# Atomization and Powder Processing of High Temperature Ferritic Stainless Steel

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**2014 NETL Crosscutting Research Review Meeting**

**Pittsburgh, PA**
**May 22, 2014**

*Support from the Department of Energy-Office of Fossil Energy is gratefully acknowledged through Ames Laboratory contract no. DE-AC02-07CH11358*

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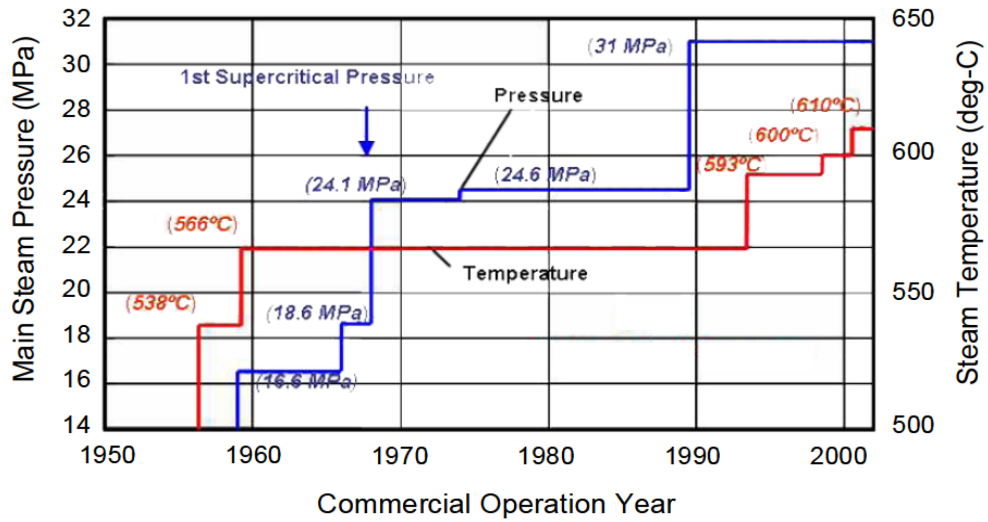
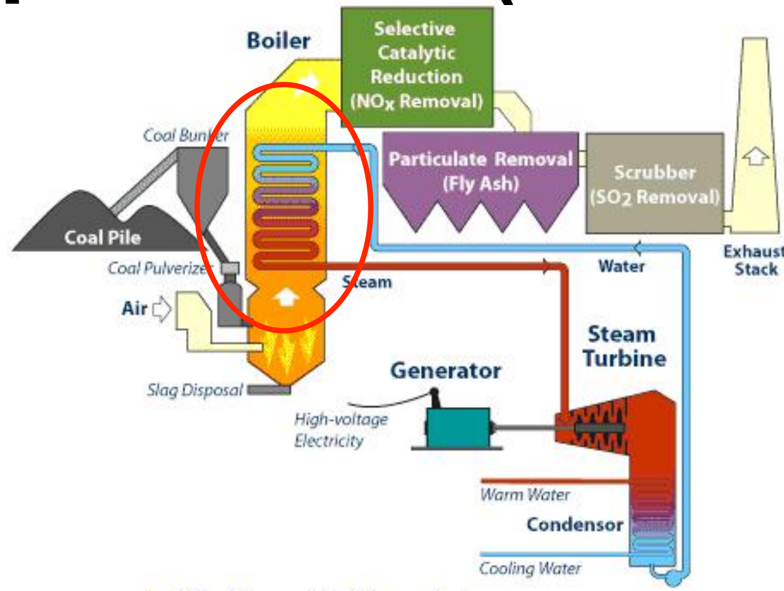
# Advanced Ultra-Supercritical (A-USC) Power Plants

- 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**)



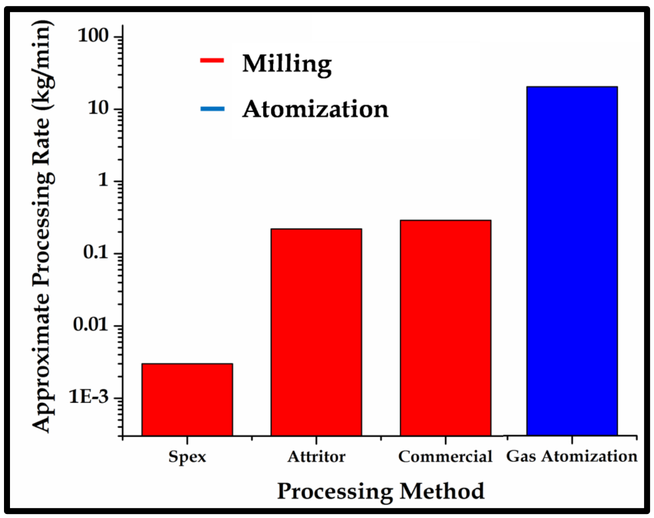

**Operation Conditions in Japan. Fukuda, Adv. In Mat. Tech. for Fossil Power Plants, 6th International Conference , 2010.**



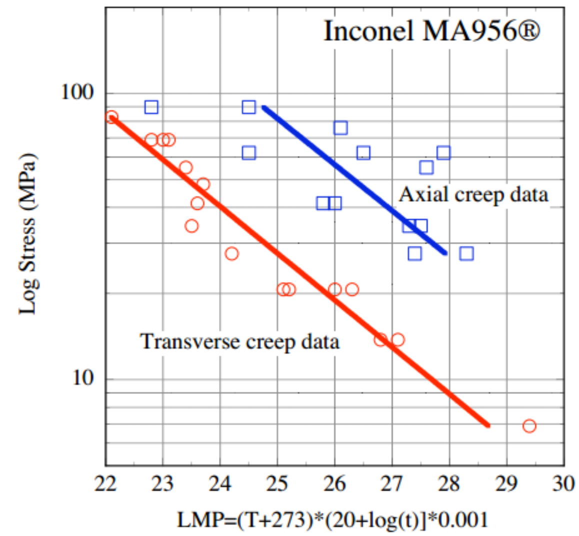

- Increases in both pressure and temperature are planned for commercial plants to increase efficiency
- **Steam temperatures of 760°C, 35MPa**
  - Tubing operates at about 785°C
- Planned lifetime of 60 years
- **Ferritic ODS alloy desired for tubing**

# 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




**Powder production rate for various methods.**
**Anderson et al, 26th annual conference on FE materials, 2012**



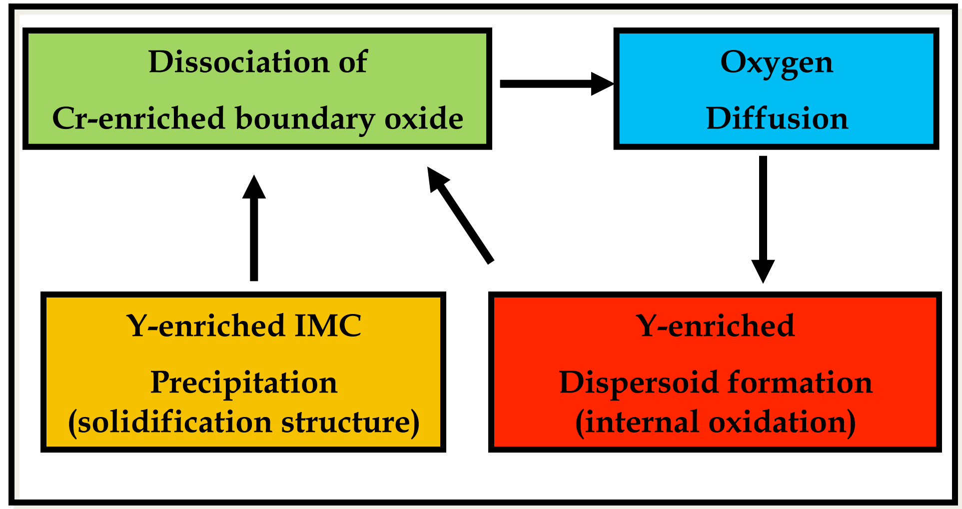

**Transverse and axial creep parameters of mechanically alloyed MA956.** ***Wright et. al. 19th Annual Conference on FE Materials 2005***

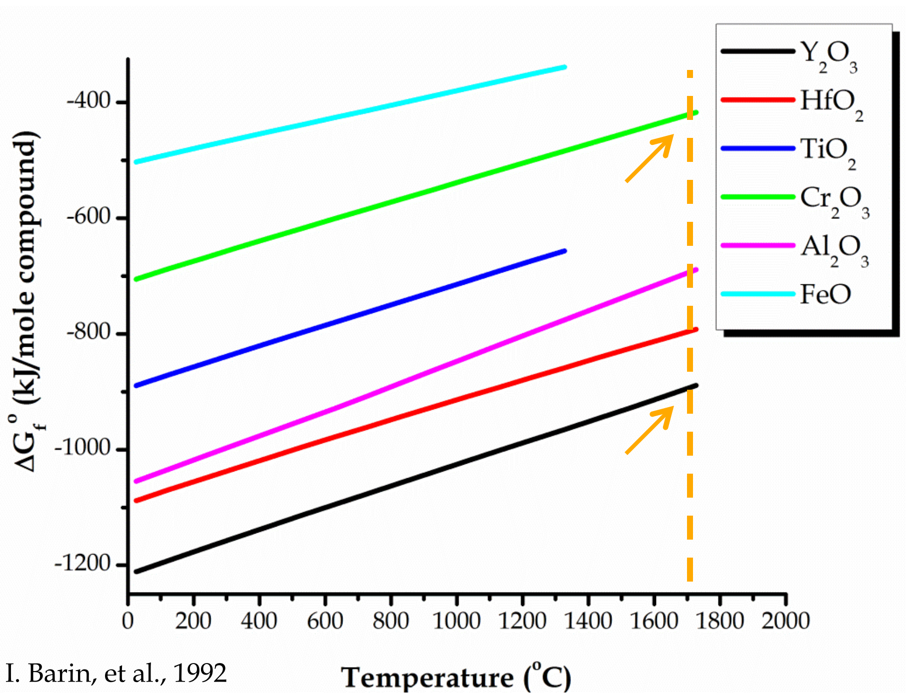
- High Material Costs
  - ODS material MA956 sheet was $165/kg
  - Caused exit from marketplace

