Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Low Cost Fabrication of ODS Alloys

GLENN GRANT, JENS DARSELL, DAVID CATALINI
PACIFIC NORTHWEST NATIONAL LABORATORY

ANTHONY REYNOLDS
UNIVERSITY OF SOUTH CAROLINA

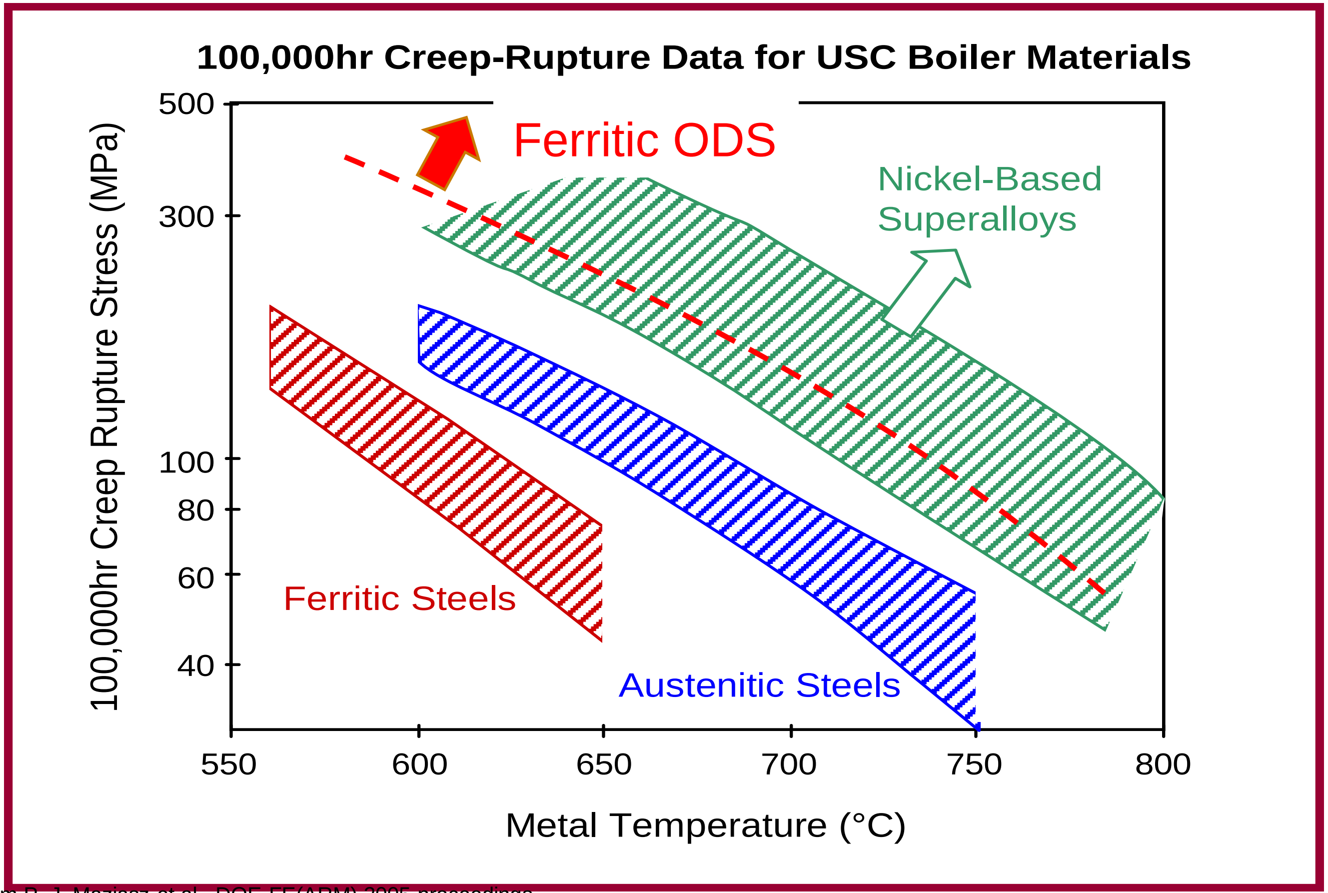
VITO CEDRO – NETL TECHNICAL MANAGER

Department of Energy – Office of Fossil Energy
National Energy Technology Laboratory
2015 Crosscutting Technology Research Review Meeting

Pittsburgh, PA
April 27 – May 1, 2015

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

Nanostructured Ferritic Alloys (NFA) including Oxide Dispersion Strengthened Alloys



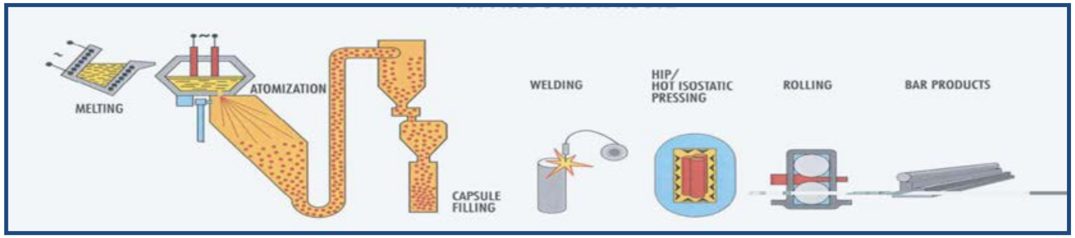
From P. J. Maziasz et al., DOE-FE(ARM) 2005 proceedings

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

Pacific Northwest NATIONAL LABORATORY

Barriers to ODS Commercialization

- **Process Cost**
  - **The high cost of ODS alloys and components is partially driven by the multistep , batch process of fabrication from powder to final product form**
  - **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 (plate / tube /pipe)**



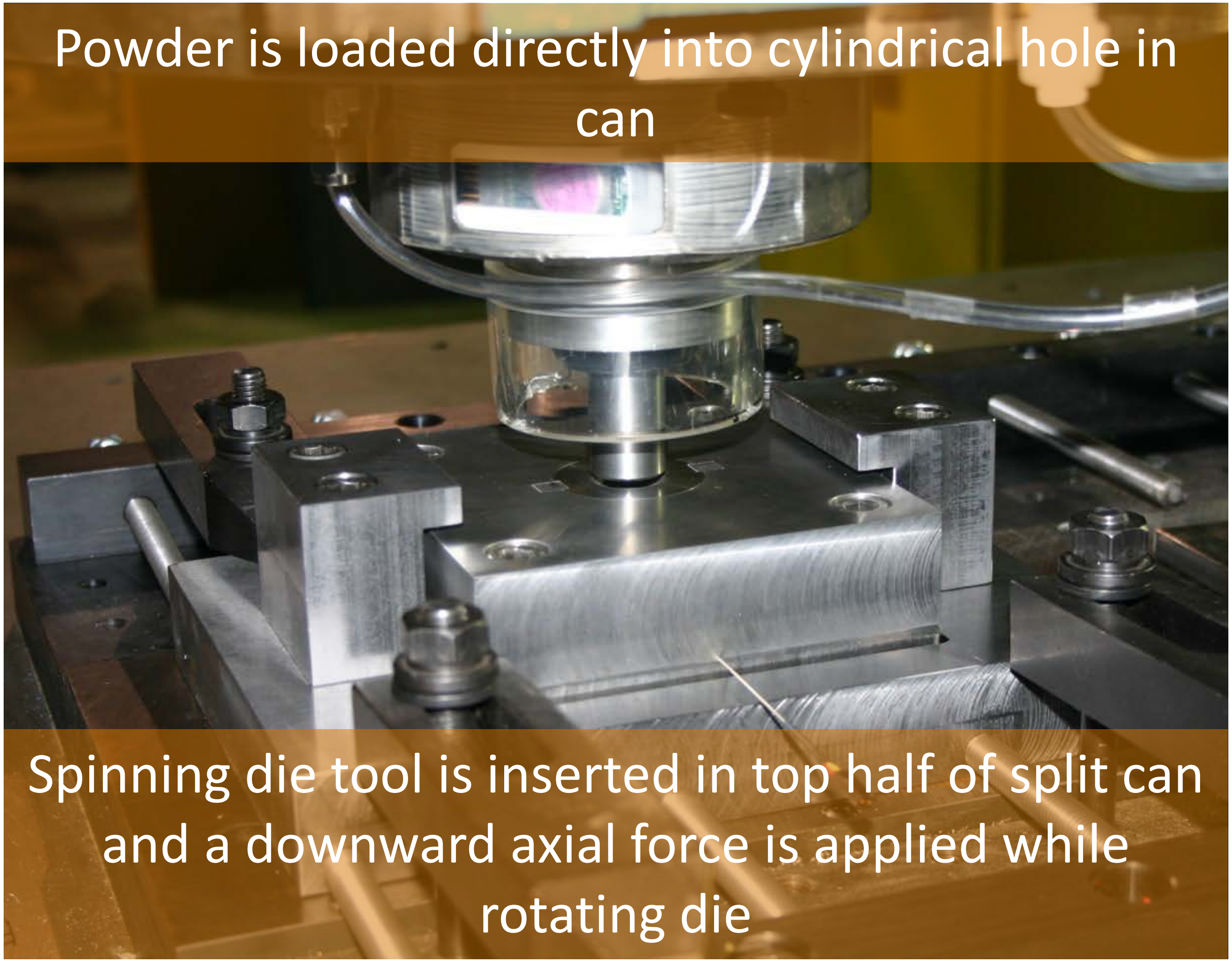
- **Challenges associated with post processing, fabrication, microstructure control / stability**
  - **ODS alloys can be hard to form, bend, pierce, draw, or pilger due to anisotropy, oxide stringering, and , in some alloys , low RT ductility**
  - **Microstructure instability can lead to good secondary recrystallization or bad secondary recrystallization**
  - **Fusion Welding can ruin the microstructure (Solid state welding may work)**

Are there alternative process routes that can remove the some of the costs and produce the right microstructure and workability when going from powder to semi-finished product ?

