NEET FY 12 Project

Accelerated Development of Zr-Containing New Generation Ferritic Steels for Advanced Nuclear Reactors

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DOE-NE Materials Crosscut Coordination Meeting

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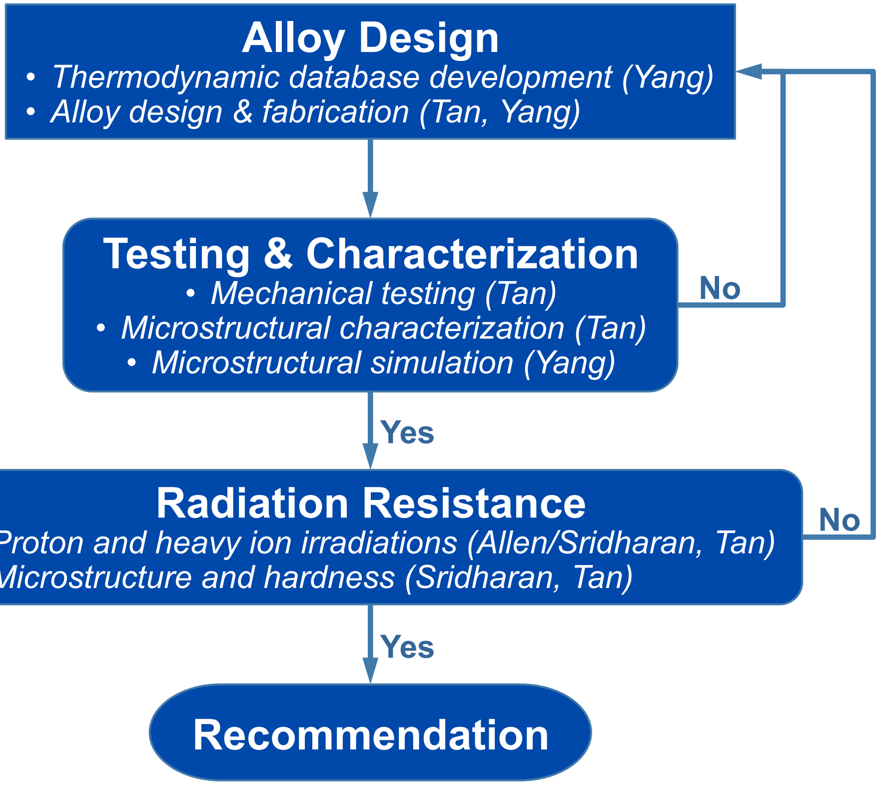
Tasks and Team Members

- **Team Members**
  - Lizhen Tan and Ying Yang (ORNL)
  - Todd Allen and Kumar Sridharan (UW-Madison)
- **Tasks**



Alloy Design
- *Thermodynamic database development (Yang)*
- *Alloy design & fabrication (Tan, Yang)*

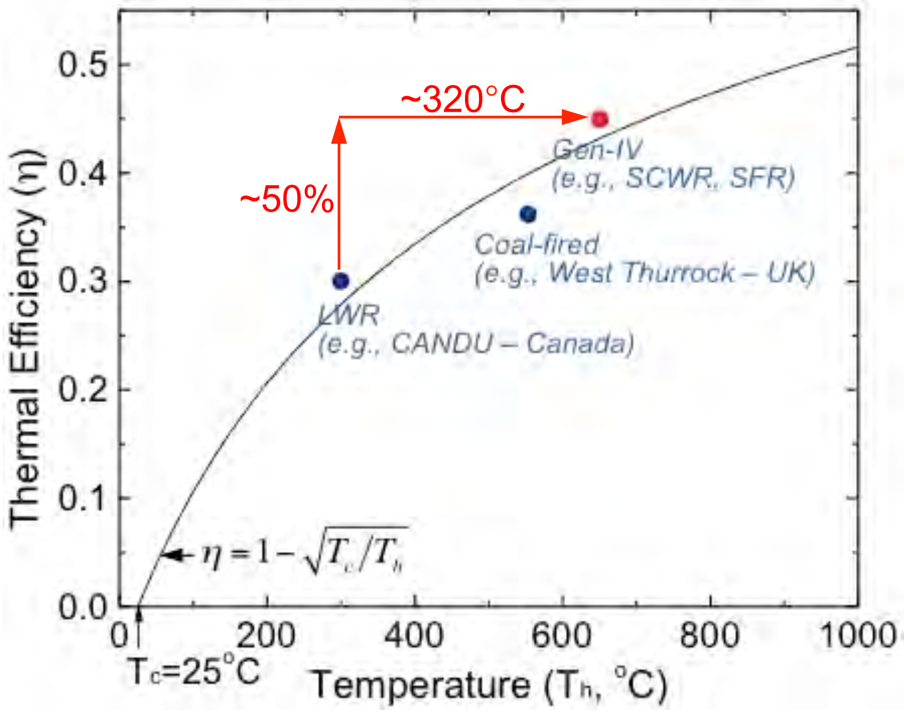
Testing & Characterization
- *Mechanical testing (Tan)*
- *Microstructural characterization (Tan)*
- *Microstructural simulation (Yang)*

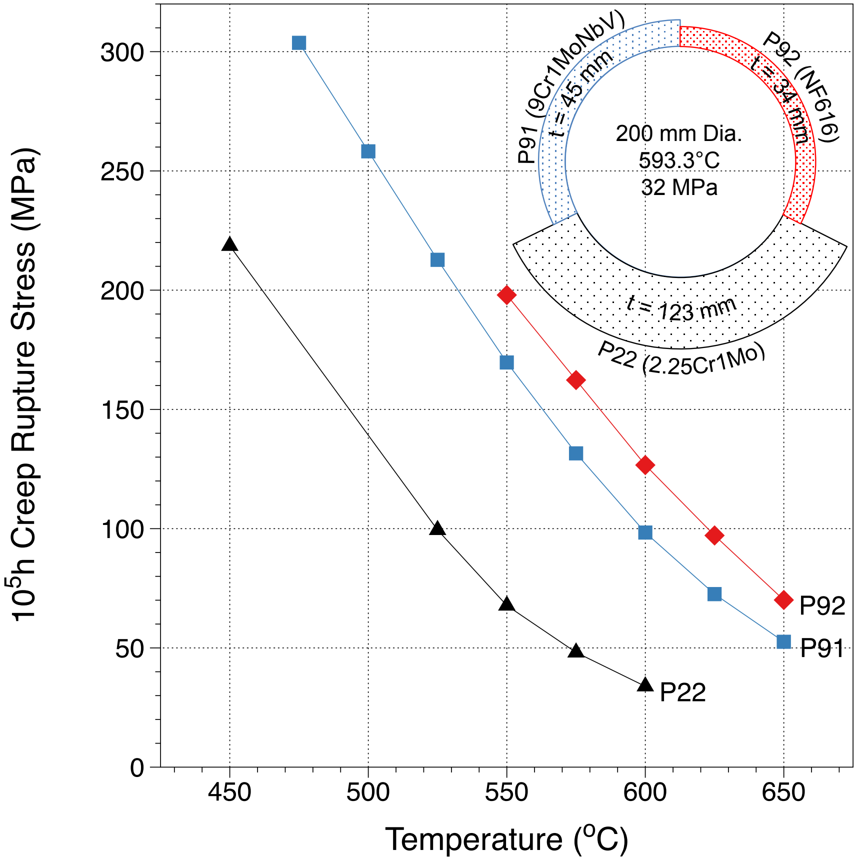
Radiation Resistance
- *Proton and heavy ion irradiations (Allen/Sridharan, Tan)*
- *Microstructure and hardness (Sridharan, Tan)*