# Chemical Reservoir ODS Alloy Design

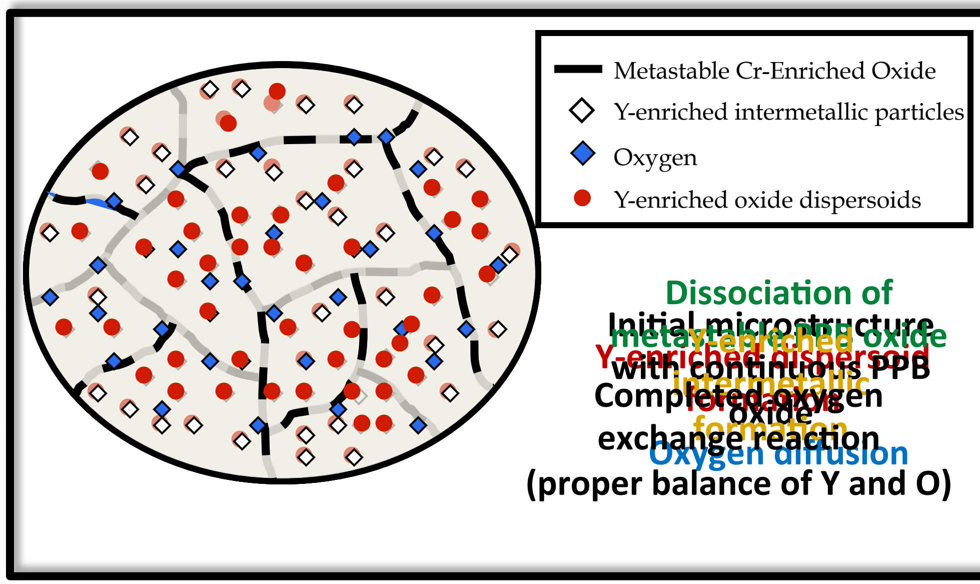
## Internal Oxygen Exchange Reaction

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



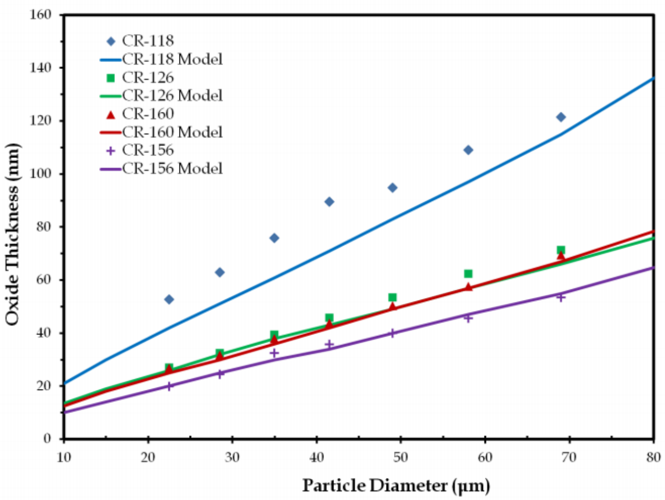




I. Barin, et al., 1992



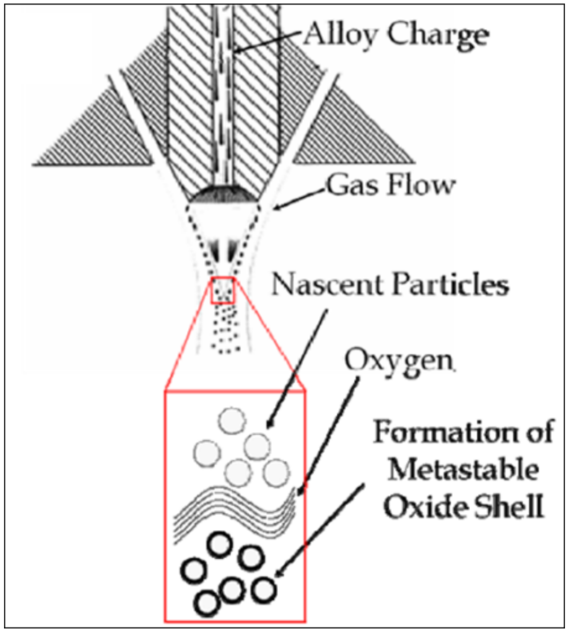
# GARS Processing of Precursor Powders with Chemical Reservoir of Oxygen

- 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



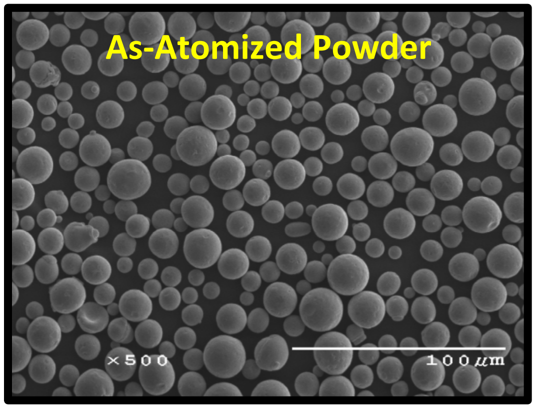

Theoretical vs. Actual oxide thickness in GARS alloys. Rieken, Iowa State University, 2011.

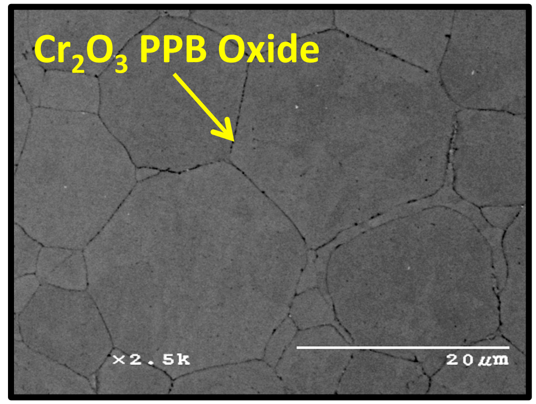
- Much higher production rate compared to milling methods
- Inert + reactive gas can be used to create surface film with controlled oxygen addition



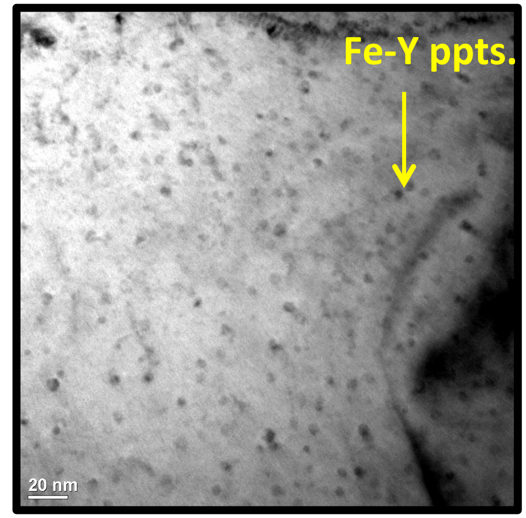

Oxide Formation During GARS. Rieken et al., Int. J. of Powder Metall., 46 (2010) 6.

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

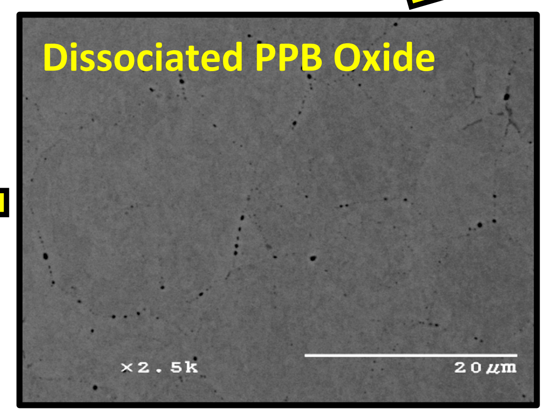


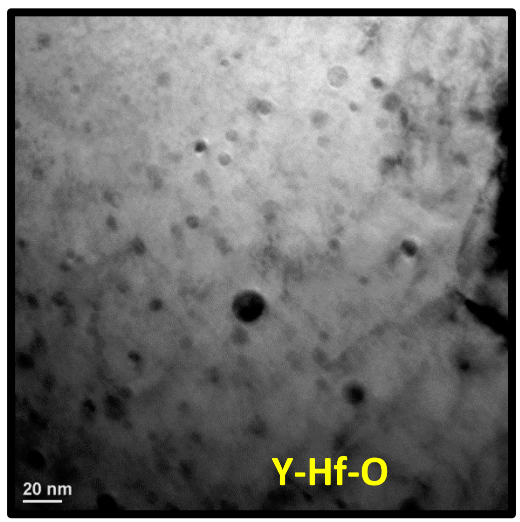

Hot Consolidated (700°C)




IMC Precipitate Formation




Heat Treated (1200°C)



