Innovative Powder Processing of High Temperature Ferritic Stainless Steel: Short Time Milling and Al Additions

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Outline

Short Time Milling Experiments:

- Gas Atomization Reaction Synthesis (GARS) Processing
- Microstructural comparison (direct consolidation vs. short ball milling)
- Hot rolling and annealing
- Mechanical Properties (hardness and hot tensile)

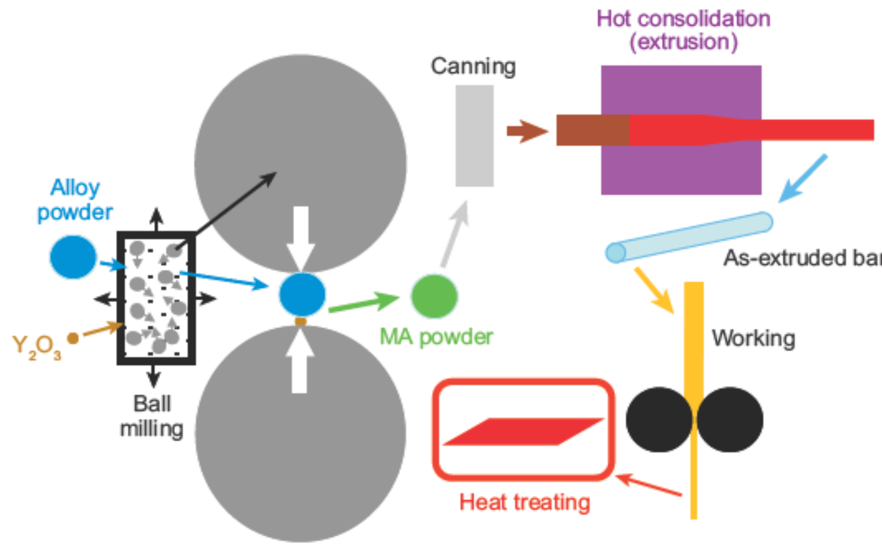
Al Additions to ODS Ferritic Stainless Steel:

- Need for Al addition in Fe-based ODS
- Modified CR Alloy with Al addition
- Gas atomization experiment results
- Initial HIP consolidation of Fe-base ODS with Al

Motivation

<u>Mechanical Alloying</u>

- Long milling times (40-80 hr)
- Batch process
- Powder contamination
- Anisotropic microstructure

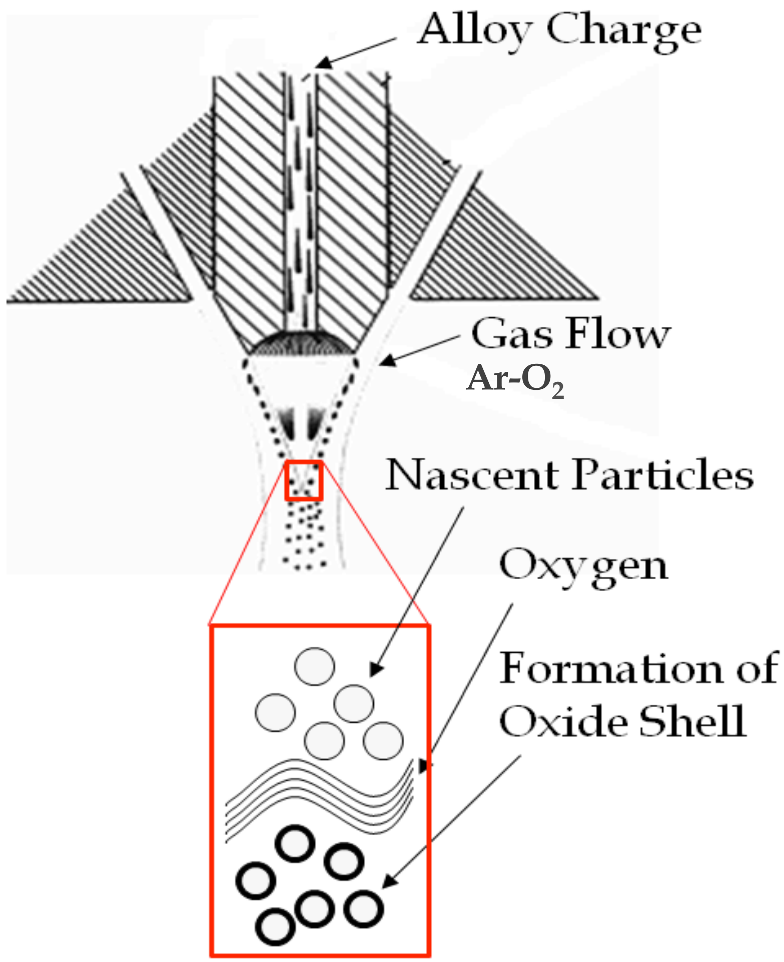


-G.R. Odette et al., Annu. Rev. Mater. Res., 2008.

Material	Cost/kg (USD)	Notes
Ferritic Stainless Steel	~$2-5	446 Plate form
Fe-based ODS	~$165, ~ $345	MA956 Sheet (Special Metals) PM 2000 (Plansee)

ODS Processing Cost!

Gas Atomization Reaction Synthesis (GARS)



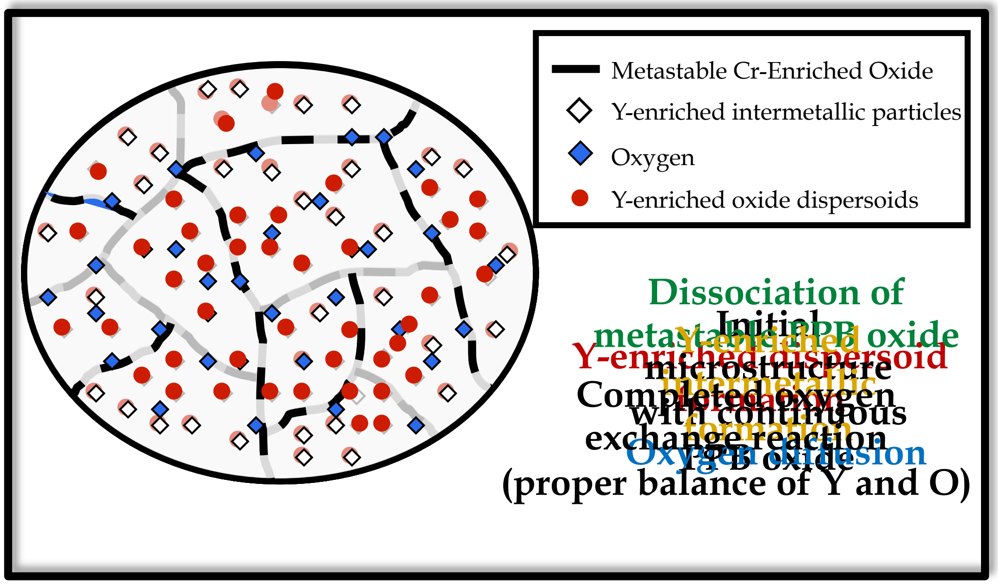
GARS Experimental Run

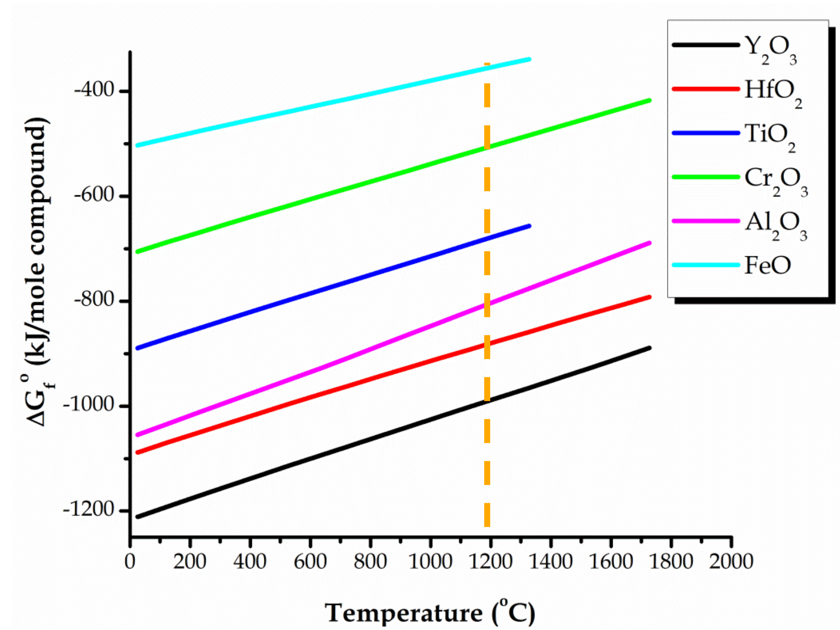
In situ alloying addition of oxygen

High speed video (4,000 fps)

Internal Oxygen Exchange Reactions

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



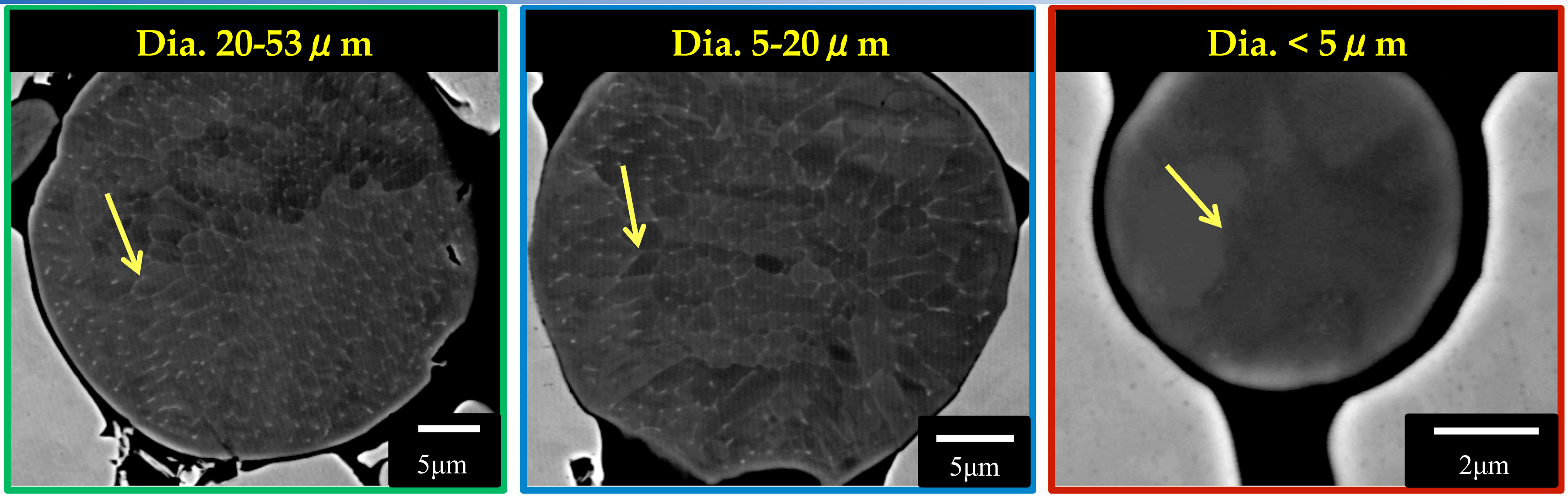


-I. Barin, et al., 1992

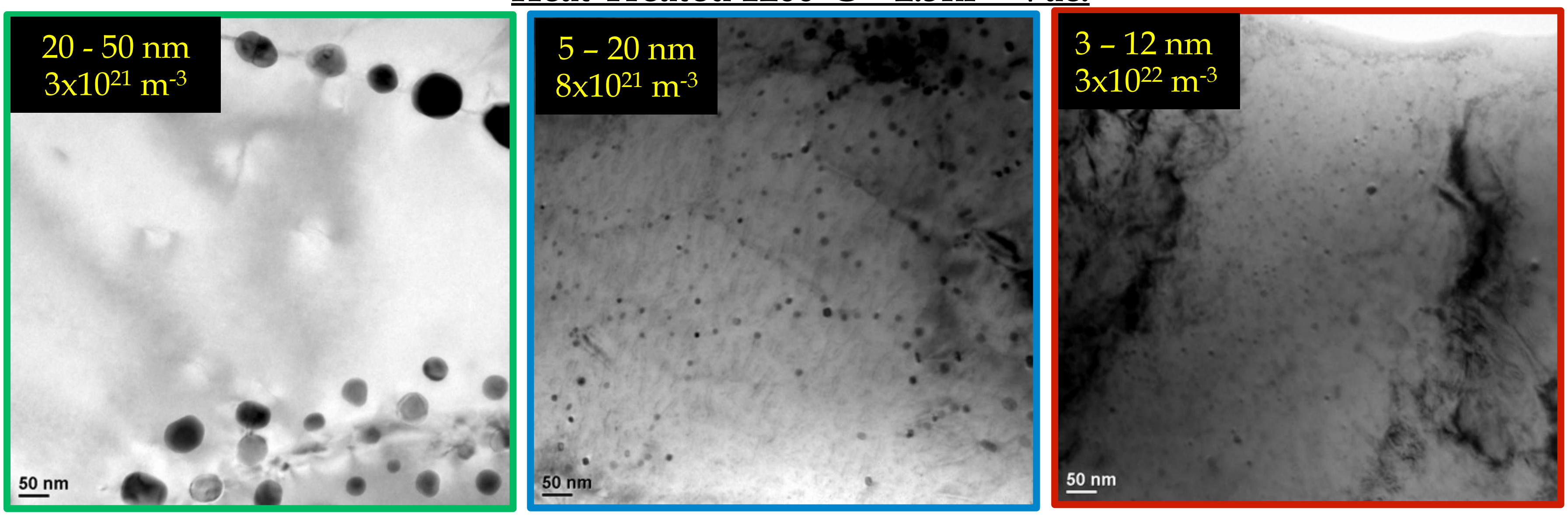
I.E. Anderson et al., USPTO no. 5,368,657, 2010.

