Atomization and Powder Processing of High Temperature Ferritic Stainless Steel

Iver E. Anderson, Joel R. Rieken, and David J. Byrd

Division of Materials Sciences and Engineering, Ames Laboratory (USDOE)

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Advanced Ultra-Supercritical (A-USC) Power Plants

• Boiler tubing exposed to two extreme environments
  – The outside is exposed to sulfidizing environments (fireside)
  – The inside of the tubing is exposed to supercritical steam (steamside)

• Increases in both pressure and temperature are planned for commercial plants to increase efficiency
  • Steam temperatures of 760°C, 35MPa
    – Tubing operates at about 785°C

• Planned lifetime of 60 years
• Ferritic ODS alloy desired for tubing
Traditional Production of Oxide Dispersion Strengthened (ODS) Alloys by Mechanical Alloying

- Highly anisotropic properties
  - Much lower transverse strength
  - Cross-rolling solution
- High contamination with ball milling
  - O, tramp metallics
  - Strict processing solution
- Long milling times
- Narrow window for hot deformation processing to final shape
- Marginal RT ductility

High Material Costs
- ODS material MA956 sheet was $165/kg
- Caused exit from marketplace
Chemical Reservoir ODS Alloy Design

**Internal Oxygen Exchange Reaction**

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

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**Diagram:**

- **Y-enriched IMC Precipitation** (solidification structure)
- **Dissociation of Cr-enriched boundary oxide**
- **Oxygen Diffusion**
- **Dispersoid formation** (internal oxidation)

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**Graph:**

- ΔG° values (kJ/mole compound) vs. Temperature (°C)
  - Y₂O₃
  - HfO₂
  - TiO₂
  - Cr₂O₃
  - Al₂O₃
  - FeO

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**Image:**

- Initial microstructure with continuous PPB oxide
- Dissociation of metastable Cr-Enriched Oxide
- Y-enriched intermetallic particles
- Oxygen
- Y-enriched oxide dispersoids

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I. Barin, et al., 1992

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**Legend:**

- Metastable Cr-Enriched Oxide
- Y-enriched intermetallic particles
- Oxygen
- Y-enriched oxide dispersoids

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**Caption:**

(Dissociation of internal oxidation)

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**Conclusion:**

Completed oxygen exchange reaction (proper balance of Y and O)
GARS Processing of Precursor Powders with Chemical Reservoir of Oxygen

- Gas Atomization Reaction Synthesis (GARS) process has been shown to produce ODS materials
- Atomization utilizes high pressure gas to produce a powder alloy
- Rapid solidification eliminates need to mix alloy through ball milling
- Much higher production rate compared to milling methods
- Inert + reactive gas can be used to create surface film with controlled oxygen addition

Theoretical vs. Actual oxide thickness in GARS alloys. Rieken, Iowa State University, 2011.

Use of Replacement Reaction with Oxygen Released from Chemical Reservoir to Form ODS Alloy

**Economically viable and high performance Fe-based ODS stainless steels**

I.E. Anderson et al., USPTO no. 8,603,213 5, 2013.
Add Corrosion Resistance with Al Addition to GARS Processed ODS Alloy

- Protective $\text{Al}_2\text{O}_3$ scale necessary for protection in steam conditions
- Chromium additions help to lower the necessary amount of aluminum
- Greater than 16 at.% Cr can cause thermal embrittlement
  - Problem for PM2000 and MA956
- **Chose composition at 16 at.% Cr and 12 at.% Al**
  - All powders will have uniform composition

Oxidation Maps adapted from *Pint and Wright, Mat Sci Forum, 2004, Tomaszewicz and Wallark, Oxi. Of Met., 1983*
Complications for Al Addition

- Large decrease in strength when Al added to traditional ODS
- Formation of $Y_2Ti_2O_7$ oxide without Al, however forms complex Y-Al oxides when added
- Y-Al oxide particles are larger and have a lower number density
  - larger spacing leads to lower strength
- Complex Y-Al oxides coarsen rapidly which can be seen by the strength difference with different rolling temperatures
- Y-Al oxides are detrimental to alloy performance