Friction Consolidation : Process description

1

Powder is loaded directly into cylindrical hole in can



2

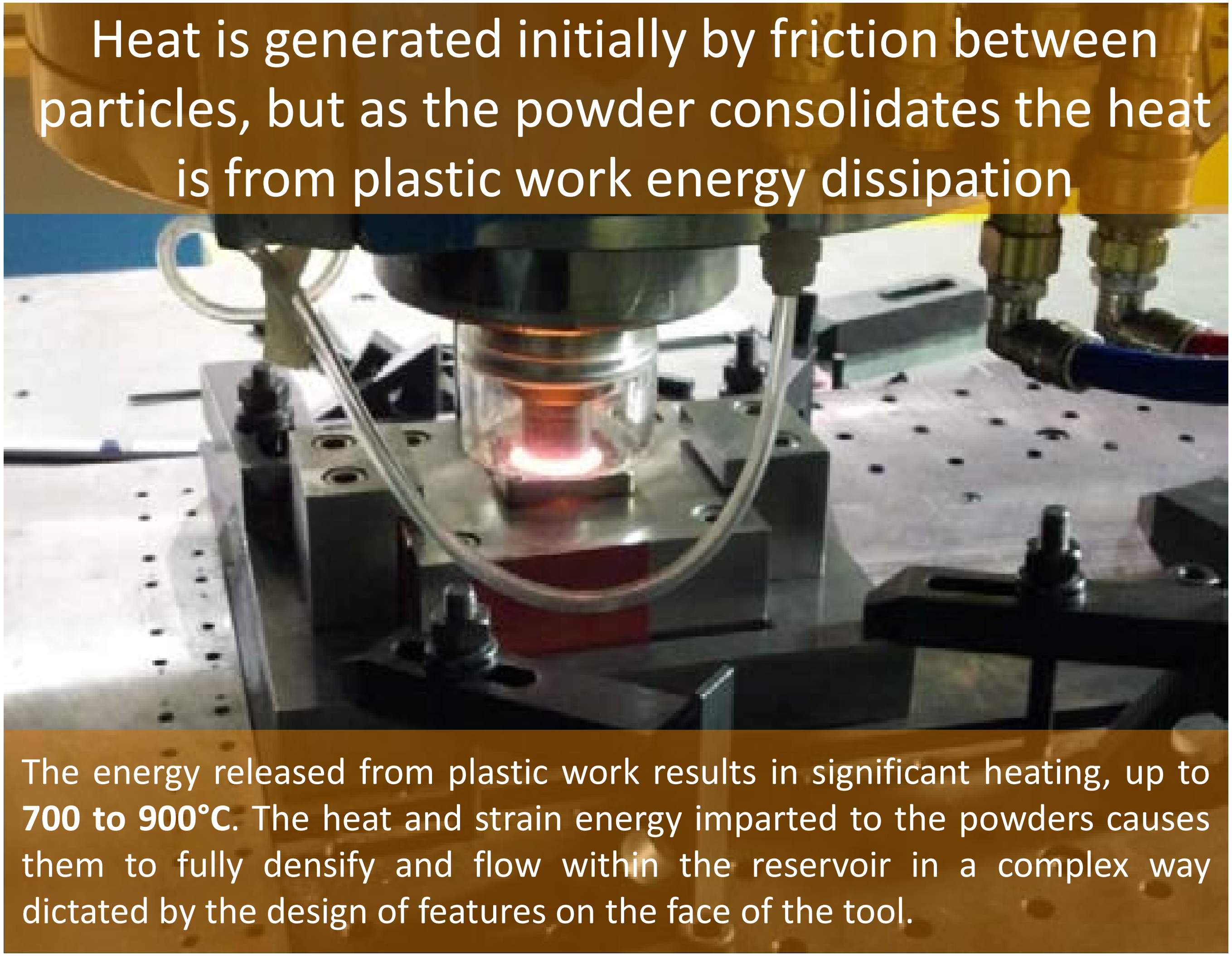
Spinning die tool is inserted in top half of split can and a downward axial force is applied while rotating die

Process description

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

3

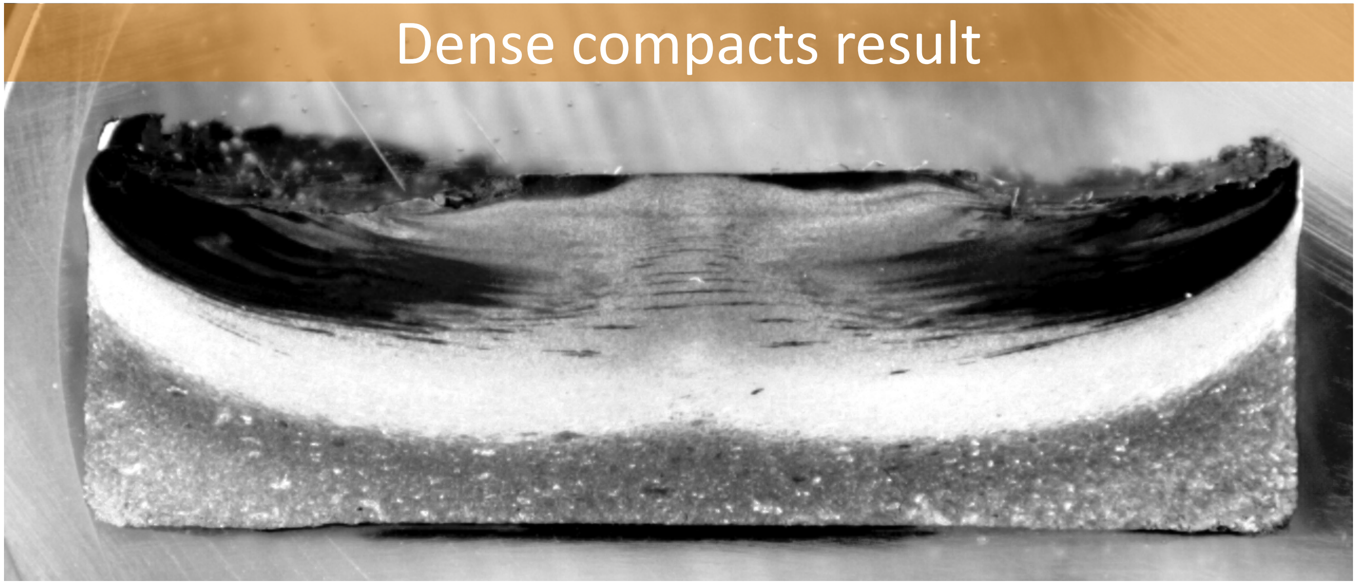
Heat is generated initially by friction between particles, but as the powder consolidates the heat is from plastic work energy dissipation



The energy released from plastic work results in significant heating, up to **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.

Process description

4



- 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 can produce good mixing of constituents and potentially “diffusion” rates high enough for good oxide mobility (dissolution) and redistribution to form nano-clusters

Objective

- Demonstrate a low-cost method of fabricating Ferritic ODS billet, rod, and tube directly from oxide-doped stainless steel powder
  - Develop the process conditions, apparatus and die configurations to produce textured wrought product forms

- Approach
  - Develop the process control and equipment to produce fully compacted billets from metallic powder feedstocks (Completed)
  - Produce lab-scale densified compacts , then, with new die designs, produce rod and tube product forms without post processing (HIPing, and rolling or extrusion, etc). (Completed)
  - Demonstrate that the oxide dispersoids are nanoscale (<20 nm in size) and uniformly distributed throughout the steel matrix (Completed)
  - Investigate scale-up issues
    - flow model development and validation (Completed)
    - Equipment design and fabrication (in process)
  - Fabricate larger rods and tubes (in process)

Feedstock Materials Investigated in the Project

- 3 Different feedstock powders

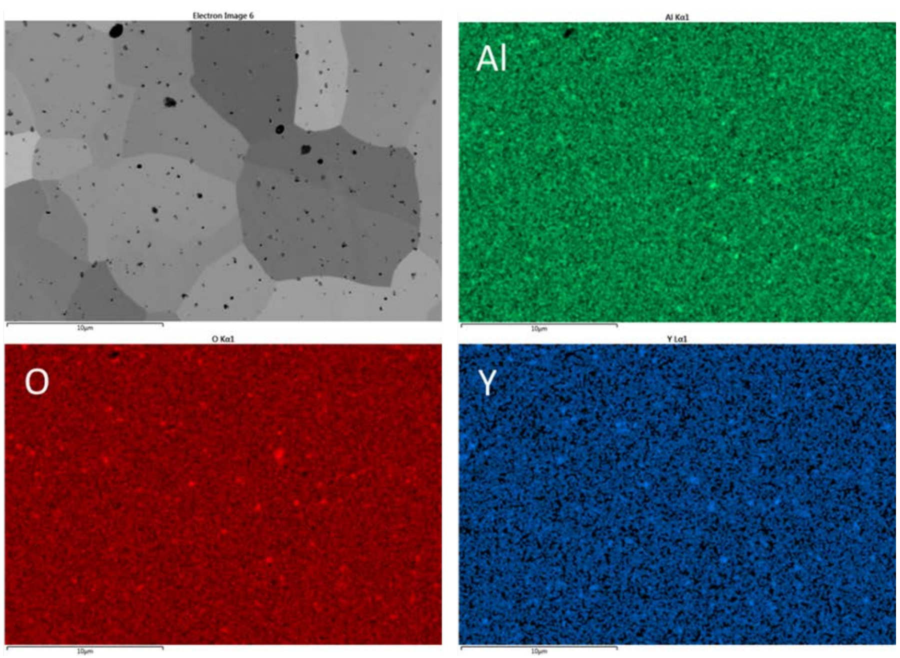
	Mechanically Alloyed Powder	Gas Atomized Powder	Steel Powder + Y_2O_3
	Special Metals	*Sandvik Osprey*	*ATI Powder Metals*
	MA956	*Fe22Cr5AlYZr*	*Custom*
Fe	Bal	Bal	Bal
Cr	19.64	22.4	18.6
Al	4.87	6	4.94
Ti	0.39	-	0.5
Y_2O_3	0.5	-	0.5
Y	-	0.07	-
Zr	-	0.42	-
Oxygen	0.25	-	-
Si	0.07	0.21	-
Mn	0.09	0.2	0.04
Ni	0.06	-	-
N	0.031	-	-
C	0.02	-	0.02
Cu	0.02	-	-
Co	0.01	-	-
S	0.007	-	0.01
P	0.006	-	-

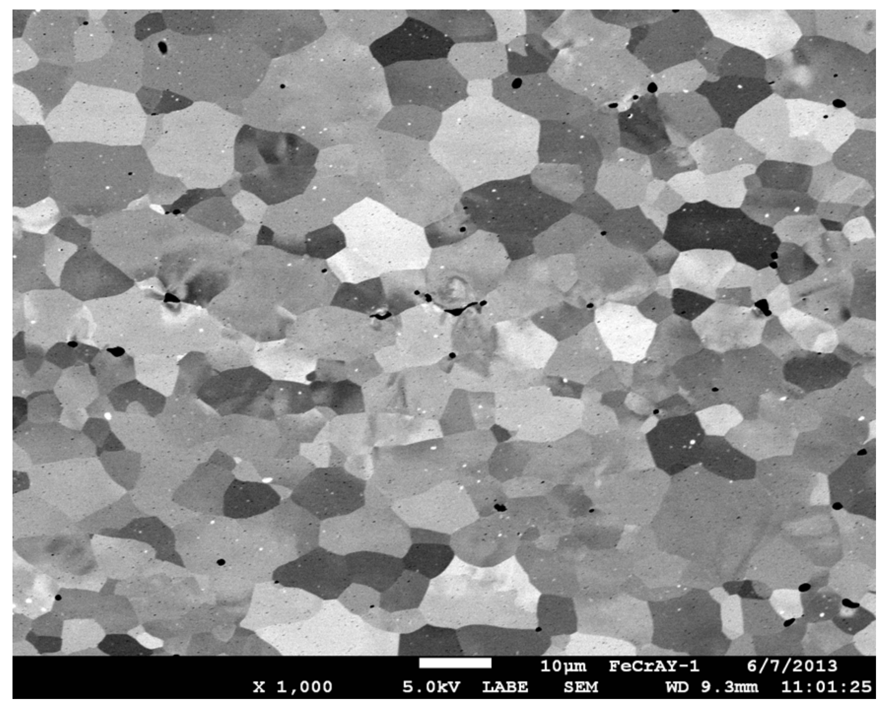
- MA – FCE can eliminate the downstream process costs but MA precursor still includes the up front MA cost
- GA - Reduces cost of “front end” powder step, but distribution of yttria may be a challenge (dependent on particle size?)
- Steel + Y - Further reduces cost of “front end”. If the primary “mixing” occurs in the Friction Consolidation process, then the distribution of Yttria in starting powder may not be as important

The mechanically alloyed powder (MA956) and the steel powder + Y2O3 have virtually the same global chemical composition.