Solidification Template → ODS Pattern

Fe-15.84Cr-0.11Hf-0.18Y at.%



<u>Heat Treated 1200°C – 2.5hr – Vac.</u>

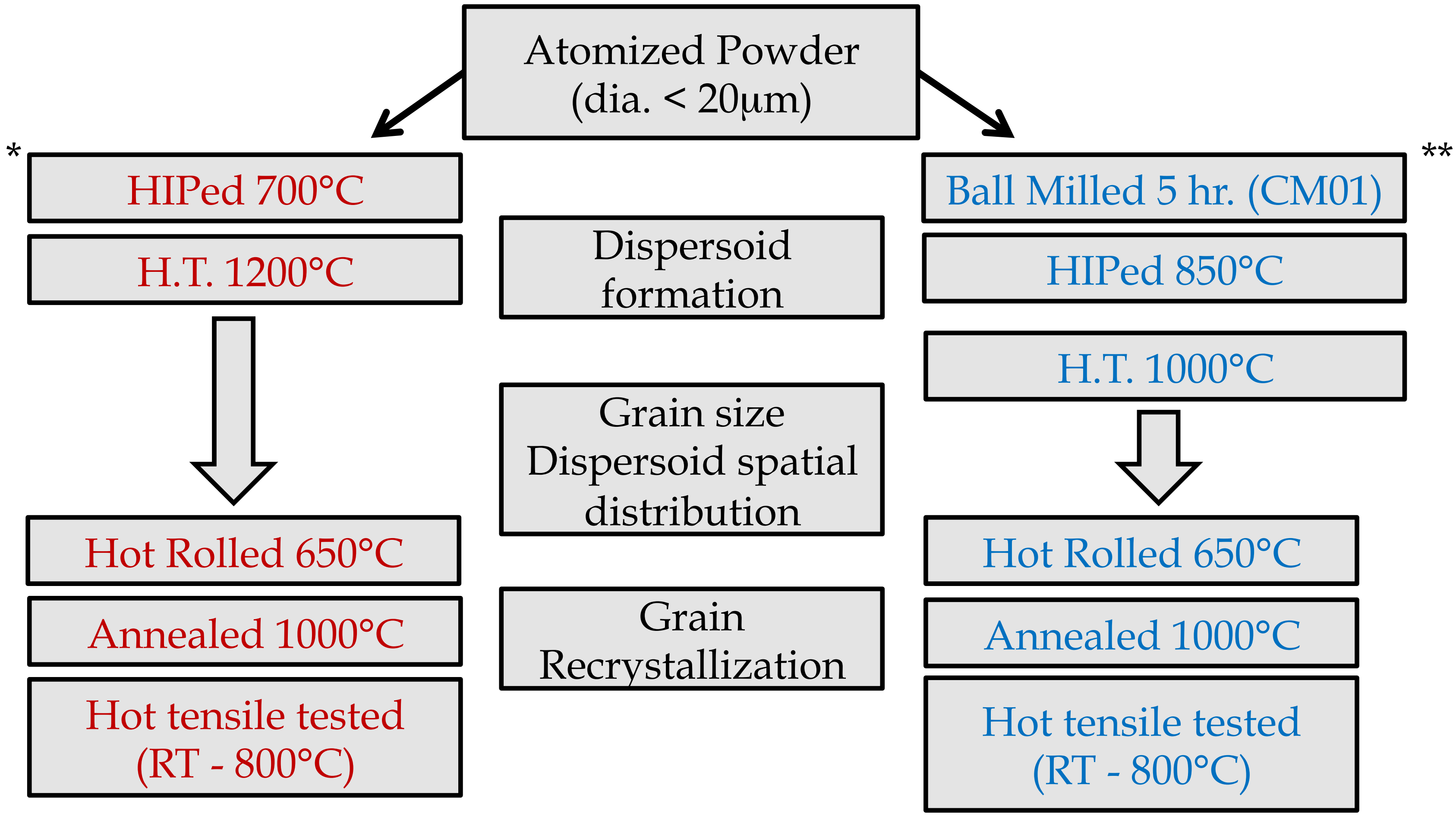


J.R. Rieken et al., J. Nucl. Mater., 2012.

Milling to Enhance Desired Yield

GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O at%

- **Current state of atomization technology generates low yields of optimum (dia. < 5μm) powders that result in ideal ODS microstructure using direct consolidation**

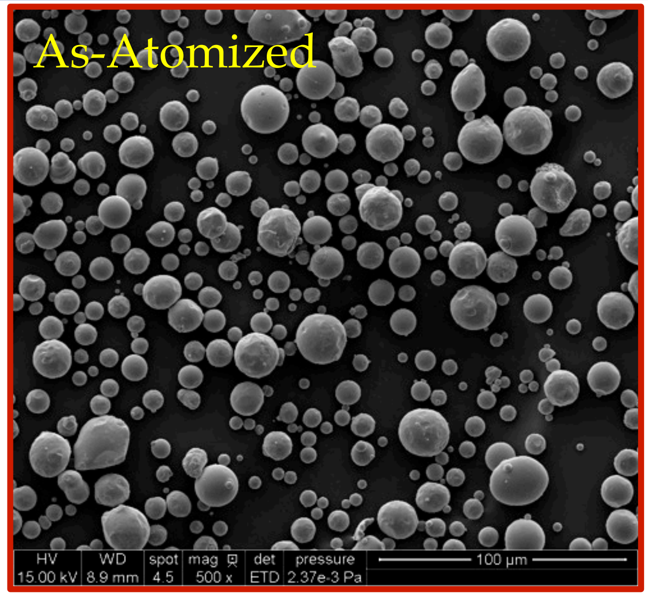


* J.R. Rieken et al., PowderMet, 2011
** D.T. Hoelzer et al., J. Nucl. Mater., 2007

Need for Powder Chemistry Control During Milling

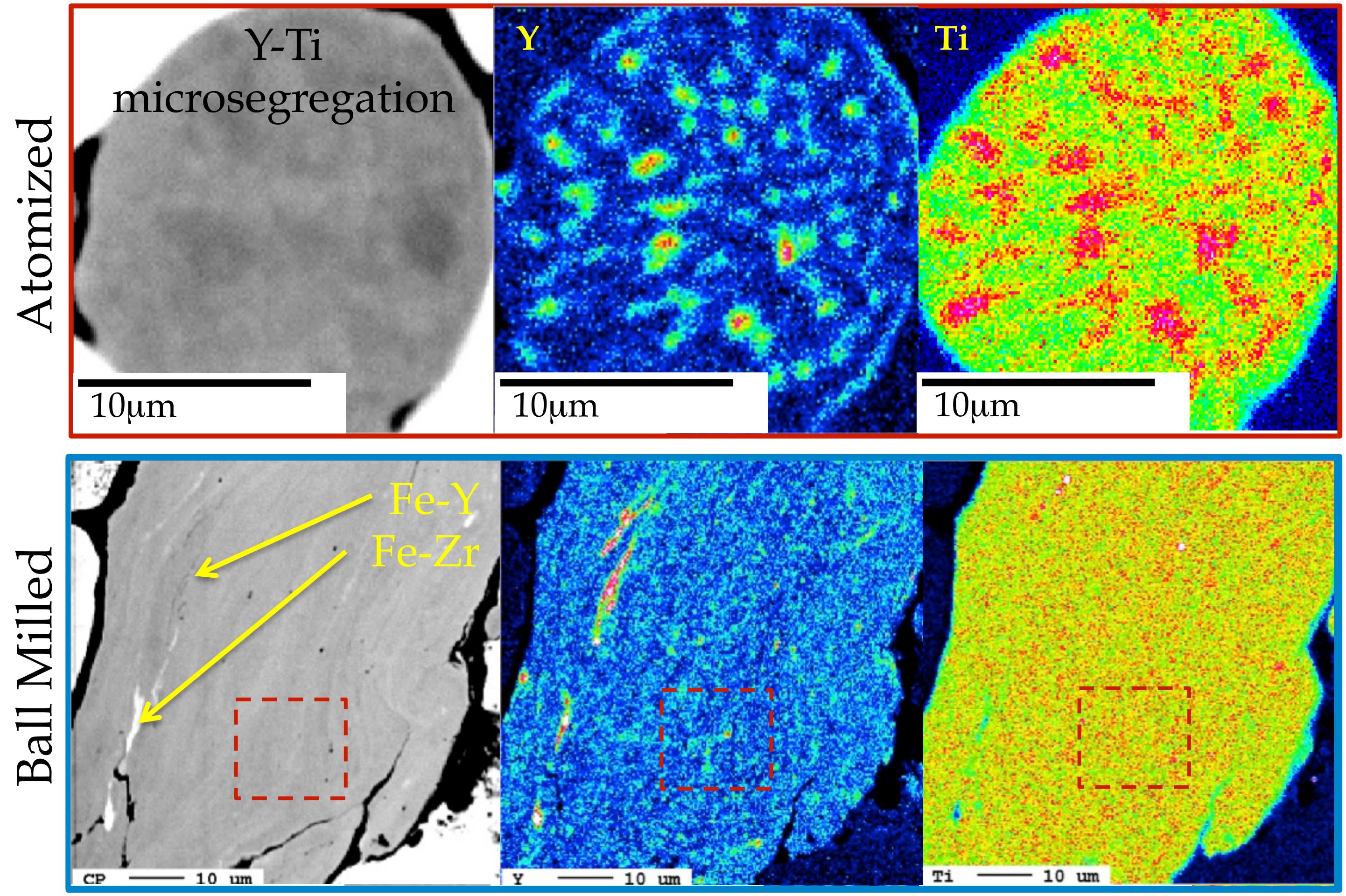
GA-130	Atomized (A) at.%	Ball Milled (BM) at.%
Fe	Bal.	Bal.
Cr	16.3	15.8
W	0.9	0.9
Ti	**0.62**	**0.61**
Y	**0.08**	**0.08**
O	**0.26**	**0.57**
Ni	-	**0.75**
Zr	-	**0.15**
Al	-	**0.11**

- **Results in ~0.40 vol.% nano-metric Y-Ti-O dispersoid phase ($Y_2Ti_2O_7$)**



Refined Microsegregation

GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O-0.75Ni-0.15Zr-0.11Al

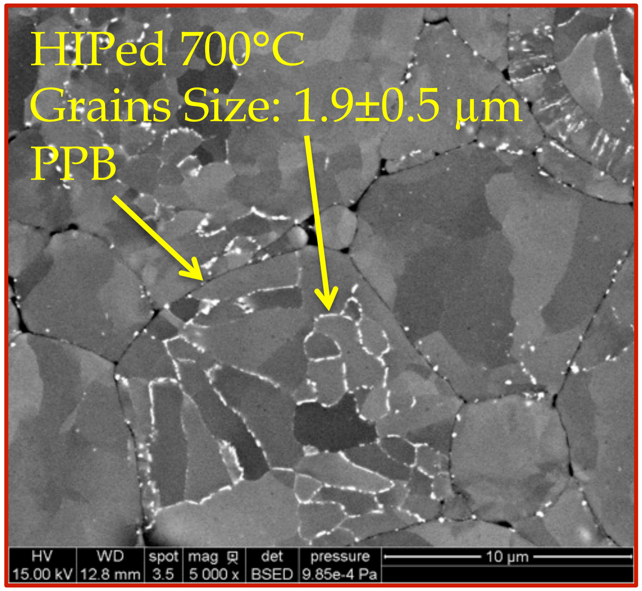


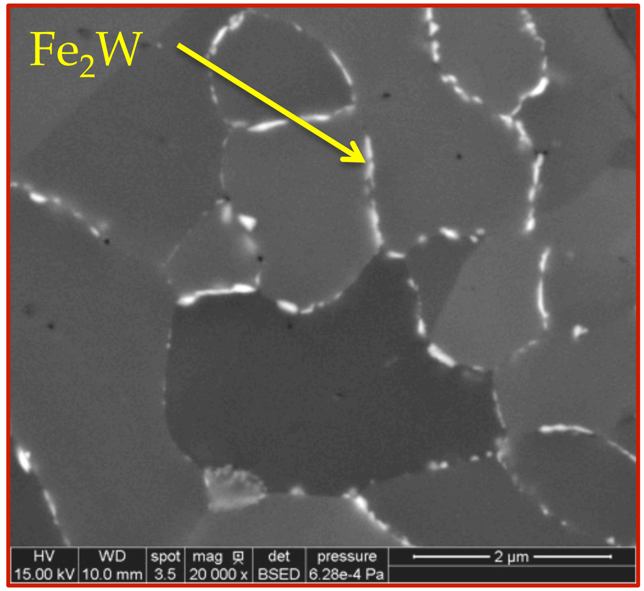
- Y and Ti microsegregation following atomization (possible $Fe_{11}TiY$)
  - Reduced microsegregation after 5 hr ball milling