Recommendation

The Need for Advanced Material Development

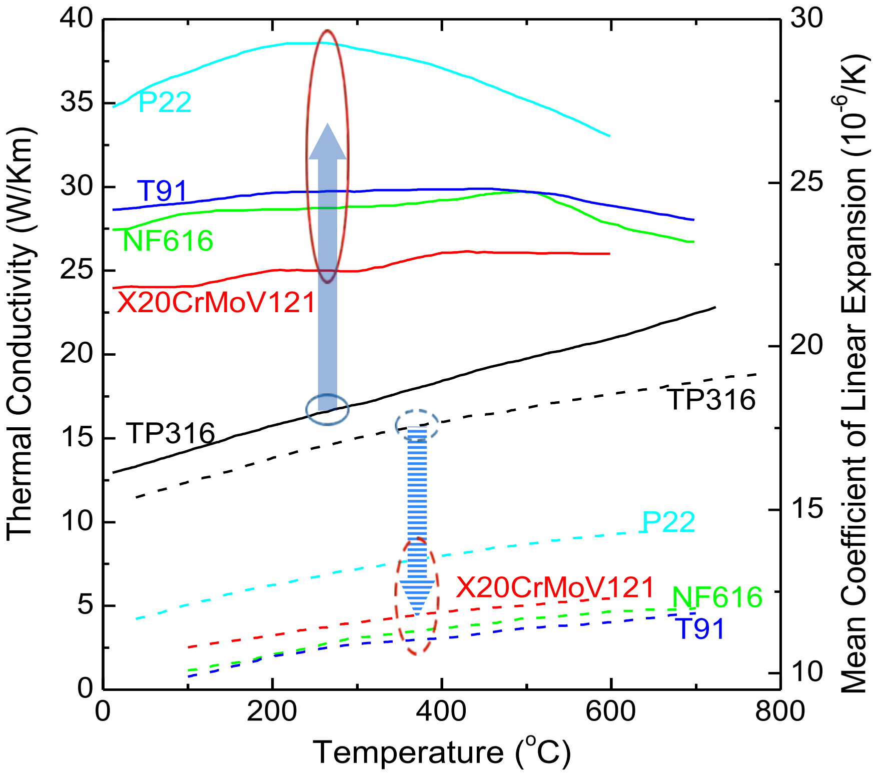
- **The escalating global clean-energy need drives higher operating temperatures of power plants for improved thermal efficiency.**
- **Advanced materials with superior high-temperature strength can effectively improve plant economics** (*reduced commodities, increased thermal efficiency, longer lifetimes*)**,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

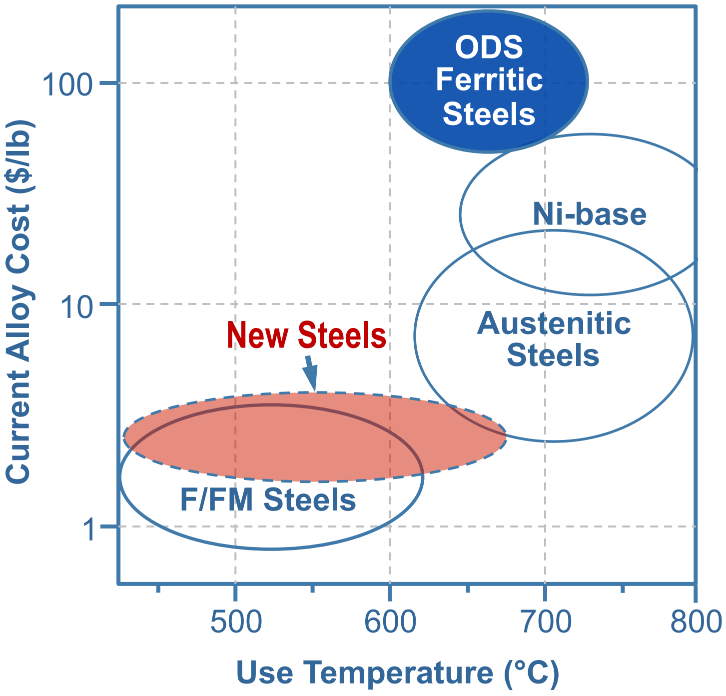




Ferritic Steels Have Outstanding Properties for Engineering Design

- **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*

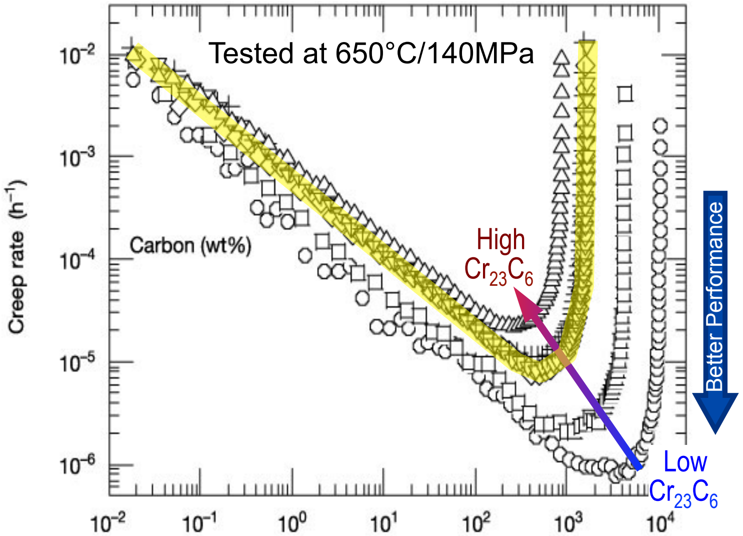




[Source: adapted from B.A. Pint]

Concerns of The Current FM Steels

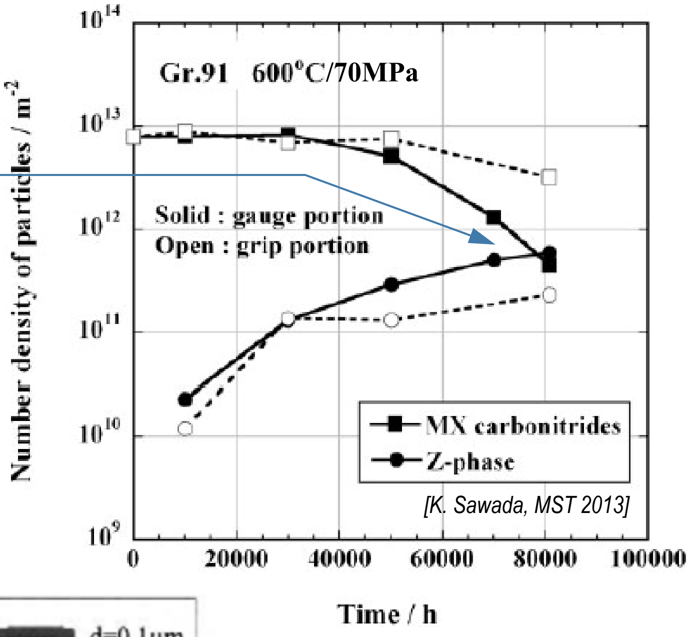
- Higher $Cr_{23}C_6$ amount results in greater creep rate.



[F. Abe, Nature 2003]

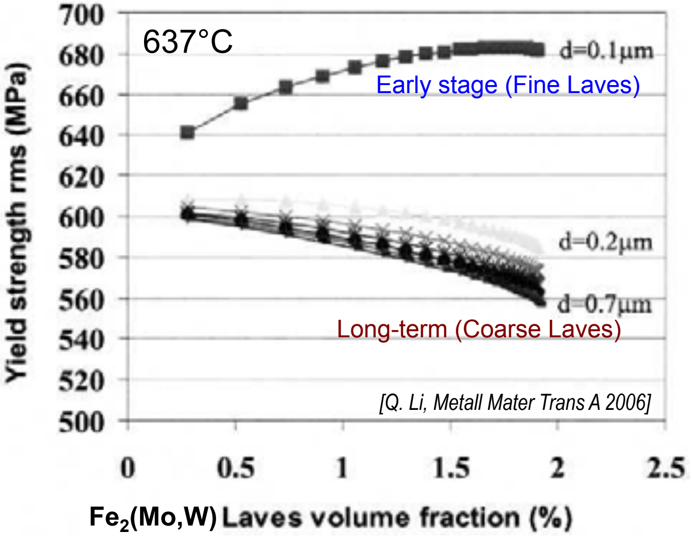
- Coarse Z-phase forms by consuming fine MX.

Stress accelerates the replacement of MX by Z-phase.