Results of Consolidation Trials

- For all three powder compositions and product forms, we were able to make fully dense compacts
- Microstructures were equiaxed, without oxide stringering
- Composition of the >50nm to 500nm particles are Al-Y-O compounds
- Structure of these precipitates changes with increasing energy input during densification from $YAlO_3$ (Perovskite-YAP) to $Y_3Al_5O_{12}$ (Garnet-YAG)

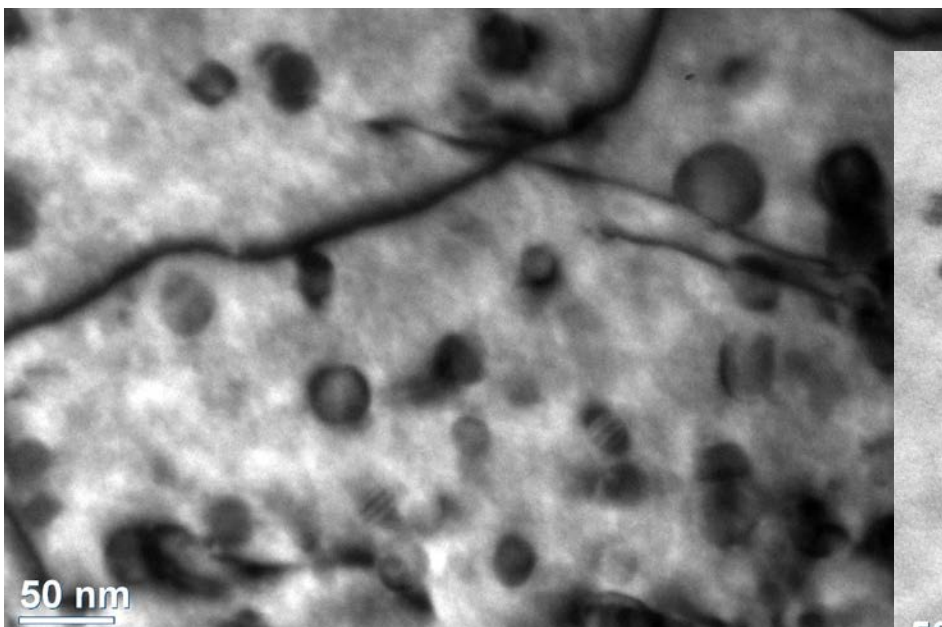


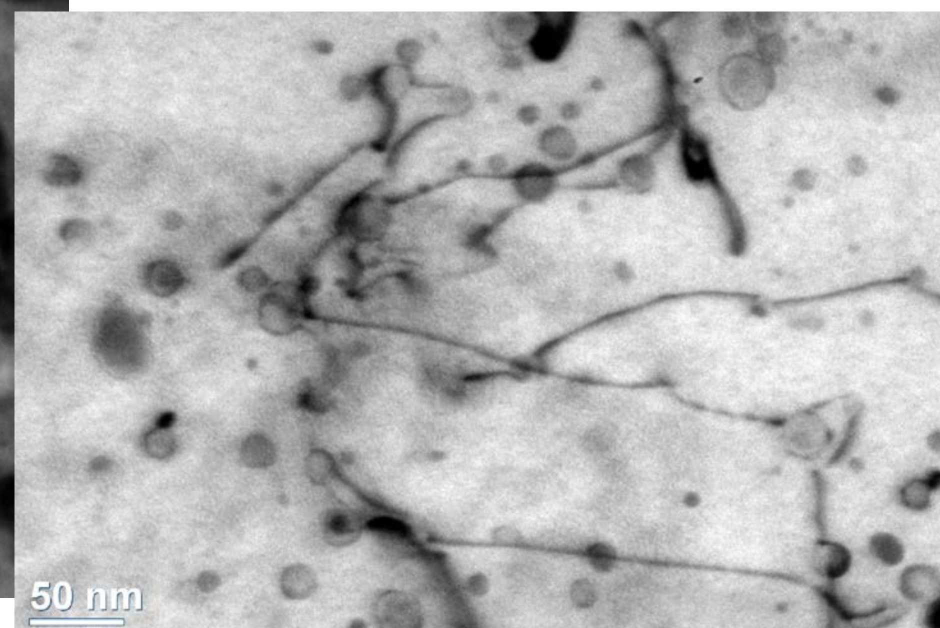


TEM results on FCE compacts

- TEM shows similar size dispersoids in the FCE processed pucks as in conventionally processed MA956
- Small 5 to 20 nm dispersoids are Al-Y-O, likely the monoclinic phase
- The FCE process may be able to make the right microstrucure in one process step

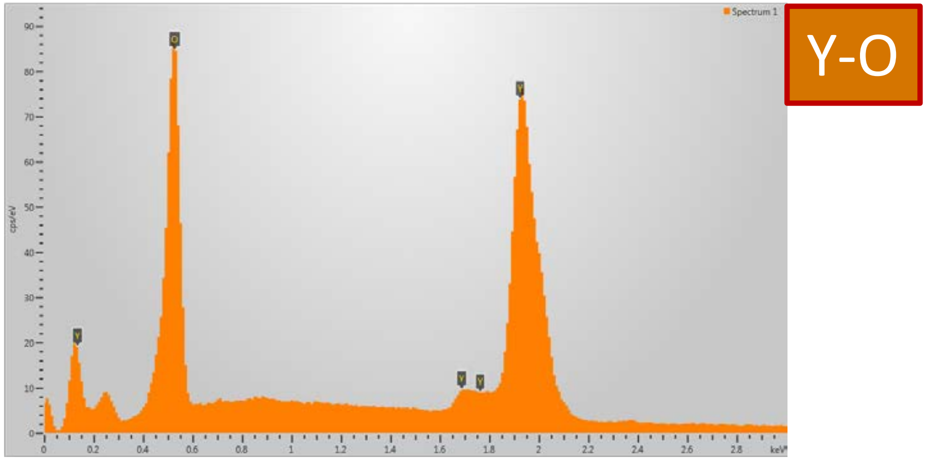
Friction Consolidation

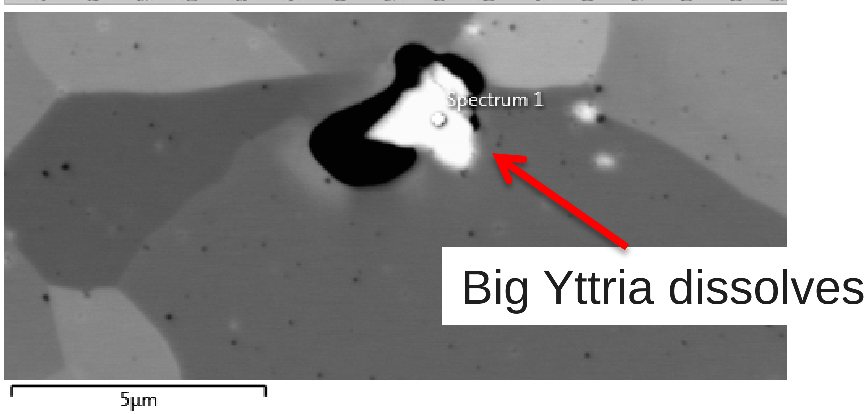


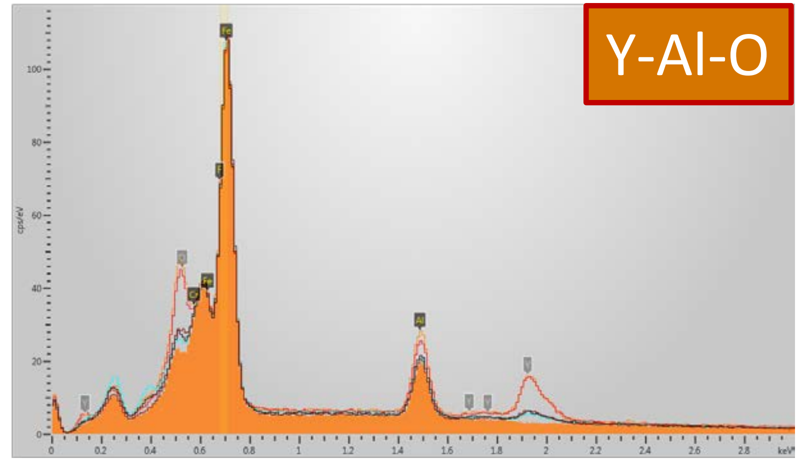


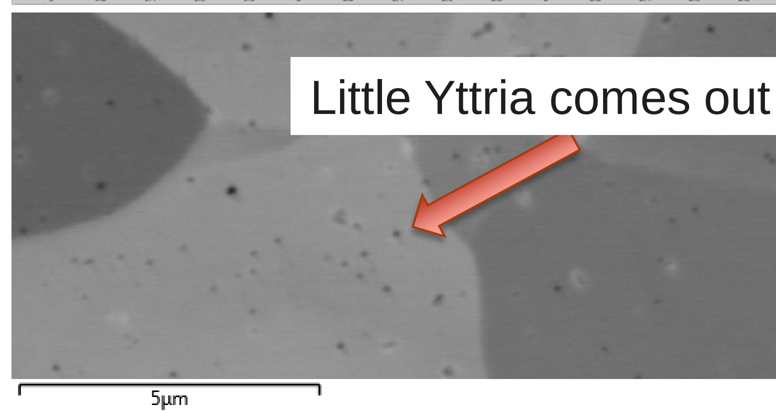
MA 956 RL

Friction Consolidated of Stainless Steel + Yttria powder





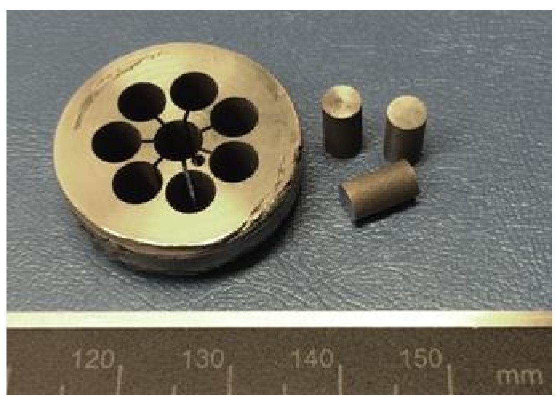




- This powder started as a 40µm steel powder mixed with 0.5% 1 to 5 µm yttria particles. Final compact shows very little coarse yttria.
- Process dissolves coarse yttria and re-precipitates dispersoid Y-Al-O