HIPped Microstructure Compared

GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O

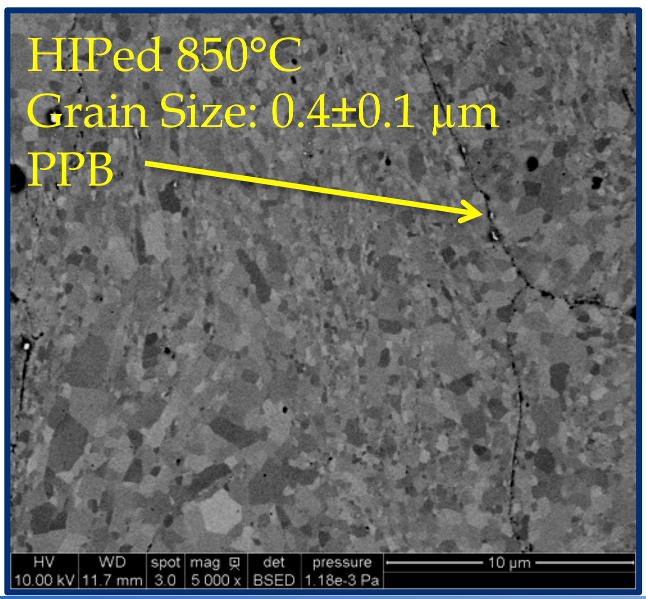
Atomized

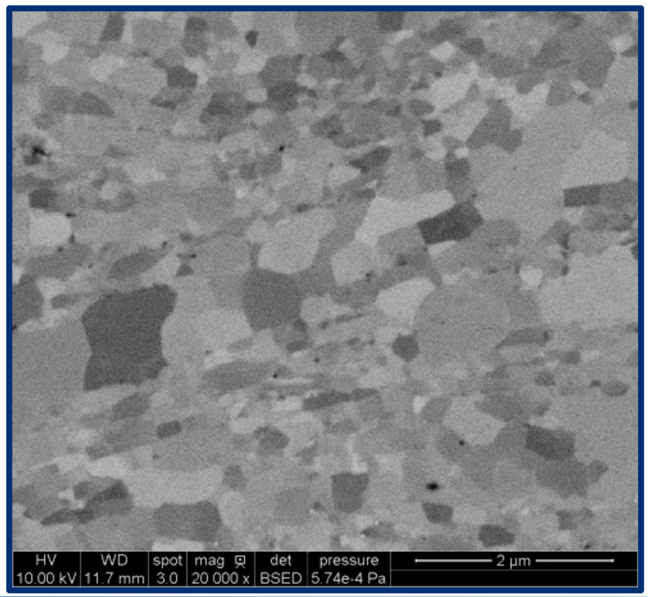




- Residual porosity
- Formation of Fe_2W phase along cell boundaries

Ball Milled



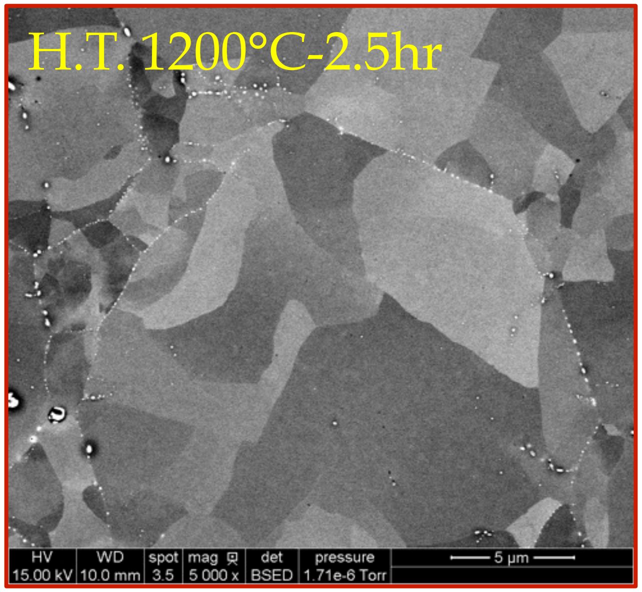


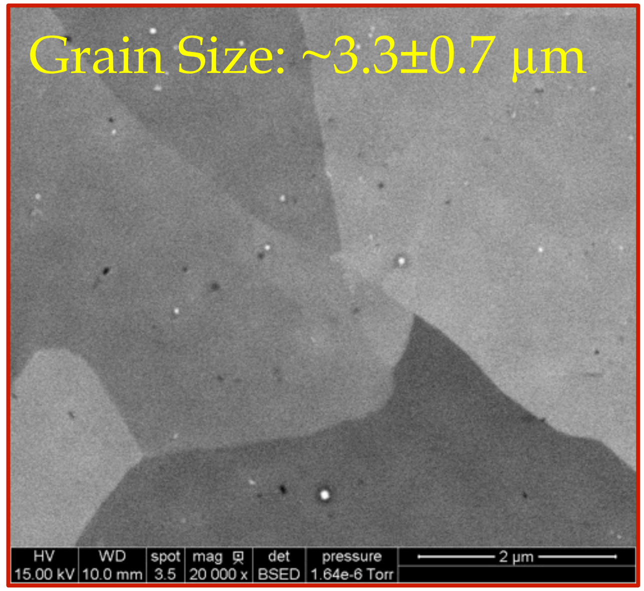
- Signification grain size reduction (5x)

Heat Treated Microstructure

GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O

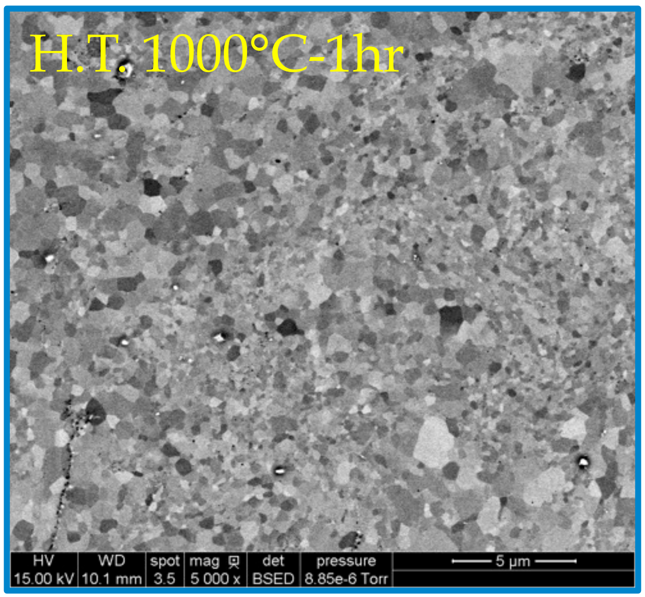
Atomized

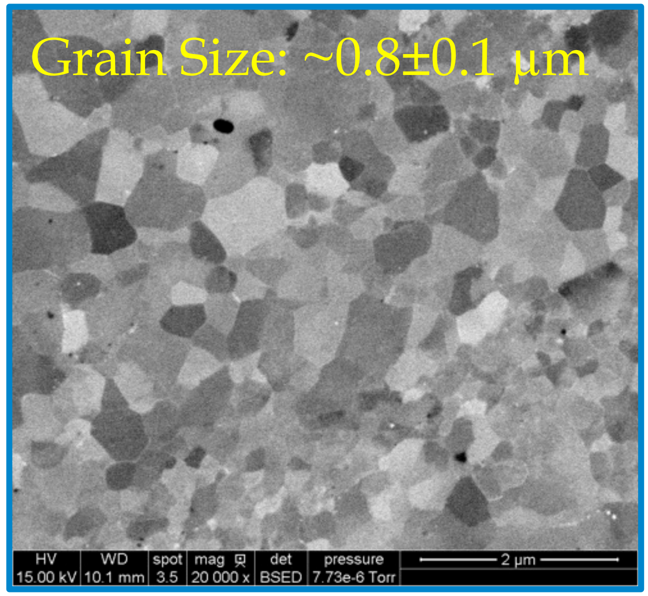




- More uniform distribution of W (Fe_2W)
- Fe_2W solvus ~800°C
- Grains pinned along PPBs

Ball Milled



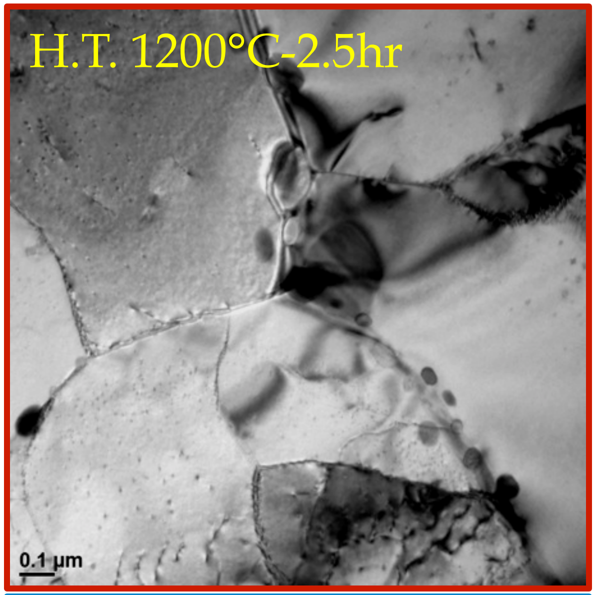


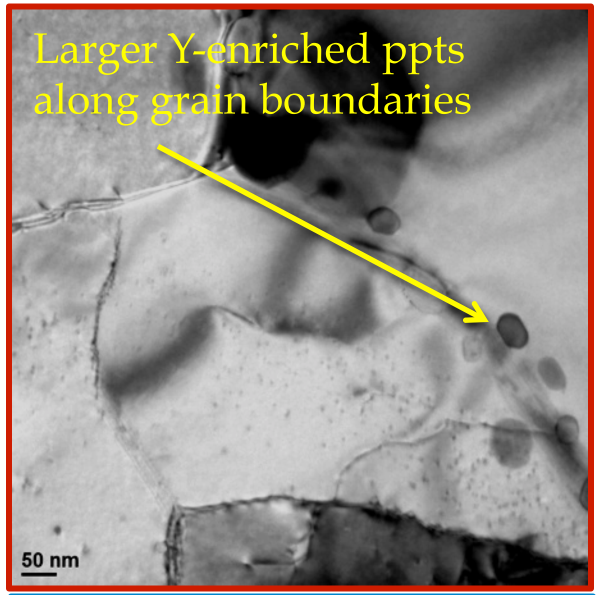
- No recrystallization observed (1000°C or 1200°C)
- Zener pinning

