Low Cost Fabrication of ODS Alloys

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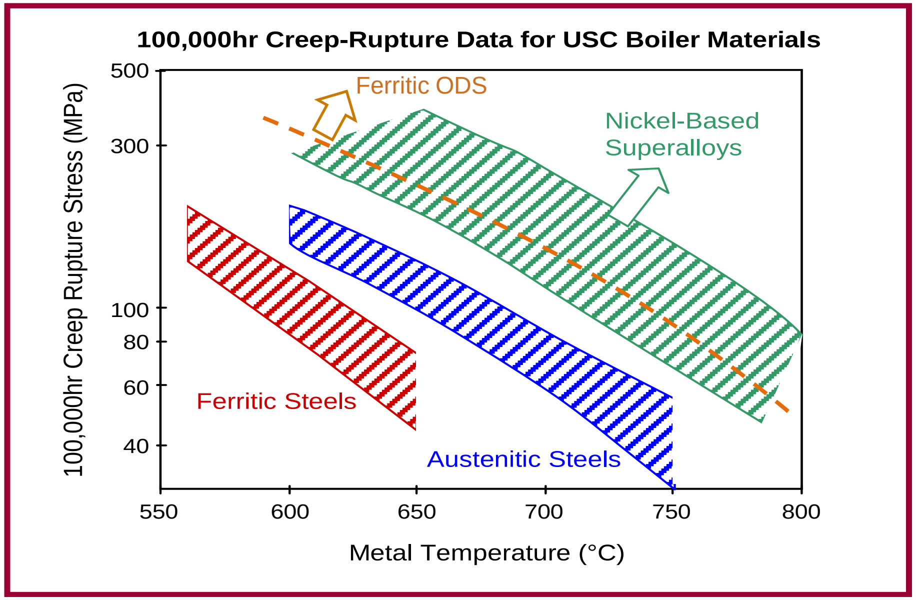
NFA / ODS Alloys have excellent performance in both creep and oxidation resistance



From P. J. Maziasz et al., DOE-FE(ARM) 2005 proceedings

So why don't we have a myriad of ODS products ?

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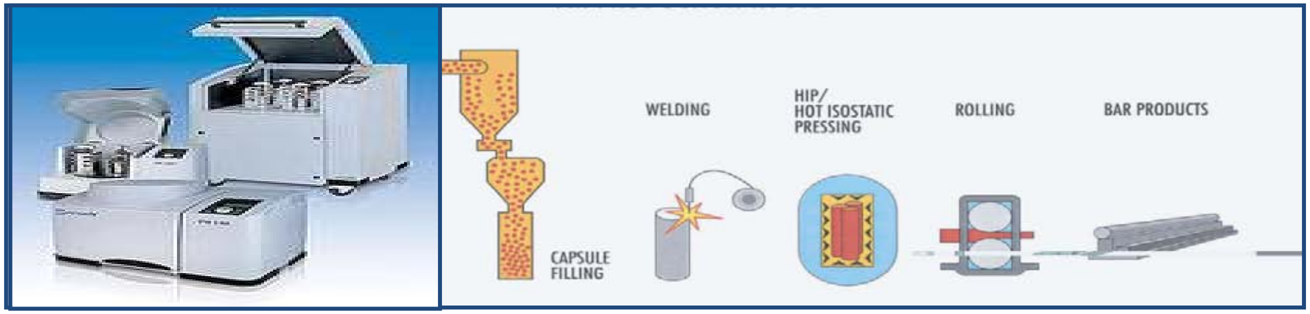
Cost

- The high cost of ODS alloys and components is driven by the multistep process of fabrication from powder
  - Make the powder in the first place, mix and mill of oxide particle, vacuum canning, densification CIP/HIP, decanning, and processing to semi-finished form (extrusion or rolling), machine or roll to tube, then heat treat for microstructure
  - Batch Process
  - Machining operations produce significant waste. Many ODS materials produced in the past for pipe or clad applications are extruded and then gun drilled.



Cost estimates for current processing route

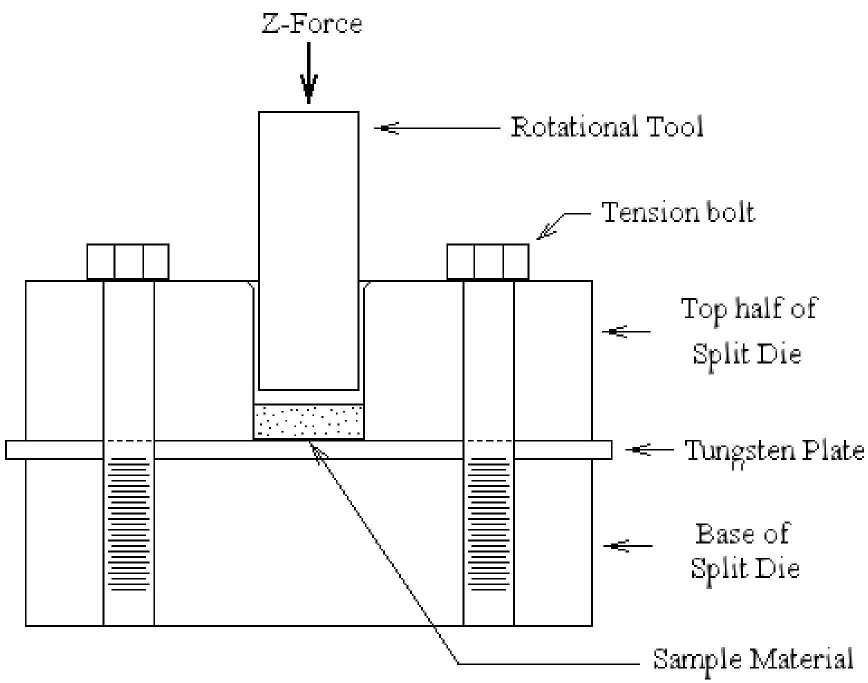
Front End (Powder processing): \$10.00/lb to \$50.00/lb
Back End (Consolidation): \$50 to \$80.00/lb

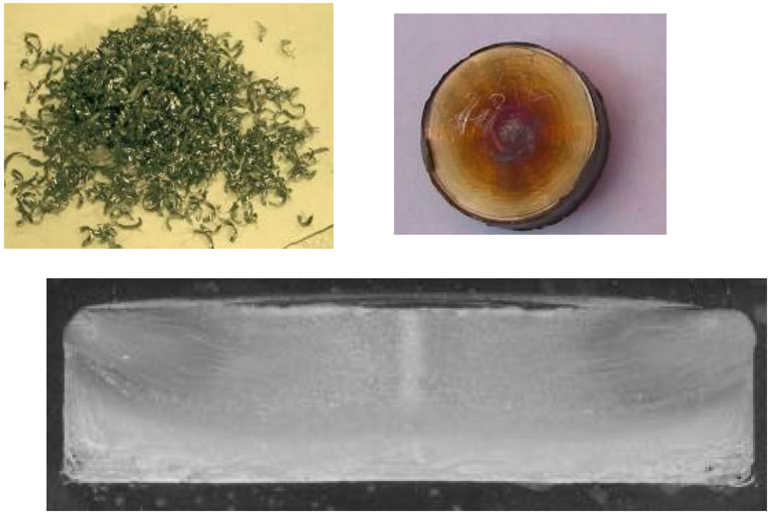
Traditional ODS materials prepared by MA routes can be \$60.00/lb to \$150.00/lb and wrought, semi-finished products can be \$200 to \$400 per lb

Are there alternative process routes that can remove the some of the cost when going from powder to semi-finished product ?

Friction Consolidation

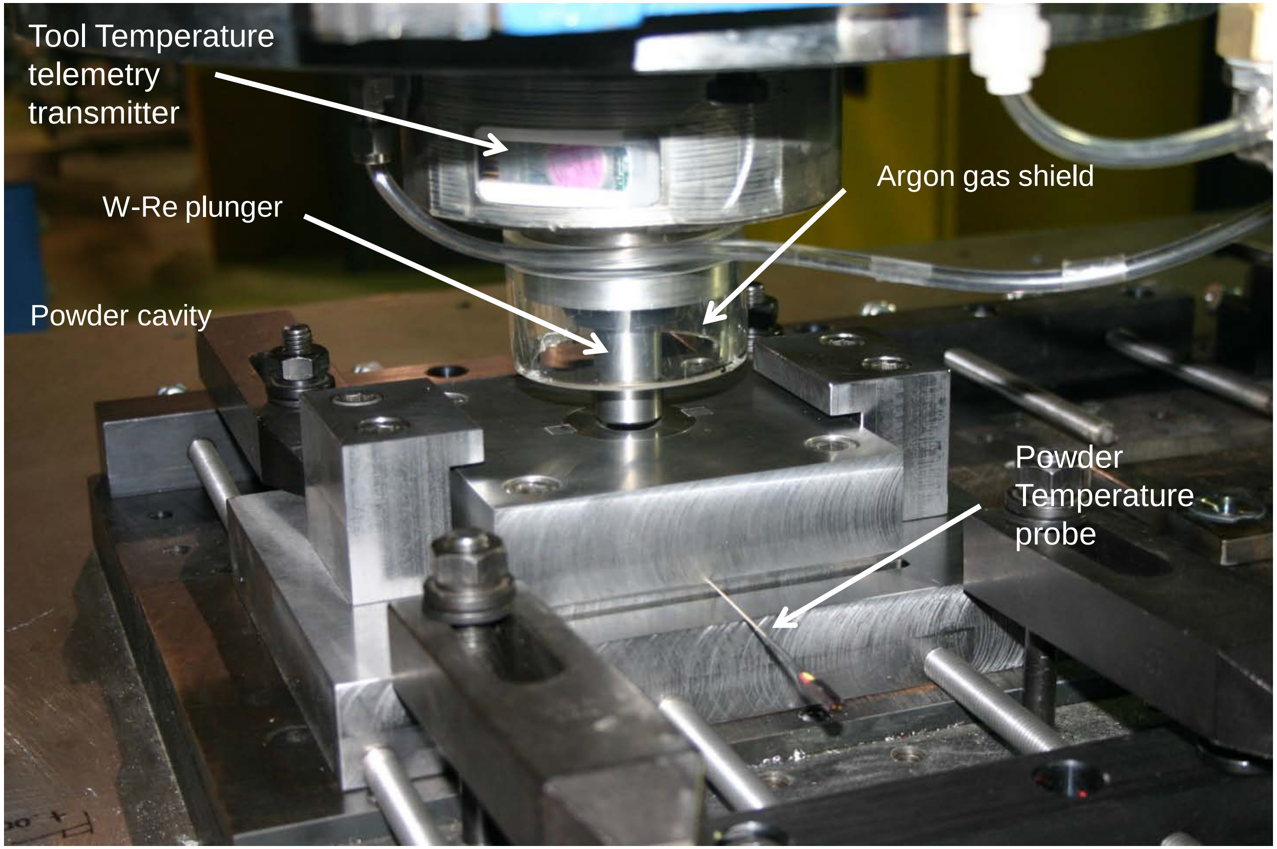
- Powder is loaded directly into cylindrical hole in die can
- Spinning cylindrical tool is inserted in top half of split die and downward axial force is applied while spinning tool
- Heat is generated initially by friction between particles, but as the powder consolidates the heat is generated by plastic work energy dissipation.
- Fully dense compacts result