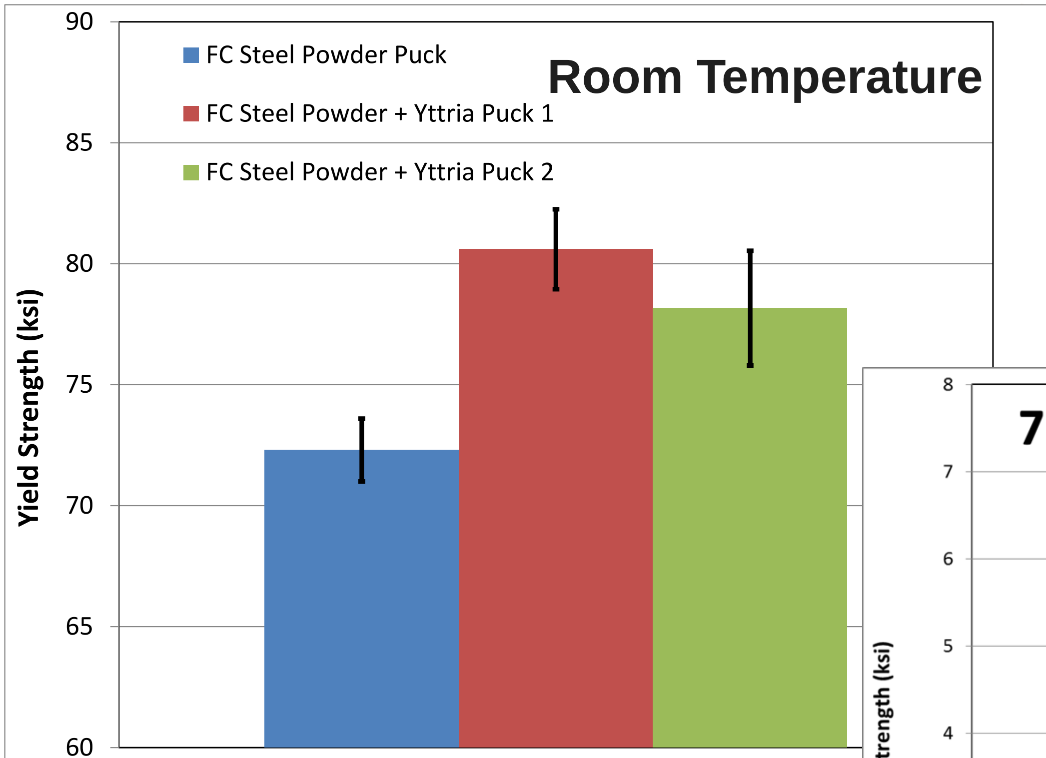
Best evidence of Yttria particle dissolution and re-precipitation might be mechanical properties

- Steel powder and steel + yttria consolidated into pucks at 300RPM, 12,500lbs, to 1000C
- Compression samples 4mm x 7mm EDM machined from pucks
- Compression testing with IN718 tension to compression fixture and following ASTM E9 – 09
- Used Ni antiseize on the top and bottom load pads – no significant barreling

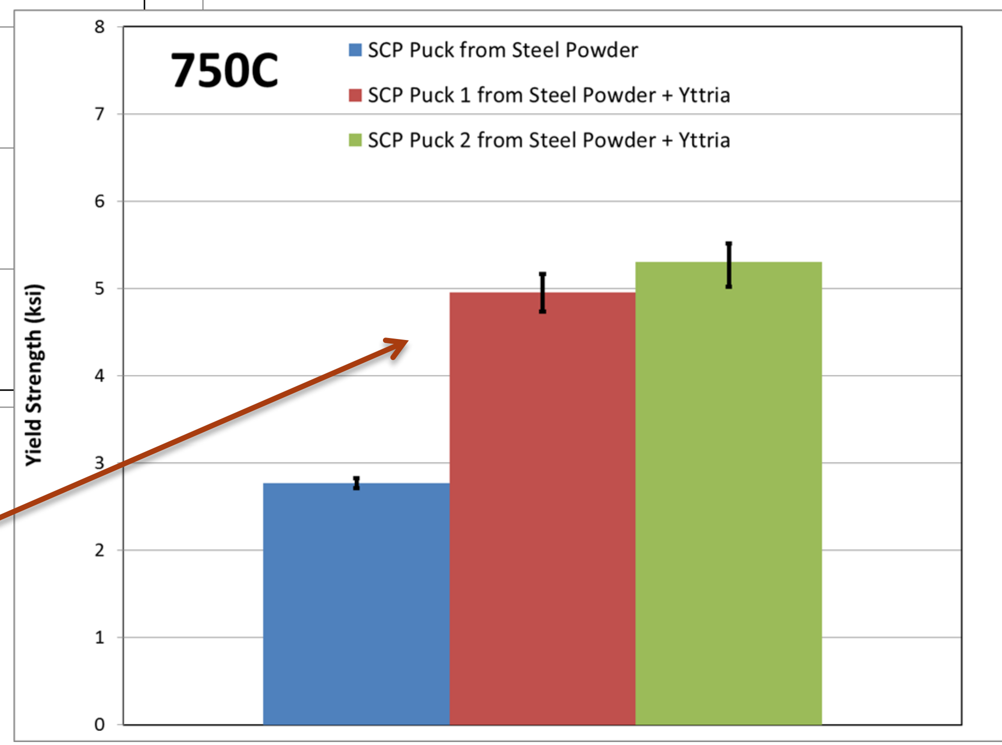


Comparison of the Compressive Yield Strength of Friction Consolidated Pucks –
Steel powder vs Steel plus coarse yttria

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



Addition of yttria and densification by FCE increases the yield strength by 6-8ksi at room temperature (8%)



Elevated temperature yield strength is up by 72% indicating probable effect of dispersion strengthening

Friction Consolidation

We have demonstrated that FC can:

- fully densify MA, gas atomized and ss+Y powders to crystalline solids with complex and process parameter dependent microstructures
- Sub 10nm dispersoids were observed in the FC processed pucks where no dispersoids were originally present in the powders
- 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)
- Can recrystallize and refine the microstructure
- Can create nanoscale Y-O and Y-Al-O dispersions from coarse elemental precursors

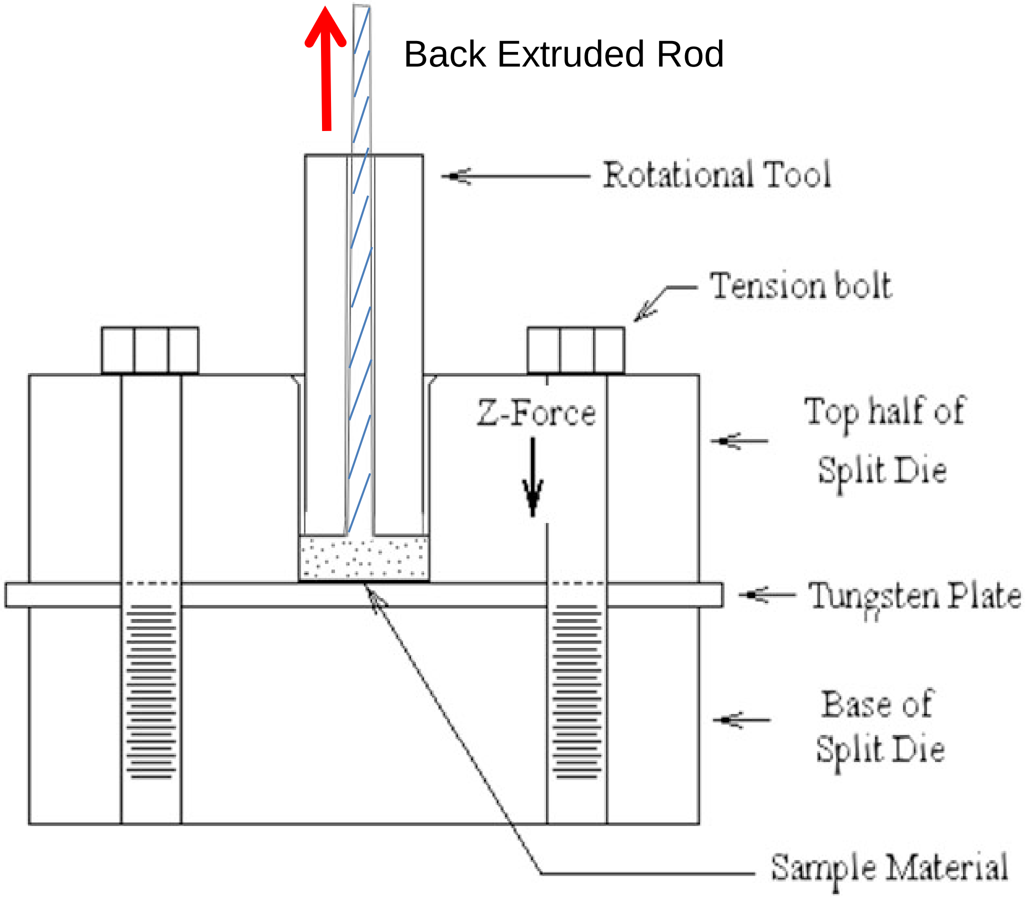
Can we make relevant product forms?

Rod extrusion

Example plunger rod with hole in center

Depending on the geometry and dimensions of the die; billets, rods and tubes can be produced by this process directly from powders.

.



