ADVANCED PROCESSING OF METALLIC POWDERS FOR FOSSIL ENERGY APPLICATIONS

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Introduction:

- Overall goal is to develop innovative powder metallurgy and gas atomization methods which can promote the implementation of USDOE Fossil Energy technologies.

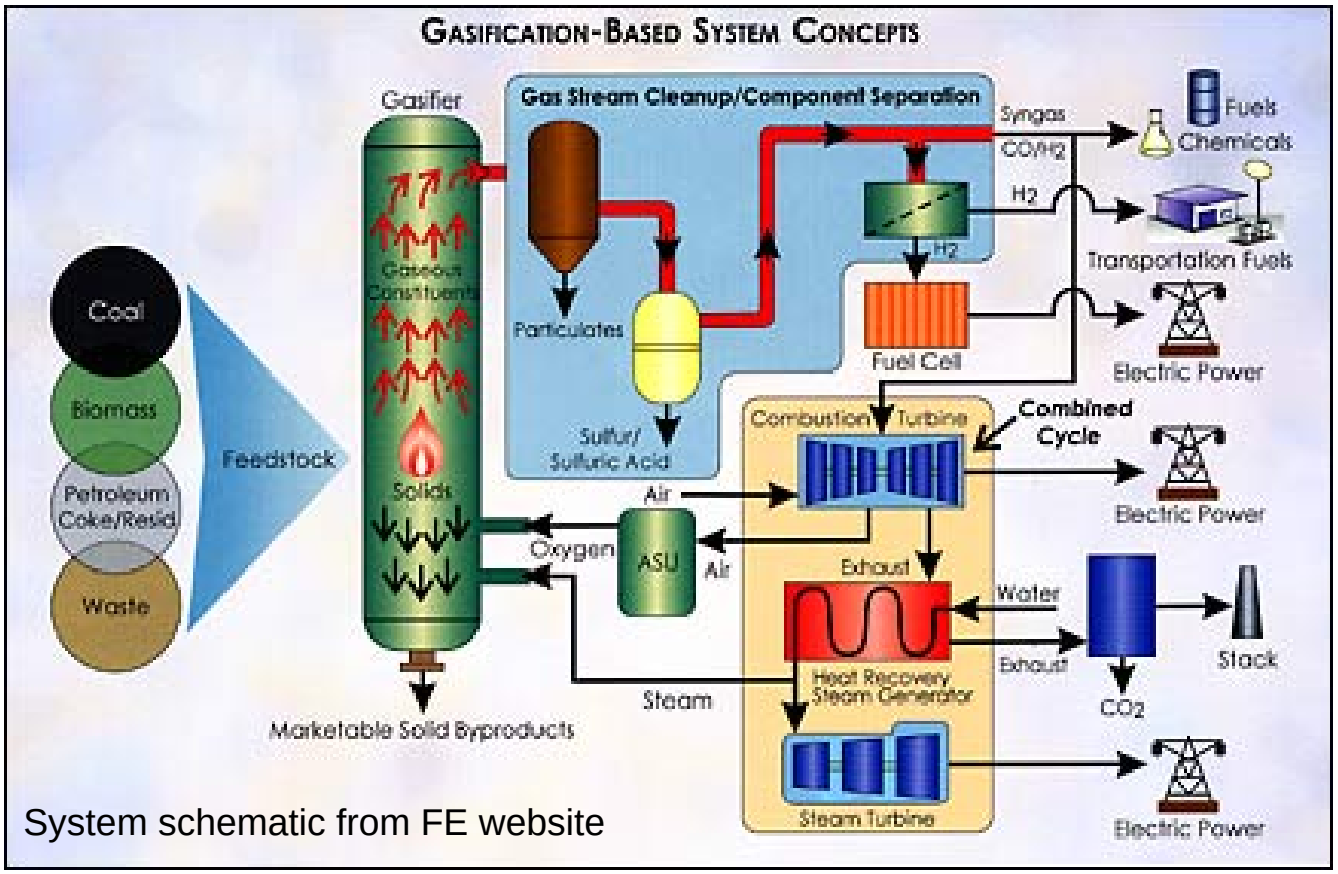
Target Technologies:

- Development of a robust porous support structure for Pd thin film used in hydrogen separation membranes; critical for carbon capture.

- Simplified production of oxide dispersion strengthened (ODS) ferritic stainless steels with isotropic microstructure/properties from reactive gas atomized precursor powder; strong potential for cost reduction and control of properties.

Need for Gas Separation Membranes

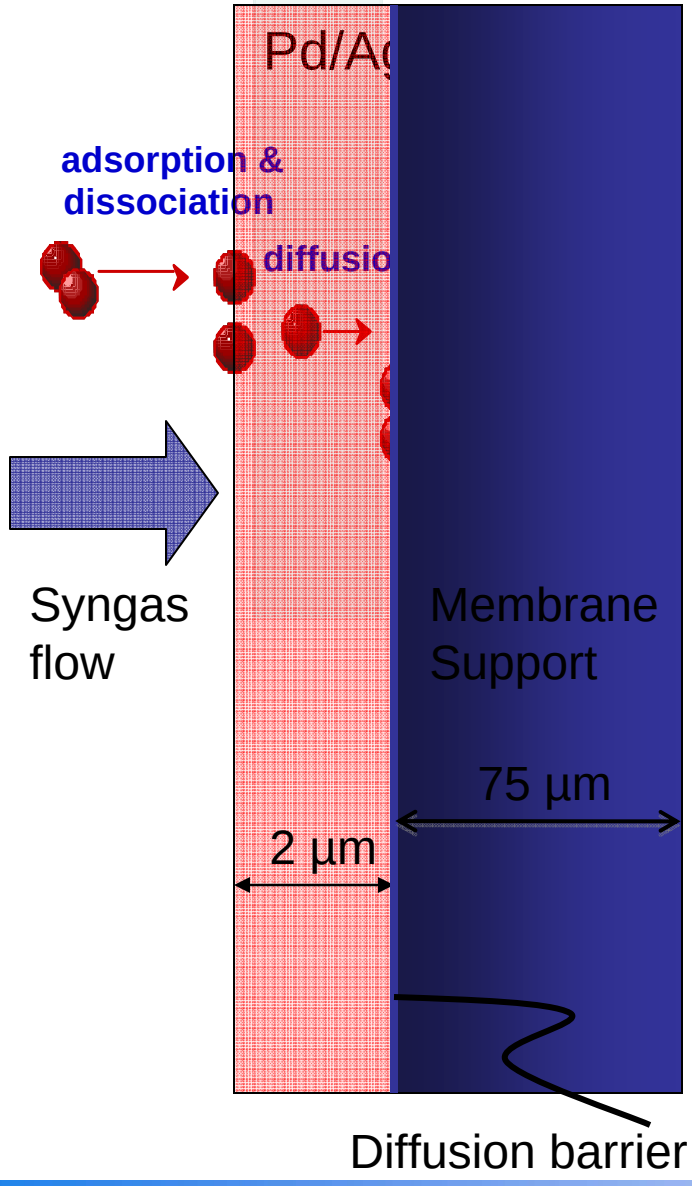
- Integrated gasification combined cycles (IGCC) power plant.
- Compatible with multiple fuel types, including bio-mass.
- Need gas separation membranes for syngas refinement.
- Generate hydrogen for co-generation, transportation fuel, or fuel cell secondary power generation.



System schematic from FE website

Iowa Energy Center BECON Facility, Nevada, Iowa

Pd-X Thin Film Hydrogen Separation



Interstitial Separation:

- Highly Gas Selective
- Low Gas Flux Rates
- Expensive
- Fragile
- Subject to Sulfur Poisoning

Technical Barriers:

Pd-X membrane

- produce pinhole-free film surface

  Lattice diffusion of hydrogen only

- maintain Pd-alloy purity

  Restrict substrate inter-diffusion

- seal external edge

  Joining to tube structure

Mem

-high permeability, sufficient strength

  Desired pore size: 0.1 - 0.5µm

- produce crack-free, low surface roughness

  Required particle size: < 3µm

Improved Support Structure Processing

Sample Material:

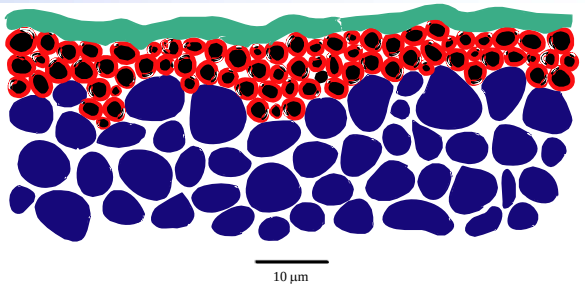
- Inconel 600 tube
  (9.6 mm OD x 6.4 mm ID)
- 316L SS/Inconel 600 frit
  with 40/10 µm pores (improved)
  (frit nested inside tube)

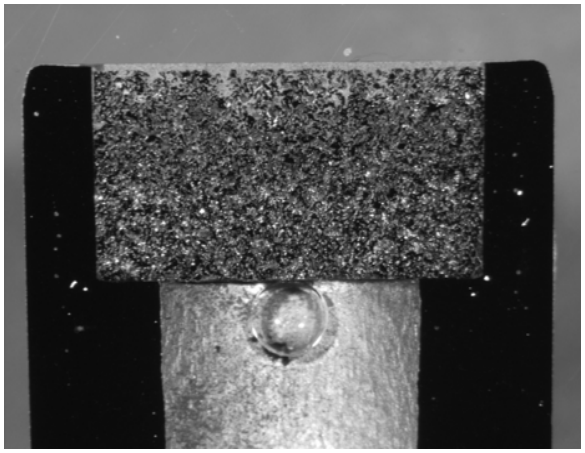
Test conditions:

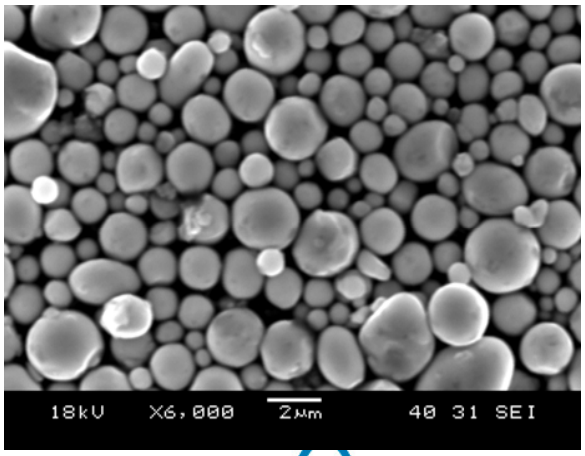
- square ended tube (initial)
- chamfer ended tube (improved)

Sintered Support Fabrication:

- Fe-16Al-2Cr (wt. %)
  < 3 µm powder (air classified)
- apply powder/methanol slurry
- "strike-off" wet surface
- vacuum sinter (10^{-6} Torr)
  4-1 h at 975-825C
- anneal to form surface diffusion barrier
  Ar atm., 24h, 800C

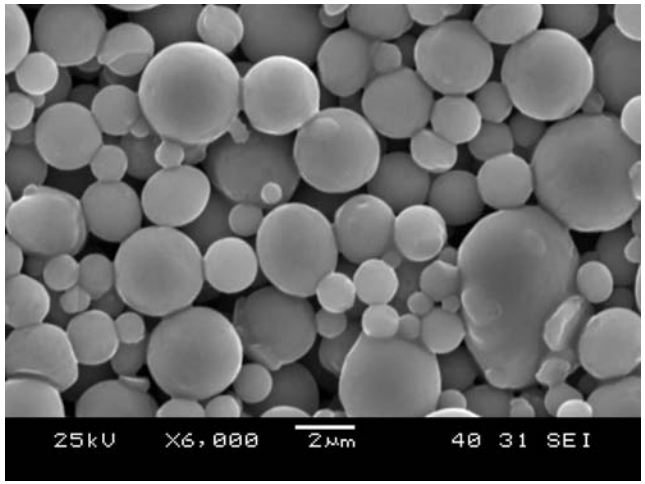






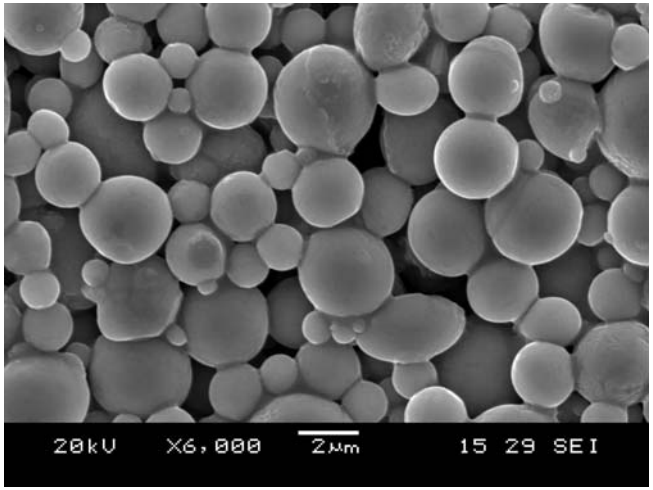
Sintered Powder Surfaces (dia. <3 µm)

Fe-16Al-2Cr (wt.%), spherical high pressure gas atomized (HPGA) powder

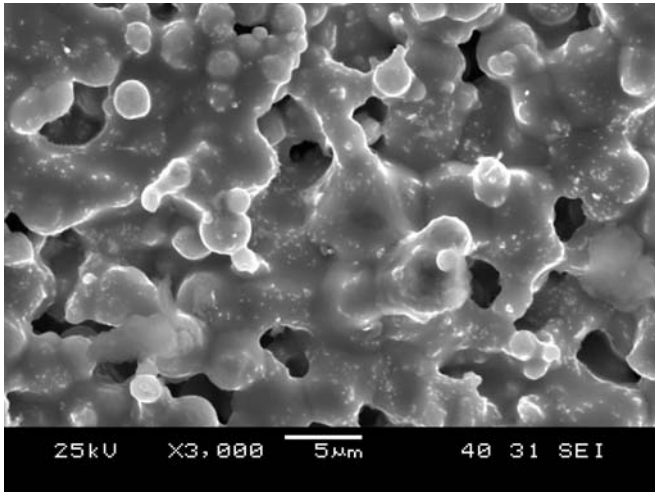


950C

975 ˚C initial selection



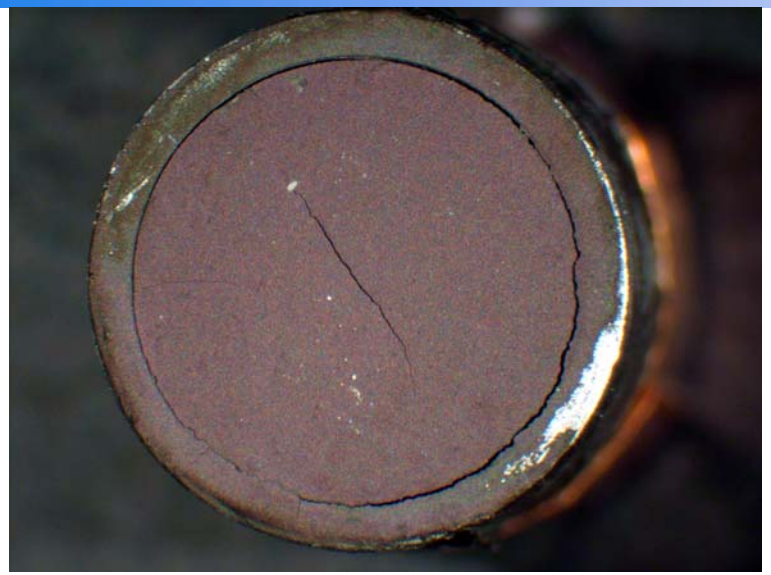
1000C

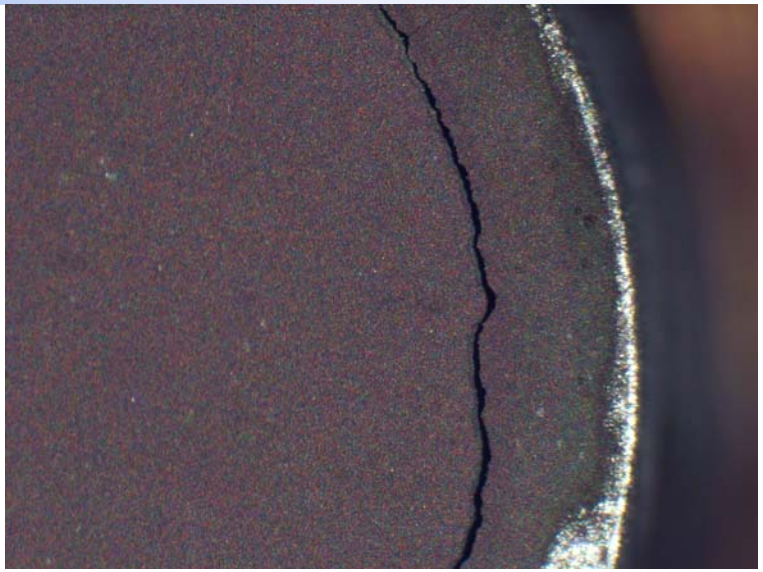


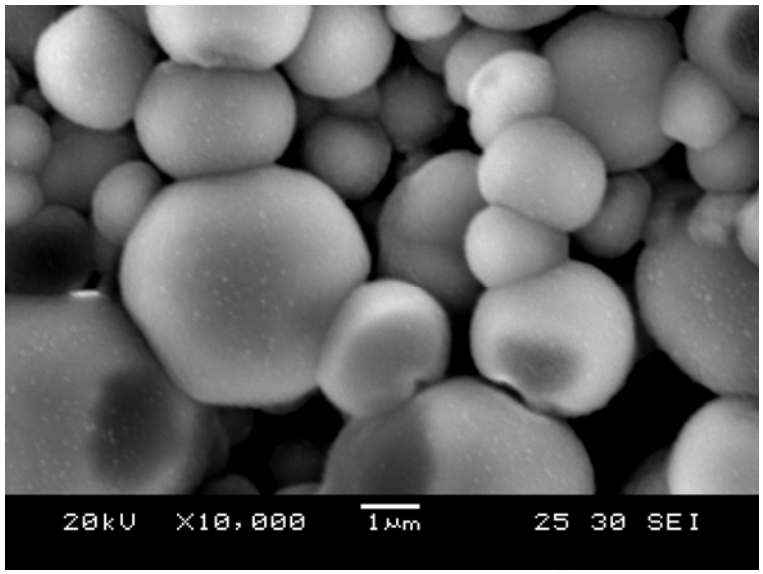
1050C

- Extreme sensitivity of ultra-fine powders to sintering temperature.
- Developed sub-support for thin layer of porous membrane support.