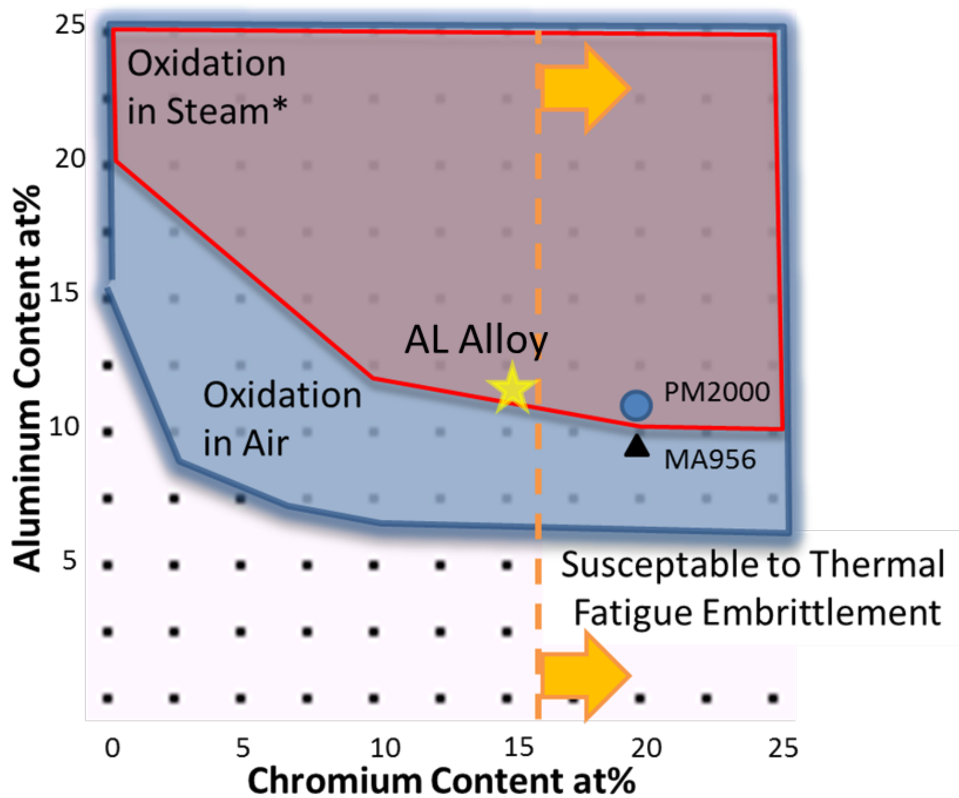

Nano-metric dispersoid formation

***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

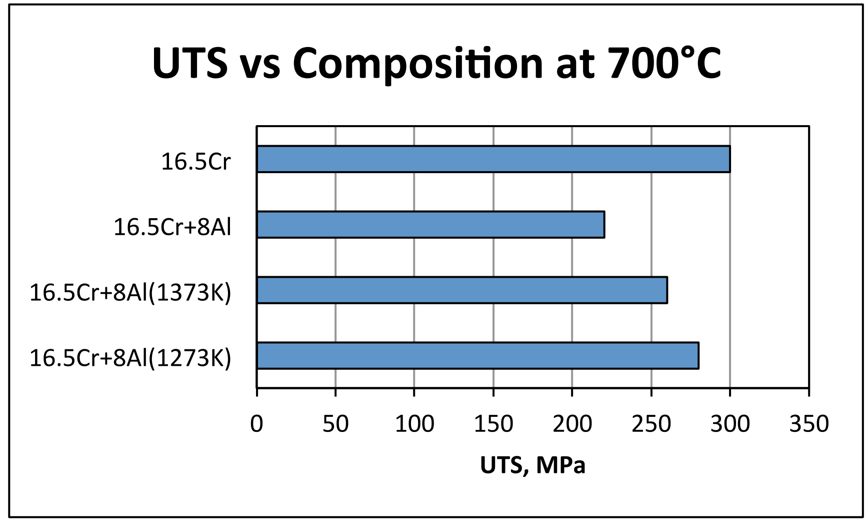
- Protective $Al_2O_3$ scale necessary for protection in steam conditions
- Chromium additions help to lower the necessary amount of aluminum
- Greater than 16 at.% Cr can cause thermal embrittlement
  - Problem for PM2000 and MA956
- **Chose composition at 16 at.% Cr and 12 at.% Al**
  - All powders will have uniform composition



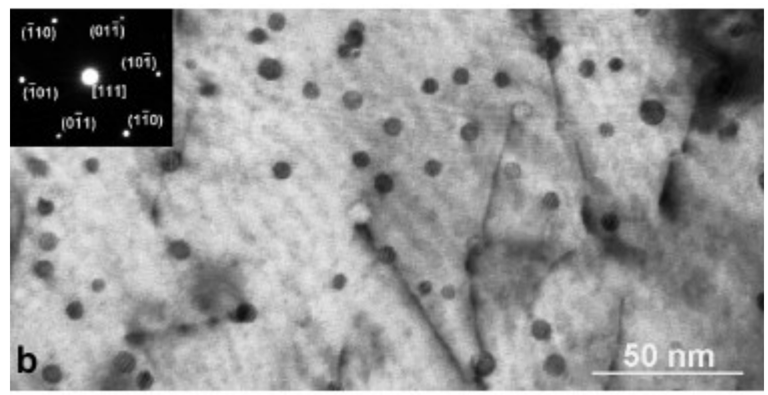

**Oxidation Maps adapted from *Pint and Wright, Mat Sci Forum, 2004, Tomaszewicz and Wallark, Oxi. Of Met., 1983***

# 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




***Adapted from Kimura et al., JoNM, 2011***



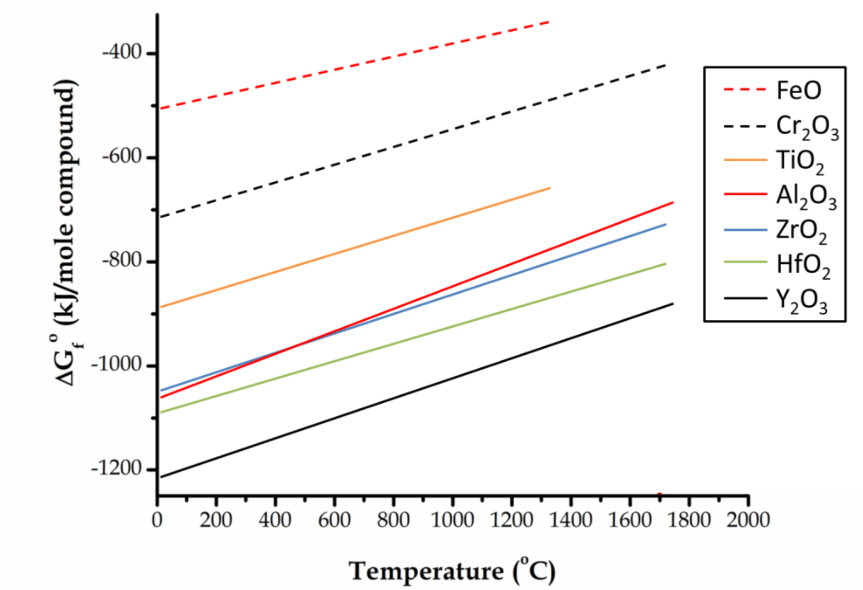

**Dispersoid Distribution, *Kimura et al., JoNM, 2011***

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

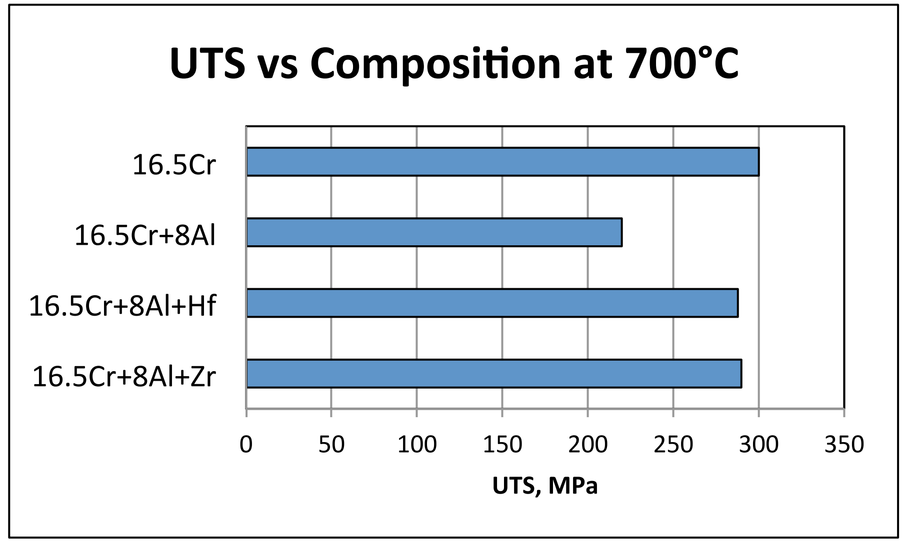
# Solution to Strength Reduction

- 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***

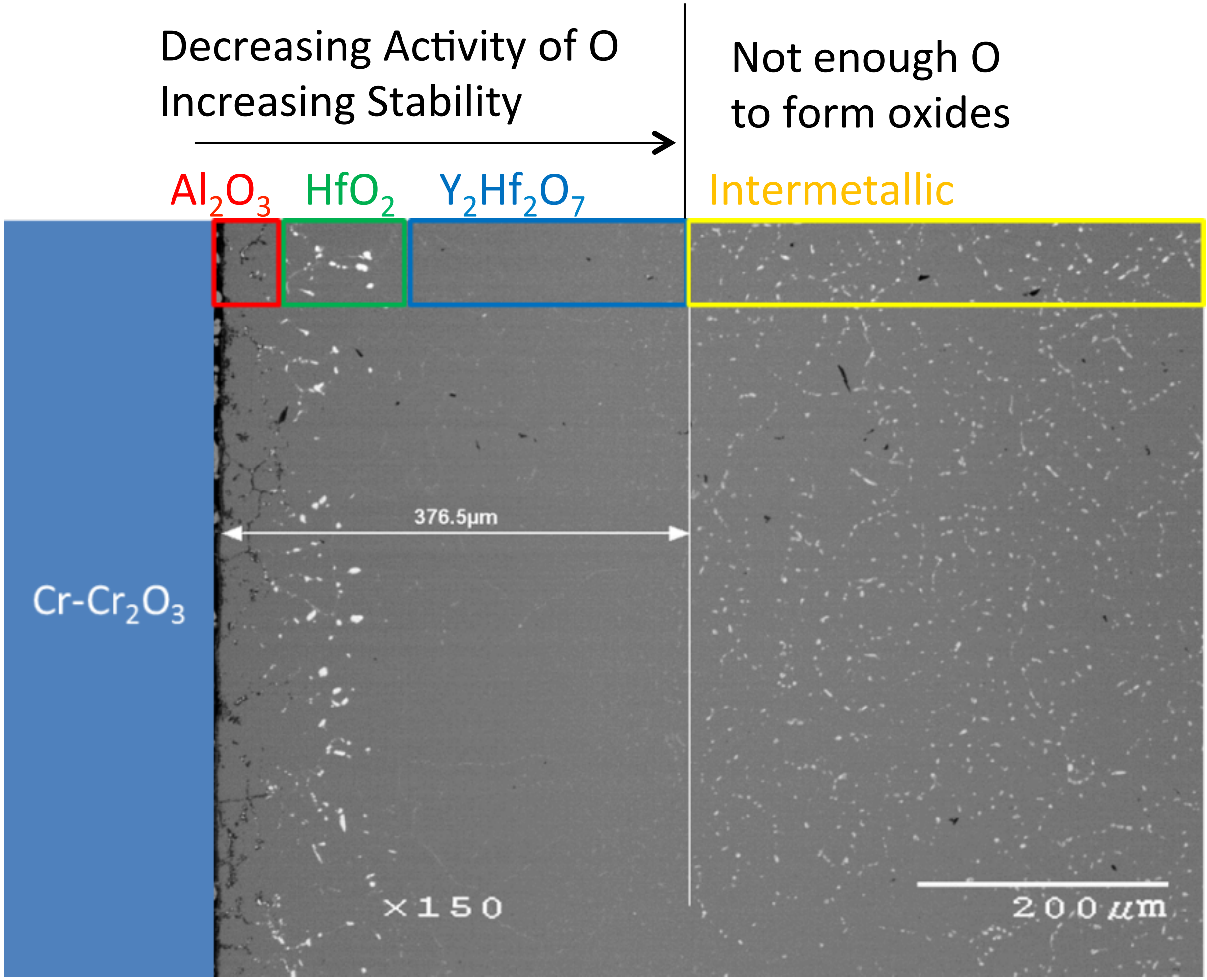



***Adapted from Kimura et al., JoNM, 2011***

- $ZrO_2$ and $HfO_2$ have lower free energy of formation than $Al_2O_3$
  - Y-Hf,Zr complex oxides more favorable than Y-Al oxides
- $TiO_2$ has a higher free energy of formation than $Al_2O_3$
  - 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




