U.S. DEPARTMENT OF ENERGY | Nuclear Energy

NEET-3 FY 2012 Award

Accelerated Development of Zr-Bearing Ferritic Steels for Advanced Nuclear Reactors

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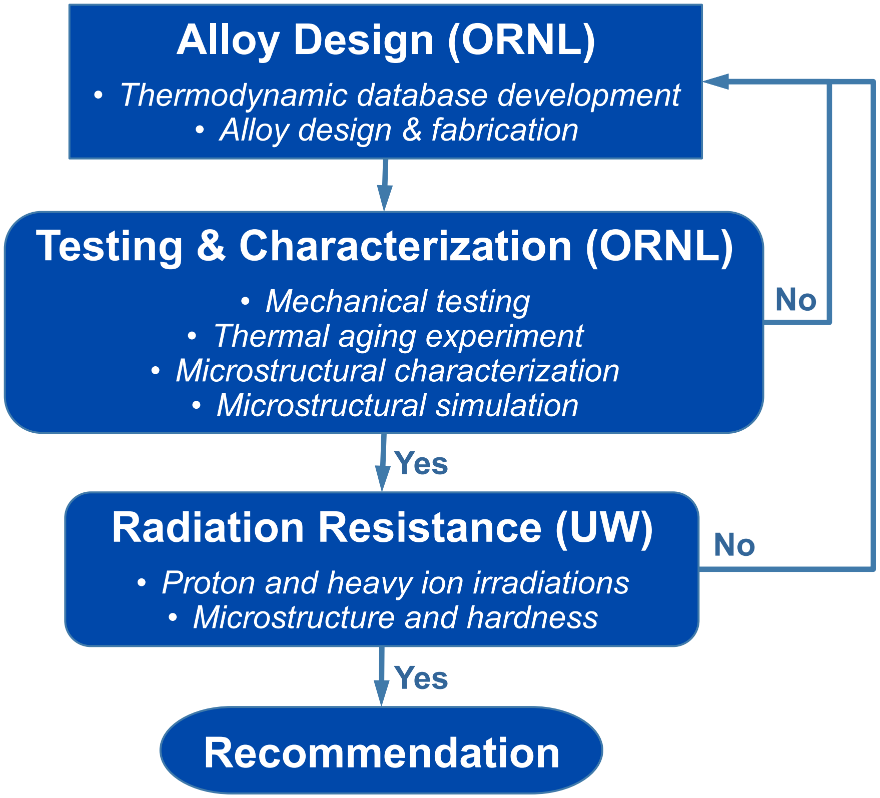
Research Plan



Alloy Design (ORNL)

- *Thermodynamic database development*
- *Alloy design & fabrication*

Testing & Characterization (ORNL)

- *Mechanical testing*
- *Thermal aging experiment*
- *Microstructural characterization*
- *Microstructural simulation*

No

Yes

Radiation Resistance (UW)

- *Proton and heavy ion irradiations*
- *Microstructure and hardness*

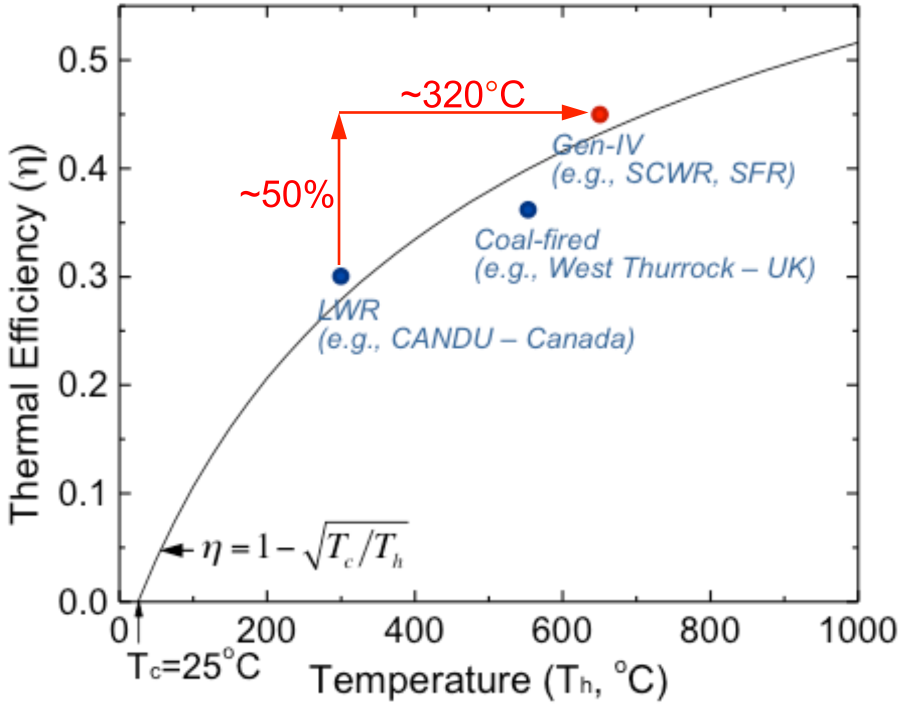
No

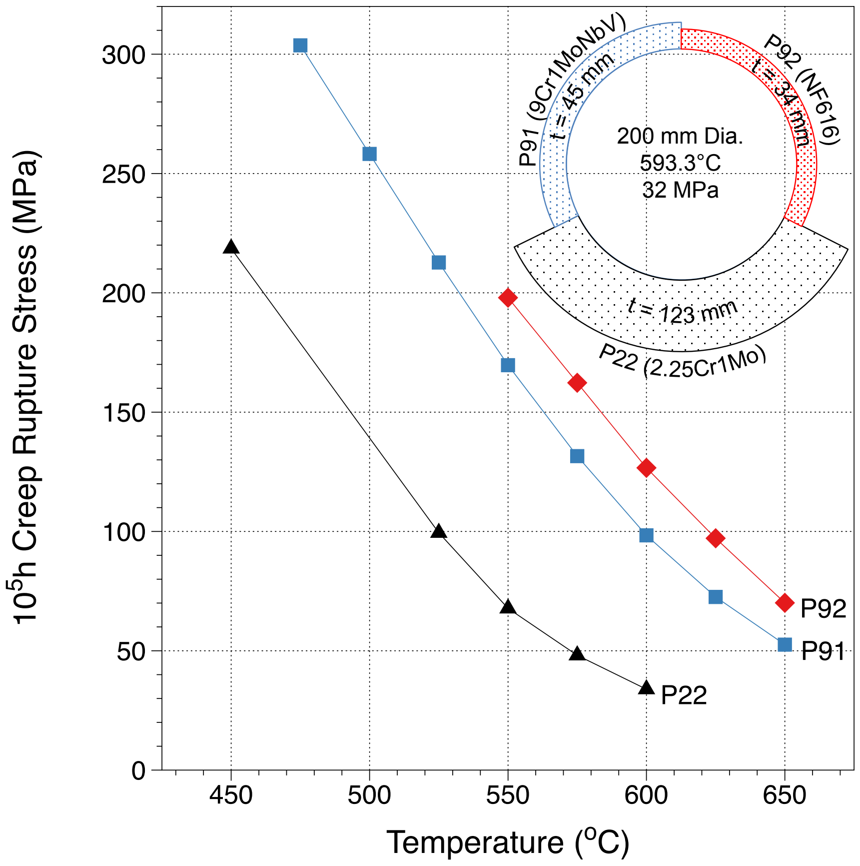
Yes

Recommendation

The Need for Advanced Material Development

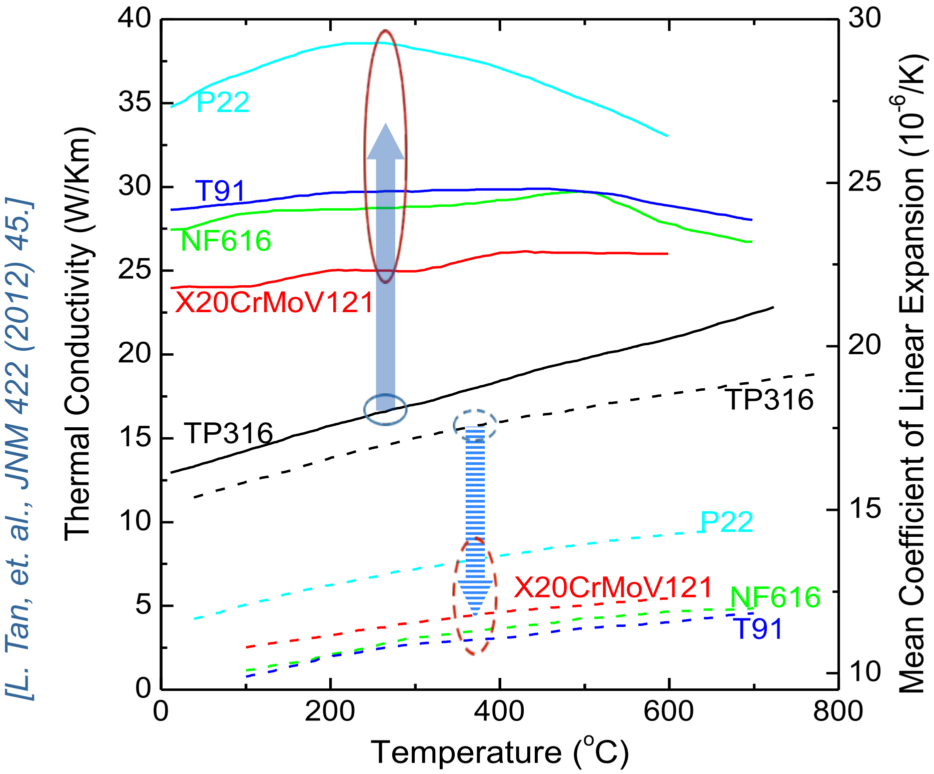
- **The escalating global clean-energy need drives higher operating temperatures of power plants for improved thermal efficiency.**
- **Advanced materials with superior high-temperature strength can effectively improve plant economics** (*reduced commodities, increased thermal efficiency, longer lifetimes*)**, safety margins, and design flexibility.**



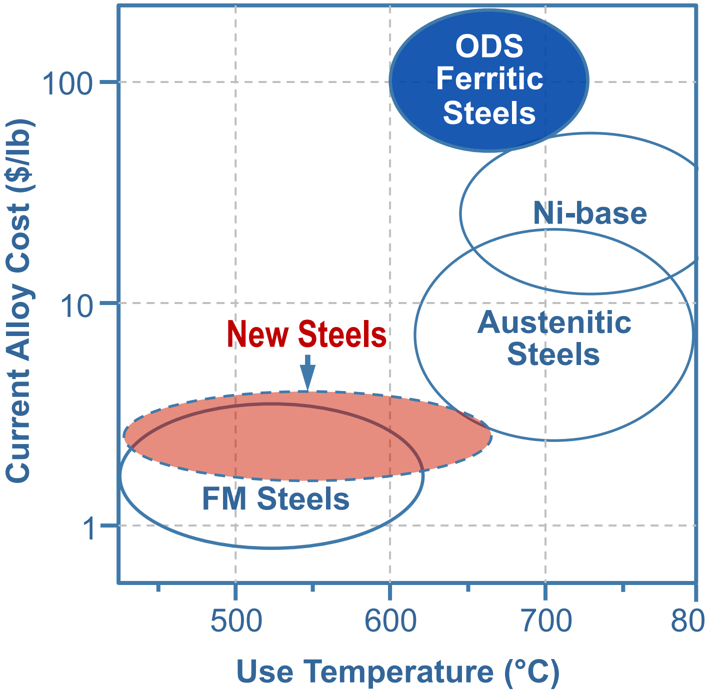


Ferritic Steels Have Outstanding Properties for Engineering Design

- **Ferritic steels are important structural materials for nuclear reactors**
  - Advantages of FM steels over austenitic stainless steels
    - *High resistance to radiation-induced void swelling (e.g., ~10 times better at temperatures above 300°C)*
    - *High thermal conductivity and low thermal expansion*
    - *Low-cost*



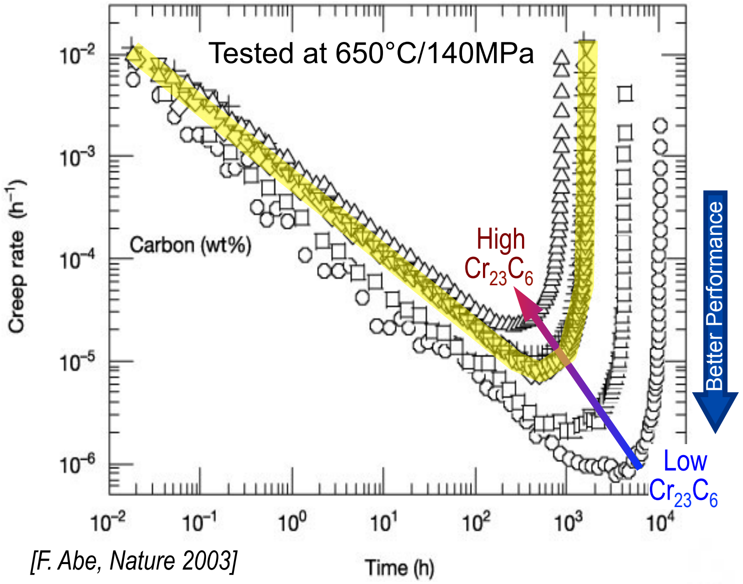
[L. Tan, et. al., JNM 422 (2012) 45.]