[K. Sawada, MST 2013]

- Laves phase coarsening deteriorates strength.



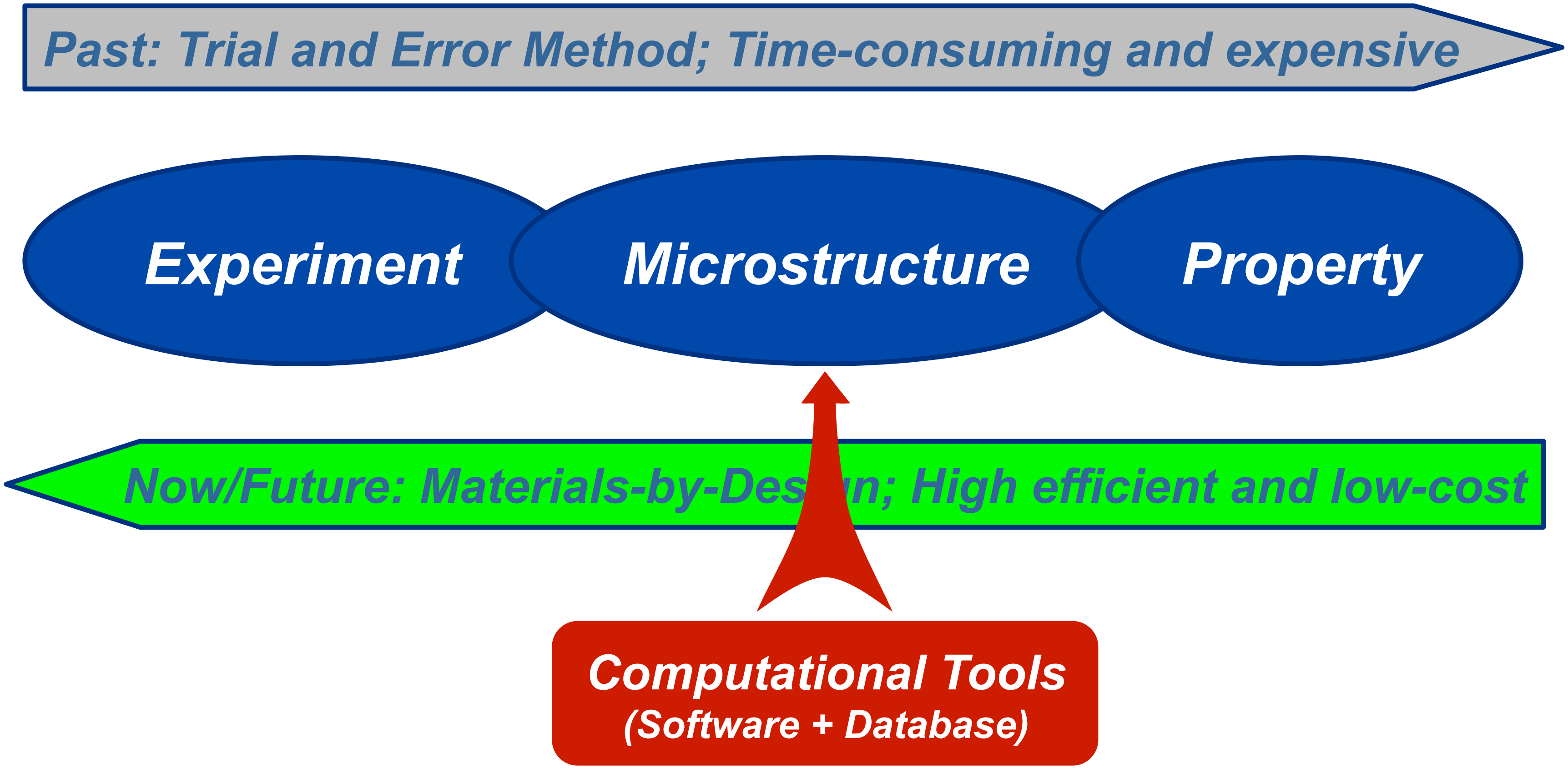
[Q. Li, Metall Mater Trans A 2006]

Potential Effects of Zr Alloying

- **Refine grain size by ZrC → Improve strength, toughness, etc.**
- **Reduce the amount of $Cr_{23}C_6$ → Improve creep resistance, reduce sensitization, etc.**
- **Reduce radiation-induced segregation (RIS) → Reduce potential SCC/IASCC.**
- **Form Zr-bearing Laves phase → Unclear.**
- **Form new phases, e.g., $Fe_{23}Zr_6$ → Unclear.**

- **Difficulty in alloy impurity control (oxygen): contrary effects**
  - Low enough oxygen → better fracture toughness
  - High oxygen → poor fracture toughness, ductility, etc.

Approach to Accelerate The Development of Zr-Containing Ferritic Steels



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

Experiment

Microstructure

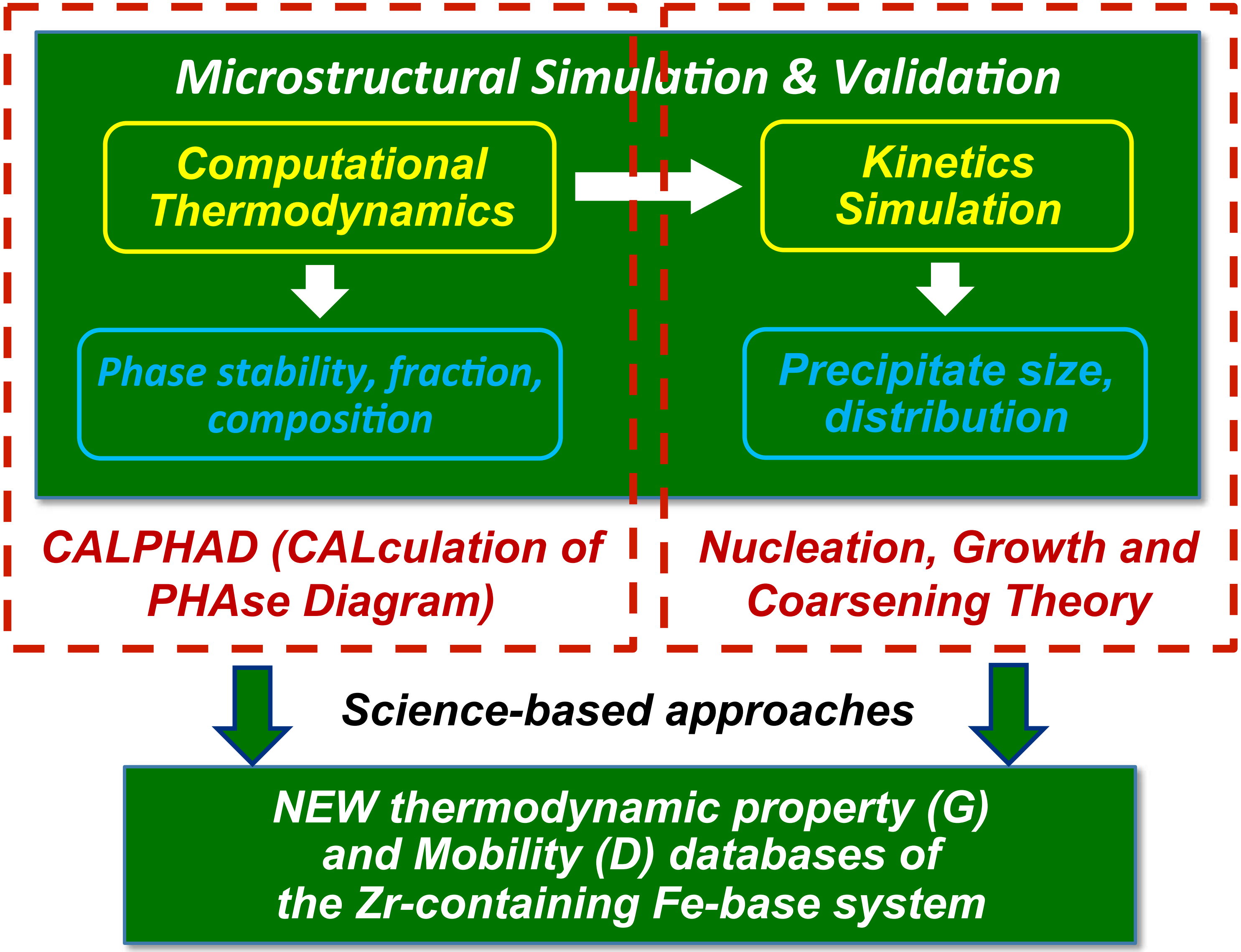
Property

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

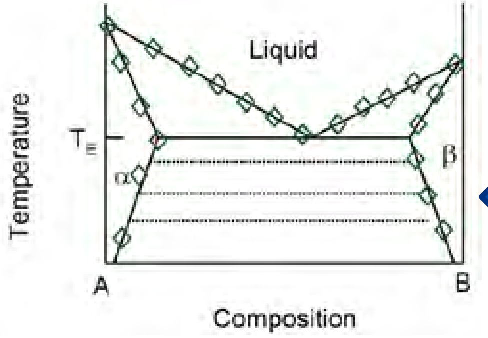
CALPHAD (CALculation of PHAse Diagram)