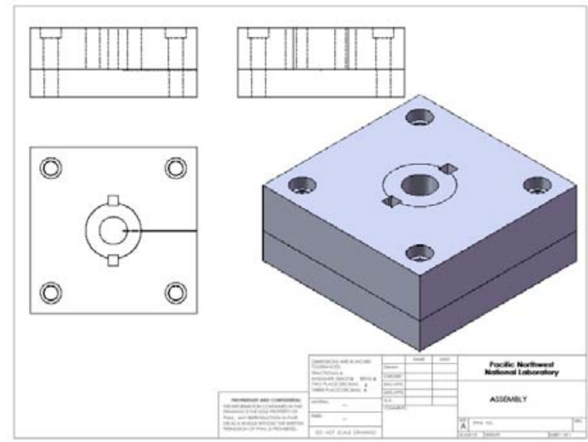


A. Reynolds, USC,2010

Friction Extrusion Die at PNNL



- Powder Chamber is approximately 1.25” in diameter



- Base plate lower half : Ni 718
- Upper half and charge chamber: H13, 718,etc.
- Spinning tool: 1.25” diam W25Re4HfC

Die and powder can mounted in high-load Friction Stir Welding machine

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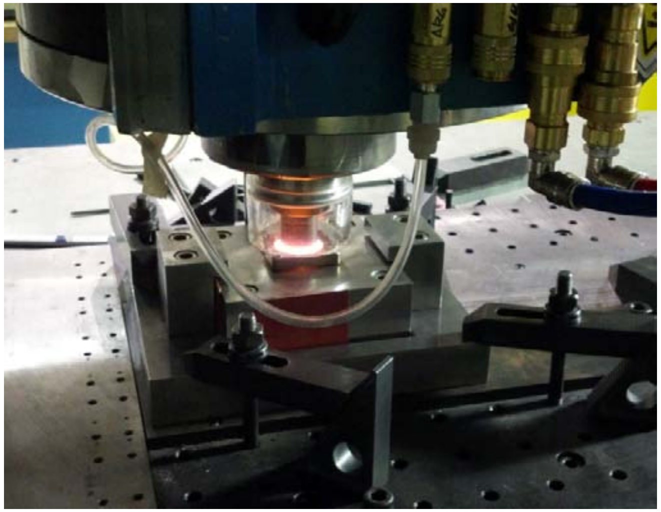
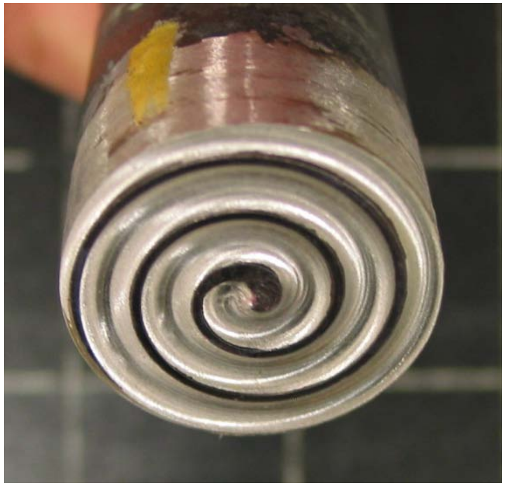
Process Description

- The energy released from plastic work results in significant heating, up to an estimated 700 to 900°C. The heat and strain energy imparted to the powders causes them to fully densify and flow within the reservoir in a complex way dictated by the design of features on the face of the tool.
- During the plastic flow event the metal is in a state of continuous dynamic recrystallization, which can result in a wide range of microstructures and final grain sizes depending on cooling rate and chemistry.





Very high levels of total strain are expected to produce extremely good mixing of constituents and potentially diffusion rates high enough for good oxide mobility and redistribution to form nanoclusters.

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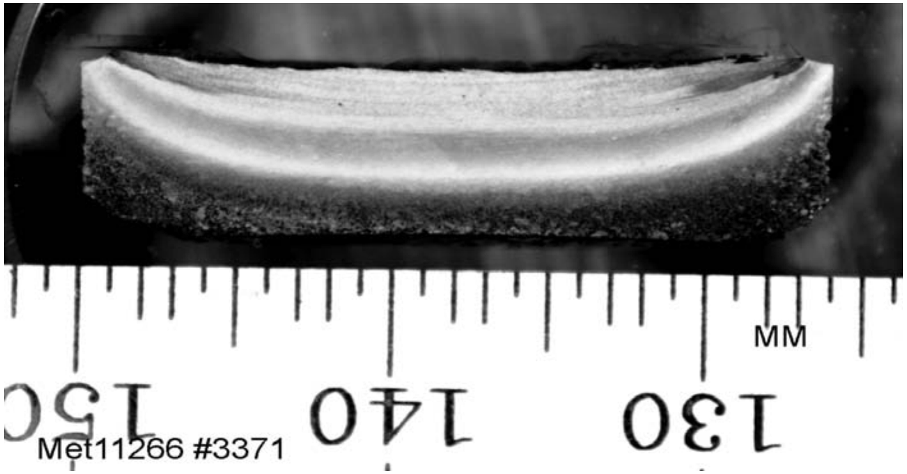
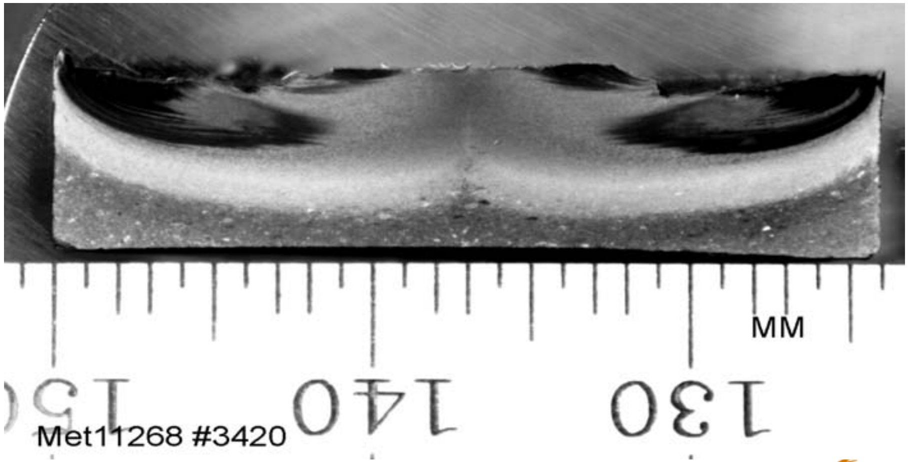
Process description

- Variables in the process include:
  - downward compressive load,
  - tool rotation speed,
  - tool design (flat, featured or scrolled),
  - time spent “stirring” at a fixed downward load
  - temperature boundary conditions (including passive or active cooling of the rotating plunger rod and die can and holder).

Flat faced tool



Featured Scroll tool



Rod extrusion

Example plunger rod with hole in center

Depending on the geometry and dimensions of the die; billets, rods and potentially back-extruded tube can be produced by this process directly from powders.

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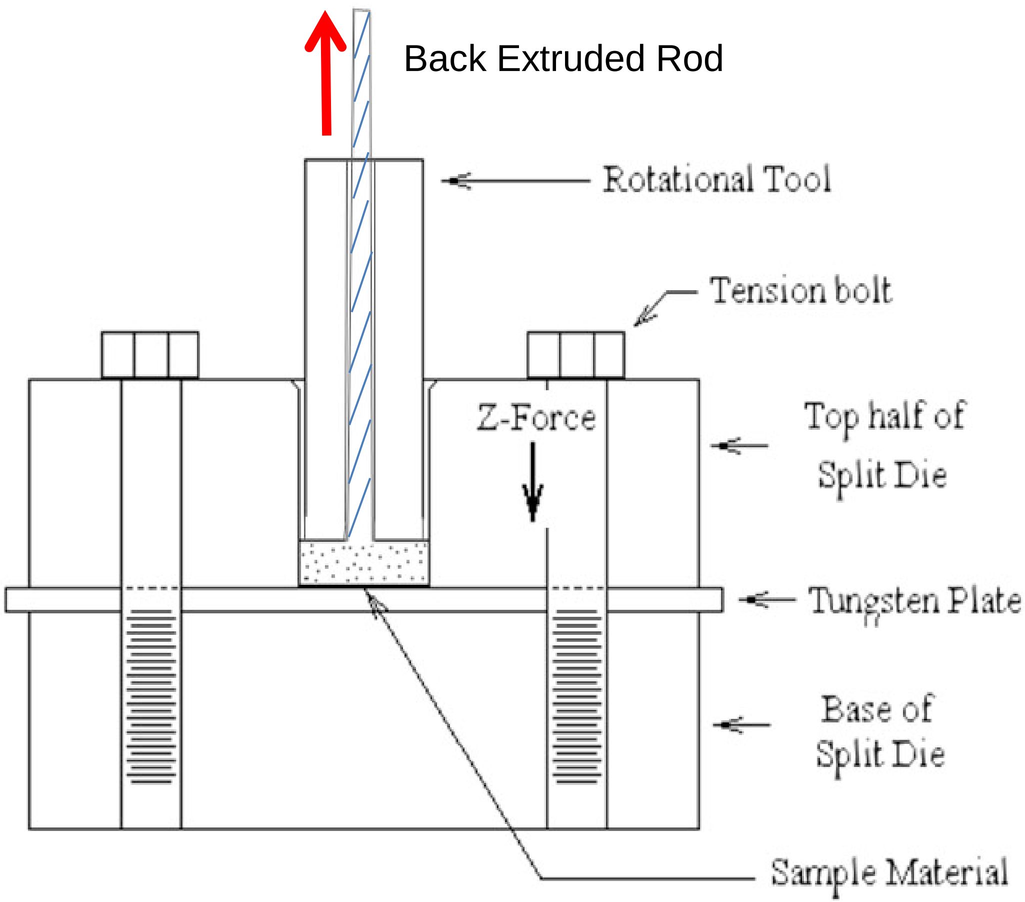

(a)

(b)

(c)

Solid Al rod fabricated directly from powder via a friction stir rod extrusion process. 2050 and 2195 rod extruded at: (a) 150, (b) 200, and (c) 250 rpm rotational speed.

A. Reynolds, USC,2009

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Objective

- Demonstrate a low-cost method of fabricating wrought ODS ferritic billet, rod, and tube directly from oxide-doped stainless steel powder, thereby eliminating costly, batch-based MA process, and can/HIP/extrude densification step

- Approach
  - Develop the process control, and equipment to produce fully compacted billets from metallic powder feedstocks
  - Produce lab-scale densified compacts , then, with new die designs, produce rod and tube product forms without intermediate steps such as powder canning, HIPing, and rolling or extrusion.
  - In evaluating the efficacy of the process, our initial focus will be to:
    - (1) verify that high density (i.e. pore-free) billet and rod forms can be fabricated by this approach,
    - (2) demonstrate that the oxide dispersoids are nanoscale (<20 nm in size) and uniformly distributed throughout the steel matrix
    - (3) the mechanical properties (creep and strength at temperature) approximate those of the current ODS alloys being evaluated for FE applications

Compaction Trials

Starting Powders

- Mechanically Alloyed Powder
  - Eliminates majority of “back end” cost of canning, HIPing / extruding, but still is moderate cost and time in the front end step (the MA step).
- Gas Atomized Powders
  - Reduces cost of “front end” MA step, but may have low yield depending on distribution of yttria in final powder product.
- Steel Powder plus Yttria Powder (simple mixing prior to friction consolidation)
  - Further reduces cost of front end. If the primary “mixing” occurs in the Friction Consolidation process, then the distribution of Yttria in starting powder may not be as important.