[Source: adapted from B.A. Pint]

Concerns of The Current FM Steels

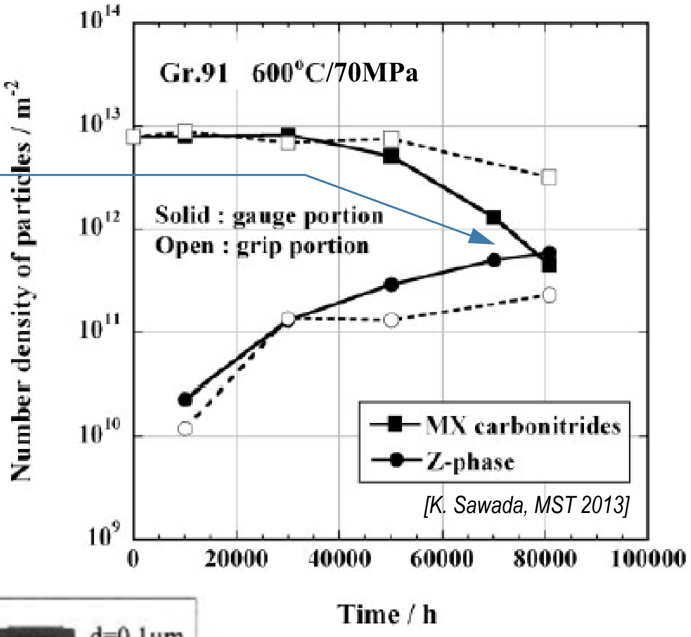
- **Higher $Cr_{23}C_6$ amount results in greater creep rate.**



[F. Abe, Nature 2003]

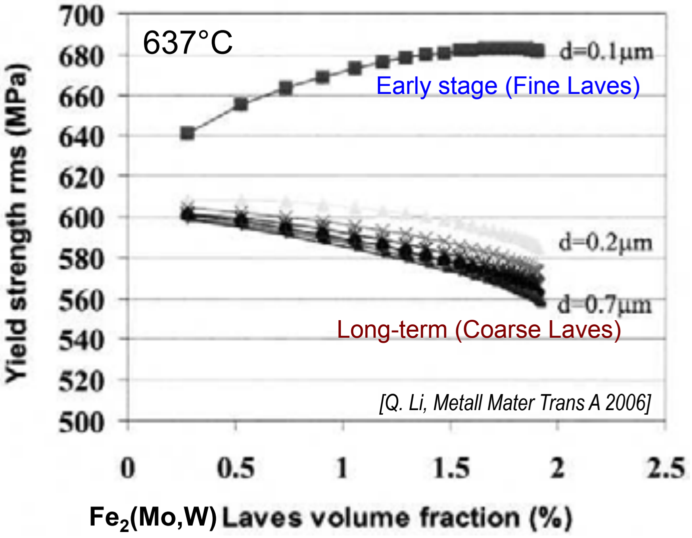
- **Coarse Z-phase forms by consuming fine MX.**

Stress accelerates the replacement of MX by Z-phase.



[K. Sawada, MST 2013]

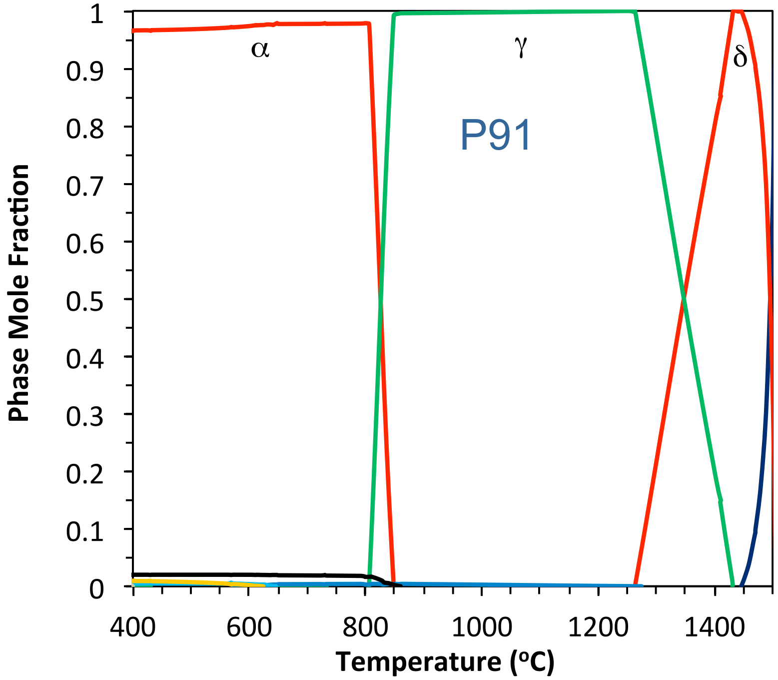
- **Laves phase coarsening deteriorates strength.**

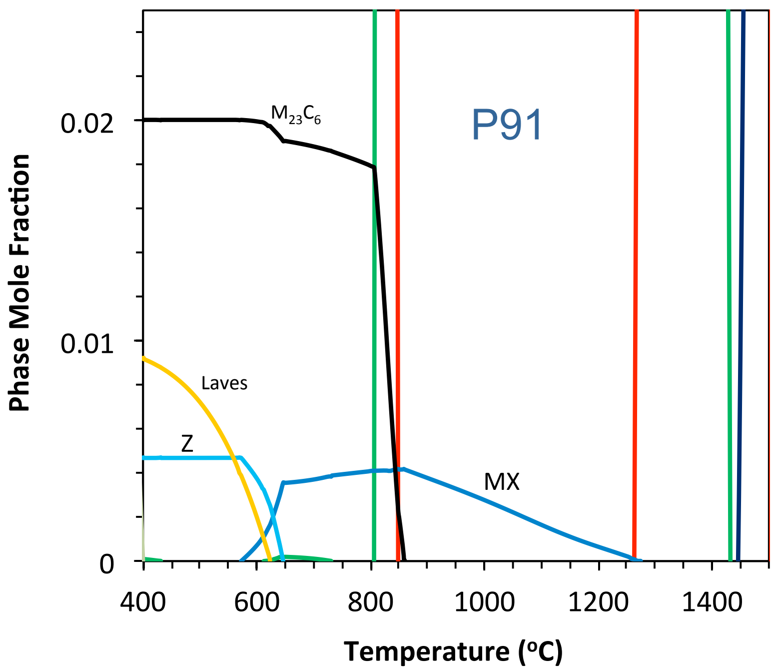


[Q. Li, Metall Mater Trans A 2006]

Alloy Design Routes

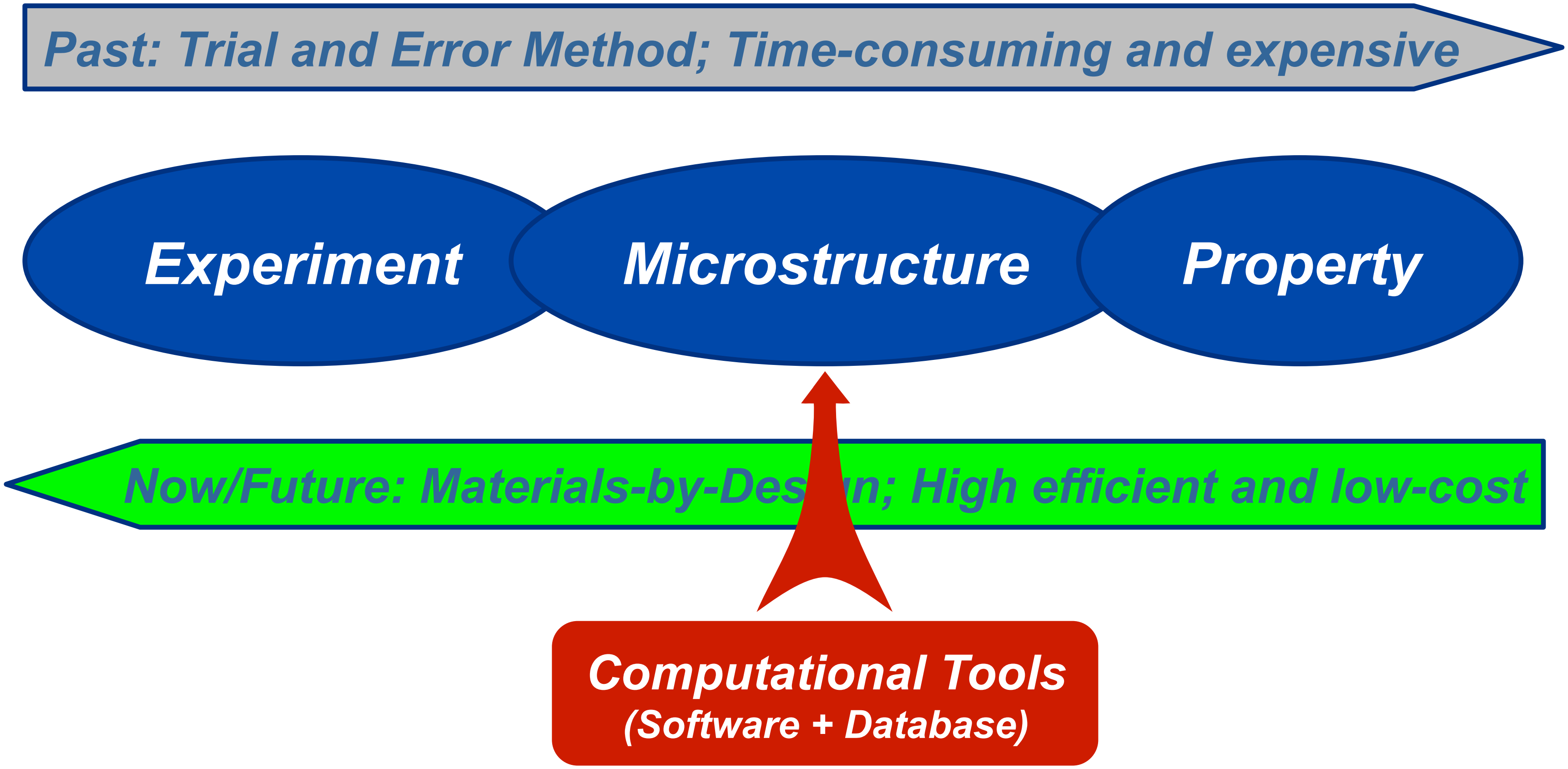
- **Route I: Advanced FM steels**
  - Adjust alloy composition to reduce $M_{23}C_6$, increase MX, and prevent Z-phase.