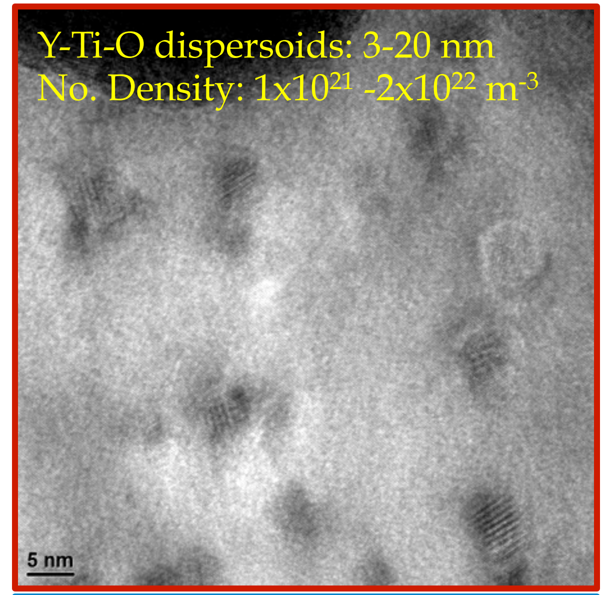
ODS Microstructure

GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O

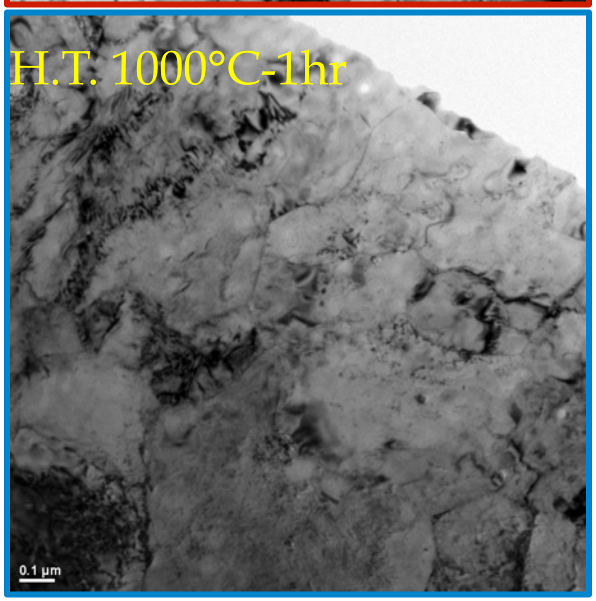
Atomized

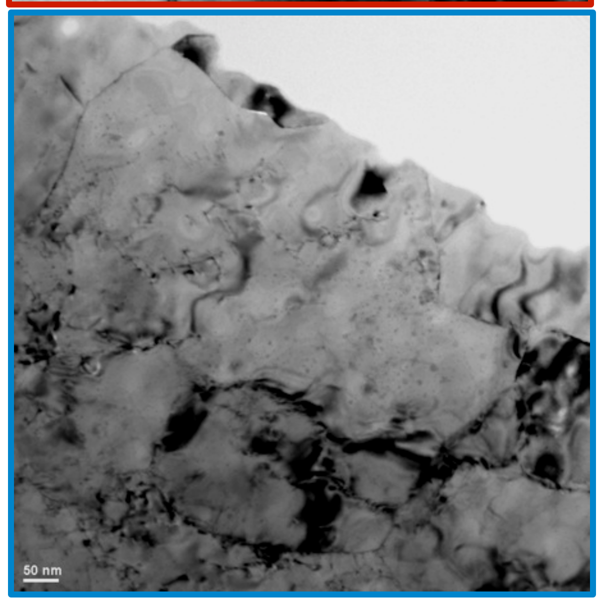


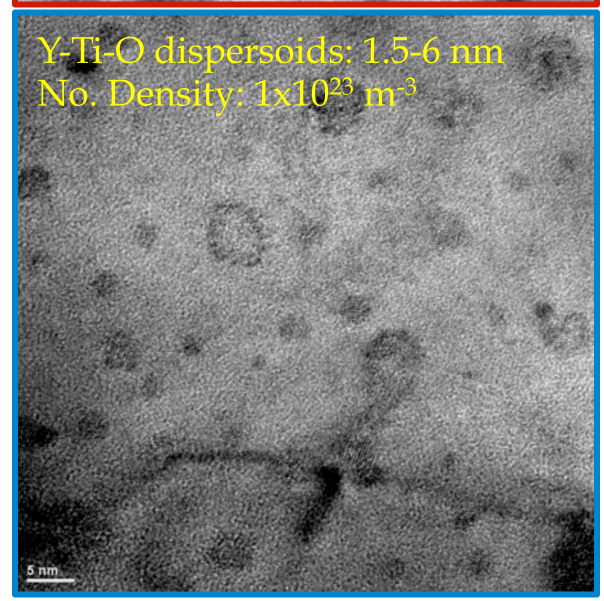




Ball Milled

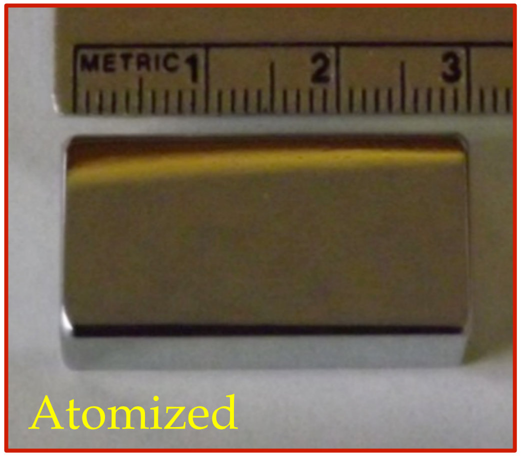


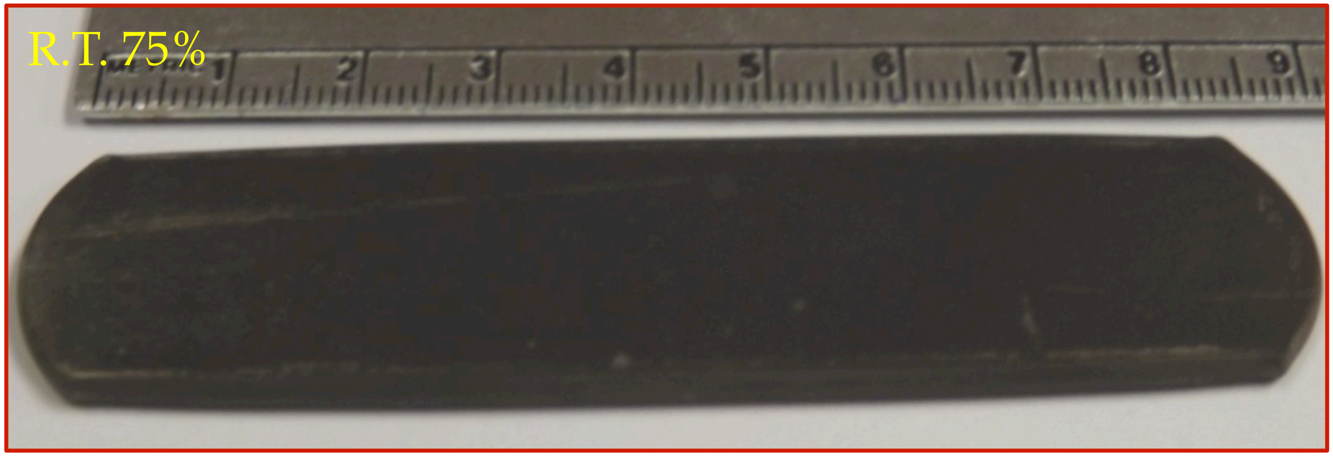


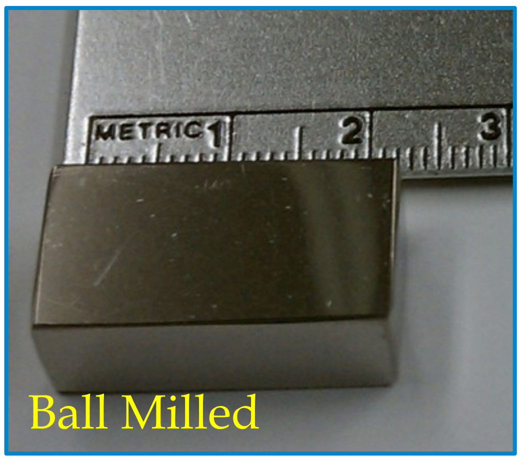


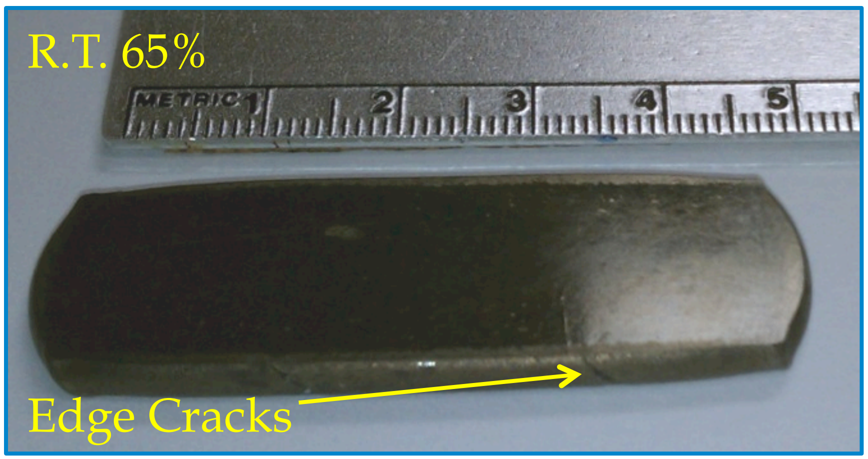
Hot Rolling (650°C)

GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O









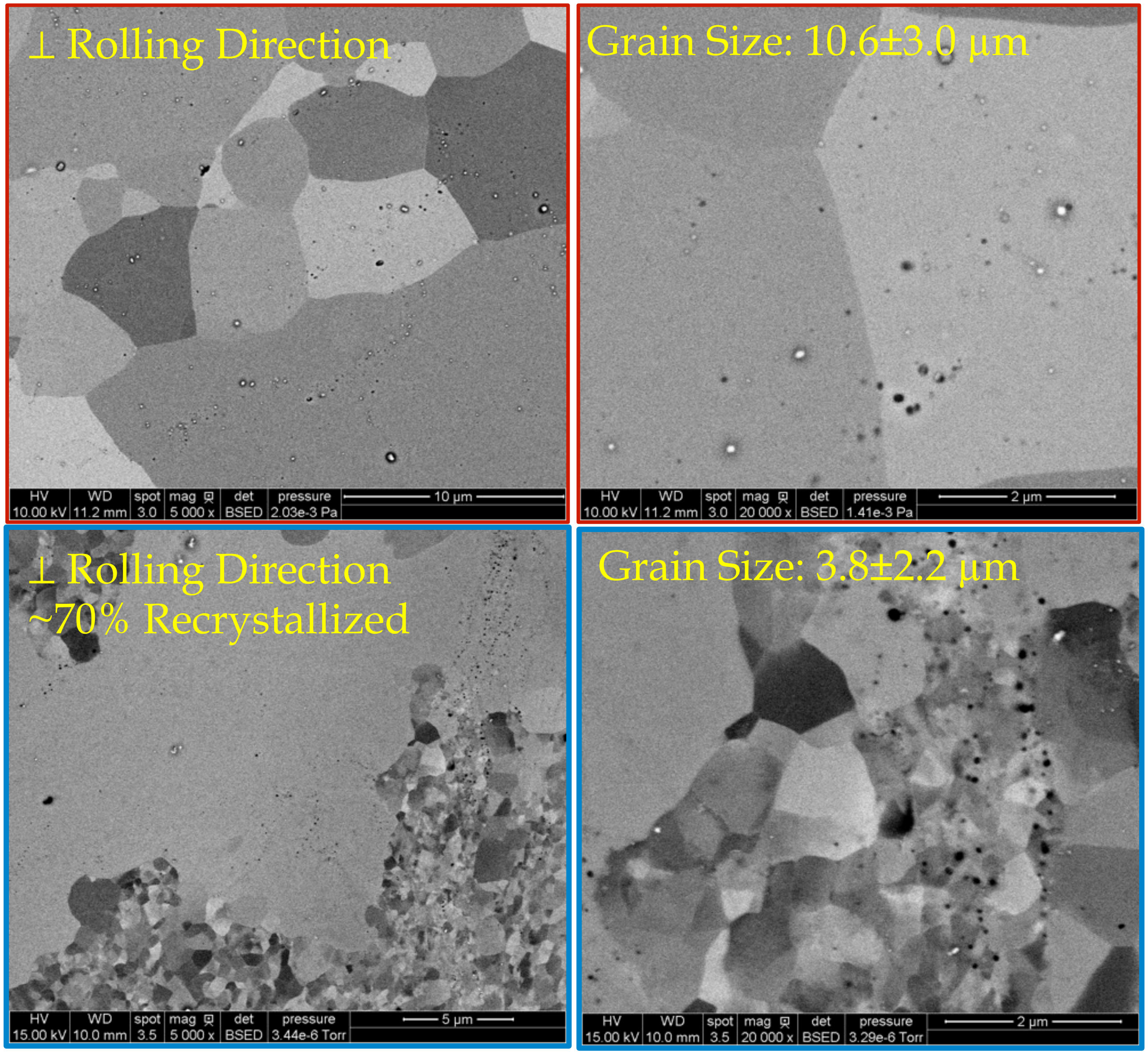
- 650°C – 30 min. initial soak time
- ~9% R.T./pass
- 10 min. hold at 650°C between passes (limited recovery)

Hot Rolled and Annealed 1000°C

GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O

Atomized

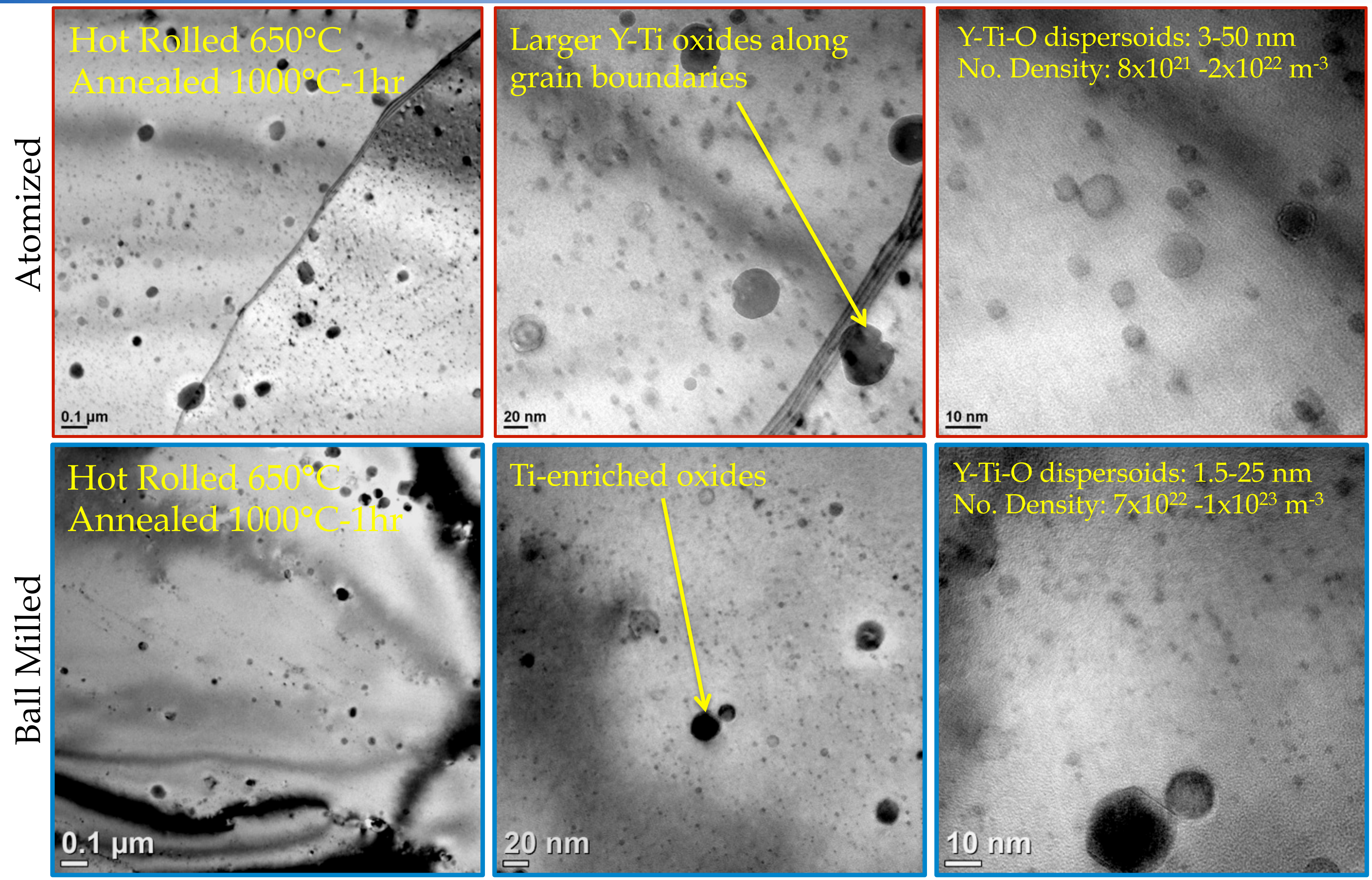
Ball Milled



- Recrystallization (abnormal grain growth) during 1000°C anneal
- Grains grown beyond PPBs (improved ductility)
- Partial dynamic grain recrystallization during hot rolling or during 1000°C anneal?
- Need for deformation processing map

Final ODS Microstructure

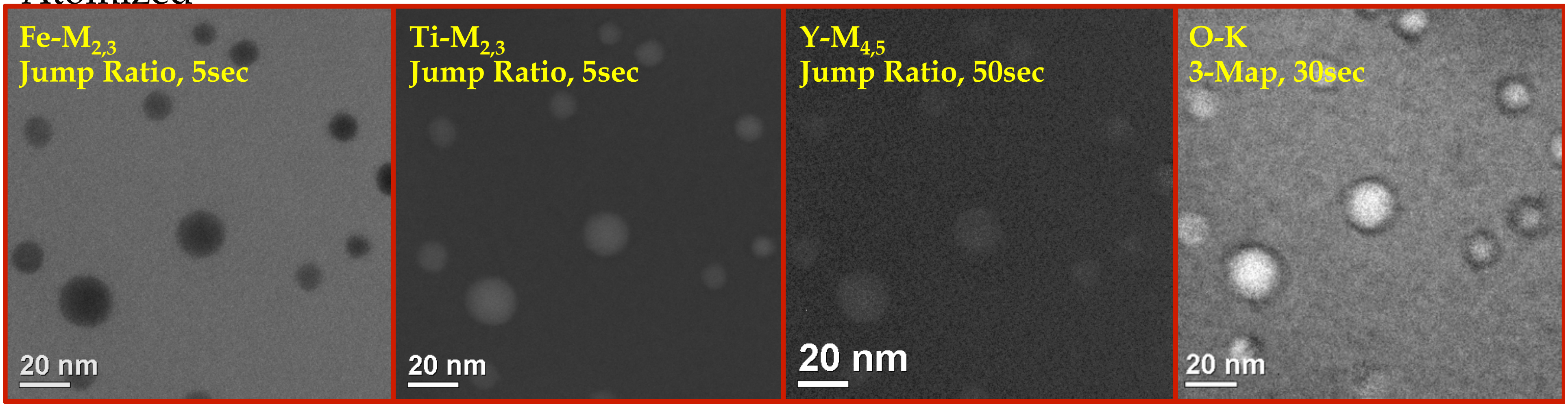
GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O