Outline

- Compaction Trials
  - Microstructures of MA956 Compacts
    - Grain size
    - Homogeneity of oxide particulate
    - The Al-Y-O system
  - Low cost powder precursors
    - Steel powder + yttria feedstock
- Summary and Next steps

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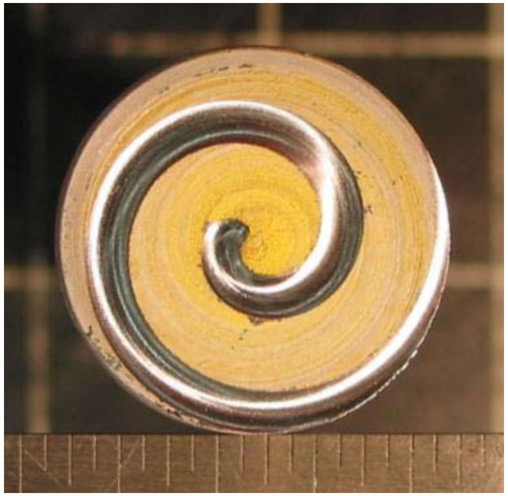
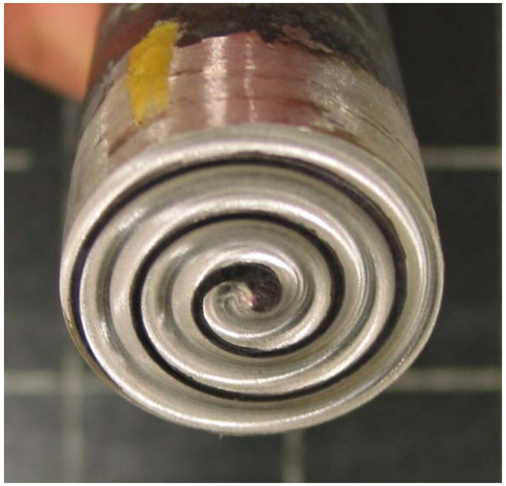
ODS Powder work (MA 956 powder from Special Metals)

Initial process responses and scrolled die

No	RPM	Z force, lbs	Time, sec	Torque, N-m	Power, W	Work (kJ)	Tool
1st	500	5000	54	101	5355	291	Smooth
3416-1	500	5000	94	86	4386	411	Scroll
3416-2	500	5000	146	80	4213	614	Scroll
3417	300	10000	121	139	4382	528	Scroll





Design of Experiment study of the effects of process variables on microstructure of the compacts is underway at University of South Carolina and at PNNL

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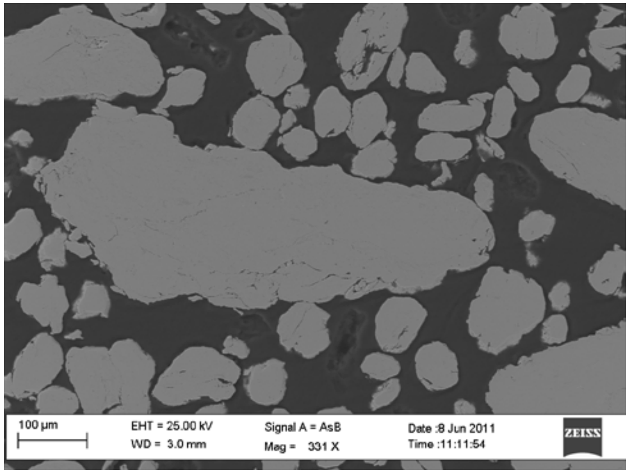
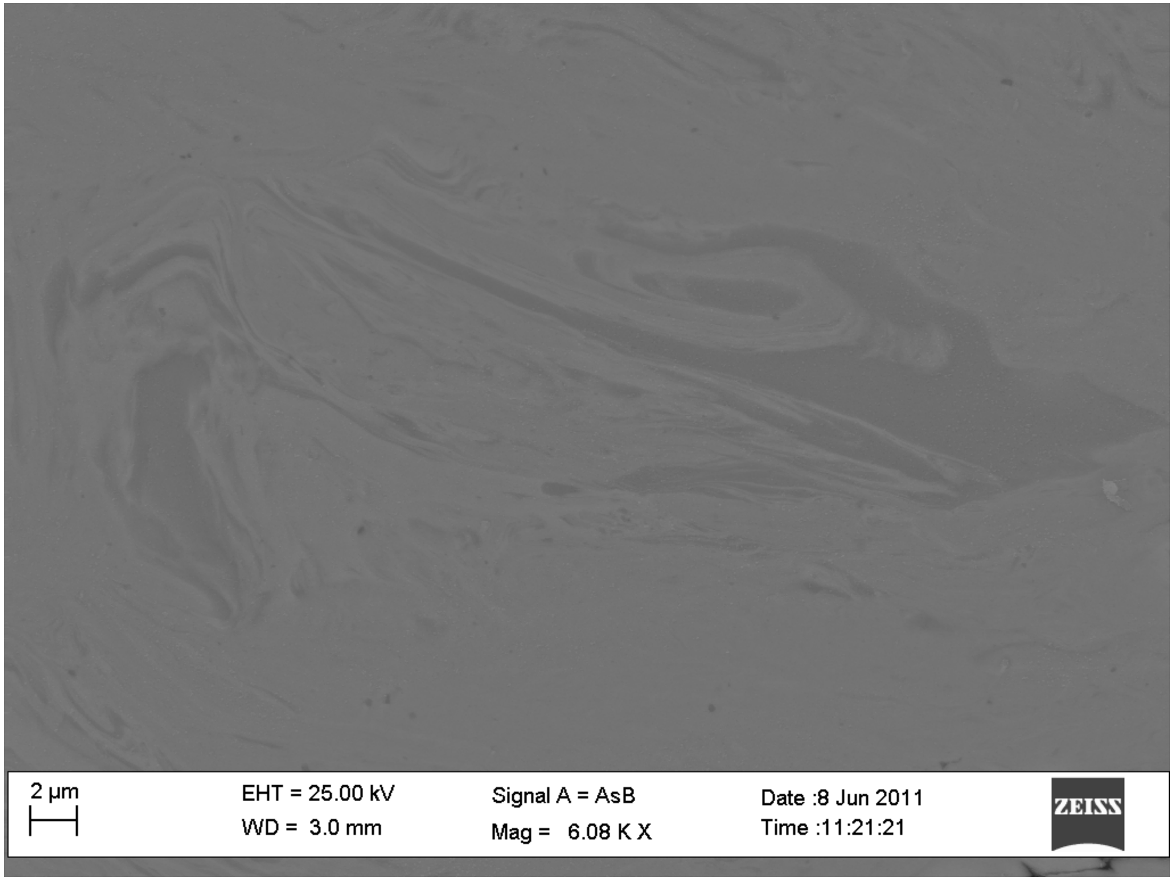
MA 956 Powder





- MA 956 is a mechanically alloyed product

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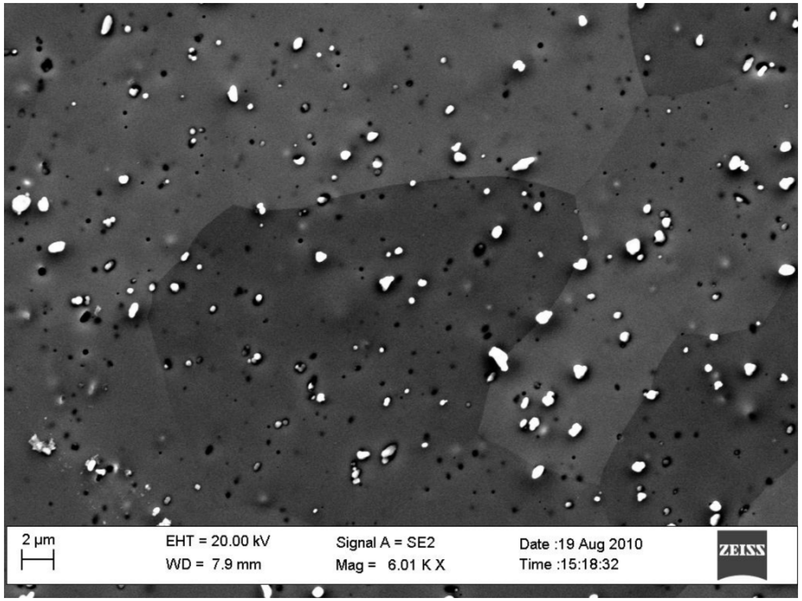
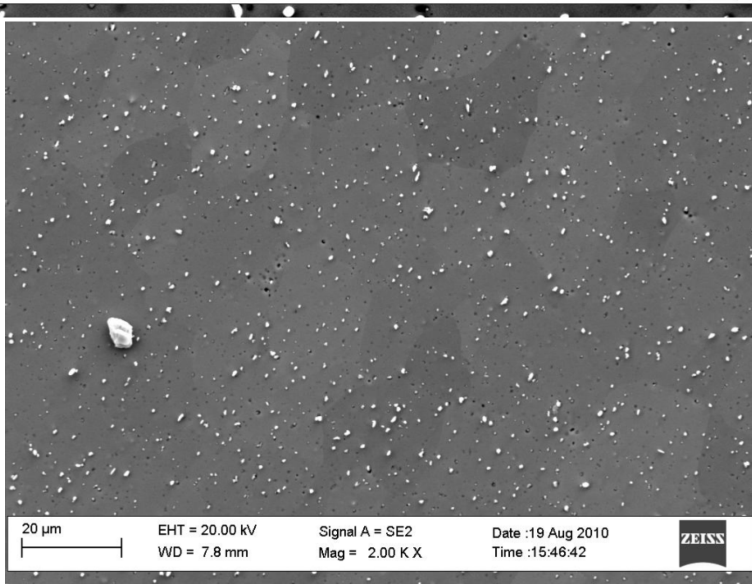
MA 956 after ~30 to 100 seconds of FC





Fully dense crystalline solid with two important features:

- **The compact has an equiaxed grain structure (This may have important implications for microstructural control during heat treatment)**
- **There is a homogeneous distribution of both coarse and fine oxides**

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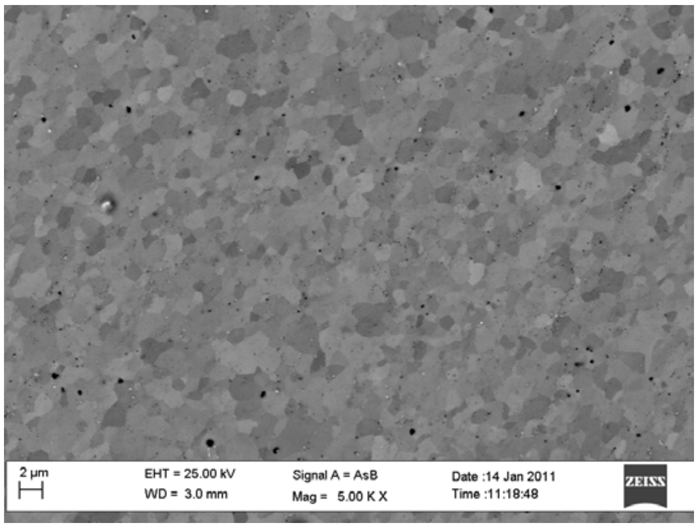
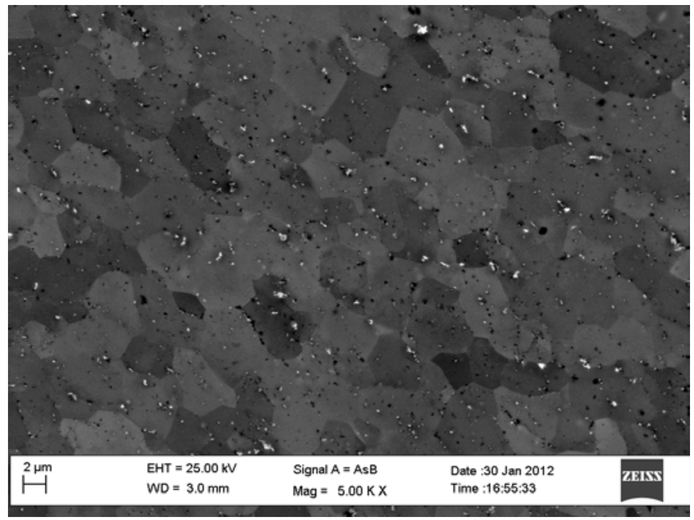
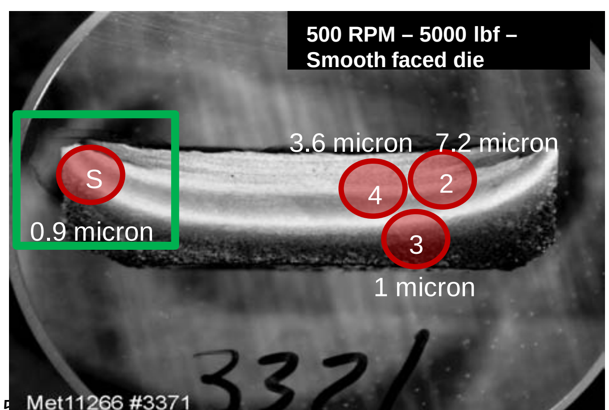
Effects of process changes