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

- 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

$$\xi=\sqrt{\frac{2D_O N_O^s t}{\nu N_B^o}}$$

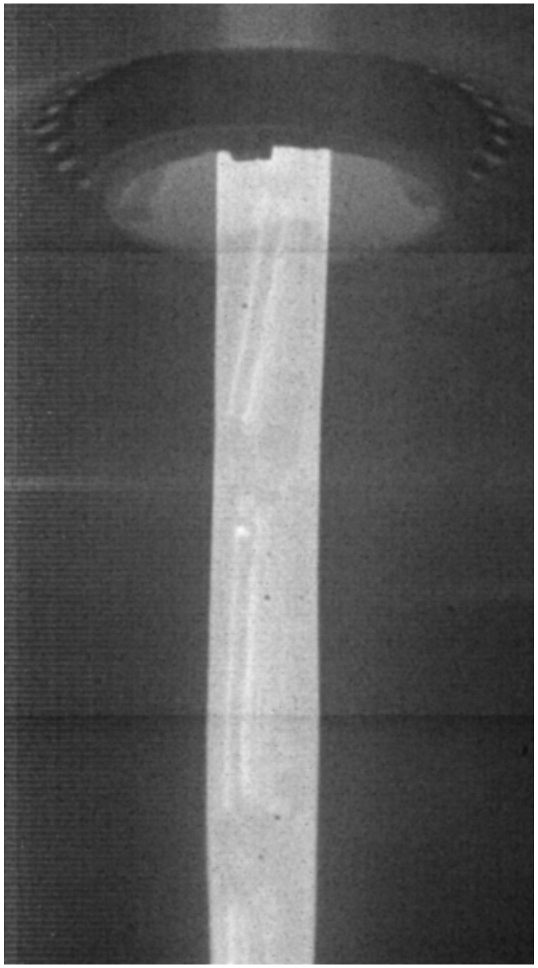
- The oxide progression into the sample shows relative oxide stability
  - **$Y_2Hf_2O_7$ oxides are the most stable**

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

# Alloy Choices

| | Al Alloy (at %) | No Al Alloy (at%) | Purpose |
|---|---|---|---|
| Fe | Bal | Bal | Ferritic matrix |
| Cr | 16 | 16 | Corrosion |
| Al | 12 | 0 | Corrosion |
| W | 0.9 | 0.9 | Strengthening |
| Hf | 0.25 | 0.25 | Dispersoid |
| Y | 0.2 | 0.2 | Dispersoid |

- 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

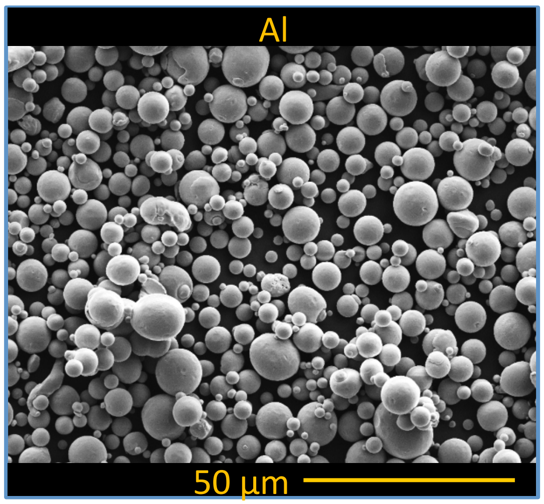


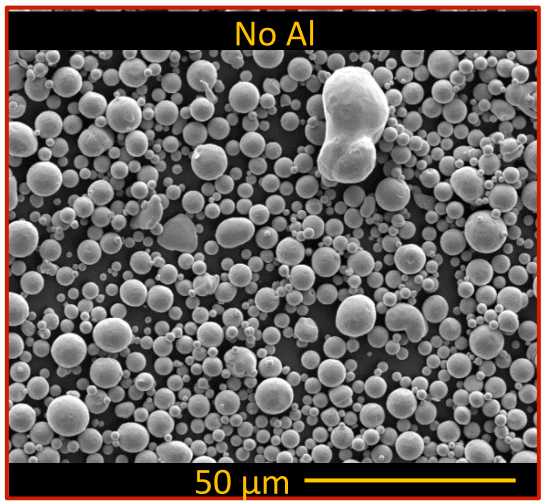
# GARS powder producation

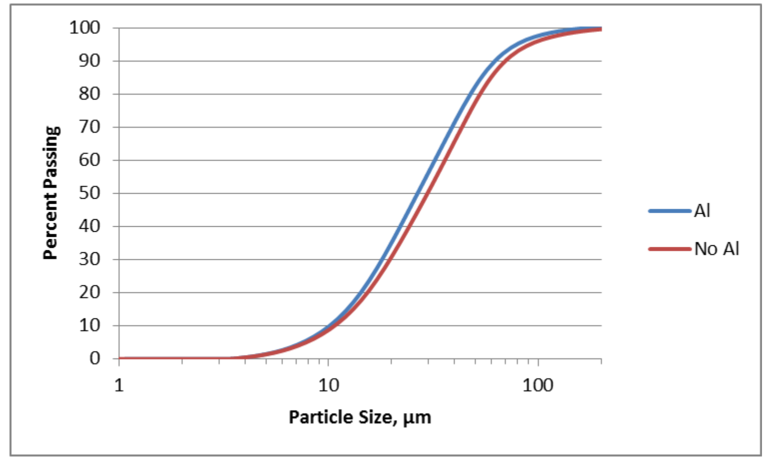
**Actual Alloy Compositions**

| Alloy (at%) | Fe | Cr | Al | W | Hf | Y |
|---|---|---|---|---|---|---|
| **Al** | Bal | 15 | **12.3** | 0.9 | 0.24 | **0.19** |
| **No Al** | Bal | 16 | **0** | 0.9 | 0.25 | **0.24** |

- Spherical powder morphology
- Elevated yttrium content in No Al alloy
  - Lower chromium content in Al alloy



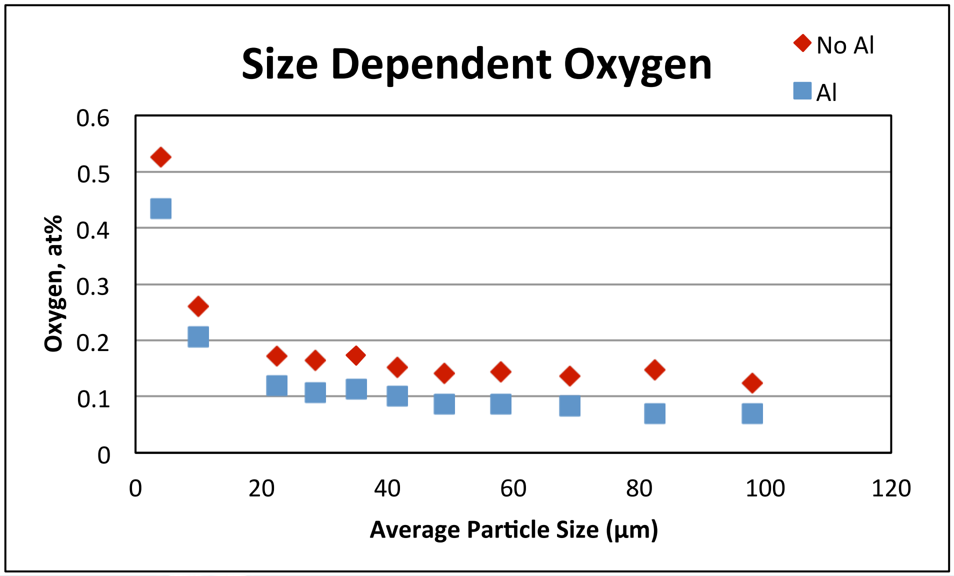



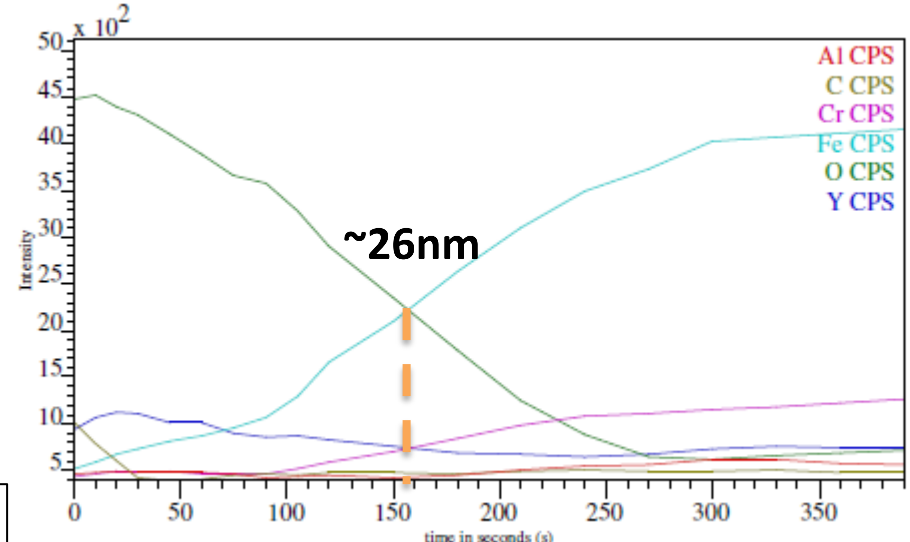




- Same gas flow parameters
- Similar size distribution between the two alloys
  - Slightly finer powder in Al alloy