- **Route II: Fully ferritic steels**
  - Prevent softening caused by the α → γ phase transformation

Approach to Accelerate The Development of Zr-Containing Ferritic Steels



Past: Trial and Error Method; Time-consuming and expensive

Experiment

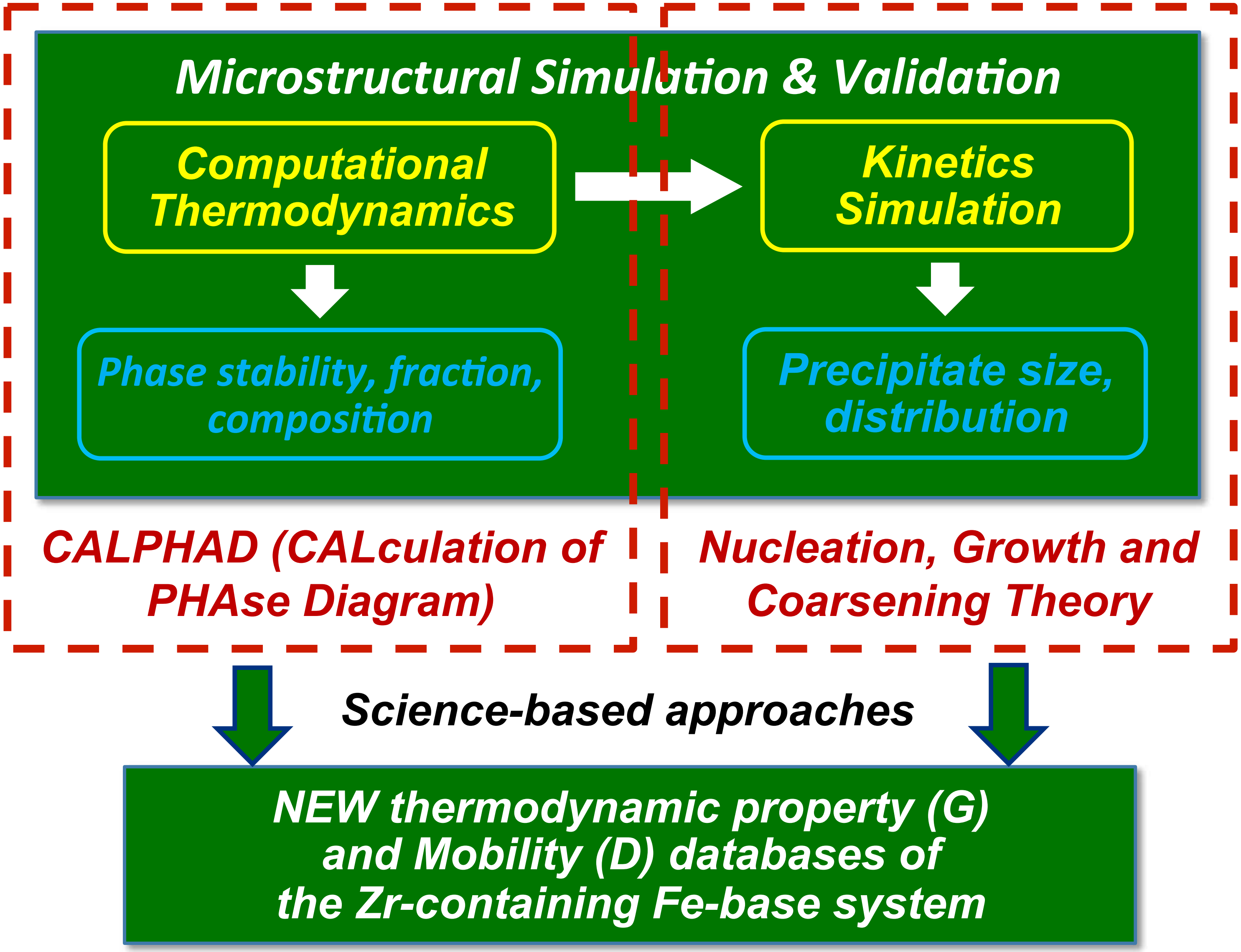
Microstructure

Property

Now/Future: Materials-by-Design; High efficient and low-cost

Computational Tools
(Software + Database)

Computational Microstructural Modeling



Microstructural Simulation & Validation

Computational Thermodynamics

Phase stability, fraction, composition

Kinetics Simulation

Precipitate size, distribution

CALPHAD (CALculation of PHAse Diagram)

Nucleation, Growth and Coarsening Theory

Science-based approaches

NEW thermodynamic property (G) and Mobility (D) databases of the Zr-containing Fe-base system

Computational tools used in this study

Software

Database

Computational thermodynamics
- *Matcalc 5.51*
- *Pandat 8.0*

Precipitation kinetics
- *Matcalc 5.51*

Thermodynamic property
- *OCTANT (in-house)*

Mobility
- *MCFe (Non-encrypt)*

OCTANT: ORNL Computational Thermodynamics for Applied Nuclear Technology

Thermodynamic database
Fe-C-Cr-Mo-Nb-Ti-W-Zr

Binaries

	C	Cr	Mo	Nb	Ti	W	Zr
Fe	🟩 Fe-C	🟩 Fe-Cr	🟩 Fe-Mo	🟩 Fe-Nb	🟩 Fe-Ti	🟩 Fe-W	🟩 Fe-Zr
C		🟩 C-Cr	🟩 C-Mo	🟩 C-Nb	🟩 C-Ti	🟩 C-W	🟩 C-Zr
Cr			🟩 Cr-Mo	🟩 Cr-Nb	🟩 Cr-Ti	🟩 Cr-Ti	🟩 Cr-Zr
Mo				🟩 Mo-Nb	🟩 Mo-Ti	🟩 Mo-W	🟩 Mo-Zr
Nb					🟩 Nb-Ti	🟩 Nb-W	🟩 Nb-Zr
Ti						🟩 Ti-W	🟩 Ti-Zr
W							🟩 W-Zr

X-Y-C Ternaries

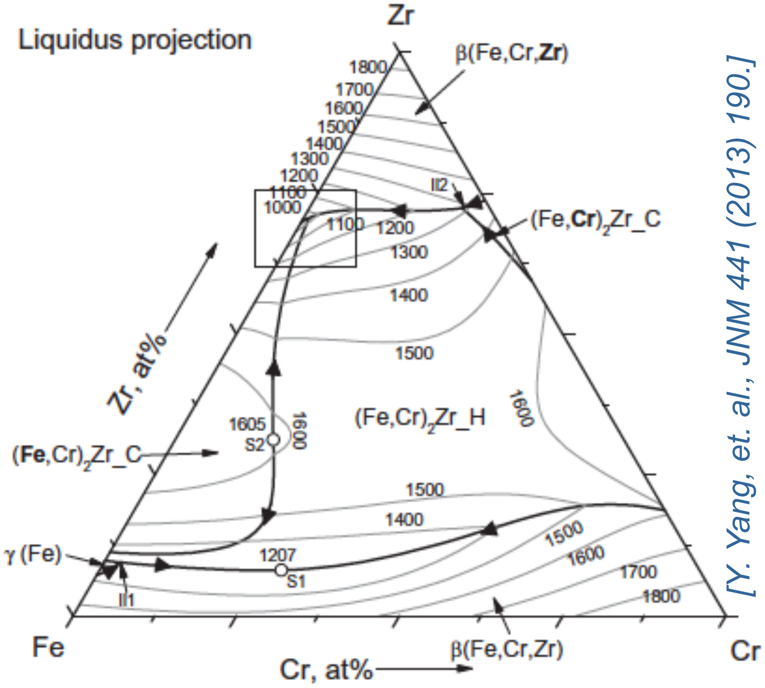
	Mo	Nb	Ti	W	Zr
Cr-C	🟨 Cr-Mo-C	🟨 Cr-Nb-C	🟨 Cr-Ti-C	🟩 Cr-W-C	🟨 Cr-Zr-C
Mo-C		🟨 Mo-Nb-C	🟨 Mo-Ti-C	🟩 Mo-W-C	🟨 Mo-Zr-C
Nb-C			🟩 Nb-Ti-C	🟩 Nb-W-C	🟨 Nb-Zr-C
Ti-C				🟩 W-Ti-C	🟨 Ti-Zr-C
W-C					🟨 W-Zr-C

Fe-X-Y Ternaries

	Cr	Mo	Nb	Ti	W	Zr
Fe-C	🟨 Fe-C-Cr	🟩 Fe-C-Mo	🟨 Fe-C-Nb	🟩 Fe-C-Ti	🟩 Fe-C-W	🟨 Fe-C-Zr
Fe-Cr		🟨 Fe-Cr-Mo	🟨 Fe-Cr-Nb	🟨 Fe-Cr-Ti	🟨 Fe-Cr-W	🟨 Fe-Cr-Zr
Fe-Mo			🟨 Fe-Mo-Nb	🟨 Fe-Mo-Ti	🟩 Fe-Mo-W	🟨 Fe-Mo-Zr
Fe-Nb				🟩 Fe-Nb-Ti	🟨 Fe-Nb-W	🟨 Fe-Nb-Zr
Fe-Ti					🟨 Fe-Ti-W	🟨 Fe-Ti-Zr
Fe-W						🟨 Fe-W-Zr

🟩 *From literature*

🟨 *From this work*



[Y. Yang, et. al., JNM 441 (2013) 190.]

Design of Zr-Bearing Alloys

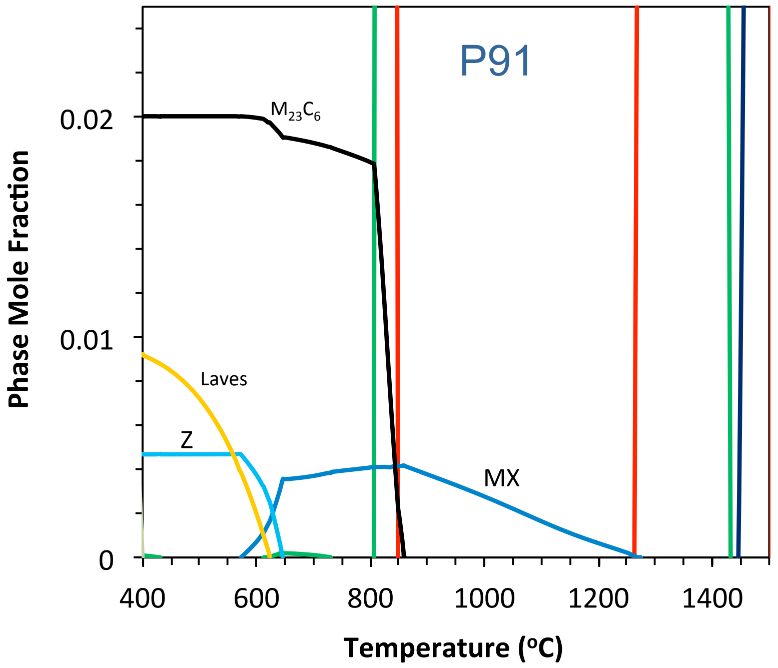
- **Route I: Advanced FM steels**
  - 9Cr ferritic-martensitic steels (T alloys): Better phase stability and lower radiation-induced DBTT shift than 12Cr FM steels.

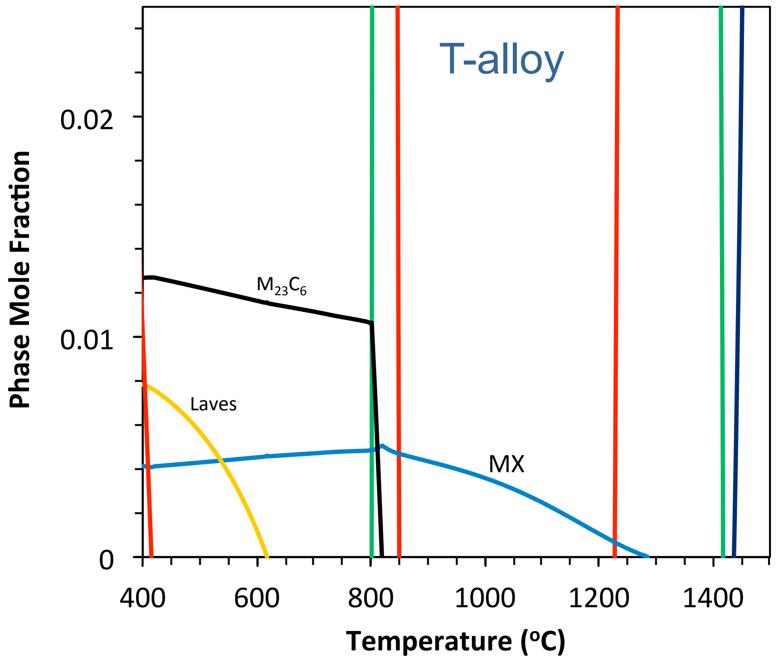
- **Router II: Fully ferritic steels**
  - 15Cr ferritic stainless steels (L alloys): Better corrosion resistance than lower Cr steels, negligible SCC issue, and without temperature-induced α – γ phase transformation in FM steels.
  - Intermetallics-strengthened ferritic alloys (Z alloys): Brand-new ferritic alloys without temperature-induced α – γ phase transformation in FM steels.