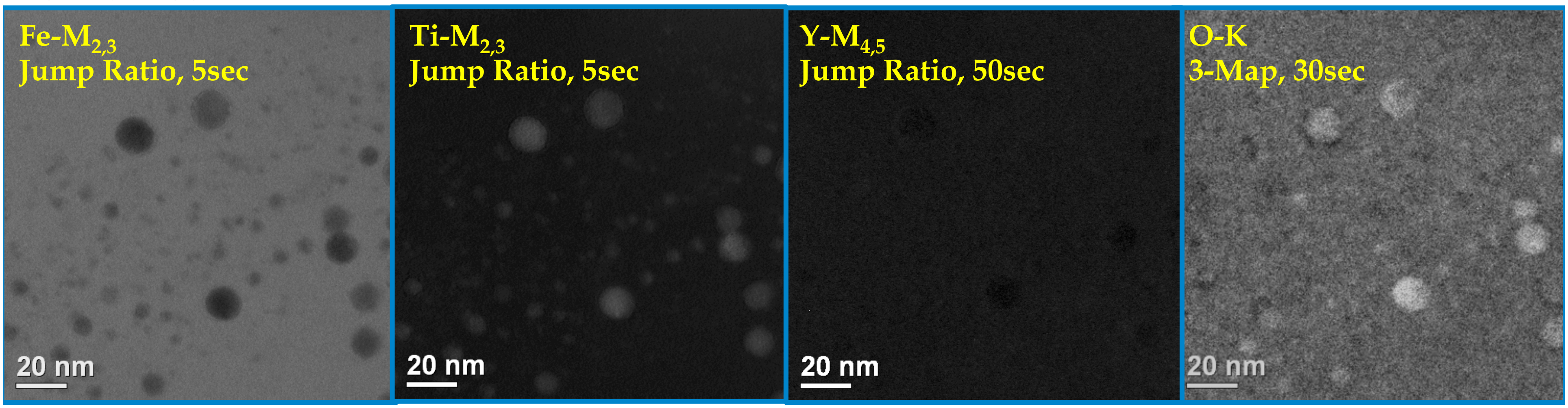
Dispersoid Chemistry (EFTEM)

GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O

Atomized

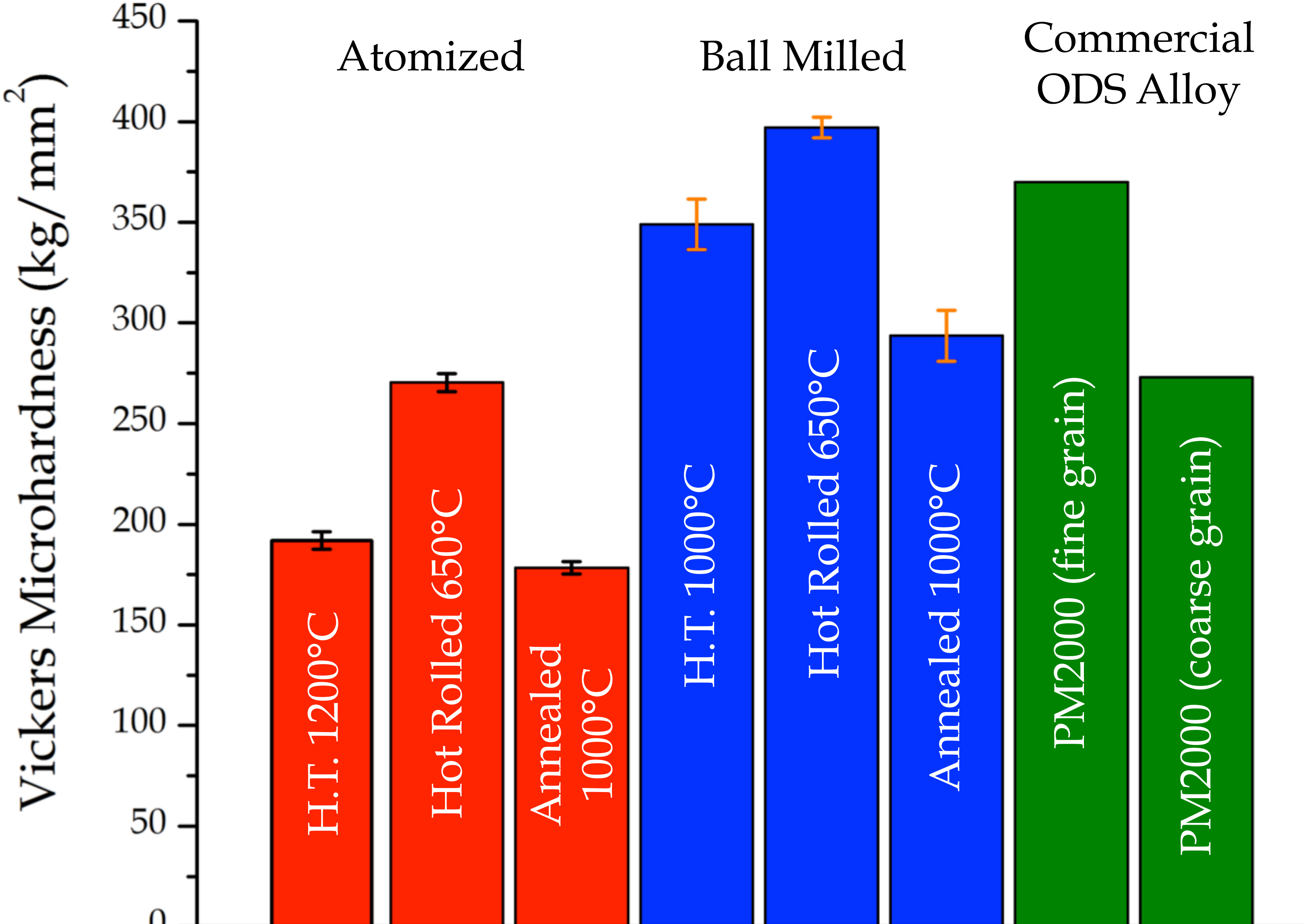


Ball Milled



Microhardness

GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O

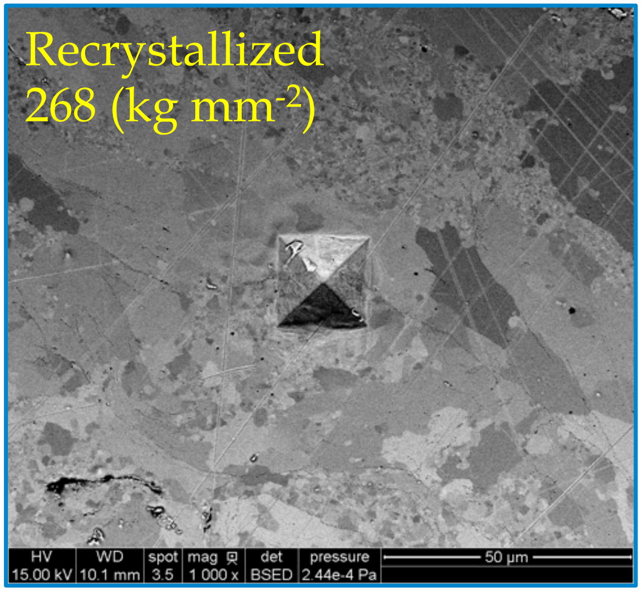


A. Alamo et al., CEA/Saclay, DOE/CEA I-NERI Prog. Review, 2003

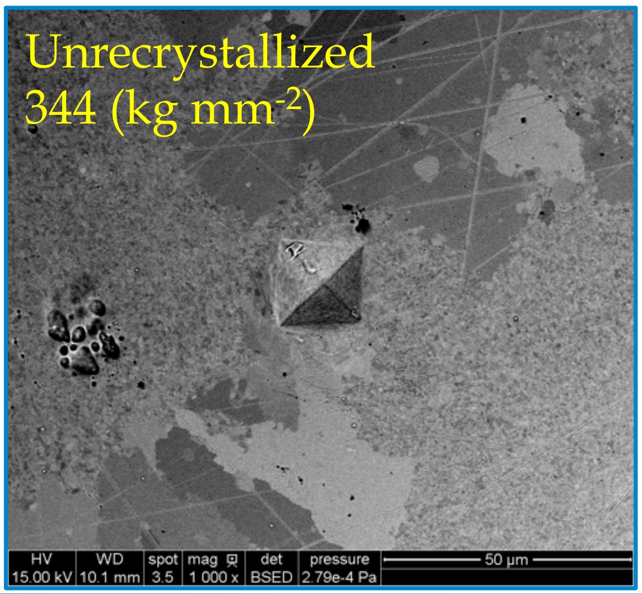
Localized Microhardness

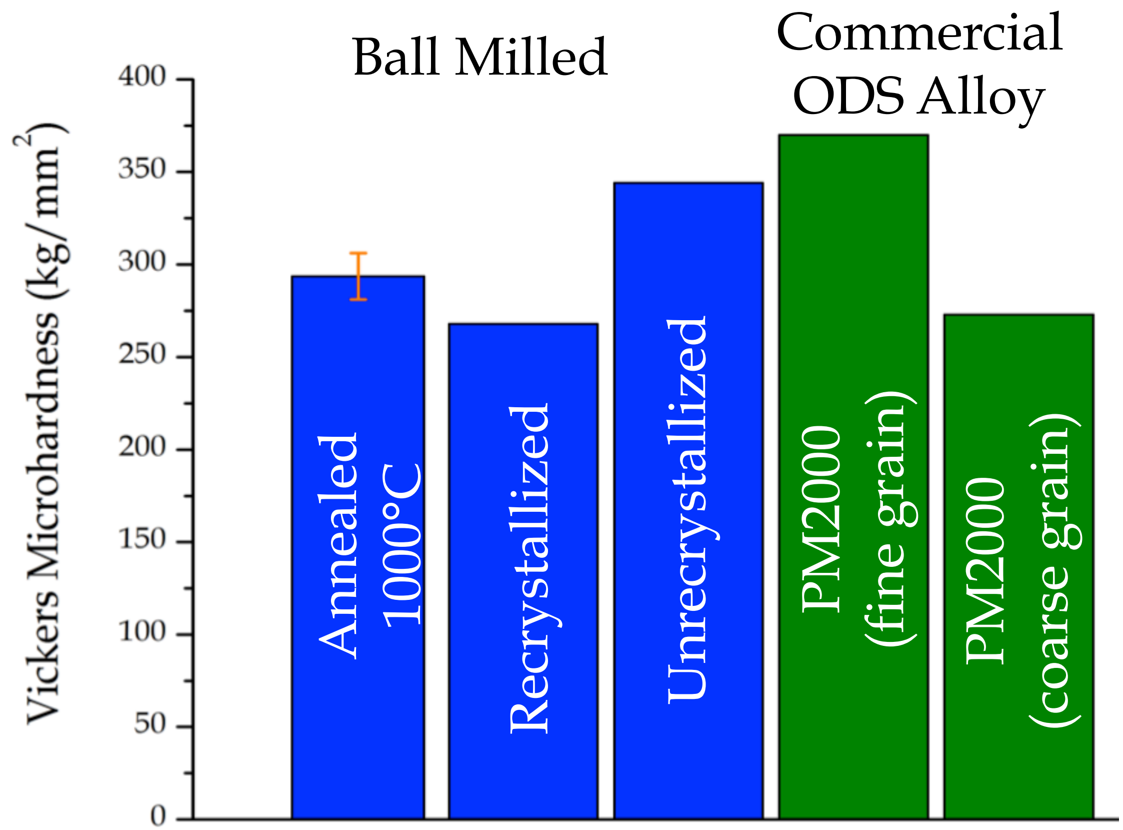
GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O

Ball Milled



Ball Milled



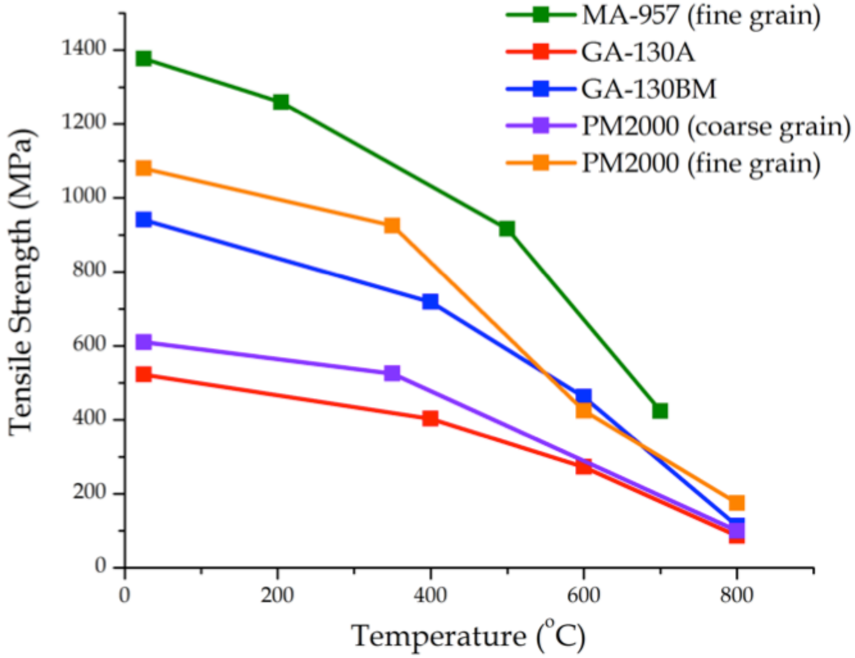


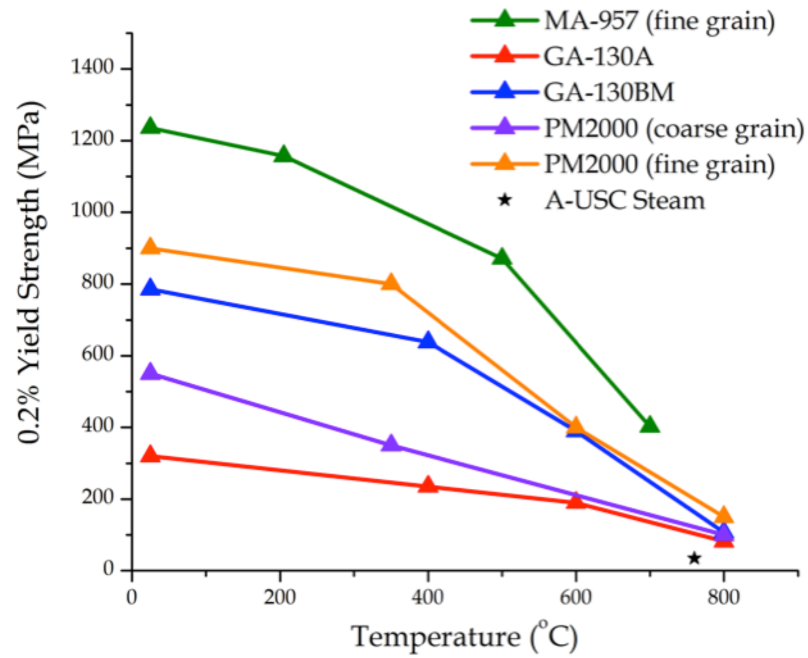
- Microhardness as a function of grain size agrees well with previously presented results on fine and coarse grained PM2000