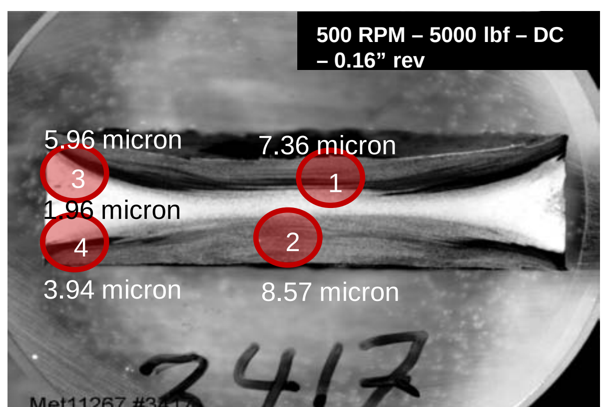
- Changing tool designs, increasing consolidation force and lowering rotation speed

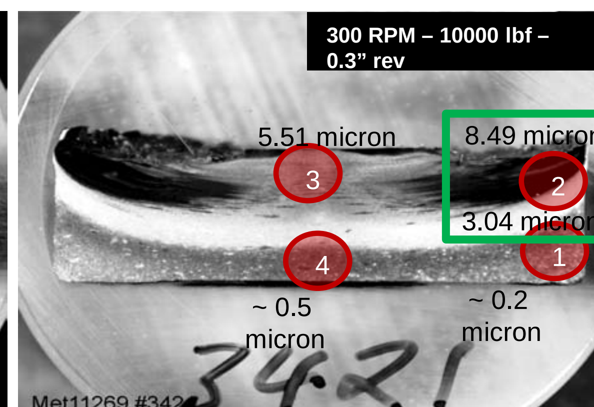




Higher tool temp
Larger grain size
More coarse oxides



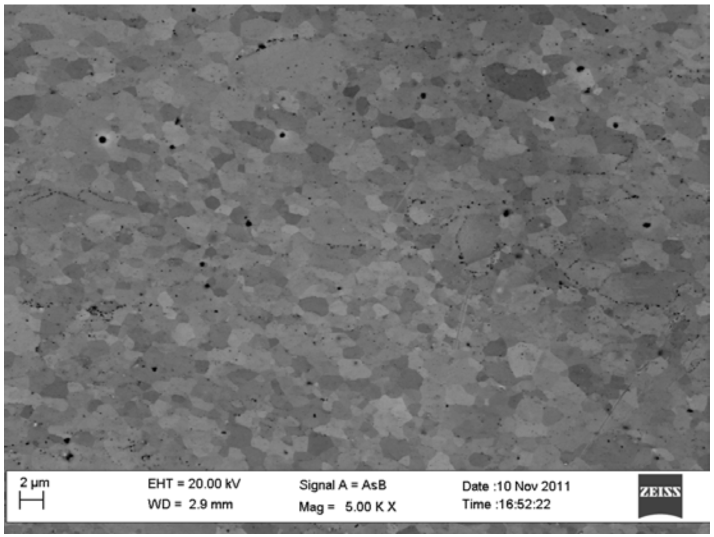


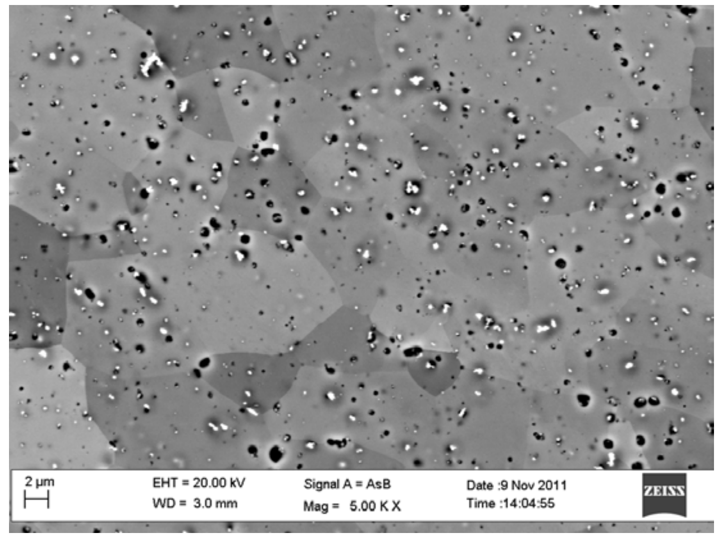


Effects of process changes

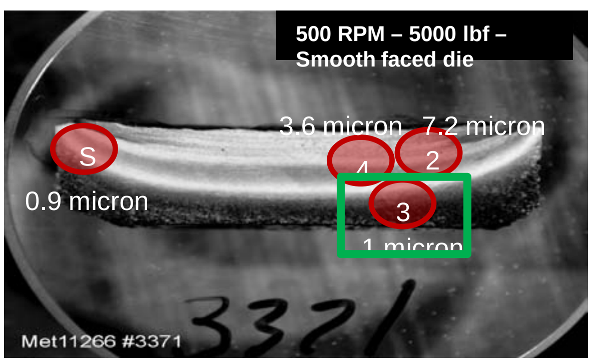
- **Effect of double processing**

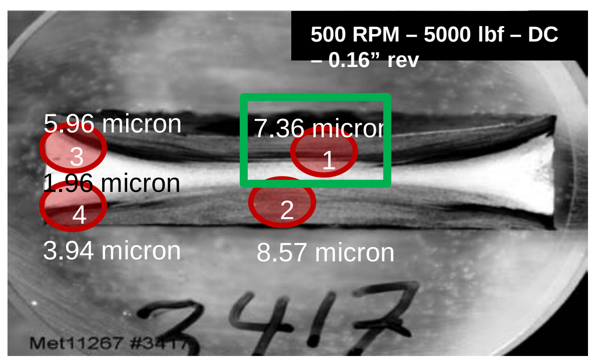
Two heat and strain cycles

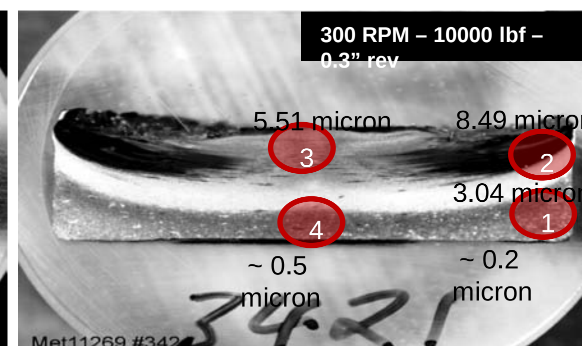




Significant coarsening of grains and oxides







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Oxides

- Fine grained areas, especially high cooling rate(?) areas of the pucks show restricted development of particles
- Also particles are coarser with increased heat and shear processing
- Particles identified in SEM as belonging to one of three particle families: Y-Al-O, Al-O, or Ti-Al-N
  - The first two were in both, the conventional and the friction stir processed sample, while the last one only in the conventionally processed sample.
- To identify them and their relation to process we did wet chemical dissolution, filtering at 20 nm, then XRD of the concentrates

Dissolution experiment and XRD

METALLOGRAPHY 8, 473-488 (1975) 473

Chemical Extraction of Refractory Inclusions from Iron- and Nickel-Base Alloys

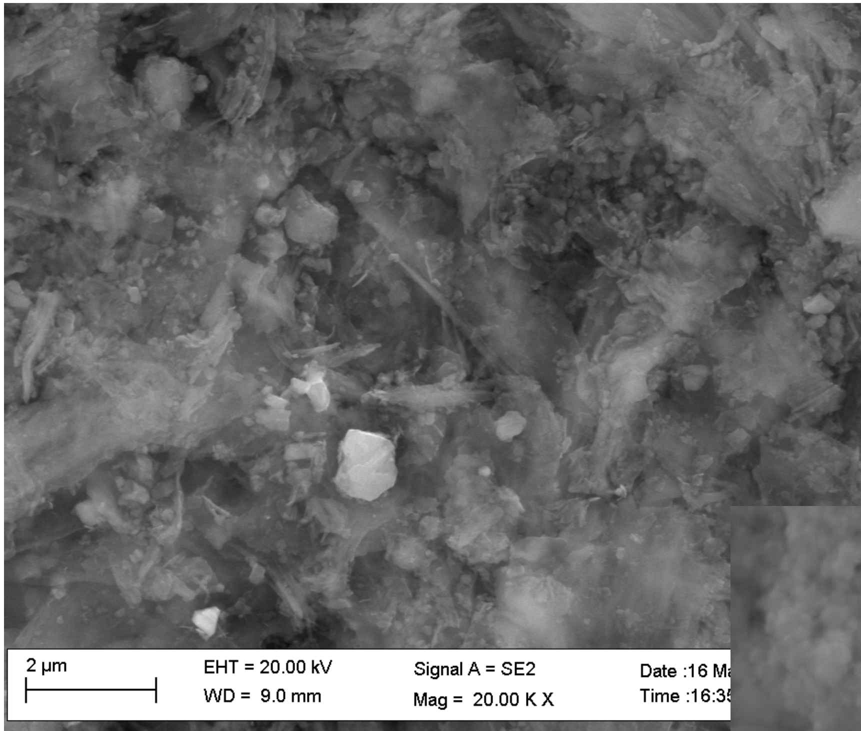
KEITH E. BURKE

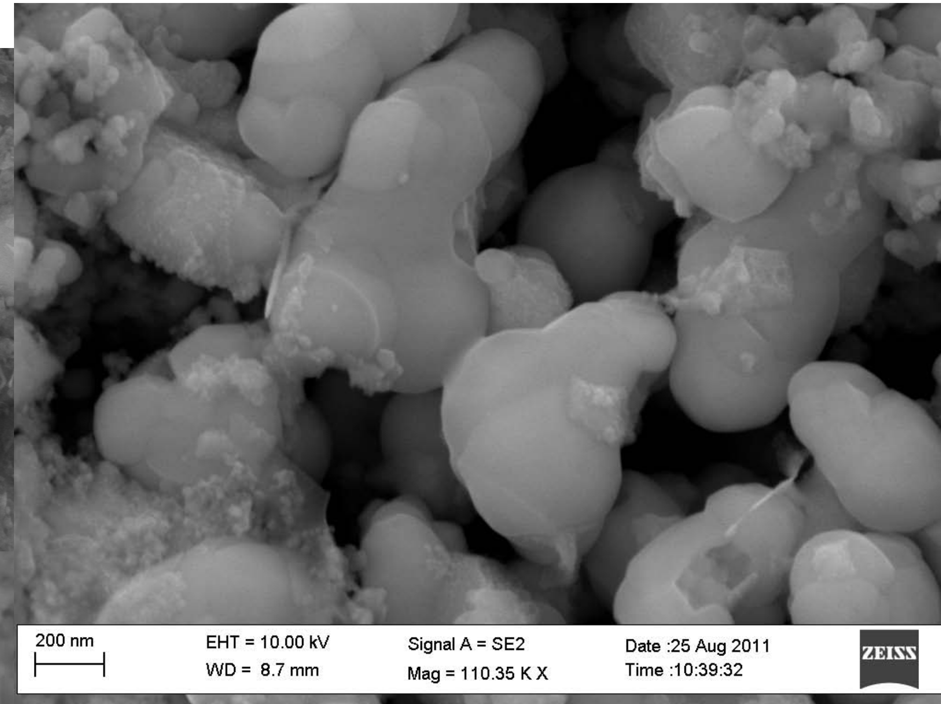
The International Nickel Company, Inc., Paul D. Merica Research Laboratory, Sterling Forest, Suffern, New York 10901