- **Reference alloy: Grade 91**

9Cr Ferritic-Martensitic Steels T-Alloys

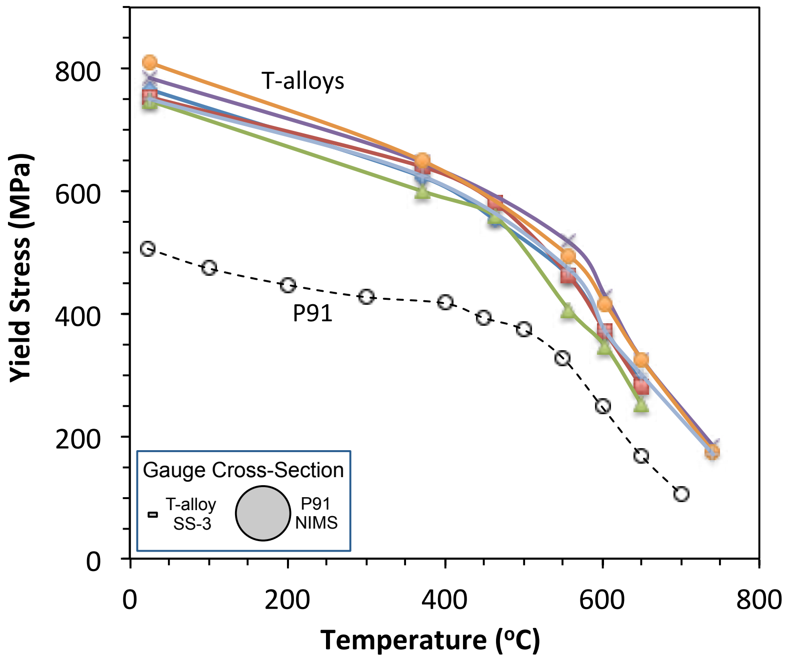
- **Aims:**
  - Increase MX;
  - Reduce $M_{23}C_6$;
  - Eliminate Z-phase;
  - Not much change to Laves phase.
- **Advantages: The experience on steelmaking and welding of conventional FM steels can be directly employed.**

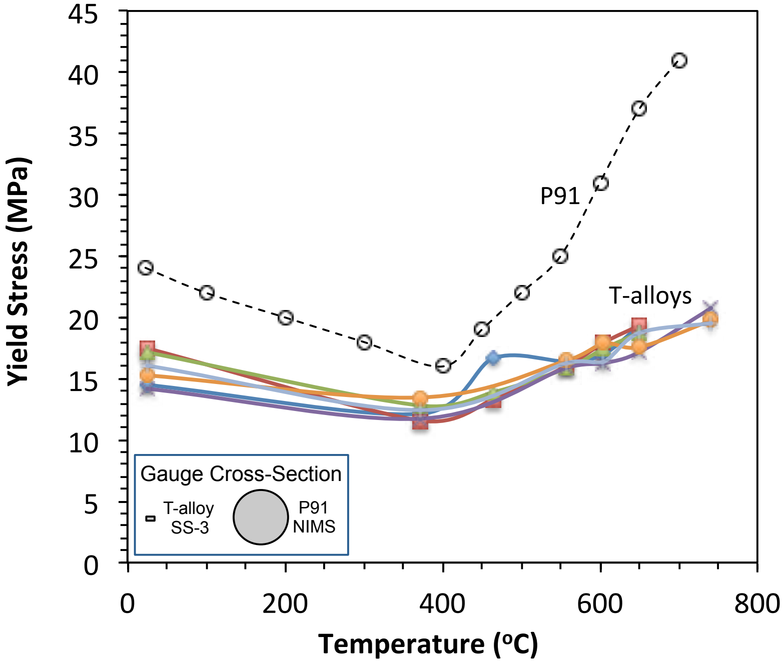




9Cr Ferritic-Martensitic Steels T-Alloys

- **T alloys showed noticeable increases in yield strength (100-300 MPa) compensated with reductions in total elongation as compared to P91.**
  - The miniature type SS-3 specimens have less material for deformation than regular specimens, partly resulting in the reduced elongation.





9Cr Ferritic-Martensitic Steels
T-Alloys

- **Precipitate-strengthening**

$$\sigma_i = 0.8\boldsymbol{MGb} / \lambda_i = 6.98\times10^{-5}\sqrt{\boldsymbol{r_i n_i}}$$

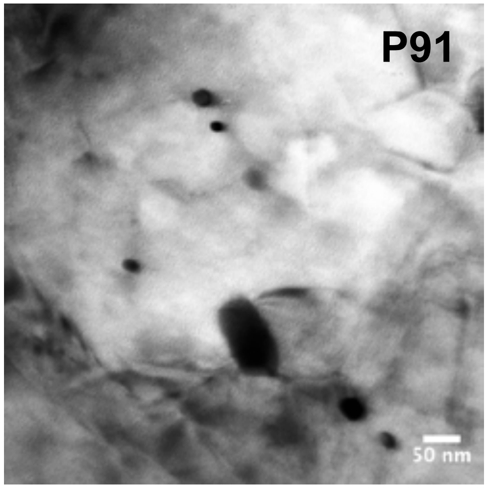
with M = 3.06, G = 83 GPa, b = 0.25 nm

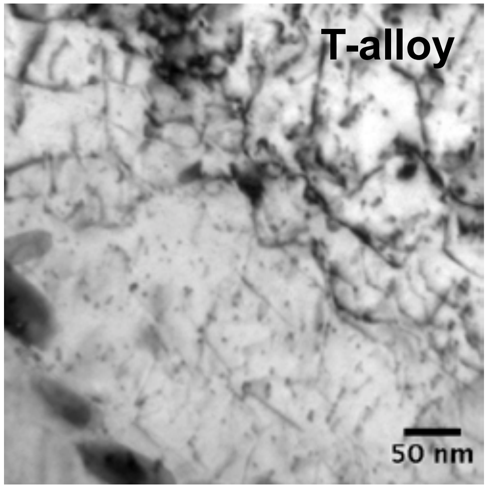
- **Dislocation-strengthening**

$$\sigma_d = 0.5\boldsymbol{MGb}\sqrt{\rho_d} = 3.17\times10^{-5}\sqrt{\rho_d}$$

	T-alloy	P91
Size of MX (r, nm)	5	20
Density of MX (n, m^{-3})	10^{22}	10^{21}
Density of dislocations (ρ_d, m^{-2})	10^{14}	10^{13}
σ_{MX}, MPa	493	312
σ_d, MPa	317	100
$\sqrt{\sigma_{MX}^2 + \sigma_d^2}$, MPa	586	328

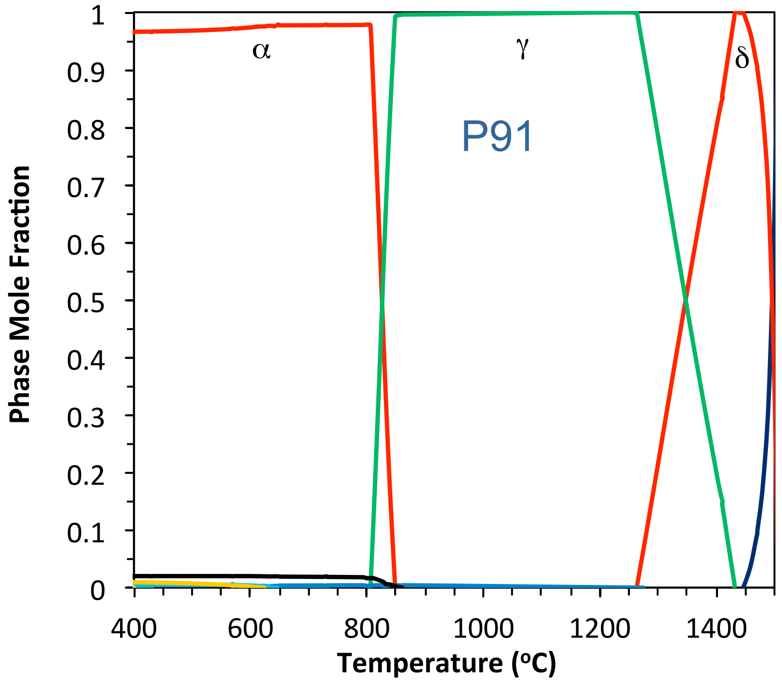
- MX precipitates exhibited greater contribution to strength than free dislocations.
- $\Delta\sigma_{calc.} = \sigma_{T\text{-}alloy} - \sigma_{P91}$ = 258 MPa, comparable to the room-temperature tensile results.

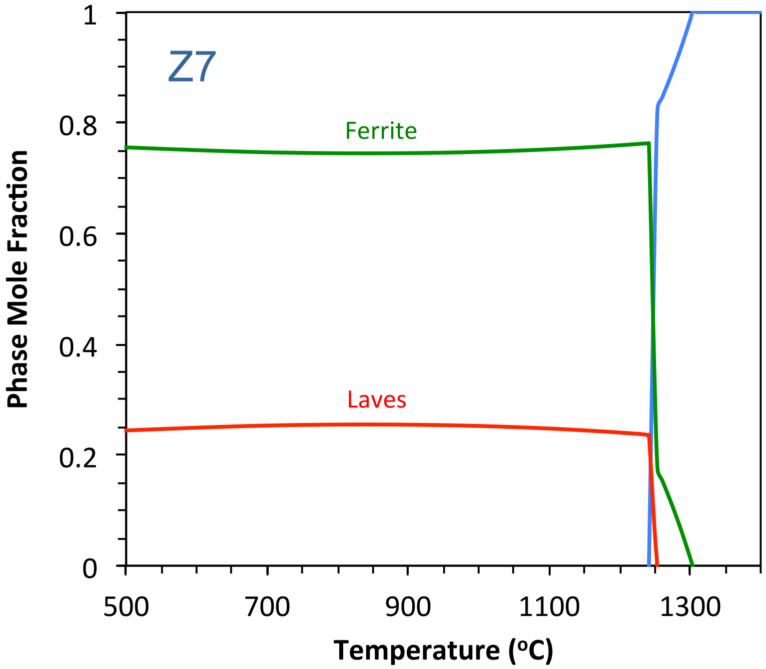




Intermetallics-Strengthened Ferritic Alloys Z-Alloys

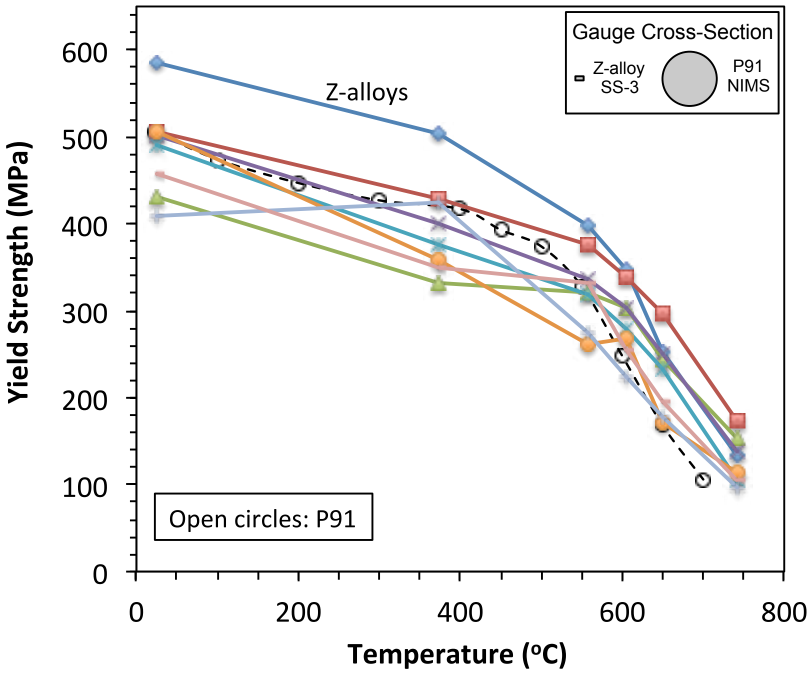
- **Aims:**
  - Develop in-situ composites composed of hard intermetallics and soft matrix;
  - Discover a balanced intermetallics-matrix microstructure for superior properties.
- **Advantages:**
  - Simpler steelmaking processes than FM steels;
  - Without α – γ phase transformation during heating and cooling.