Nucleation, Growth and Coarsening Theory

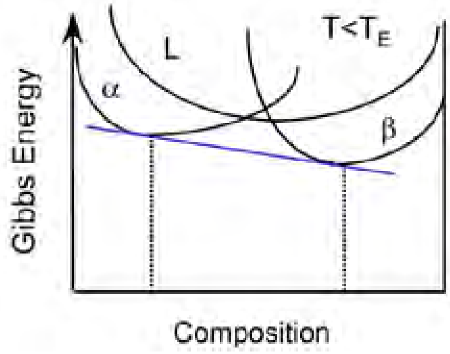
Science-based approaches

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

Multicomponent Thermodynamics (CALulation of PHAse Diagram-CALPHAD)



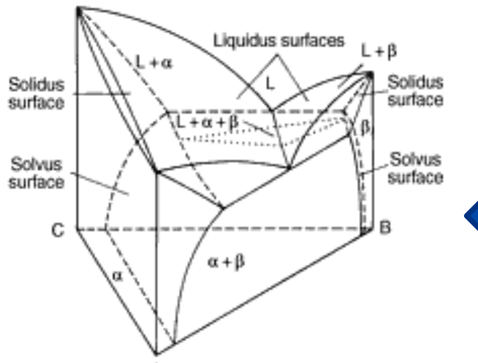
Binary phase diagram Thermochemical Data



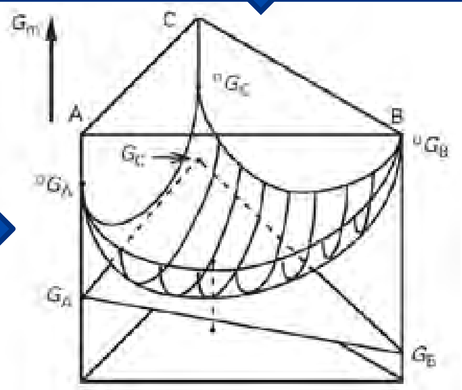
$G=f(T,P,x_B)$

$G=\sum X_i G_i^0 + RT\sum X_i \ln X_i$

$+\text{Binary } G^{ex}$



Ternary phase diagram Thermochemical Data



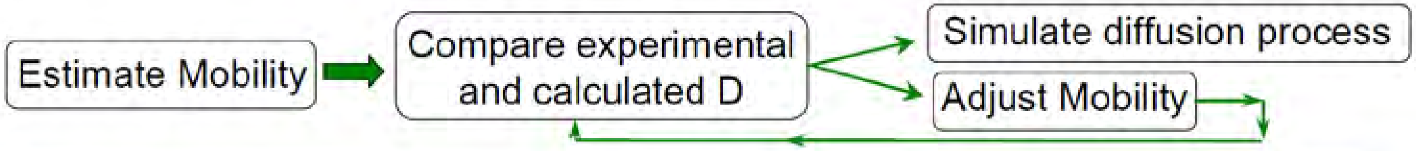
$G=f(T,P,x_B,x_C)$

$+\text{Binary } G^{ex} + \text{Ternary } G^{ex}$

Phase diagram ⟷ **Thermodynamics**

$+\text{Binary } G^{ex} + \text{Ternary } G^{ex}$
$+n\text{th order } G^{ex}$

Computational diffusivity

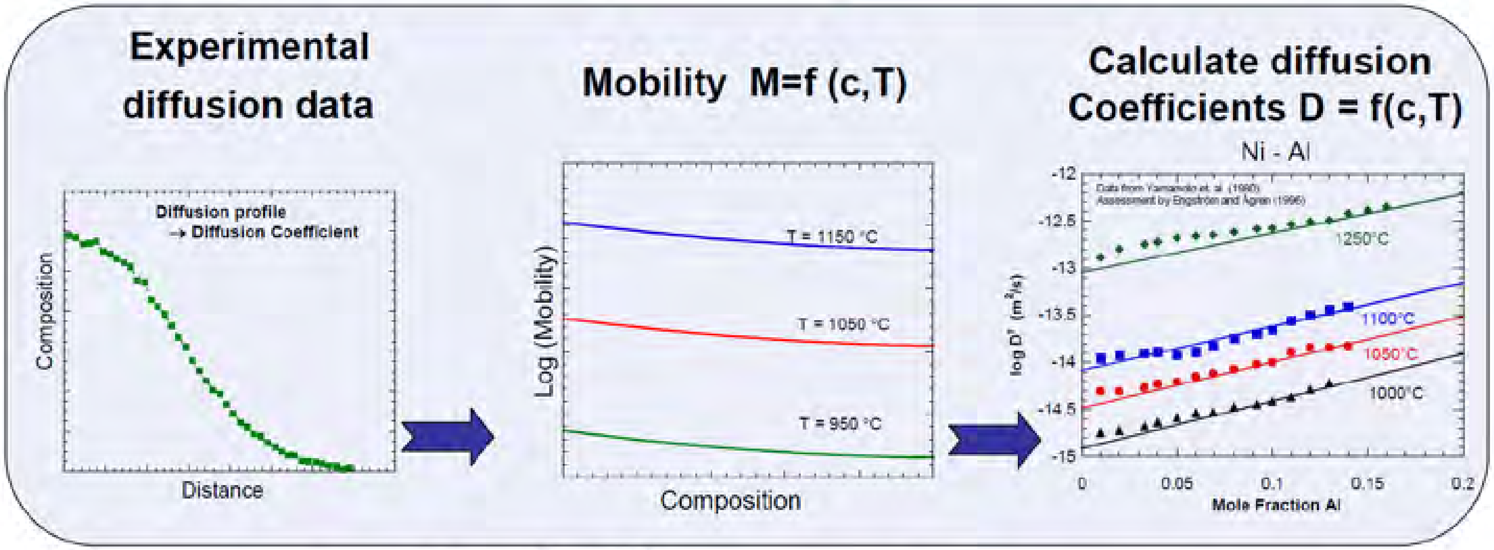


Estimate Mobility

Compare experimental and calculated D

Simulate diffusion process

Adjust Mobility



Experimental diffusion data

Mobility M=f (c,T)

Calculate diffusion Coefficients D = f(c,T)

$$M_i = \frac{M_i^\circ}{RT}\exp\left(\frac{-\Delta Q_i}{RT}\right) \text{ where } \Delta Q_i = f(c_i,T) \text{ and } M_i^\circ = 1$$

For a binary: $Q_i^\phi = c_i Q_i^i + c_j Q_i^j + c_i c_j \left(A_i^{i,j} + (c_i - c_j)B_i^{i,j} + (c_i - c_j)^2 C_i^{i,j} + \ldots\right)$

$D_k^* = RTM_k \ (k=A,B)$

$D_k = RTM_k \boxtimes_k ; \boxtimes_k = 1 + \partial\ln(f_k)/\partial\ln(X_k) ; (k=A,B)$

