Atomization and Powder Processing of High Temperature Ferritic Stainless Steel

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Application Goals

➢ Create a simplified process for production of precursor powders and oxide dispersion strengthened ferritic stainless steel alloys

A-USC Steam Coal Fired:

• Boiler / Burner Materials
• Heat exchanger tubing
• Exhaust liner

• 760°C at 35MPa Supercritical Steam
Highly Demanding Operating Conditions for Fe

<table>
<thead>
<tr>
<th>Strengthening Mechanism</th>
<th>Effective Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work Hardening</td>
<td>~0.3 $T_m$</td>
</tr>
<tr>
<td>Grain Size</td>
<td>~0.3 $T_m$</td>
</tr>
<tr>
<td>Solid Solution Strengthening</td>
<td>~0.4 $T_m$</td>
</tr>
<tr>
<td>Precipitation Strengthening</td>
<td>~0.6 $T_m$</td>
</tr>
<tr>
<td>Oxide Dispersion Strengthening</td>
<td>~0.9 $T_m$</td>
</tr>
</tbody>
</table>

- Oxide dispersion strengthening is best option for elevated temperature microstructure stability and creep resistance of Fe-base alloys.

![Graph showing A-USC conditions](image)
Dislocation Substructure

- TMT can be used to develop a dislocation substructure for increased alloy strengthening
- Sub-grain stability is highly dependent on the spatial distribution of the dispersoids
- Critical balance between driving and dragging forces (Zener pinning)

B.A. Wilcox, et. al., 1967.

**Fe-Based ODS Processing Comparison**

* Mechanical Alloying
  - Long milling times
  - Batch commercial process (< 2000 kg)
  - Powder contamination (C, O, N, Ar)
  - Anisotropic microstructure

** Gas Atomization (RSP)
  - Higher processing rates (10-20 kg/min)
  - Continuous processing capacity
  - Minimized contamination
  - Isotropic microstructure capability

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<table>
<thead>
<tr>
<th>Material</th>
<th>Cost/kg (USD)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferritic Stainless Steel</td>
<td>~$2-5</td>
<td>446 Plate form</td>
</tr>
<tr>
<td>Fe-based ODS</td>
<td>~$165, ~$345</td>
<td>MA956 Sheet (Special Metals), PM 2000 (Plansee)</td>
</tr>
<tr>
<td>Ni-based</td>
<td>~$30-35</td>
<td>Inconel 718 Sheet (Special Metals), Inconel 617 (Special Metals)</td>
</tr>
</tbody>
</table>

* R.M. German, 2005.

ODS Processing Cost!
Gas Atomization Reaction Synthesis

In situ alloying addition of oxygen (primarily) as transient powder surface oxide.

<table>
<thead>
<tr>
<th>Alloy Element</th>
<th>Primary Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>Surface reactant, Oxidation resistance</td>
</tr>
<tr>
<td>Y</td>
<td>Dispersoid former</td>
</tr>
<tr>
<td>Ti</td>
<td>Surface reactant, Dispersoid stabilizer</td>
</tr>
<tr>
<td>Hf</td>
<td>Surface reactant, Dispersoid stabilizer</td>
</tr>
<tr>
<td>O</td>
<td>Surface oxidant, Dispersoid former</td>
</tr>
</tbody>
</table>
Internal Oxygen Exchange Reaction

- Y-enriched intermetallic compound (IMC) precipitation (Y reservoir)
- Dissociation of Cr-enriched prior particle boundary (PPB) oxide (O reservoir)

I. Barin, et al., 1992
Chemical Reservoir Phase Evolution

As-Atomized Powder

HIP Consolidation 850°C

HIP Consolidation 1300°C

Fe-15.70Cr-0.20Y-0.49Ti-1.16O (at%)
GARS Process Control
Resulting Oxygen Content Control Approach

- Rapid oxidation kinetics
- Empirically determined linear oxidation dependence on $p_{O_2}$
  \[ k_p \propto (P_{O_2})^{1/n} \]
  Where, $n = 1$
- Decreased oxidation kinetics when Y present in the surface oxide layer
- Sensitive to atomization processing parameters (i.e., gas nozzle and pour tube design)

Surface Oxide Analysis (AES)