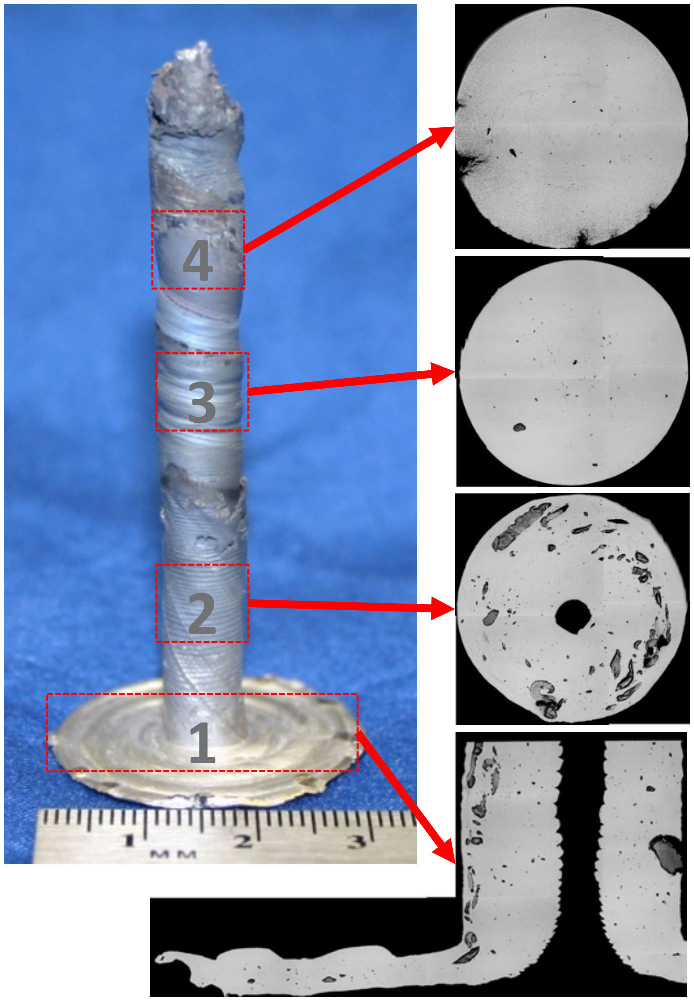
Solid Al rod fabricated directly from powder via a friction stir rod extrusion process. 2050 and 2195 rod extruded at: (a) 150, (b) 200, and (c) 250 rpm rotational speed.

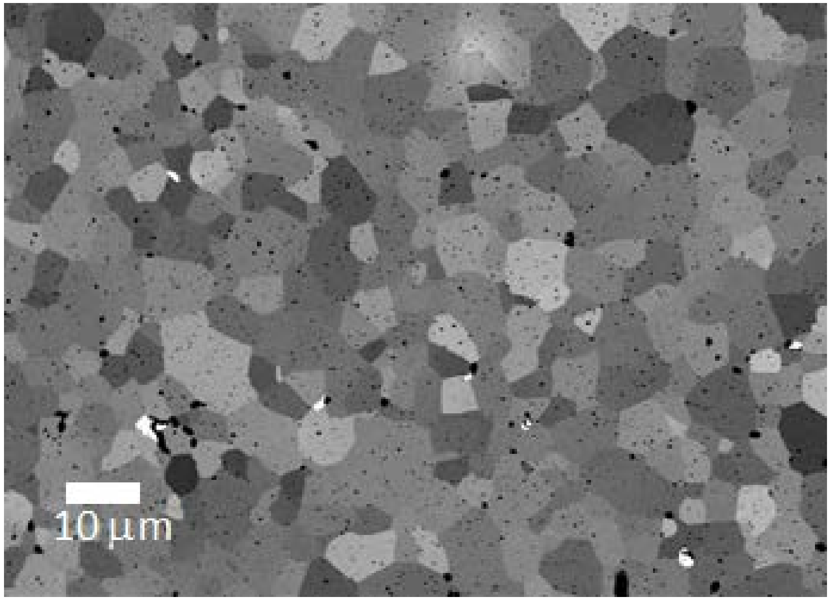
A. Reynolds, USC, 2008

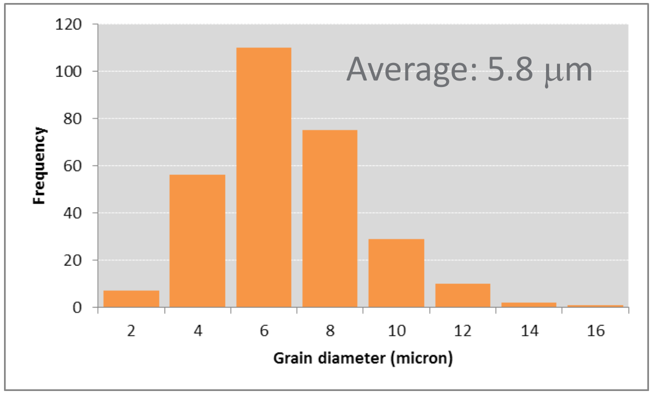
Pacific Northwest
NATIONAL LABORATORY

Friction Consolidated and Extruded Rod of MA956 from MA powder

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*



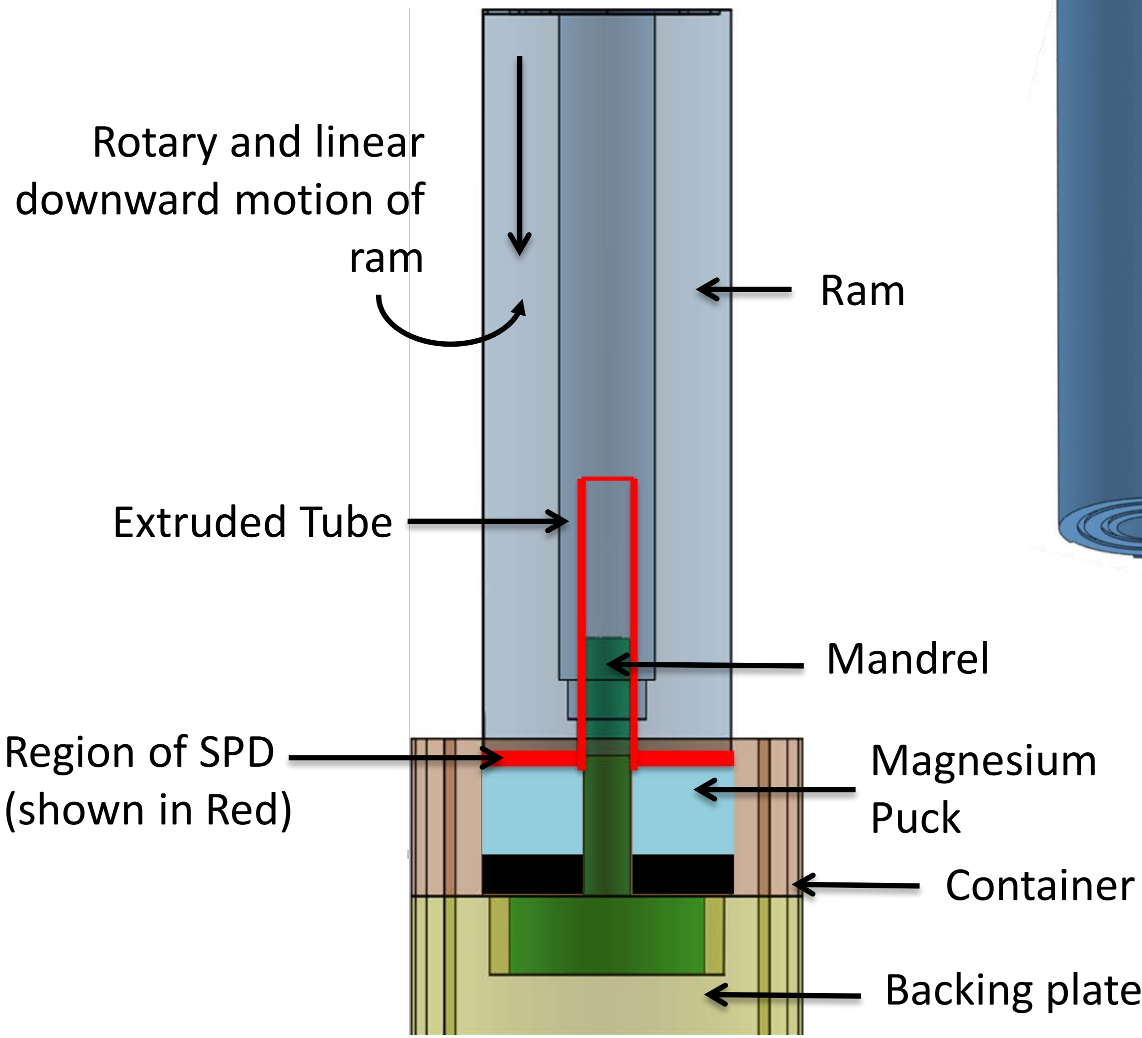


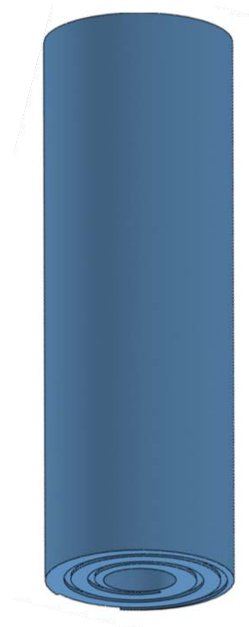


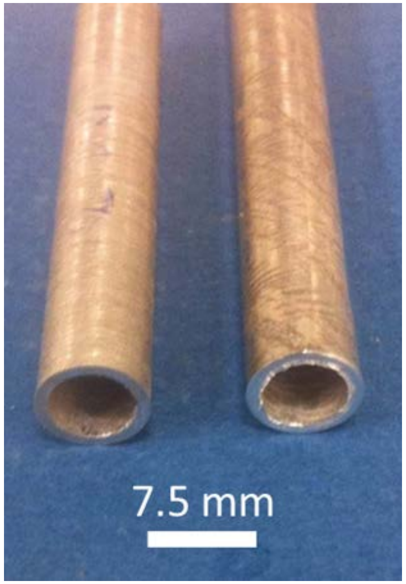
Tool used for extrusion, with a hole in the center.

- Equiaxed grain structure
- Grain are NOT elongated in the longitudinal direction. (implication for anisotropy?)
- No oxide stringering

Shear Assisted Indirect Extrusion Process
Evidence of efficacy from Magnesium trials

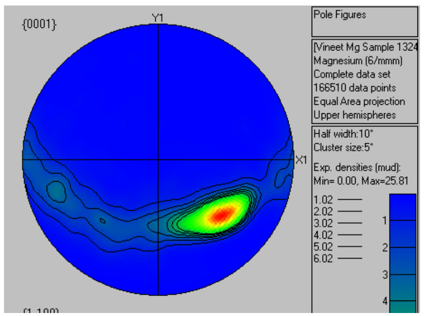


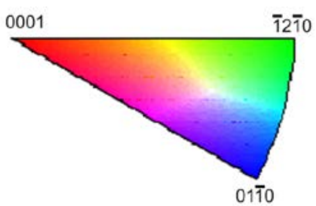


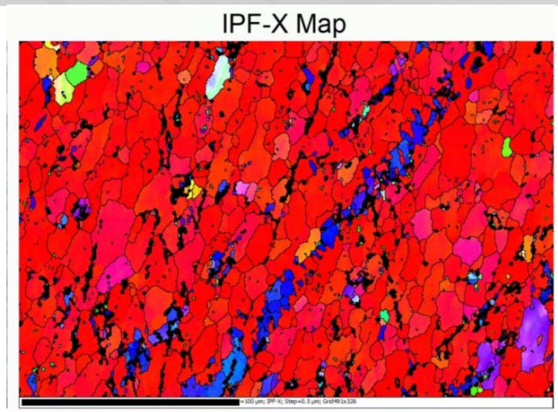


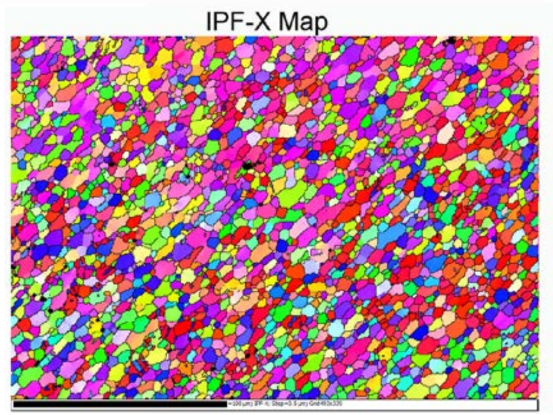
Flute/ Scroll profile on the Ram

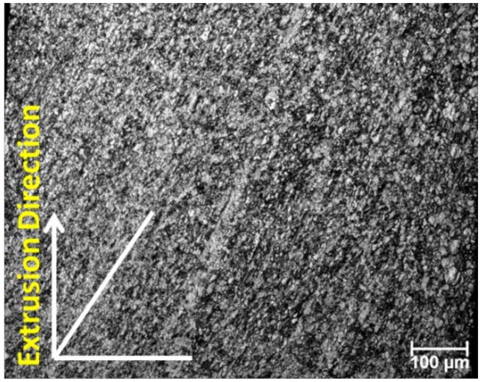
Unique Textures and Microstructures are possible (mag ZK60 example)