$\tilde{D} = x_B D_A + x_A D_B$

Computational tools used in this study

Software

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

Precipitation kinetics
- ***Matcalc 5.51***

Database

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

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

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

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

🟩 *From literature*

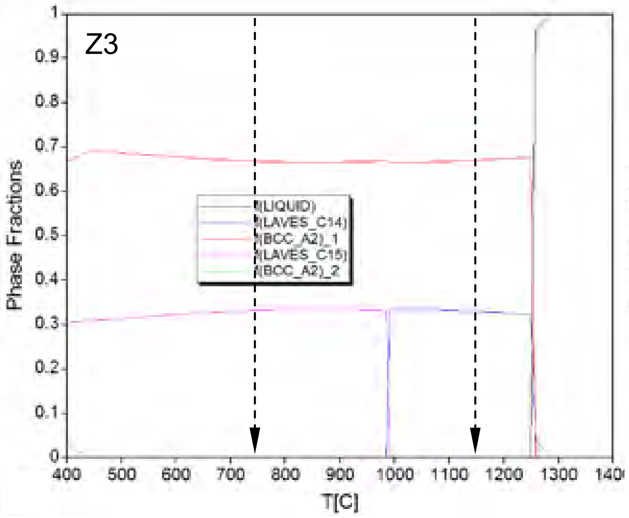
🟨 *From this work*

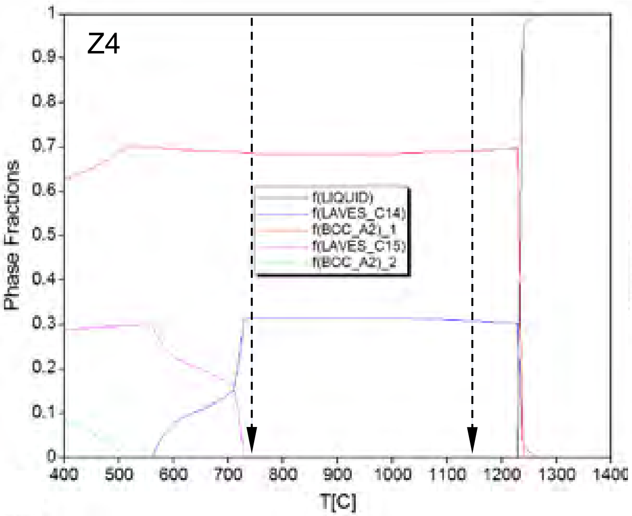
Design of Alloys Containing Zr

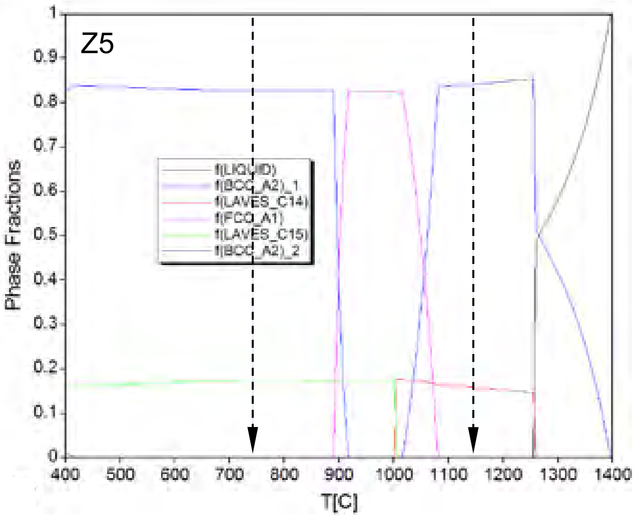
- **Class I: Intermetallics-strengthened alloys**
  - Support fundamental Zr-bearing thermodynamic database development
  - Explore Zr-bearing Laves phase and potential $Fe_{23}Zr_6$ effects
- **Class II: 9Cr ferritic steels**
  - Better phase stability than 12Cr
  - With Grade 91 and 92 as references
- **Class III: High-Cr ferritic steels**
  - Better corrosion resistance than lower Cr steels, negligible SCC issue
  - With AISI 439/444 and 304 as references

Class I:
Intermetallics-Strengthened Alloys

- **Three intermetallics (Fe_2Zr) strengthened alloys Z3, Z4, and Z5 were designed with**
  - Phase transformation of Fe_2Zr from C14-type at high-temperature to C15-type at low-temperature
  - Similar amount of Fe_2Zr in Z3 and Z4, but about ½ amount reduced in Z5.
- **Conditions**
  - As-received: 1150°C + 50% reduction deformation + AC
  - Aging: 750°C for 1800 h to obtain C15-type in Z3 and Z5, comparing its effect to C14-type in Z4.

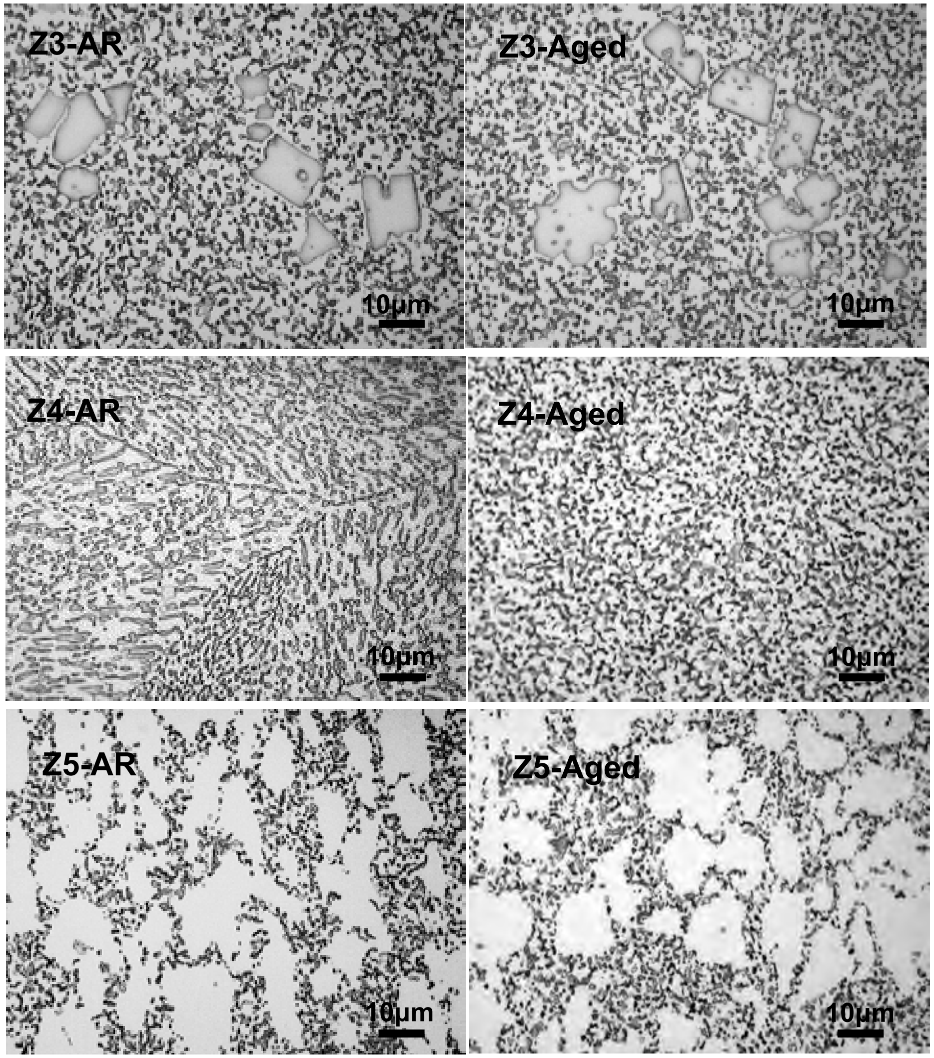






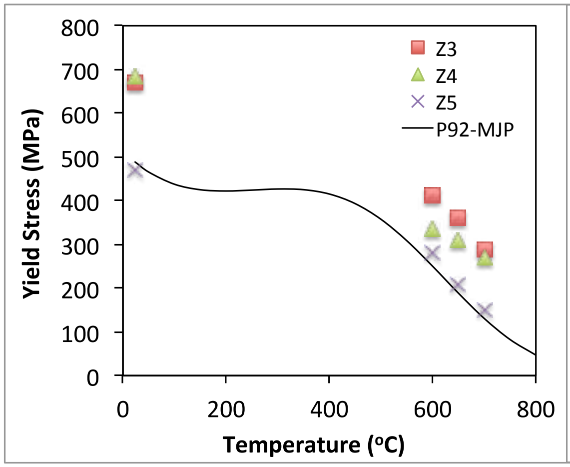
Class I: Intermetallics-Strengthened Alloys

