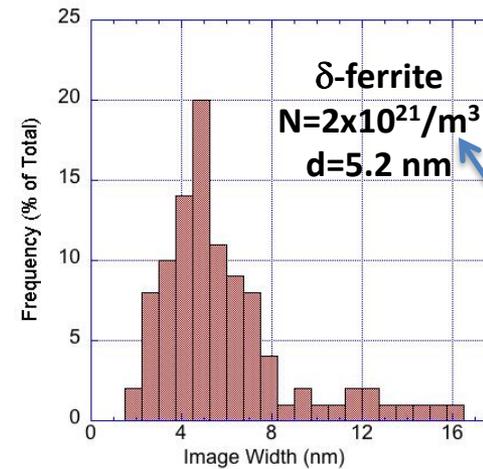
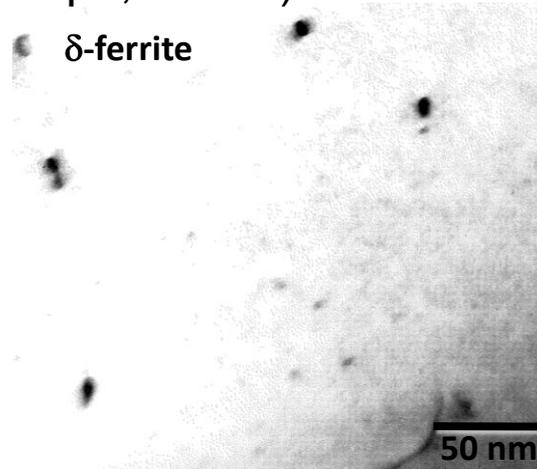
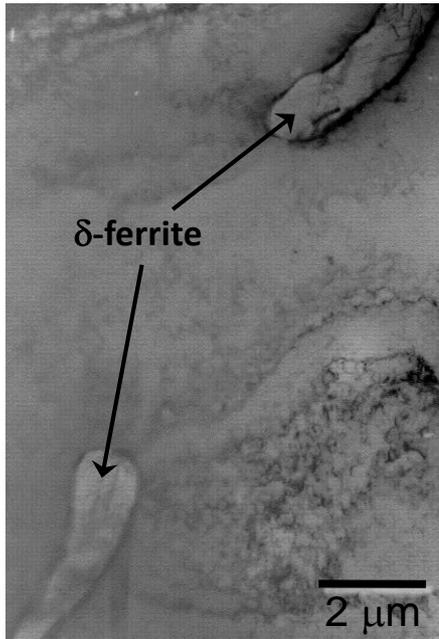


Flight test of LEAP engine with SiC/SiC parts

Approaches for radiation resistance 2: Utilize matrix phases that are resistant to defect accumulation (e.g., BCC or noncrystalline phases)

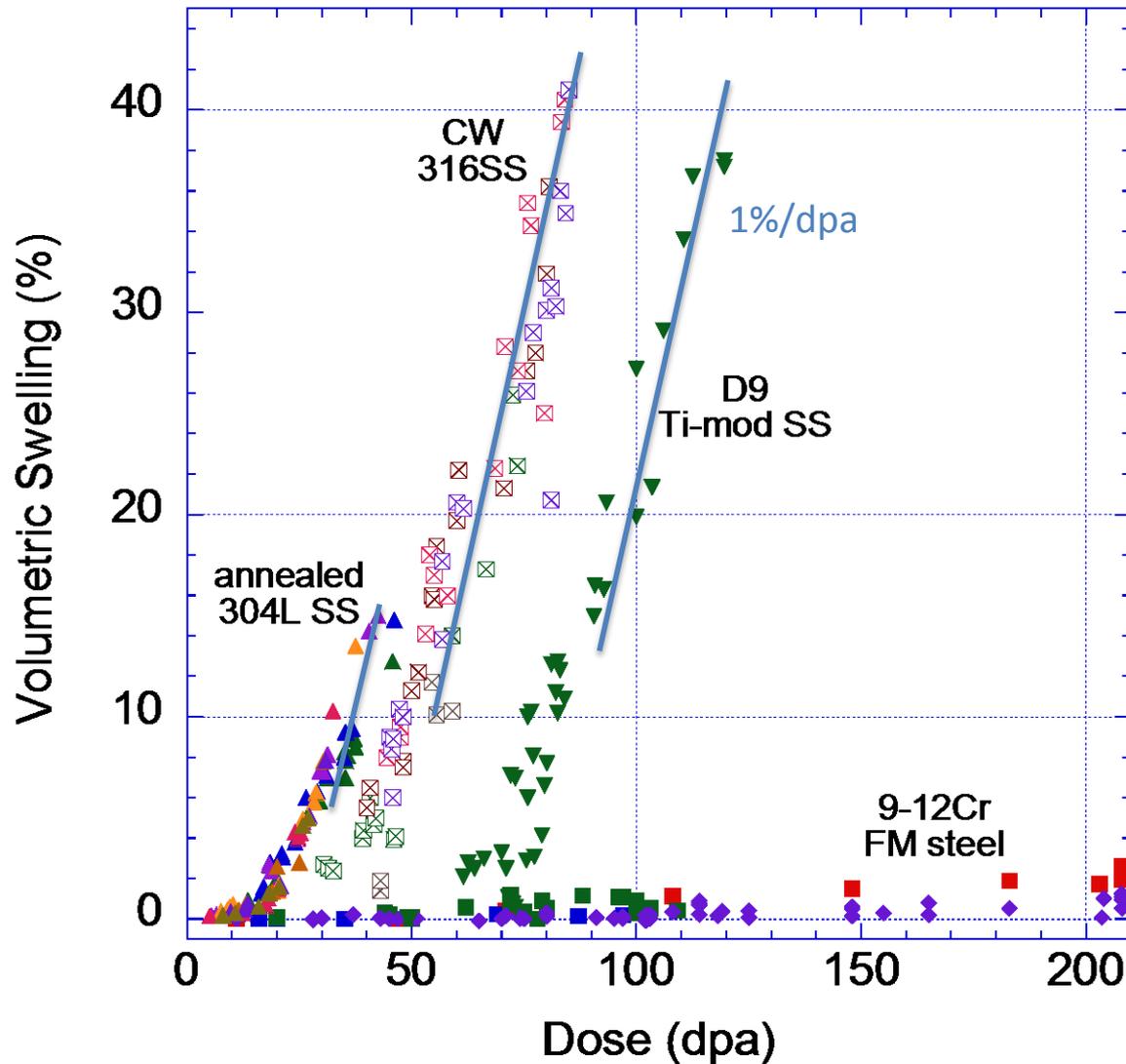
Comparison of defect cluster formation in neutron irradiated austenitic and ferritic stainless steel (0.065 dpa, 120°C)

Type 308 stainless steel weld metal

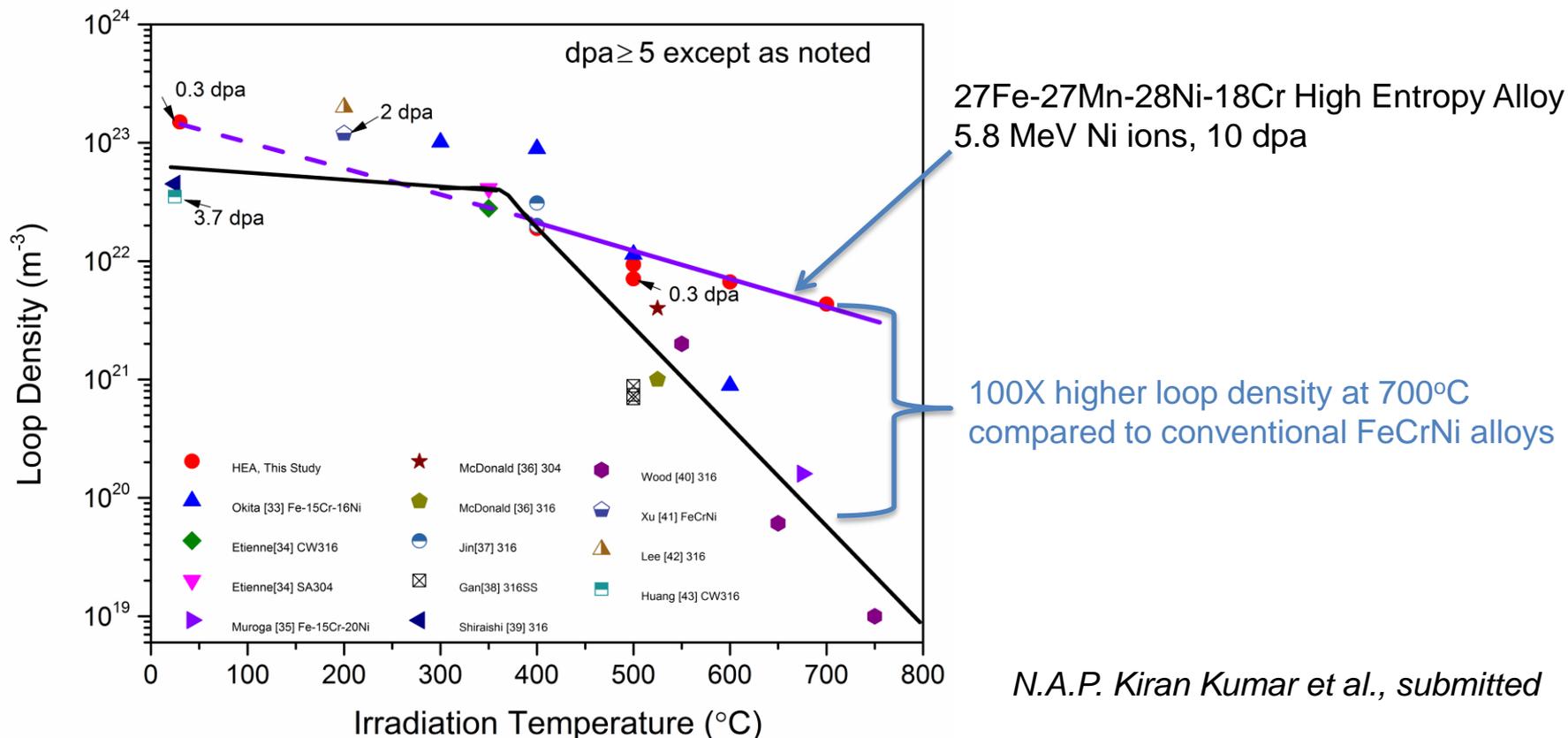


30x lower visible defect accumulation for BCC phase

Comparison of Volumetric Swelling in Fast Fission Reactor Irradiated Austenitic & Ferritic-Martensitic Steels



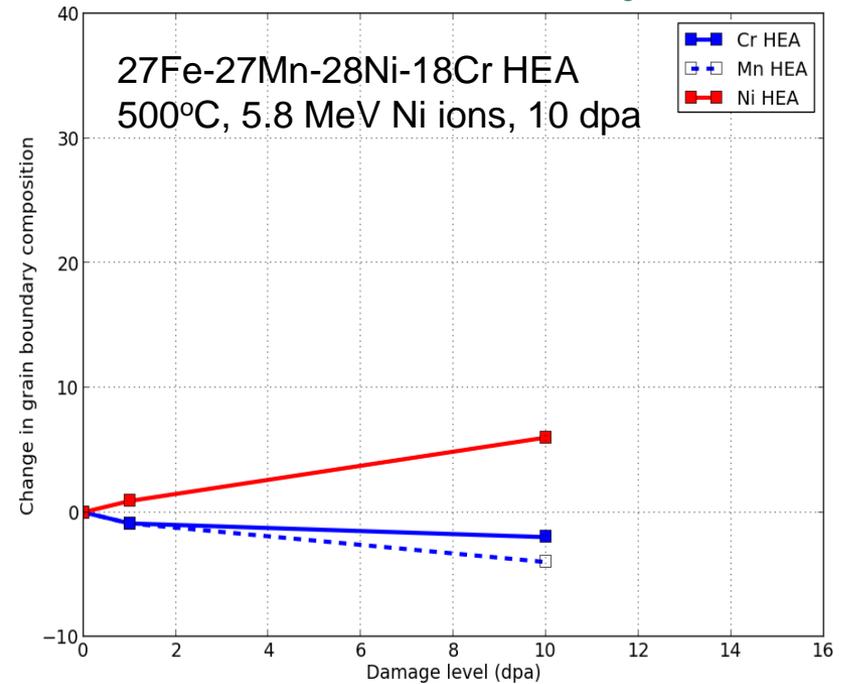
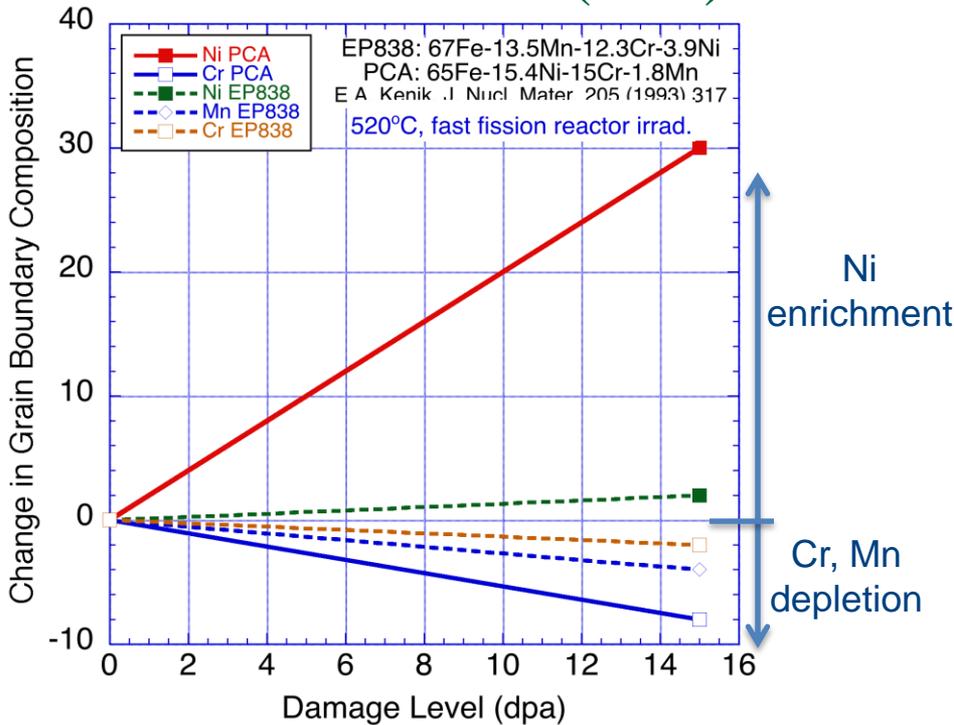
Dislocation loop temperature dependence is less pronounced in irradiated Fe-Cr-Ni-Mn HEA FCC alloy



High temperature loop density is much higher and loop size much smaller for High Entropy Alloy compared to traditional FCC FeCrNi(Mn) alloys

=> HEA effect on solute diffusivities?

Radiation Induced Solute Segregation in Irradiated Fe-Cr-Ni-(Mn) Face Centered Cubic Alloys



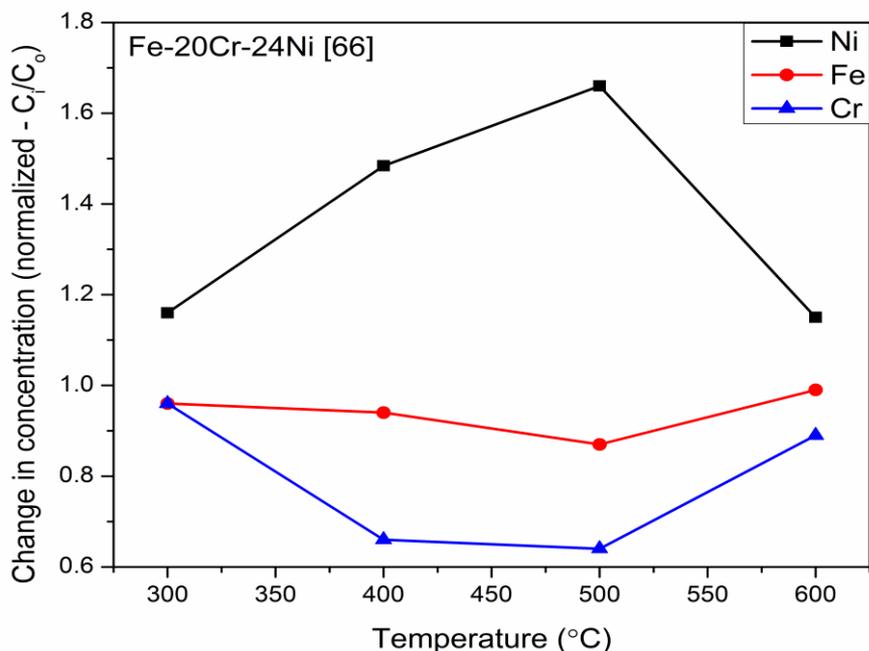
N.A.P. Kiran Kumar et al., submitted

RIS behavior for High Entropy Alloys is more sluggish than traditional FCC FeCrNi(Mn) Alloys

=> HEA effect on solute diffusivities

Depletion of solute A if $\frac{D_A^v}{D_B^v} - \frac{D_A^i}{D_B^i} > 0$

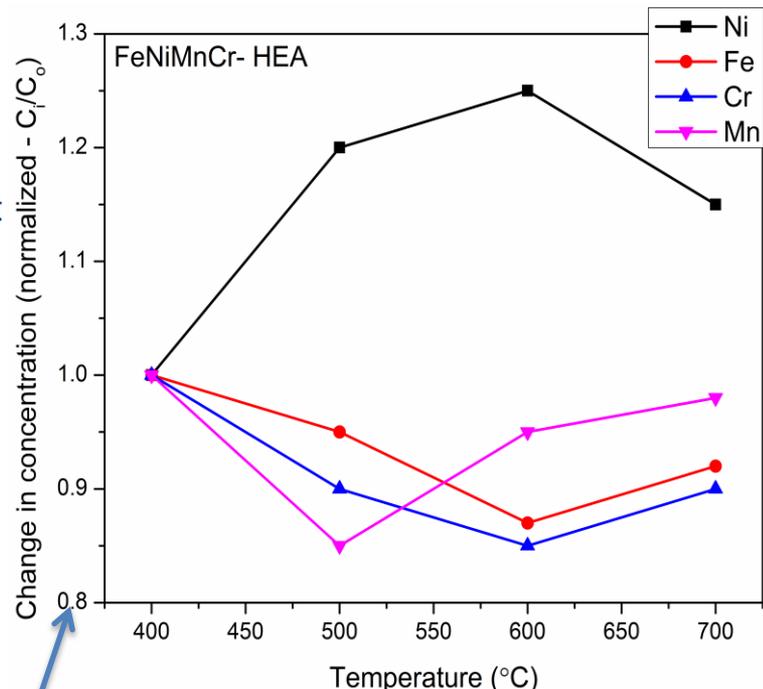
Radiation Induced Solute Segregation in Ion-Irradiated Fe-Cr-Ni-(Mn) Face Centered Cubic Alloys



Ni
enrichment

Cr, Fe
depletion

Note magnified scale



N.A.P. Kiran Kumar et al., submitted

Qualitatively similar RIS behavior for High Entropy Alloys but magnitude is lower and shifted to higher temperatures than traditional FCC FeCrNi(Mn) alloys

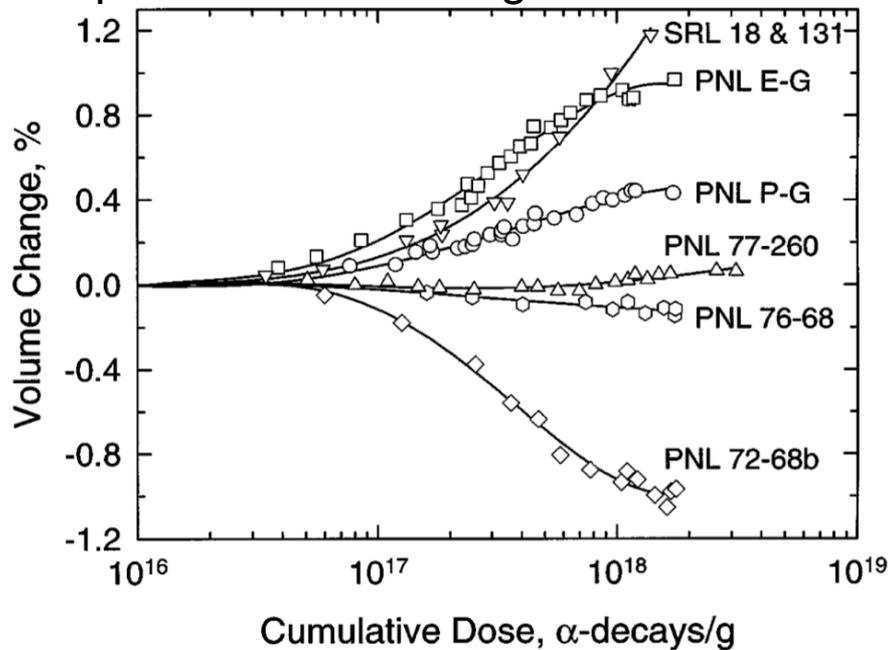
=> HEA effect on solute diffusivities?