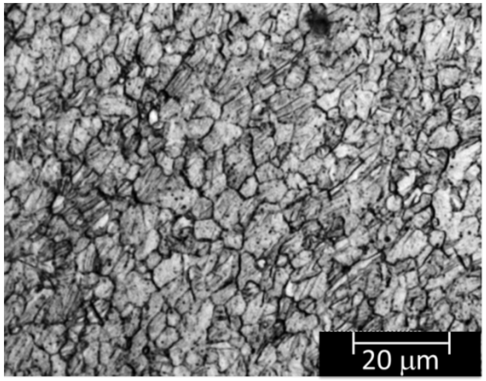








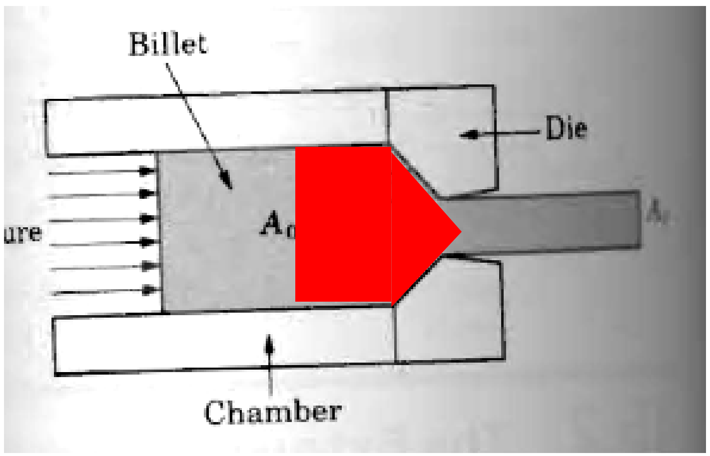




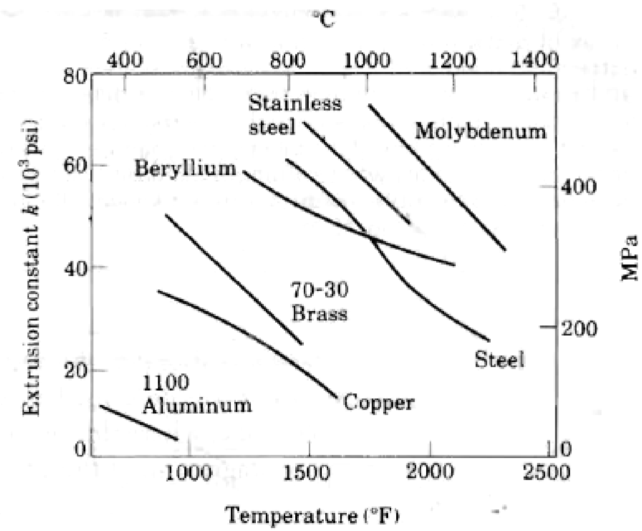
- Grain size less than 5 microns and oriented 45deg to the extrusion axis
- The texture direction is influenced by the ratio of the rotation rate to the extrusion rate
- In ODS alloys that have secondary recrystallization behavior this may allow for growth of elongated grains in a unique (spiral) direction in the tube/pipe

“Shear Assisted” Extrusion vs. Conventional Direct Extrusion

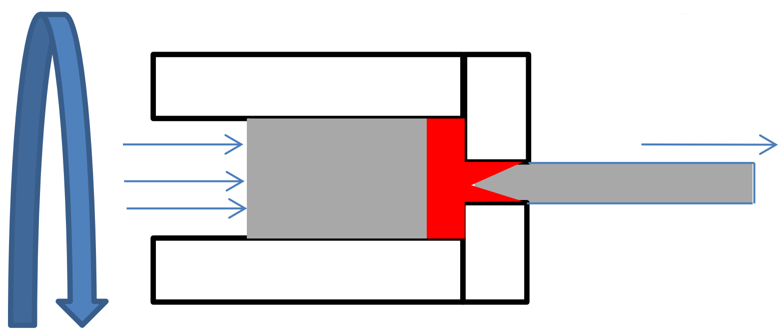
- Do normal extrusion guidelines apply? No
- Ram loads are 1/10 that estimated from conventional extrusion



F = Ao*k*ln(Re)
Re = Ao/Af
K = extrusion constant



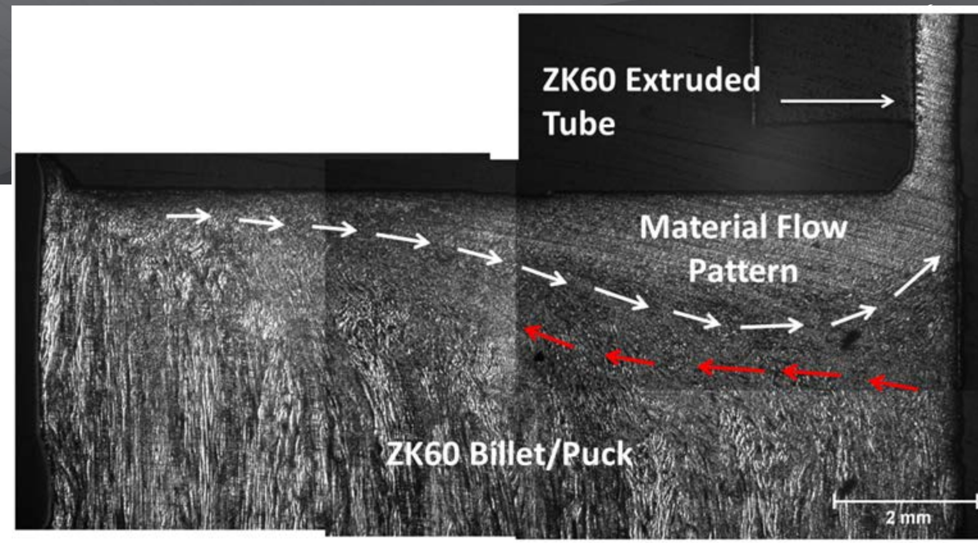
- Why? -
  - Deforming volume is much smaller ?
- This is extremely good for scale up considerations

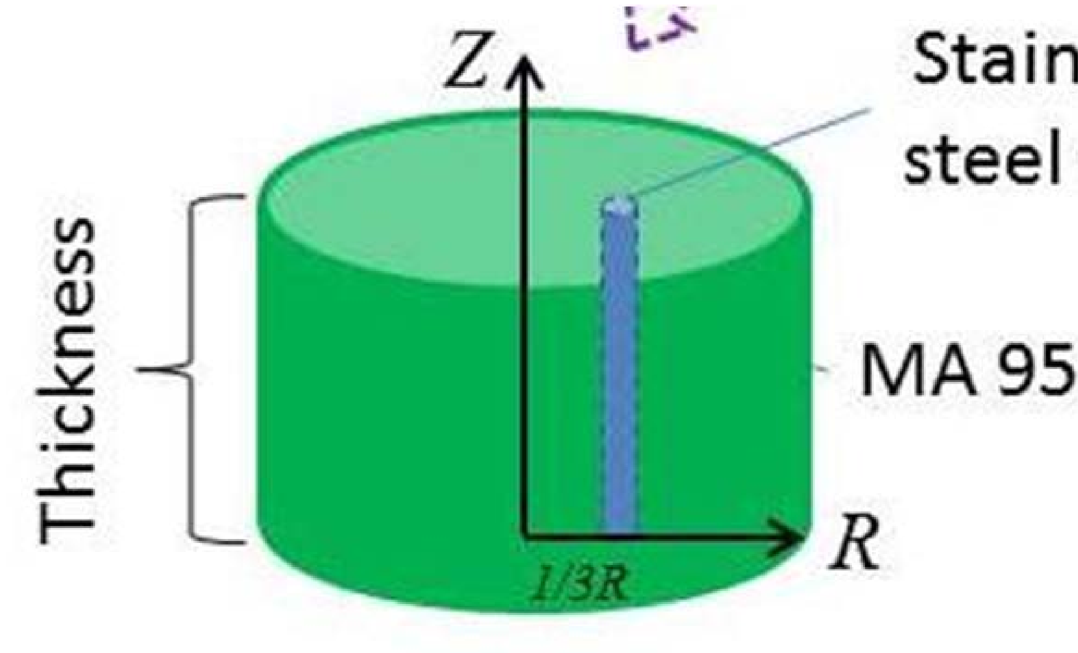


Pacific Northwest
NATIONAL LABORATORY

Material flow is different than conventional extrusion

- How does material flow progress during extrusion and how is texture developed?
  - Marker Studies and Flow Modeling





Extrusion parameters for all marker **experiments were as follows:**

Extrusion/processing force: 22,500 N (5000lbf)

Die rotation rate: 300, 500, 700 RPM

Die: 25 mm diameter, single scroll, W-25% Re
Processing time: 27 s
Billet height: 6.4 mm

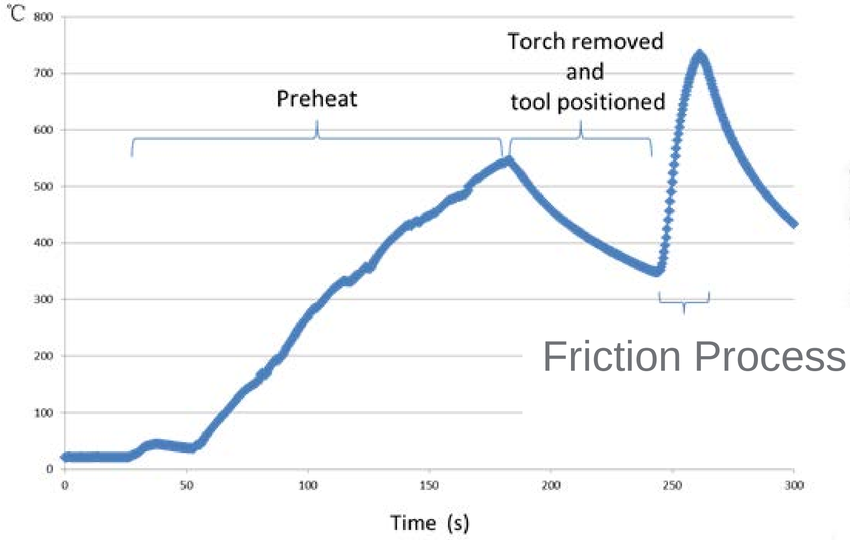
Work done by Dr. Anthony Reynolds, University of South Carolina