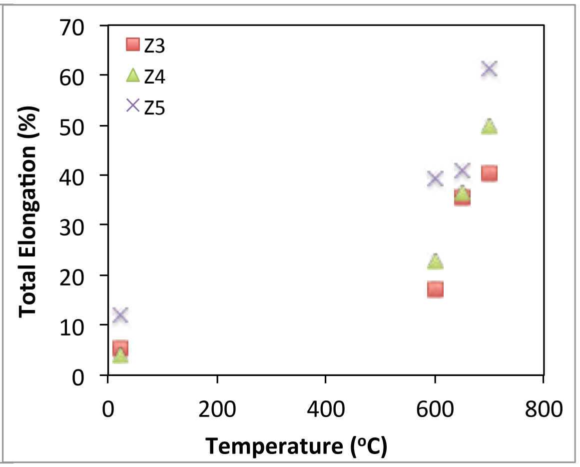
- **Intermetallics in as-received:**
  - Z3 is primarily composed of dispersive fine intermetallics with a few large size intermetallics.
  - Z4 is dominated by dispersive fine intermetallics with minor orientations (or texture) in different grains.
  - Z5 has less amount of fine intermetallics forming a network.
- **The aging did not lead to noticeable changes to the microstructures of Z3 and Z5. But the texture in Z4-AR was eliminated by the aging.**

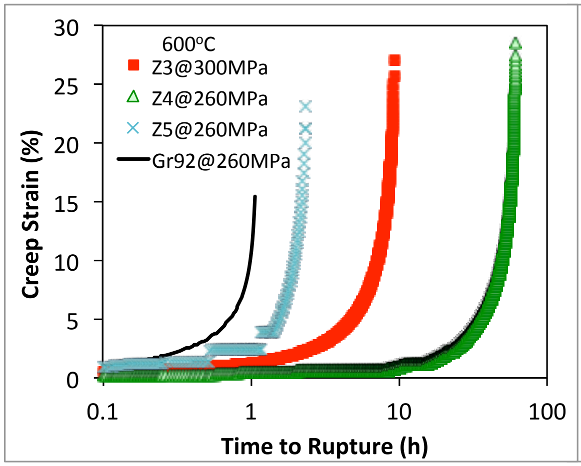


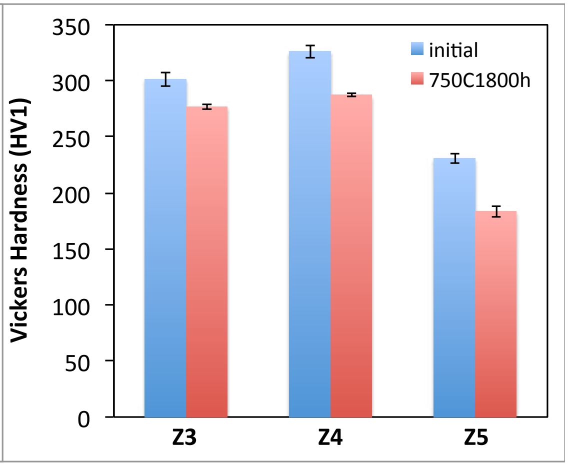
Class I: Intermetallics-Strengthened Alloys

- **Tensile testing results:**
  - Yield stresses of Z3 are similar to Z4, about 40-60% higher than P92. Yield stress of Z5 is comparable to P92.
  - Total elongations of the alloys are comparable or better than P92 at high temperatures, but poor at room temperature.
- **Creep testing at 600°C indicated different levels of improvement in creep resistance in both life and ductility.**
- **The aging slightly reduced the hardness of the alloys.**
- **The aging may alter the mechanical properties of the alloys, e.g., room temperature ductility.**