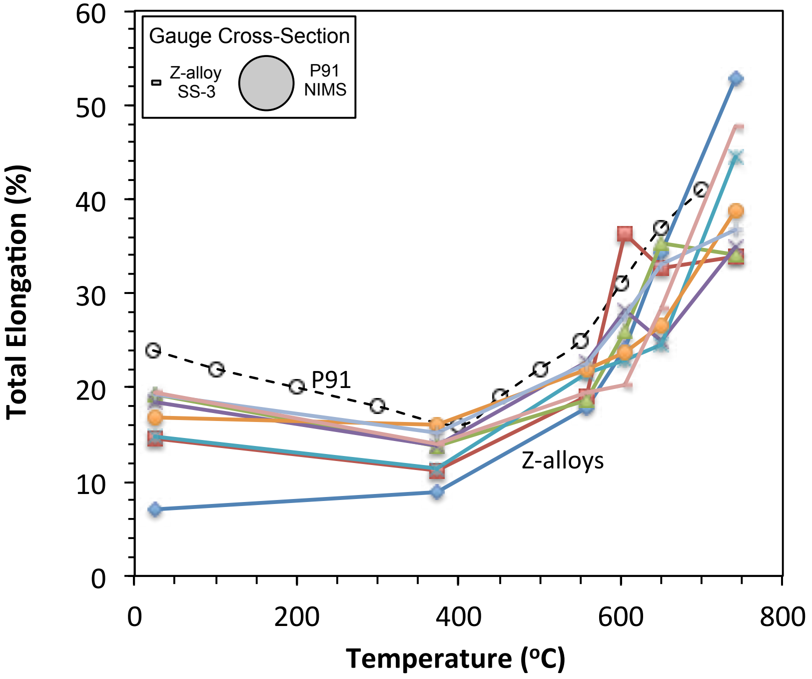




Intermetallics-Strengthened Ferritic Alloys
Z-Alloys

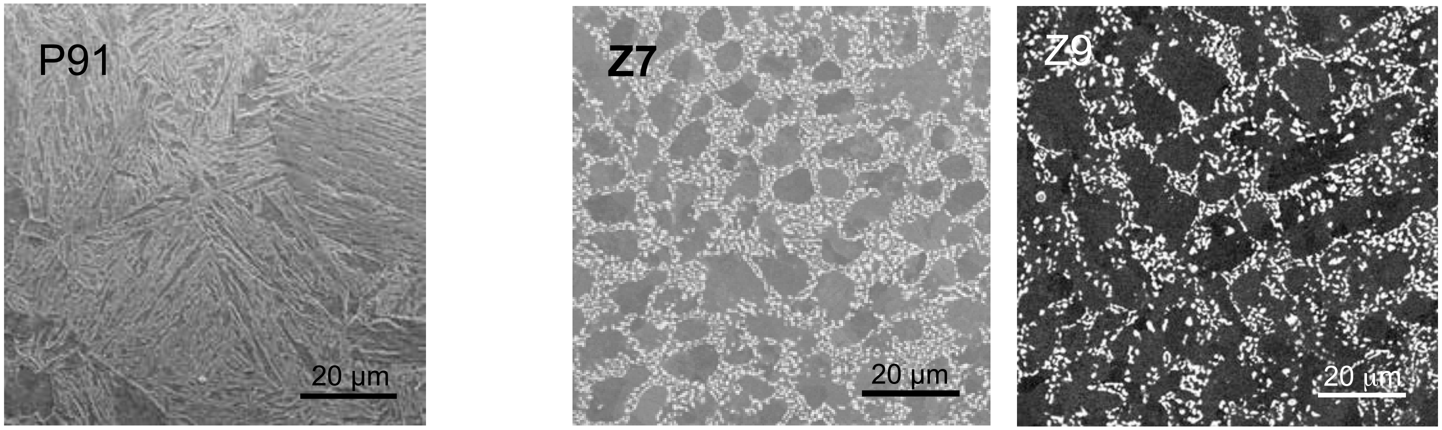
- **Z-alloys showed comparable or greater yield strength than P91, especially at temperatures above ~600°C.**
  - Ductility (total elongation) of the Z-alloys can be adjusted by microstructural (composition) control of the alloys.



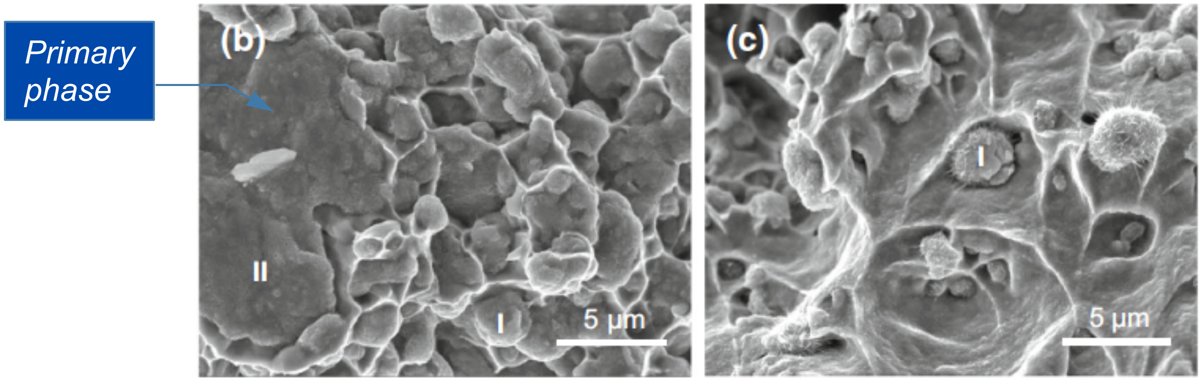


Intermetallics-Strengthened Ferritic Alloys Z-Alloys

- **Different from P91, Z-alloys are composed of eutectic network in a ferritic matrix, which are strongly dependent on alloy composition.**



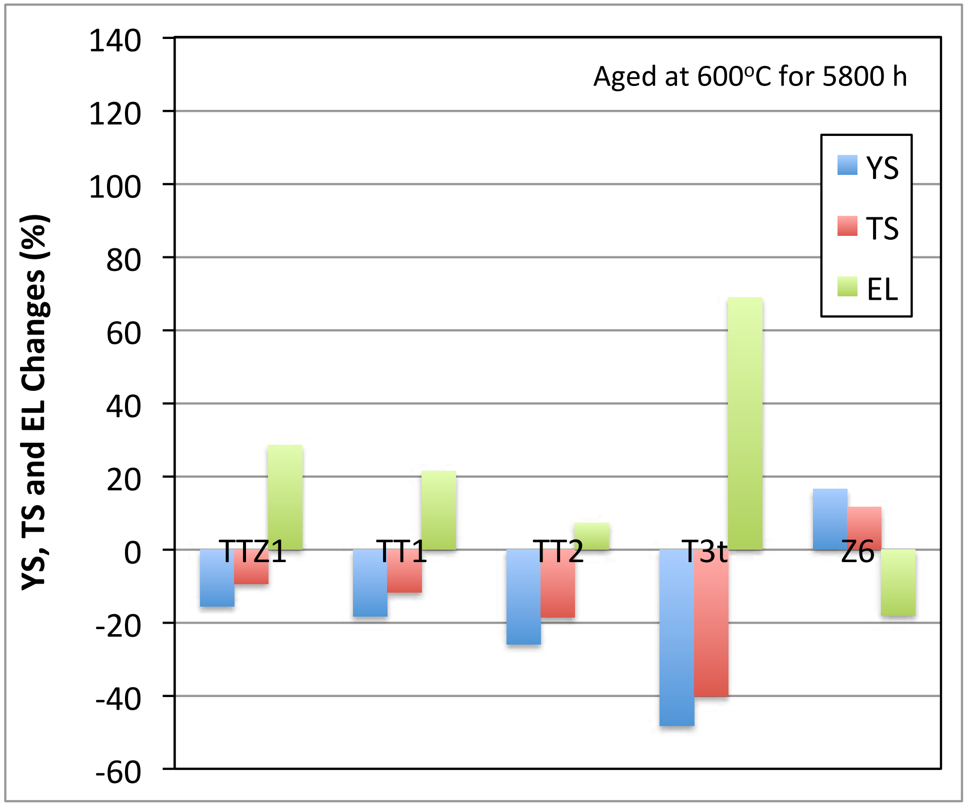
- **Primary phase need to be eliminated in the Z-alloys, which had brittle fracture, in contrast to the intermetallic particles favored ductile facture.**

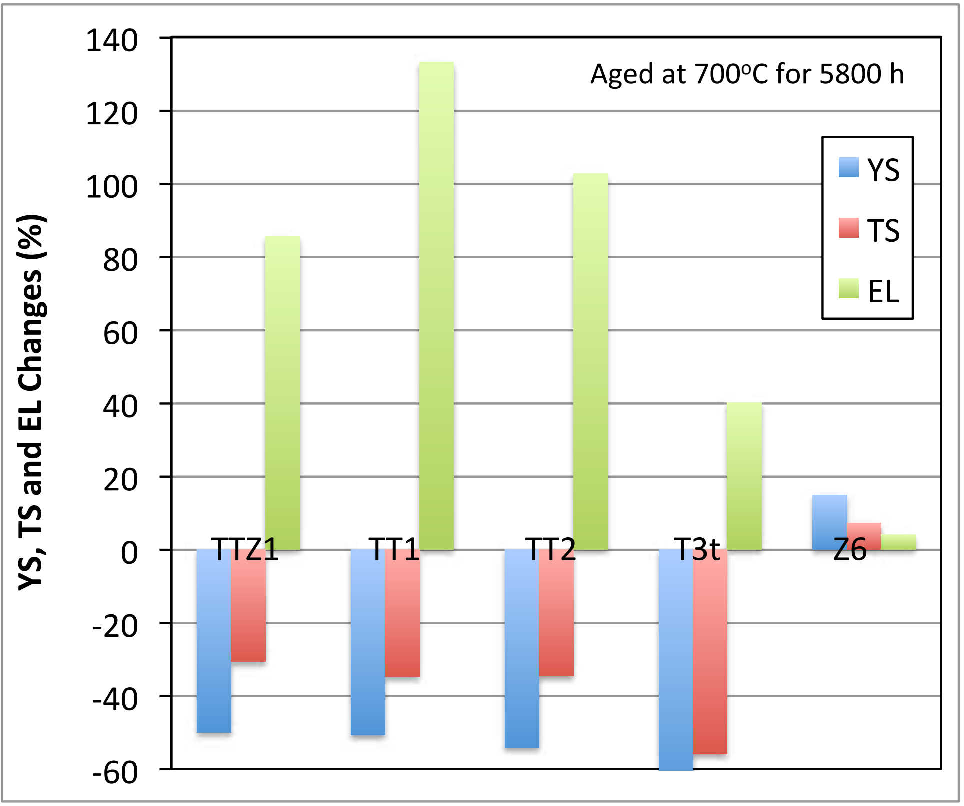


[L. Tan, et al., MMTA 46 (2015) 1188.]