CR-156Y-Hf: Fe-15.84Cr-0.11Hf-0.18Y at.%

Decreasing particle size

Decreased surface oxidation
Resulting Surface Oxide Layer Thickness

- Why is there a particle size dependence?
- All oxygen is in the form of a uniform surface oxide layer
- Cr$_2$O$_3$ surface oxide formation

Assumptions

\[
\xi_{ox} = \frac{\Delta m_{O_2}W_{ox}}{S_dW_{O_2}y\rho_{ox}}
\]

Where, $M_{aO_y}$

Confirmed using TEM

Predicted Oxide Layer Thickness

- Utilizing the droplet cooling curves (T vs. t)
- Oxidation reaction deemed complete when $\delta < 400 \text{ nm sec}^{-1}$
- Majority of oxidation occurs prior to droplet solidification

Cr$_2$O$_3$ formation

Solidification

**Parabolic Oxidation Rate Constant**

$$k_p = B \exp \left( \frac{-E}{RT} \right)$$

Where, $E=249\text{kJ/mol}$ (Gulbransen et al., 1957)

$B=5 \text{g}^2\text{cm}^{-4}\text{s}^{-1}$ (experimental)

$$k_p \propto (P_{O_2})^{\frac{1}{n}} \quad n=1 \text{ (experimental)}$$

**Oxygen Mass Gained**

$$\Delta m_{O_2}(\Delta t) = \left( \frac{k_{p,i} + k_{p,f}}{2} \right)^{\frac{1}{2}} \cdot 2S_d \left( t_f^{\frac{1}{2}} - t_i^{\frac{1}{2}} \right)$$

**Resulting Oxide Layer Thickness**

$$\xi_{ox} = \frac{\Delta m_{O_2}W_{ox}}{S_dW_{O_2}y_{\rho_{ox}}}$$

**Oxide Growth**

$$\delta = \frac{\Delta \xi_{ox}}{\Delta t}$$
Comparison with Experimental Results

- Initially optimized for CR-118 (parabolic oxidation pre-factor)
- Modified atomization processing parameters and ran model for each similar CR-alloy
- Recommended as a processing tool to predict and control in situ O additions during atomization
ODS Microstructure Control
As-Atomized Solidification Structure

- Microsegregation observed in coarser powders
- Apparent solute trapping in ultra-fine (dia. < 5µm) powders
- APT highlighted intermetallic clusters

CR-156Y-Hf: Fe-15.84Cr-0.11Hf-0.18Y at.%

Fe-(Y,Hf) Cluster
Size: 2-5 nm
No. Density: 2-6x 10^{22} m^{-3}
**Calculated Solidification Velocity**

\[
\Omega \equiv \frac{T_L - T_N}{\Delta H_f / C_d}
\]

**Approximation of the Ivanstov Function**

\[
Pe_t = a \left( \frac{\Omega}{1 - \Omega} \right)^b
\]  
(Wang et al., 1993)

**Truncated LKT Model**

\[
r_{den} = \frac{\Gamma / \tau^*}{(\Delta H_f / C_d) Pe_t (1 - n)}
\]

(Lipton, Kurz, and Trivedi, 1987)

**Planar Stability, when \( \Omega \geq 1 \)**

\[
(V_{den})_{abs} = \frac{\alpha_L \Delta H_f}{\Gamma c_{dL}}
\]

(Trivedi and Kurz, 1986)
Calculated Solidification Velocity

Planar (microsegregation-free) growth

\[(V_{den})_{abs} = \frac{\alpha L \Delta H_f}{G_c d L}\]  
(Trivedi and Kurz, 1986)

\[Q_{re} = \Delta H_f V_{den} A_d \rho_d\]
Precursor IMC Precipitate Distribution

CR-156Y-Hf: Fe-15.84Cr-0.11Hf-0.18Y at.%

As-HIPed 700°C – 300MPa – 4hr

Fe-(Y,Hf) IMC precipitates

Dia. 20-53 µm

Dia. 5-20 µm

Dia. < 5 µm

Fe-(Y,Hf) IMC precipitates

Fe-(Y,Hf) IMC precipitates

Fe-(Y,Hf) IMC precipitates
Resulting ODS microstructure

Heat Treated 1200°C – 2.5hr – Vac.