16.5Cr Base:Fe-16.5Cr-8Al-0.6W-0.17Ti-0.17Y (at.%)
Rolled at 1423K unless otherwise noted

Adapted from Kimura et al., JoNM, 2011

Dispersoid Distribution, Kimura et al., JoNM, 2011
Solution to Strength Reduction

• Strength can be recovered through additions of Hf, Zr

• Strength recovery can be attributed to formation of a more stable oxide phase without Al

-Zhang et al., Acta Met. 2009

Free energy of formation for various oxides

UTS vs Composition at 700°C

Adapted from Kimura et al., JoNM, 2011

• ZrO₂ and HfO₂ have lower free energy of formation than Al₂O₃
  – Y-Hf,Zr complex oxides more favorable than Y-Al oxides

• TiO₂ has a higher free energy of formation than Al₂O₃
  – Y-Al oxides form in Ti containing alloys

16.5Cr Base: Fe-16.5Cr-8Al-0.6W-0.17Ti-0.17Y (at.%)
Oxygen Diffusion in Cast Alloys

- Reaction front penetration showed promise for dissociation during replacement reaction of CR oxygen
- For this case the reaction front can be calculated with the following equation

$$\xi = \sqrt{2D \downarrow O N \downarrow O \uparrow s t/vN \downarrow B \uparrow o}$$

- The oxide progression into the sample shows relative oxide stability
  - $Y_2Hf_2O_7$ oxides are the most stable

Example of Rhine’s Pack sample after heat treatment at 1160°C for 10 hours

Fe-16Cr-10Al-0.25Hf-0.2Y (at.%)
Alloy Choices

<table>
<thead>
<tr>
<th></th>
<th>Al Alloy (at%)</th>
<th>No Al Alloy (at%)</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Bal</td>
<td>Bal</td>
<td>Ferritic matrix</td>
</tr>
<tr>
<td>Cr</td>
<td>16</td>
<td>16</td>
<td>Corrosion</td>
</tr>
<tr>
<td>Al</td>
<td>12</td>
<td>0</td>
<td>Corrosion</td>
</tr>
<tr>
<td>W</td>
<td>0.9</td>
<td>0.9</td>
<td>Strengthening</td>
</tr>
<tr>
<td>Hf</td>
<td>0.25</td>
<td>0.25</td>
<td>Dispersoid</td>
</tr>
<tr>
<td>Y</td>
<td>0.2</td>
<td>0.2</td>
<td>Dispersoid</td>
</tr>
</tbody>
</table>

- Cr chosen to avoid embrittlement and Al to compliment for oxidation protection
- Designed to form 1 vol% $Y_2Hf_2O_7$
- Tungsten added as solid solution/laves phase strengthening mechanism
  - Also shown to benefit creep rupture strength
- No Al alloy for direct comparison
GARS powder production

Actual Alloy Compositions

<table>
<thead>
<tr>
<th>Alloy (at%)</th>
<th>Fe</th>
<th>Cr</th>
<th>Al</th>
<th>W</th>
<th>Hf</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Bal</td>
<td>15</td>
<td>12.3</td>
<td>0.9</td>
<td>0.24</td>
<td>0.19</td>
</tr>
<tr>
<td>No Al</td>
<td>Bal</td>
<td>16</td>
<td>0</td>
<td>0.9</td>
<td>0.25</td>
<td>0.24</td>
</tr>
</tbody>
</table>

- Spherical powder morphology
- Elevated yttrium content in No Al alloy
  - Lower chromium content in Al alloy
- Same gas flow parameters
- Similar size distribution between the two alloys
  - Slightly finer powder in Al alloy
Alloy Oxygen Content

- Increased oxygen levels in No Al alloy
  - Elevated in all powder sizes
- Oxide thickness measured through Auger depth profiling
  - Oxides show Yttrium Enrichment
  - Still found to be amorphous through XRD

![Size Dependent Oxygen](chart)

**Example thickness measurement on Al containing alloy 32-38 µm powder using SiO₂ standard for etching**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>~13µm Powder</th>
<th>~35µm Powder</th>
<th>~68µm Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA-1-198</td>
<td>9 nm</td>
<td>25 nm</td>
<td>32 nm</td>
</tr>
<tr>
<td>GA-1-204</td>
<td>11 nm</td>
<td>26 nm</td>
<td>34 nm</td>
</tr>
</tbody>
</table>