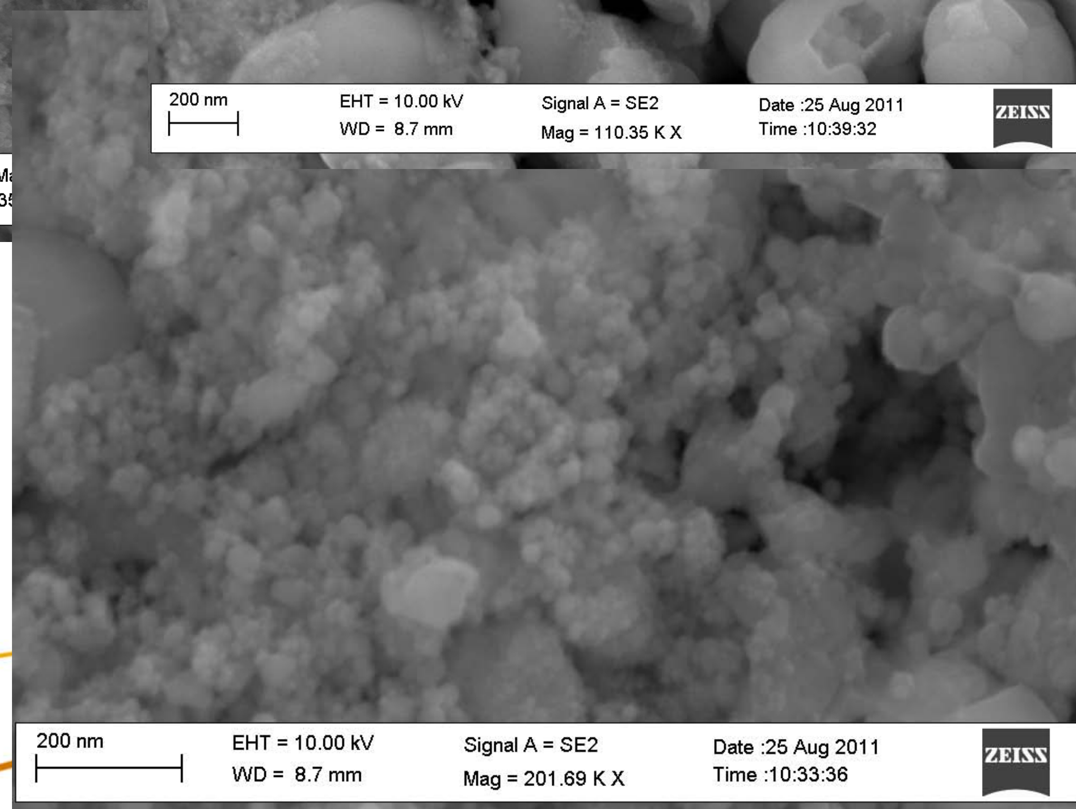
TABLE 6

Solubility of Various Compounds in the Berzelius Reagent

Compounds	% Insoluble
NbC, B_4C, $\boxed{TiN}$, Cr_5B_3, ZrO_2, TiP, CrP	99 ± 1
$Cr_{23}C_6$, Cr_3C_2, $\boxed{TiC}$, WC, TaC, VC, Cr_2N	96 ± 1
Cr_7C_3, WTiC(50/50), WTiC(70/30), VN, $\boxed{Al_2O_2}$, TiS_2	93 ± 1
W_2C, $\boxed{3Y_2O_3 \cdot 5Al_2O_3}$, NiO	90 ± 1
Fe_3C, MoC, Mo_2C, TiB_2, $\boxed{Y_2O_3}$, La_2O_3, Nd_2O_3	<2


2 µm
EHT = 20.00 kV
WD = 9.0 mm
Signal A = SE2
Mag = 20.00 K X


200 nm
EHT = 10.00 kV
WD = 8.7 mm
Signal A = SE2
Mag = 110.35 K X
Date :25 Aug 2011
Time :10:39:32
ZEISS


200 nm
EHT = 10.00 kV
WD = 8.7 mm
Signal A = SE2
Mag = 201.69 K X
Date :25 Aug 2011
Time :10:33:36
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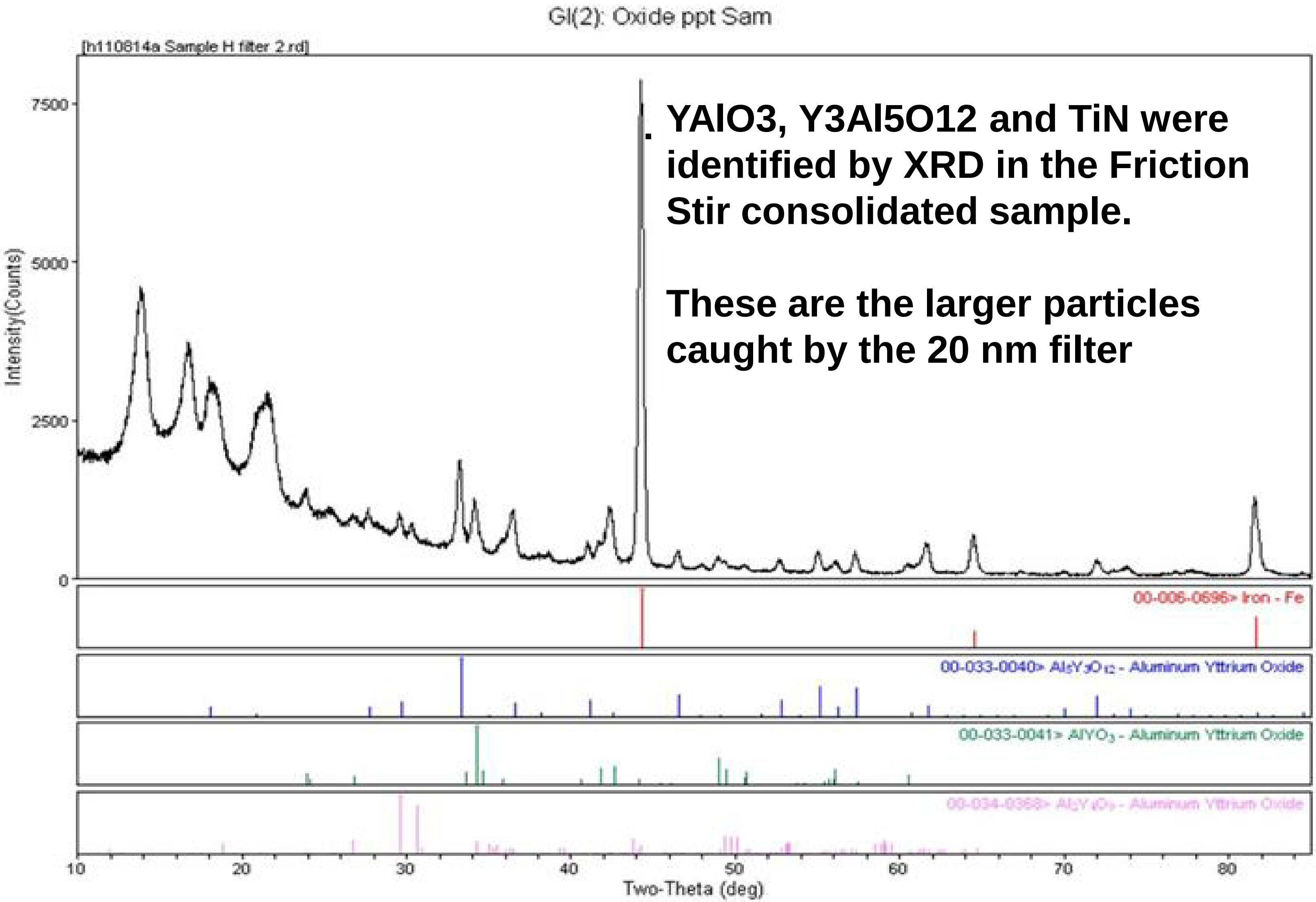
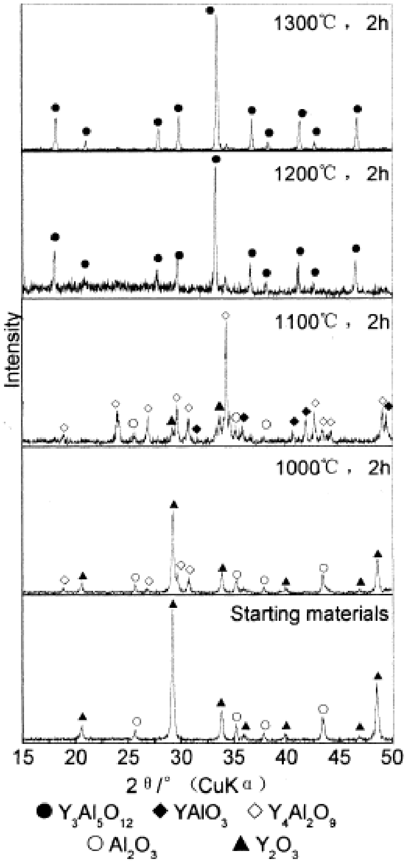
XRD on insolubles



YAlO3, Y3Al5O12 and TiN were identified by XRD in the Friction Stir consolidated sample.