# 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



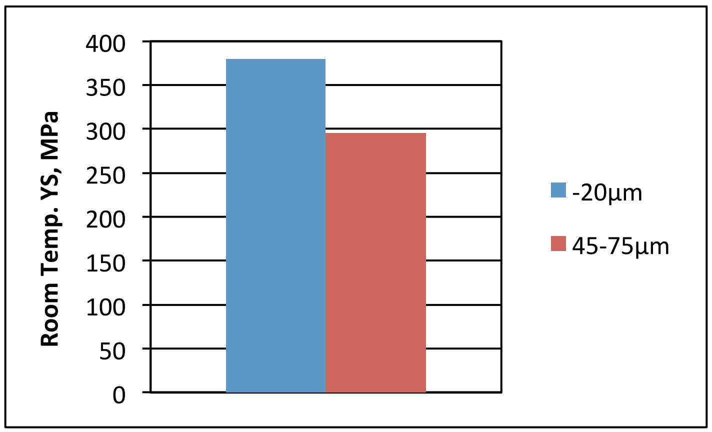

**Example thickness measurement on Al containing alloy 32-38 µm powder using $SiO_2$ standard for etching**

| Alloy | ~13µm Powder | ~35µm Powder | ~68µm Powder |
|---|---|---|---|
| GA-1-198 | 9 nm | 25 nm | 32 nm |
| GA-1-204 | 11 nm | 26 nm | 34 nm |

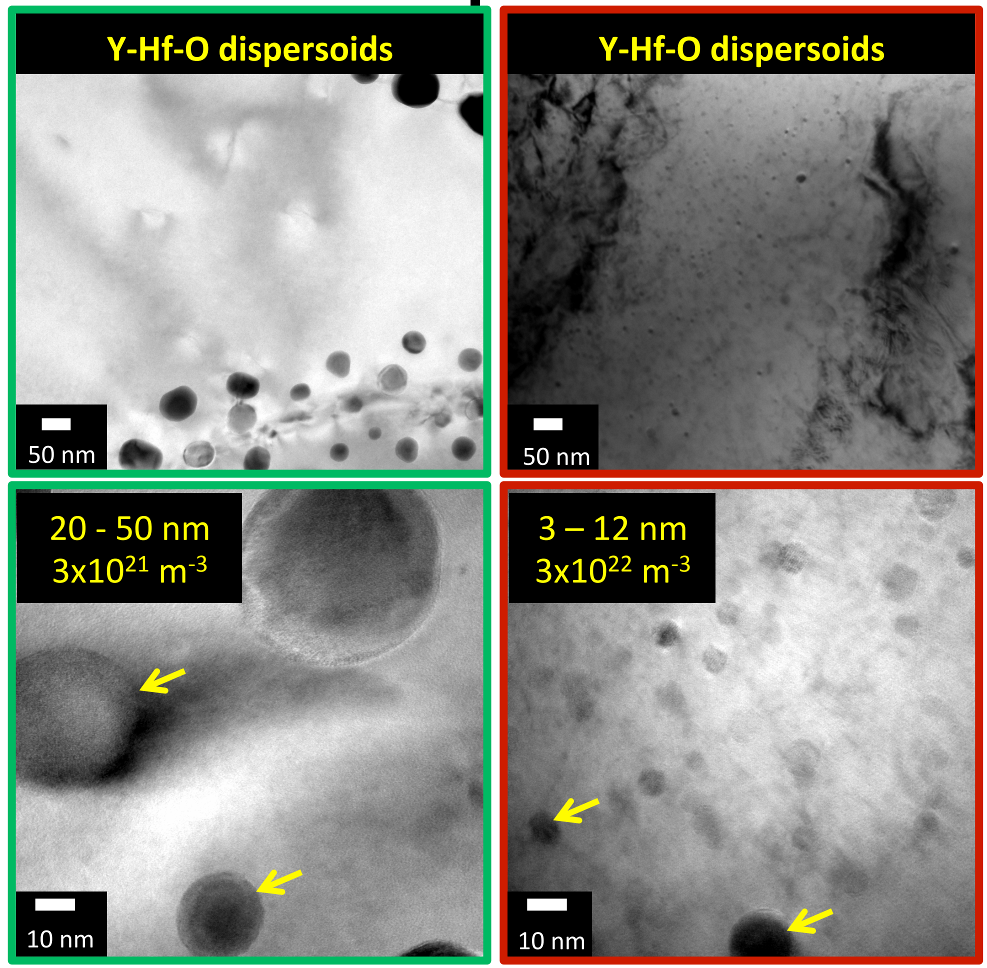
- Elevated oxygen caused by slightly higher pour temperature in No Al alloy

# 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***



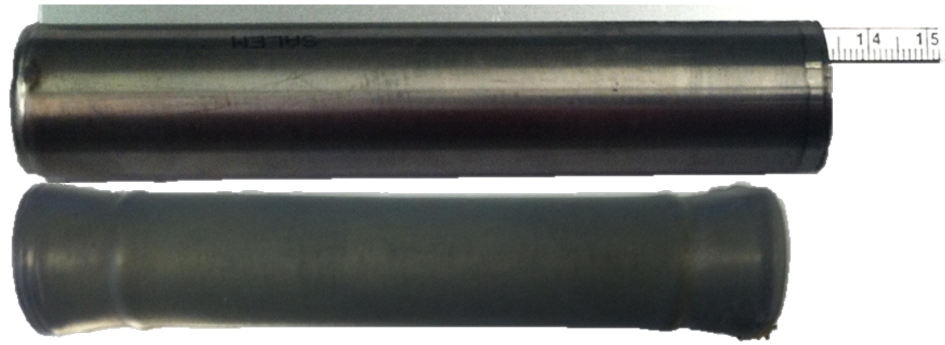

**20-53µm Powder** **<5µm Powder**

***Rieken et al., JNM, 2012***

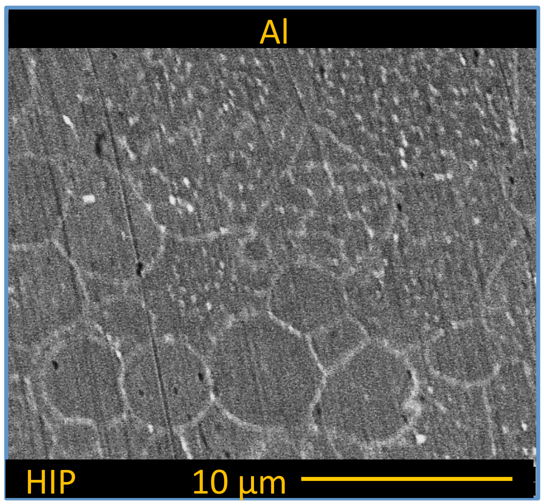
# Alloy Consolidation

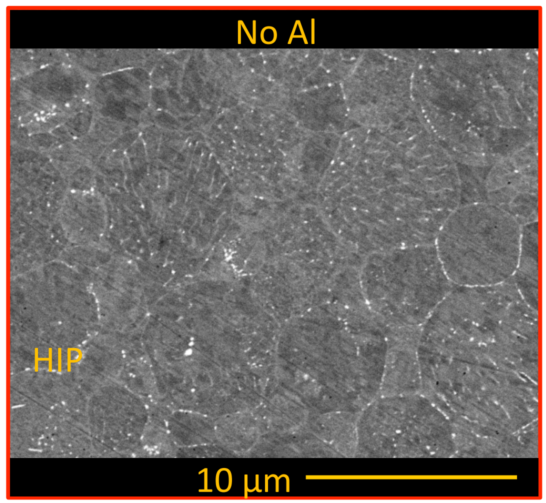
- -8 µm powder chosen for consolidation
  - Closest to ideal oxygen content (0.7 at%)
  - Smaller powder will have better distribution
  - Still have enough for full HIP can

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



Al HIP can prior to consolidation (top); Al HIP can after consolidation at 850°C 300 MPa for 4 hours



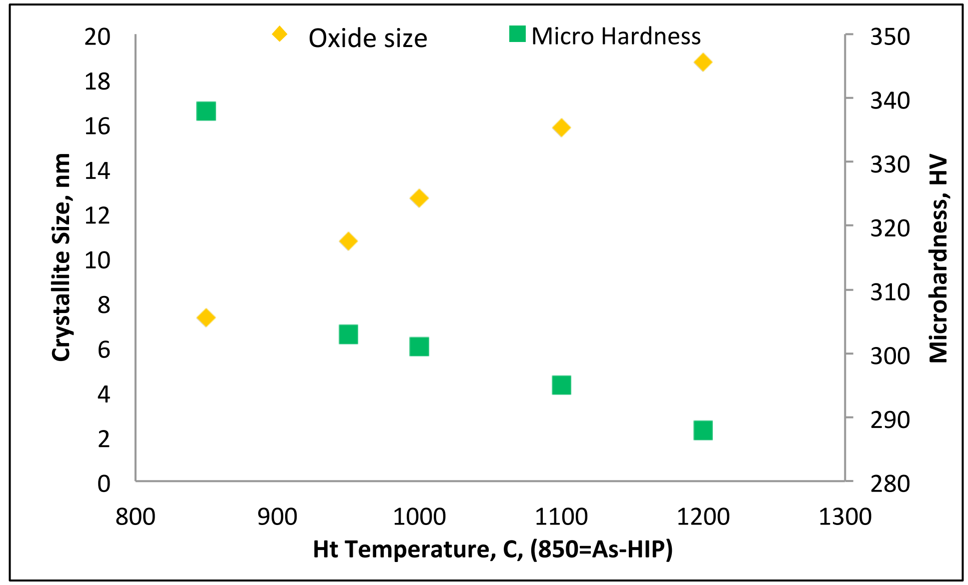



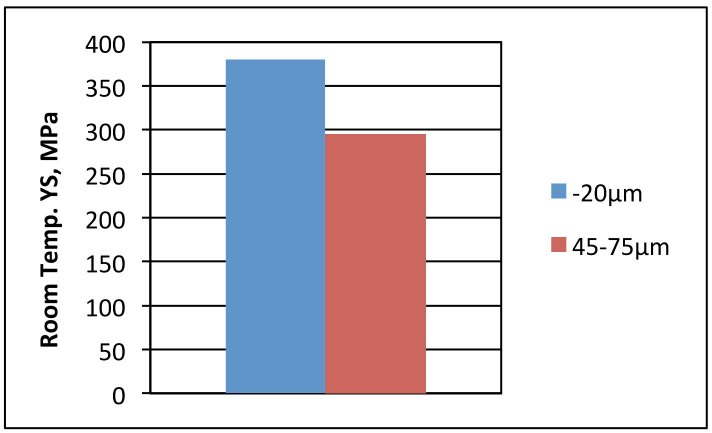

- Hot Isostatic Pressing (HIP) for Consolidation
  - 850°C hold temperature
  - 300 MPa hold pressure
  - 4 hour hold time