-A. Alamo et al., CEA/Saclay, DOE/CEA I-NERI Prog. Review, 2003

Elevated Temp. Tensile Strength

GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O



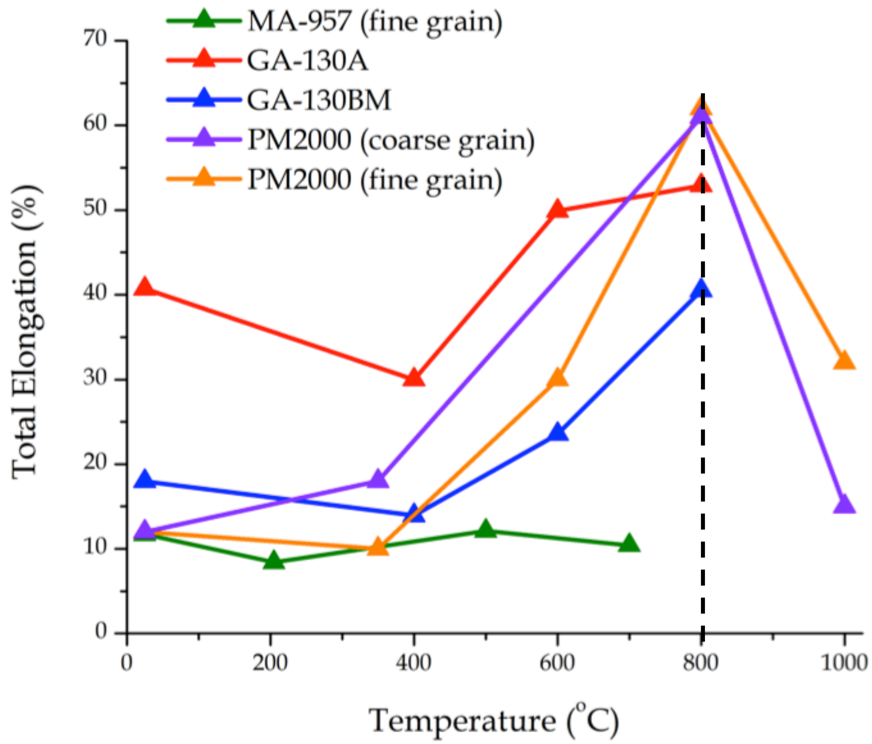


Alloy	Dispersoid (vol.%)	Grain Size (μm)
MA-957 (fine)	~1.0	Unrecrystallized (dia. < 1)
GA-130A	**~0.4**	**Recrystallized (10.6 ±3.0)**
GA-130BM	**~0.4**	**Partially recrystallized (3.8 ±2.2)**
PM2000 (coarse)	~1.0	Recrystallized (~500-1,000)
PM2000 (fine)	~1.0	Unrecrystallized (dia. < 10)

J.J. Fischer, US Patent 4,075,010,21, 1978 (MA-957)
A. Alamo et al., CEA/Saclay, DOE/CEA I-NERI Prog. Review, 2003

Enhanced Total Elongation

GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O



- GA-130A and GA-130BM illustrate good ductility with only modest decrease in elevated temperature ductility (800°C) compared to PM2000, possibly related to residual PPB oxide (GA-130A) or contamination (GA-130BM)

- Ductility peak (800°C) associated with transition between transgranular and intergranular fracture

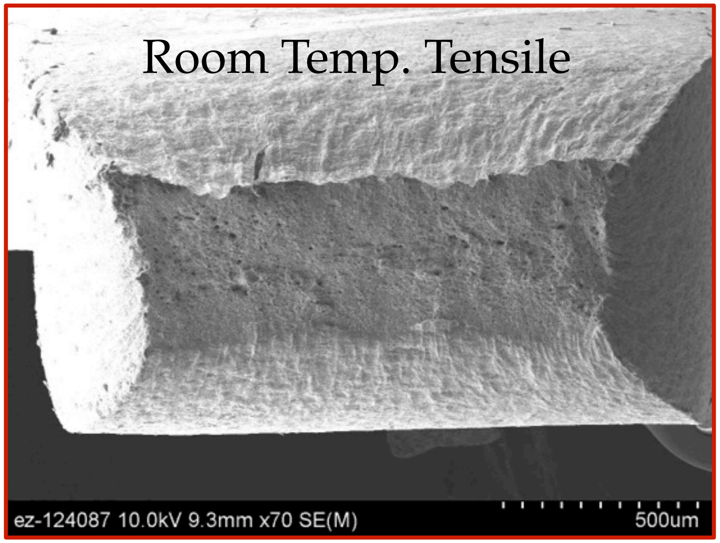
-A. Steckmeyer et al., J. Nucl. Mater., 2010.

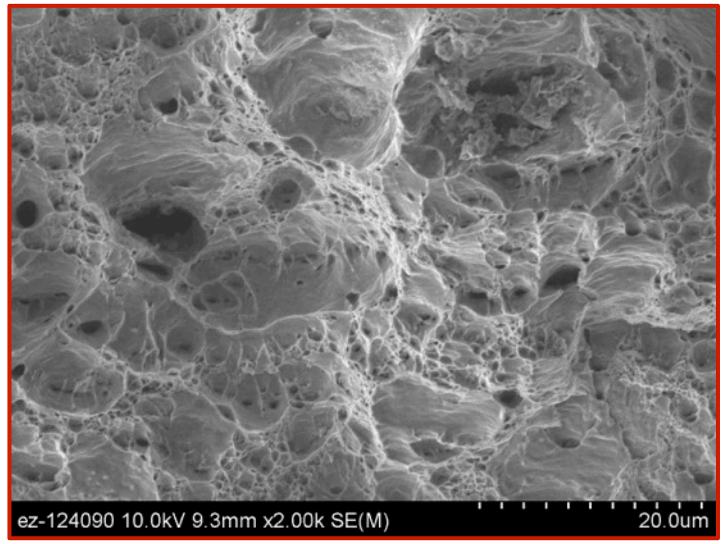
J.J. Fischer, US Patent 4,075,010,21, 1978 (MA-957)
A. Alamo et al., CEA/Saclay, DOE/CEA I-NERI Prog. Review, 2003

Fracture Analysis

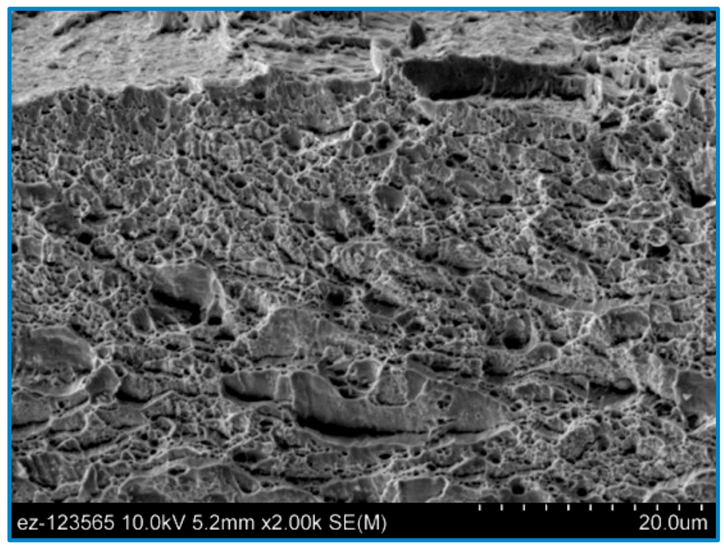
GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O

Atomized





Ball Milled



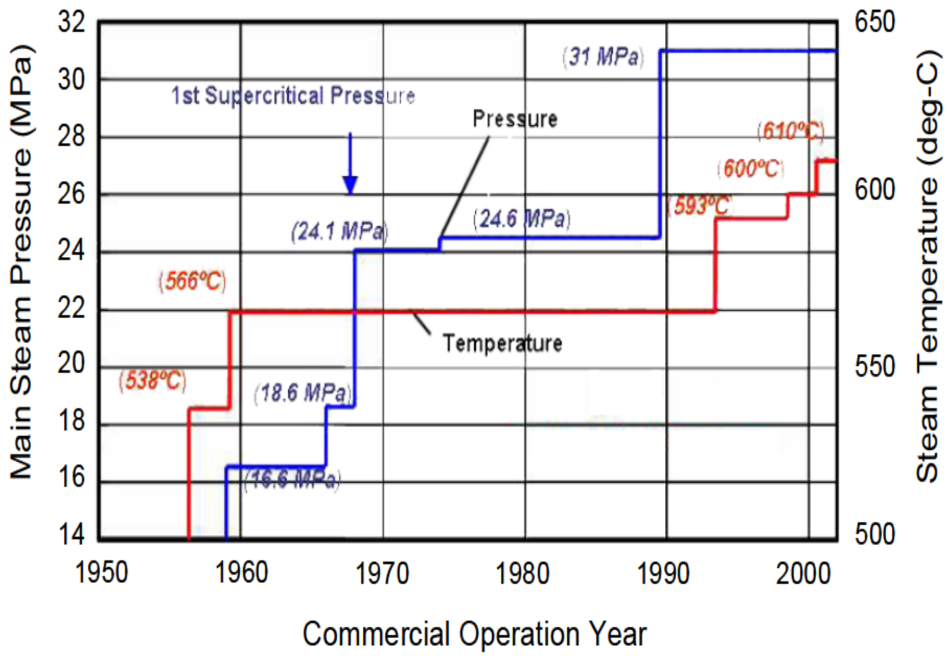
Summary

GA-130A: Fe-16.3Cr-0.9W-0.6Ti-0.08Y-0.26O
GA-130BM: Fe-15.8Cr-0.9W-0.6Ti-0.08Y-0.57O

- Two manufacturing routes were highlighted as viable methods for improved processing efficiency of Fe-based ODS alloys (i.e., direct consolidation or short ball milling of GARS powders)
- Short ball milling (5 hr) of GARS powders resulted in reduced Y-microsegregation, yielding smaller and more uniformly distributed nano-metric oxide dispersoids (Y-Ti-O)
- Both alloys illustrated good workability at 650°C (rolled to ~65% RT)
- Partial or full recrystallization occurred during 1000°C anneal following hot rolling (need for deformation processing map)
- GA-130A (direct consolidation) displayed hot tensile properties similar to recrystallized PM2000, while GA-130BM (ball milled) exhibited strengths similar to unrecrystallized PM2000, and both alloys showed good high temperature ductility (T.E. ≥ 40% at 800°C)

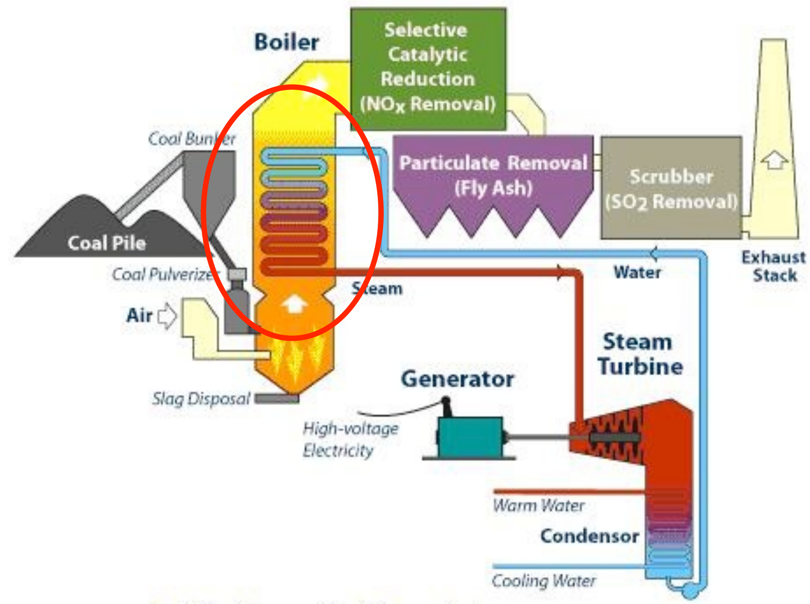
Advanced Ultra-Supercritical Power Plants (A-USC)

- Boiler tubing exposed to two extreme environments
  - Outside exposed to sulfidizing environments (**fireside**)
  - Inside exposed to supercritical steam (**steamside**)