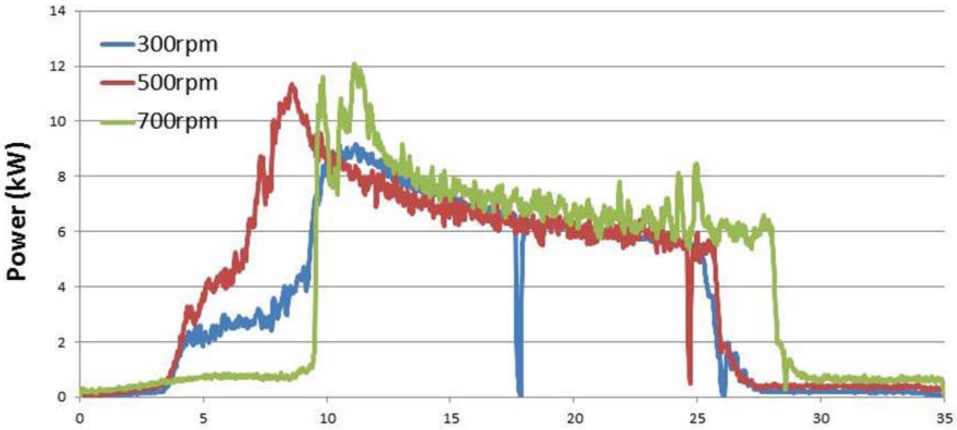
Marker Studies

Serial sectioning through billet

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- MA956 needed pre-heat to reduce die wear and loads at startup





Initial position of marker in all sections

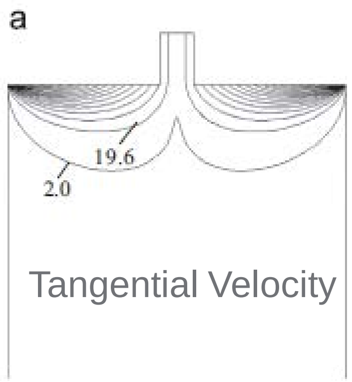
- Spiral pattern (highest strain) is at die face and decreases with depth
- Deformation extended 2 -3 mm into puck after 27 seconds

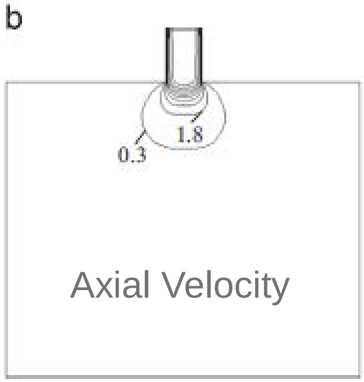
U. of S. Carolina Modeling the process

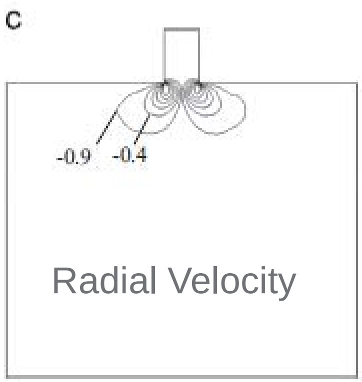
H. Zhang, X. Zhao, X. Deng, M.A. Sutton, A.P. Reynolds, S.R. McNeill, X. Keb University of South Carolina and Correlated Solutions,Inc. have been modeling the process.

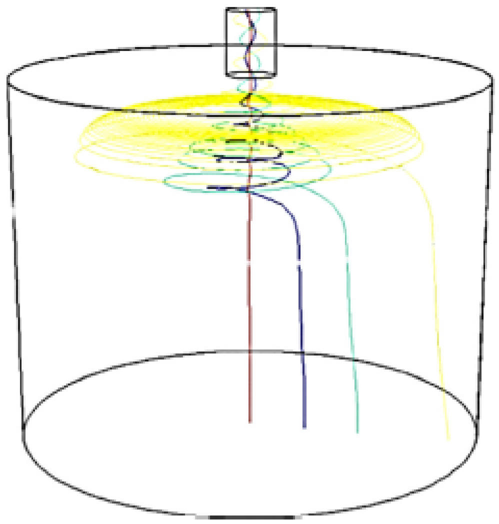
three-dimensional computational fluid dynamics(CFD) model with a no-slip contact condition between the rotating tool and the material being processed.

During processing the material is treated as a non-Newtonian fluid with a viscosity that is temperature and strain rate dependent.









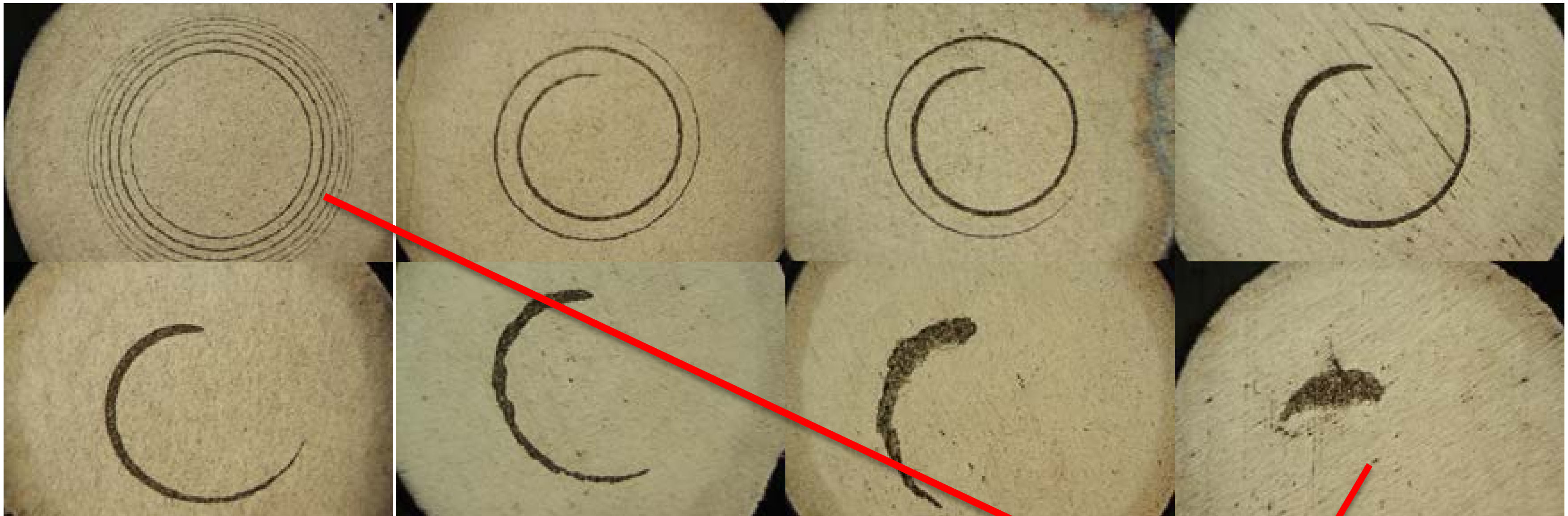
Paths taken by markers

Tang W, Reynolds AP., Production of wire via friction extrusion of aluminum alloy machining chips., J Mater Process Technology 2010; 210:2231–7

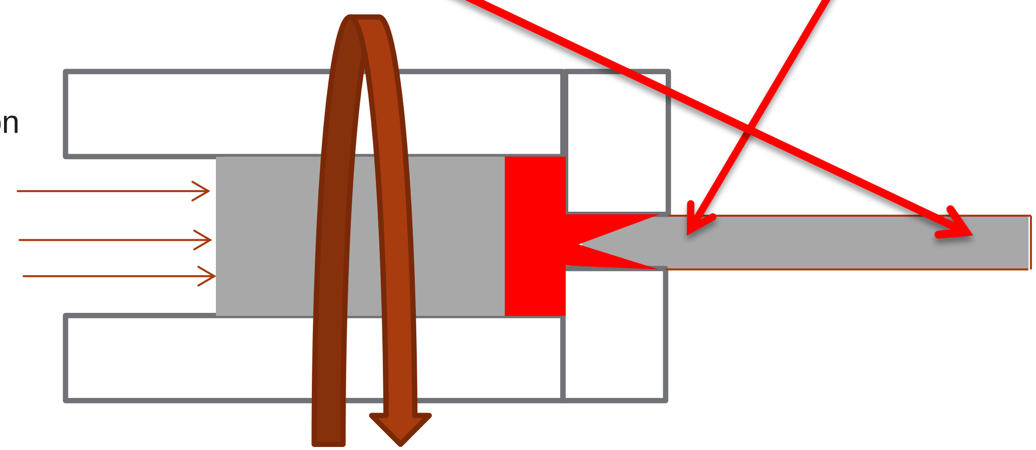
H. Zhang, X. Zhao, X. Deng, M.A. Sutton, A.P. Reynolds, S.R. McNeill, X. Keb, Investigation of material flow during friction extrusion process; International Journal of Mechanical Sciences 85 (2014)130–141

Marker Study in an Aluminum analog

How texture might be customized



- Spiral pattern is seen in the wire cross section
- Because this extrusion proceeded at constant force and increasing temperature, the extrusion rate constantly increased
- Increasing rate lead to a change in the tangential component of strain.
- The extrudate was more like a conventional extrusion at high rate



If process conditions could be controlled, we should be able to dial in $\varepsilon_{tangential} / \varepsilon_{axial}$ and potentially set texture direction

What are the knobs we can turn to control the product properties?