- Elevated oxygen caused by slightly higher pour temperature in No Al alloy
Solidification Structure Importance

- Previous work with:
  - CR-156 (Right)
    Fe-15.84Cr-0.11Hf-0.18Y at%
  - CR-166 (Below)
    Fe-15.91Cr-0.12Ti-0.09Y at%

- Dispersoids follow distribution of intermetallic phases

- Finer dispersoid distribution leads to increased yield strength

Adapted From Anderson et al., 26th Ann. Conf. on FE Mat., 2012

20-53μm Powder

Rieken et al., JNM, 2012
Alloy Consolidation

- 8 µm powder chosen for consolidation
  - Closest to ideal oxygen content (0.7 at%)
  - Smaller powder will have better distribution
  - Still have enough for full HIP can

- Sealed in 316L stainless steel can
  - Outgassed at 600°C and sealed under vacuum

- Hot Isostatic Pressing (HIP) for Consolidation
  - 850°C hold temperature
  - 300 MPa hold pressure
  - 4 hour hold time

- Can turned off on lathe
  - Samples EDMed and polished
Microstructure Evaluation

- Al samples used in heat treatments

- Samples placed in furnace at temperature and water quenched

- FeHf$_2$ ht phase found to be present in all heat treatment samples except 1200°C; through XRD analysis

- Decrease in hardness found with increase in heat treatment temperature
  - Conversion of dispersoids to oxygen lean composition leads to increase in dispersoid crystallite size (found through Scherrer analysis)

Adapted From Anderson et al., 26th Ann. Conf. on FE Mat., 2012
Temperature Effects on Microstructure

- Cannot see dispersoid phase through SEM
  - TEM would be required to resolve at nano-scale

- Clusters of FeHf$_2$ precipitates found in 1000°C and 950°C
  - Could be detrimental during rolling processes

- No noticeable FeHf$_2$ in 1100°C sample
  - Even though small presence detected in XRD
FeHf$_2$ ht Phase Prevention

- Preventing formation of FeHf$_2$ ht phase through homogenization at 1200°C
  - FeHf$_2$ ht phase is possible site for crack initiation during rolling

- FeHf$_2$ ht phase was not found present after homogenization

- Unknown phase present in both Al and No Al samples
  - Unknown phase is not Y-Al oxides

- 1200°C chosen for HT temperature

X-ray diffraction data obtained with Co tube; FeHf$_2$ ht phase noted with red arrows
Comparison of Alloy Microstructure

- Samples heat treated at 1200°C for 5 hours
  - Ramp rate of 1200°C/hour

- As-HIP microstructures have the same cellular intermetallic compounds in larger powders
  - Not as prominent in the heat treated condition

- Larger precipitates seen in No Al alloy in the heat treated condition

Al (Fe-15Cr-12.3Al-0.9W-0.24Hf-0.19Y)
No Al (Fe-16Cr-0.0Al-0.9W-0.25Hf-0.24Y)
Rolling Study

- Samples prepped through EDM and polishing
  - Prevent Crack Formation

- Soaked at 1050°C prior to rolling and between rolling passes
  - Rolling Achieved through 10% reduction in thickness passes
  - Total reduction in thickness of 70% (~50% Reduction in cross-sectioned area)

- Surface Grinding to ensure flat parallel surfaces

Al (Fe-15Cr-12.3Al-0.9W-0.24Hf-0.19Y)
No Al (Fe-16Cr-0.0Al-0.9W-0.25Hf-0.24Y)
As-Rolled Microhardness

- Slightly lower microhardness in longitudinal direction of No Al
  - Transverse strength in MA956 is ~35% of longitudinal
  - Wright et. al., 19th annual conference on FE materials, 2005

- Al alloy had fully isotropic microhardness values

Microhardness values indicate that GARS produced ODS alloy does not exhibit anisotropic strength like MA ODS

Al (Fe-15Cr-12.3Al-0.9W-0.24Hf-0.19Y)
No Al (Fe-16Cr-0.0Al-0.9W-0.25Hf-0.24Y)
Comparison of Alloy Tensile Properties