CR-156Y-Hf: Fe-15.84Cr-0.11Hf-0.18Y at.%

Y-Hf-O dispersoids

Dia. 20-53 μm

Dia. 5-20 μm

Dia. < 5 μm

Y-Hf-O dispersoids

50 nm

50 nm

50 nm

50 nm

Y-Hf-O dispersoids

20 - 50 nm

3x10^{21} m^{-3}

5 - 20 nm

8x10^{21} m^{-3}

3 - 12 nm

3x10^{22} m^{-3}

Dia. 20-53 μm

Dia. 5-20 μm

Dia. < 5 μm
Thermal Mechanical Treatment
**ODS Microstructure**

CR-166 (< 20 µm): Fe-15.91Cr-0.12Ti-0.09Y-0.49O at.%
CR-166 (45-75µm): Fe-15.91Cr-0.12Ti-0.09Y-0.33O at.%

**Cellular Pattern**
- Interior Core Structure
  - ~0.5 vol.% dispersoids

**Y₂Ti₂O₇ Dispersoids**
- No. Density: ~1-4x10²¹ m⁻³

**Cellular Pattern**
- ~0.5 vol.% dispersoids

**Dispersoids**
- No. Density: ~1-10x10²⁰ m⁻³
Cold Rolled Microhardness

- CR-166 (< 20 µm): Fe-15.91Cr-0.12Ti-0.09Y-0.49O at.%
- CR-166 (45-75µm): Fe-15.91Cr-0.12Ti-0.09Y-0.33O at.%

Cold Rolled to ~85 % Reduction in Area

- ~2X increase in microhardness
- Cold work threshold
- Microstructure dependent (Zener Limit)
Annealed Microstructure

Heat Treated 1200°C

Cellular Pattern Interior Core

Cold Rolled 85% RA + Annealed 500°C-1hr-Air

Cold Rolled 85% RA + Annealed 500°C-1hr-Air + 800°C-1hr-Air

CR-166 (< 20 µm): Fe-15.91Cr-0.12Ti-0.09Y-0.49O at.%
CR-166 (45-75 µm): Fe-15.91Cr-0.12Ti-0.09Y-0.33O at.%

Grain size ~1.1 µm
Grain size ~0.3 µm
Grain size ~13 µm

Grain size ~0.3 µm
Grain size ~1.1 µm
Grain size ~14 µm
Mechanical Properties

CR-166 (< 20 µm): Fe-15.91Cr-0.12Ti-0.09Y-0.49O at.%
CR-166 (45-75µm): Fe-15.91Cr-0.12Ti-0.09Y-0.33O at.%

- Mean free path for dislocation movement (Orowan)
- Dislocation climb and detachment stress (interfacial pinning)
- A threefold increase in total elongation
Thermal Stability
Thermal Stability (1200°C)

CR-164HfY: Fe-15.55Cr-0.12Hf-0.09Y-1.04O at.%
CR-166TiY: Fe-15.91Cr-0.12Ti-0.09Y-0.49O at.%

1200°C 2.5 hr
- Y-Hf-O Dispersoids
  No. Density: $\sim 3 \times 10^{21} \text{ m}^{-3}$

1200°C 100 hr
- Y-Hf-O Dispersoids
  No. Density: $\sim 2 \times 10^{21} \text{ m}^{-3}$

1200°C 1,000 hr
- Y-Hf-O Dispersoids
  No. Density: $\sim 9 \times 10^{20} \text{ m}^{-3}$

- Y-Ti-O Dispersoids
  No. Density: $\sim 3 \times 10^{21} \text{ m}^{-3}$

- Y-Ti-O Dispersoids
  No. Density: $\sim 2 \times 10^{21} \text{ m}^{-3}$

- Y-Ti-O Dispersoids
  No. Density: $\sim 6 \times 10^{20} \text{ m}^{-3}$
Microstructure Evolution

CR-164HfY: Fe-15.55Cr-0.12Hf-0.09Y-1.04O at.%
CR-166TiY: Fe-15.91Cr-0.12Ti-0.09Y-0.49O at.%

\[ R_c = \frac{4r}{3f} \]

(C.S. Smith, 1948)

Hf vs. Ti

Microhardness drop

\[ t \approx \frac{k\lambda}{\beta \cos \theta\beta} \]