Aging Effect on Strength and Ductility

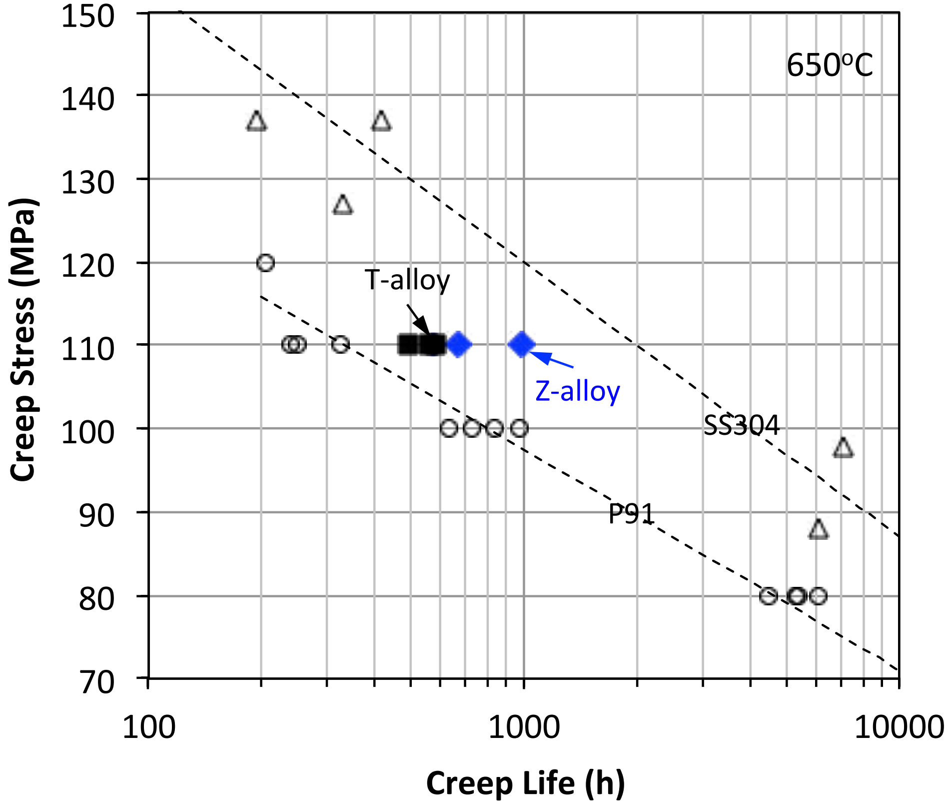
- **Aging resulted in softening of FM steels (T-alloys) but strengthening of ferritic steels (Z-alloys).**
- **Composition adjustment can noticeably mitigate aging-induced softening in FM steels.**
  - As compared to alloy TT1, Zr-alloying (alloy TTZ1) mitigated the aging-induced softening.

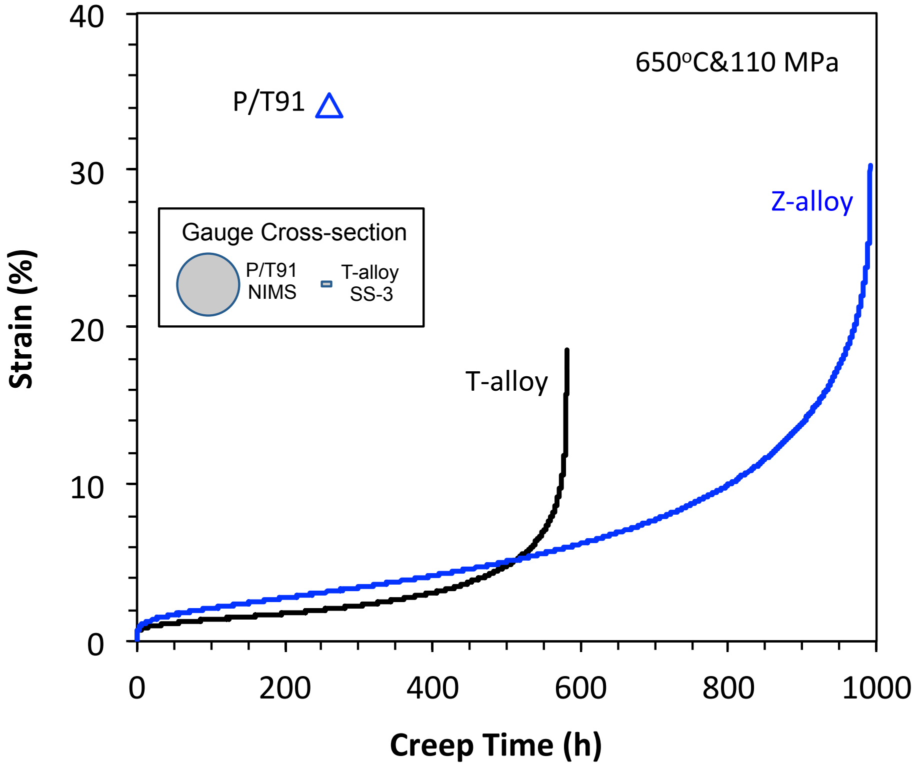




Creep Resistance of The New Alloys

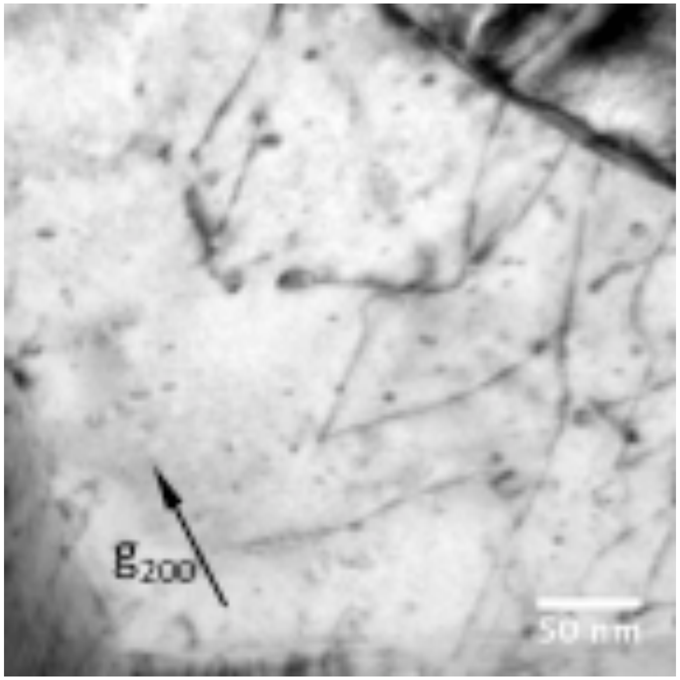
- **T-alloys and Z-alloys showed comparable or greater creep rupture life than P91 at 650°C.**
  - Generally, Z-alloys have greater creep life and strain than T-alloys.

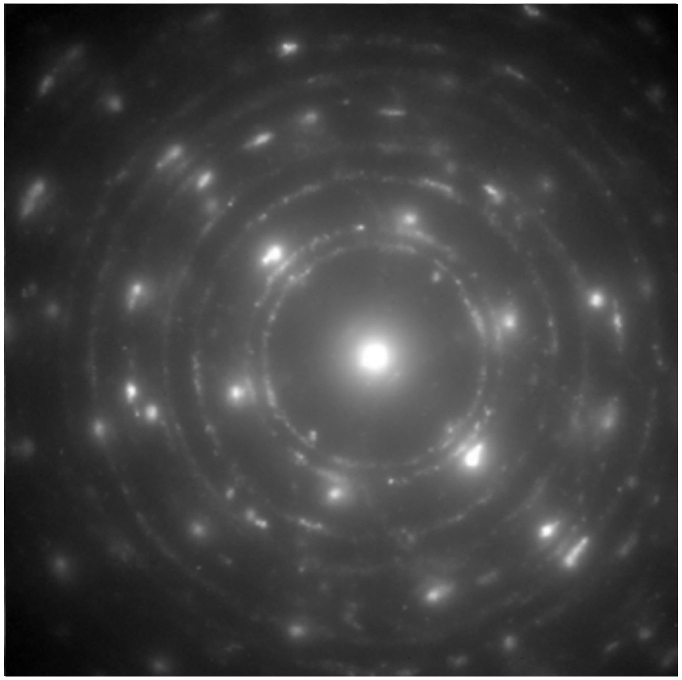




Intermetallics-Strengthened Ferritic Alloys Z-Alloys

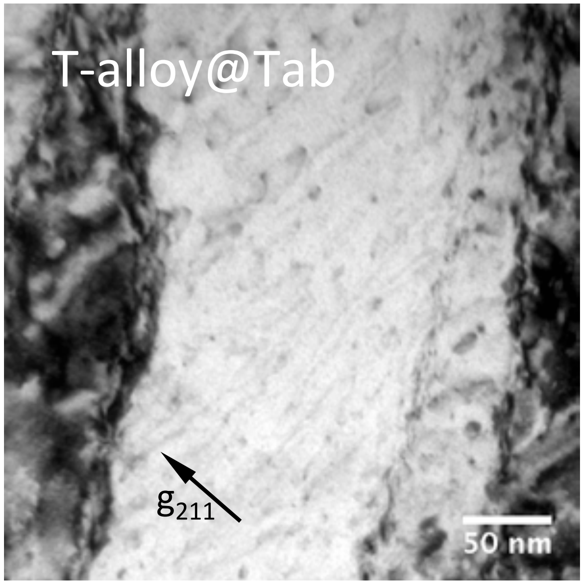
- **High densities of precipitates (10^{19} to 10^{22} m^{-3}) formed in the Z-alloys during creep testing at 650°C, which enhanced creep resistance of the alloys but did not impair creep ductility.**

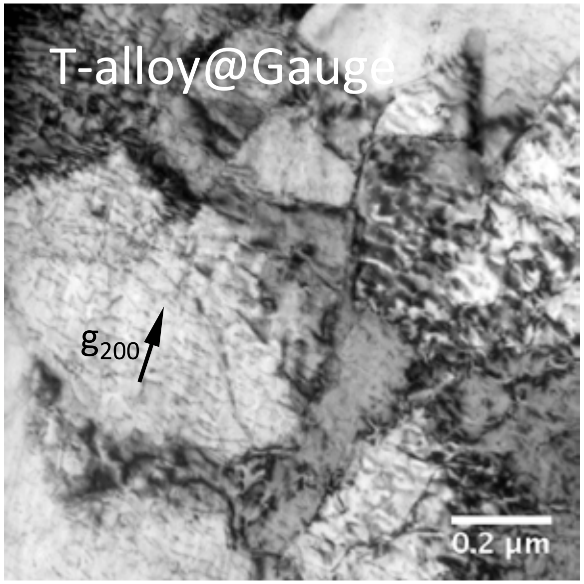


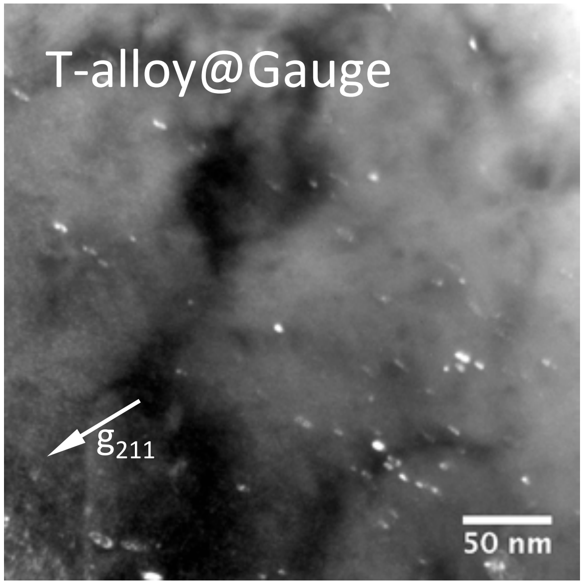


9Cr Ferritic-Martensitic Steels
T-Alloys

- **Creep at 650°C resulted in significant amount of dislocations and recovery of lath boundaries, but not much effect on precipitates.**
- **Recovery of lath boundaries is the primary mechanism resulting in softening of T-alloys, similar to general 9-12% Cr FM steels.**

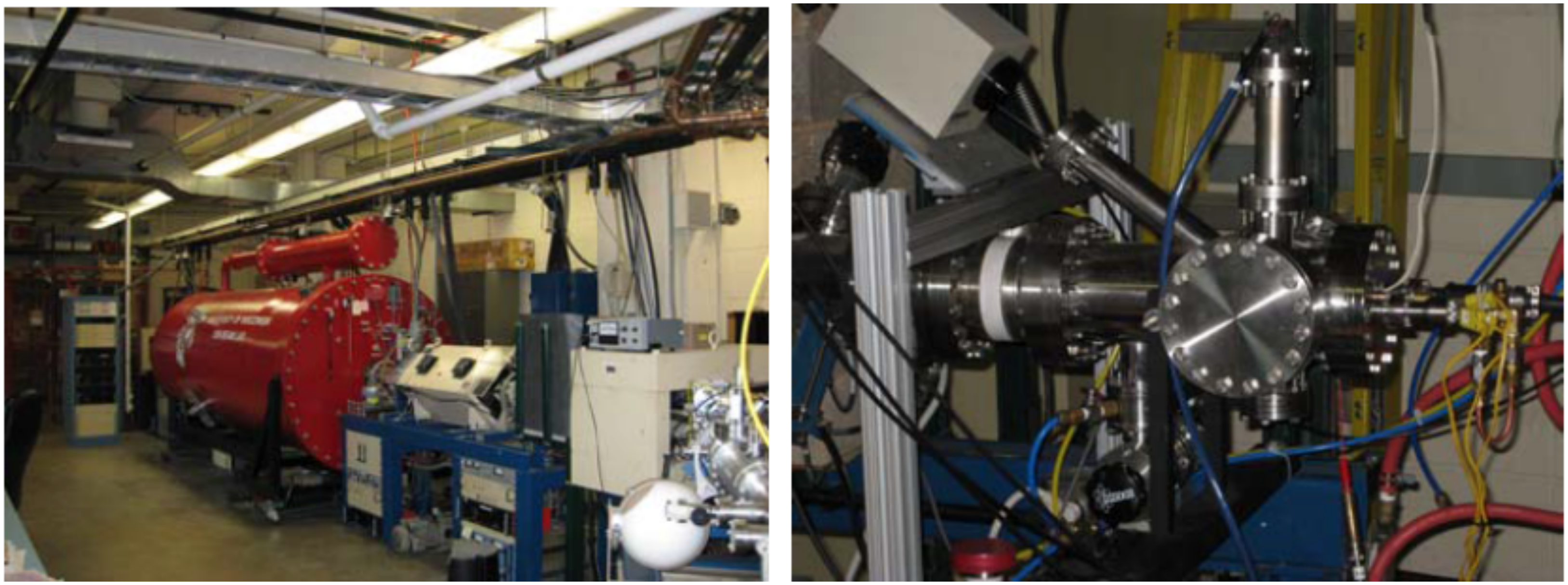






Ion-Irradiation Experiments

- **Radiation resistance of the alloys has being evaluated using proton ion irradiation. Heavy ion (Fe^{2+}) irradiation experiments will be conducted.**
  - Radiation-hardening, radiation-induced phase stability, swelling and segregation will be studied.