These are the larger particles caught by the 20 nm filter

Interactions of Y and Al oxides



Reaction	Temperature
➢ $2\ Y_2O_3 + Al_2O_3 = Y_4Al_2O_9$ (Monoclinic-YAM)	900 – 1100ºC
➢ $Y_4Al_2O_9 + Al_2O_3 = 4YAlO_3$ (Perovskite-YAP)	1100 – 1250ºC
➢ $3\ YAlO_3 + Al_2O_3 = Y_3Al_5O_{12}$ (Garnet-YAG)	1400 – 1600ºC

➢ Starting material: Y:Al = 3:5

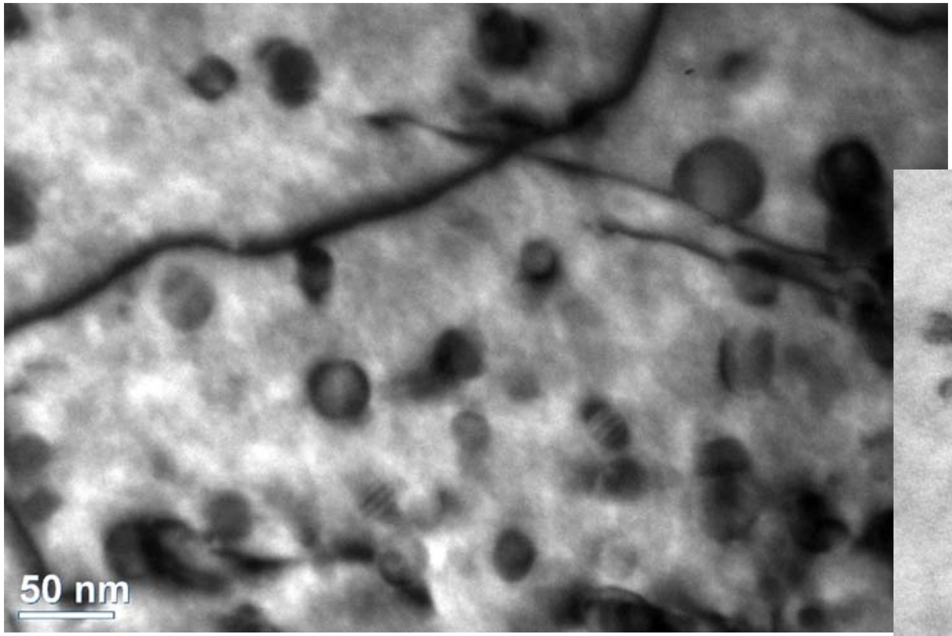
➢ Diffusion of Al^{3+} into Yttria, and the first phase to develop during heat treatment is the yttrium-rich YAM phase. With further increase in temperature Al^{3+} also diffuses into YAM to form YAP

➢ Finally, Al^{3+} reacts with YAP to form YAG

There is much debate about this in the literature

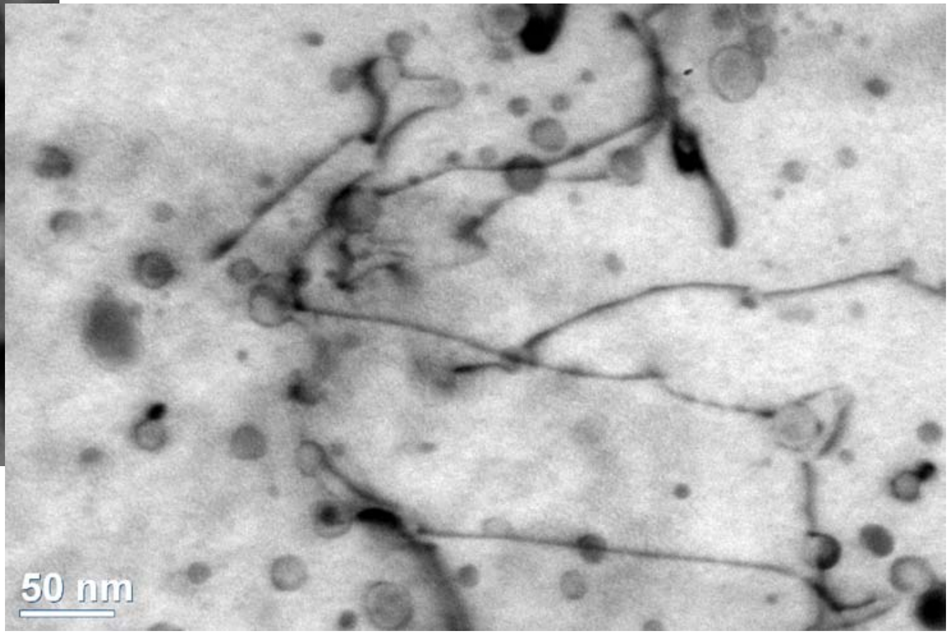
What do we have?

- Clearly the coarse oxides in the compacts are YAP and YAG.
- What about the fine grain parts of the compacts with relatively few particles? Where is the AL-Y-O?

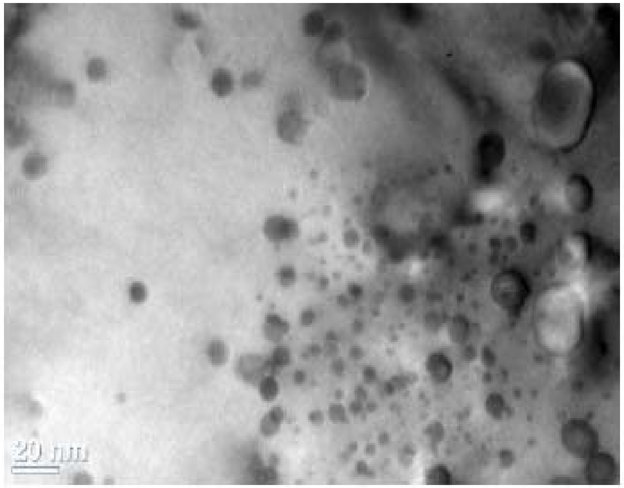


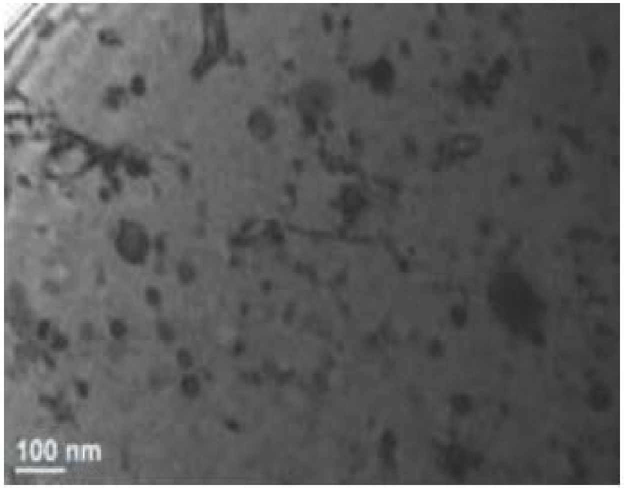
MA 956 RL

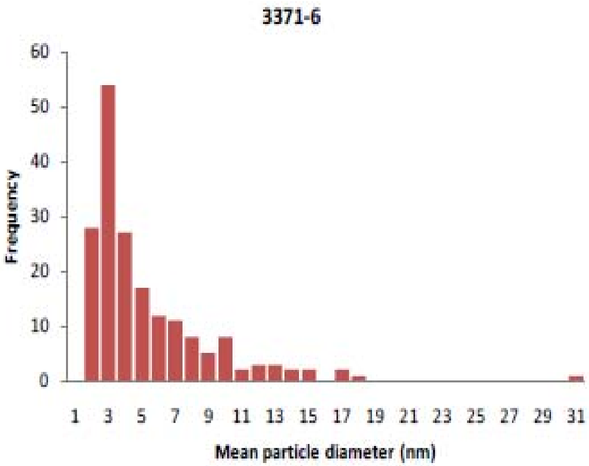
Friction Consolidation

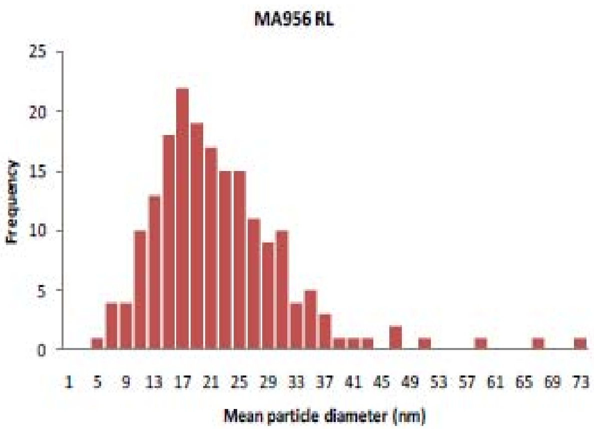


Dispersoid size FC compacts









- **Average dispersoid size in SCP compacts: 4.8nm**
- **Average dispersoid size in MA956RL product: 21.1 nm**

We think these are YAMS. APT time.

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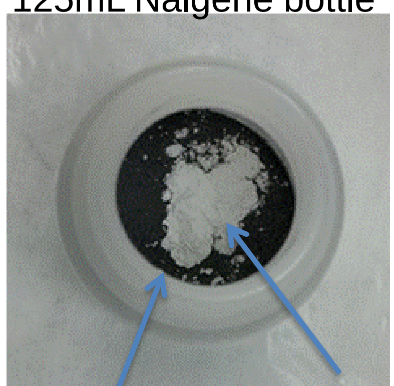
An even lower cost route to an ODS may be to start with stainless powder and coarse yttria

- 15µm 430LSS powders were mixed with 1wt% 5-10µm yttria powders and consolidated
- Ball mixed (<50vol% milling media) with 8mm YSZ balls for 1hr
- Pre-consolidated in 1.25” diameter die at 5000lbs
- Consolidated with 1.25” W-La scrolled tool at 300RPM, 5000lbs

Material	Fe	Cr	C	Si	Mn	Al	Ti	Y2O3	Mo
MA956	bal.	18.5-21.5	0.1 max.	NA	0.30 max.	3.75-5.75	0.2-0.6	0.3-0.7	NA
MA957	bal.	13.5-15.2	0.012-0.017	0.02-0.07	0.05-0.12	0.055-0.17	0.95-1.38	0.19-0.28	0.28-0.32
430L	bal.	17	0.02	0.9	0.2	NA	NA	NA	NA

99g 430SS + 1g Y2O3 in 125mL Nalgene bottle

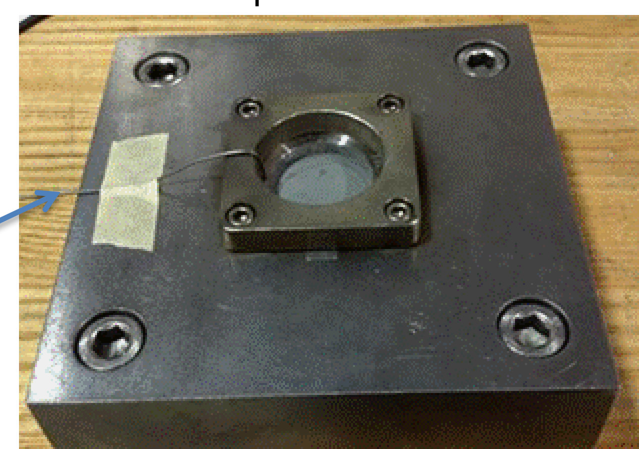


Y2O3

430SS

Mixed powders in die

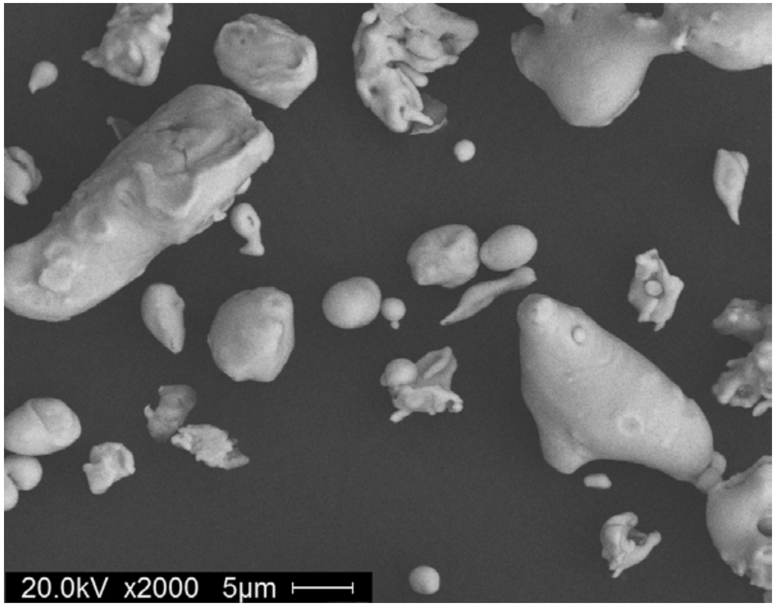
TC



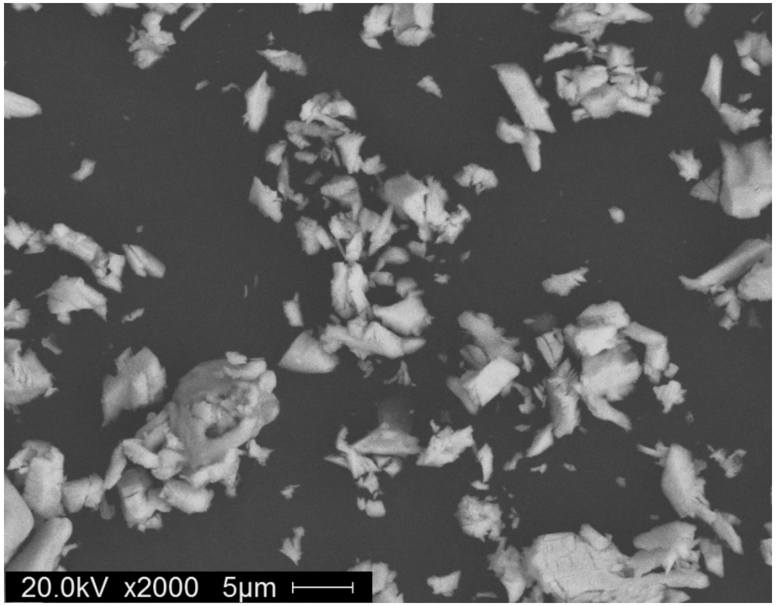
SEM of as-received powders

- 430-L stainless steel powder appeared as round globules approximately 2-20µm
- Yttria powder appears as irregularly shaped flakes 1-5µm in size with larger agglomerations