Results for Square End Tube (4 h sinter)



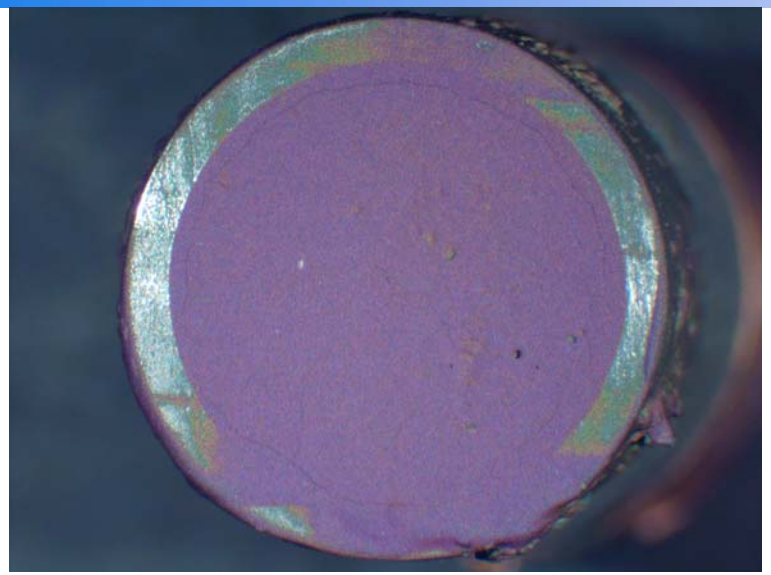


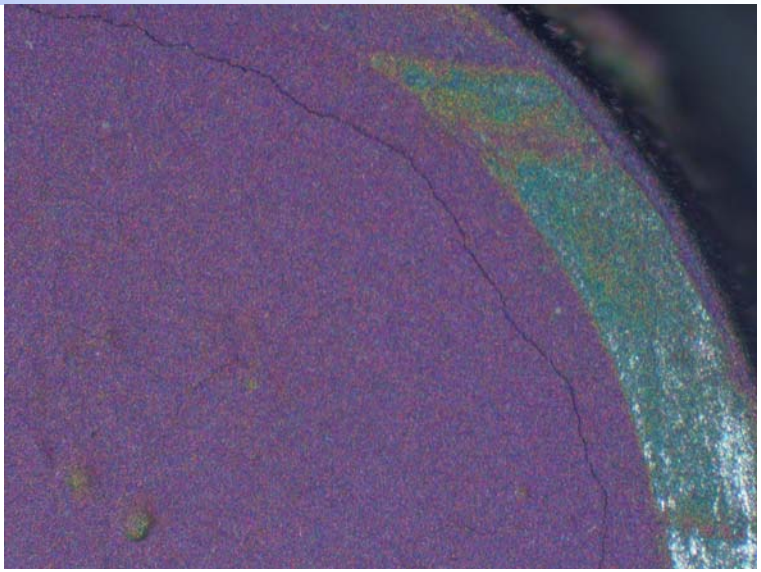


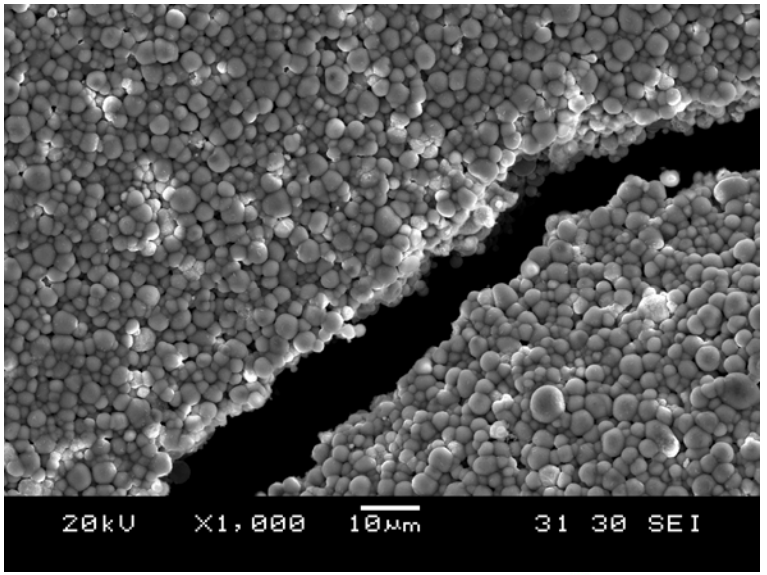
Analysis of Initial Results:

- Powder sintering time (4 h) at 975C is too long.
- Excess sintering shrinkage stress promotes centerline and rim cracking.
- Stress generated in middle and at interface with tube interior wall.

Results for Square End Tube (1 h sinter)





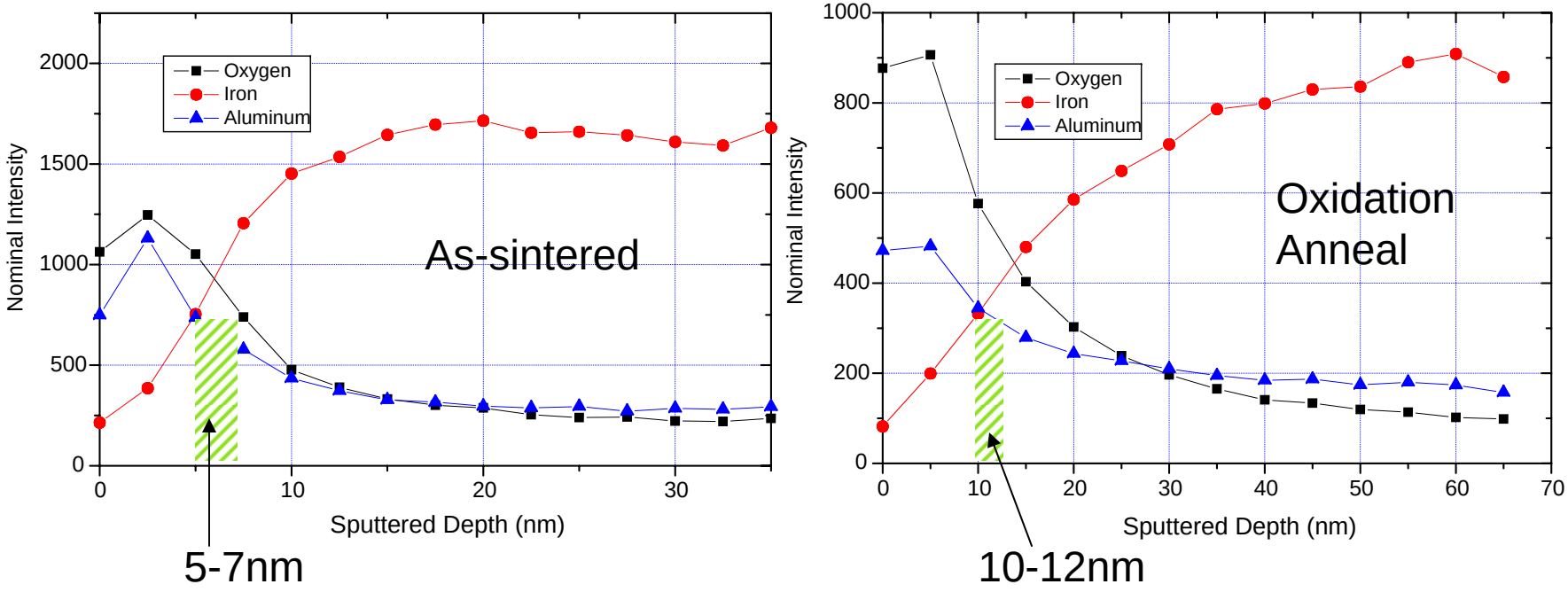


Analysis of Initial Results:

- Powder sintering time (1 h) sufficient (surface roughness?).
- Sintering shrinkage stress still promotes rim cracking.

- Need additional stress relief mechanism at interface with tube end.

Increased Oxide Thickness from Anneal



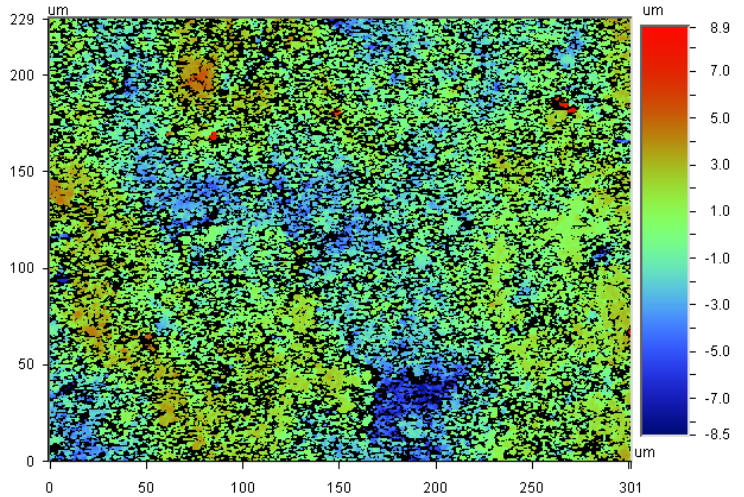
Analysis:

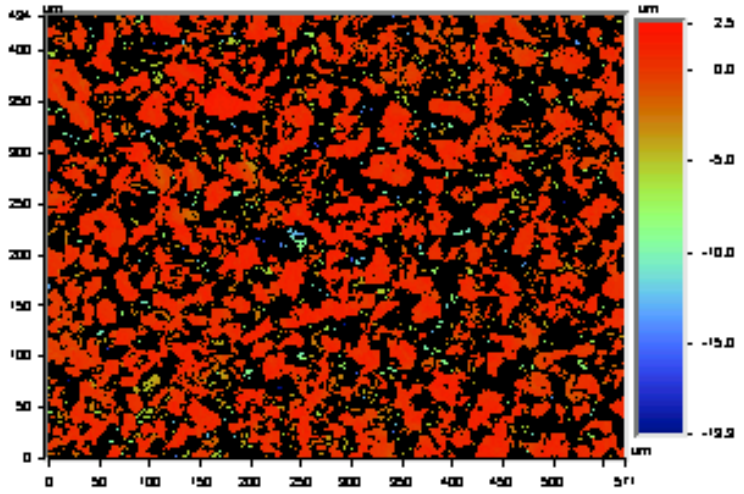
- Anneal at 800C for 24 h in UHP Ar.performed to increase oxide barrier film.
- Aluminum oxide is dominant surface oxide.

- Oxide thickness doubled by anneal.
- Need to test diffusion barrier effectiveness after permeability testing.

Preliminary Porous Support Assessment

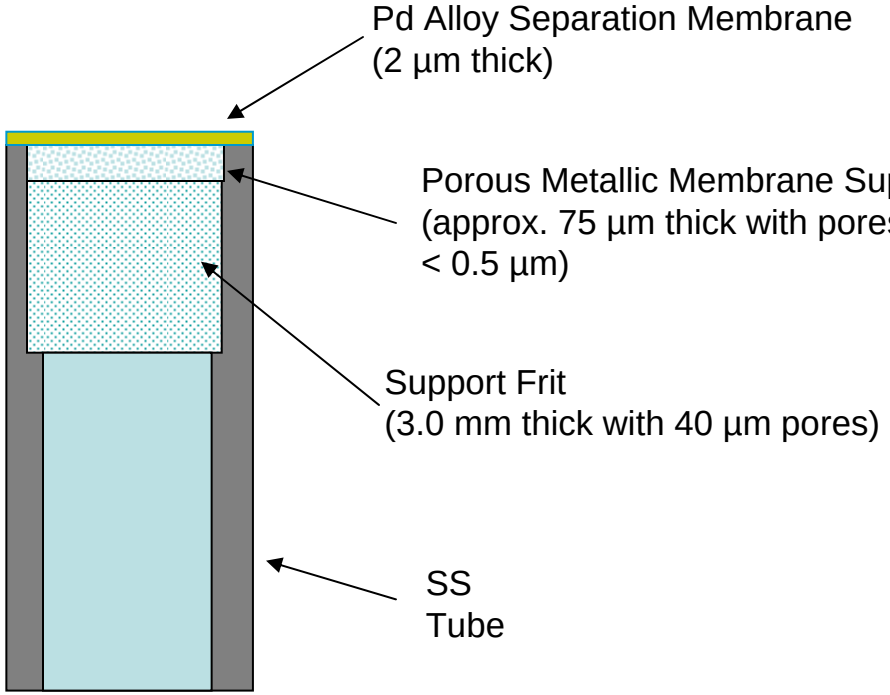
- Low surface roughness and open porosity are keys for support of a thin, defect-free Pd film.
- Commercial Inconel support(0.1µm pores): R_a= 907nm
- Large roughness range produces pinholes in Pd.
- Large particles restrict open flow area.
- Ames Fe-16Al-2Cr support: R_a=1.46 µm
- Ultrafine particles promote high open flow area.



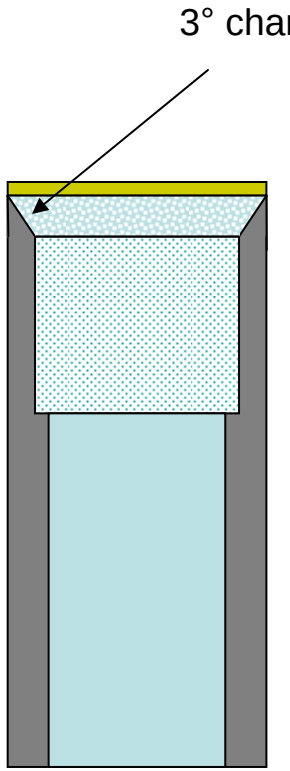


Further Defect-Free Support Development

- Tried chamfer to provide gradual stress accommodation (sliding) during sintering.



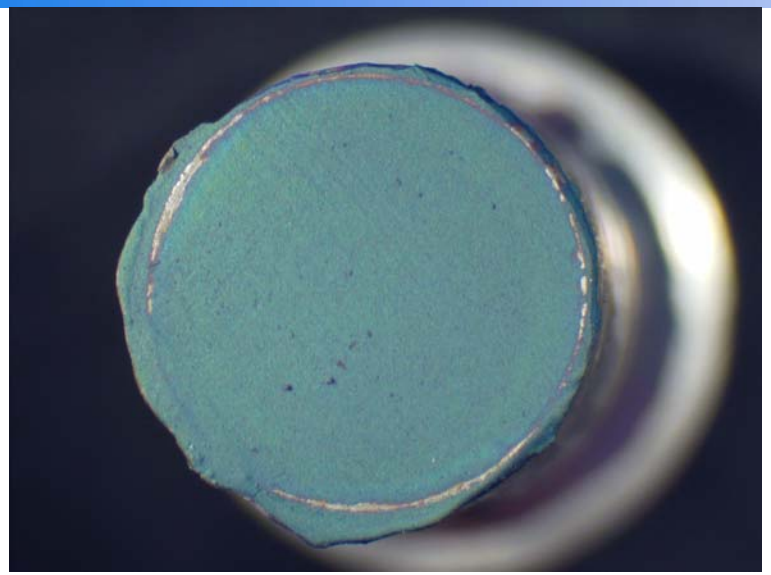
Square tube cavity

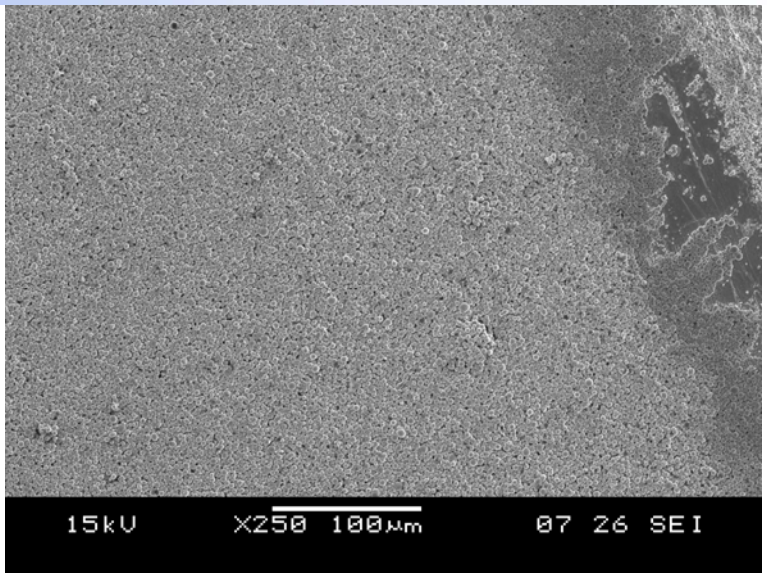


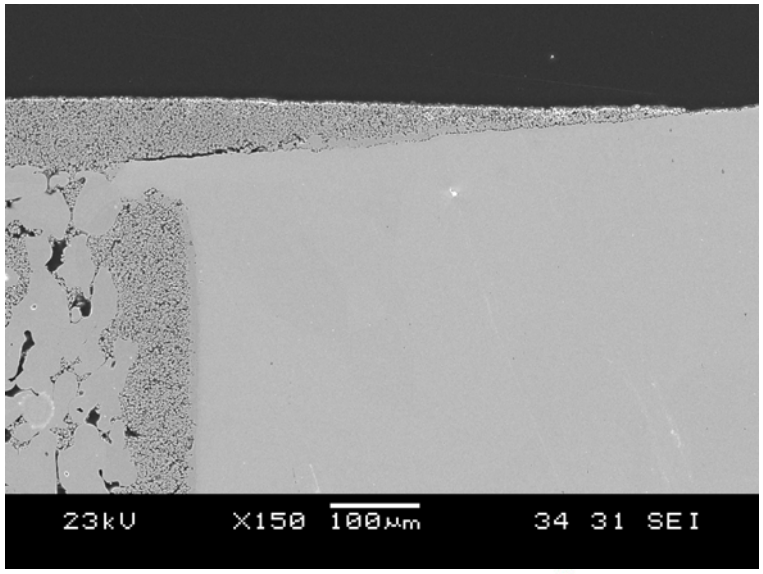
Chamfered tube cavity

Not to Scale

Results for Chamfered Tube (1 h sinter)



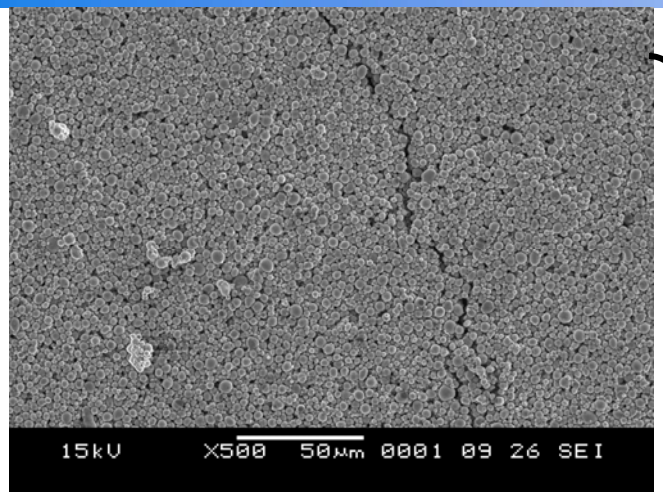


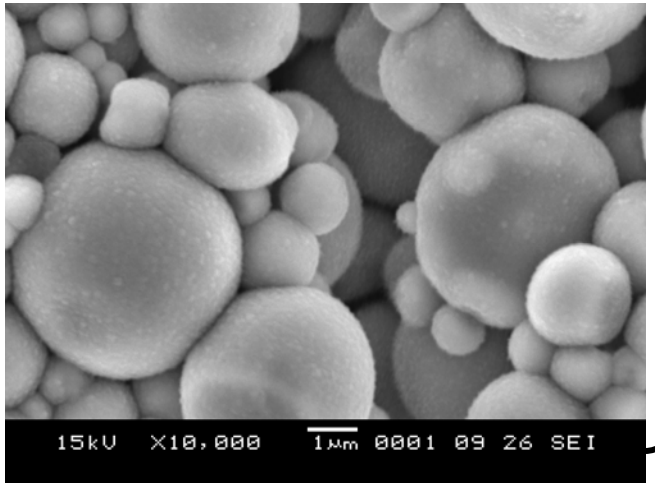


Analysis of Further Results:

- Same powder sintering time used (1 h).
- Sintering stress accommodation eliminated rim cracking.
- Stress relief mechanism acts at chamfered interface with tube end.

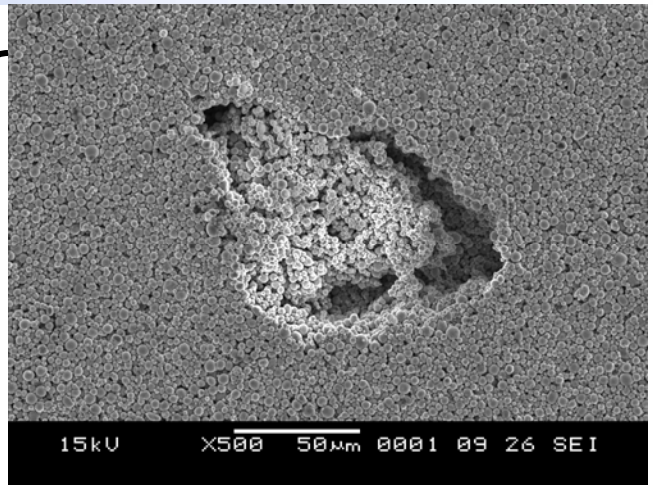
Closer Examination Detects Minor Defects



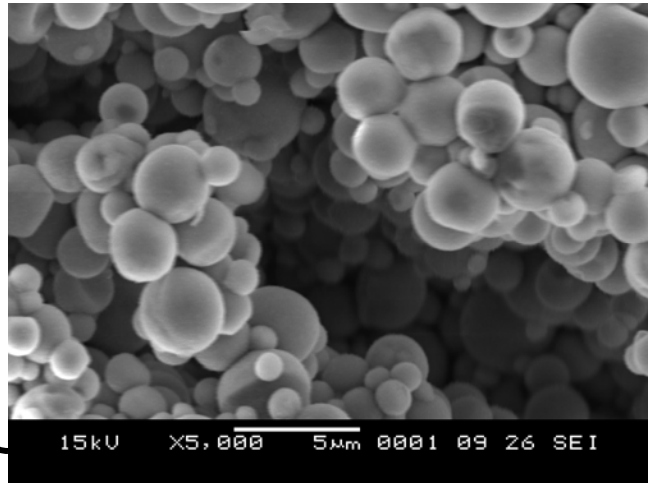


Implications:

- Superficial surface cracks.
- Pd thin film may bridge gap.