1.7 MV Tandem Accelerator Ion Beam @ UW-Madison

Proton Irradiation Experiments

- **Twelve (12) different alloys were irradiated using protons to 0.1 and 1 dpa at 420°C and a dose rate of $3\text{x}10^{-6}$ dpa/s.**

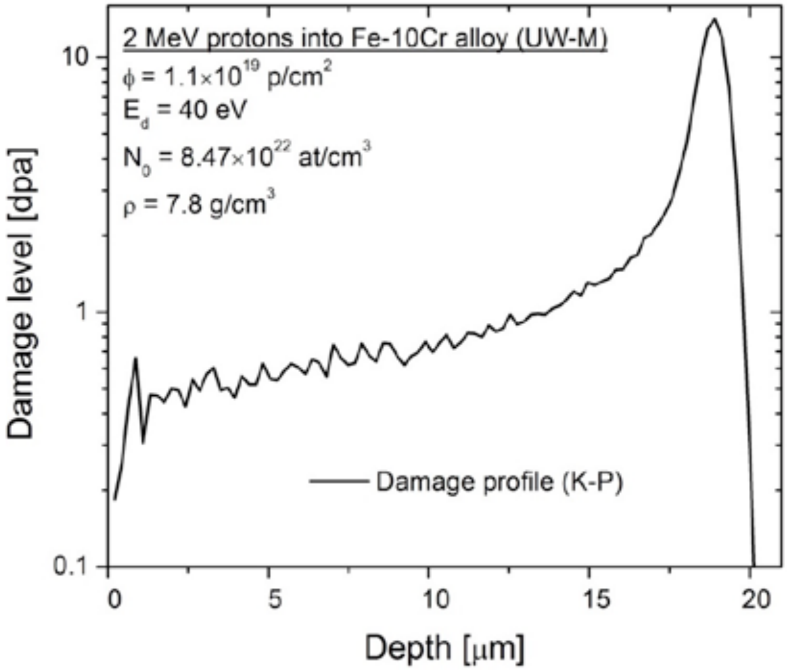
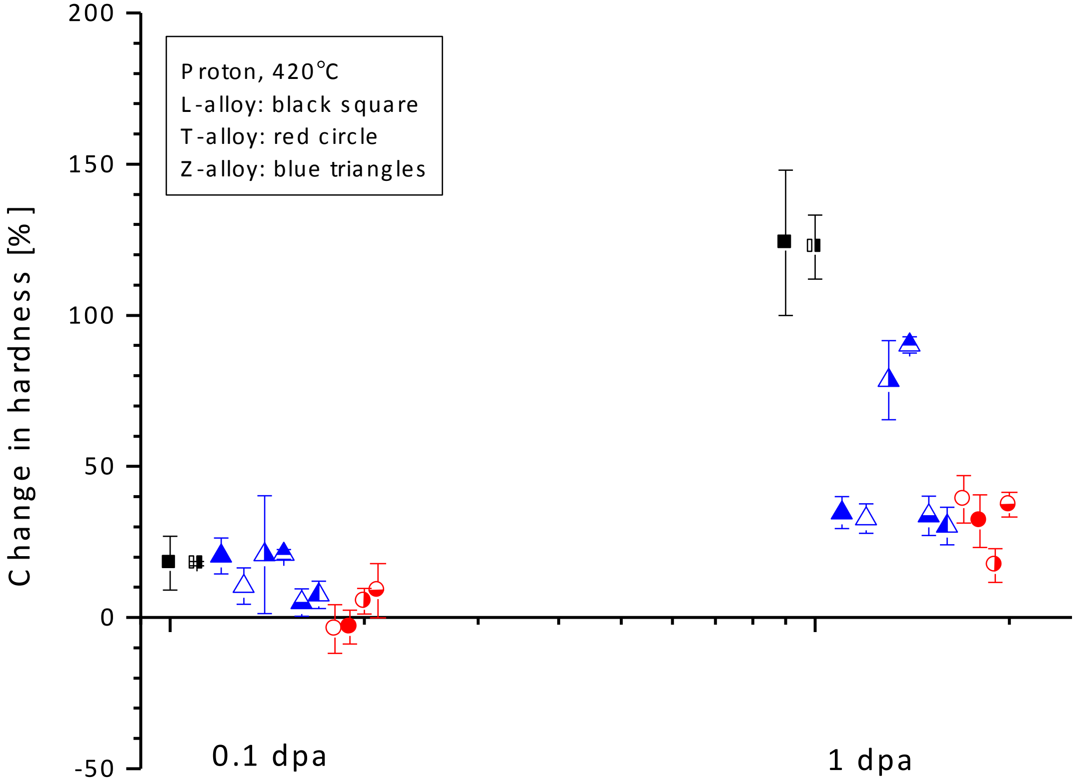


Fig. 1: Damage profile in Fe-10Cr irradiated with 2 MeV proton to 1 dpa.

Fig. 2: Picture of L-alloys before and after proton implantation.

Radiation Hardening
Vickers Microhardness

- **Vickers micro-indentation with 25 gf (~1.9–2.6 μm = ~10% of Rp):**
  - L-alloys exhibited the greatest hardening (120%) after 1 dpa proton irradiation.
  - Z-alloys had a large variation in hardening (~30-90%) after ~1 dpa, indicating a strong effect of solute elements on radiation hardening.
  - T-alloys showed a small level of hardening (20-40%) after up to 2 dpa.
  - As compared with Grade 91 (open circle) with ~40% hardening, the T-alloys and selective Z-alloys have lower hardening.



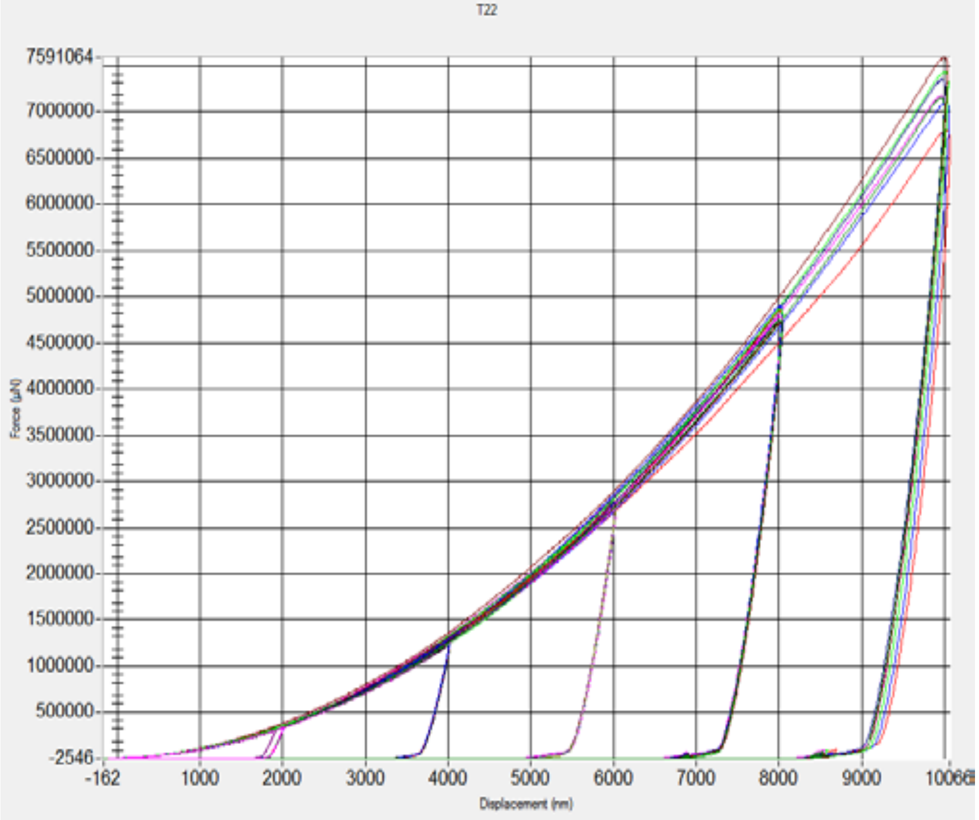
Radiation Hardening Nanoindentation

Hardness calculated by Olive-Pharr method:

$$H = P_{max} / A_c$$

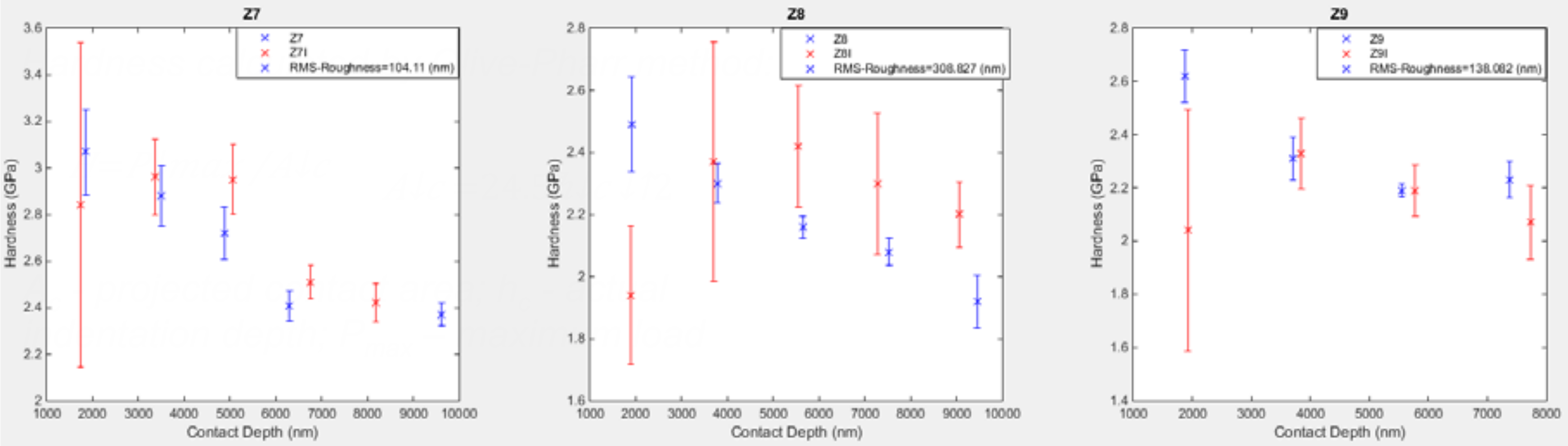
$$A_c = 24.5 h_c^2$$

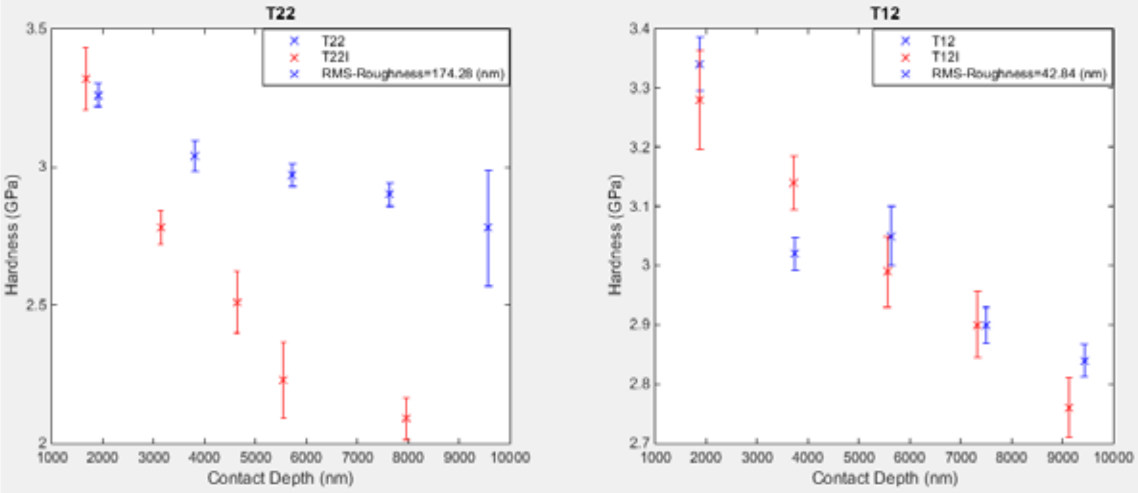
A_c - *projected contact area;* h_c - *actual indentation depth;* P_{max} *– maximum load*