430L SS powder



99.99% Yttria powder



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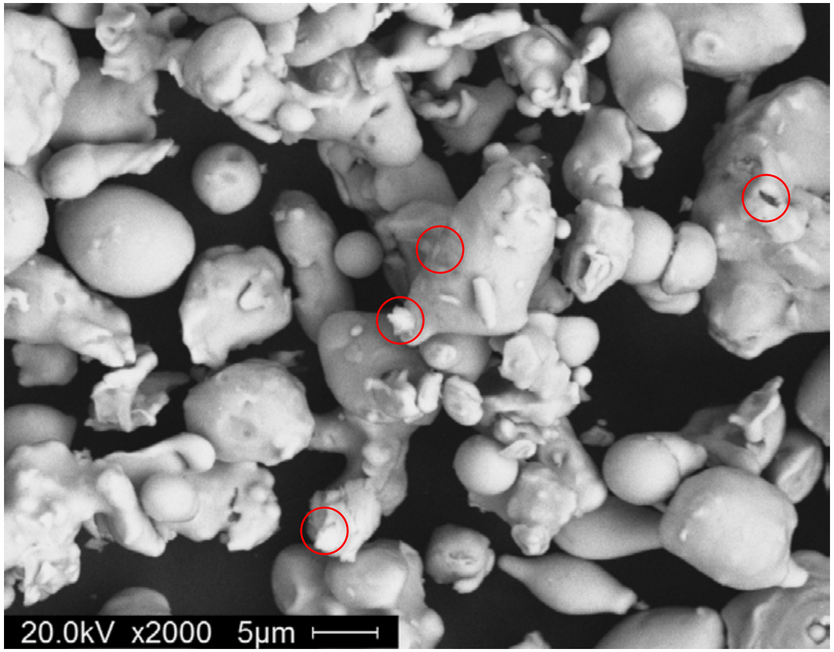
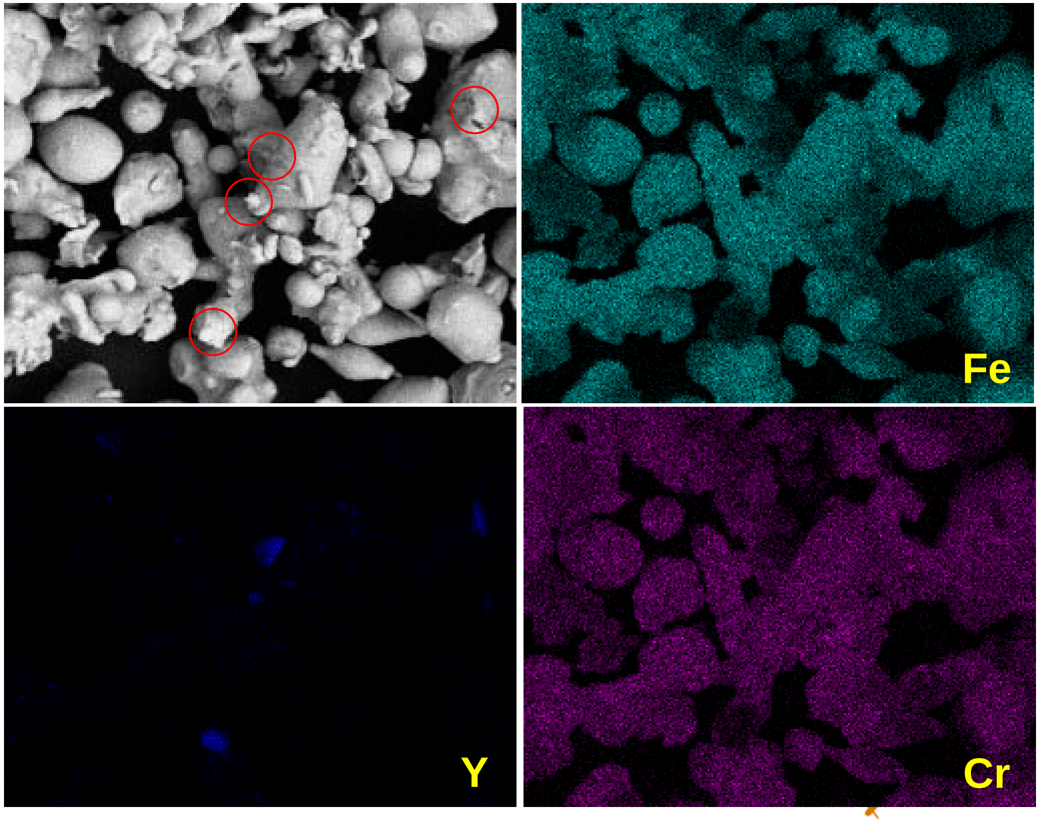
SEM of mixed powders

- After ball mixing, yttria appears as separate irregular particles and some are embedded into the 430L particles



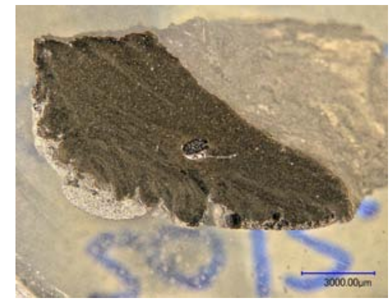
EDS maps



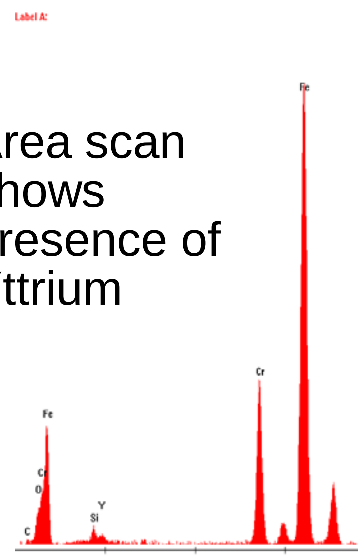
Results

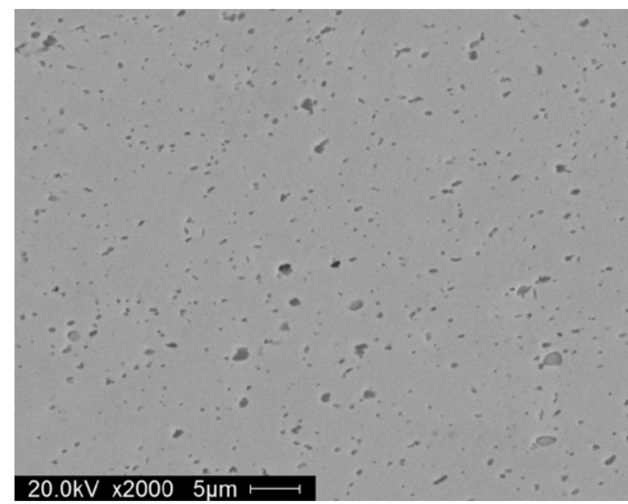
- Temperature of IN 718 ring increased rapidly to 800C at which point the run was aborted

- Consolidated sample was sectioned at two different points and mounted and polished for SEM