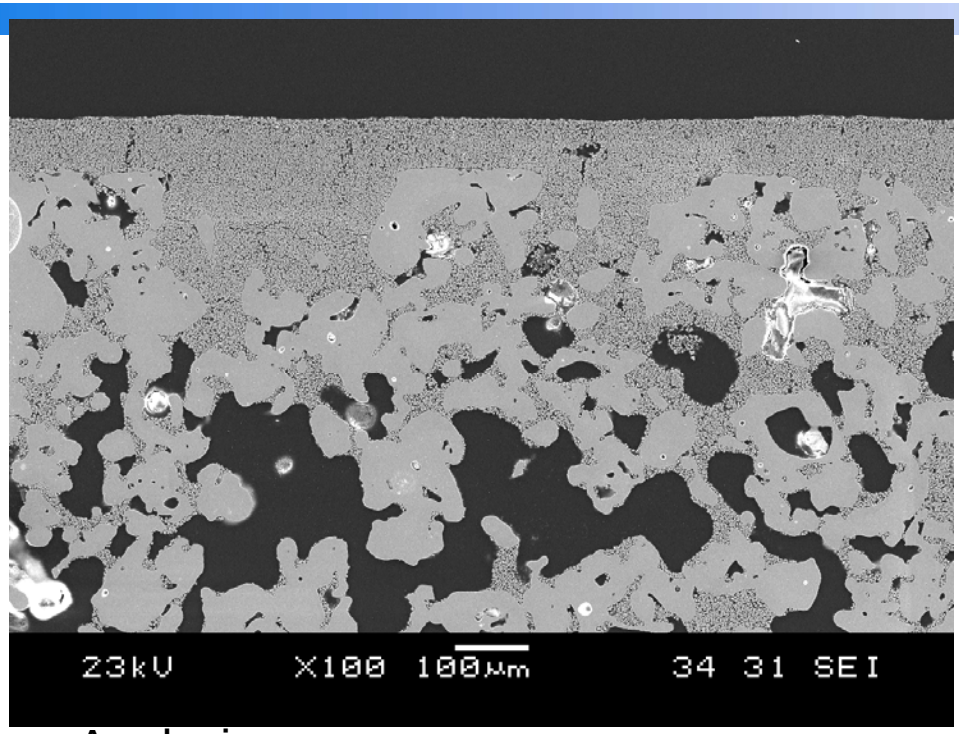


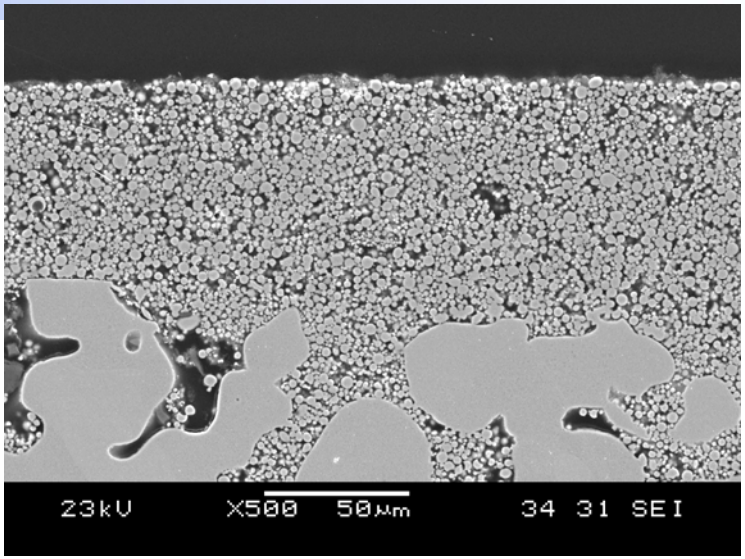
- "Sink hole" pit/depression.
- Pd thin film insufficient to bridge pit.

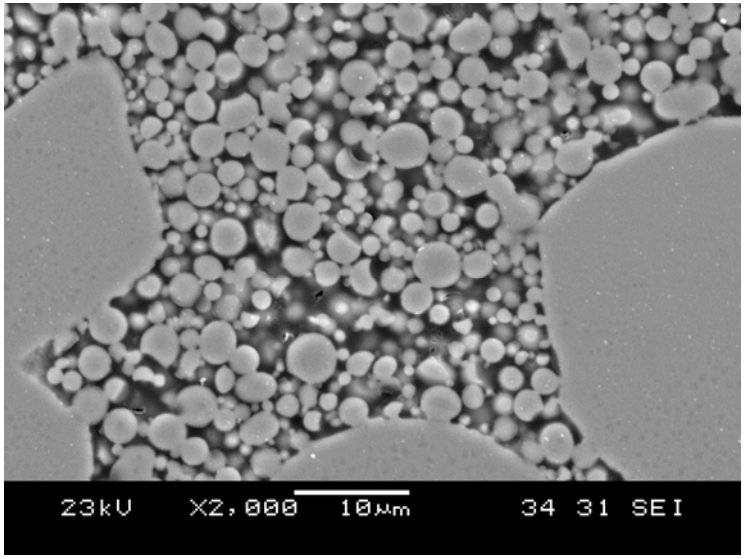


- Need to fill-in sink hole source.

Cross-section Reveals Sink-hole Source





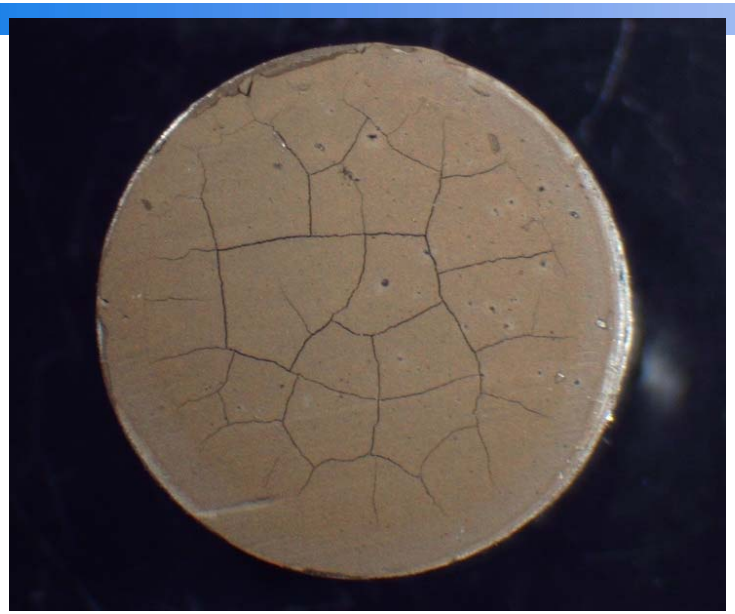


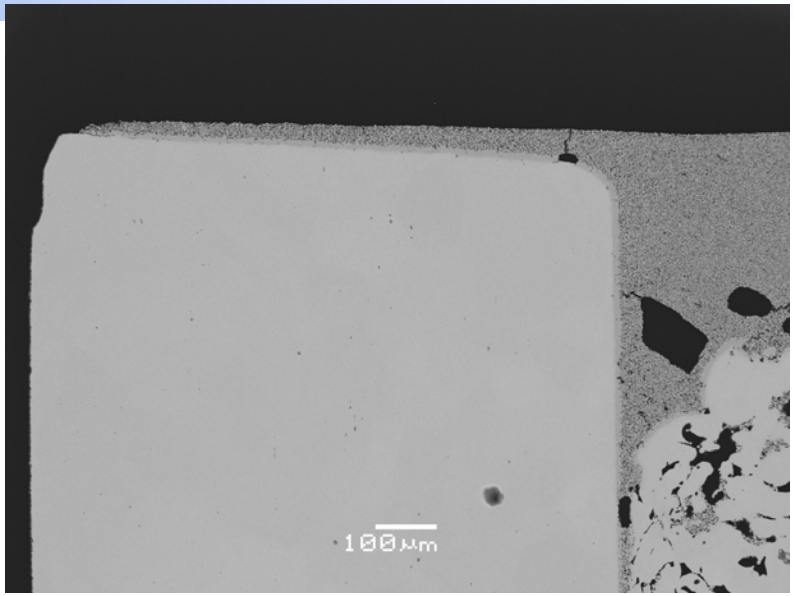
Analysis:

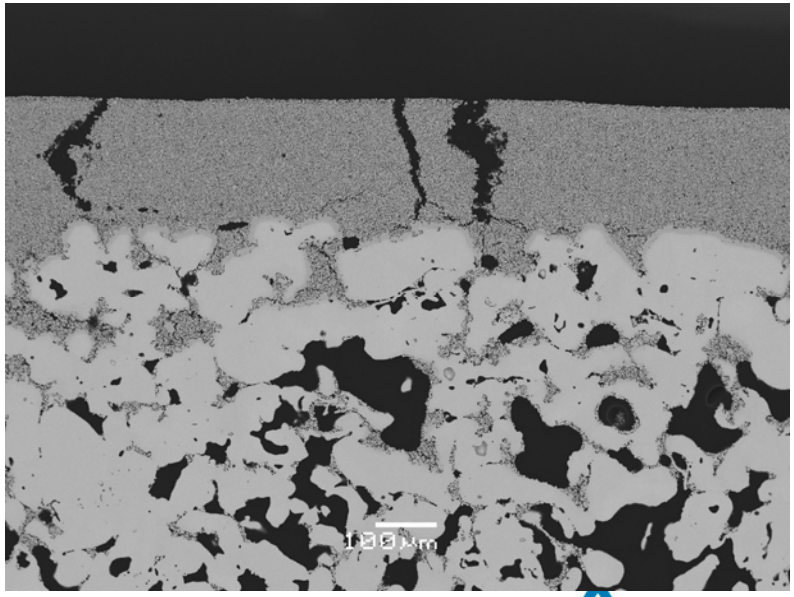
- Excess penetration of ultrafine powders down into large (40µm) frit porosity.
- Carrier fluid (methanol) assists powder flow down into “sink hole.”

- Need for ***frit with smaller pore size (<10µm)***.

Chamfered Tube, 10µm Frit, Inconel 600







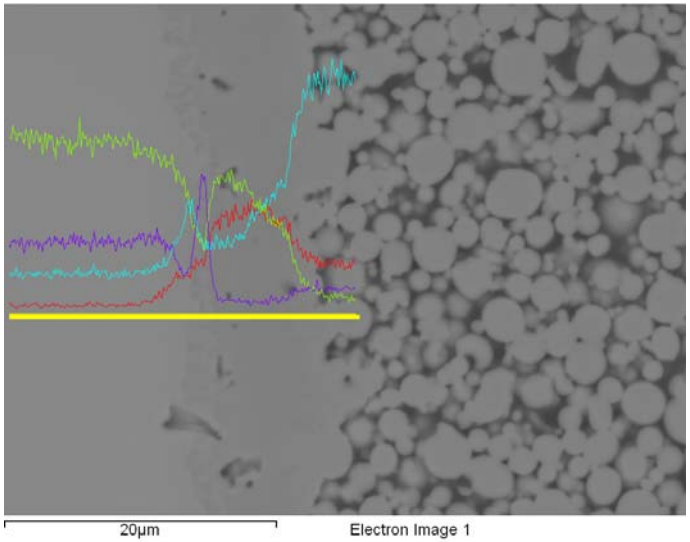
Analysis:

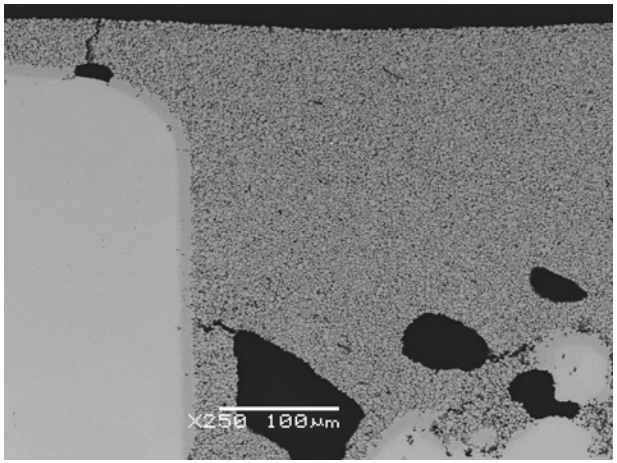
- Effect of switch to 10µm (Inconel) frit masked by other deficiencies.
- Wide mud-cracks reappeared.
- Reaction layer with Inconel frit and depression of frit at wall suspected.

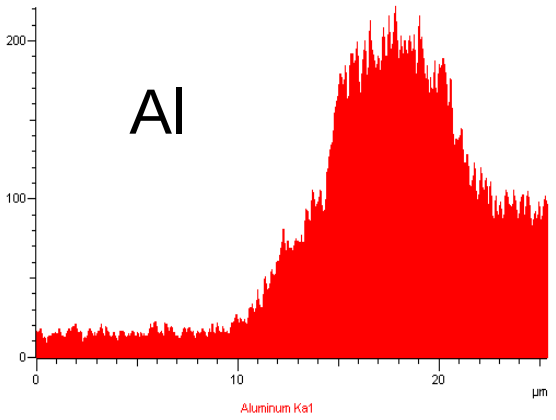
- Try reduced sintering temperature and inverted frit position (flatness)

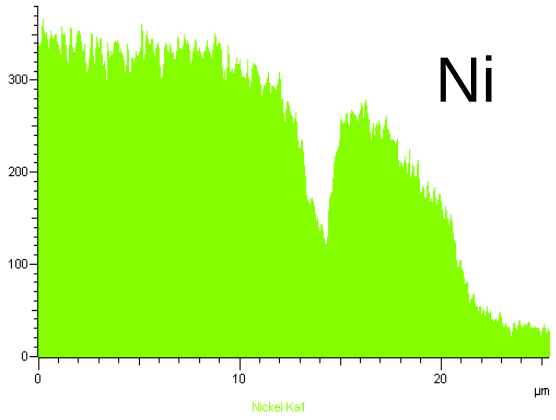
EDS Revealed Inconel/Fe-Al-Cr Reaction Layer

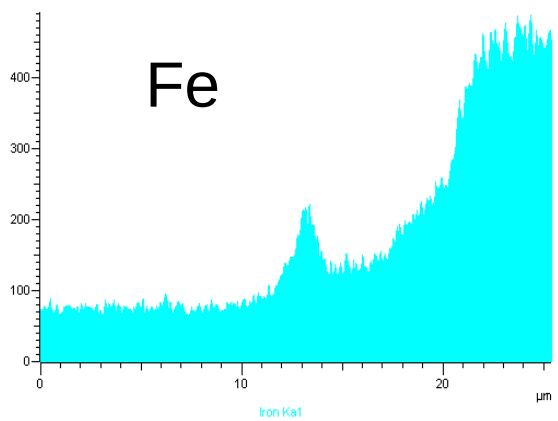
Sintering at 975C too high.

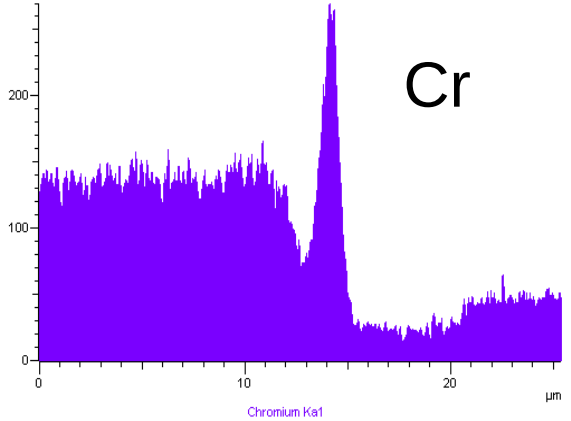






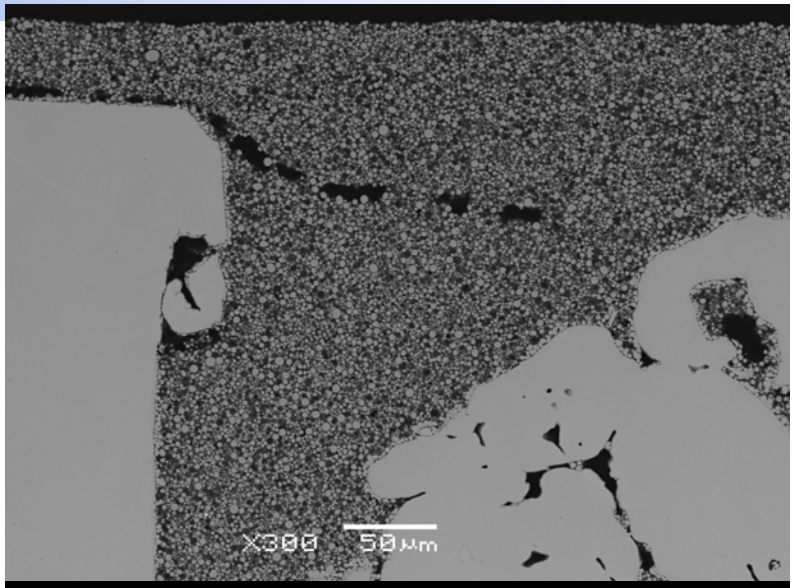


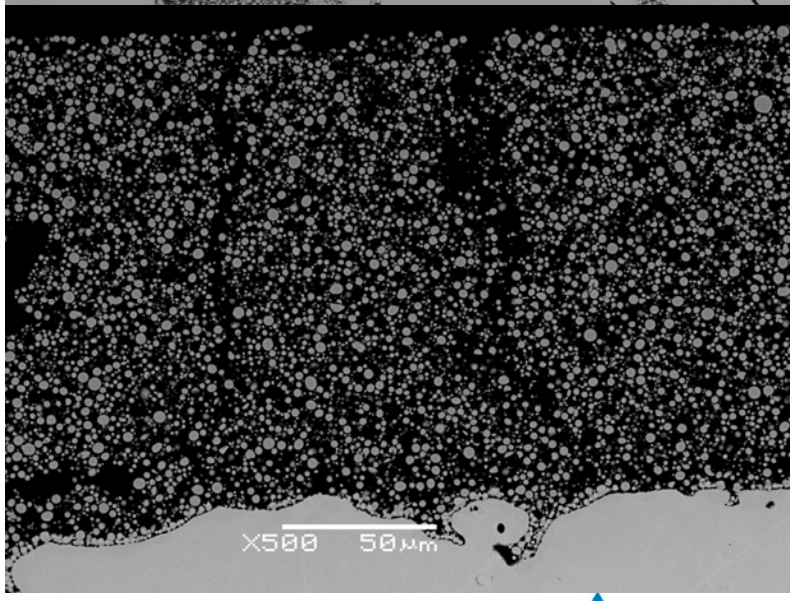




- Probable Ni aluminide (exothermic) reaction
- Reduce sintering temperature.