Another rad-resistant possibility (2): noncrystalline phases

NB: many glasses exhibit variable stability to irradiation
Acceptable stability was observed during irradiation of "BAM-11" ($Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$) metallic glass

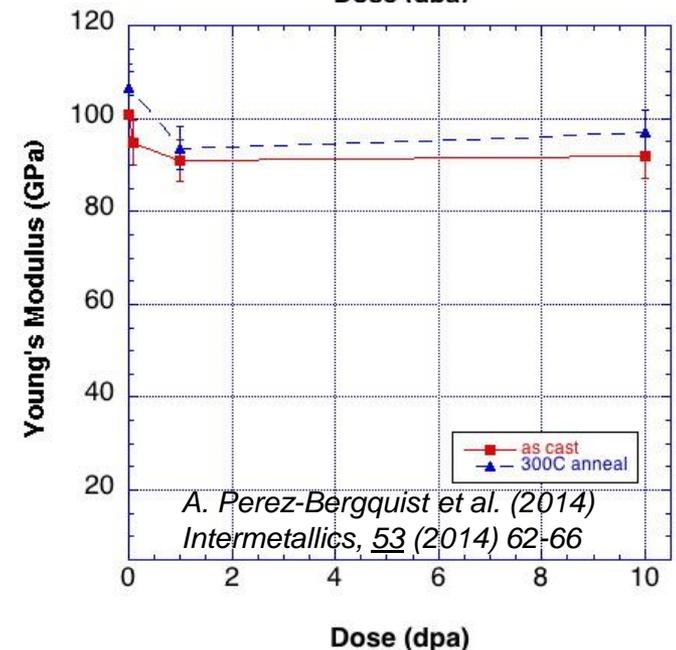
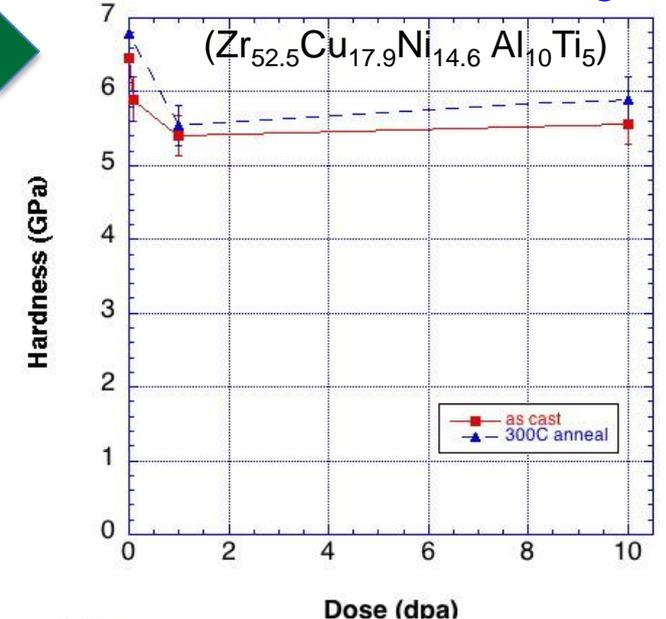
3 MeV Ni ion irradi. BAM-11 glass

Volume changes in several actinide-doped nuclear waste glasses



W.J. Weber et al., *J. Mater. Res.* 12 (1997) 1946

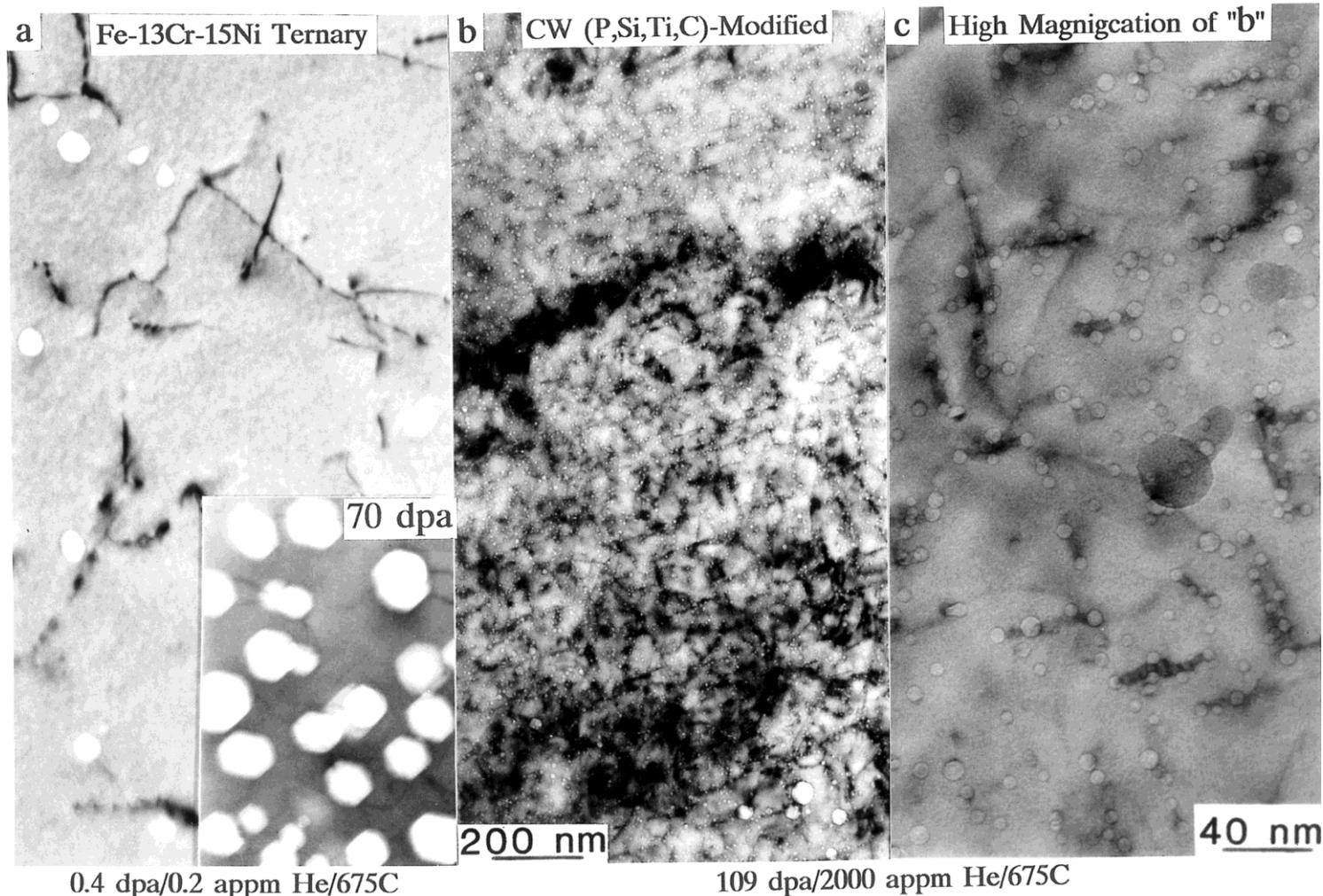
Numerous short-range ordered states can occur in glasses; good stability occurs if "radiation-disrupted" SRO is similar to initial SRO



A. Perez-Bergquist et al. (2014)
Intermetallics, 53 (2014) 62-66

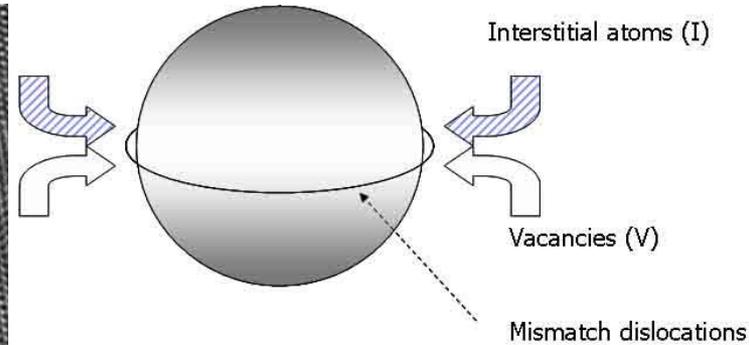
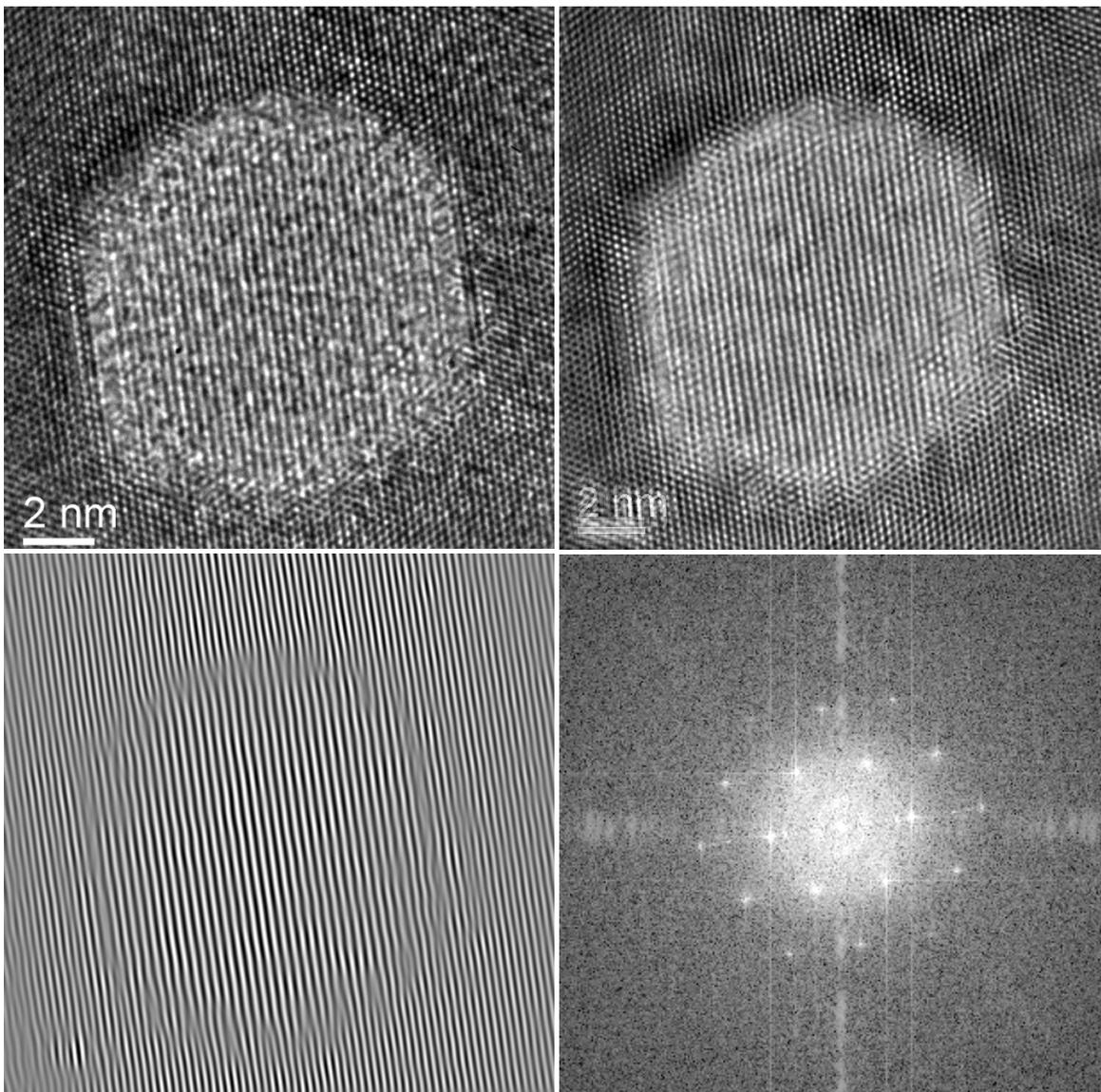
Approaches for radiation resistance 3: High sink strength

- “Traditional mainstream” strategy for radiation resistance is based on a high density of nanoscale precipitates or particles (e.g., Ti-modified austenitic stainless steel)
 - Nanoscale multilayer interfaces is an analogous approach



Dual-beam Ni+He irradiation

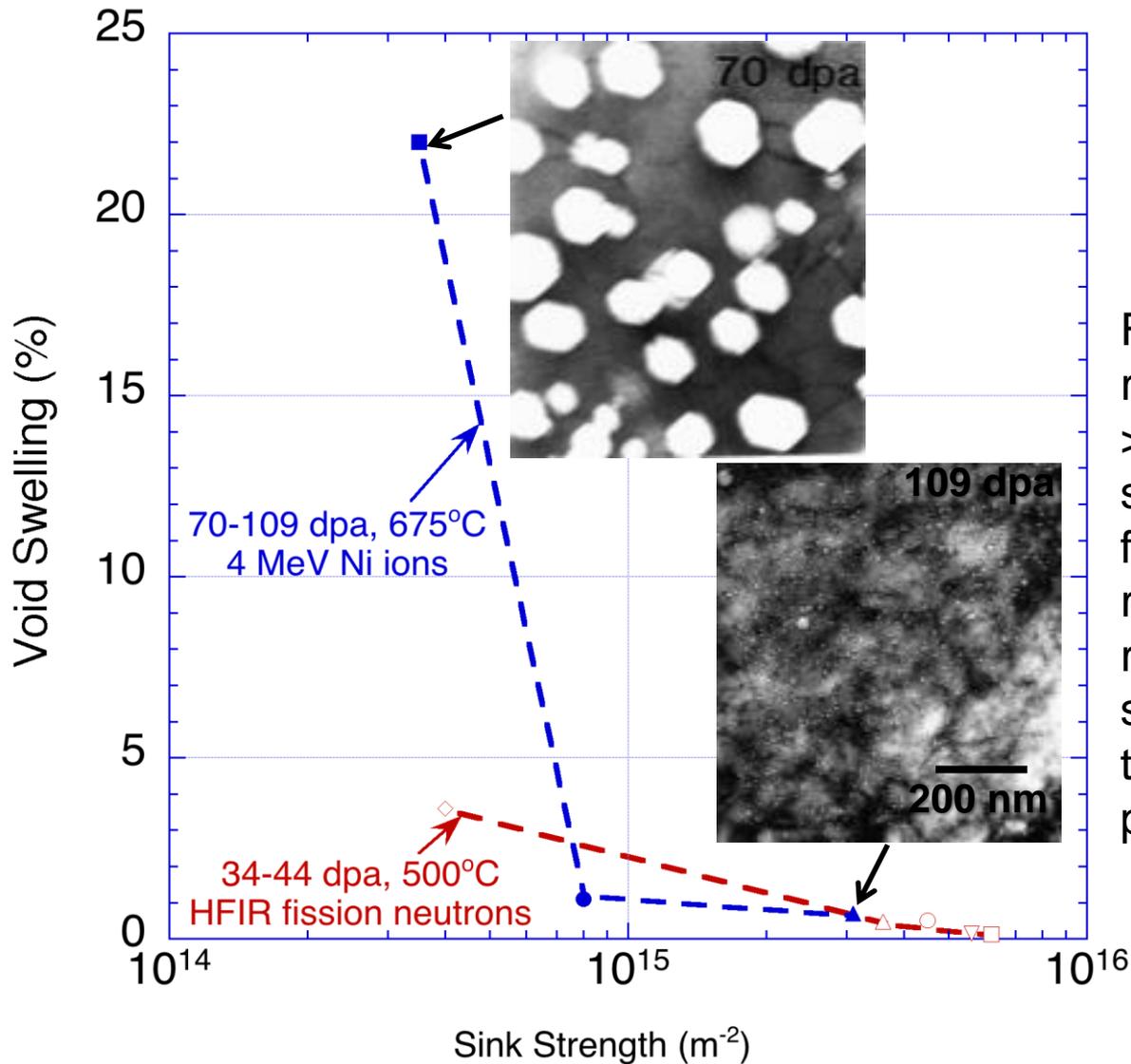
Mechanisms of excellent irradiation resistance: oxide dispersion strengthening (ODS) particles



- ◆ **Semi-coherent interface acts as mutual recombination site for point defects**
- ◆ **Very high particle densities can be achieved for ODS steels (much higher than conventional precipitates)**

