NEET FY 12 Project

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

Lizhen Tan
Materials Science and Technology Division
Oak Ridge National Laboratory

DOE-NE Materials Crosscut Coordination Meeting

August 20, 2013
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*

![Graph showing thermal conductivity and expansion properties of different steels](image)

- **Low-cost**

[Source: adapted from B.A. Pint]
Higher Cr$_{23}$C$_6$ amount results in greater creep rate. Coarse Z-phase forms by consuming fine MX. Laves phase coarsening deteriorates strength.

Stress accelerates the replacement of MX by Z-phase.
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

**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

\[ G = \sum_{i} X_i \ln X_i + RT \sum_{i} X_i \ln X_i \]

Gibbs Energy

\[ G = f(T, P, x_B) \]

Ternary phase diagram
Thermochemical Data

\[ G = f(T, P, x_B, x_C) \]

Phase diagram
Thermodynamics

\[ + \text{Binary } G^{\text{ex}} \]

\[ + \text{Binary } G^{\text{ex}} + \text{Ternary } G^{\text{ex}} \]

\[ + \text{Binary } G^{\text{ex}} + \text{Ternary } G^{\text{ex}} + \text{nth order } G^{\text{ex}} \]
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 \( D = f(c, T) \)

\[
M_i = \frac{M_i^o}{RT} \exp \left( -\frac{\Delta Q_i}{RT} \right)
\]

where \( \Delta Q_i = f(c_i, T) \) and \( M_i^o = 1 \)

For a binary:

\[
Q_i^d = c_i Q_i^d + c_j Q_j^d + c_i c_j \left( A_i^{i,j} + (c_i - c_j) B_i^{i,j} + (c_i - c_j)^2 C_i^{i,j} + ... \right)
\]

Evaluate diffusion coefficient as

\[
D \downarrow k \overset{f}{\Rightarrow} \text{RTM} \downarrow k \\Rightarrow G_{BDA} \downarrow k + G_{BAD} \downarrow k = 1 + \frac{\partial n(f \downarrow k)}{\partial n(X \downarrow k)}; \quad (k = A, B)
\]

\[
D = x_{BAD}A + x_{ADB}
\]
Computational tools used in this study

<table>
<thead>
<tr>
<th>Software</th>
<th>Database</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Computational thermodynamics</strong></td>
<td><strong>Thermodynamic property</strong></td>
</tr>
<tr>
<td>- Matcalc 5.51</td>
<td>- OCTANT (in-house) Mobility</td>
</tr>
<tr>
<td>- Pandat 8.0</td>
<td>- MCFe (Non-encrypt)</td>
</tr>
<tr>
<td><strong>Precipitation kinetics</strong></td>
<td></td>
</tr>
<tr>
<td>- Matcalc 5.51</td>
<td></td>
</tr>
</tbody>
</table>

**OCTANT**: ORNL Computational Thermodynamics for Applied Nuclear Technology
### Binaries

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>Nb</th>
<th>Ti</th>
<th>W</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe-C</td>
<td>Fe-Cr</td>
<td>Fe-Mo</td>
<td>Fe-Nb</td>
<td>Fe-Ti</td>
<td>Fe-W</td>
<td>Fe-Zr</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>C-Cr</td>
<td>C-Mo</td>
<td>C-Nb</td>
<td>C-Ti</td>
<td>C-W</td>
<td>C-Zr</td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td></td>
<td>Cr-Mo</td>
<td>Cr-Nb</td>
<td>Cr-Ti</td>
<td>Cr-Ti</td>
<td>Cr-Zr</td>
</tr>
<tr>
<td>Mo</td>
<td></td>
<td></td>
<td></td>
<td>Mo-Nb</td>
<td>Mo-Ti</td>
<td>Mo-W</td>
<td>Mo-Zr</td>
</tr>
<tr>
<td>Nb</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Nb-Ti</td>
<td>Nb-W</td>
<td>Nb-Zr</td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ti-W</td>
<td>Ti-Zr</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W-Zr</td>
<td></td>
</tr>
</tbody>
</table>
## Thermodynamic database

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

### Fe-X-Y Ternaries

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Mo</th>
<th>Nb</th>
<th>Ti</th>
<th>W</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-C</td>
<td>Fe-C-Cr</td>
<td>Fe-C-Mo</td>
<td>Fe-C-Nb</td>
<td>Fe-C-Ti</td>
<td>Fe-C-W</td>
<td>Fe-C-Zr</td>
</tr>
<tr>
<td>Fe-Cr</td>
<td></td>
<td>Fe-Cr-Mo</td>
<td>Fe-Cr-Nb</td>
<td>Fe-Cr-Ti</td>
<td>Fe-Cr-W</td>
<td>Fe-Cr-Zr</td>
</tr>
<tr>
<td>Fe-Mo</td>
<td></td>
<td></td>
<td>Fe-Mo-Nb</td>
<td>Fe-Mo-Ti</td>
<td>Fe-Mo-W</td>
<td>Fe-Mo-Zr</td>
</tr>
<tr>
<td>Fe-Nb</td>
<td></td>
<td></td>
<td></td>
<td>Fe-Nb-Ti</td>
<td>Fe-Nb-W</td>
<td>Fe-Nb-Zr</td>
</tr>
<tr>
<td>Fe-Ti</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe-Ti-W</td>
<td>Fe-Ti-Zr</td>
</tr>
<tr>
<td>Fe-W</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe-W-Zr</td>
</tr>
</tbody>
</table>

### X-Y-C Ternaries

<table>
<thead>
<tr>
<th></th>
<th>Mo</th>
<th>Nb</th>
<th>Ti</th>
<th>W</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-C</td>
<td>Cr-Mo-C</td>
<td>Cr-Nb-C</td>
<td>Cr-Ti-C</td>
<td>Cr-W-C</td>
<td>Cr-Zr-C</td>
</tr>
<tr>
<td>Mo-C</td>
<td></td>
<td>Mo-Nb-C</td>
<td>Mo-Ti-C</td>
<td>Mo-W-C</td>
<td>Mo-Zr-C</td>
</tr>
<tr>
<td>Nb-C</td>
<td></td>
<td></td>
<td>Nb-Ti-C</td>
<td>Nb-W-C</td>
<td>Nb-Zr-C</td>
</tr>
<tr>
<td>Ti-C</td>
<td></td>
<td></td>
<td></td>
<td>W-Ti-C</td>
<td>Ti-Zr-C</td>
</tr>
<tr>
<td>W-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W-Zr-C</td>
</tr>
</tbody>
</table>

*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
Three intermetallics (Fe$_2$Zr) strengthened alloys Z3, Z4, and Z5 were designed with
- Phase transformation of Fe$_2$Zr from C14-type at high-temperature to C15-type at low-temperature
- Similar amount of Fe$_2$Zr in Z3 and Z4, but about $\frac{1}{2}$ 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.
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.
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.
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.
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.
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.

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.

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

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.