Lower T (850C) Sinter, 10µm Frit, Inconel



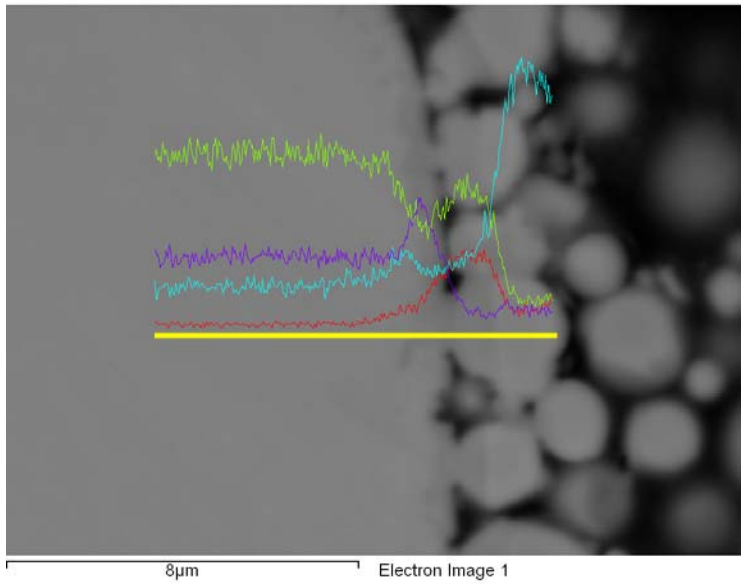


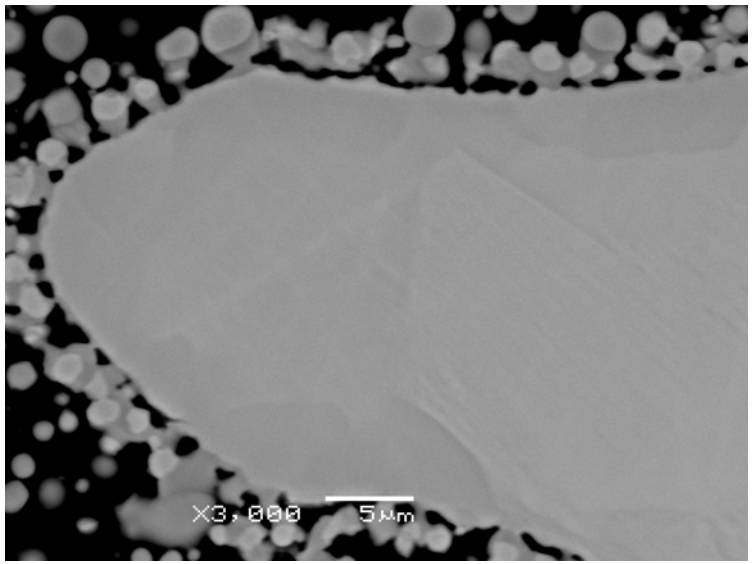
Analysis:

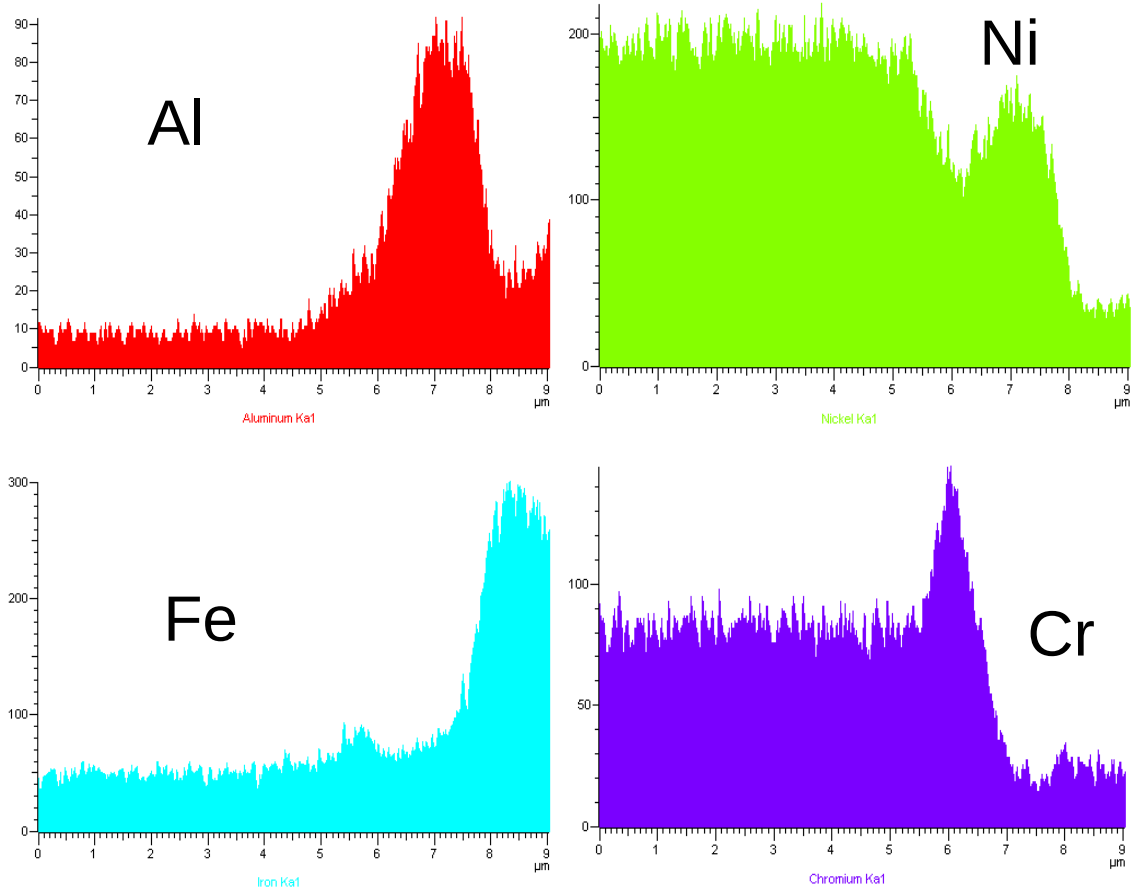
- Reduced sintering temperature decreased apparent reaction layer.
- Superficial mud-cracks remained (slight reaction layer?).
- Residual frit wall defect “pinning.”

- Try final sintering temperature reduction and improve frit insertion.

Thinner Reaction at Inconel/Fe-Al-Cr Interfaces

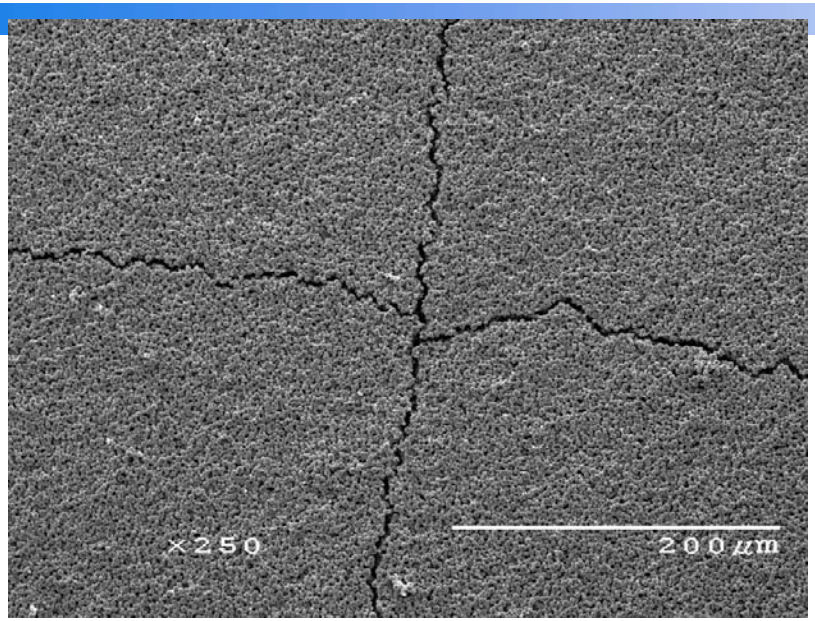


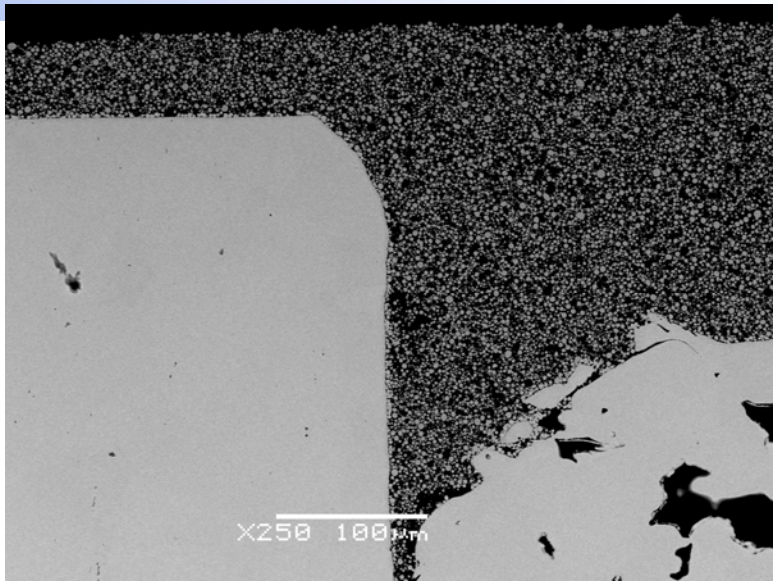


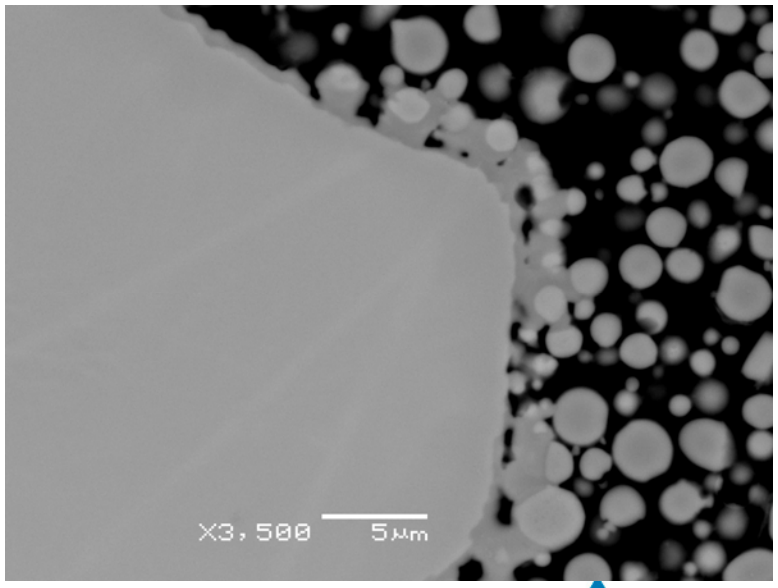


- 850C still too high.
- Frit interface bonding remains--reduce T
- Maintain interparticle “tack” sintering?

Lowest T (825C) Sinter, 10µm Frit, Inconel





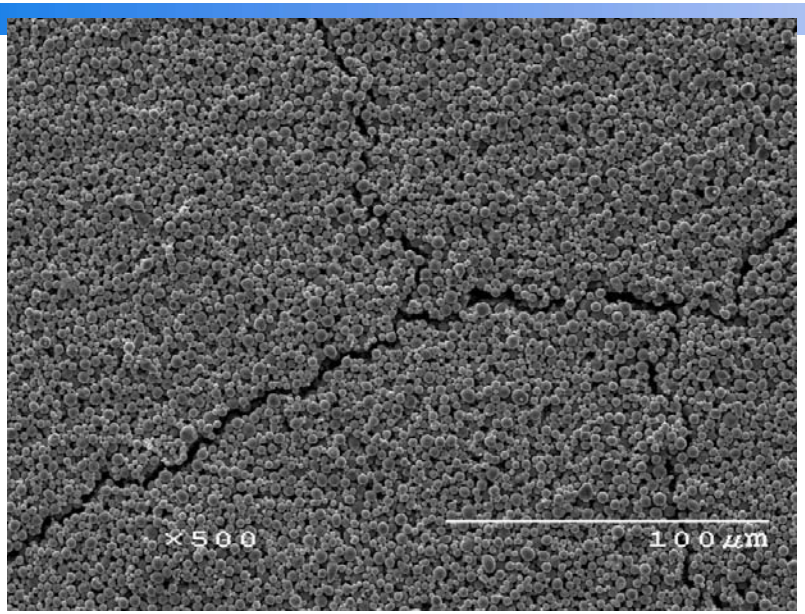


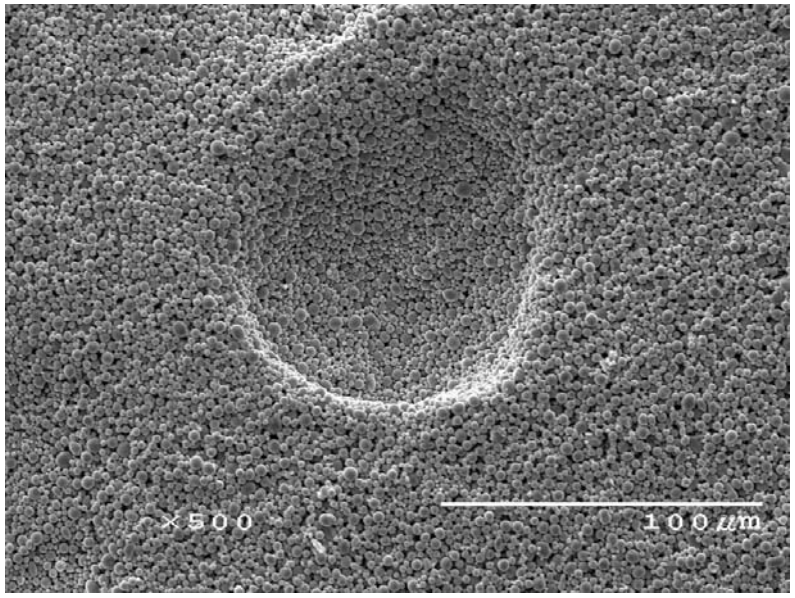
Analysis:

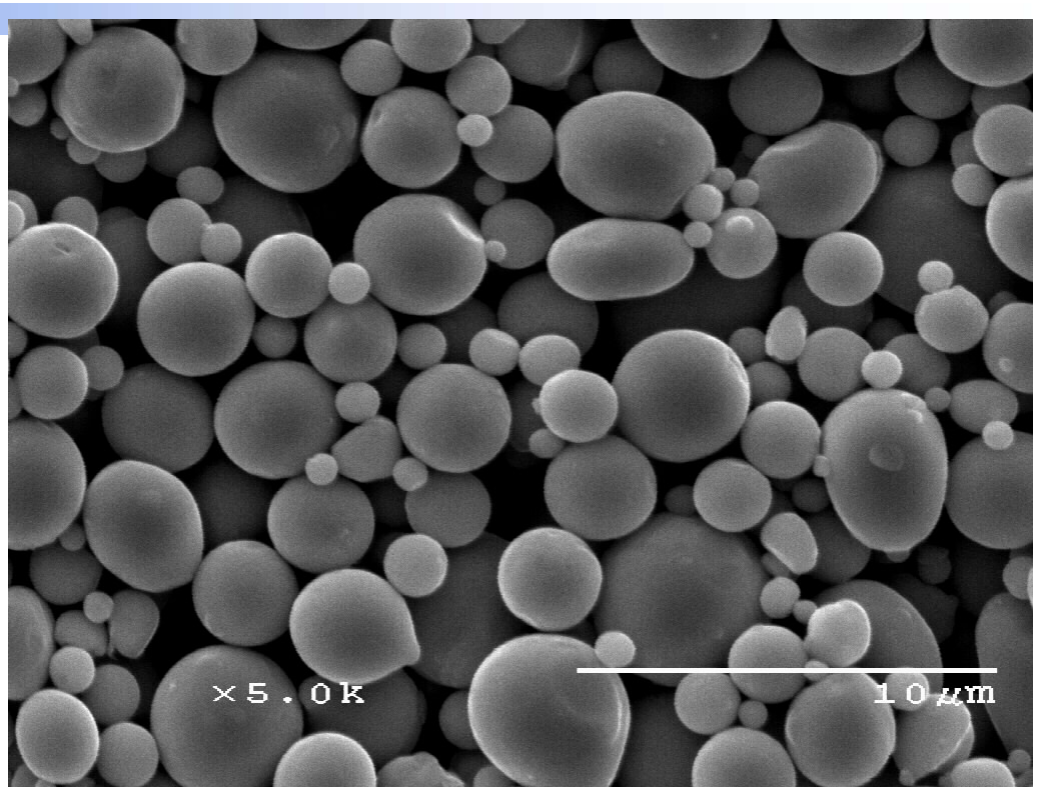
- Lowest sintering temperature resulted in pull-out porosity and surface roughness.
- "Micro-mud-cracks" remain (residual interfacial bonding---cannot avoid).
- Slight frit wall depression "pinning."

- Switch back to SS frit and raise frit level to restore frit glide surface.

Roughness from Insufficient Tack Sintering

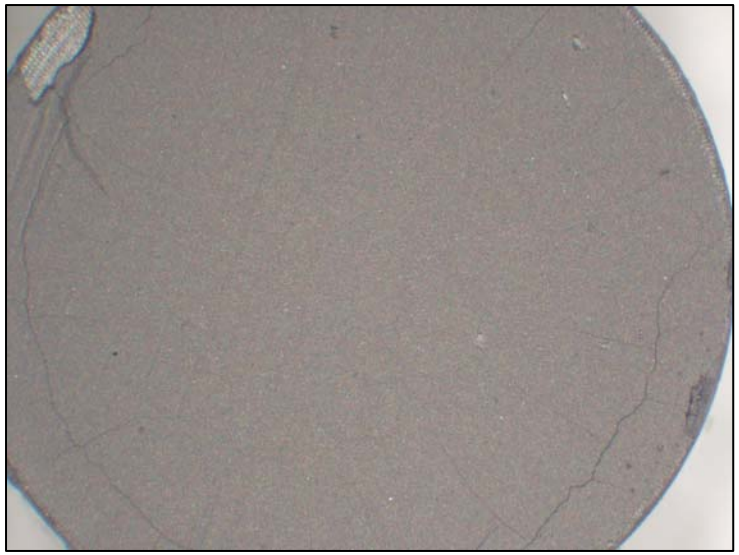


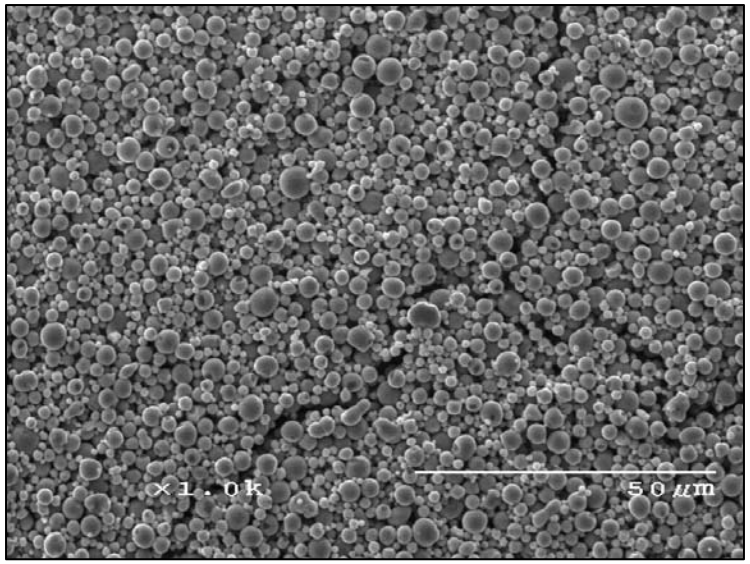




- Substrate sample inverted and impacted to free un-bonded particles.
- Excess surface roughness and surface dimples resulted.
- Insufficient sintering---raise sintering Temp.