- 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



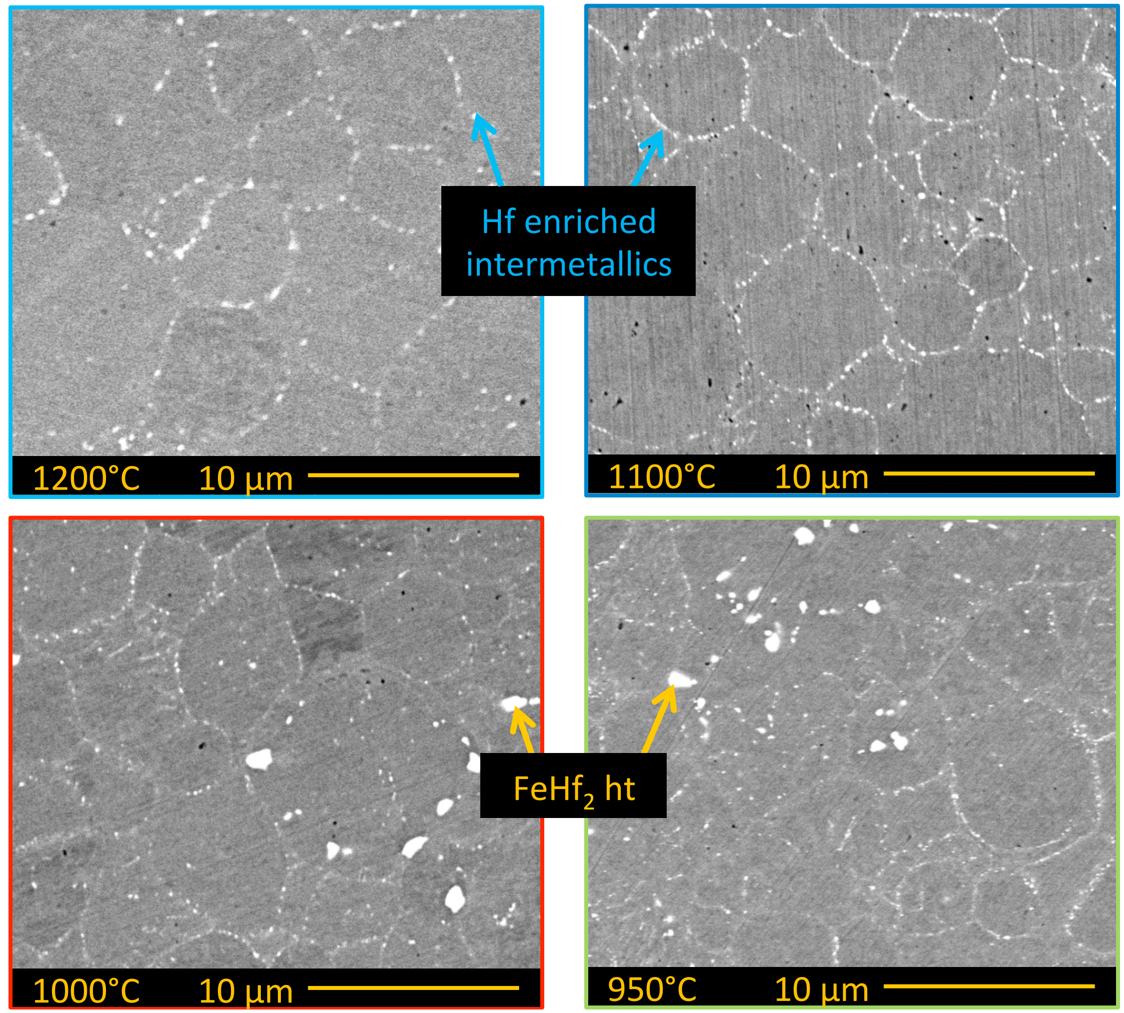




- Decrease in hardness found with increase in heat treatment temperature
  - Conversion of dispersoids to oxygen lean composition leads to increase in dispersoid crystallite size (found through Scherrer analysis)

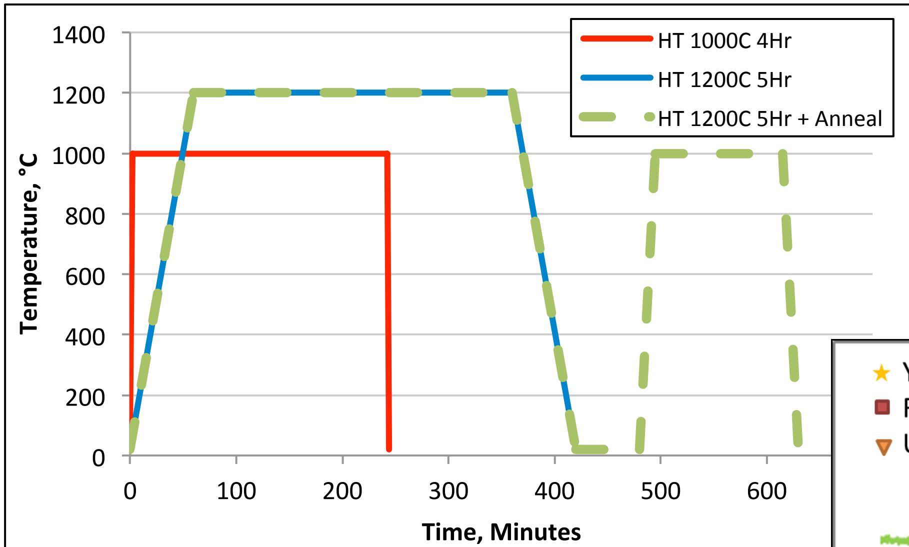
**Adapted From *Anderson et al., 26th Ann. Conf. on FE Mat., 2012***

# Temperature Effects on Microstructure

- Cannot see dispersoid phase through SEM
  - TEM would be required to resolve at nano-scale
- Clusters of $FeHf_2$ ht precipitates found in 1000°C and 950°C
  - Could be detrimental during rolling processes
- No noticeable $FeHf_2$ ht in 1100°C sample
  - Even though small presence detected in XRD



# $FeHf_2$ ht Phase Prevention

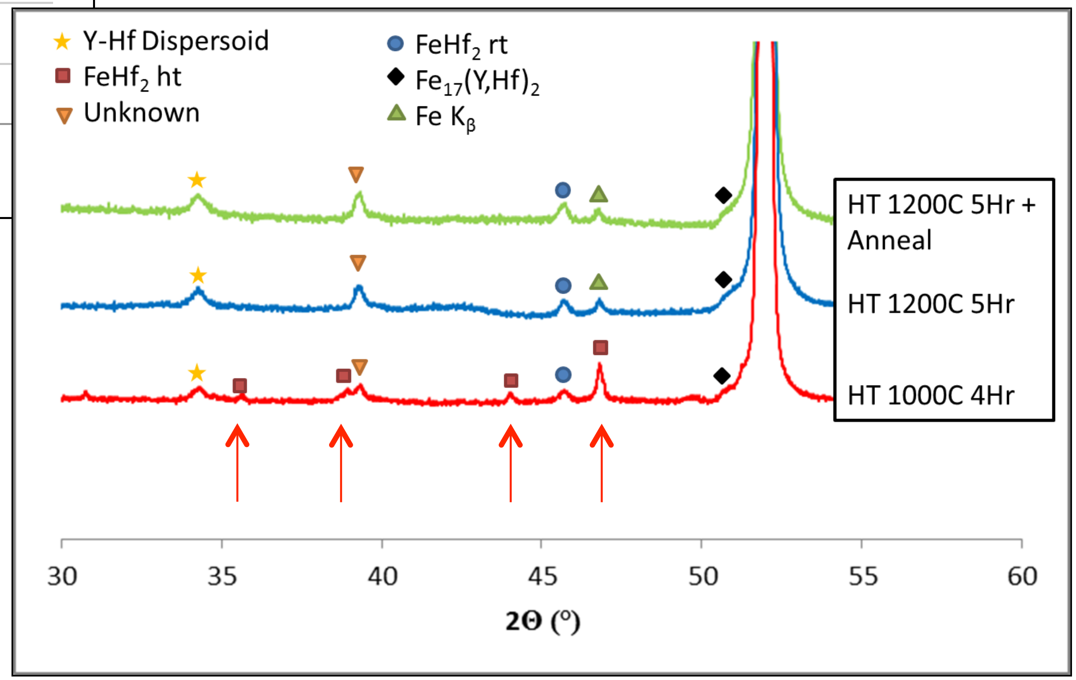



- Preventing formation of $FeHf_2$ ht phase through homogenization at 1200°C
  - $FeHf_2$ ht phase is possible site for crack initiation during rolling