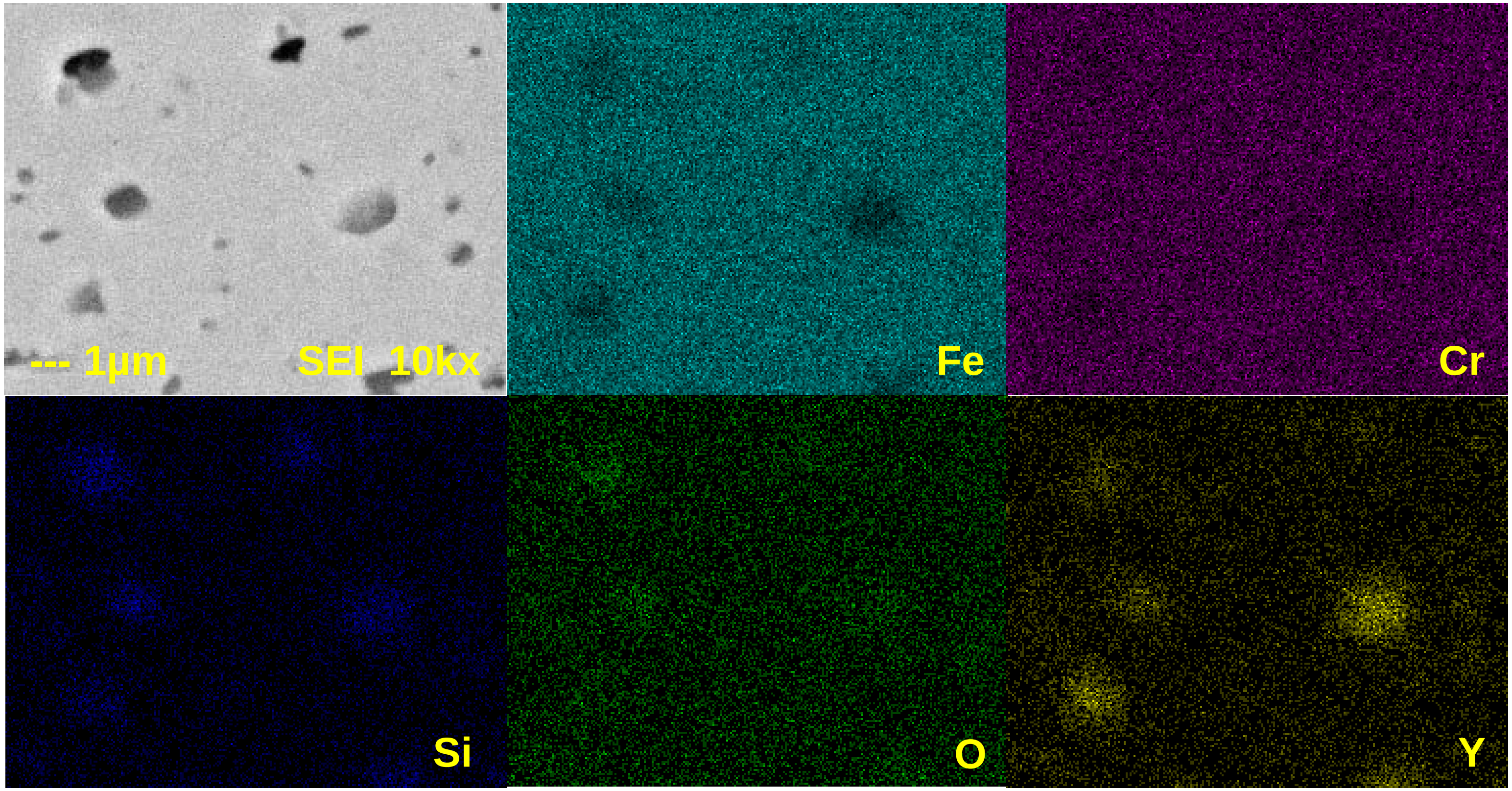
- Area scan shows presence of Yttrium



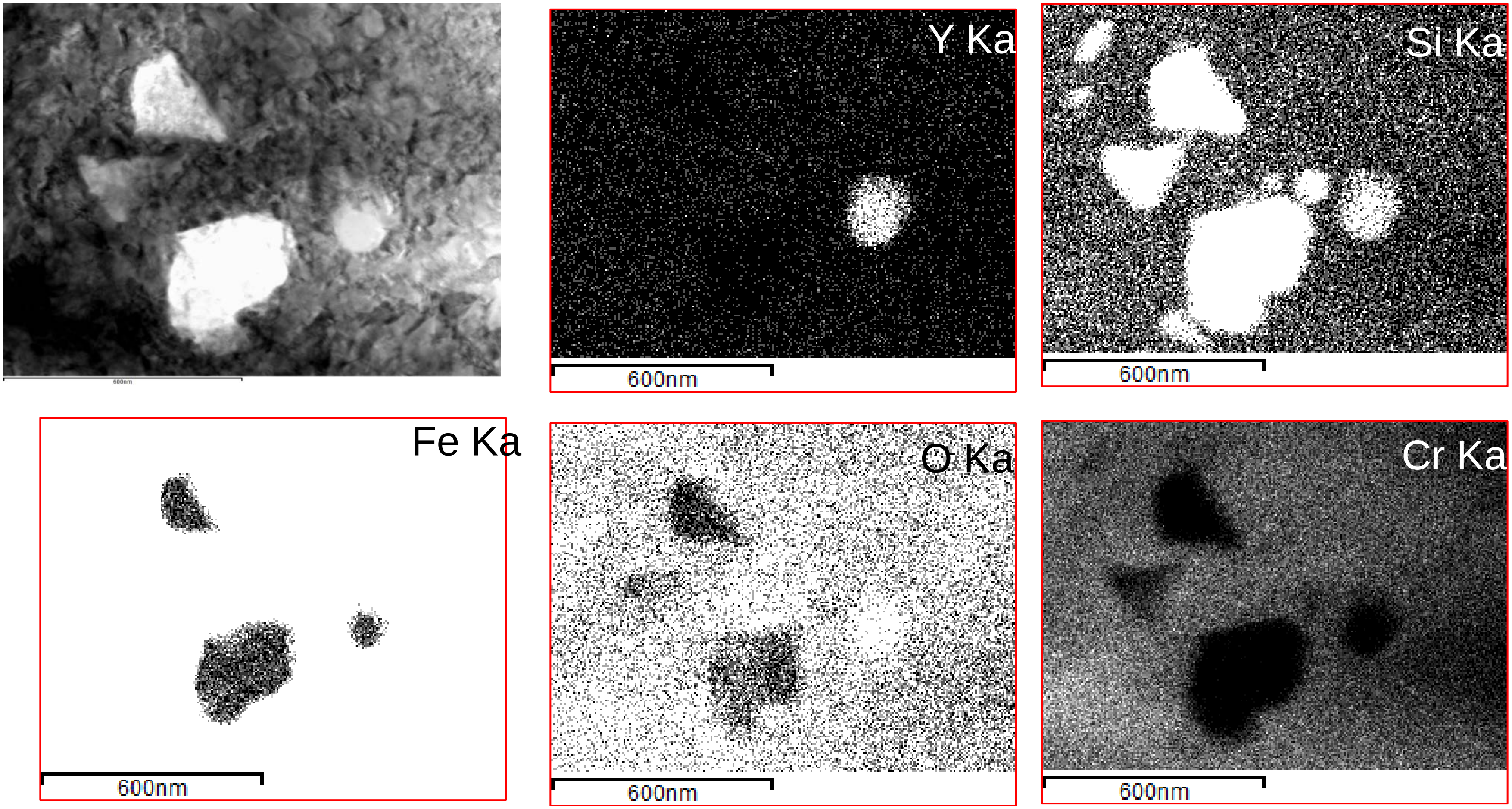


EDS map

- Yttria appears in part with Si, and possibly in small amounts with the FeCr base



Element map searching for small Y-rich particles



Small nano-scale Y-only particles were not identified through the EDX mapping. But coarser (100-200nm) Y-Si-O rich areas are seen

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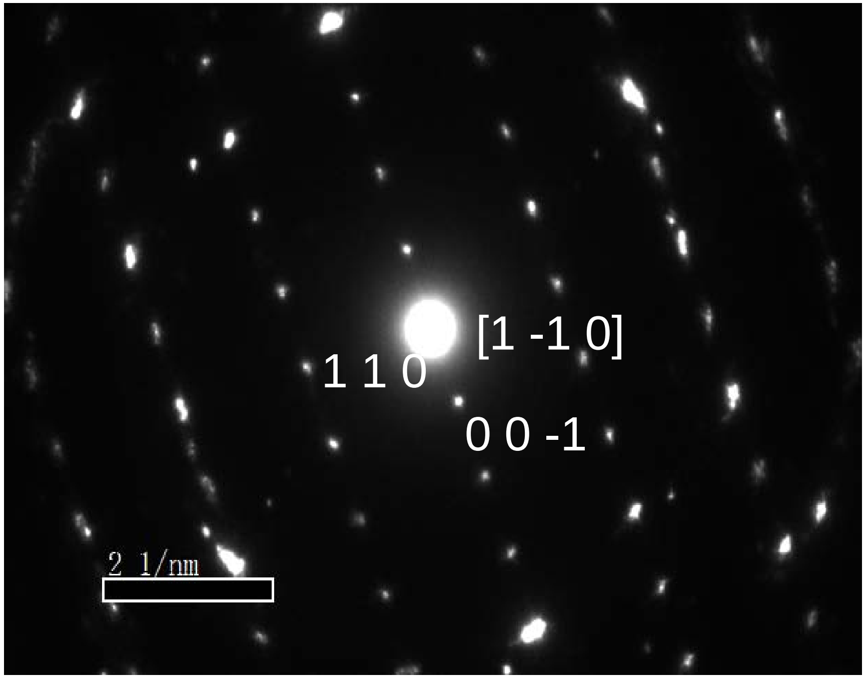
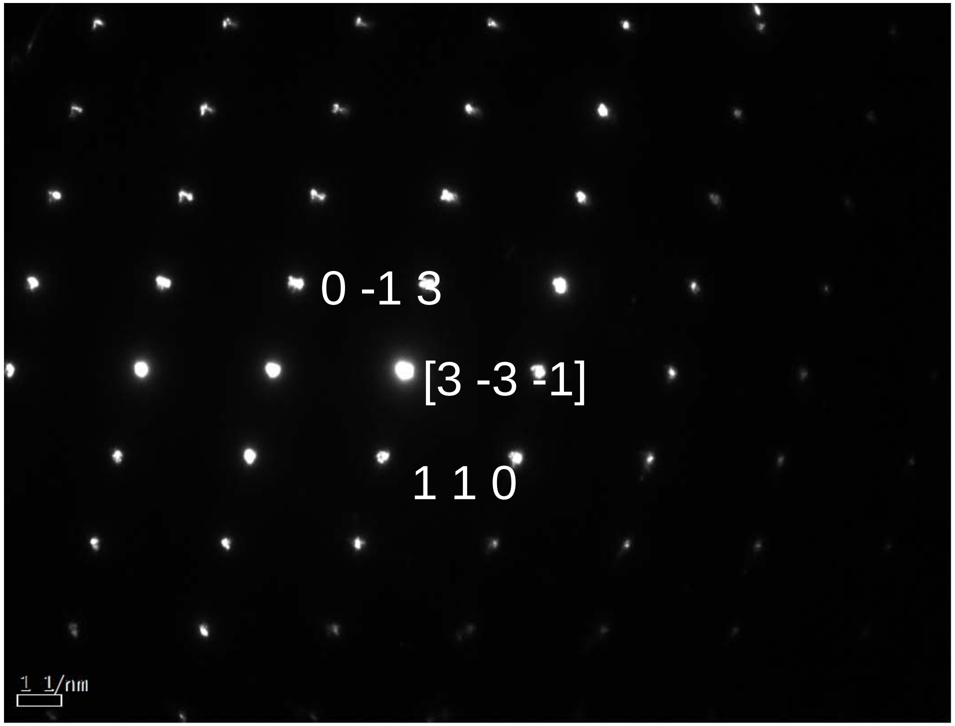
Phase of Y-rich particles





- Y_2SiO_5, monoclinic, Space Group #15
- Unit Cell: a=10.41, b=6.72, c=12.49, α=90, β=102.6, γ=90

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Summary of work on “elemental” powders

- Yttrium did react. No evidence of yittria particles in the matrix. This determination is complicated because of the very fine grain size of the FSW matrix
- However yttria is apparently tied up with silica, forming a separate phase of Y_2SiO_5.
- Might consider annealing the material. This might allow a clearer picture of the grain interiors to reveal any small yittria particles.
- Question of sub 10nm dispersoids is still open
- However probably best to get an alloy powder that does not contain silicon and try again. Ideally a Fe-Cr-AL powder.

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Summary

- FC process fully densifies both MA and ss+Y powders to crystalline solids with complex and process parameter dependent microstructures
- Sub 10nm dispersoids were observed in the FC processed MA compacts where no dispersoids were originally present.
- Process time <60 sec on average
- Al-Y-O phases developed are process parameter dependent, especially formation of YAP and YAG in the solid allowing for tailoring of the Al, Y, or O available to form nano YAM (the dispersoid of interest)

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Next Steps

- More Process Development
- Die design optimization
  - Scroll depth and pitch
  - Active control of die can temperature
- Billet or Compact Characterization
  - Microstructural
  - Mechanical Performance
    - Creep performance similar to MA alloys?
    - What is the toughness of this microstructure (fatigue, etc)
- Rod Extrusion
  - Extrusion die design
  - Mechanical properties of the rod or tube
- Scale up issues
  - Length
  - Diameter
  - Glass lubricants on die can
- Continued work on using low-cost un-alloyed powders
- Feasibility of using low cost gas atomized powders

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Potential Applications and Benefits

- **Ability to produce product forms directly from powder, eliminating numerous /costly processing steps (e.g. mechanical alloying, canning, HIPing, extrusion, etc.**
  - **Application to near-net shape processes (Rod or plate? Or shape?)**
  - **Application to tubing and piping (back extrude tube around plunger)**
  - **Production of hollow billets for tubular extrusion**
  - **Potentially change from batch to continuous process**

- **Process has the potential to produce appropriate microstructures**
  - **Process can create equiaxed microstructure, and possible isotropic mechanical properties (Heat treat studies pending)**
  - **Process also has the potential to break up stringers allowing for reduced roll processing and reduction in probability of defects and low fracture toughness due to stringers**
  - **Strain induced mixing may allow even poorly mixed Fe-Cr-AL-Y powders to be used as feed stocks**
- **Ability to process novel alloy compositions and microstructures without melt solidification steps - critical to ODS alloys and other non-equilibrium systems**

These features are anticipated to lead to a substantial reduction in the cost of producing ODS alloy product.

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