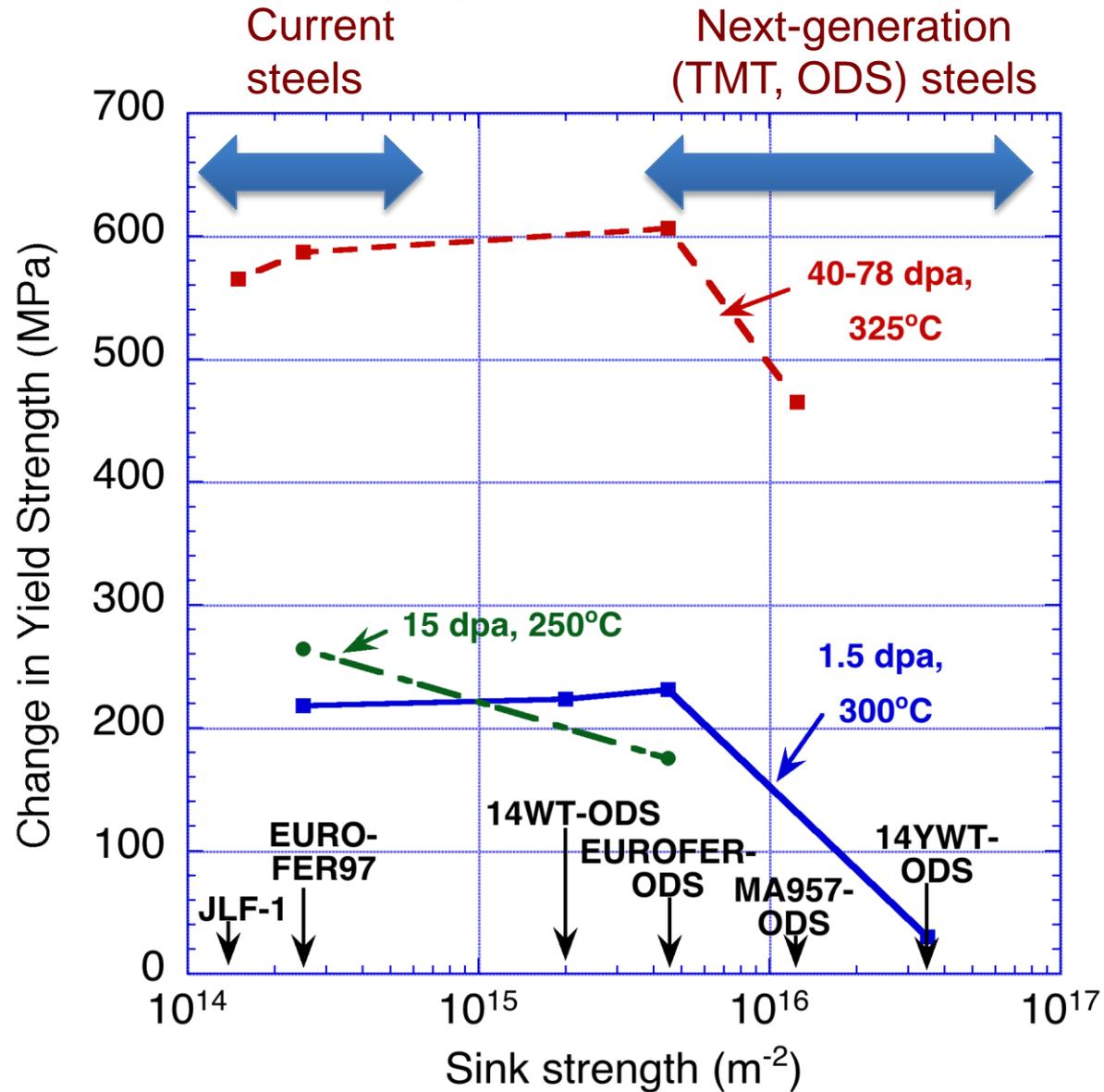
P. Dou, Chongqing Univ., 2nd Asia Nuclear Fuel Conf., Sendai, Japan, Sept. 2014

Effect of Sink Strength on the Volumetric Void Swelling of Irradiated FeCrNi Austenitic Alloys

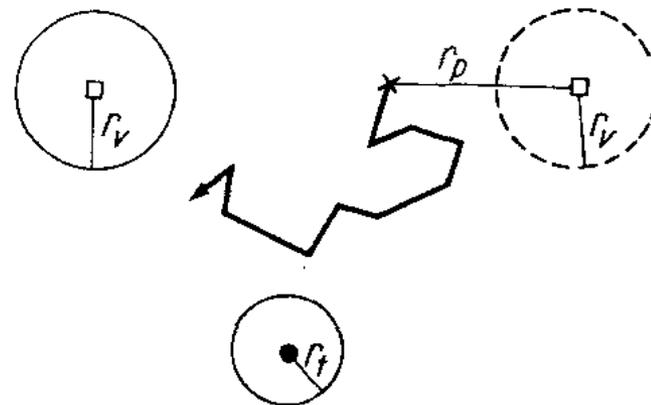
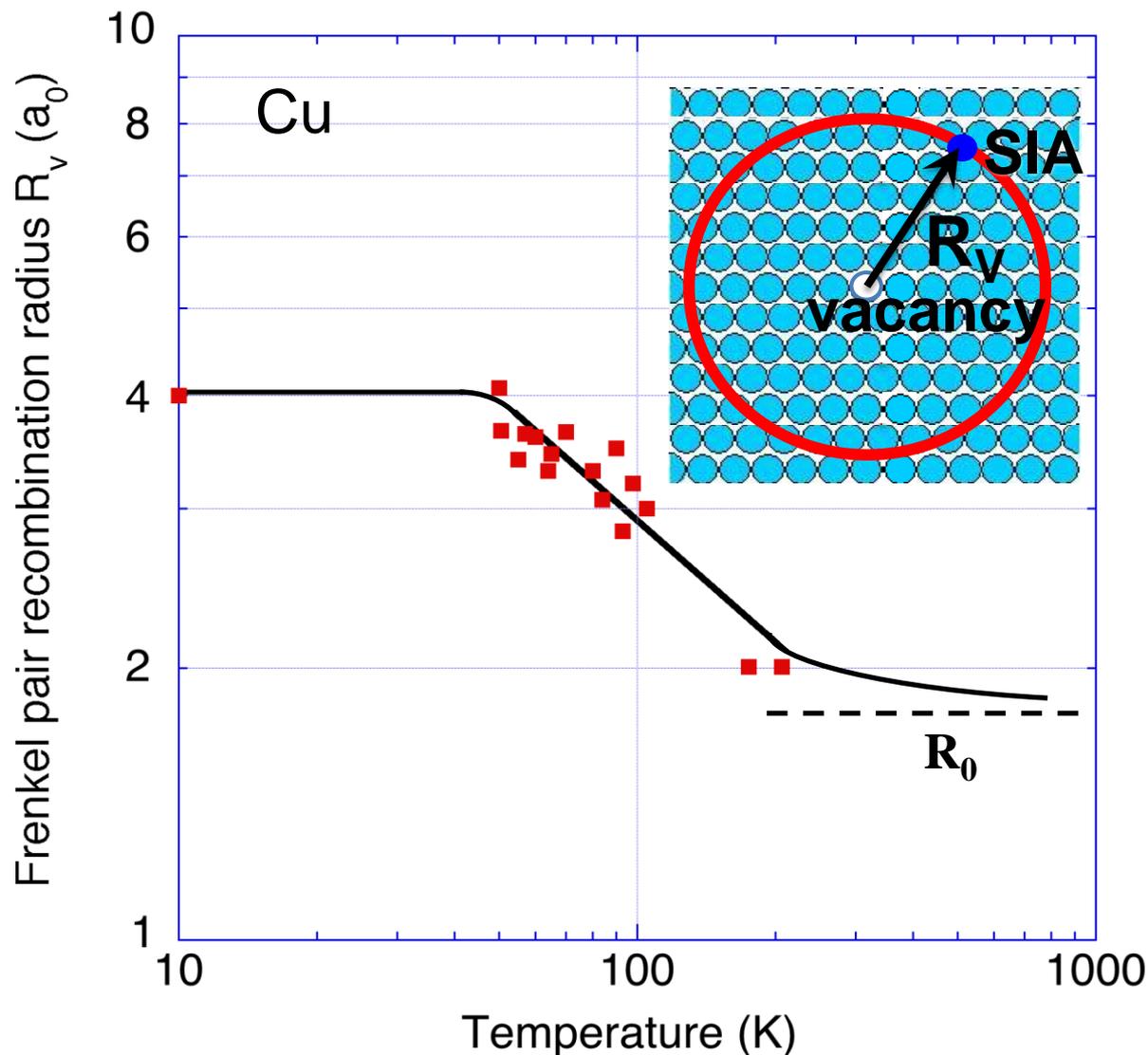


For void swelling resistance, sink strengths $>10^{15}/m^2$ are generally sufficient for light water fission reactors; fusion reactor irradiation may require even higher sink strengths ($>10^{16}/m^2$?) due to transmutant He production

Effect of Initial Sink Strength on the Radiation Hardening of Ferritic/martensitic Steels



Sink spacings approaching the spontaneous defect recombination distance will enhance i-v recombination



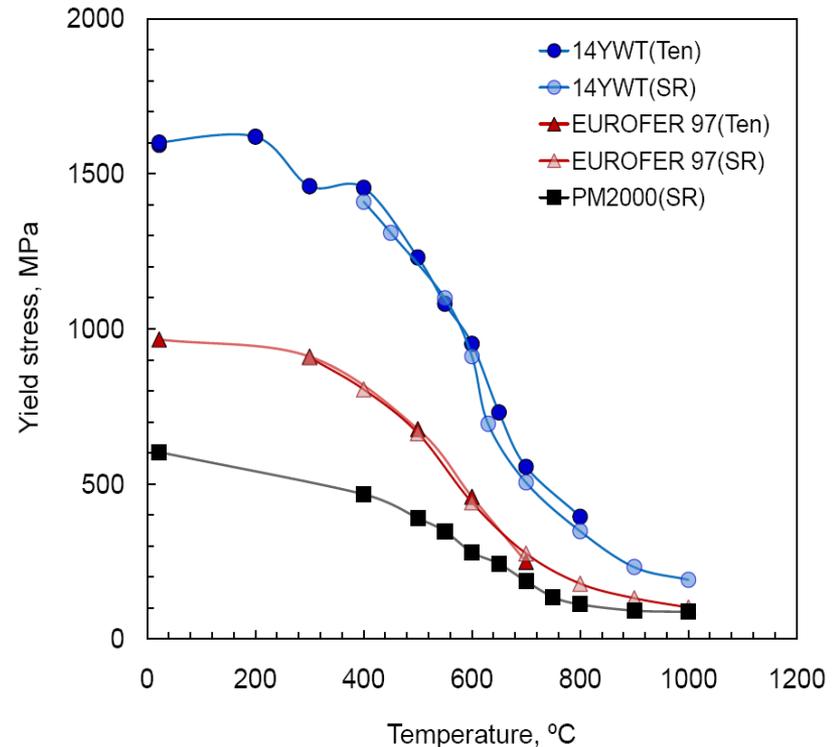
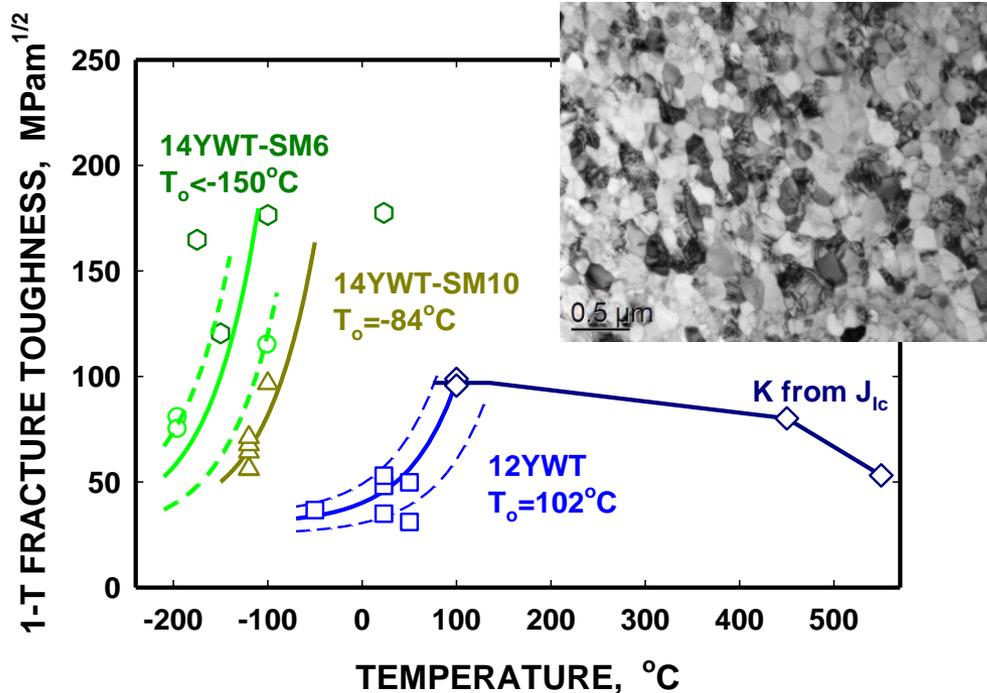
R_v =vacancy recombination radius

R_0 =spontaneous recombination radius

after D.E. Becker et al., Phys. Stat. Sol. (b) 54 (1972) p. 455 and R. Lennartz et al., J. Phys. F 7 (1977) 2011

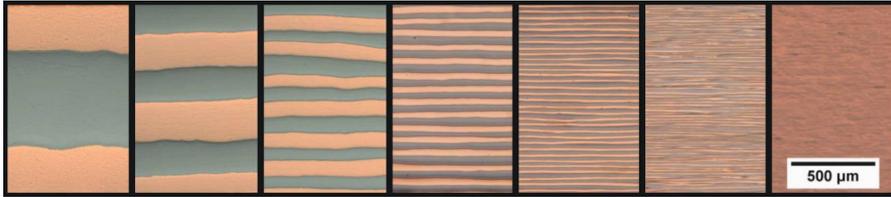
ODS ferritic steels

Fracture toughness of 14YWT is superior to earlier ODS ferritic alloys



- The fracture toughness transition temperature (L-T orientation) was higher for 14YWT heats containing fine grains (-150°C to -84°C) is significantly lower than that of 12YWT (102°C) which has larger grains
 - Small grain size itself is not the only factor in establishing good fracture toughness
- The fracture toughness in the T-L orientation (crack propagates parallel to extrusion direction) is 18°C; **anisotropy due to hot extrusion is still a problem**

Bulk nanolayered composites show superior radiation damage tolerance than nanocrystalline metals



Cu-Nb nanolayered composites processed via accumulative roll bonding (ARB) exhibit lower void density than nanocrystalline (nc) Cu of comparable grain size.

Interphase boundaries in lamellar geometry may provide optimal point defect sink strength and low interface energy for irradiation stability. Conventional nanocrystalline metals show grain growth and poor radiation tolerance during high-temperature irradiation.

Research Details

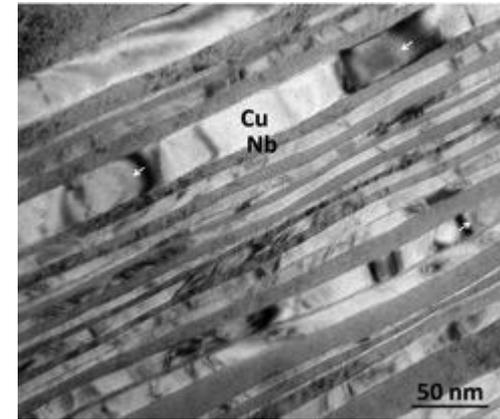
ARB nanolayered Cu-Nb and nc Cu (average layer and grain size =20 nm), coarse grain Cu and single crystal Cu.

He ion irradiation at 450 ° C.

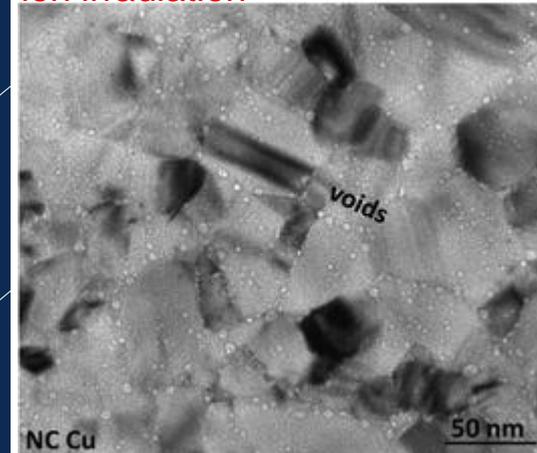


T. Nizolek et al., Adv. Mater. & Proc. 173 (2015) p. 18

ARB nanolayered Cu-Nb: No voids after He ion irradiation



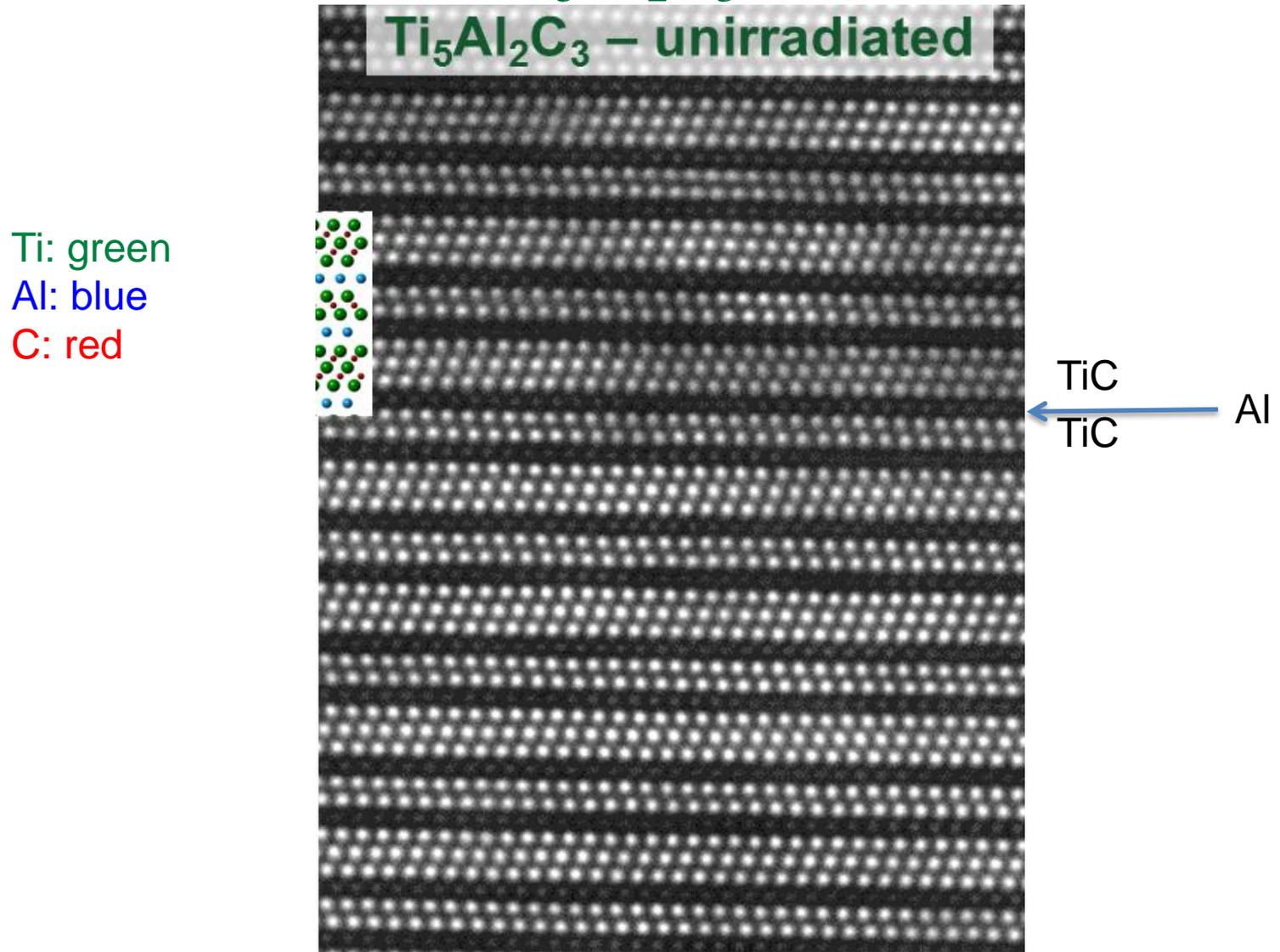
Nanocrystalline Cu: Voids at gb's and grain growth after He ion irradiation