- $FeHf_2$ 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

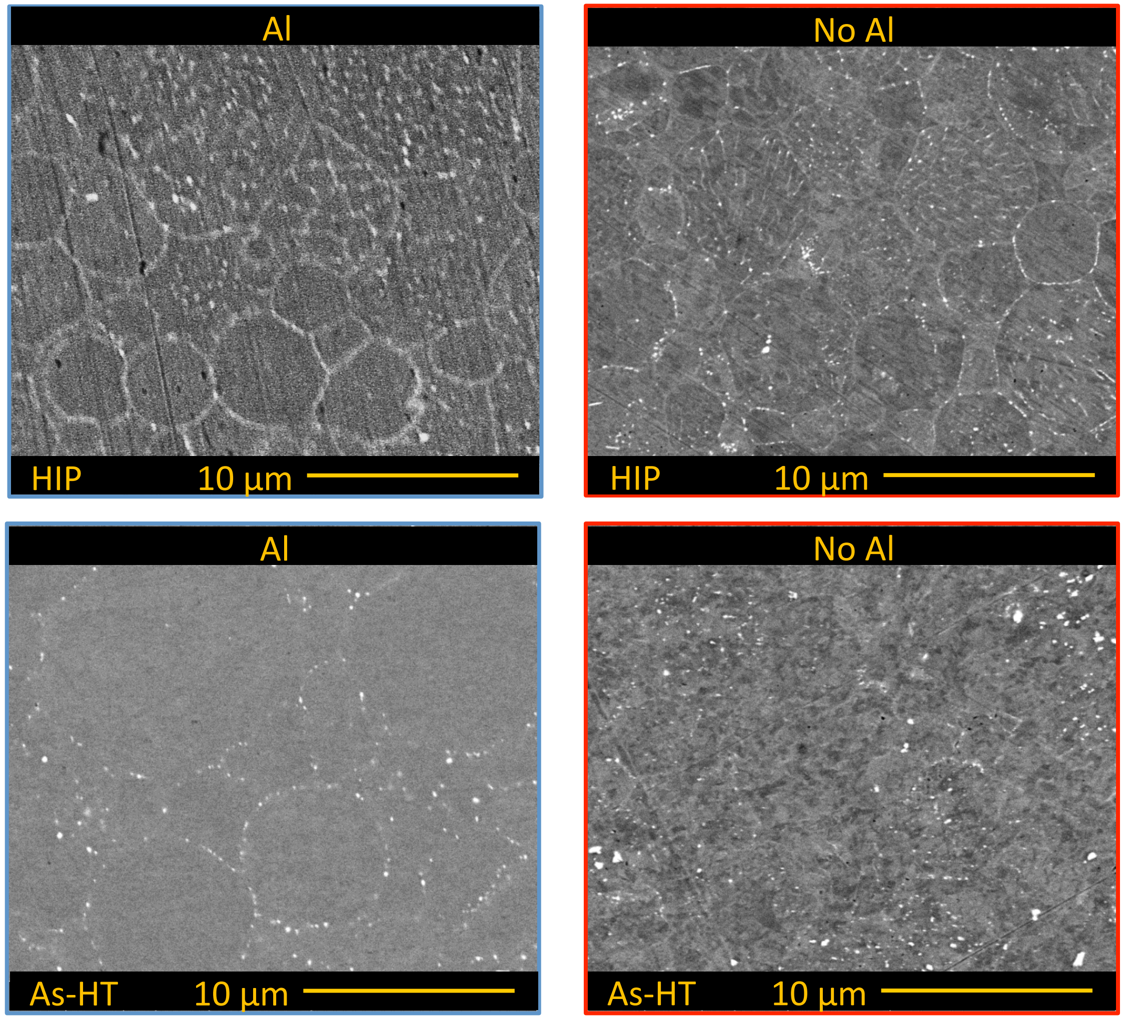
- **1200°C chosen for HT temperature**




**X-ray diffraction data obtained with Co tube; $FeHf_2$ ht phase noted with red arrows**

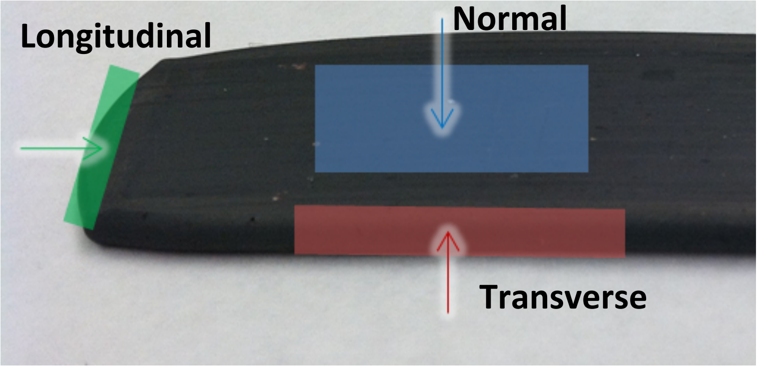
# Comparison of Alloy Microstructure

- 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)

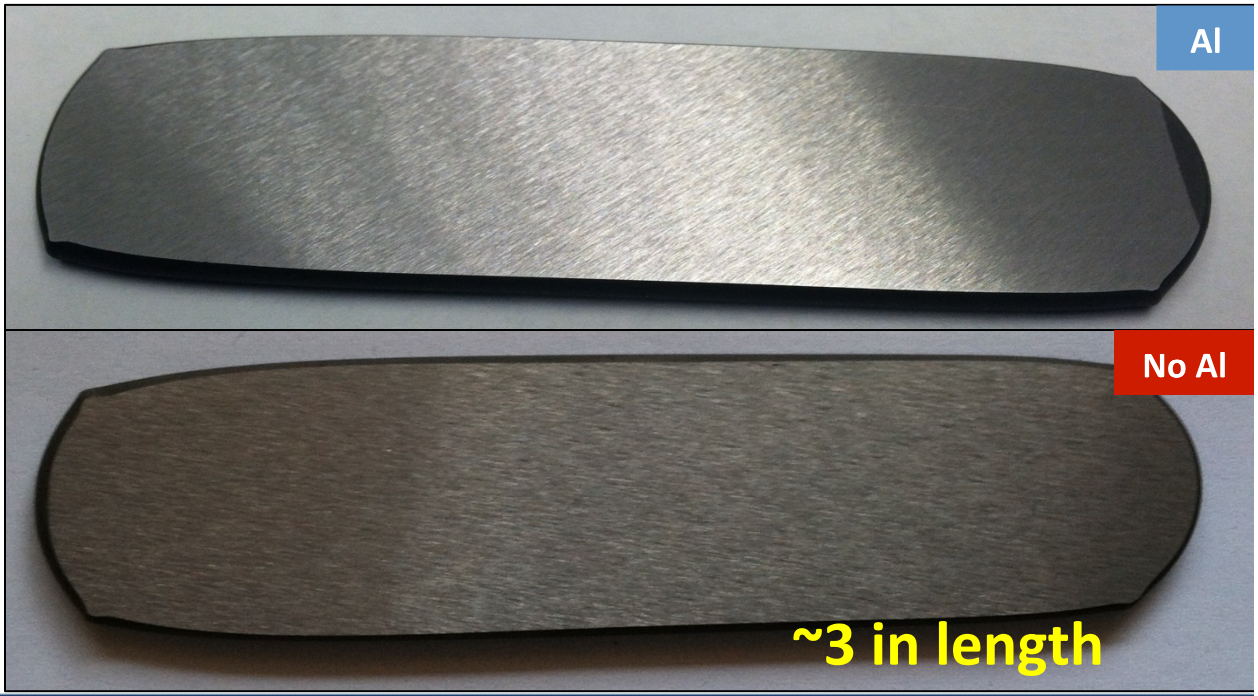
# Rolling Study




Three Orthogonal Rolling Directions

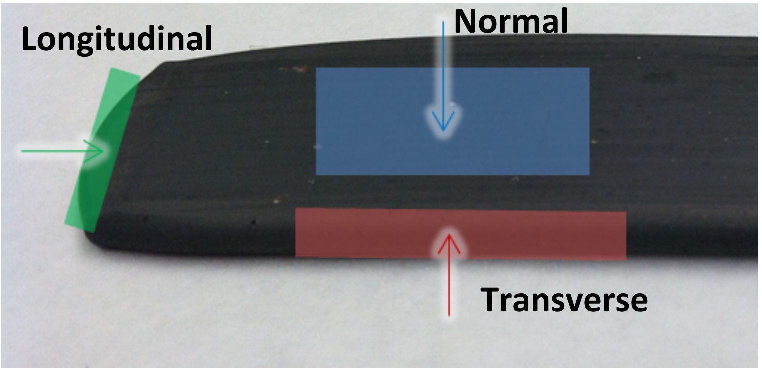
- Samples prepped through EDM and polishing
  - Prevent Crack Formation

- 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

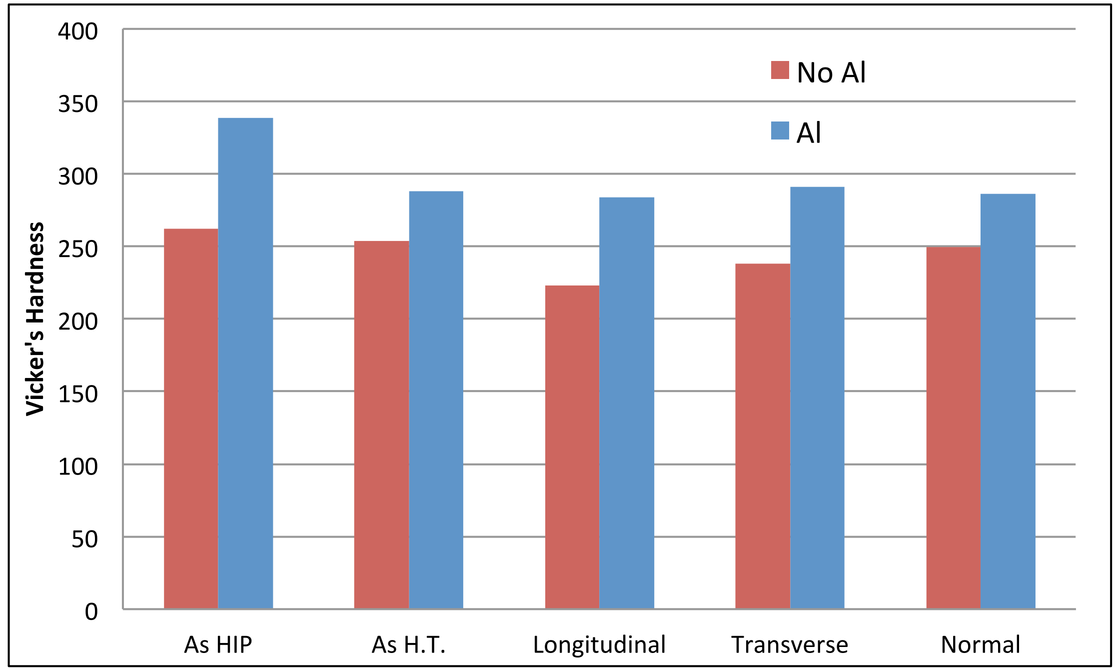



Al (Fe-15Cr-12.3Al-0.9W-0.24Hf-0.19Y)
No Al (Fe-16Cr-0.0Al-0.9W-0.25Hf-0.24Y)