Loading curve for irradiated T22 alloy (1 dpa)

Nano-hardness -- results



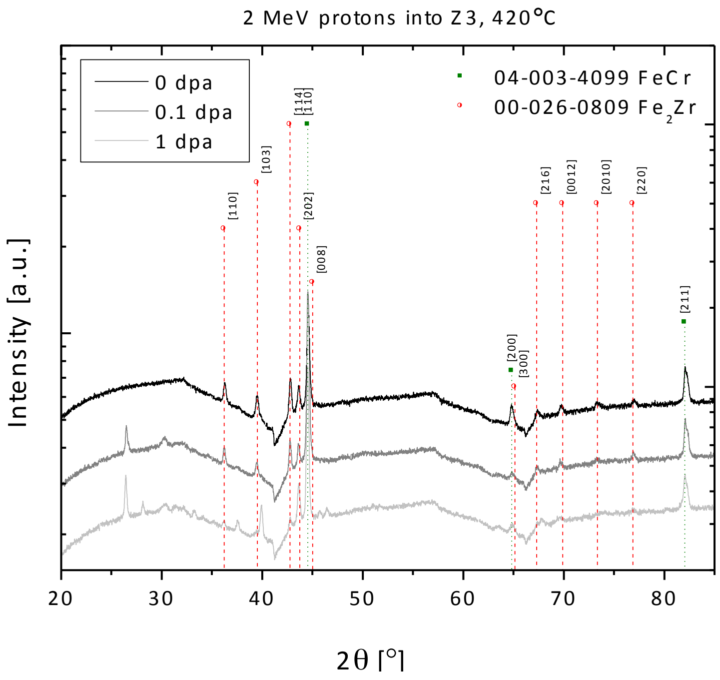


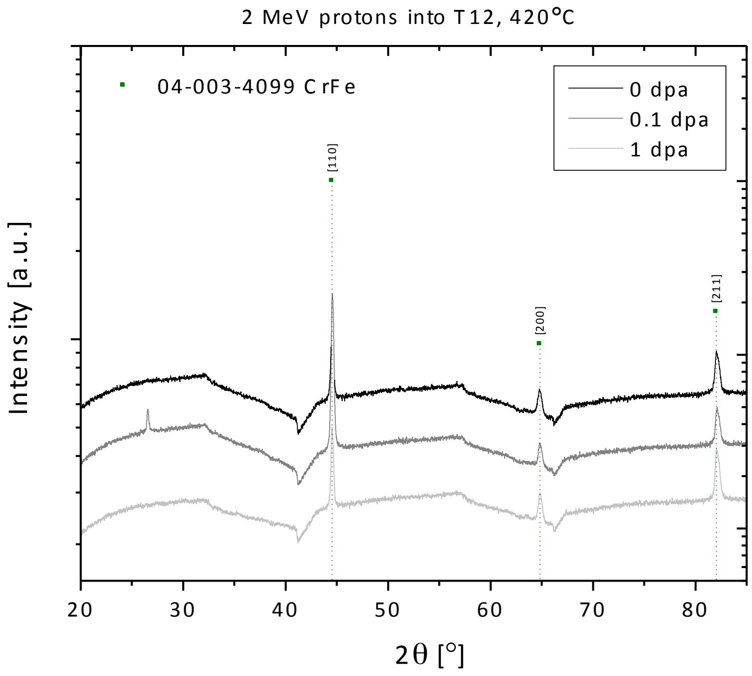
- Surface roughness causes increase in standard deviation a the 2um mark.
- Roughness correction can be applied using the advanced nonlinear Olive-Pharr method.
- Irradiated T22 alloy shows steel softening possible due to presence of voids.

Hardness vs contact depth for all irradiated steel samples (red) as compared to un-irradiated base material (blue).

XRD analysis

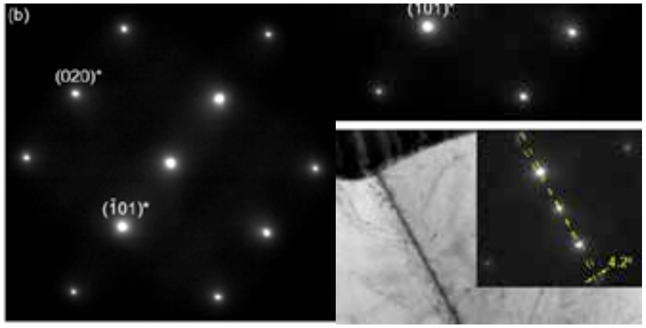
- T-alloys are most resistant to precipitate formation/phase changes due to proton irradiation, which results in the best hardness performance
- Z-alloys underwent some phase change during proton irradiation at various damage levels. Fe_2Zr hexagonal phase could be clearly identified, especially in the samples with a higher Zr content.



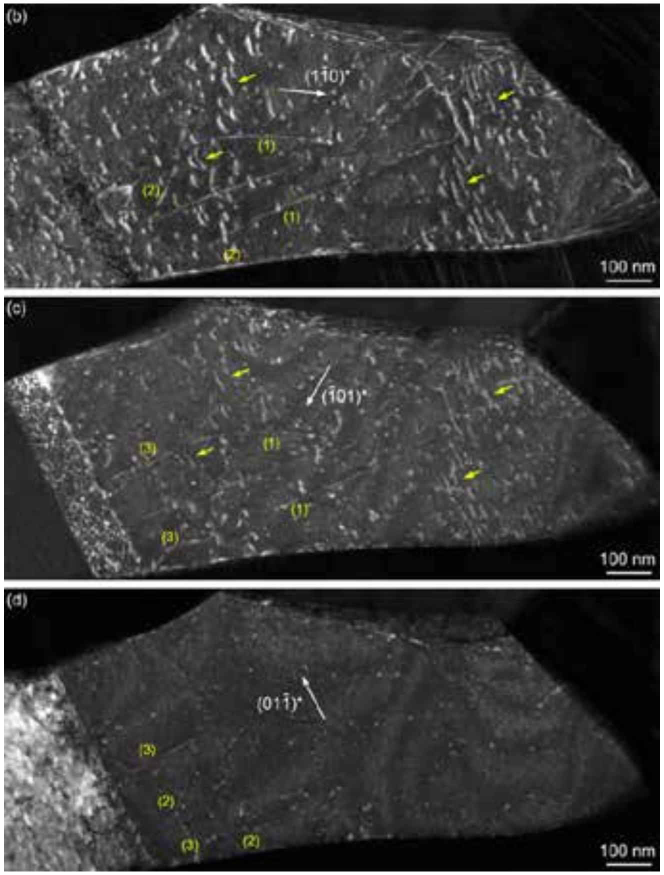


Microstructure of Z-Alloy Ferritic Matrix

- BCC single phase ($d_{(110)}$ = 1.97 Å) accords with α-Fe.
- Dislocation lines with Burgers vectors of <111>/2 or <100>
- Long dislocation lines are mostly nucleated from matrix grain boundaries or phase interfaces
- Short dislocation threads (10~100 nm) are uniformly dispersed throughout the grain. They are identified as edge dislocations with Burgers vector of <100>



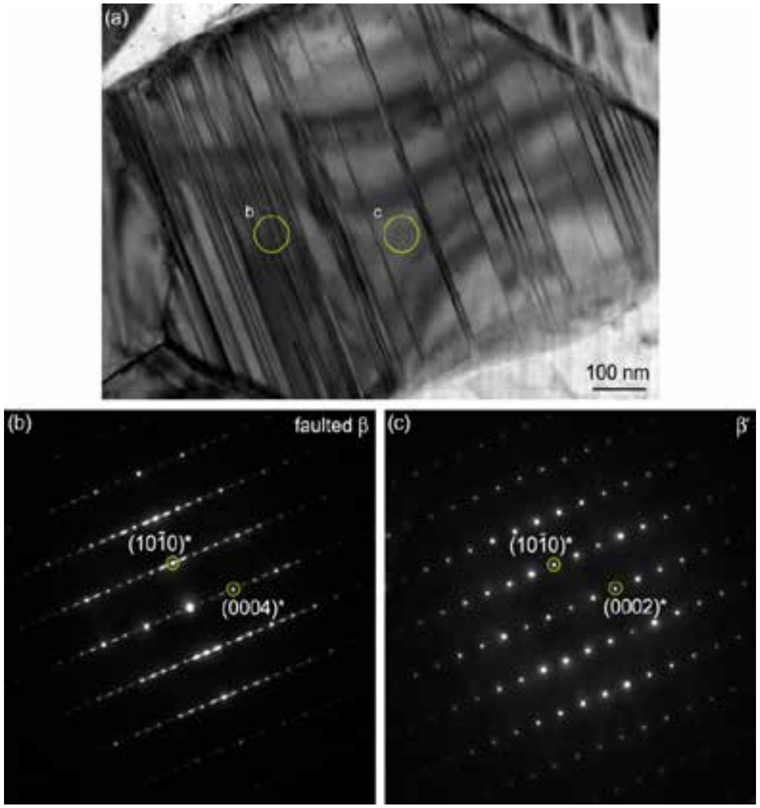
Diffraction patterns in [101] zone axis of α-Fe. (d) Bright-field TEM image of the grain boundary. Defects and/or strain field are noticed near the boundary. (Inset) diffraction pattern showing a small misorientation angle.



WBDF TEM image of the same grain at different **g** vectors. All images were recorded in (**g**, 3.1**g**) condition

Microstructure of Zr/W-rich Phase

- Aberration-corrected HRSTEM revealed high density of planar defects in the β-Fe_2Zr, a C36 type ($P6_3/mmc$) Laves phase (b-circle), and β’-Fe_2Zr, a C14 type ($P6_3/mmc$) Laves phase (c-circle).
- The stacking order of structural units agrees perfectly with structure models of faulted C36 and pristine C14 Laves phases
- Atomic ratio between Fe and Zr in these Laves phases is about 2.6 – chemically imperfect



Crystal structure of Zr/W-rich phase. (a) Bright-field TEM image shows severely faulted bands divided by defect-free bands. (b, c) Selected area diffraction patterns from circle b and c in (a), respectively.

Summary

- Two classes of alloys with Zr-alloying were developed, i.e., T-alloys (advanced FM steels) and Z-alloys (intermetallics-strengthened alloys), which showed promising results for superior high-temperature performance as compared with Grade 91.
  - Increased yield/tensile strength (by ~100–300 MPa from ~700 to 25°C) compensated with some decreases in ductility.
  - Improved creep resistance with significantly greater creep lives.
- Alloy composition exhibited noticeable effect on radiation hardening/ softening for both Z-alloys and T-alloys.