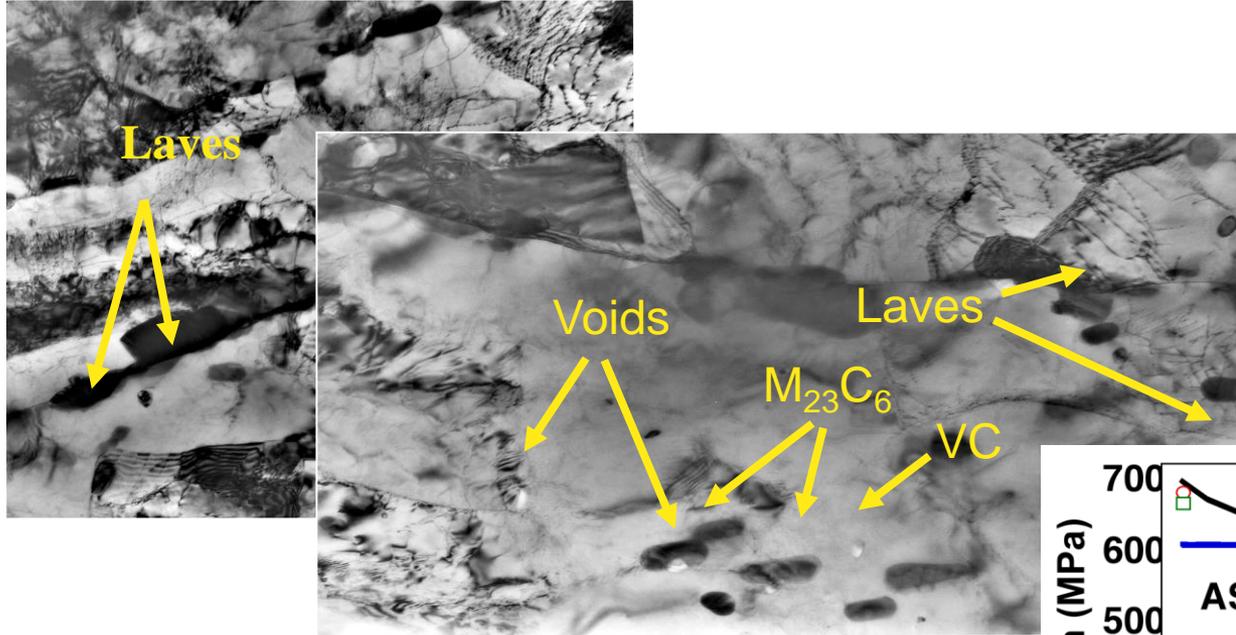
References:

1. W. Han *et al.*, Advanced Materials, **25** (2013) 6975-79.
2. W. Han *et al.*, Journal of Materials Research, **28**(20), (2013), 2763-70. (JOURNAL COVER)

High sink strength via internal multilayers in MAX phase ceramics: Example for $\text{Ti}_5\text{Al}_2\text{C}_3$

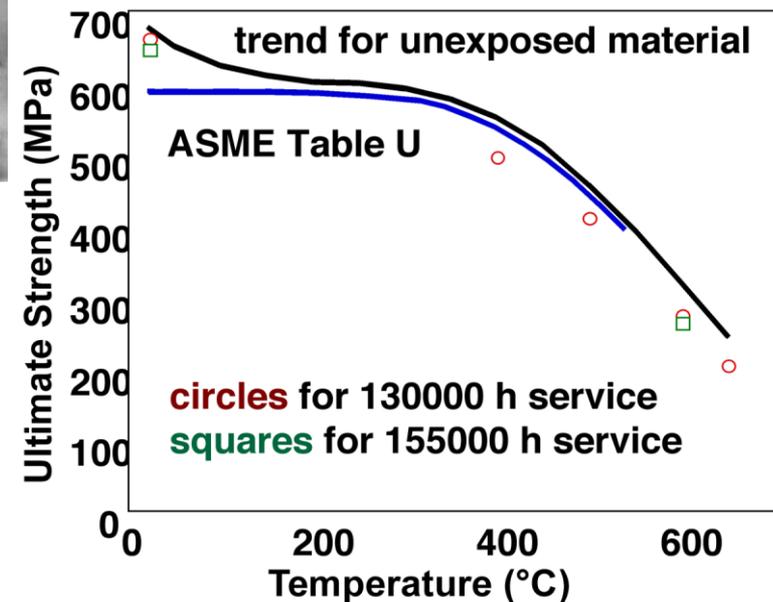


Today We Know That Very Long Time Service Causes The Properties of 9Cr-1MoVNb to Decrease to a Greater Extent Than Anticipated In Initial Alloy Design



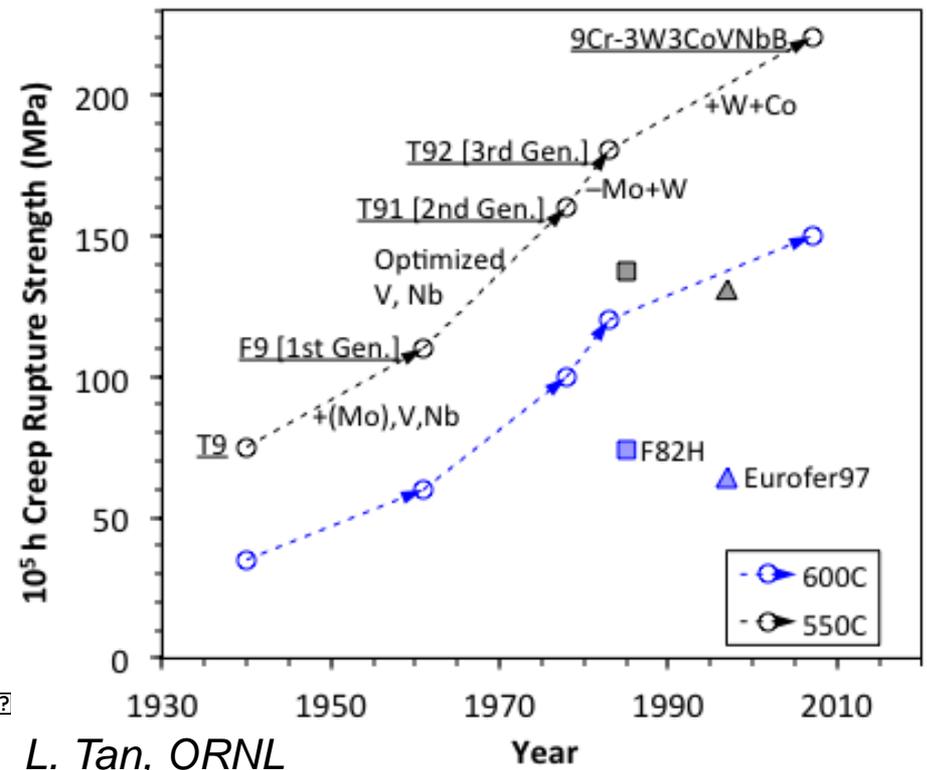
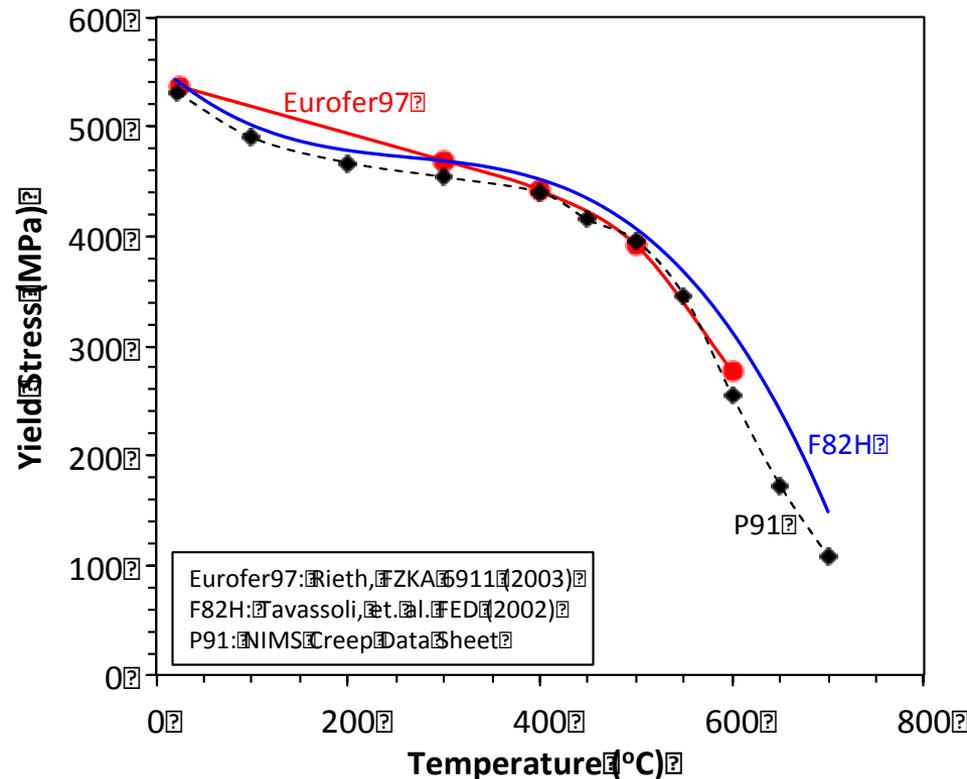
Exposure of 9Cr-1MoVNb Tubing for 155,000 h at 550-590° C Produces Laves Phase Precipitation and Substructure Recovery

The Tensile Strength of 9Cr-1MoVNb Decreased 15% As A Result Of Long-Time Steam Boiler Tubing Service



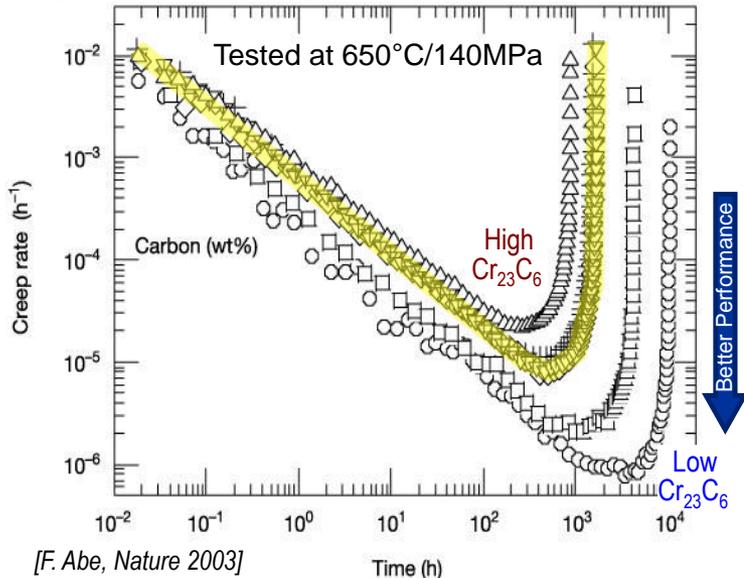
Development of RAFM Steels

- USA, Japan, and European Union initiated development of RAFM steels in 1980s, and came up with respective alloys such as 9Cr-2WVTa, F82H, and Eurofer97 (adopted in 1997). China, India, Korea, etc. started relevant R&D activities afterwards.
- Despite comparable tensile properties as compared with the ASME codified Grade 91, RAFM steels have significantly lower creep strength at temperatures above $\sim 500^\circ\text{C}$.

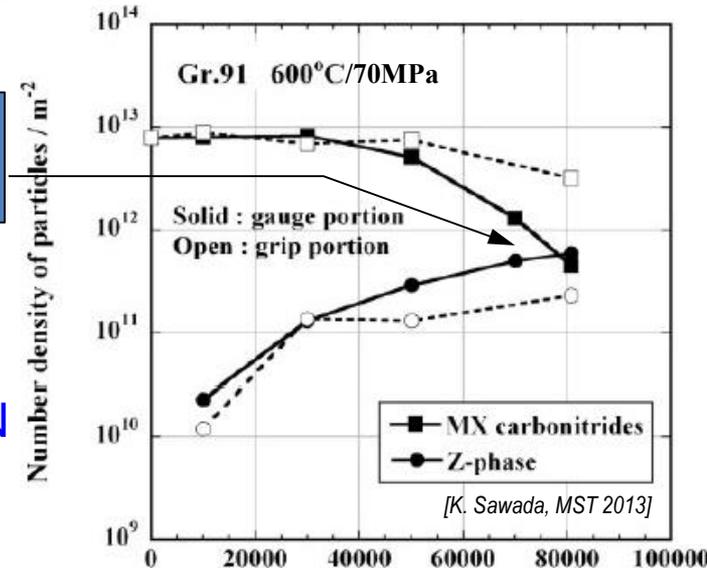
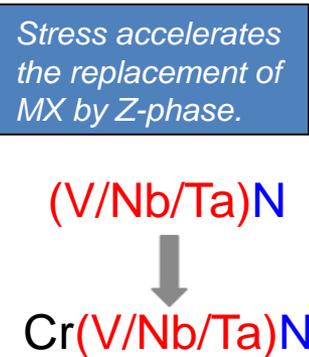


Concerns of Current 9-12Cr FM Steels

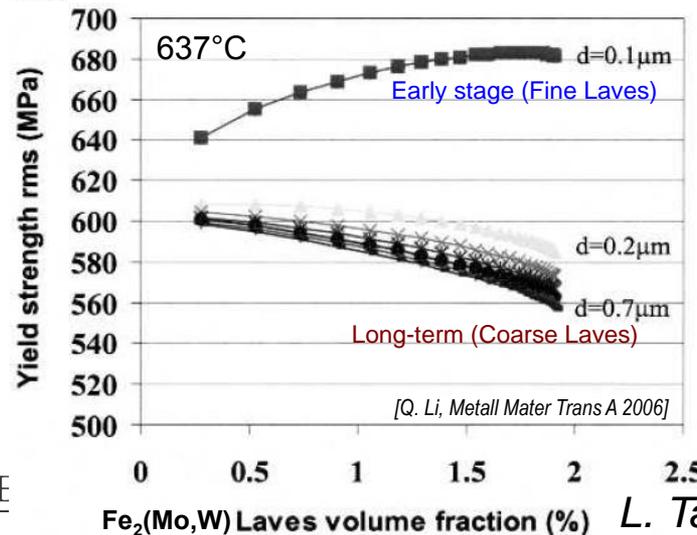
- Higher Cr_{23}C_6 amount results in greater creep rate.



- Coarse Z-phase forms by consuming fine MX during long-term services.



- Laves phase coarsening degrades strength.

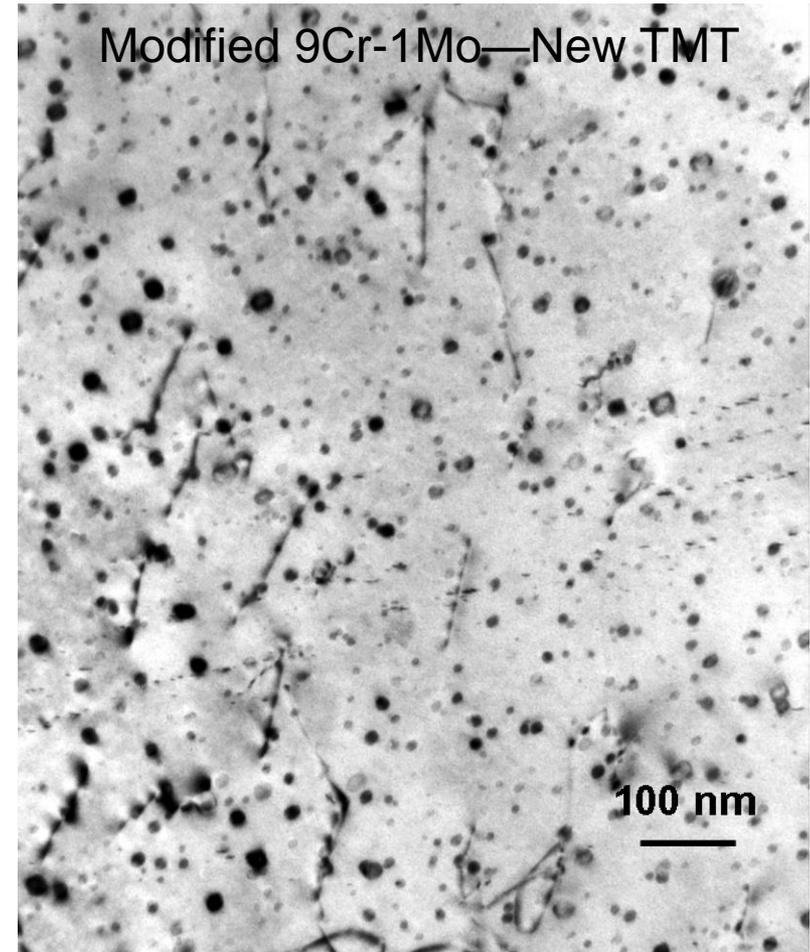


	Time / h	
	T91	T92
V, wt%	32.4	34.8
Cr	44.0	44.2
Nb	19.4	16.3
Fe	4.2	4.7
@600°C	34,141h	39,540h
Size	166 nm	155 nm
Fraction	0.7%	0.3%

Computational thermodynamics modeling identified potential new thermomechanical treatment (TMT) processes for commercial 9-12%Cr steels: 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
 - Up to 1000X increase in density (TMT precipitate density is $0.2\text{-}1 \times 10^{22}/\text{m}^3$; $d \sim 4\text{-}8$ nm)

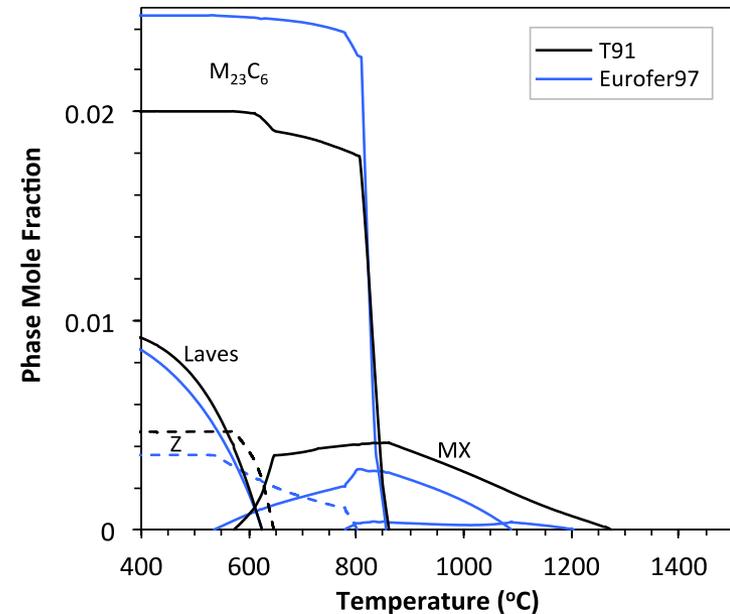
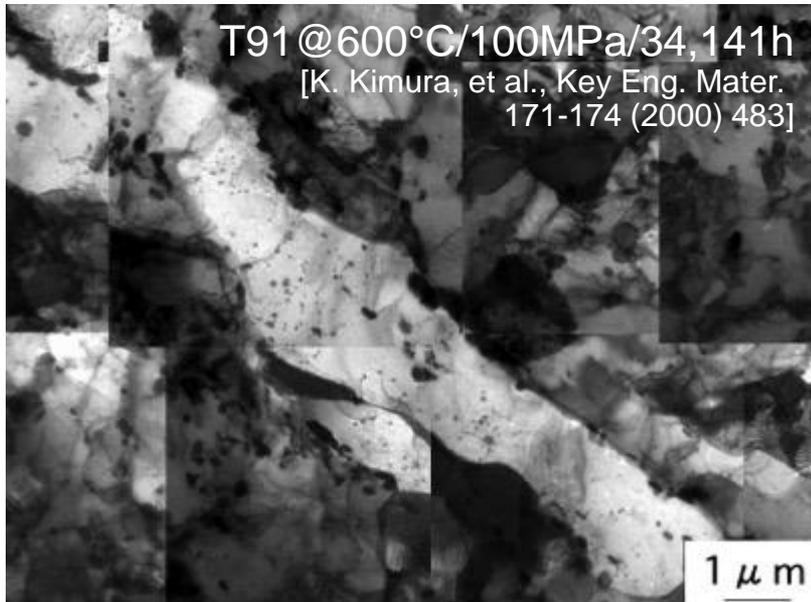
Potential drawback: TMT may be difficult to implement in some product forms, and can't be retained in weldments