# As-Rolled Microhardness




**Three Orthogonal Rolling Directions**




**Orientational effects on alloy 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*

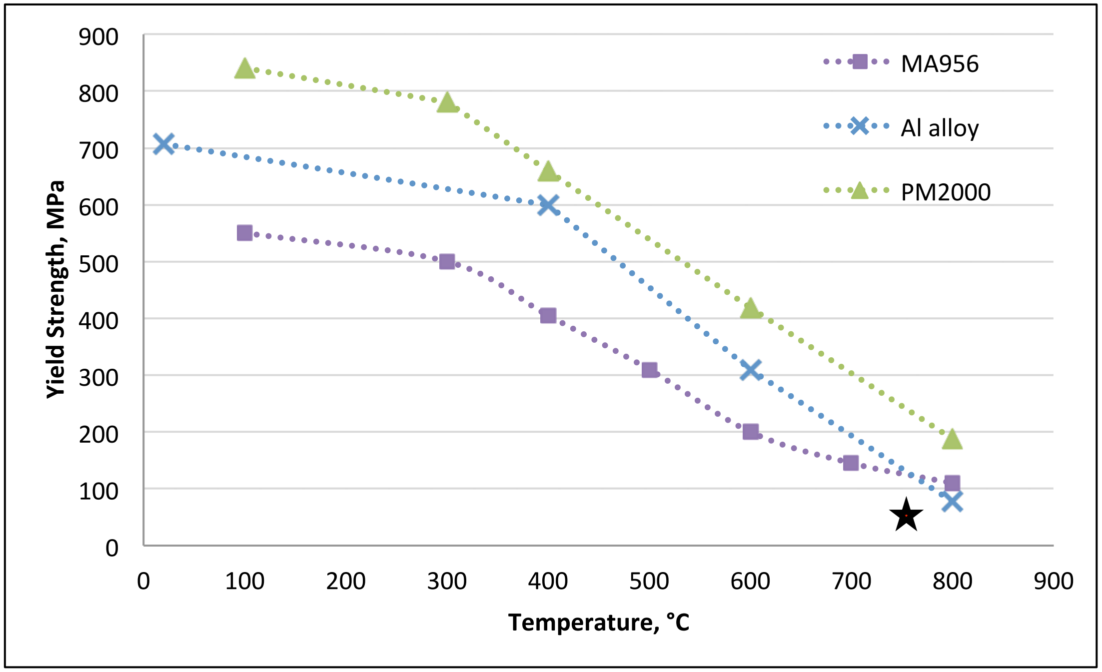
- Al alloy had fully isotropic microhardness values

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



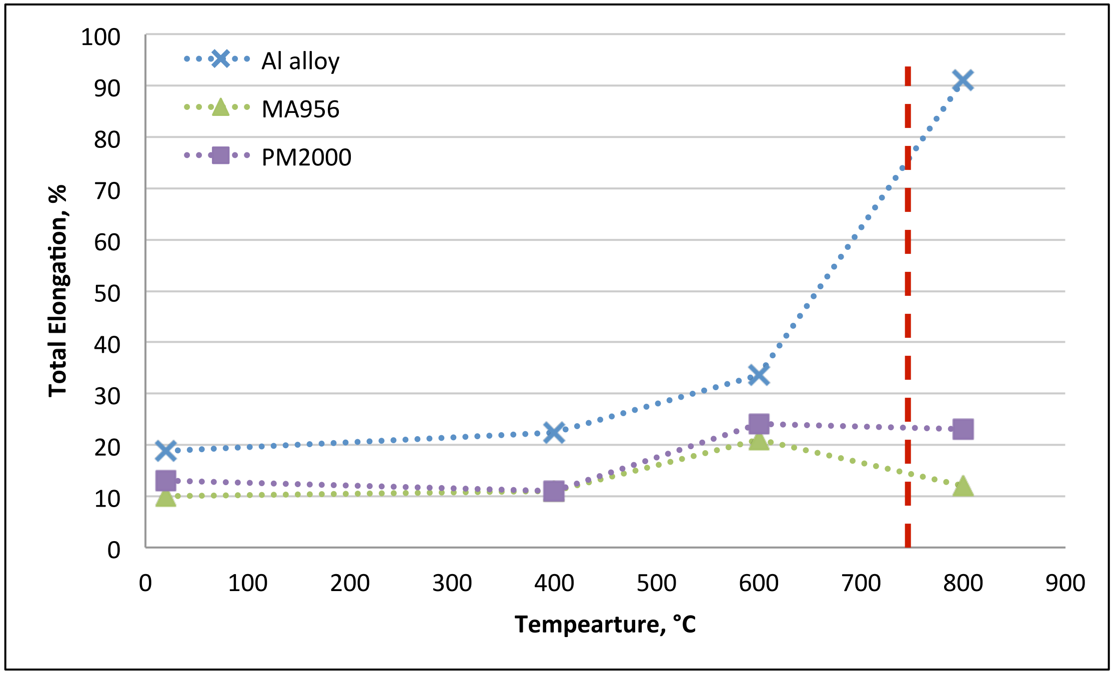

**Tensile strength of GARS produced alloys compared to previously commercial available MA956 and PM2000 (data provided by manufacturers)**

YS meets threshold stress for A-USC operation conditions (further creep testing planned)

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

- 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

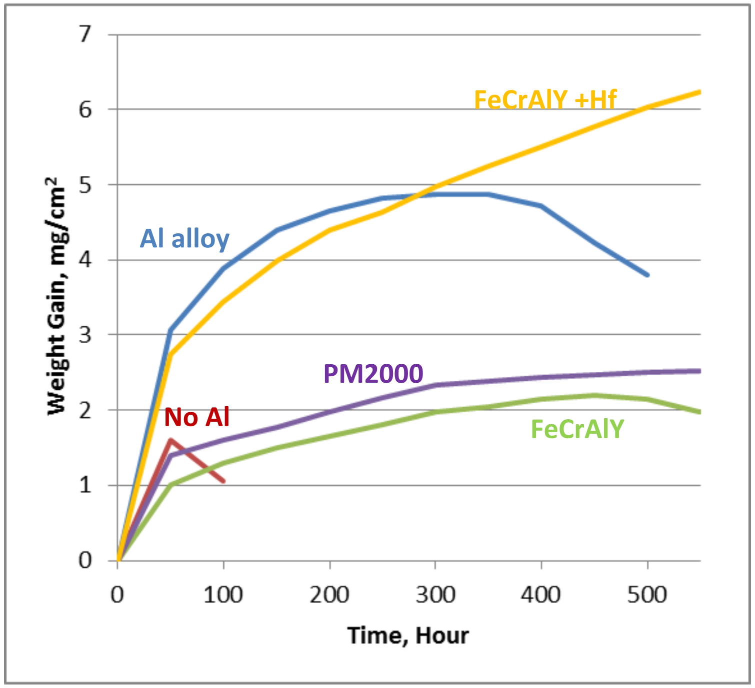



**Total Elongation of GARS produced alloys compared to previously commercial available MA956 and PM2000 (data provided by manufacturers)**

3X increased HT elongation compared to MA alloys---will be benefit for hot deformation

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 dry air at 1200°C

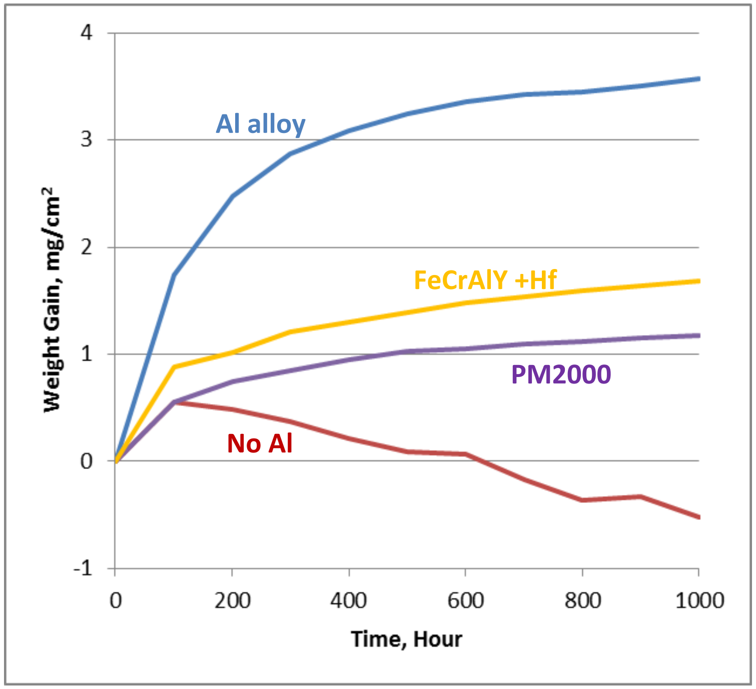



**Mass gains in dry air at 1200°C, cycle times of 1 hour. Data obtained by Bruce Pint at ORNL**

- 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




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

- 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**

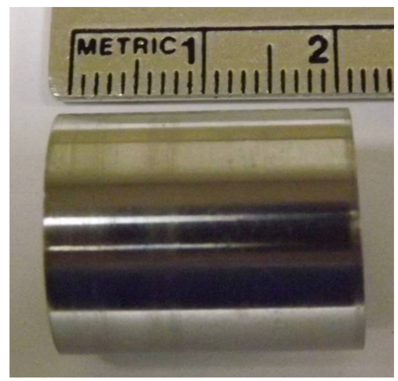
Al (Fe-15Cr-12.3Al-0.9W-0.24Hf-0.19Y)
No Al (Fe-16Cr-0.0Al-0.9W-0.25Hf-0.24Y)

# 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


- This study was sponsored by the Department of Energy, Office of Fossil Energy (Cross-Cutting program) through Ames Laboratory contract no. DE-AC02-07CH11358 and is gratefully acknowledged.