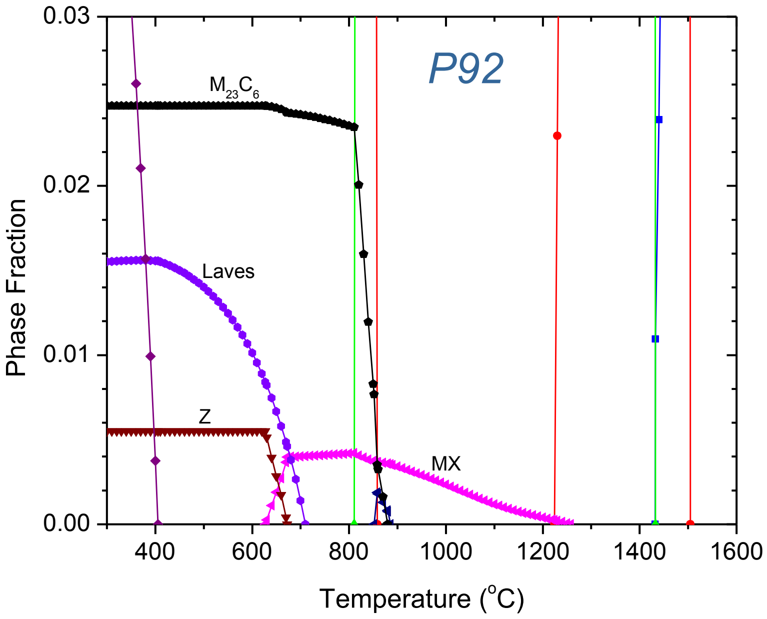


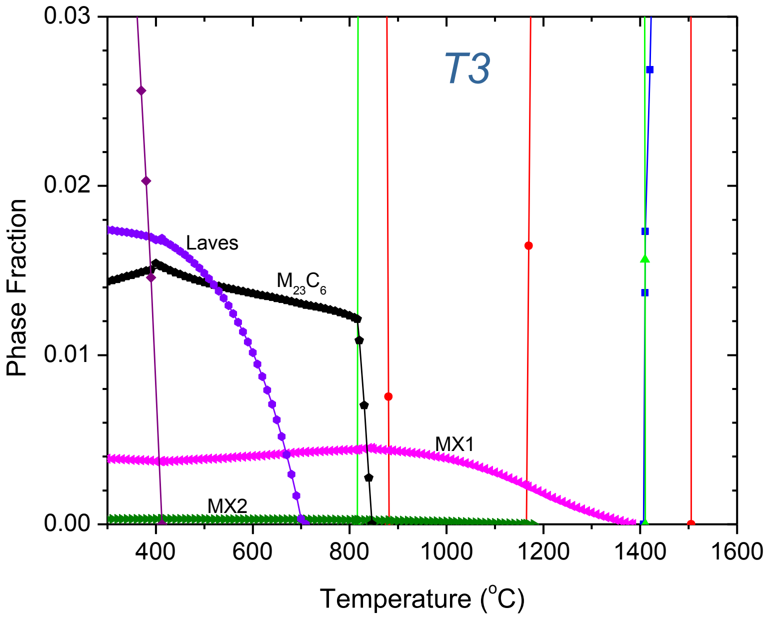




Class II:
9Cr Ferritic Steels

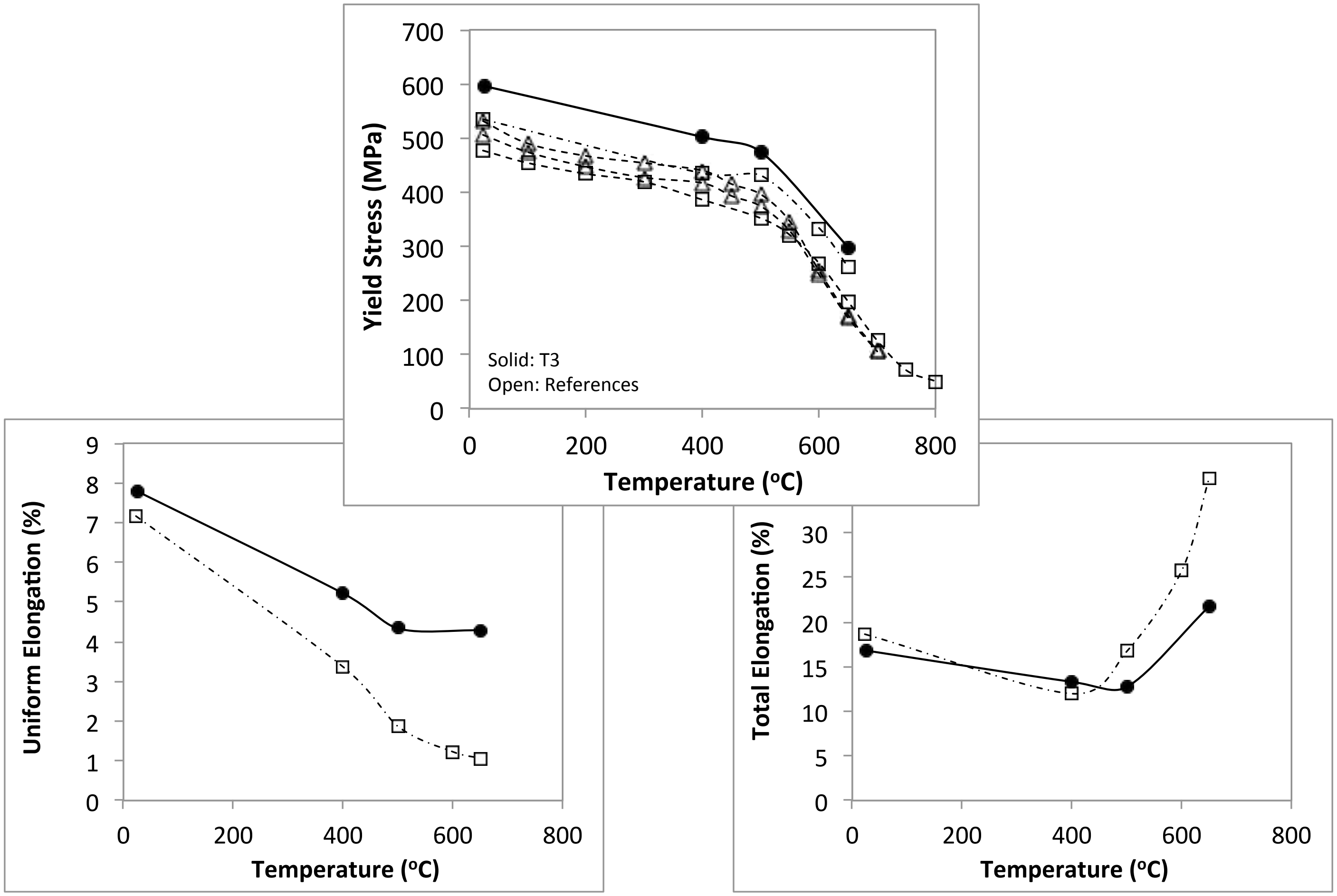
- **Aims:**
  - Eliminate Z-phase and reduce $M_{23}C_6$.
  - Changes to Laves phase content is not considered.





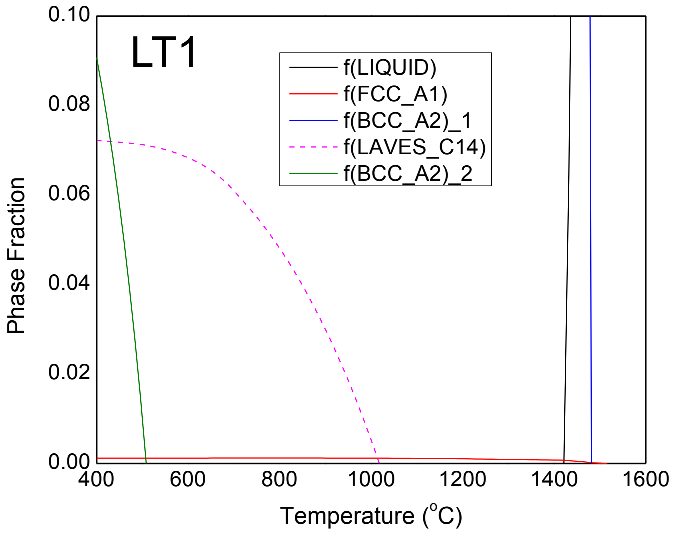
Class II:
9Cr Ferritic Steels

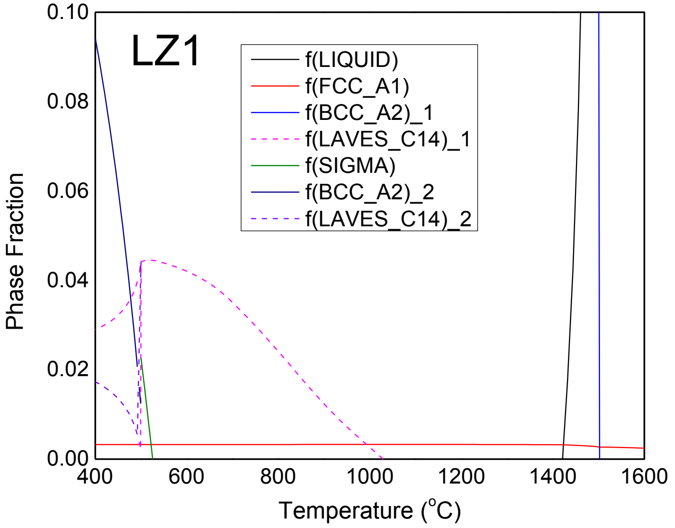
- **Tensile testing results of alloy T3 showed moderate increase in yield strength (10-15%) and comparable or slightly lower total elongation, but noticeably improved uniform elongation.**

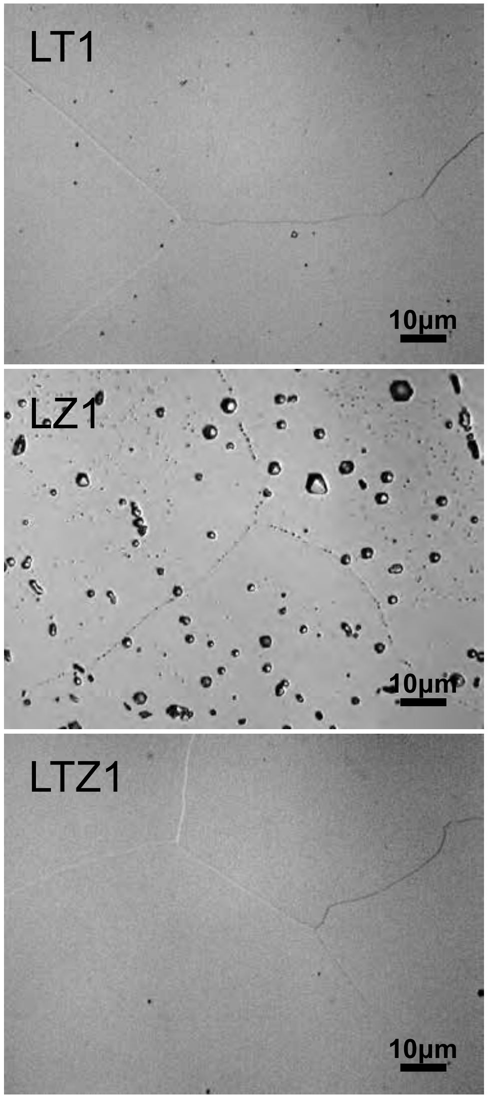


Class III: High-Cr Ferritic Steels

- High-Cr (15Cr) ferritic alloys were designed to have Laves-phase strengthening.
- The poor control of oxygen and nitrogen in LZ1 alloy resulted in a lot of large particles, harmful to mechanical properties.