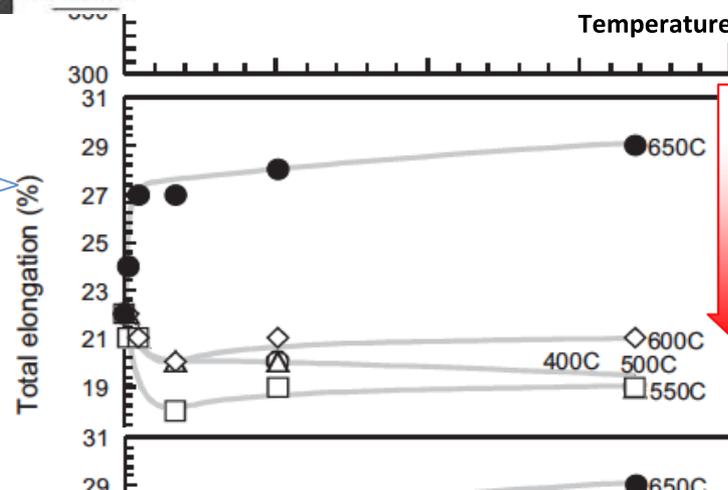
R.L. Klueh et al., *J. Nucl. Mat.* 367-370 (2007) 48; *Scripta Mat.* 53 (2005) 275

Motivation for Castable Nanostructured Alloys (CNAs) based on 9Cr ferritic steel

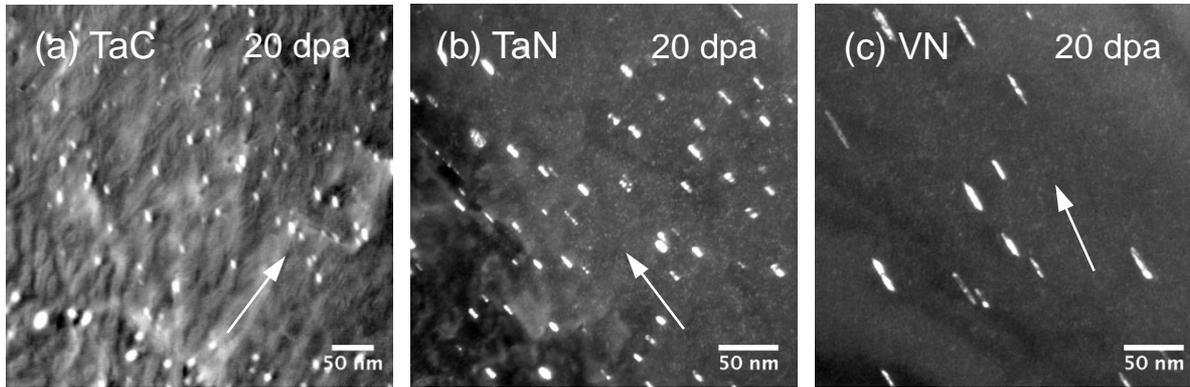
- The significant recovery of T91 at 600° C and 100 MPa suggests that the low amount of MX in the current RAFM steels (e.g., Eurofer97) may lower resistance to recovery.



Noticeable aging-induced softening in F82H-IEA at T > 500°C.
[K. Shiba, et al., *Fus. Eng. Des.* 86 (2011) 2895.]

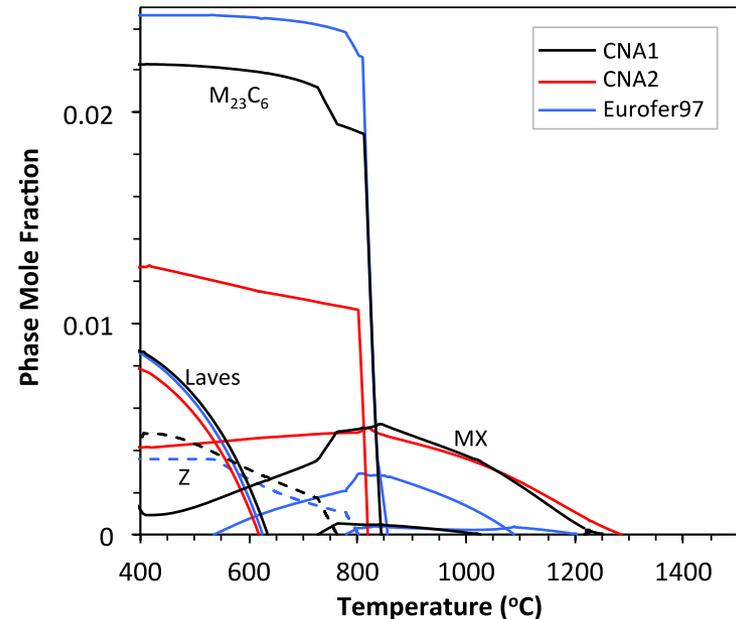


Design of Strengthening Precipitates in 9Cr steels



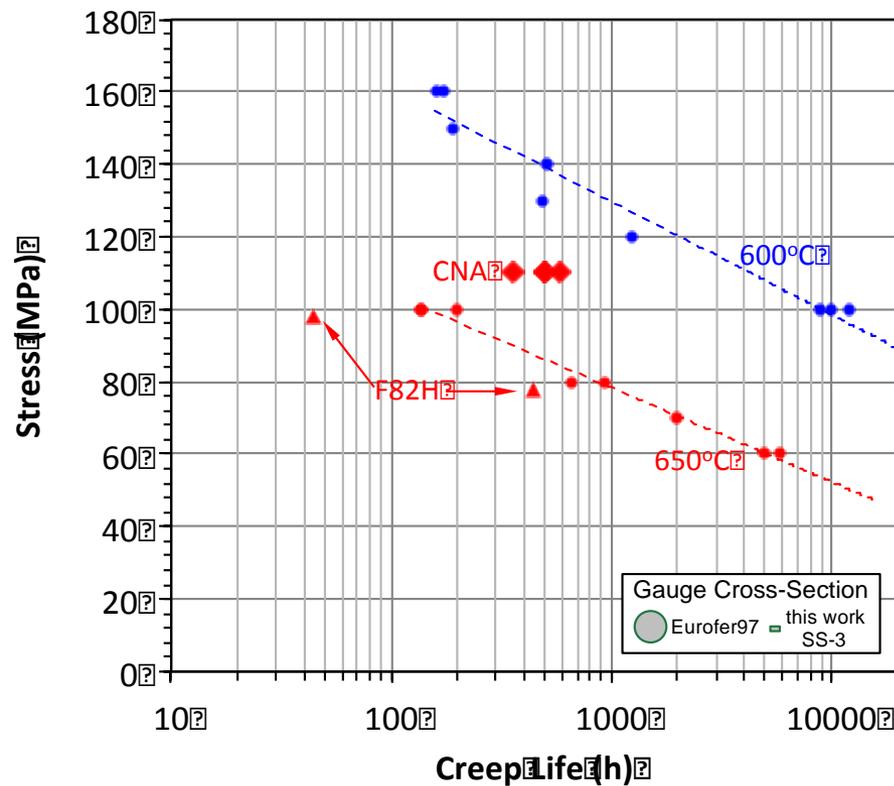
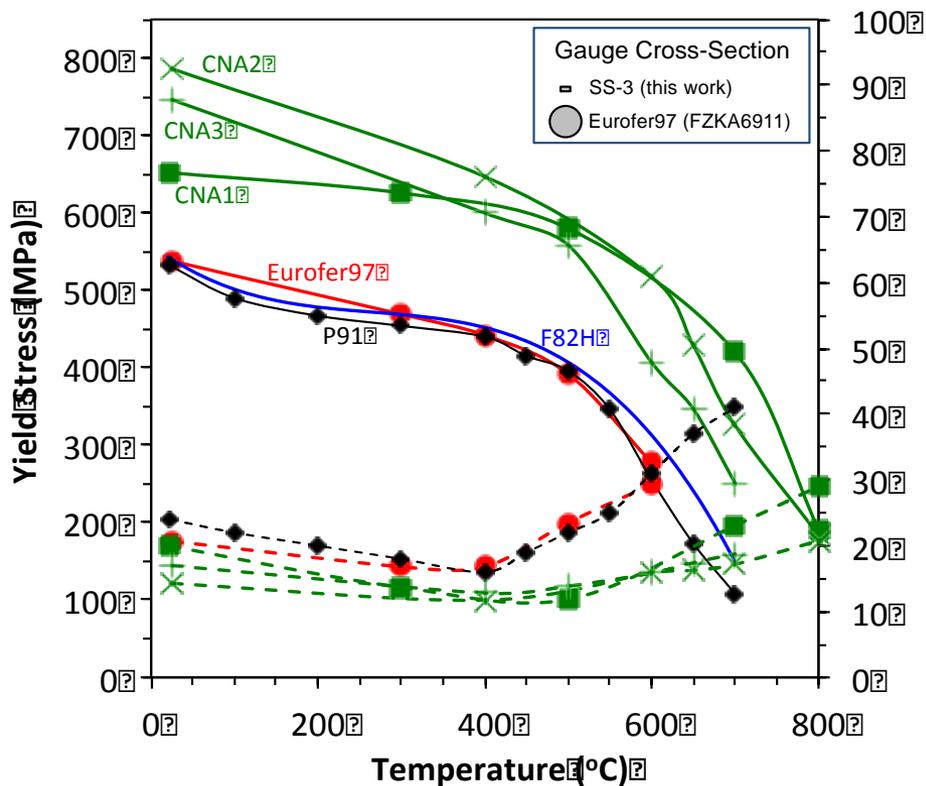
[L. Tan, et al. J. Nucl. Mater. 445 (2014) 104; Acta Mater. 71 (2014) 11]

- The superior stability of TaC under thermal, stress, and irradiation as compared with TaN and VN, inspired the development of MC-strengthened instead of MN-strengthened CNAs.
- The CNAs are designed to have
 - Increased MX, e.g., MN (with Z-phase) in CNA1 and MC (without Z-phase) in CNA2;
 - Reduced $M_{23}C_6$;
 - Comparable amount Laves phase.



Tensile and Creep Resistance of CNAs

- CNAs exhibited ~100–300 MPa increases in yield strength compensated by some reductions in ductility as compared with the FM/RAFM steels.
- Creep at 650° C showed superior creep resistance of CNAs as compared with Eurofer97 and F82H.



Microstructure of CNAs

- Lath boundary width (λ_{sgb} : 200–500 nm) is comparable to or less than conventional FM/RAFM steels (350–500 nm).

$$\sigma_{sgb} \approx 10Gb / \lambda_{sgb}$$

~700 vs. ~500 MPa **>1X** ↗

- MX nanoprecipitate (d_i : ~5 nm) density (n_i : 10^{22} m^{-3}) in CNA2 is two orders of magnitude higher than that in Eurofer97 ($\geq \sim 20 \text{ nm}$; 10^{20} m^{-3}).

$$\sigma_i \approx aMGb \sqrt{d_i n_i}$$

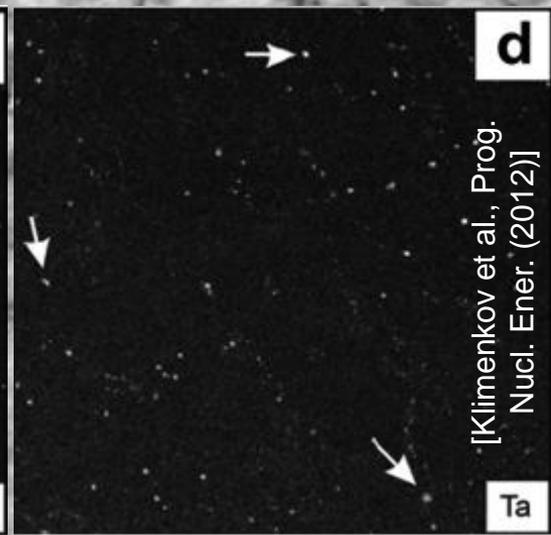
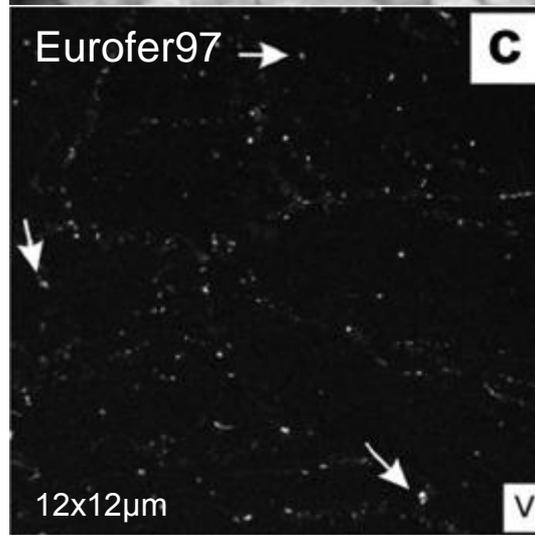
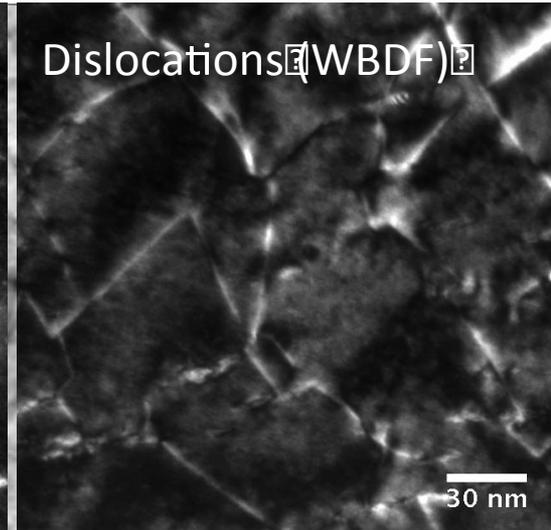
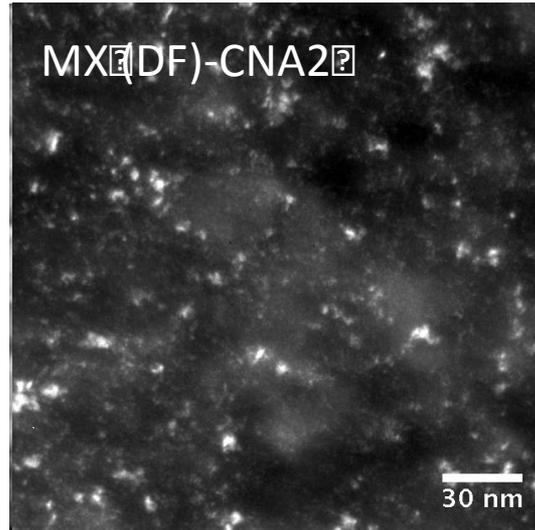
~200 vs. ~80 MPa **>2X** ↗

- Free dislocation density (ρ_d : 10^{14} m^{-2}) is comparable to that in FM/RAFM steels.

$$\sigma_d \approx 0.5MGb \sqrt{\rho_d}$$

~300 vs. ~300 MPa **~1X**

~780 vs. ~580 MPa

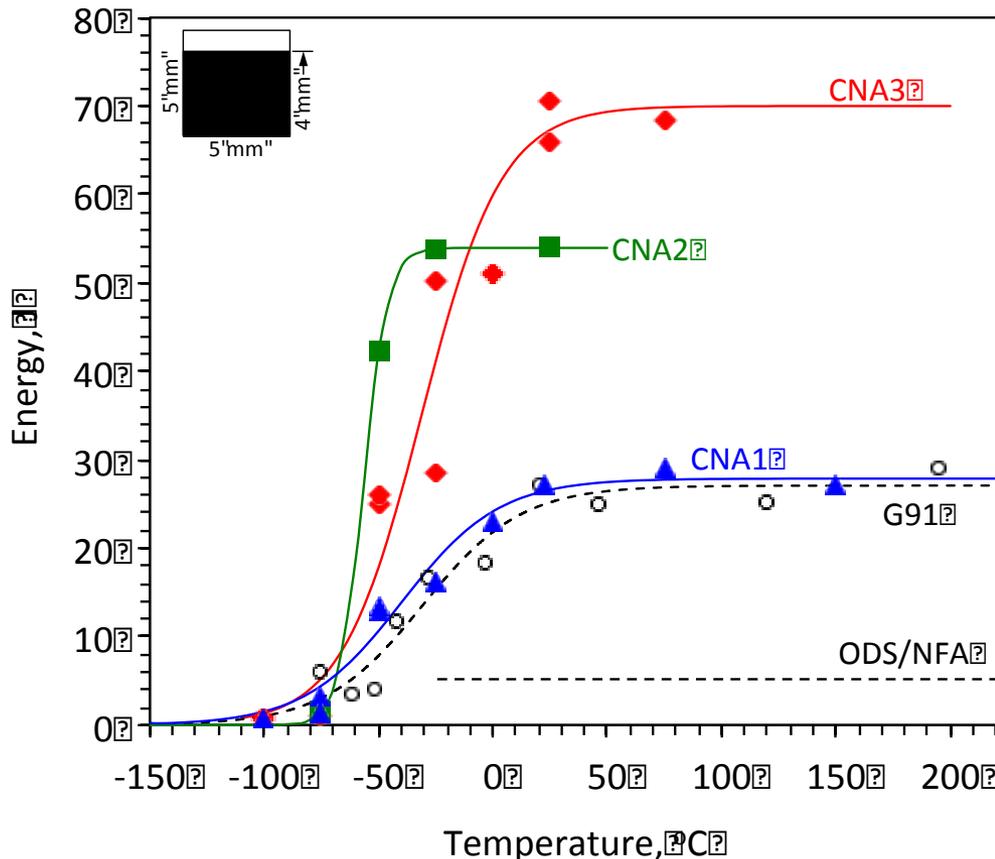


~200MPa ↗

L. Tan, ORNL

Charpy Impact Toughness of CNAs

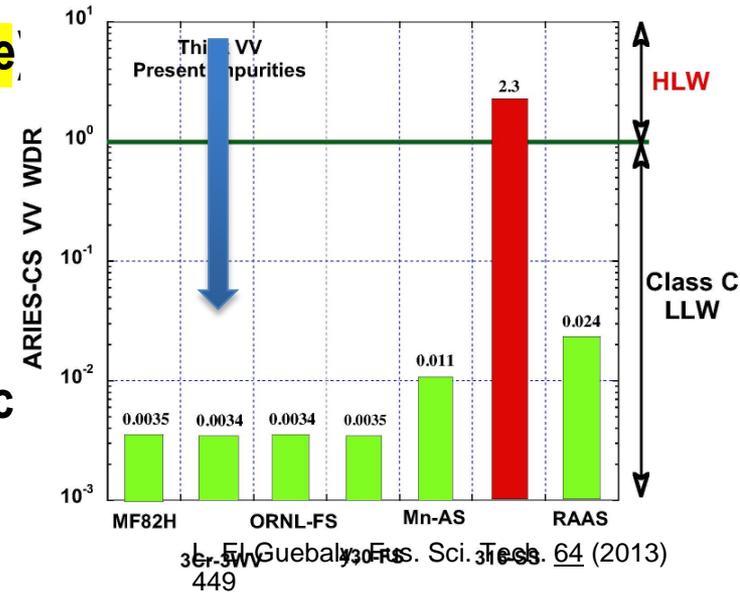
- CNA1 (primarily MN) exhibited USE and DBTT comparable to Grade 91.
- CNA2 and CNA3 (primarily MC) showed significantly increased USE with comparable or lower DBTT as compared with Grade 91.
- The CNAs and FM steel have remarkably higher USE as compared to the general value of 12-14Cr ODS/NFA.