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

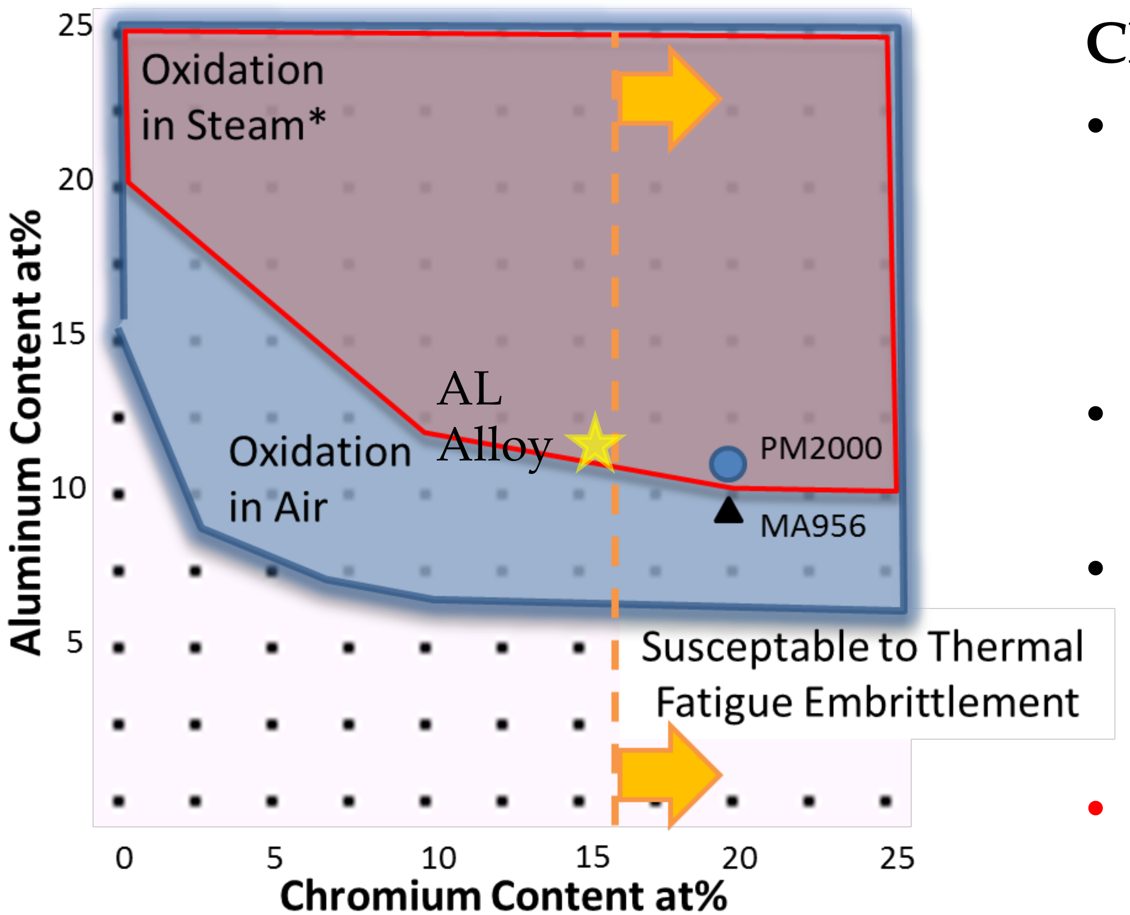
Schematic of Coal-fired Power Plant



- Increases in pressure and temperature planned for commercial plants to increase efficiency.
- A-USC conditions of 760°C, 35MPa
  - Tubing may be at 785°C
- Lifetime of 60 years

P.D. Sharma, Supercritical Coal-Fired Power Plant (2009)

Steamside Oxidation Resistant Alloy Design with Cr+Al



*Steam Conditions of 700°C with 10 vol% H_2O and Air conditions at 800°C

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

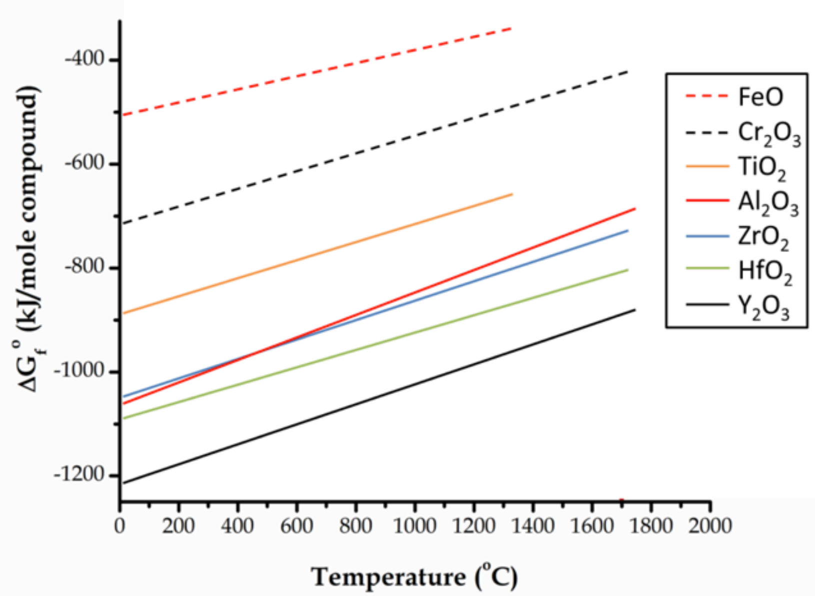
Choices:

- Less than 16 wt% Cr to avoid thermal issues
  - Previous ODS alloys contained too much Cr
- Design for conditions on steamside tubing
- Fireside will need to be protected by coatings

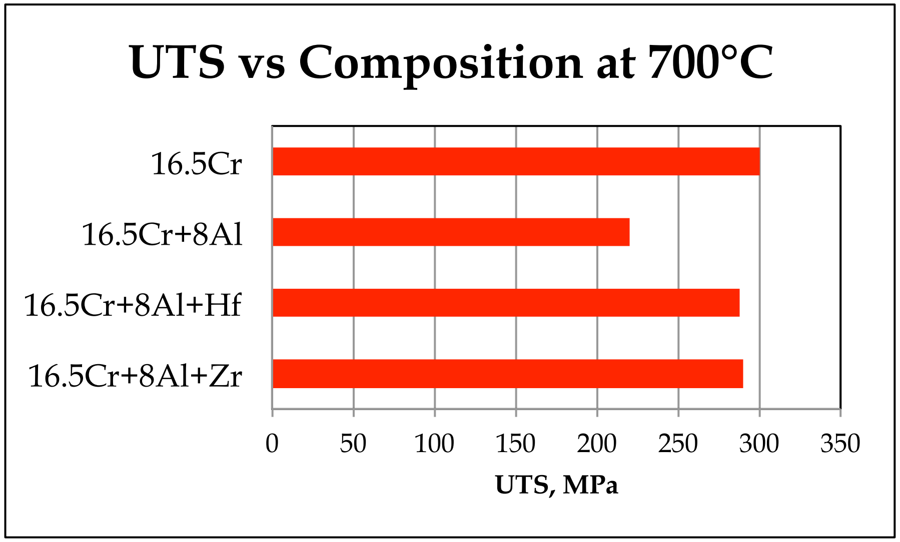
- Alloy selected with 16 at% Cr and 12 at% Al

Why Not Simple Al Addition to ODS Ferritic Steels?

- Large decrease in strength when Al added to traditional ODS
  - Attributed to distribution of Y-Al oxide instead of Y-Ti
- Strength can be recovered through additions of Hf, Zr



Free energy of formation for various oxides

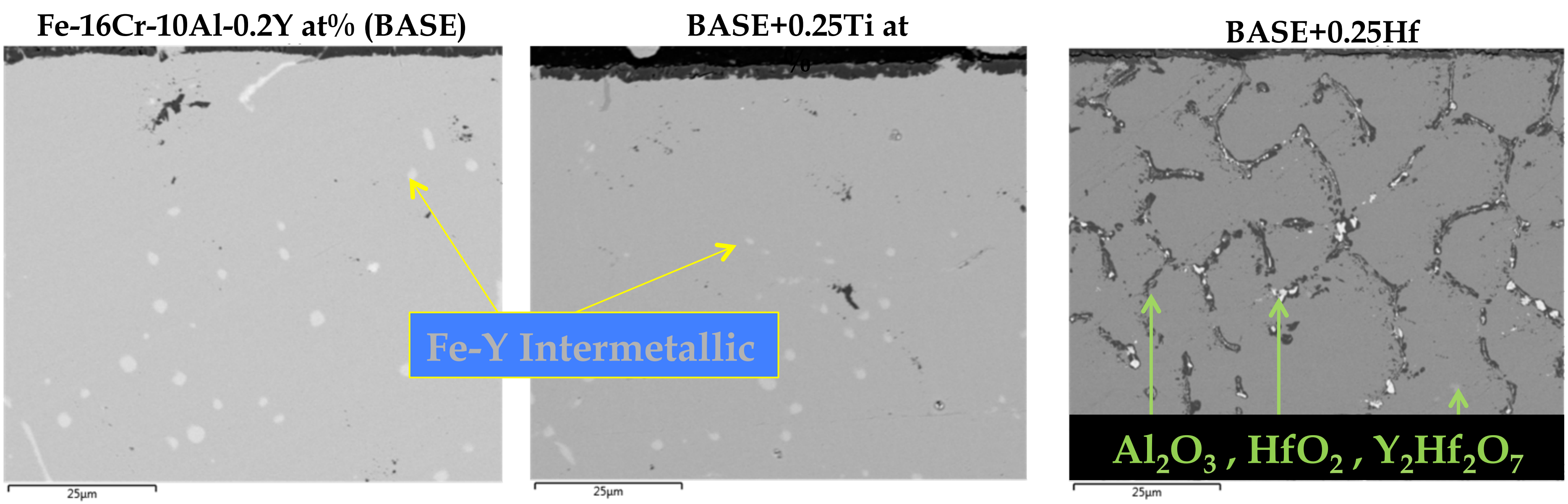


Adapted from Kimura et al., Jo.NM, 2011

- ZrO_2 and HfO_2 have higher negative 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.%)

Surface Oxide Penetration in Cast Alloys

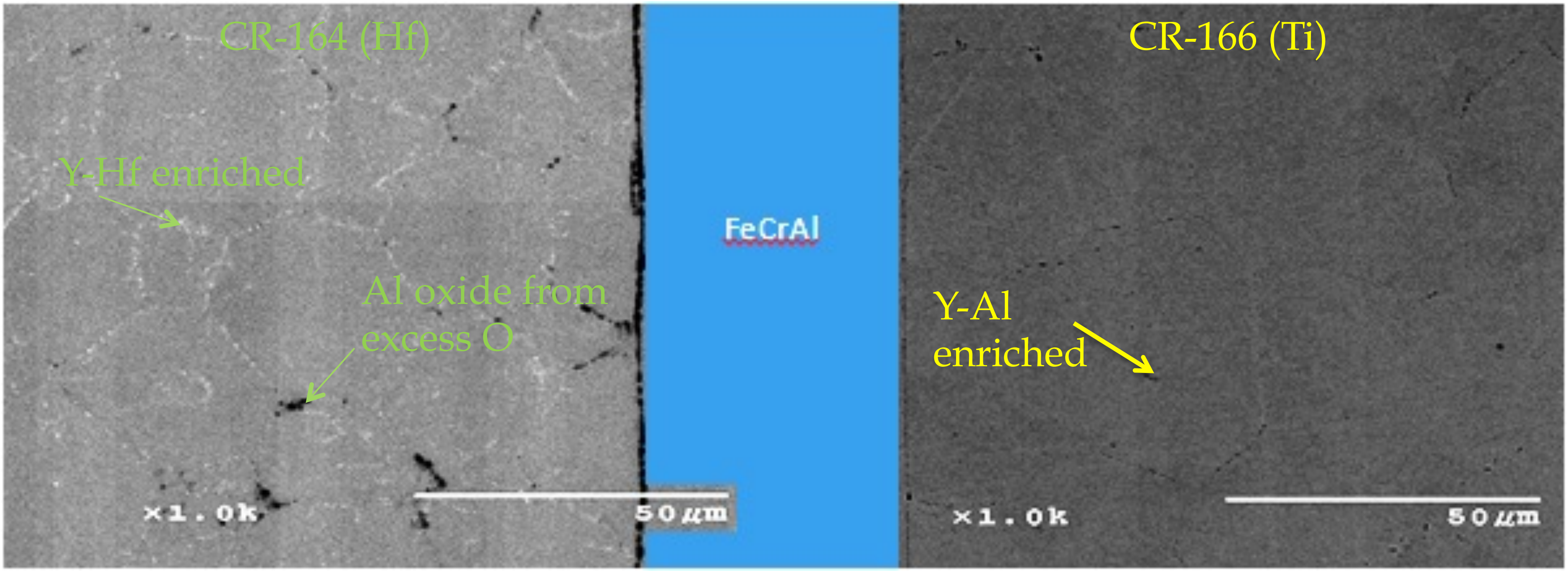


- Rhines' Pack used to simulate GARS exchange reaction (post-consolidation)
- HT with Cr-Cr_2O_3 at 1160°C for 10 hr.
- All alloys formed surface Al_2O_3
- Base and Ti-added samples had little to no oxygen penetration and formed some complex Y-Al oxides
- Hf-added sample had extensive oxygen penetration within cast microstructure – about 400 µm
  - Al_2O_3 and HfO_2 were not present closer to interface of reaction
- Hf addition seems to prevent Y diffusion to surface to react with Al

Alloy	Fe	Cr	Y	Hf	Ti	O
CR-164	Bal	15.55	0.09	0.12	0	0.69
CR-166	Bal	15.91	0.09	0	0.12	0.42

Al Diffused into ODS Alloys

HT at 1000°C for 24 hours



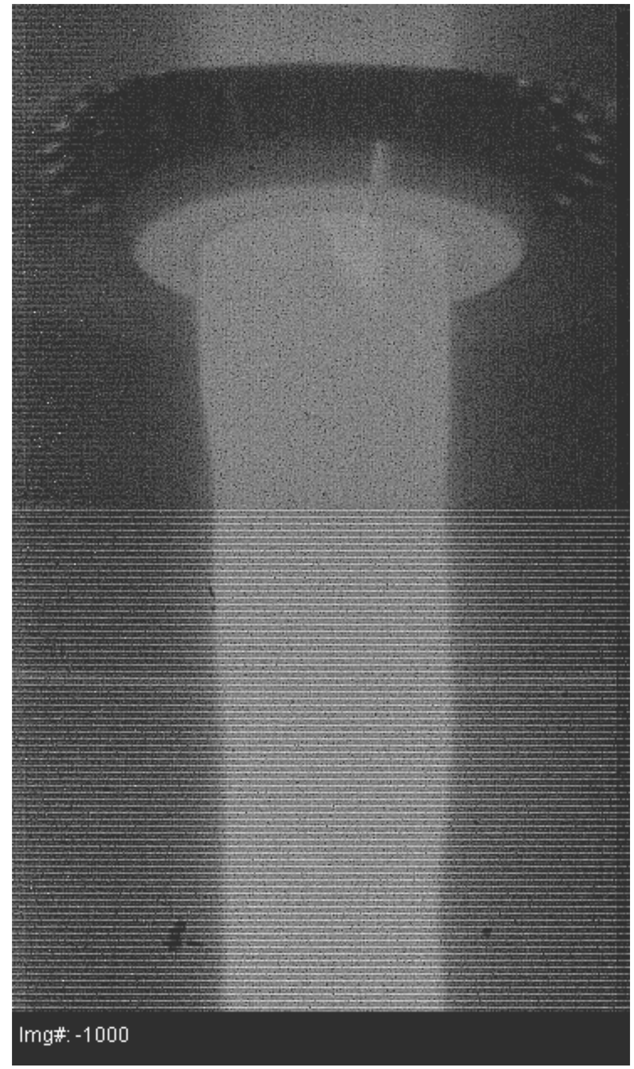
- ODS Alloys from GARS powders/HIP
- Diffusion couples were set up to investigate stability of previously formed Y-Hf or Y-Ti oxides
- Al content of approximately 18at.% was found in CR-164 and 13at.% in CR-166