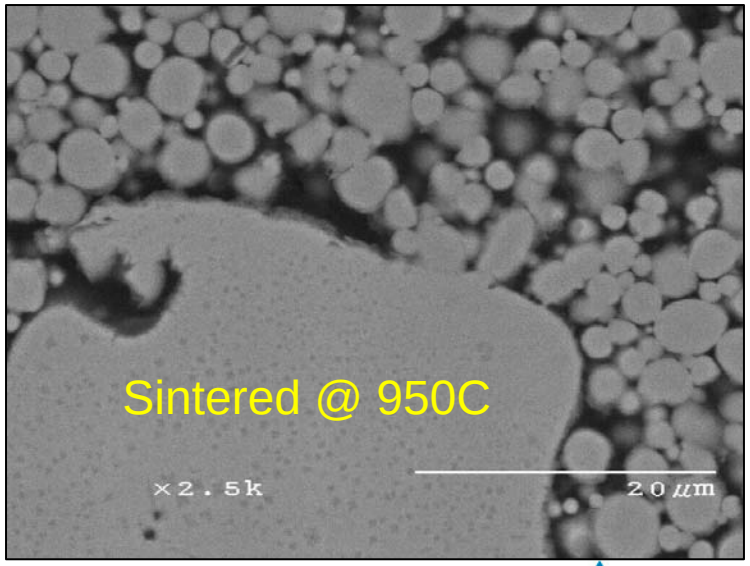
Increased T (875C) Sinter, 10µm Frit, 316L SS





Analysis:

- No reaction detected at SS frit interface, most mud cracks eliminated.
- Only noticeable cracking seen along circumference---Inconel tube suspected.
- No apparent surface dimpling.
- Only surface microstructural analysis completed (i.e., not cross-sectional images)



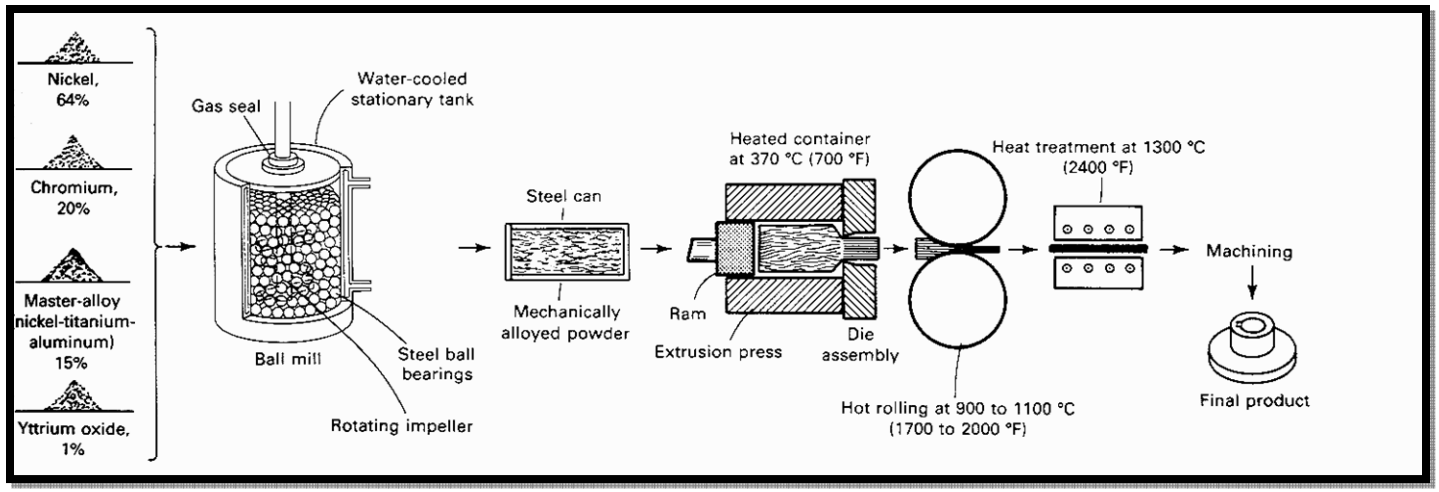
Membrane Support Summary:

- Selected sintering conditions (850-900C, 1h) and size fraction (<3µm) of gas atomized Fe-16Al-2Cr (wt.%) to produce suitable porous membrane support structure with areas of ideal flatness.
- Chamfered edge of support tube helps to prevent rim cracking.
- Pore size of porous frit is important to provide adequate base for application of ultrafine powder slurry (<10 µm suitable) without significant surface defects.
- Alloy choice for tube and frit important to inhibit excessive interfacial reaction and bonding, i.e., SS better than Inconel.
- Flat frit surface that matches with chamfer edge provides more ideal “glide surface” for sintering shrinkage.
- Effect of oxide diffusion barrier film on Fe-16Al-2Cr needs to be tested (suppression of Fe and Cr diffusion into Pd).

Motivation: *ODS alloys superior for high temperatures*

Current ODS Processing Starts with Mechanical Alloying:

- An energetic mixing process that introduces a base metal, alloying additions, and nonmetal powders (dispersoid phase) in a high-energy mill (time > 48 hours)
- *Hot deformation consolidation leads to an anisotropic microstructure and anisotropic mechanical properties (limits applications)
- Time intensive, multiple step process produced high cost Fe-based alloys (i.e. 150-300 USD/kg for as-consolidated MA-956 tubing-Sandvik 2003)
- **Commercial alloys (MA-956 and PM 2000)---no longer in production



Critical ODS Stainless Steel Applications:

◆High P heat exchanger tubing.

* J.D. Whittenberger et al. , Met Trans A 12A (1981) 845-851
**R.L. Klueh et al., Oak Ridge National Labs, J. Nuclear Mat. 341 (2005) 103-114

Goal: Simplify the Manufacturing Process

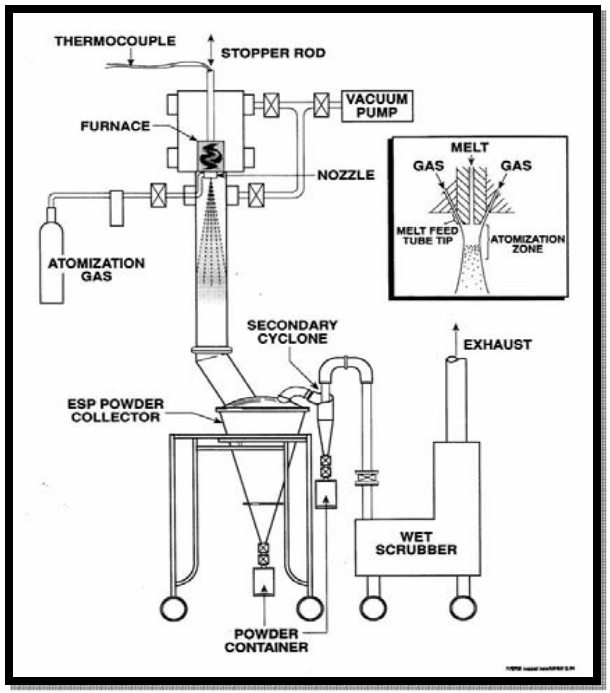
Precursor Atomized Powder, Consolidation, and Heat Treatment:

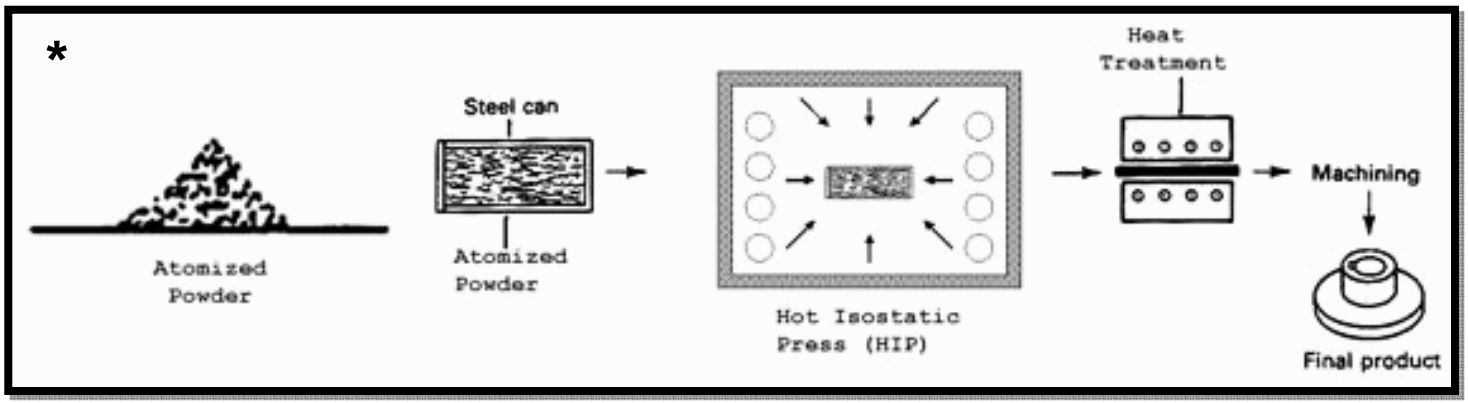
[1] Gas atomization reaction synthesis (GARS) using Ar-O_2 gas mixtures to produce powder.

[2] Hot isostatically pressed (or vacuum hot pressed) to full density retaining an equiaxed grain structure and isotropic mechanical properties.

[3] Heat treated to assist further formation of dispersoid phase

Eliminates mechanical alloying and directional deformation processing





* Terpstra, R.L, Simplified powder processing of oxide dispersion stainless steel, Advances in Powder Metallurgy and Particulate Materials, 2006.

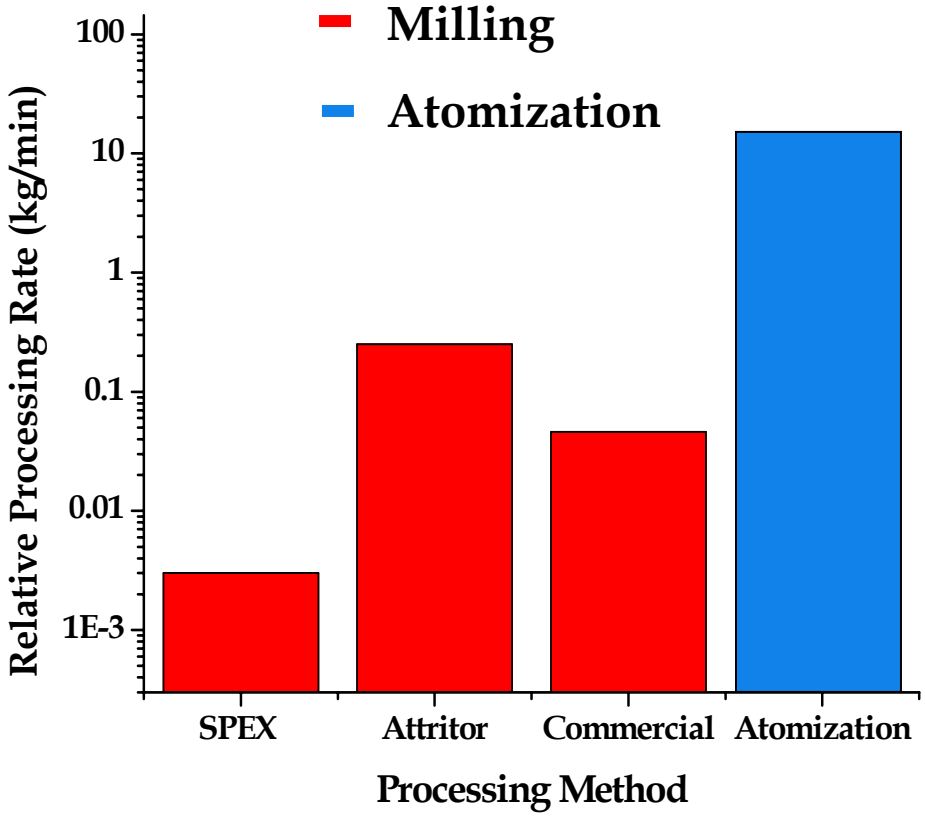
Processing Comparison

* **Mechanical Alloying**

- Long milling times
- Batch commercial process (≈ 200 kg)
- Powder contamination (carbon and milling debris)
- Anisotropic microstructure

** **Gas Atomization (RSP)**

- Higher processing rates (capabilities of up to 100 kg/min)
- Continuous commercial processing
- Minimized contamination
- Isotropic microstructure



The powder processing rate using gas atomization can be an order of magnitude larger than that of mechanical milling

*C. Suryanarayana, ASM Handbook, Vo. 7, ASM International, Materials Park, OH, 1998, pp. 80-90.

**R.M. German, *Powder Metallurgy and Particulate Materials Processing*, 2005, MPIF, Princeton, NJ.

New Precursor Powder Processing

Alloy Design Considerations:

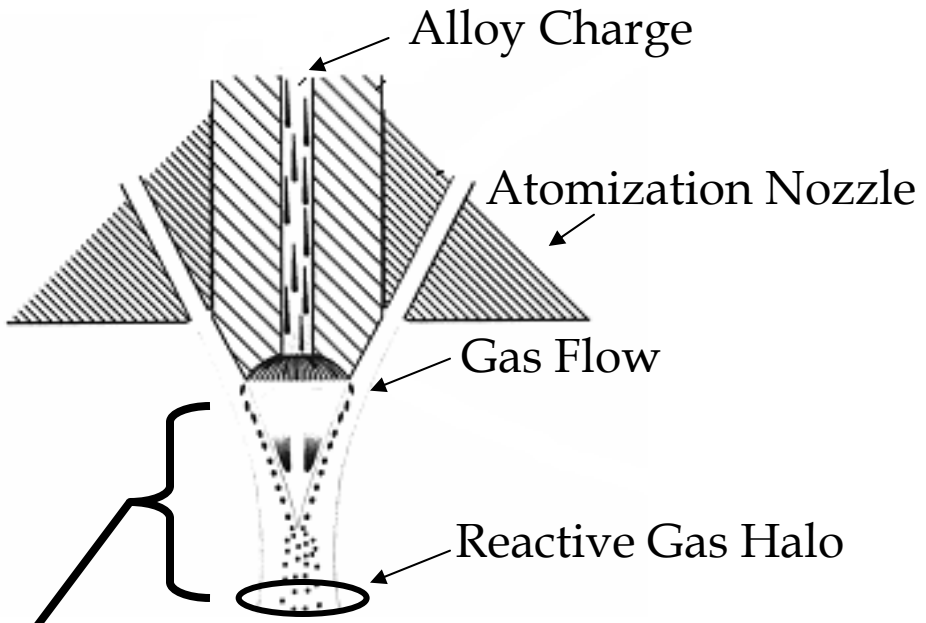
- Ferrite matrix (e.g., Fe-Cr SS)
- Reactive surface oxidation element (e.g., Cr , Ti)
- Oxide dispersion forming element (e.g., Y, Ti)

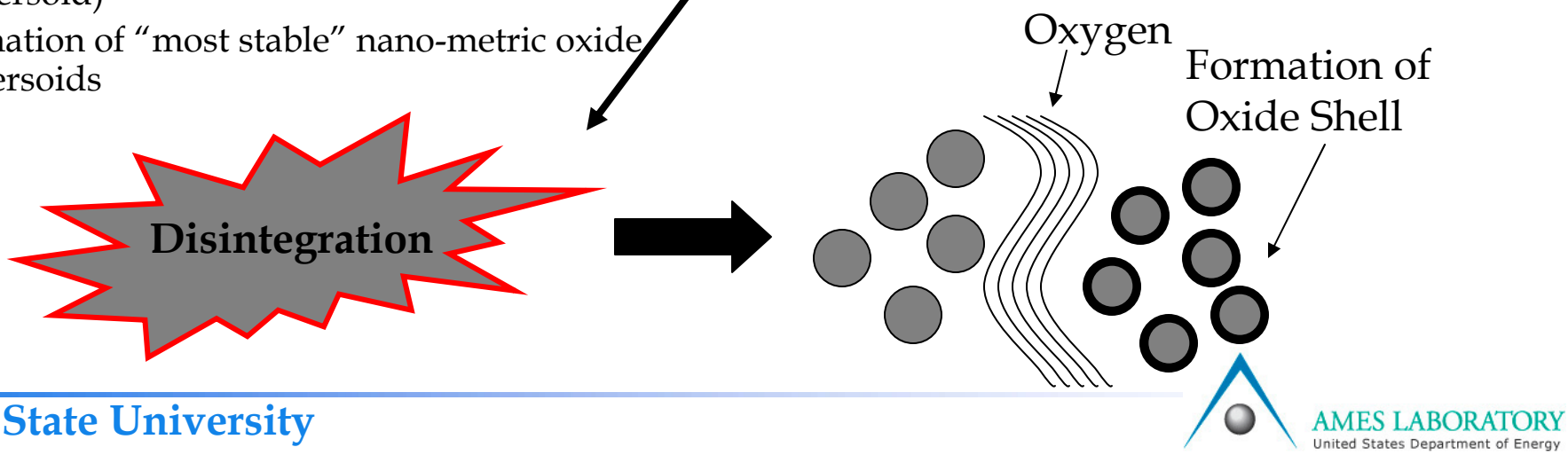
Gas Atomized Reaction Synthesis:

- Rapid solidification process
- Reactive atomization gas (Ar-O_2)
- In situ oxidation of reactive surface oxide element
- Kinetically favored surface oxide formation

Consolidation and Heat Treatment:

- Oxygen exchange reaction (PPB Oxide + Y → Dispersoid)
- Formation of "most stable" nano-metric oxide dispersoids

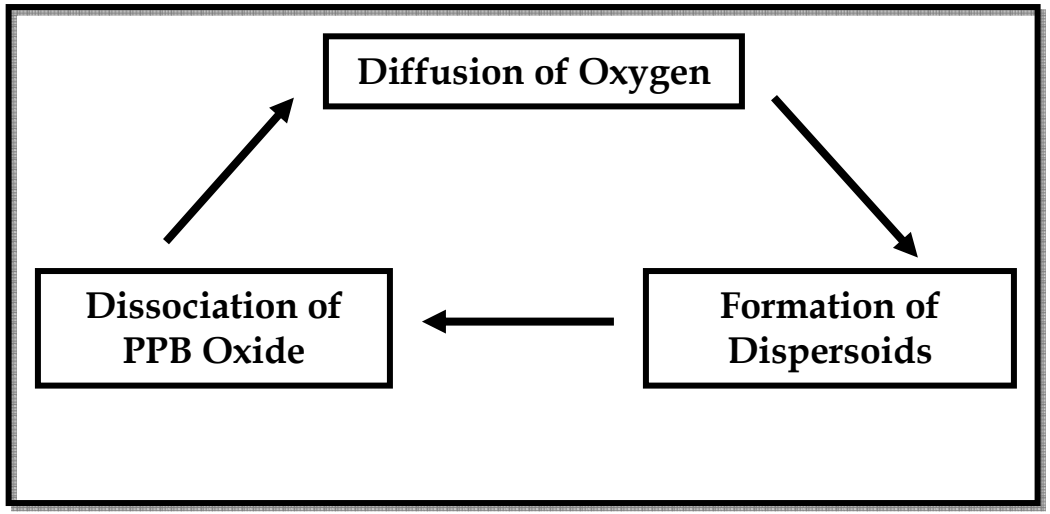


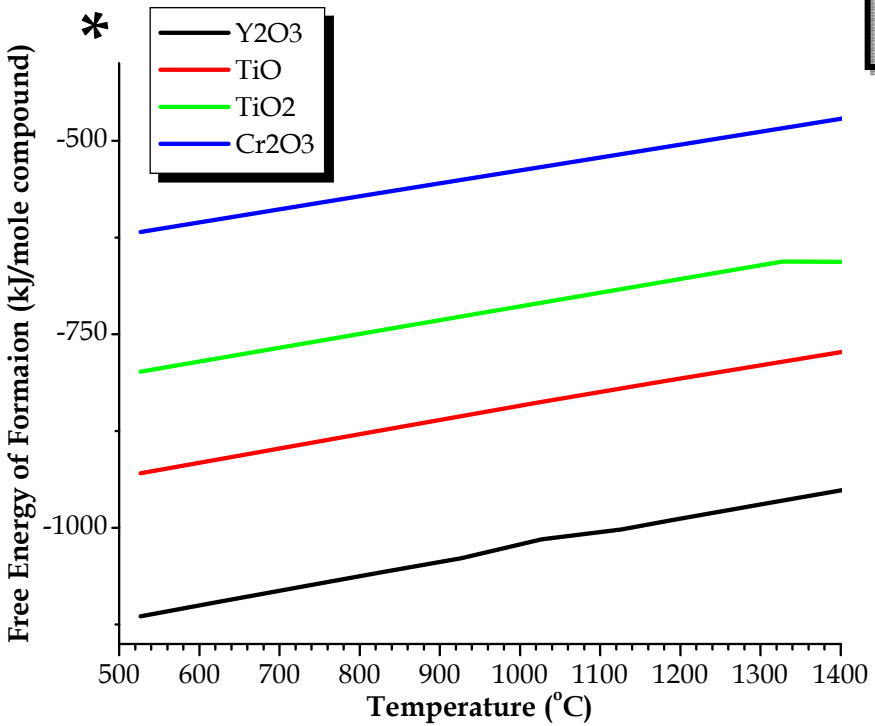


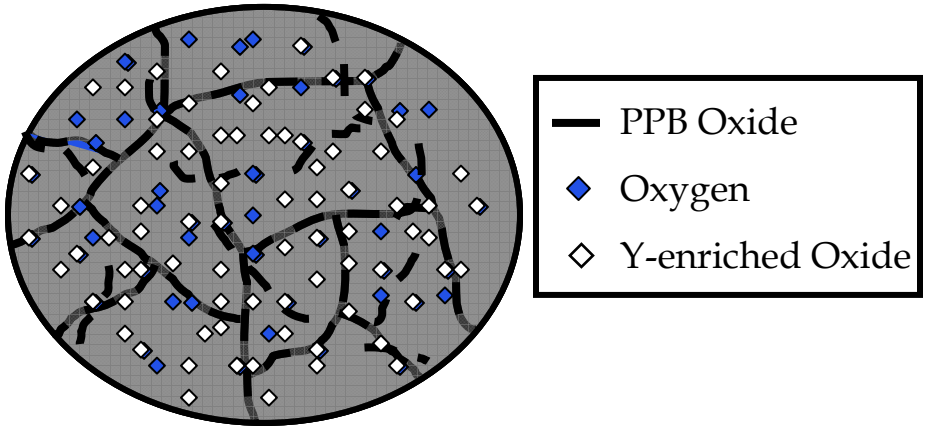
Oxygen Exchange Reaction

- PPB oxide dissociation
- Oxygen diffusion
- Nano-metric yttrium-enriched oxide formation

Full dissociation of PPB oxide will be necessary for ideal properties







* Sauert F., Schultze-Rhonhof E., Sheng W.S., Thermochemical Data of Pure Substances, 2nd Edition 1992.