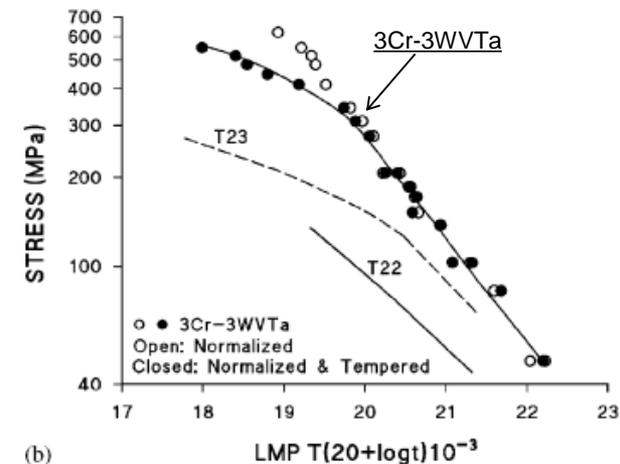
Overview of Bainitic Steel Development

>100X lower waste disposal burden vs. 316SS

- Target: Fusion structural applications in next-step fusion devices (FNSF or DEMO);
 - Vacuum vessel (>400-500° C, relatively low dose)
 - Structural ring, magnet shields
- Why 3Cr-3WV(Ta) steels?:
 - Inexpensive low alloy steel
 - Improved creep properties due to formation of carbide-free acicular bainite ferrite (lower bainitic microstructure)
 - potentially no requirement of PWHT, suitable for large volume components



- Approach:
 - Computational thermodynamics for alloy design
 - Effect of minor alloying additions on transformation kinetics
 - Phase equilibrium of strengthening second-phases
 - Property evaluation of 3Cr-3WV(Ta) steels
 - Production of CCT diagrams
 - Mechanical property / weldability



LMP plot of 3Cr-3WV(Ta) steel, compared with 2.25Cr-1Mo (T22) and 2.25Cr-1.6WVNB (T23)
R. Klueh, JPVP (2007)

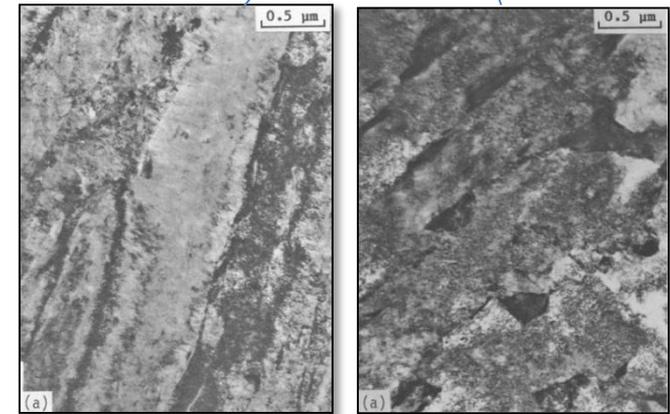
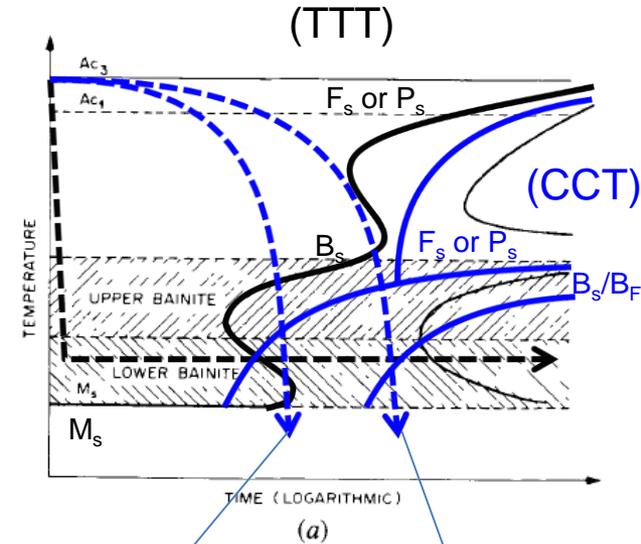
3 Cr Alloy Design Strategy

1. Carbide-free acicular bainite ferrite

- Appeared when rapidly cooled, contributing better properties (creep resistance, toughness, low DBTT)
- Requires to lower B_s and retard F_s/P_s

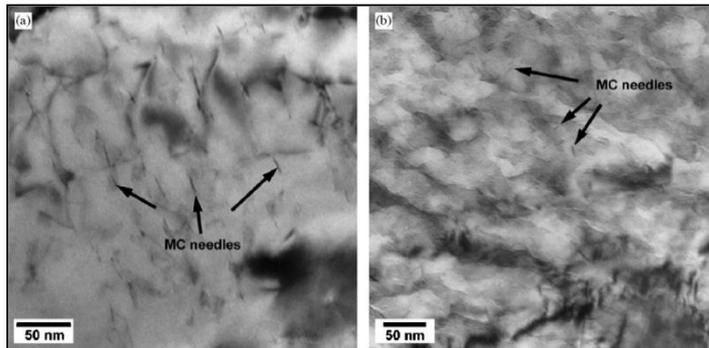
2. Second-phase strengthening

- **Mn + N additions** stabilize austenite phase and increase solubility of MX (e.g. VN, TaC);
 - ✓ **Advantage:** large amounts of stable, strengthening second-phase precipitates
 - ✓ **Disadvantage:** retained austenite/martensite, transmutation of nitrogen



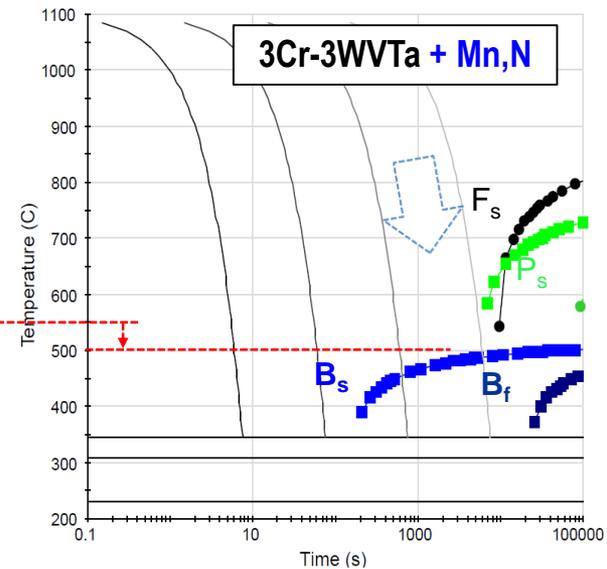
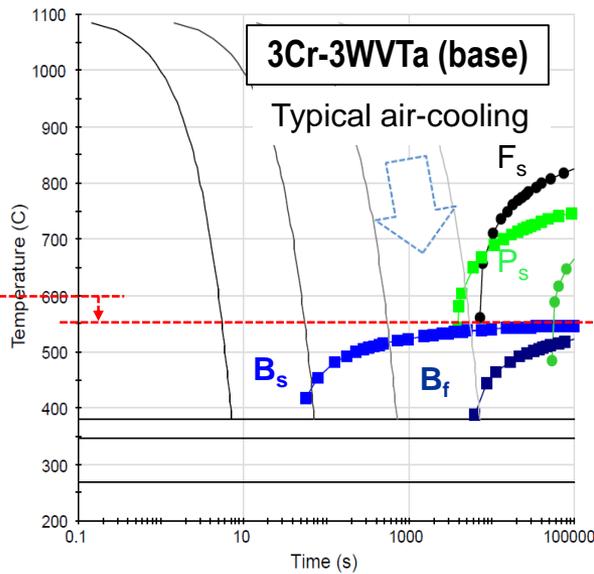
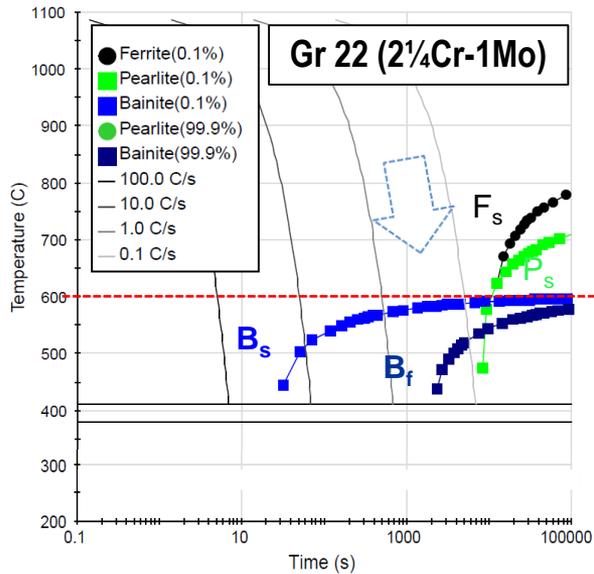
TEM images of 3Cr-1.5Mo-0.1V steels (a) quenched + tempered, (b) normalized and stress-relieved.

R. Klueh, MMTA, 1987



TEM images of normalized + tempered steels (a) 3Cr-3WV, and (b) 3Cr-3WVTa
R. Klueh, JPVP, 2007

Consideration From Calculated CCT curves



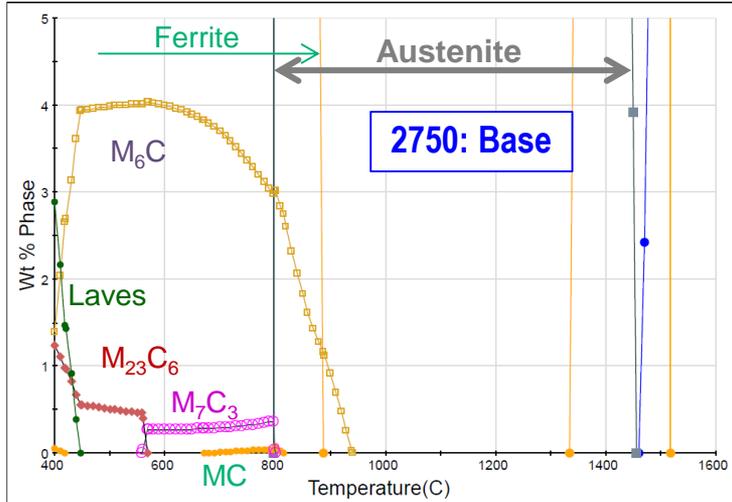
(calculated by JMatPro v.8 with Fe database)

- **3Cr-3WVTa (base)** showed “lower B_s + promoted P_s ” compared to **Gr 22**
 - Good: High Cr/W contributed to form carbide-free acicular bainite ferrite
 - Bad: Potential formation of the ferrite/pearlite when the material was slowly cooled
- **3Cr-3WVTa + Mn, N** showed “further lower B_s + retarded F_s/P_s ” compared to **the base**
 - Overall 100°C calculated reduction in B_s compared to Grade 22
 - Good: Additions of Mn+N stabilized austenite to promote acicular bainite formation
 - Bad: Potential formation of martensite when the material was cooled rapidly

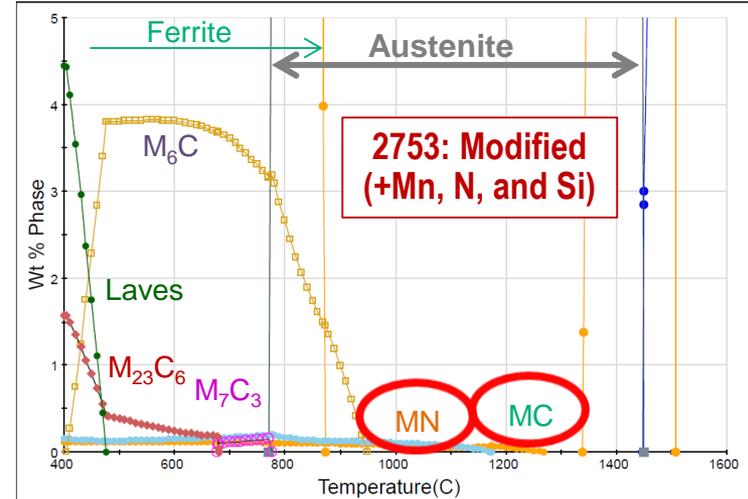
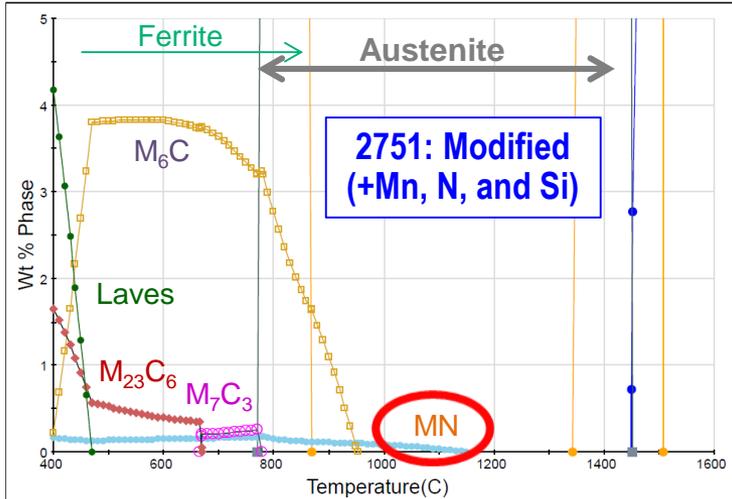
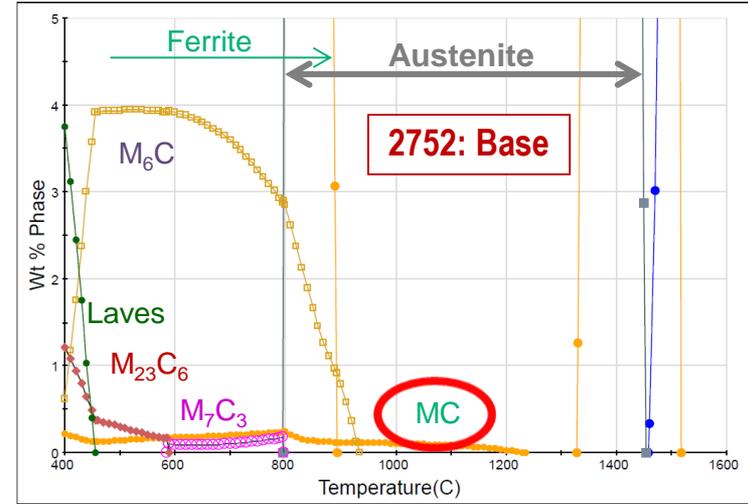
Improved Stability of Second-phases in 3Cr Steel

- Minor alloying additions stabilized MC (M: mainly Ta) + MN (M: mainly V)

3Cr-3WV base



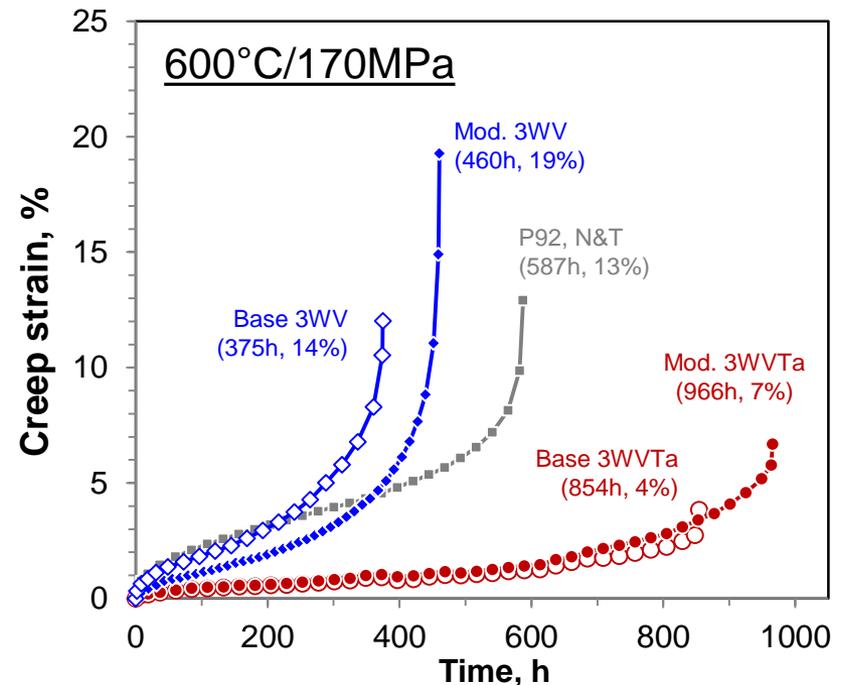
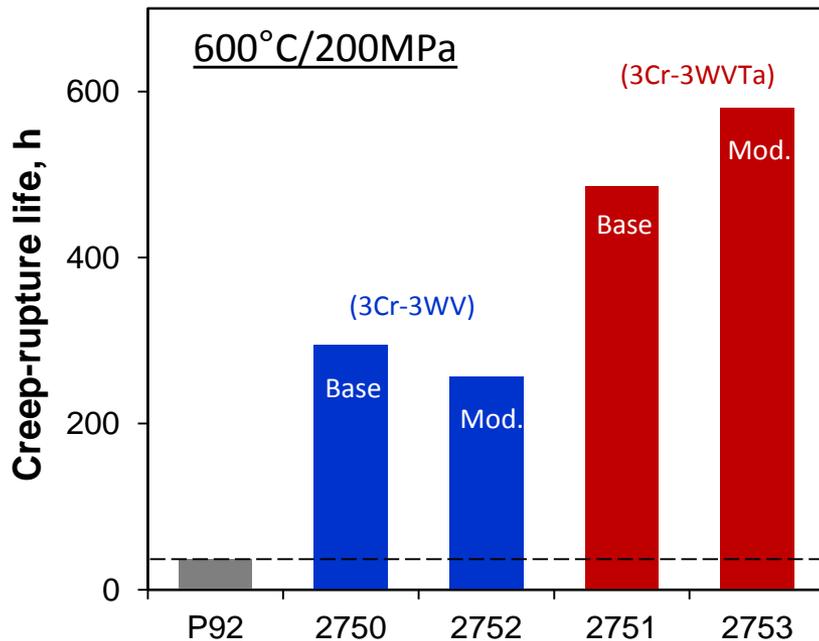
3Cr-3WVTa base



(calculated by JMatPro v.8 with Fe database)

Improved Creep-rupture Properties in 3Cr Steels

- Better properties compared to P92 F-M steels:
 - All 3Cr-3WV(Ta) steels at 600 ° C-200MPa
 - Only 3Cr3WVTa steels at 600 ° C-170MPa (test in progress)
- Modified alloys tend to show improved properties at lower stress range:
 - Requires multiple long-term creep testing (lower-temperature, lower-stress) to verify



Conclusions

- Nearly all commercially available structural alloys are not optimized for peak performance
- Multiple approaches are available for designing high performance radiation-resistant structural materials
 - High sink strength (Ti-mod-SS, ODS steels, modified ferritic/martensitic steels with fine scale precipitates, nanolaminates, MAX phase?)
 - Negligible vacancy mobility (SiC; W MMCs?)
 - Radiation-resistant matrices (BCC, HEAs?, BMGs?)