- WDS analysis showed some oxides enriched in Y and Al in CR-166 with none in CR-164
- Y-Hf oxides stable
- Y-Ti oxides began conversion to Y-Al oxides

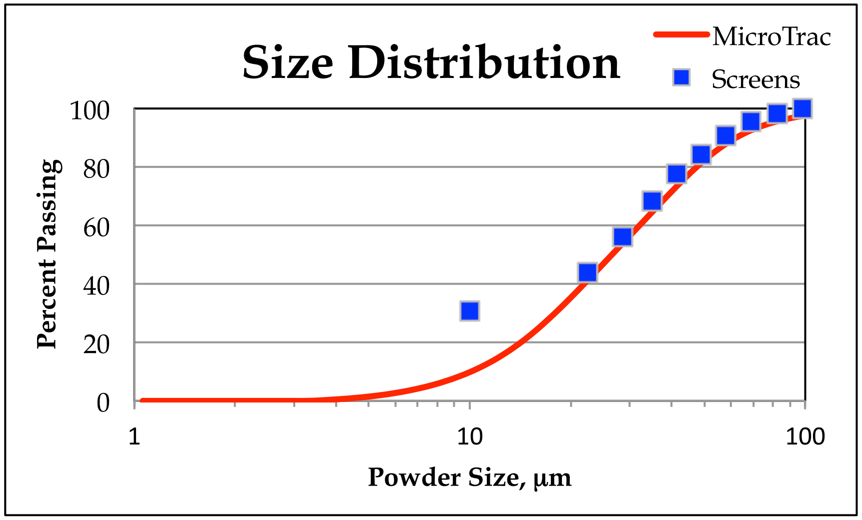
Selected ODS Precursor Powder Alloy Composition

	Comp (at.%)	Comp (wt.%)	Purpose
Fe	Bal.	Bal.	Base Material
Cr	16	15.6	Corrosion
Al	12	6.1	Corrosion
W	0.9	3.1	Strengthening
Hf	0.25	0.84	Dispersoid
Y	0.2	0.33	Dispersoid

- Reduced Cr chosen to avoid embrittlement with sufficient Al 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
- Atomized with reaction gas of Ar-0.19vol% O_2

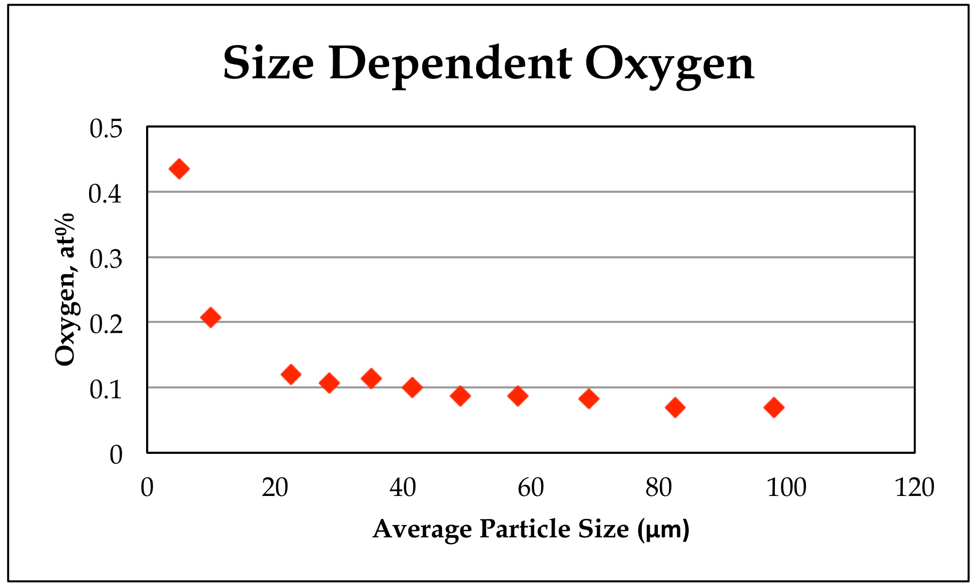


Successful GARS Powder Production



- Reaction gas oxygen value tuned for fine powders (-10 µm)
  - Finer particles will have increased oxygen (surface area)
  - Oxygen in large powders can be increased through reactive processing (HVOF or ball milling)

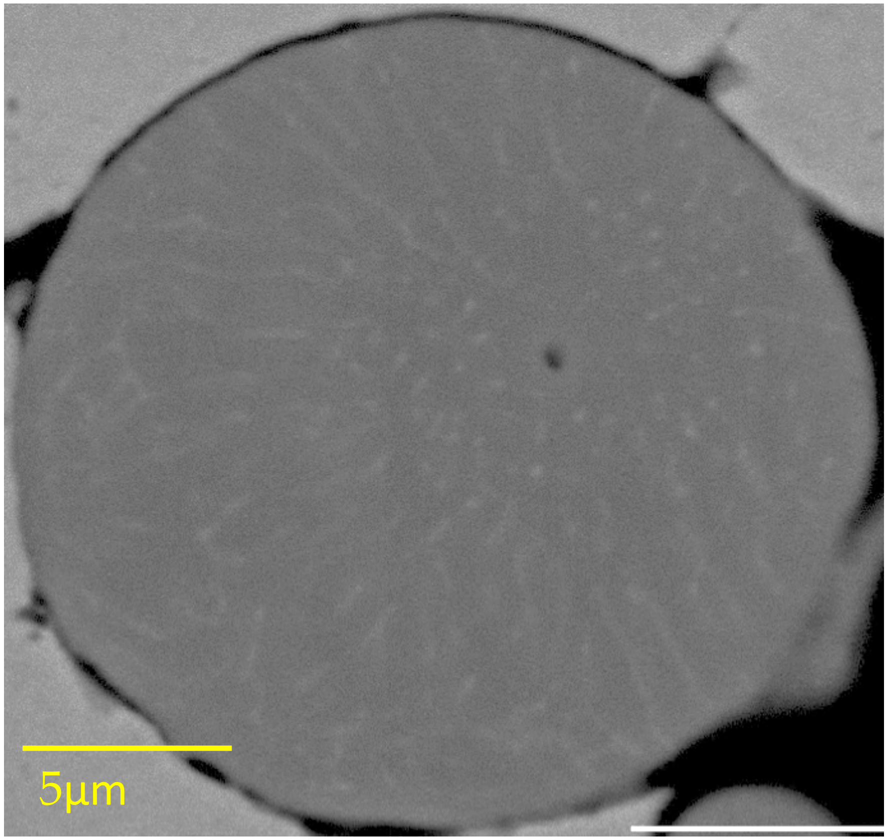
- d_{50} = 27 µm
- Composition verified through NSL analysis
  - Oxygen values taken from stack of screens
- Surface Oxide Enriched in Y or Fe

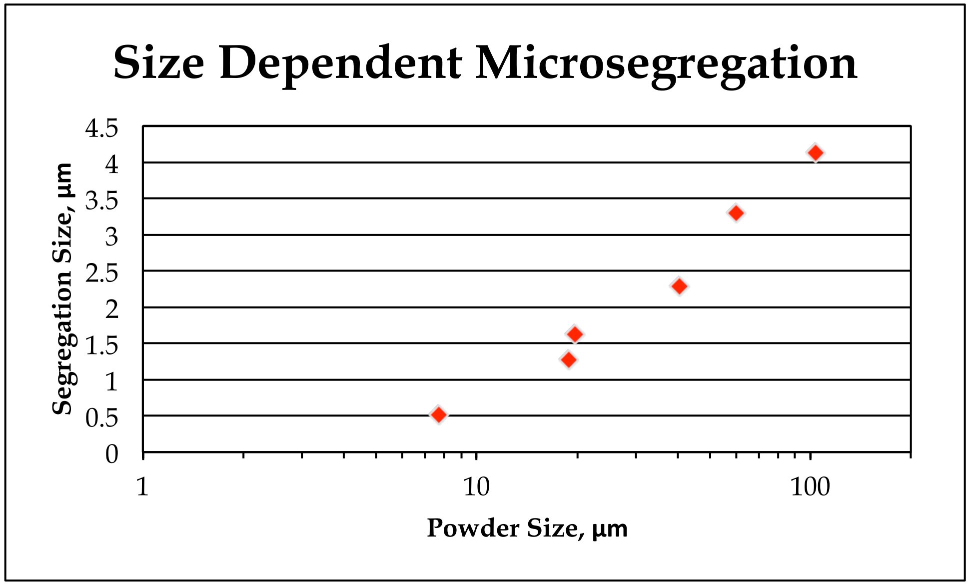


Alloy (at%)	Fe	Cr	Al	W	Hf	Y
Nominal	Bal	16	12	0.9	0.25	0.2
Actual	Bal	15	12.3	0.9	0.24	0.19

Microsegregation Trend due to Rapid Solidification

- Powders cold isostatic pressed with 75vol% Cu to analyze cross-sections

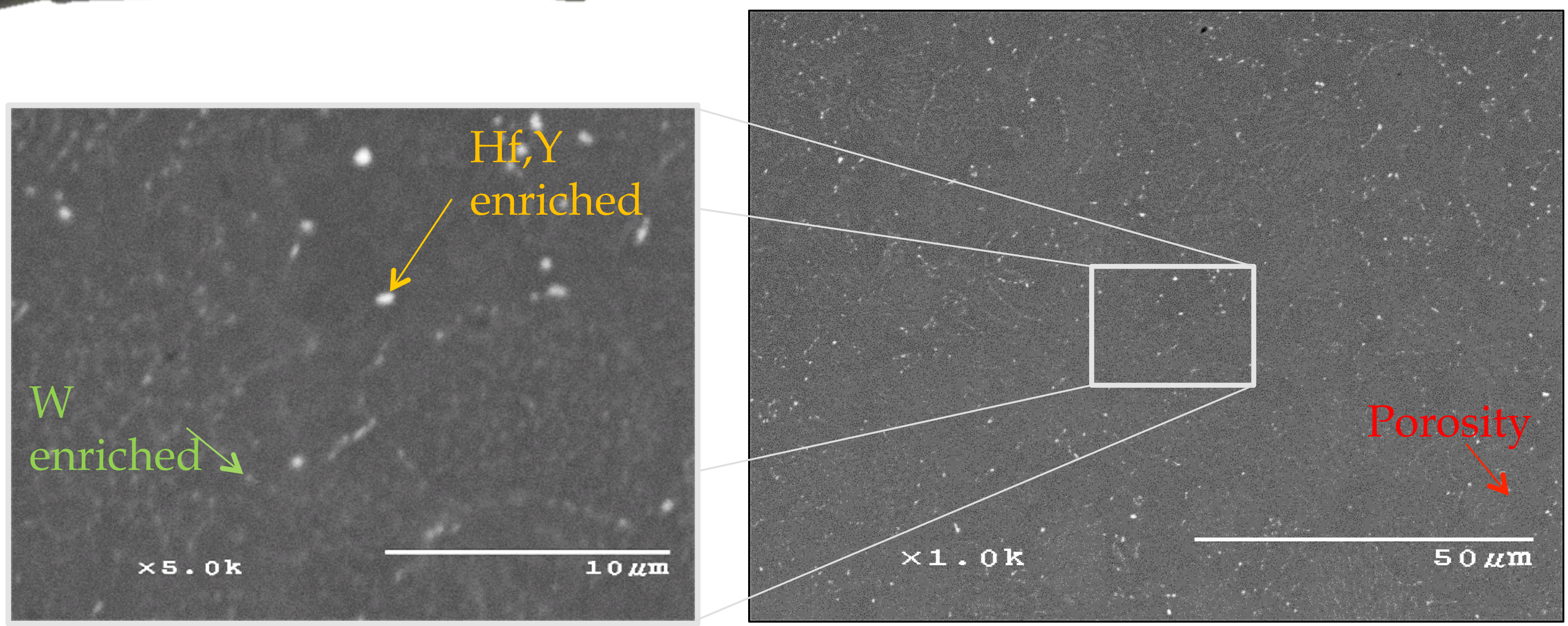




- Finer powders quenched (gas cooled) faster and display high undercooling.
- Solute segregation suppressed by rapid solidification
- Segregation size (spacing) should approach 0 (solute trapping) at approximately 7 µm
- Segregation phase enriched in Y and Hf
  - W not present in intercellular phase

HIP Consolidation of Fine Powder

- Sieved to dia.< 20µm powder
- Loaded in 316 SS can and outgassed
- Vacuum sealed by e-beam welding
- Consolidation by hot isostatic pressing (HIP)
  - Desired temperature of 850°C 300MPa for 4h
  - Error caused HIP to stop at 850°C 200MPa for 13h then was raised to 300MPa for 4h



Summary

Al Additions to ODS Ferritic Stainless Steel:

- Need for Al addition in Fe-based ODS
  Designed alloy to resist steamside oxidation.
- Modified CR Alloy with Al addition
  Developed Hf additive to assist in Al incorporation in ODS alloy.
- Gas atomization experiment results
  Performed successful GARS experiment on Al containing ODS alloy.
- Initial HIP consolidation of Fe-base ODS with Al
  Will perform processing and characterization studies.

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