(B.D. Cullity, 1967)
Future Work
## New Fe-based ODS atomization trial

### GARS Process Control

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fe-16Cr-0.30Hf-0.20Y-0.70O at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size Range Goal</td>
<td>Dia. &lt; 10(\mu)m</td>
</tr>
<tr>
<td>Reaction Gas</td>
<td>Ar-0.06O(_2) vol.%</td>
</tr>
<tr>
<td>Dispersoid Phase</td>
<td>(\text{Y}_2\text{Hf}_2\text{O}_7)</td>
</tr>
</tbody>
</table>

### Atomization Parameters

<table>
<thead>
<tr>
<th>Nozzle</th>
<th>45° (closed wake)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>600 psi</td>
</tr>
<tr>
<td>Pour Tube</td>
<td>Super heating composite</td>
</tr>
<tr>
<td>Metal Flow Rate</td>
<td>1 kg/min</td>
</tr>
</tbody>
</table>
Superheat Pour Tube Module

- Efficiently add ~250°C of superheat to the molten alloy as it is transported from the crucible to the high pressure atomization gas
- Prevents “freeze-out” during atomization runs that utilize low metal flow rates
Fe-16.8Cr-0.90W-0.62Ti-0.08Y-0.26O at.%(Fe-15.1Cr-2.95W-0.53Ti-0.12Y-0.07O wt.%)
Alloy Design (Al Additions)

- Simulate and identify internal O-exchange reactions within Fe-base alloys containing Al additions
- Evaluate the ability to form and sustain mixed Y-Hf-O dispersoids with Al present in the α-Fe matrix
- Resist YAG/YAM/YAP oxide dispersoid formation

Fe-15.6Cr-10Al-0.36Hf-0.12Y at% (Fe-15Cr-5Al-1.2Hf-0.2Y wt%)

Chill Cast Fingers
Polished (6 mm cubes)
Cr/Cr$_2$O$_3$ Rhines Pack (controlled $P_O$)
Heat treated at 1200°C

- L. Zhang et al., Acta Mat. 57, 2009
Microstructure Evolution

Fe-15.6Cr-10Al-0.36Hf-0.12Y at%  
(Fe-15Cr-5Al-1.2Hf-0.2Y wt%)

Initial intermetallic ppts  
(Fe_{17}Y_{2})

Internal oxidation zone

HT 1200°C for 2.5 hr

HT 1200°C for 10 hr

Continuous surface oxide formation
Continuous surface layer of $\alpha$-Al$_2$O$_3$

No detectable Y$_3$Al$_5$O$_{12}$ (YAG), YAlO$_3$ (YAP), or Y$_4$Al$_2$O$_9$ (YAM) at the surface or within the internal oxidation zone

Mixed Y-Hf-O ($Y_2Hf_2O_7$) throughout the internal oxidation zone
Conclusions

- GARS was successfully demonstrated as a simplified method to produce precursor powders for ODS ferritic stainless steel alloys
- Droplet cooling curves were used to formulate a theoretical oxidation model to accurately predict the resulting surface oxide layer thickness
- Microstructural results showed a clear ability to manipulate oxide and intermetallic phases within each CR-alloy using elevated temperature consolidation and heat treatment
- Phase analysis confirmed the operation of an O exchange reaction between PPB oxide and Y-enriched IMC precipitates, resulting in the formation of nano-metric dispersoids
- Initial Y-enriched IMC precipitate spatial distribution was shown to be highly dependent on powder particle size (i.e., solidification rate)
Conclusions

- Dispersoid thermal stability was enhanced through the addition of Hf as a substitute for Ti in these CR-alloys.

- ODS microstructures fabricated from ultra-fine (dia. < 5µm) powders resulted in the most ideal spatial distribution of nano-metric oxide dispersoids (dia. < 10 nm).

- This solidification dependence suggests the need to modify the atomization processing parameters to dramatically increase the yield of ultra-fine powders, in order to achieve a more ideal ODS microstructure while maintaining this simplified processing scheme.

- Initial elevated temperature mechanical testing revealed that these simplified CR-alloys contained a Y.S. similar to MA-956, while maintaining a threefold increase in total ductility.
Acknowledgement

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