Nuclear energy offers several attractive advantages, but the competition for 21st century energy options is strong

- **Dramatic changes in public perception/ acceptance of risk tolerance in the past 50 years**
 - Transportation (automotive, airplane)
 - Public health (smoking)
- **Alternative energy concepts with attractive environmental attributes are making steady advances**
 - Fossil energy with ultrasupercritical Rankine power conversion
 - Solar photovoltaic
 - Wind

Science grand challenge:

- **Is it feasible to envision Gen II-III nuclear power that would not require public evacuation for any design-basis accident?**

There are four potential strategies for improved accident tolerance

Minimize core enthalpy input

- Reduced steam-cladding oxidation rate
- Reduced heat of oxidation for cladding

Minimize combustible hydrogen generation

- Reduced steam-cladding oxidation rate
- Enhanced hydrogen sequestration and chemical conversion



Improved fuel containment of fission products

- Enhanced retention of fission products
- Minimize fuel relocation / dispersion
- Lower operating temperatures
- Inhibit clad internal oxidation
- Increased fuel melting safety margin

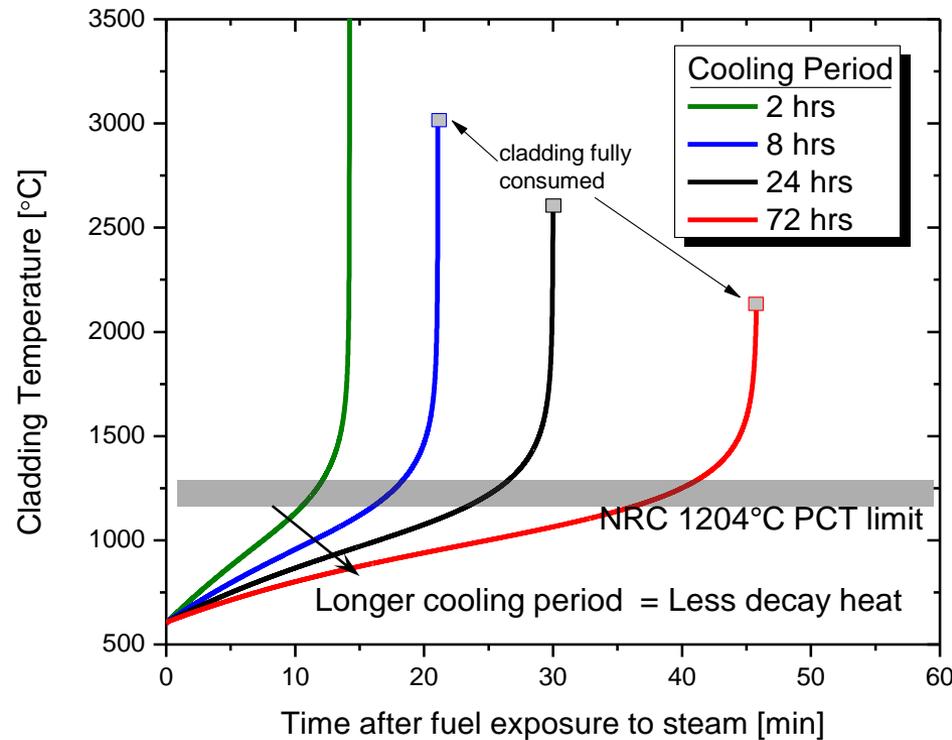
Improved cladding to maintain core coolability and retain fission products

- Improved high temperature clad strength and fracture resistance
- Thermal shock resistance
- Increased melting temperature
- Resistance to hydrogen embrittlement

- potential options for fuel cladding include:
 - Oxidation-resistant austenitic steels
 - Oxidation-resistant coatings on Zr alloy cladding
 - Ceramic matrix composite cladding
- Potential options for fuel include dispersed particle fuels

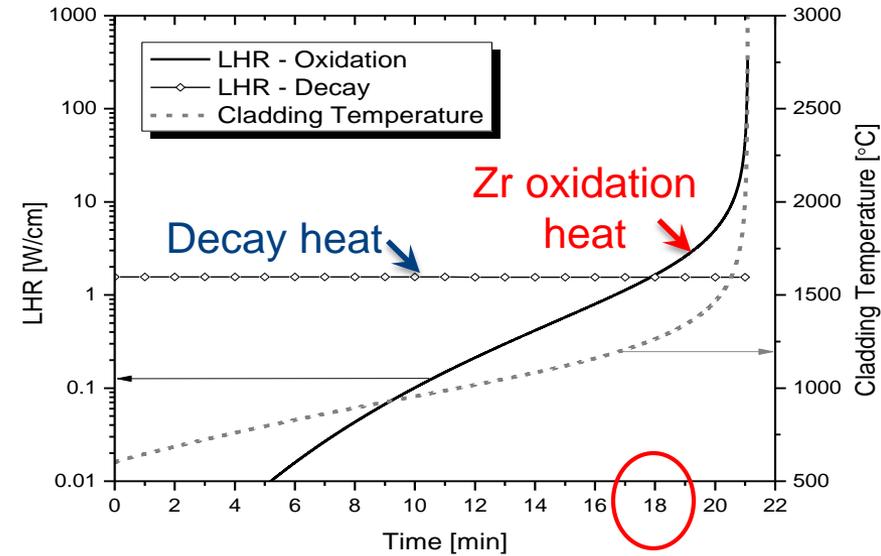
Oxidation behavior of zircaloy cladding under LOCA conditions

Cladding temperature evolution (600°C steam) for different cooling periods

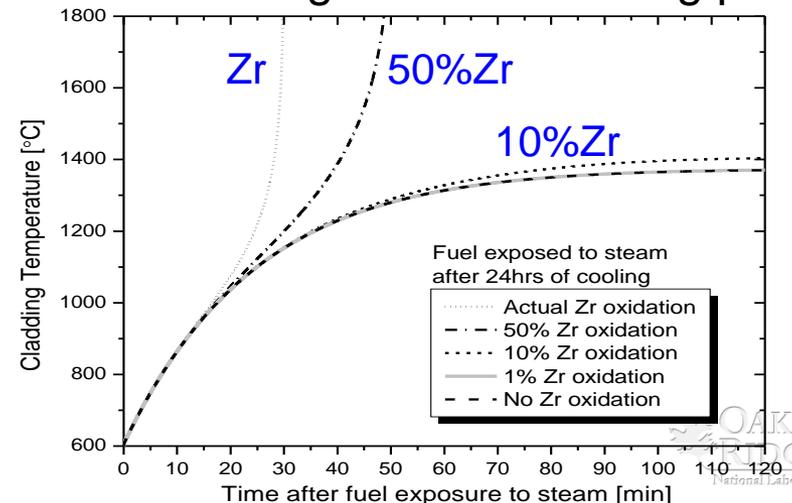


K. Terrani, L. Snead, S. Zinkle et al.,
J.Nucl. Mater., **448** (2014) 420

Cladding heat evolution due to oxidation (600°C steam) after 8h cooling period

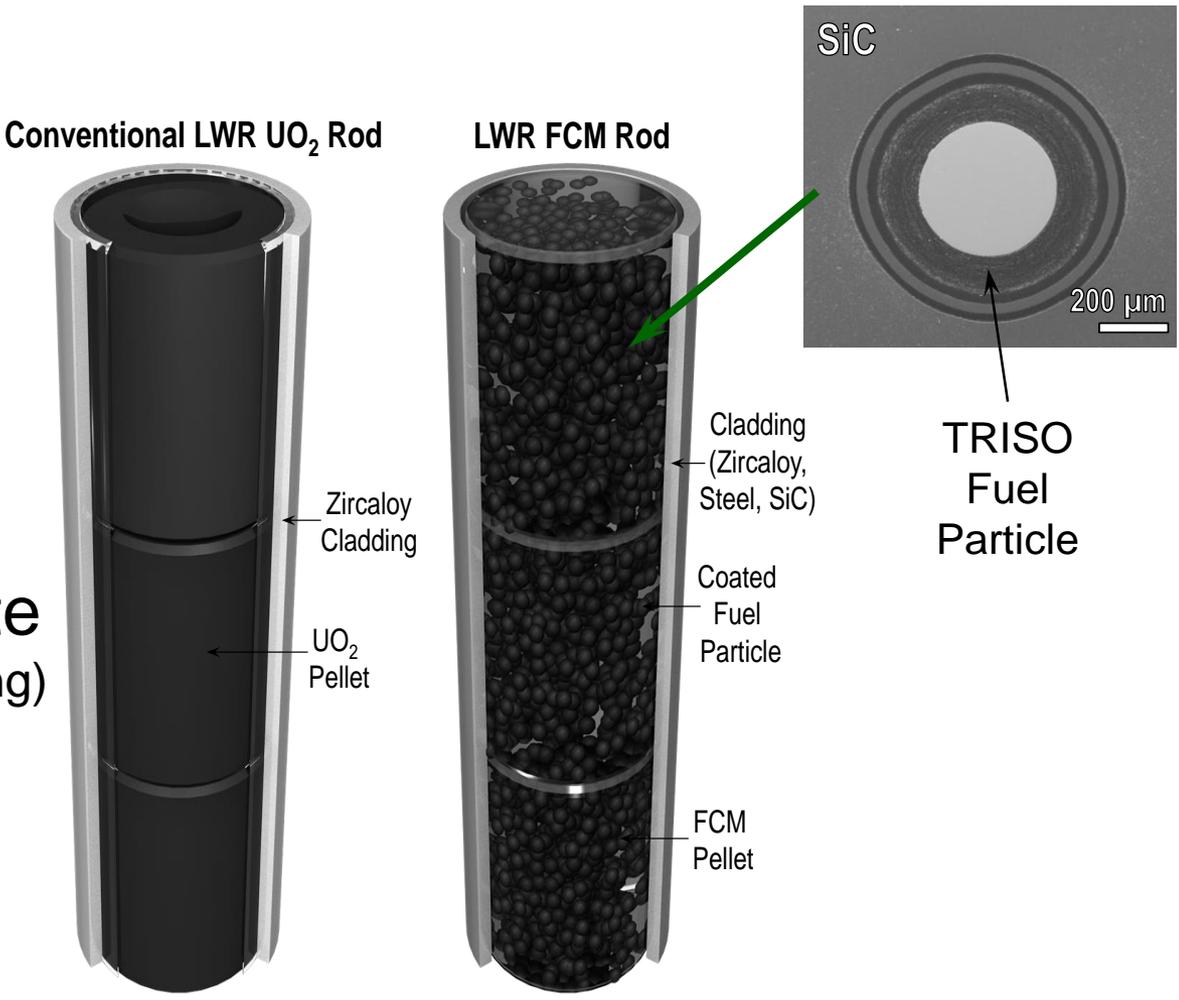


Cladding temperature evolution due to oxidation heating after 24h cooling period

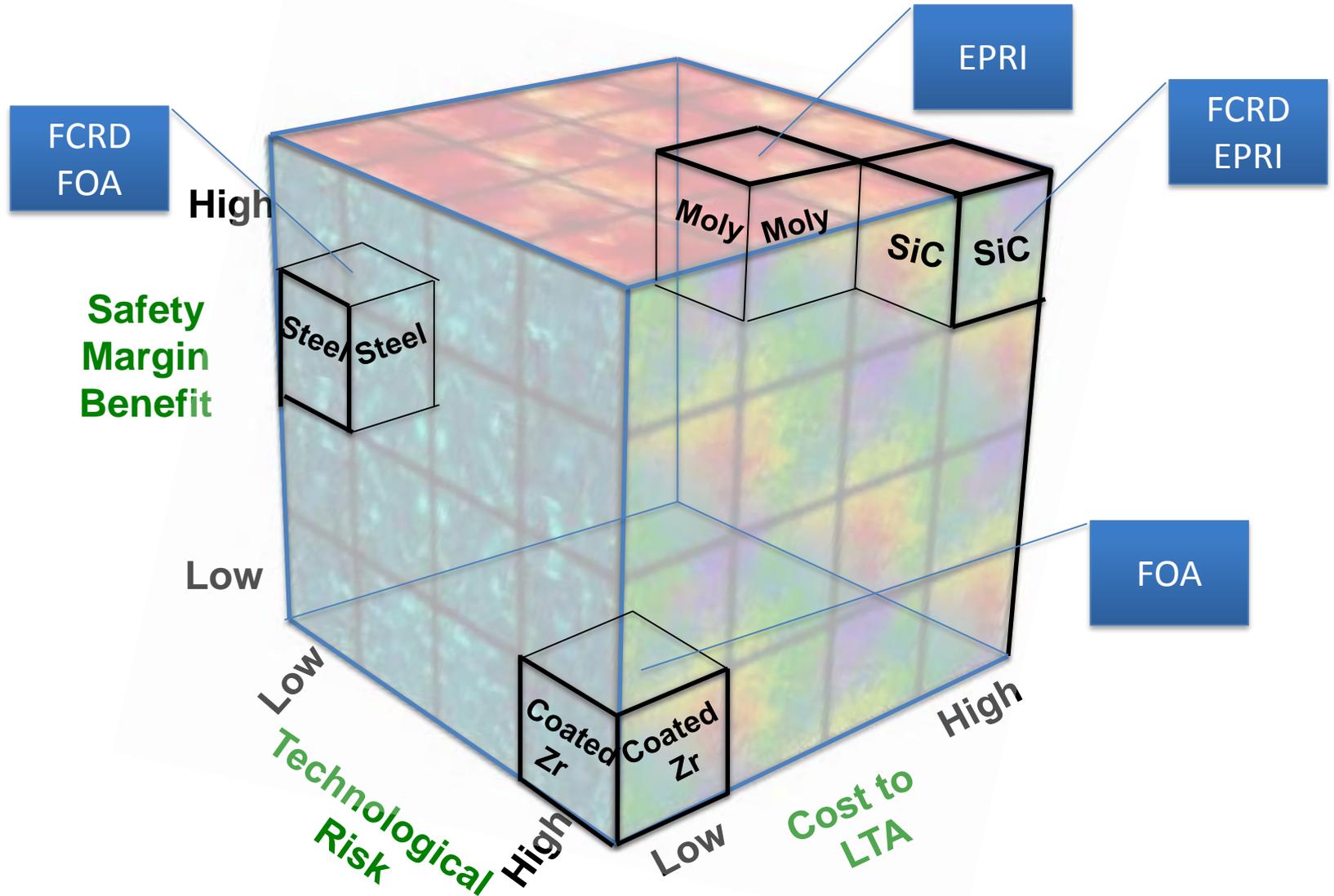


Several Accident Tolerant Fuel Concepts are Under Consideration, including:

- UO_2 – Zircaloy
(Base Case)
- UO_2 – FeCrAl
(oxidation resistant Steel)
- UO_2 – SiC composite
(oxidation resistant CFC cladding)
- FCM – FeCrAl
(Fully Ceramic Microencapsulated Fuel)

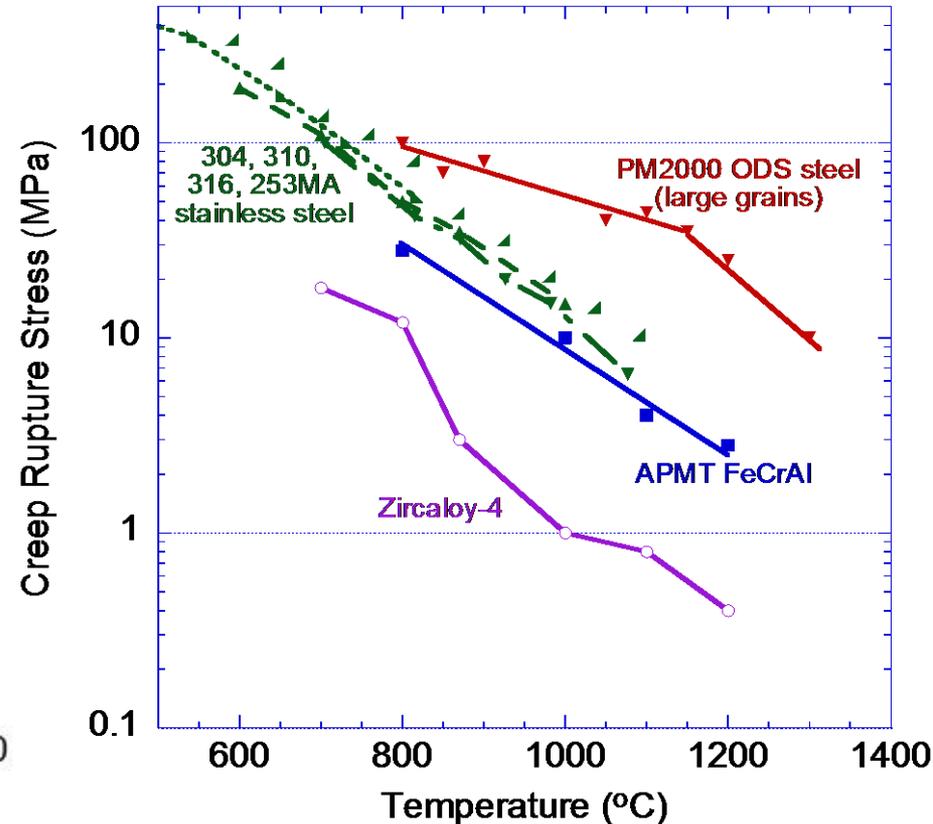
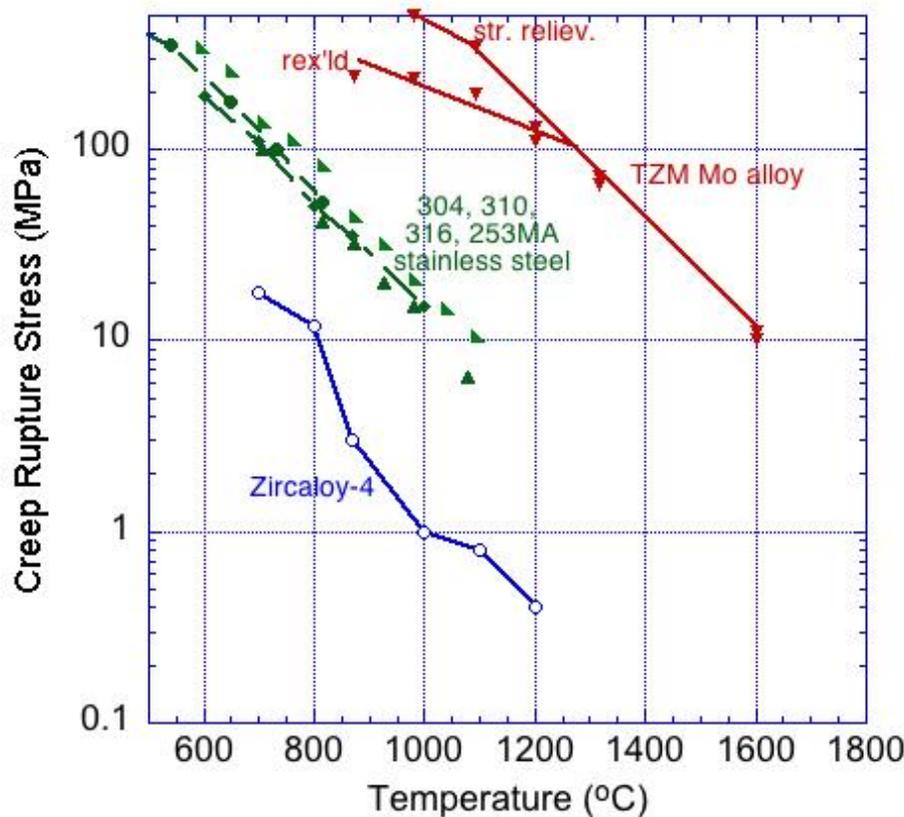