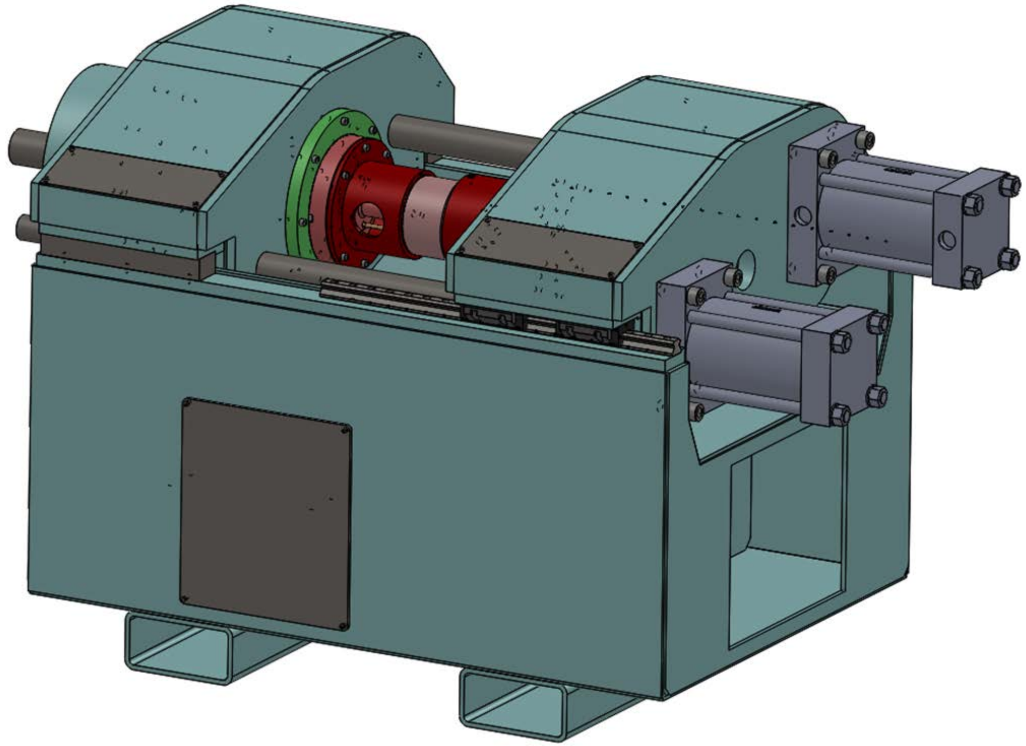
- **Die RPM** : largest effect on thermal gradient. Higher RPM- higher temperature of the deformation zone and possibly steeper the thermal gradient
- **Extrusion Rate:** set by a combination of temperature at the face, extrusion ratio, material properties. Ratio of RPM to extrusion rate may set texture in extrudate. Spiral or off axis textures observed.
- **Extrusion Force:** High forces are needed to initially compact the powders but during extrusion, force is probably dictated by material condition
- **Die face feature** : a scroll feature on die face promotes strong flow of material at the die face. This could help feed die throat and contribute to texture development. Also has strong effect on mixing and homogenization
- **Boundary Conditions:** Active cooling/heating is important (controlled fast cooling rates after the cessation of dynamic recrystallization can help minimize grain growth, or slow cooling rates could promote secondary recrystallization for creep resistance), atmosphere control in billet chamber may be important to control oxidation in ODS alloy fabrication

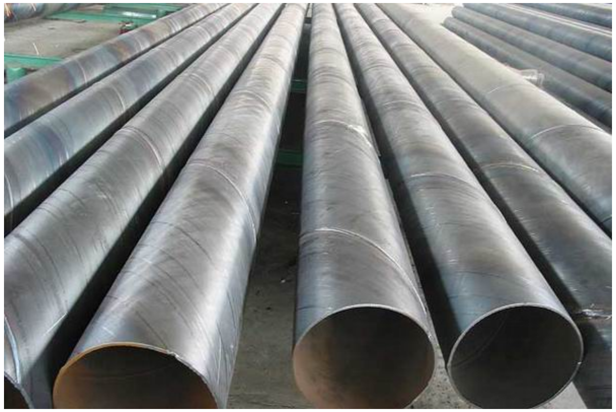
FCE is a thermo-mechanical process. We can have control over the microstructure, and hence on the properties, by adjusting process variables.

Scroll feature on die tool face

Next step – Scale up

- We need better control of process and higher forces to extrude reasonable sized tubes
- The machine at right should be installed at PNNL in mid-Fall.
- First of its kind “rotary extruder”
  - 100 Ton axial feed
  - 700 ft-lb rotation torque
  - 10 inch stroke
  - Controlled rate, force, torque, die temperature





Summary - Lowering the cost of ODS Alloys

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 shape?)
  - Application to tubing and piping
  - Production of hollow billets for tubular extrusion
- Process has the potential to produce appropriate microstructures
  - Process can create equiaxed microstructure – reduction of anisotropic behavior?
  - Process does not produce oxide stringers
    - reduced roll processing
    - 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

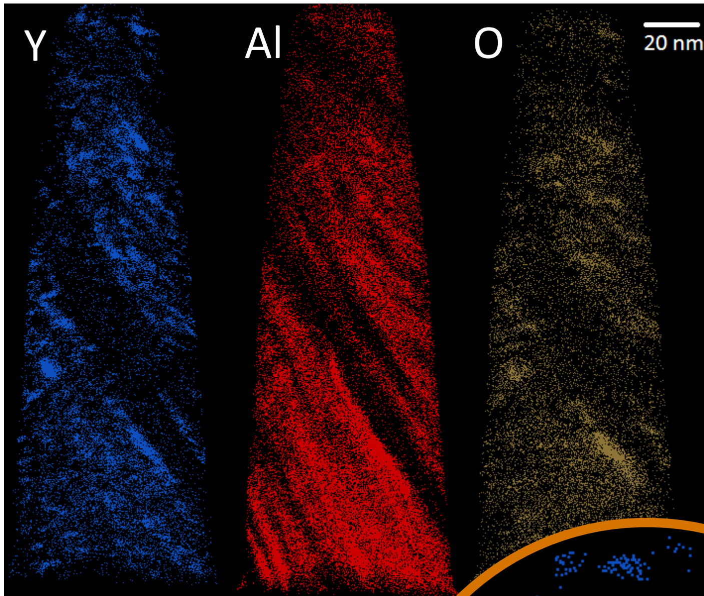
These features may lead to a substantial reduction in the cost of producing ODS alloy products

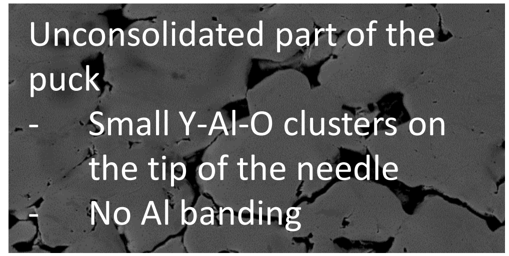
Pacific Northwest
NATIONAL LABORATORY

END

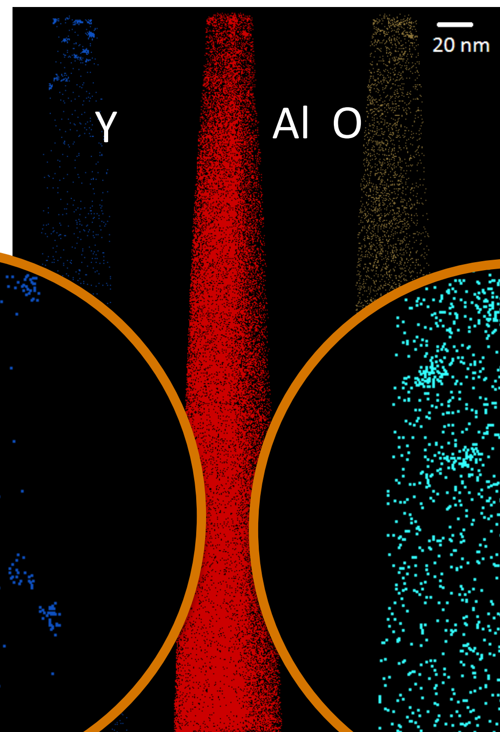
Atom Probe Tomography (APT) of Friction Consolidated MA956

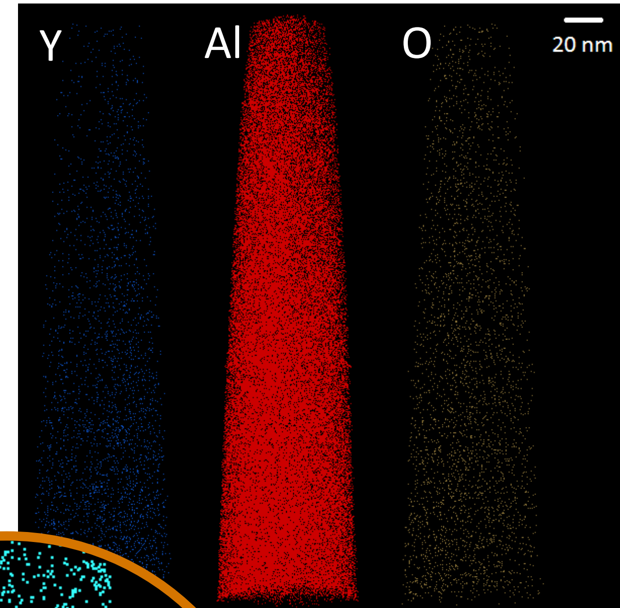
Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



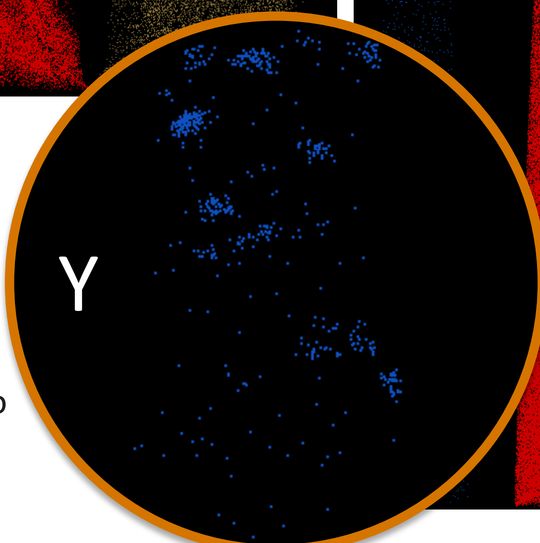


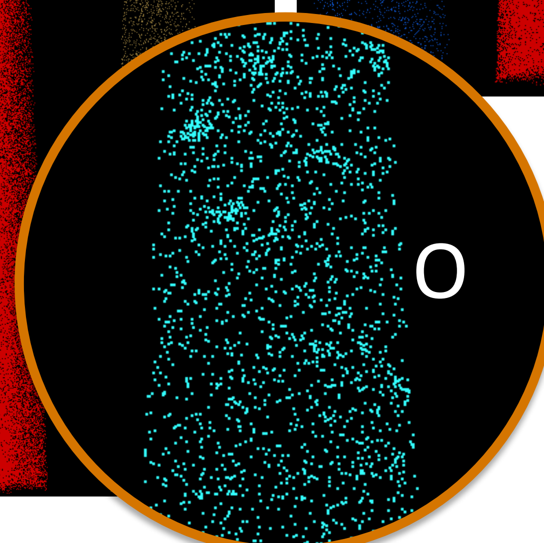
Unconsolidated part of the puck
- Small Y-Al-O clusters on the tip of the needle
- No Al banding





Powder before consolidation
- Y is present in clusters
- Al shows banding
- O also correlates to some Y locations





Consolidated Puck
- Y is very finely divided
- Al is homogeneously distributed
- O is very finely divided