• Type SS3 tensile specimens machined from rolled samples
  – Tensile data taken as an average of transverse and longitudinal
• Comparable strength to previous mechanically alloyed PM2000 and MA956
• YS slightly higher than goal strength at operation temperature
  – Some strength loss due to increased dispersoid size caused by low oxygen content
  – Increased oxygen can be added in simple process modification

YS meets threshold stress for A-USC operation conditions (further creep testing planned)
Comparison of Alloy Tensile Properties

- Al data taken as an average of transverse and longitudinal directions
  - Higher elongation in transverse direction

- Al containing alloy had much higher ductility at 800°C than previous ODS alloys

- Ductility peak at 600°C followed by decrease in mechanically alloyed ODS materials
  - Caused by transition from transverse to intergranular failure

**Graph:**

- Total Elongation of GARS produced alloys compared to previously commercial available MA956 and PM2000 (data provided by manufacturers)

**Key Points:**

3X increased HT elongation compared to MA alloys---will be benefit for hot deformation
Corrosion in dry air at 1200°C

- No Al alloy had spallation occur after 100 cycles
  - Significantly more protection with aluminum additions

- Al alloy had much higher mass gains than PM2000 or cast FeCrAlY
  - Similar to FeCrAlY + Hf due to internal oxidation

- Internal oxidation forms pegs which can increase oxidation resistance
  - Large pegs can be places for crack initiation
    - Allam et al, Oxidation of Metals, 13 (4) 1979

- Low oxygen content caused large excess of reactive intermetallics (Y and Hf)

Al (Fe-15Cr-12.3Al-0.9W-0.24Hf-0.19Y)
No Al (Fe-16Cr-0.0Al-0.9W-0.25Hf-0.24Y)
Corrosion in wet air at 1100°C

- Water containing atmosphere to simulate steamside of boiler tubing
  - Higher temperature for accelerated effects

- No Al alloy had mass loss occur after 1 cycle
  - Consistent mass loss shows that No Al alloy is not protective in this atmosphere

- Al alloy had increased mass gain compared to other PM2000 and cast FeCrAlY + Hf
  - Caused by internal oxidation due to low oxygen content in alloy

- Al alloy showed protective scale formation for 1000 hours with water vapor present

Mass gains in 10 volume % water vapor at 1100°C, cycle times of 100 hours. Data obtained by Bruce Pint at ORNL.

Al (Fe-15Cr-12.3Al-0.9W-0.24Hf-0.19Y)
No Al (Fe-16Cr-0.0Al-0.9W-0.25Hf-0.24Y)
Specific Conclusions

- A desirable composition for GARS processing to ODS alloy for enhanced corrosion resistance, dispersoid formation, and other factors is: Fe-16Cr-12Al-0.9W-0.25Hf-0.2Y at.%

- After full density consolidation by HIP, heat treatment conditions of 1200°C for 5 hours appears to be optimum
  - Prevents high temperature phase formation and solutionizes for hot rolling

- Direct comparison enabled by processing same ODS alloy with and without Al addition
  - Higher strength found for aluminum containing alloy
  - Comparable strength to PM2000 and MA956

- Aluminum containing alloy had better corrosion resistance in dry and wet air
  - Higher than normal corrosion in Al alloy compared to PM2000 and cast alloys due to high Hf
  - Completion of oxidation reaction for Y+Hf intermetallics will improve corrosion resistance

- Awaiting corrosion and strength results from short time ball milling with higher oxygen level
General Conclusions

- New A-USC operating conditions require new materials to be developed
  - Aluminum additions for steamside corrosion resistance
  - Oxide dispersion strengthening (ODS) for high temperature strength
- Previously available commercial ODS alloys produced by mechanical alloying were targeted
  - MA processed alloy too costly for desired shapes (e.g., tubes) and no longer in marketplace.
- GARS processing method in advanced development stage for producing ferritic ODS alloys
  - Much lower net-shape (tube) cost likely in ODS alloys from GARS precursor powders (NE funds).
  - Recent CRADA project with commercial powder maker established GARS processing pilot plant.
Acknowledgement

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