Enhancing Safety Margin with Advanced Fuels: Cladding Options



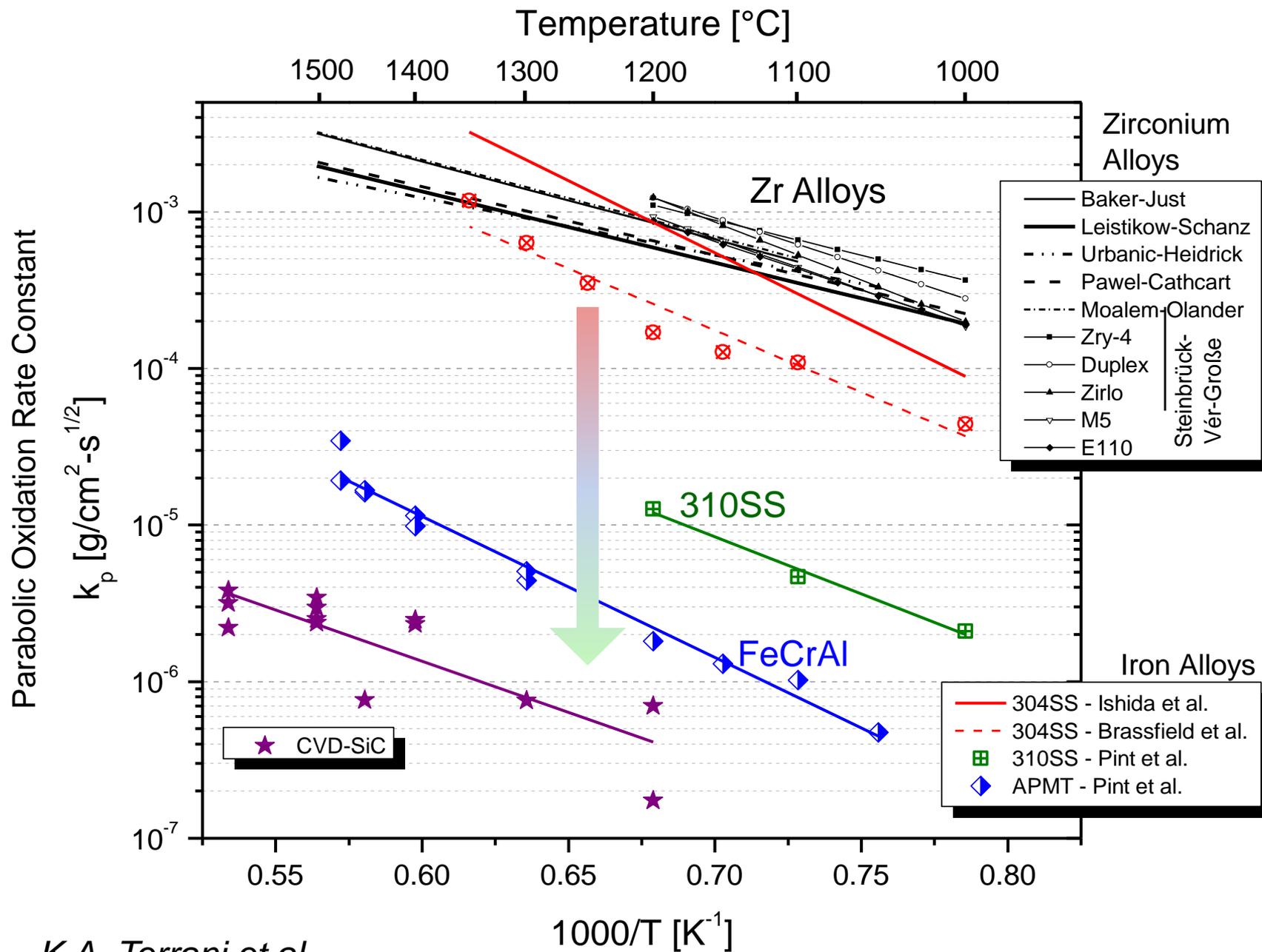
Short-term (100 h) thermal creep strength of some candidate cladding materials

Comparison of 100 h creep rupture strengths of candidate fuel cladding materials



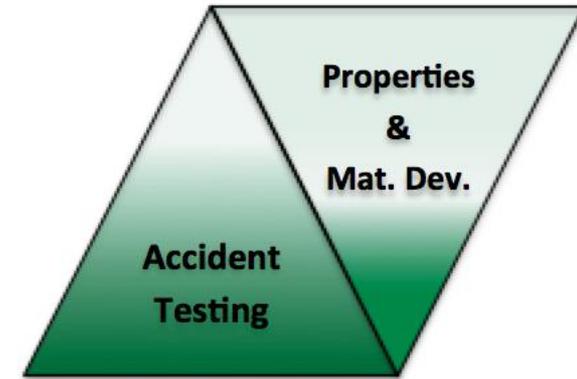
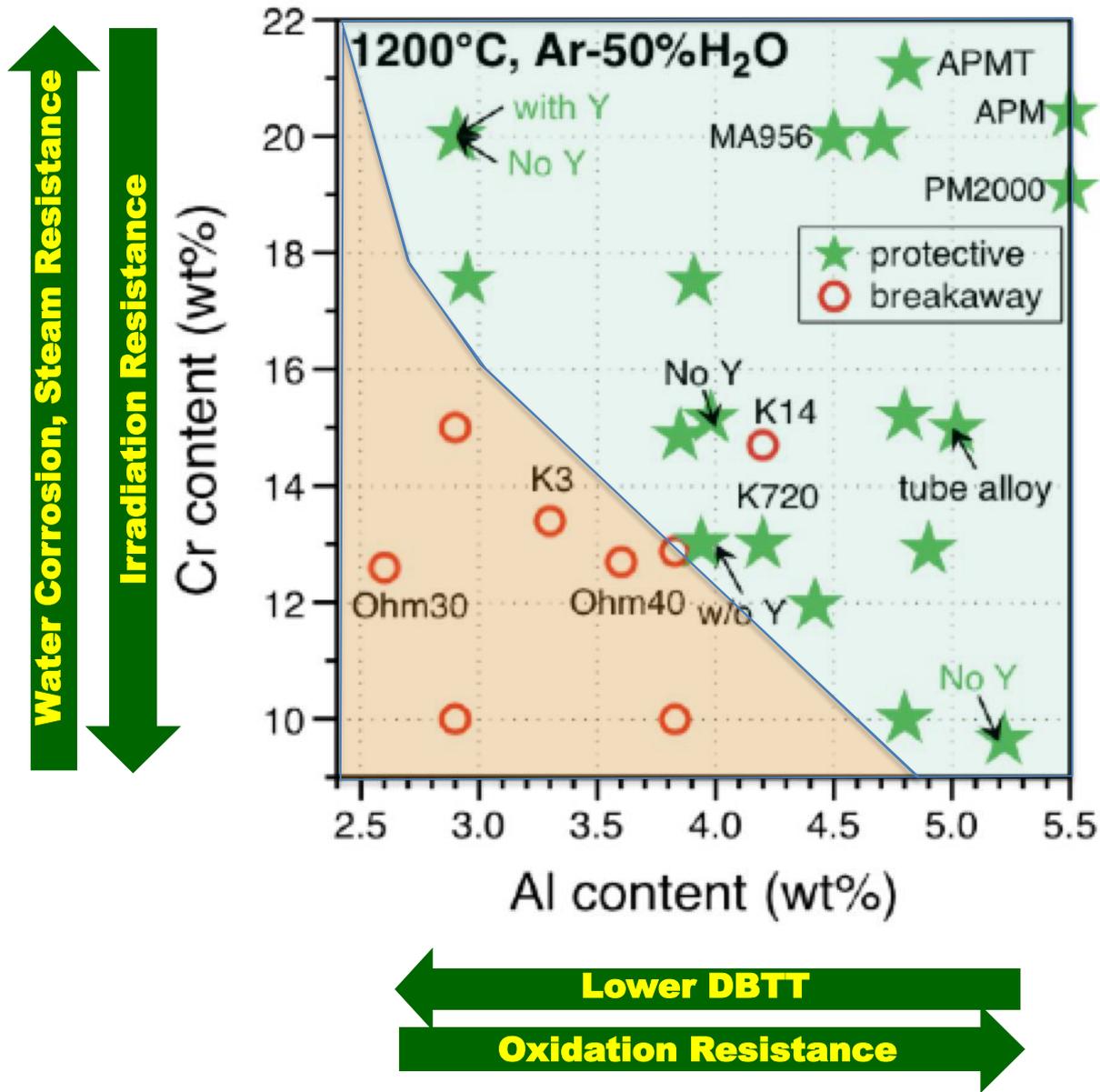
- Mo alloys and steels (and SiC/SiC, not plotted) offer improved high temperature thermal creep strength

Fundamentals of Steam Oxidation Kinetics

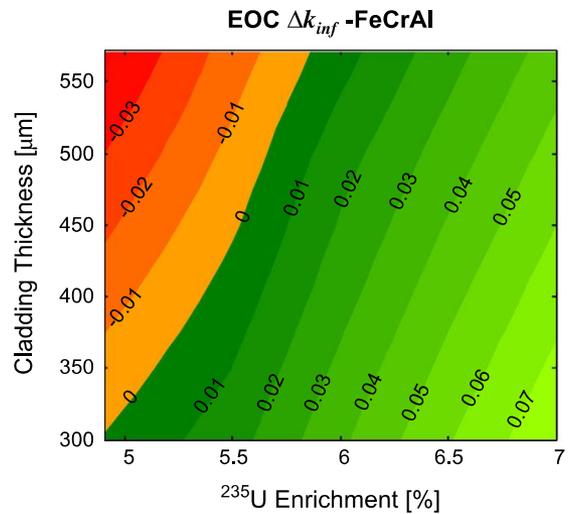
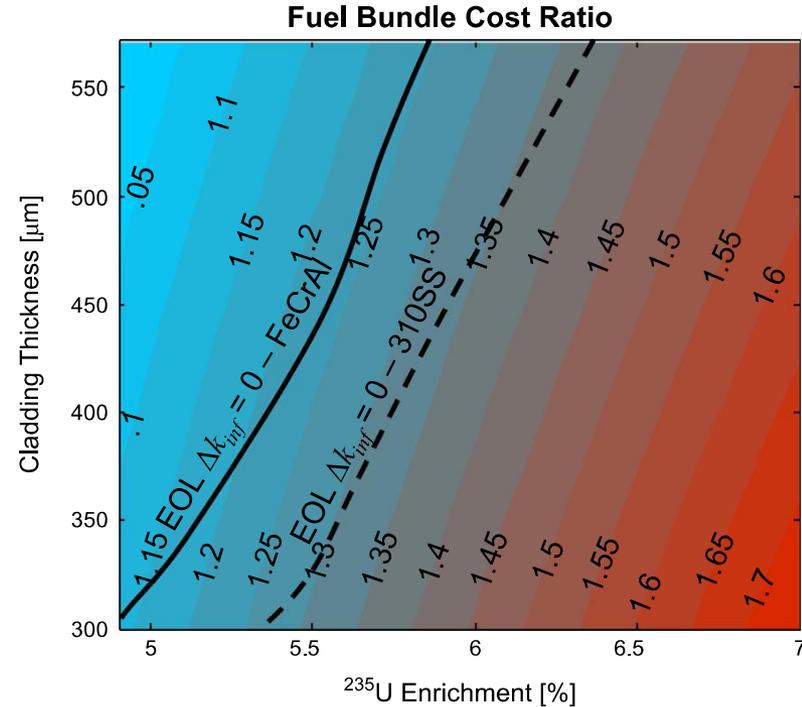
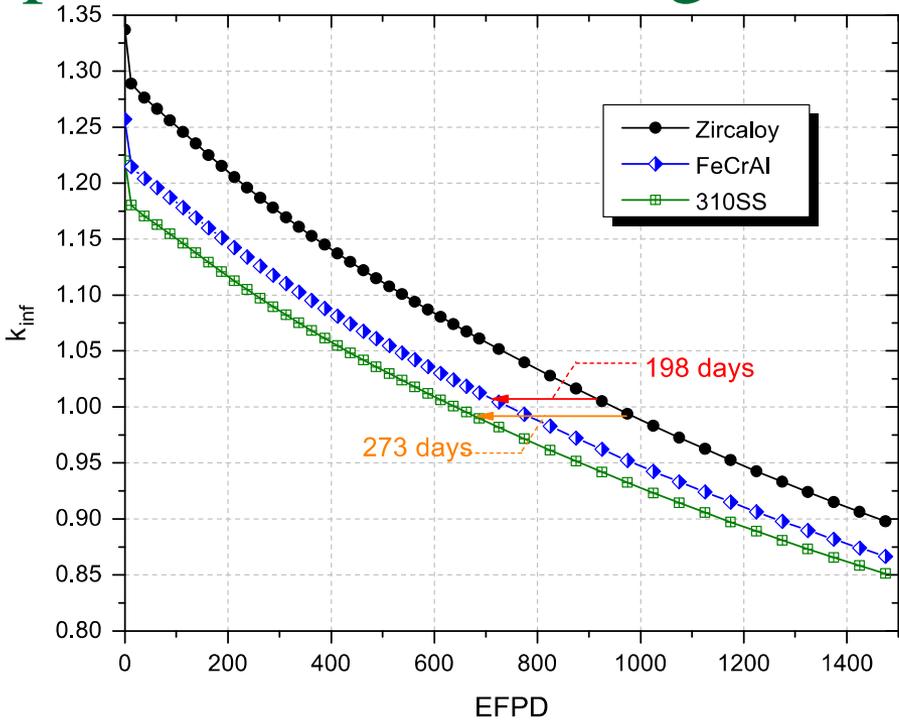


Advanced Ferritic Alloys:

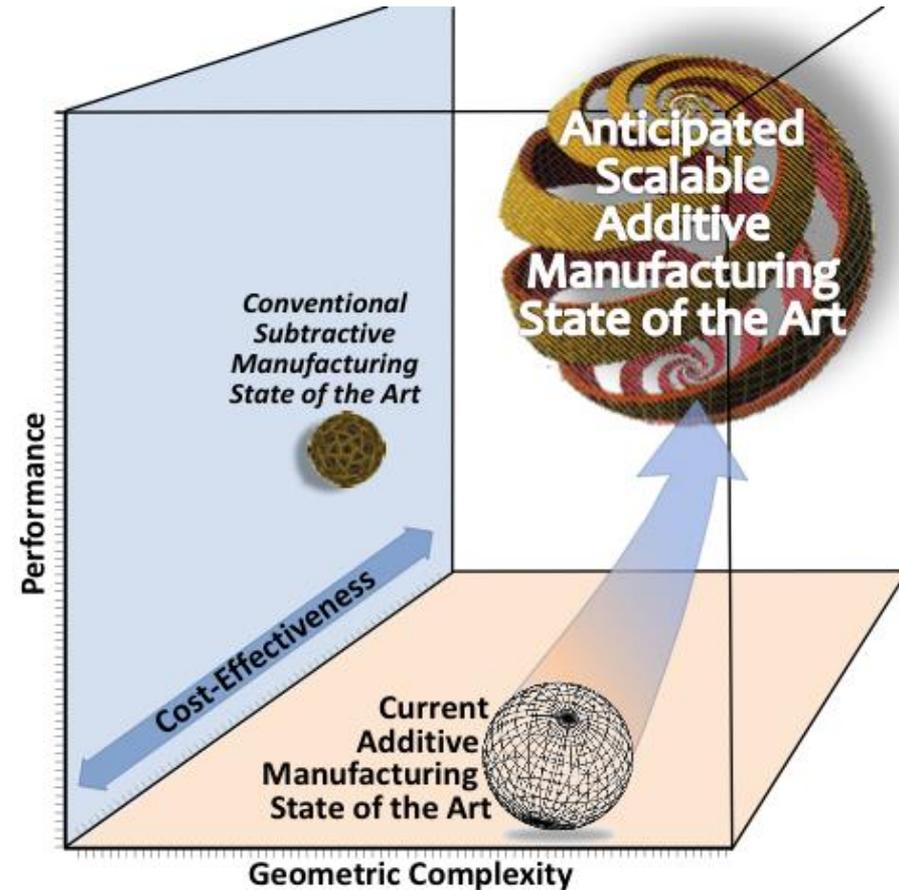
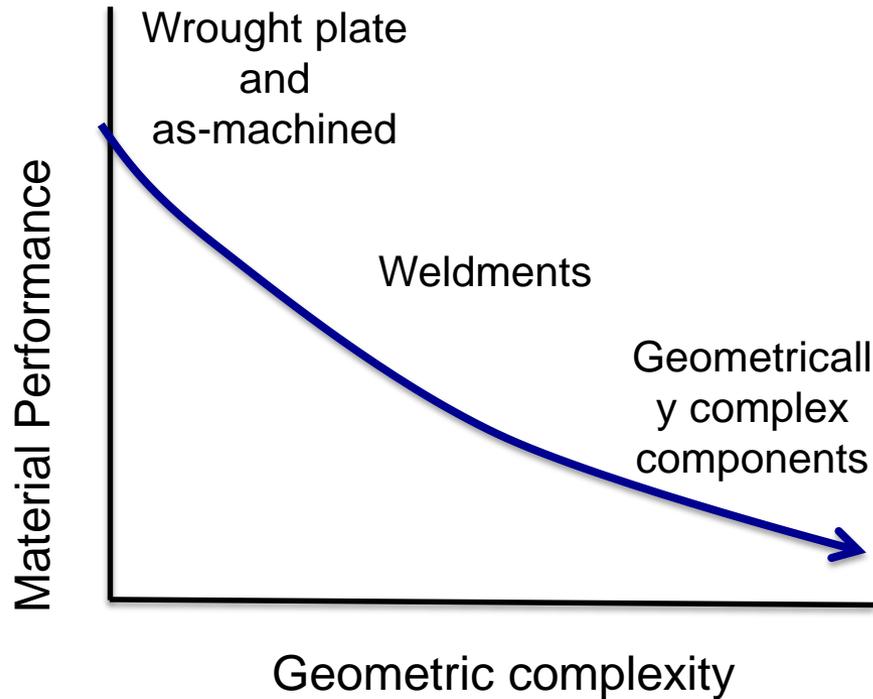
- Oxidation Resistance under Accident Test Conditions -



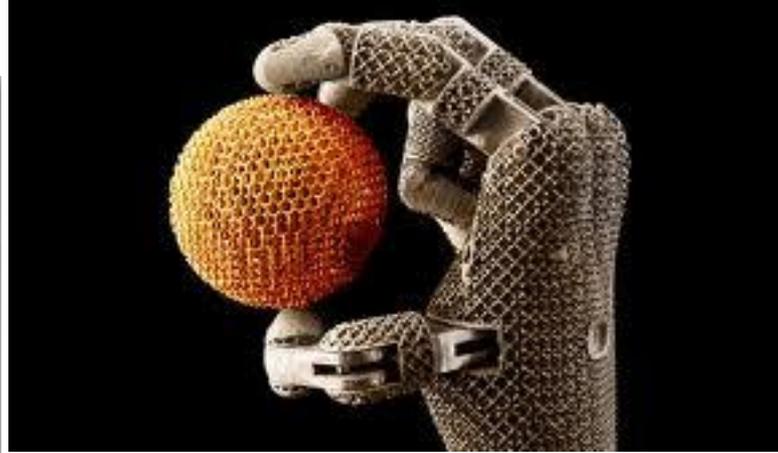
Impact of steel cladding on LWR neutronics



Conventional manufacturing often results in property degradation, and cannot produce spatially complex parts



Advanced manufacturing technologies will reshape how we fabricate engineering components in the 21st century



Shelby Cobra made by 3D printing in ~24 h (ORNL)

North American International Auto Show, Detroit, Jan. 2015