Alloy Powder Compositions

As-Charged Composition

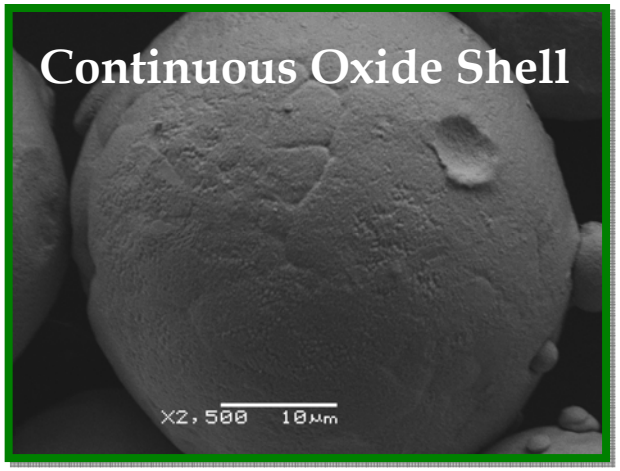
- ***CR-96: Fe-12.5Cr-1.0Y (wt.%) → Secondary Reaction Zone**
- **CR-112: Fe-15.0Cr-0.5Y (wt%)**
- **CR-118Ti: Fe-15.0Cr-0.5Y-0.54Ti (wt.%) → addition of Ti**

* Preliminary Results

Results

1. As-Atomized Oxide Shell Thickness
2. As-Consolidated Microstructure
3. Dispersoid Composition Analysis
4. Initial Mechanical Properties
5. Fracture Analysis

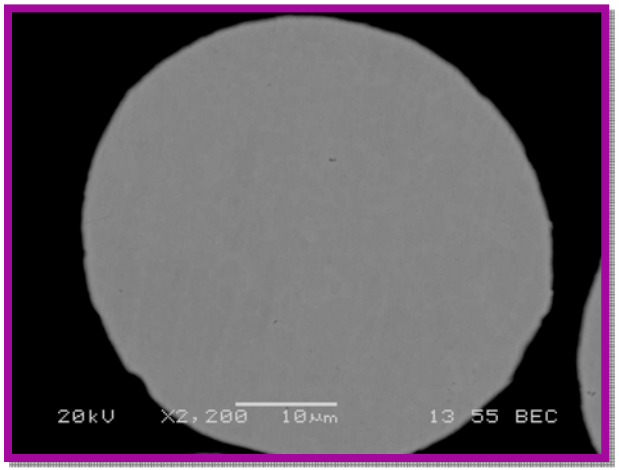
As-Atomized Powder Morphology

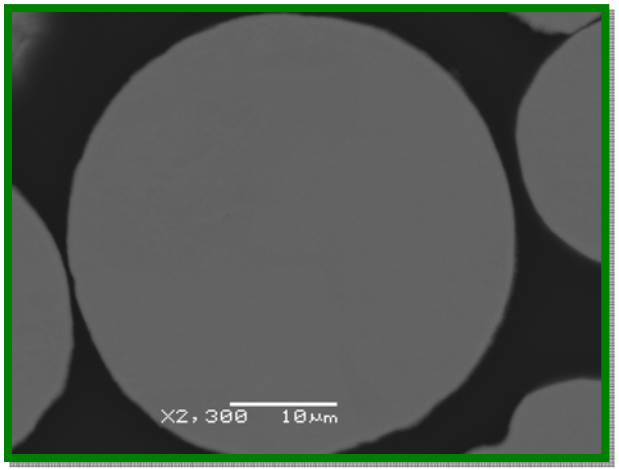


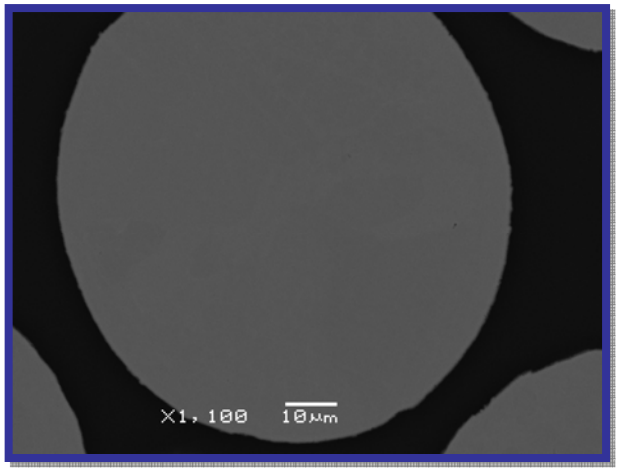
Fe-12.5Cr-1.0Y-0.08O wt.%

Fe-15.0Cr-0.5Y-0.4O wt.%

Fe-15.0Cr-0.5Y-0.54Ti-0.4O wt.%

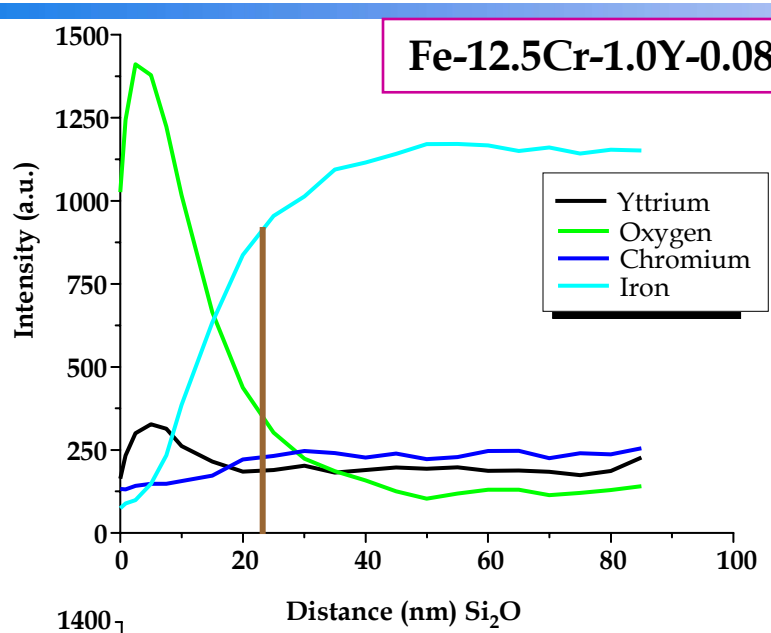


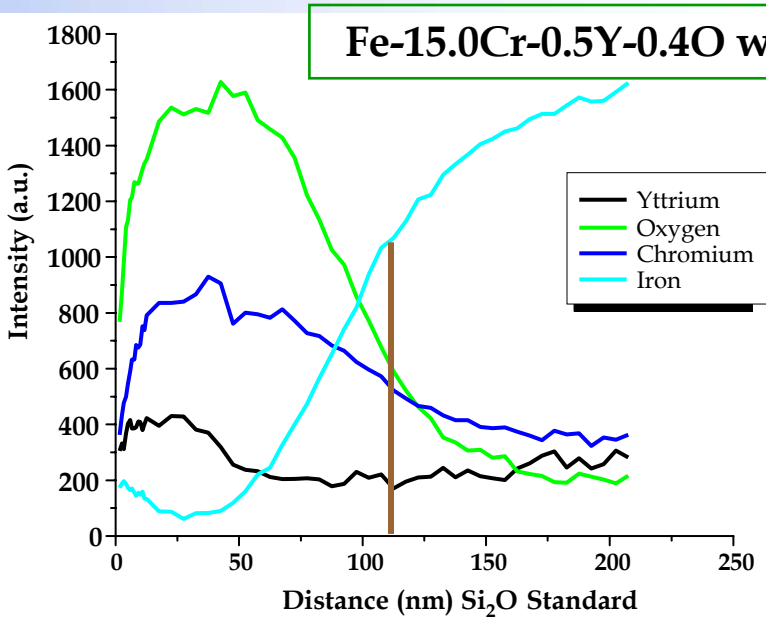


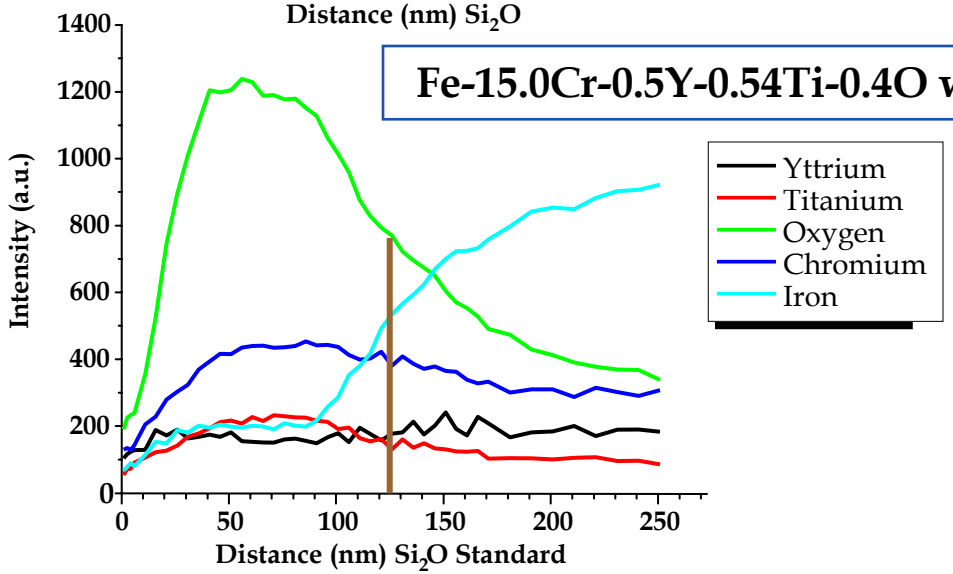


Spherical and relatively satellite free powder

Surface Oxide Coating

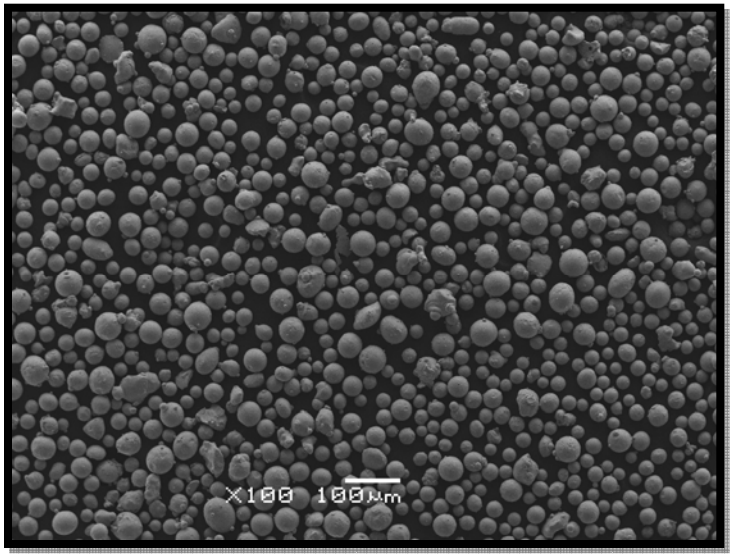


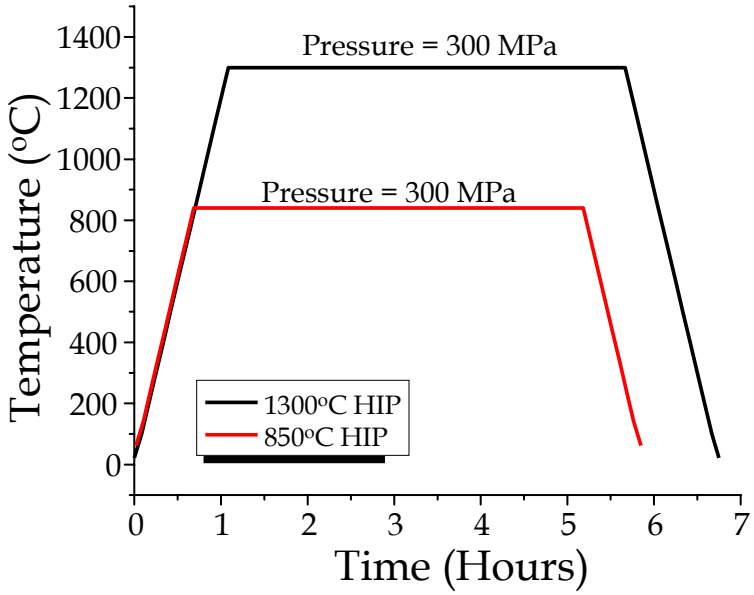




- **Relative surface chemistry and oxide thickness identified using Auger electron spectroscopy**
- **Surface oxide characteristics are dependant on processing parameters**

Powder Consolidation





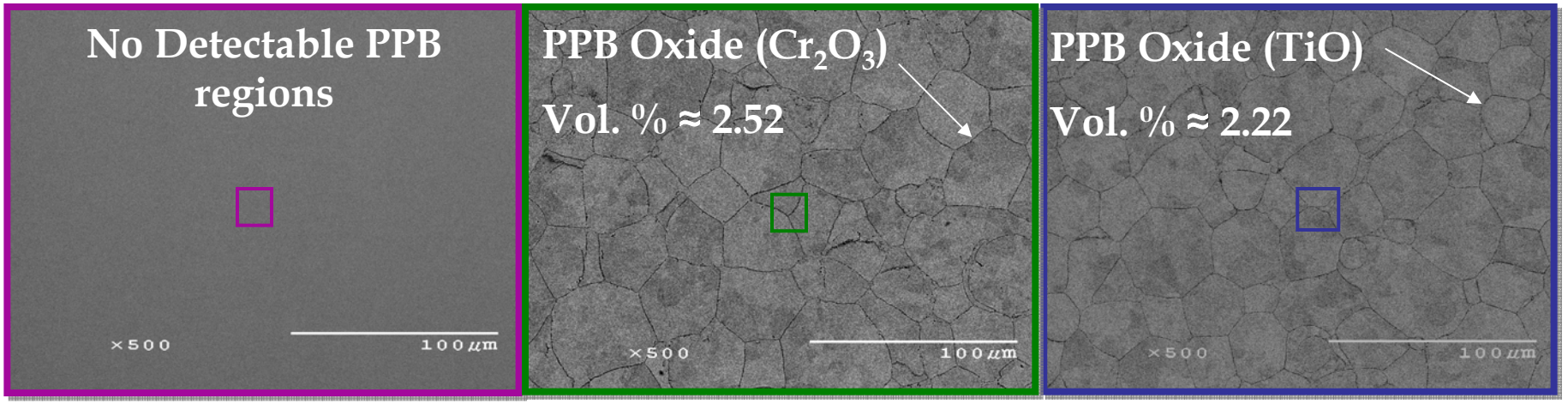
850°C HIP

- Complete consolidation (low strength)
- Limited oxygen exchange reaction

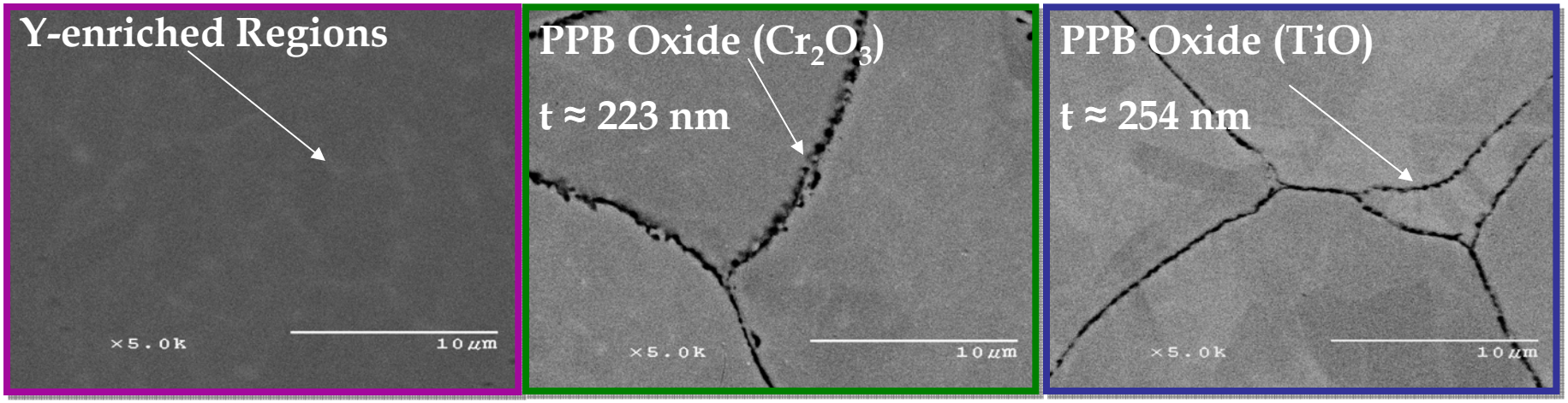
1300°C HIP

- Complete consolidation (high strength)
- Nearly full oxygen exchange reaction

Low Temp. Consolidation (850°C)

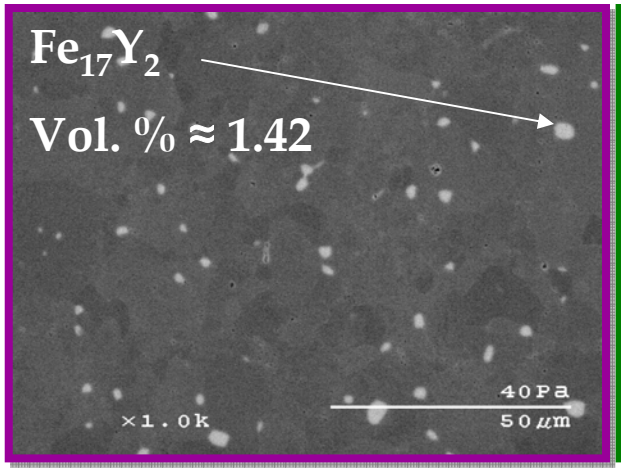


Fe-12.5Cr-1.0Y-0.08O wt.% **Fe-15.0Cr-0.5Y-0.4O wt.%** **Fe-15.0Cr-0.5Y-0.54Ti-0.4O wt.%**

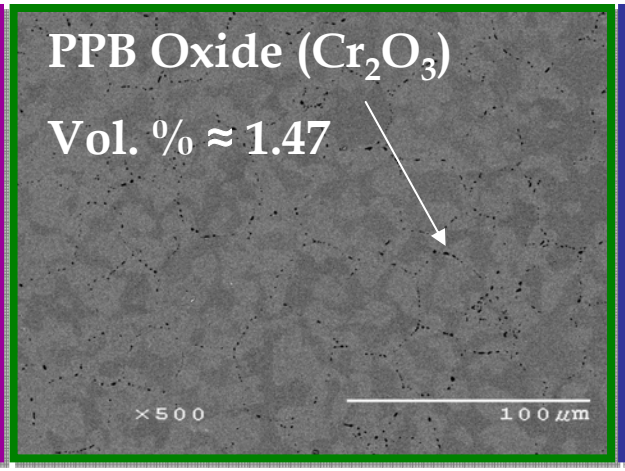


Note: CR-96 (i.e. purple border) has significantly less oxygen and more yttrium than the other two alloys

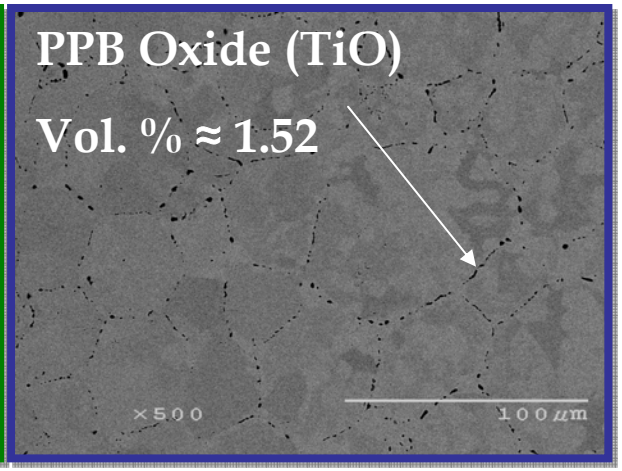
High Temp. Consolidation (1300°C)