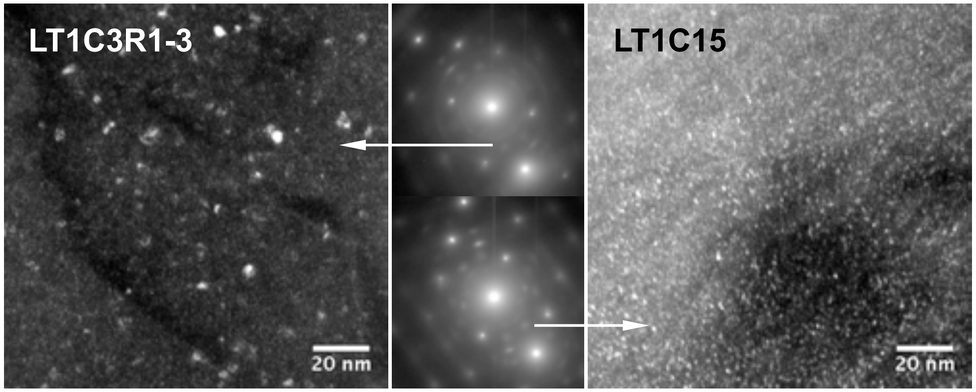




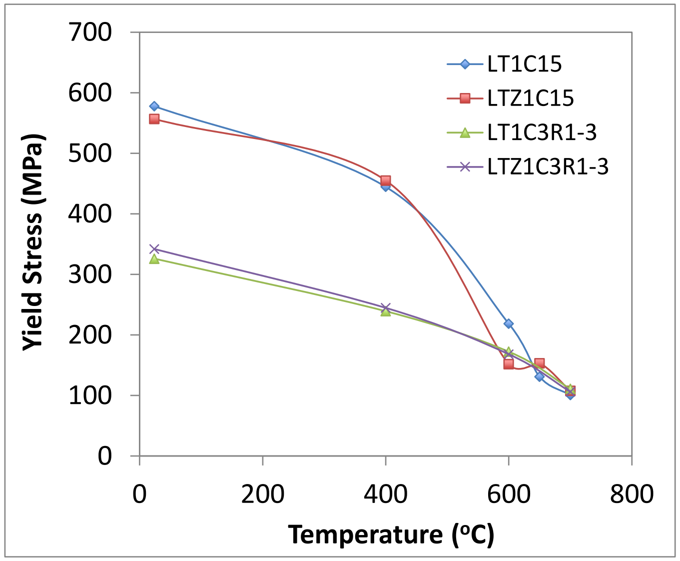


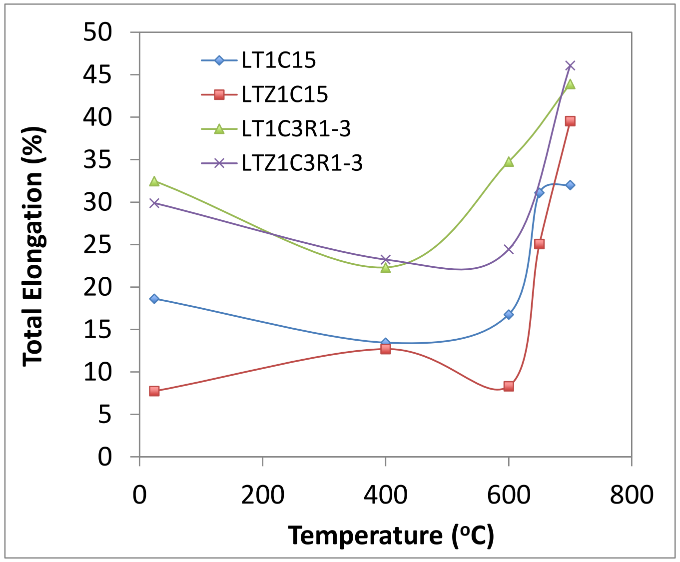
Class III:
High-Cr Ferritic Steels

- **The alloys' strength is adjustable by thermomechanical treatment, which is comparable or superior to AISI 304.**
  - The increased strength would be primarily attributable to the significantly increased amount of ultrafine precipitates.



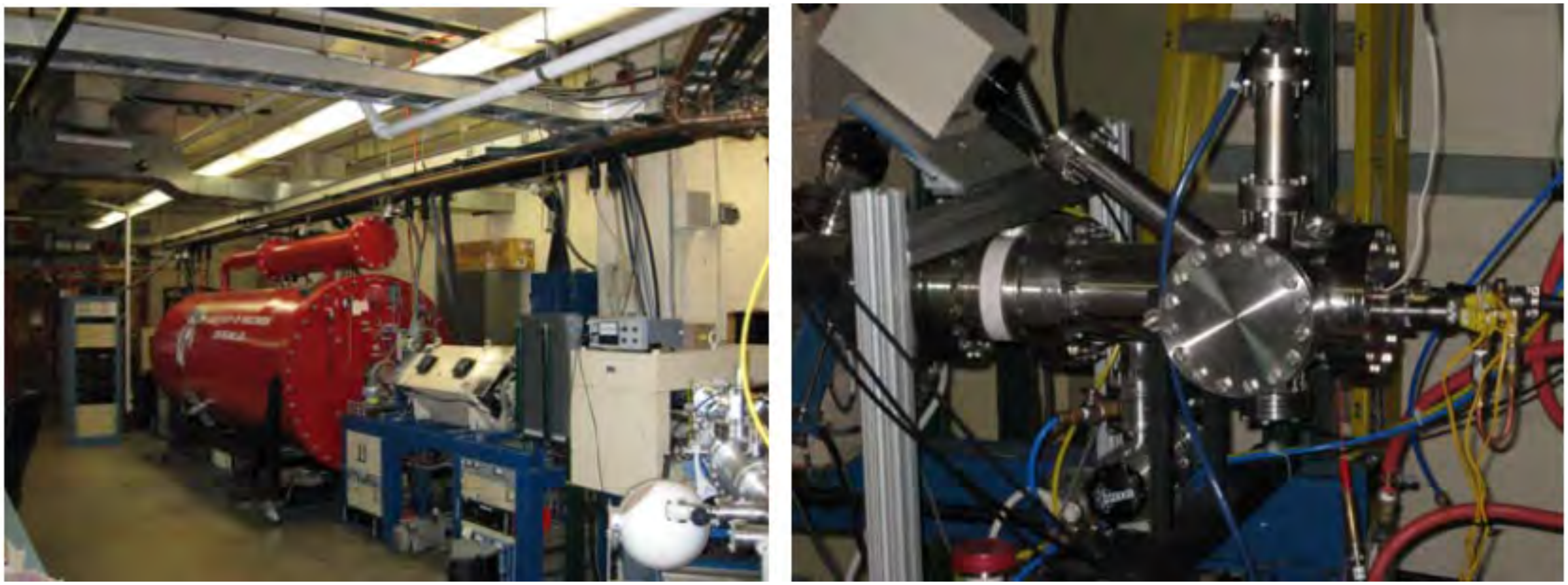
- **The alloys showed decent ductility.**
  - The occasional low ductility was resulted from aggregated Zr-oxide inclusions.





Ion-Irradiation Experiments

- **Radiation resistance of the alloys is to be evaluated using proton and heavy ion (e.g., Fe^{2+}) irradiations.**
  - Radiation-hardening, radiation-induced phase stability and segregation will be studied.
- **Radiation resistance screening of the first set of samples has been initiated.**



1.7 MV Tandem Accelerator Ion Beam @ UW-Madison

Summary

Zr-alloying would improved mechanical properties and radiation resistance. Approaches to solve the difficulty in alloy chemistry control will be explored by collaborating with commercial vendors, e.g., Carpenter Tech.

FY 2013

- Three classes of alloys are being explored by experiments assisted with computational thermodynamics.
  - Intermetallics-strengthened
  - 9Cr ferritic
  - Higher-Cr (15Cr) ferritic
- Ion irradiation experiments of selected alloy samples are initiated.

FY 2014

- Development and down selection of the 3-class of alloys for larger heats production and mechanical property assessment.
- Ion irradiation study of selected alloy samples.

FY 2015

- Continue testing, ion-irradiation, and characterization of the down-selected alloys.
- Recommend superior alloy(s) for further investigation.