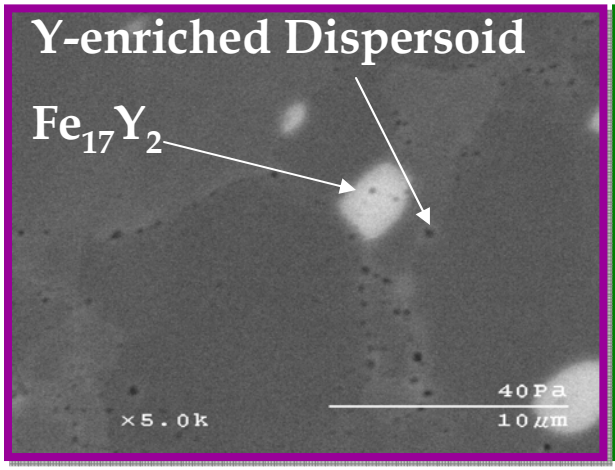
Fe-12.5Cr-1.0Y-0.08O wt.%

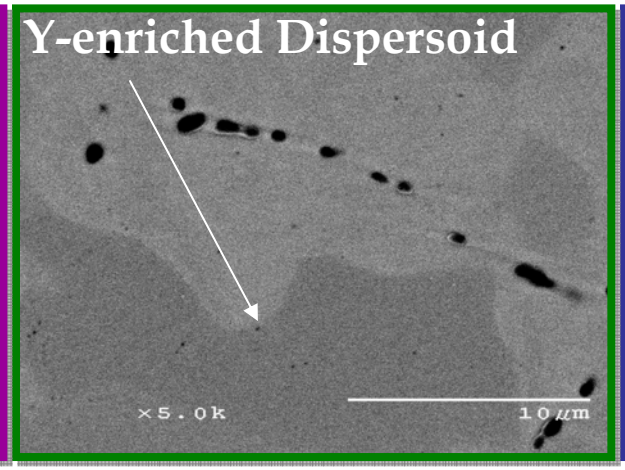


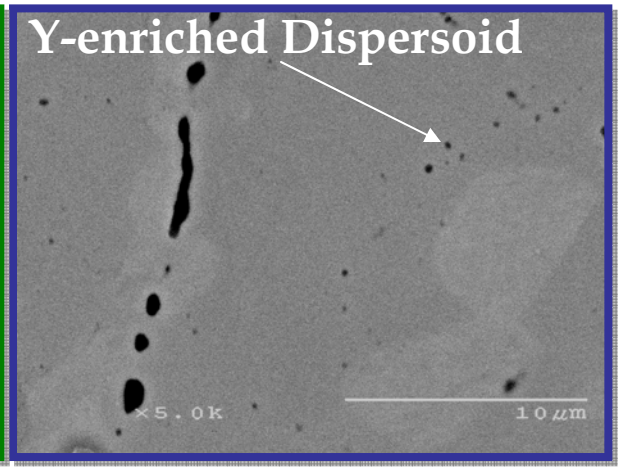
Fe-15.0Cr-0.5Y-0.4O wt.%



Fe-15.0Cr-0.5Y-0.54Ti-0.4O wt.%

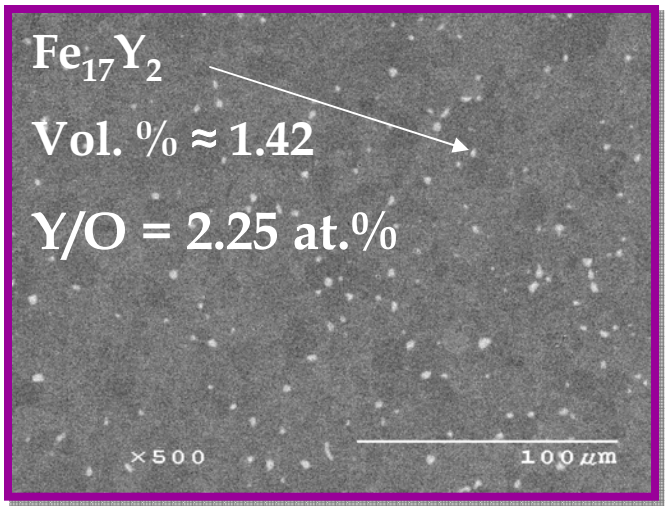




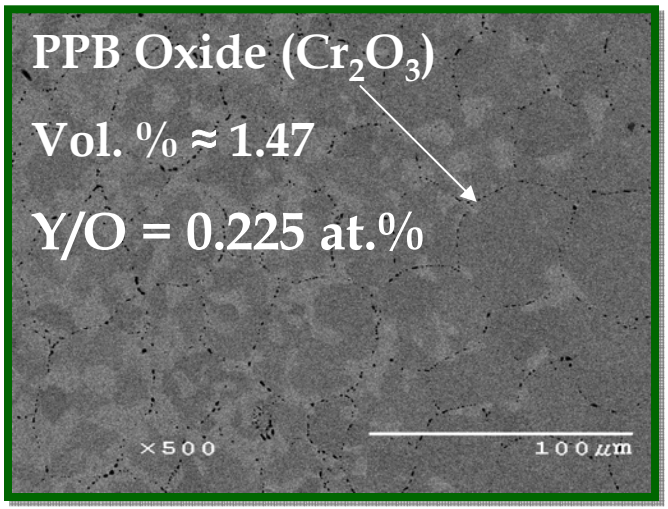


Residual non-ideal phases (i.e. $Fe_{17}Y_2$ or PPB oxide) remain at a similar volume percentage

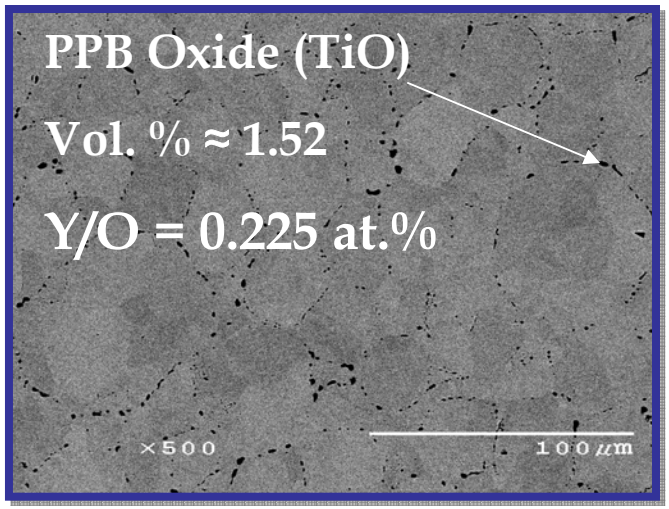
Ratio Dependence of Reactive Constituents



Fe-12.5Cr-1.0Y-0.08O wt.%



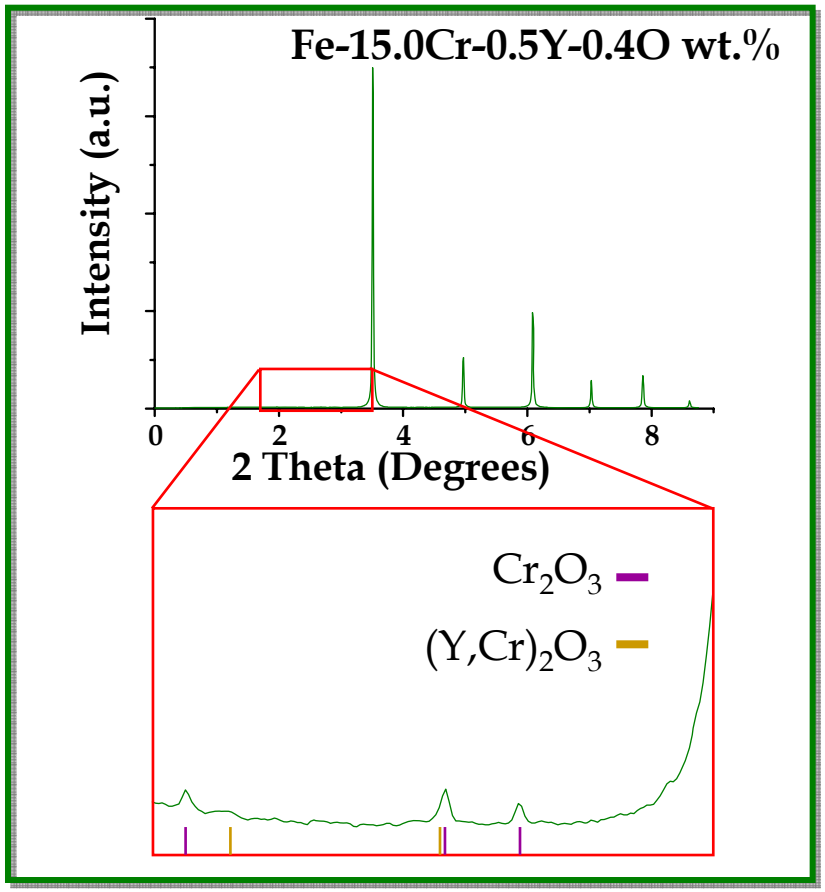
Fe-15.0Cr-0.5Y-0.4O wt.%

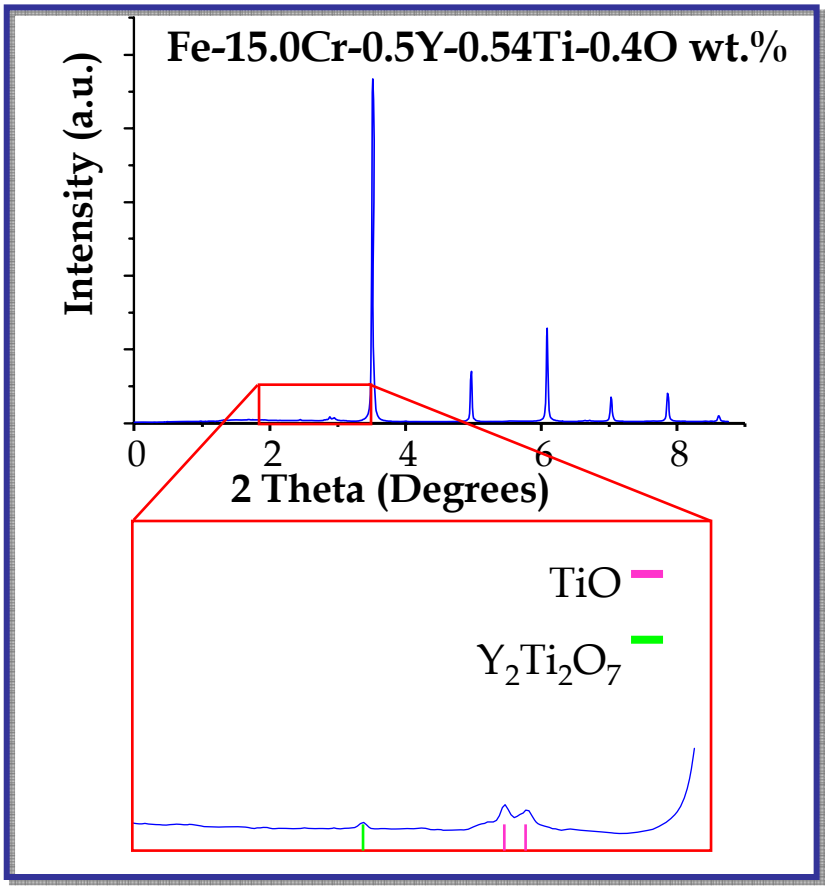


Fe-15.0Cr-0.5Y-0.54Ti-0.4O wt.%

- **Formation of an ideal microstructure is dependant on the as-atomized yttrium-to-oxygen ratio**
- **Yttria (Y_2O_3) requires a yttrium-to-oxygen ratio of 0.667 at.%**
- **Typical alloying addition of 0.5 wt.% yttrium should require approximately 0.135 wt.% oxygen**

Phase Identification-Synchrotron

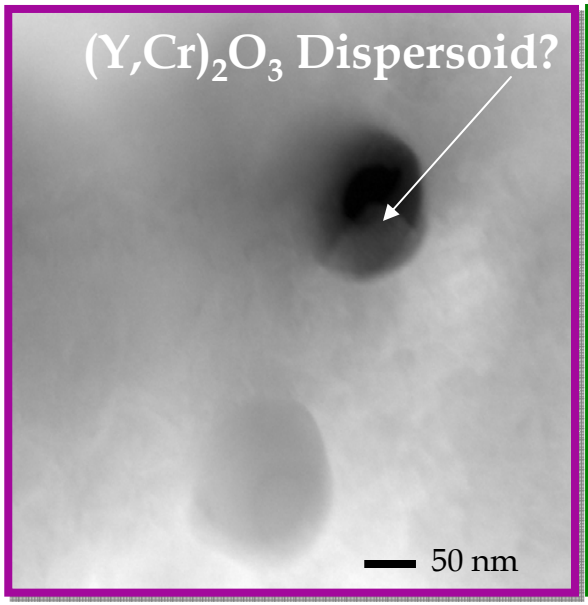




- As-consolidated (1300°C HIP) sample
- Phase analysis based on phase patterns and not full refinement
- Good agreement with chemical phase analysis (i.e. wave dispersive spectroscopy)

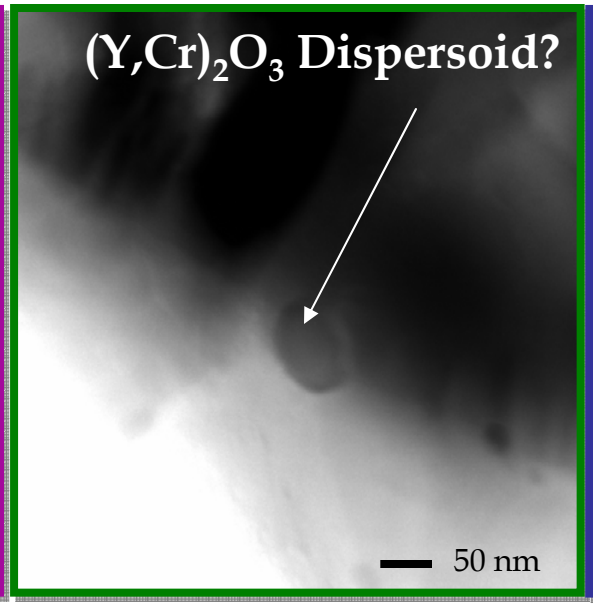
Phase Identification-STEM/EDS

Fe-12.5Cr-1.0Y-0.08O wt.%



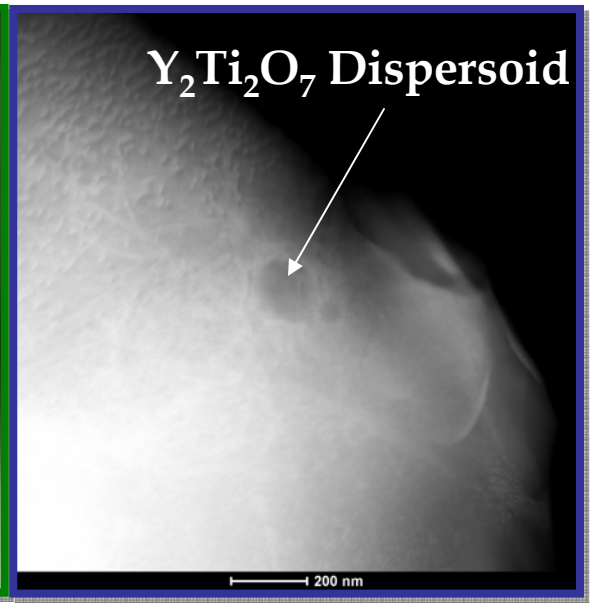
Element	Atomic %
Oxygen	59.19
Chromium	16.02
Yttrium	24.78

Fe-15.0Cr-0.5Y-0.4O wt.%



Element	Atomic %
Oxygen	63.14
Chromium	18.61
Yttrium	18.24

Fe-15.0Cr-0.5Y-0.54Ti-0.4O wt.%



Element	Atomic %
Oxygen	63.66
Titanium	20.35
Yttrium	15.98

- Dispersoids of similar size to those detected within the SEM
- Particle analysis selection based on location to minimize matrix interaction

Dispersoid Composition Importance

- Dispersoid composition is dependent on alloying constituents
- The ideal ratio of yttrium-to-oxygen can vary with dispersoid phase composition
- In all cases the dispersoids form as mixed oxides

Initial Alloy Design Y/0 ≈ 0.667 at.%

Y_2O_3	Atomic %	Weight %
Yttrium	0.400	0.500
Oxygen	0.600	0.135

Fe-Cr-Y Y/0 ≈ 0.33 at.%

$(Y,Cr)_2O_3$	Atomic %	Weight %
Yttrium	0.200	0.500
Oxygen	0.600	0.270

Fe-Cr-Y-Ti (wt.%) Y/0 ≈ 0.285 at.%

$Y_2Ti_2O_7$	Atomic %	Weight %
Yttrium	0.181	0.500
Oxygen	0.636	0.320

As-Consolidated Mechanical Testing

Tensile Bar Specimen:

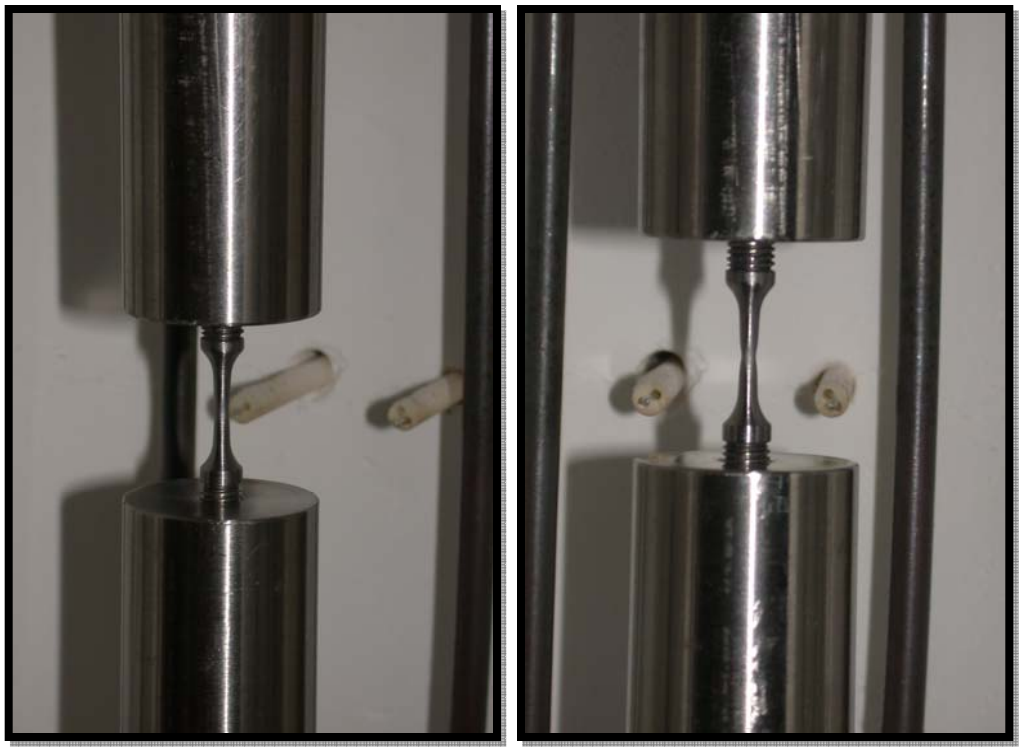
- As-HIP 1300°C – 4.0 hrs. – 303 MPa
- Finite Element Analysis Design

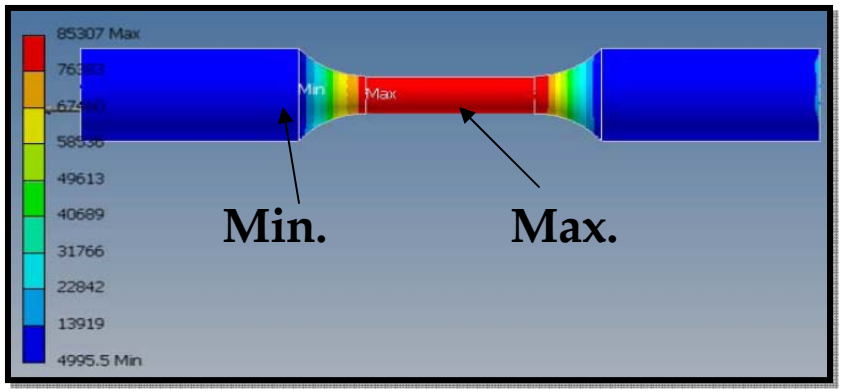
Open Air Tensile Test Machine:

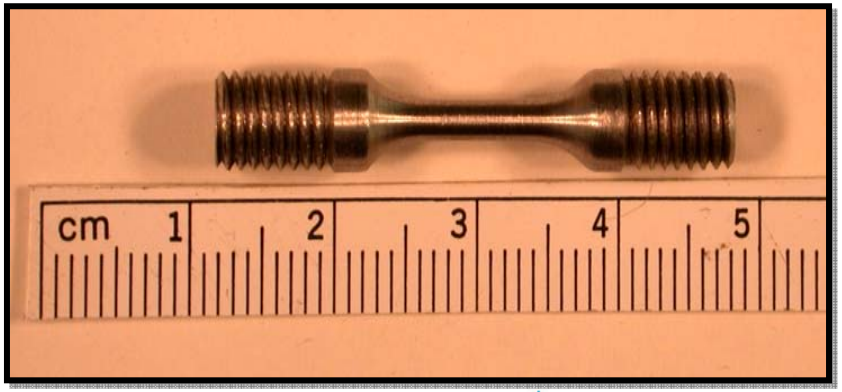
- 810 MTS-657.01 HT Furnace
- Temperature Range RT-700°C

Test Procedure:

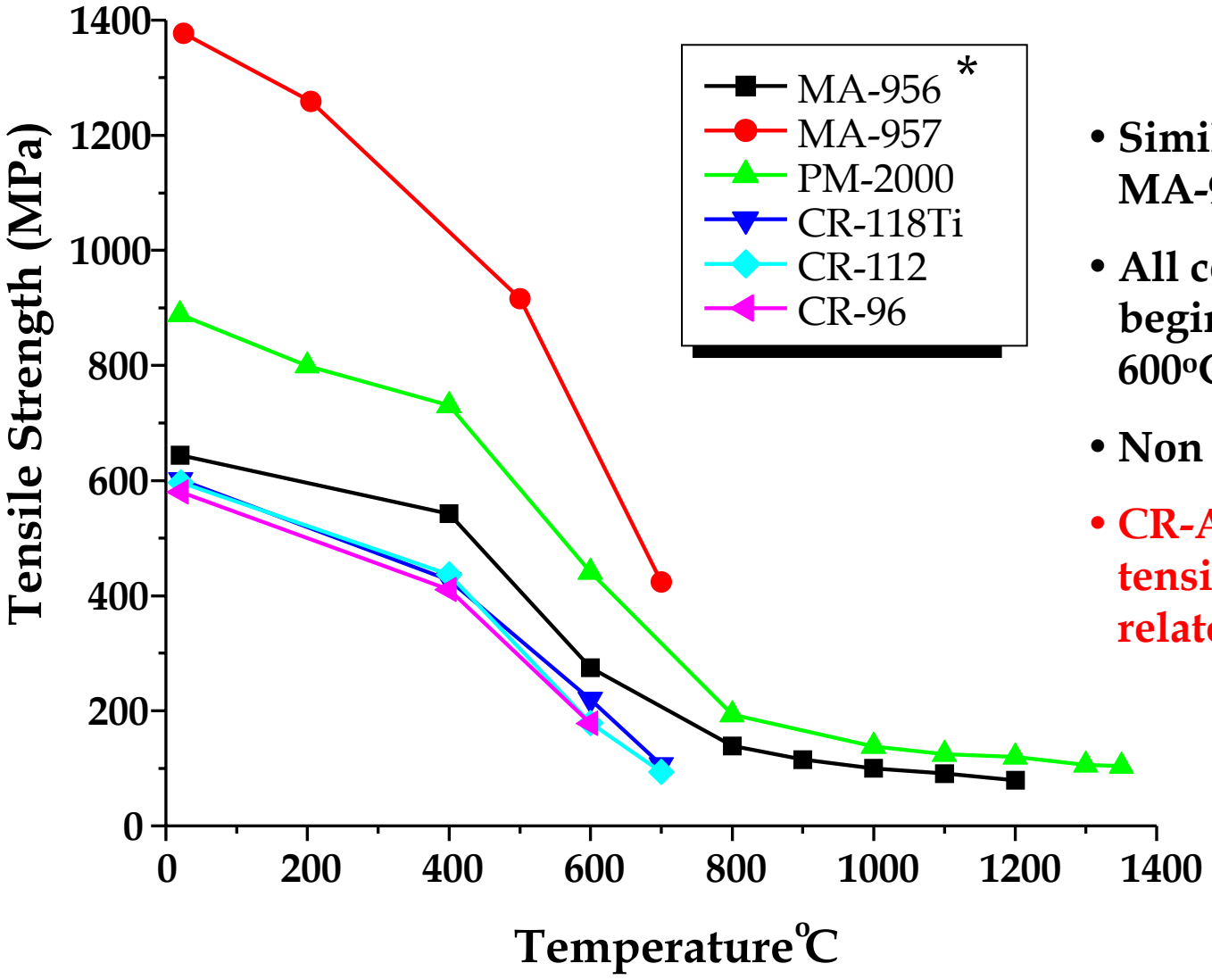
- ASTM-E 21-05 (HT Tensile Testing)
- Displacement velocity = 0.1 mm/min.







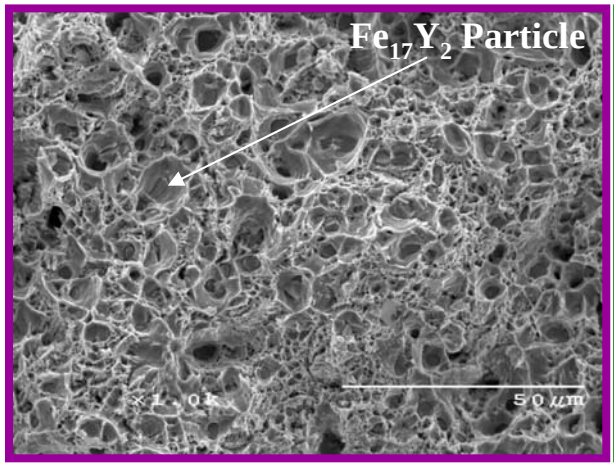
Tensile Strength Comparison



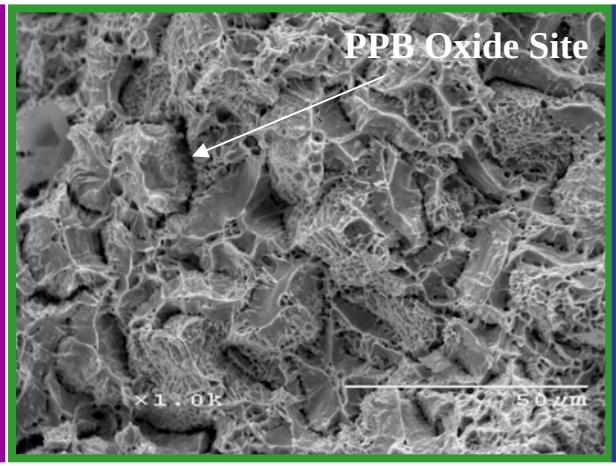
- **Similar tensile strength as MA-956**
- **All commercial alloys begin to converge above 600°C**
- **Non ideal microstructure**
- **CR-Alloys illustrate similar tensile strength due to related microstructures**

*R.L. Klueh et al., Oak Ridge National Laboratory, Journal of Nuclear Materials 341 (2005) 103-114

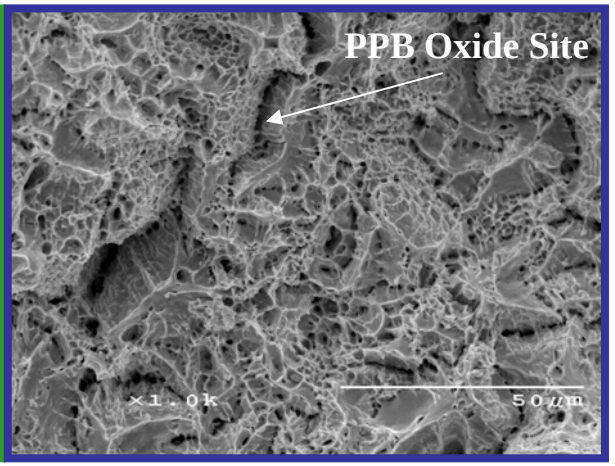
Failure Analysis-Microstructure



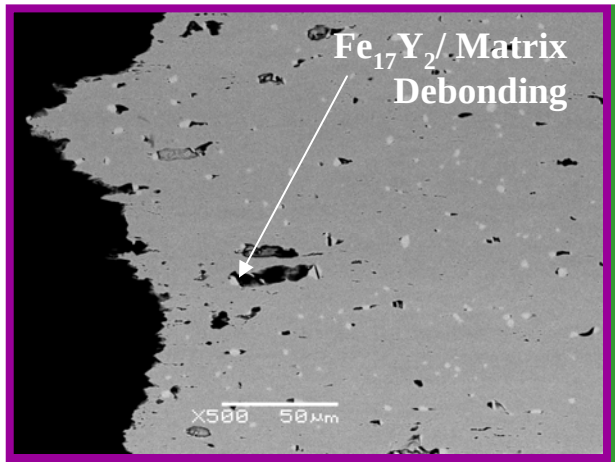
Fe-12.5Cr-1.0Y-0.08O wt.%

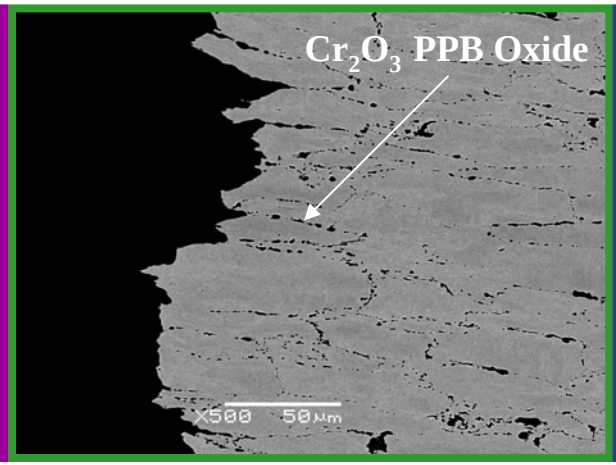


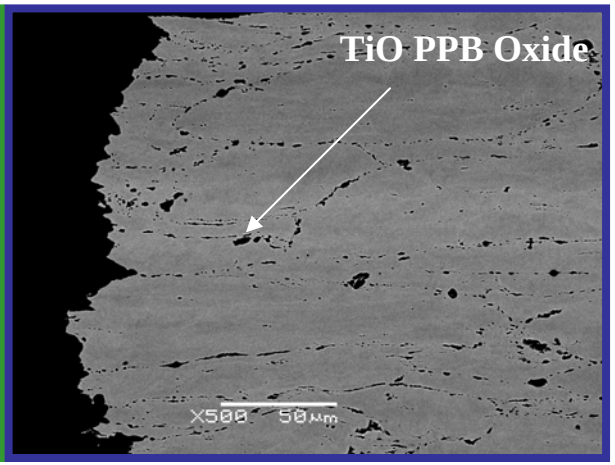
Fe-15.0Cr-0.5Y-0.4O wt.%



Fe-15.0Cr-0.5Y-0.54Ti-0.4O wt.%

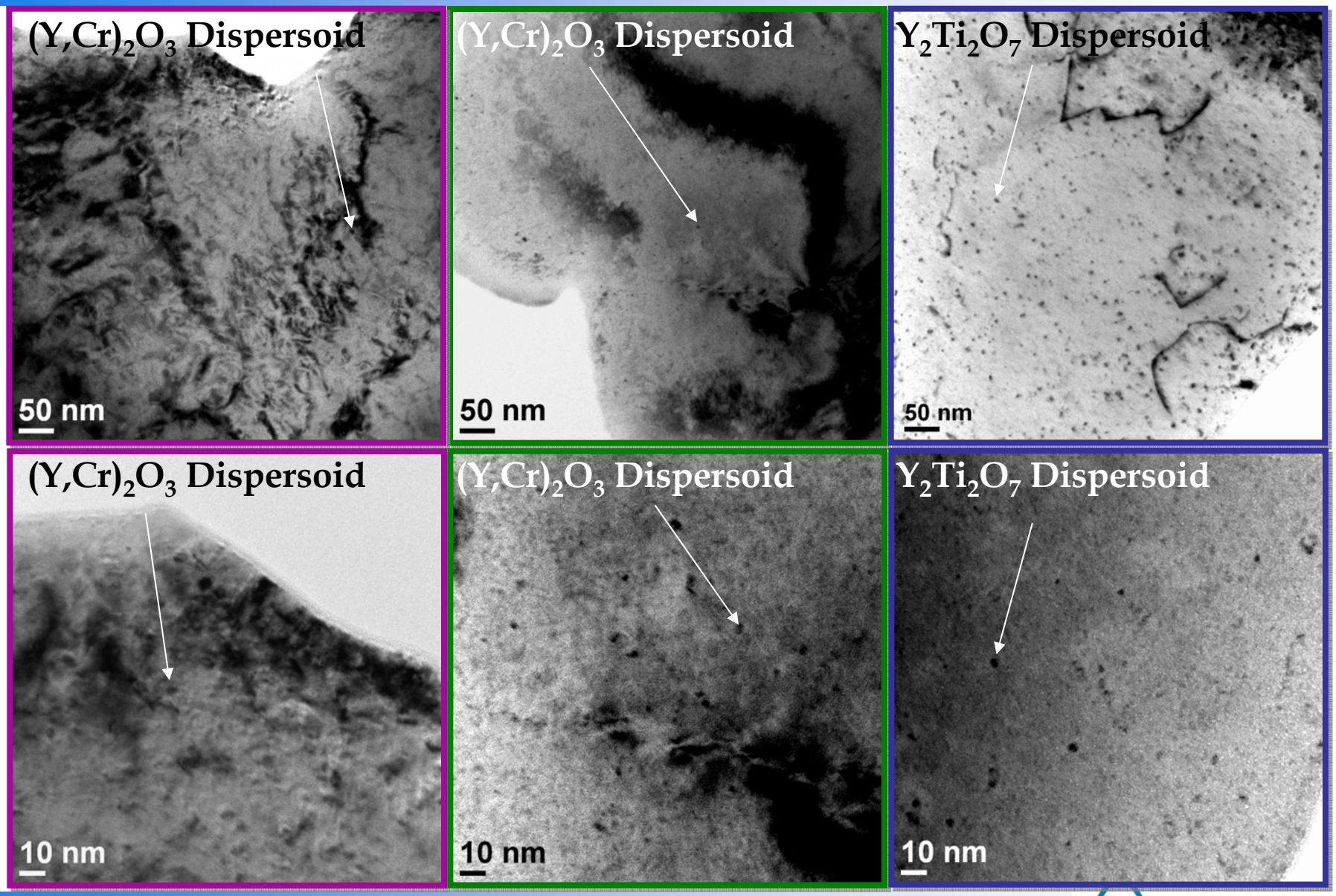






Failure occurs from micro void formation resulting from the debonding of the matrix from residual non-ideal phases (i.e. $Fe_{17}Y_2$ or PPB oxide)

Failure Analysis-Nanostructure

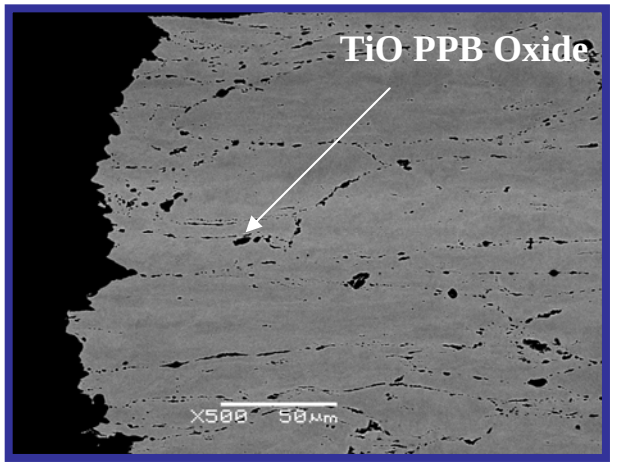


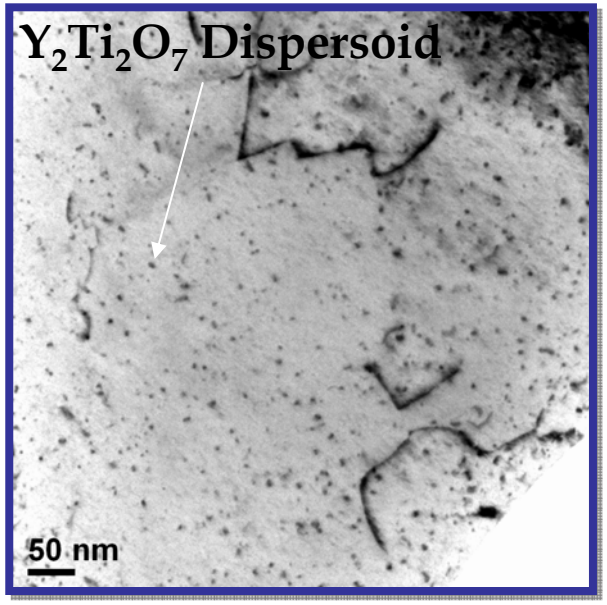
Summary

- A new simplified processing technique involving gas atomization and in situ oxidation has been developed to produce precursor ferritic stainless steel powder that can be consolidated into an oxide dispersion strengthened alloy with an isotropic microstructure
- Atomization parameters can be used to control the concentration of oxygen introduced into the alloy system during the in-situ oxidation procedure, eventually producing a desired ODS microstructure
- Initial results have shown a clear ability to manipulate the phase microstructure using high temperature consolidation
- Preliminary phase analysis illustrates the formation of nano-metric yttrium enriched oxide dispersoids

Summary

- Alloy tensile strength seems limited to the interfacial bond strength between $Fe_{17}Y_2$ or residual PPB oxide and the α-Fe matrix
- Global microstructure needs improvement (i.e. preventing $Fe_{17}Y_2$ phase formation and full dissociation of PPB oxide) to achieve ideal strength
- Local nano-structure shows the formation of nano-metric yttrium enriched oxide dispersoids and demonstrates that this process has the unique potential to effectively form an ODS ferritic stainless steel alloy





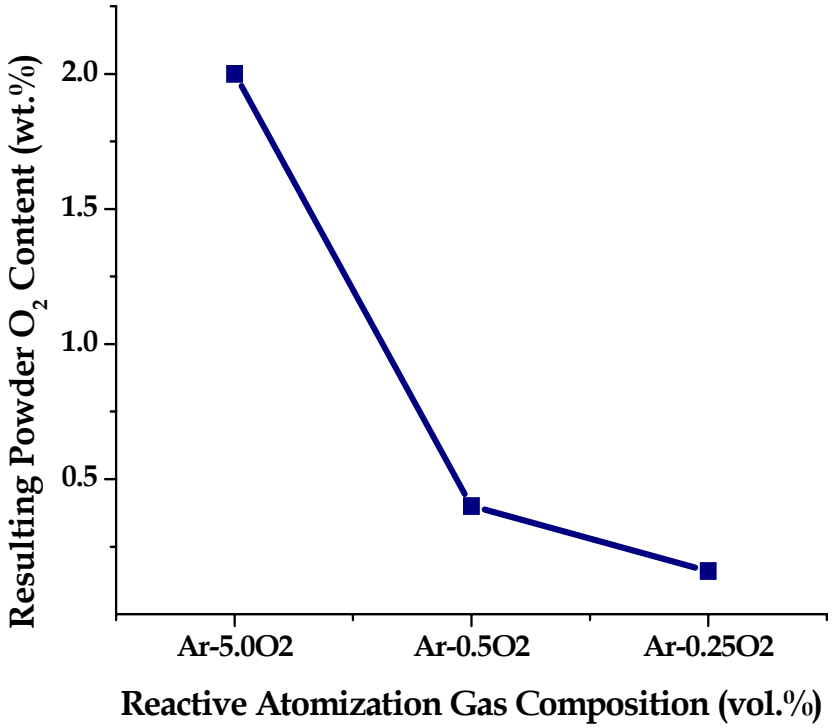
Future Work

Alloy Design

- Cr (≈ 15.0 wt.%) Ferrite Stabilizer
- Y (≈ 0.5 wt.%) Dispersoid Former
- Ti (≈ 0.5 wt.%) Dispersoid Former
- W (≈ 3.0 wt.%) Solid Solution Strengthener

Processing Parameters

- Reaction gas % and injection method
- Pouring temperature



Heat treatment procedure development

- Synchrotron (X-ray) phase analysis (post HT)
- TEM analysis (powder and as-consolidated)
- Mechanical testing (micro hardness and tensile strength)

By modifying the reactive gas composition the oxygen content within the powder particles can be controlled