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Fabrication of iron nitride based soft magnets for transformer cores

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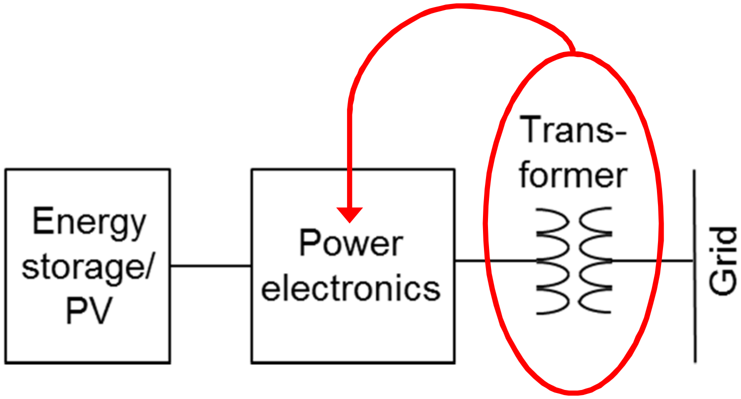
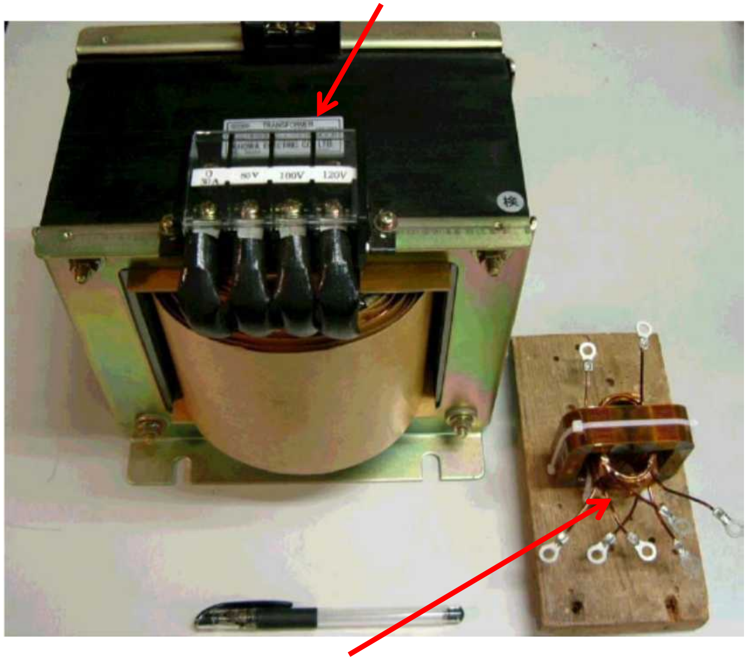
Benefits of a High Frequency Transformer



Line frequency (50 Hz) transformer



High frequency (20 kHz) transformer

S. Krishnamurthy, Half Bridge AC-AC Electronic Transformer, IEEE, 1414 (2012).

- Integrate output transformer within power conversion electronics
- Leverage high switching speed and high temperature performance of WBG semiconductors
- Transformer core materials for high frequency transformers have been an afterthought (no current material meets all needs)

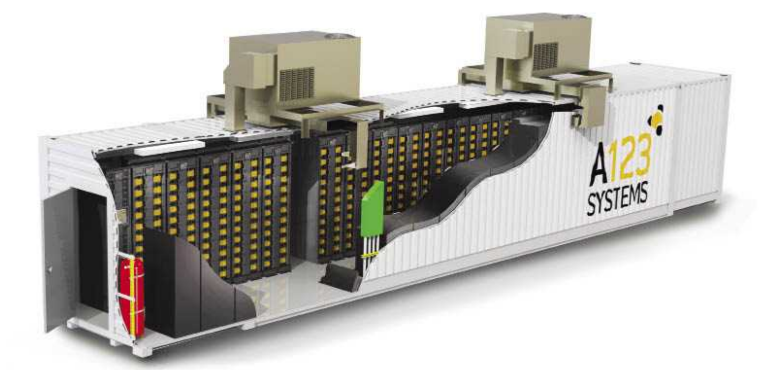
Material requirements:

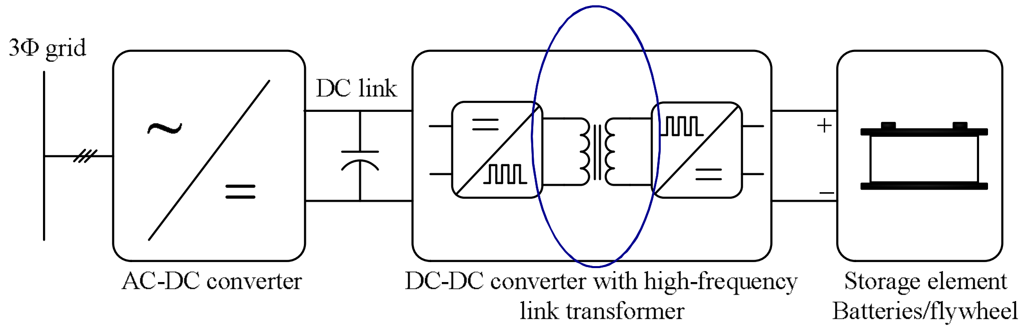
- Low loss in ~ 10-30 kHz frequency range
- High permeability (low coercivity)
- High saturation magnetizations
- Low magnetostriction
- High temperature performance
- Rapid and scalable manufacturing
- Affordable

Transportable Energy Storage and Power Conversion Systems (PCS)

Benefits of Energy Storage:

- **Maintaining power quality and reliability**
- **Improve stability and defer upgrades**
- **Improved control such as load leveling, peak, power factor control, frequency and voltage regulation**
- **Increase the value of variable renewable generation**





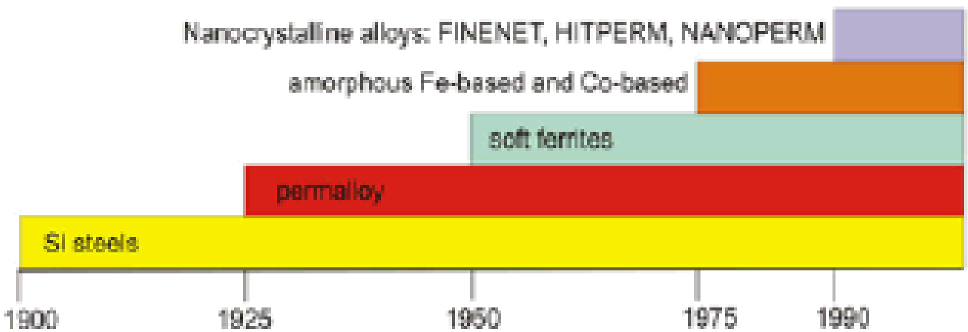
Benefits of Transportable Systems:

- **Faster installation**
- **Lower cost**
- **Modular design allows for quick deployment to multiple sites**
- **PCS can represent 20-60% of total energy storage system cost**

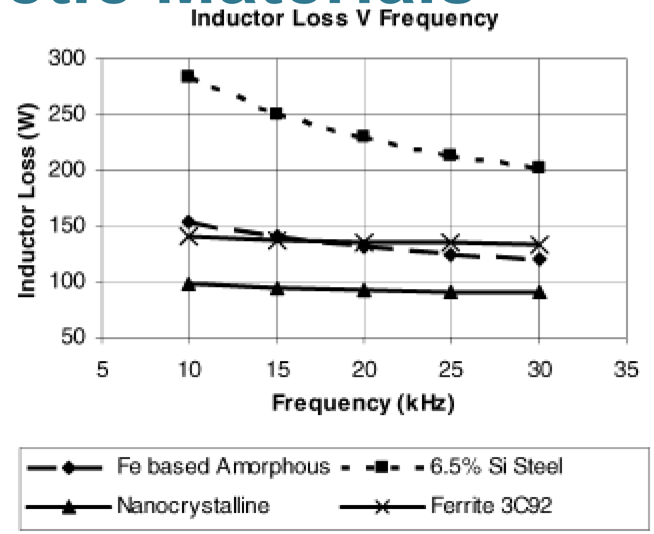
Military Microgrid

- **Almost identical challenges facing modernization of civilian electrical grid**
- **Desire to deploy systems in a small number of ISO containers**
  - **Requirement to reduce space of power conversion system**

Development of Soft Magnetic Materials



L.A. Dobrzański, M. Drak, B. Ziębowicz, Materials with specific magnetic properties, Journal of Achievements in Materials and Manufacturing Eng., 17, 37 (2006).



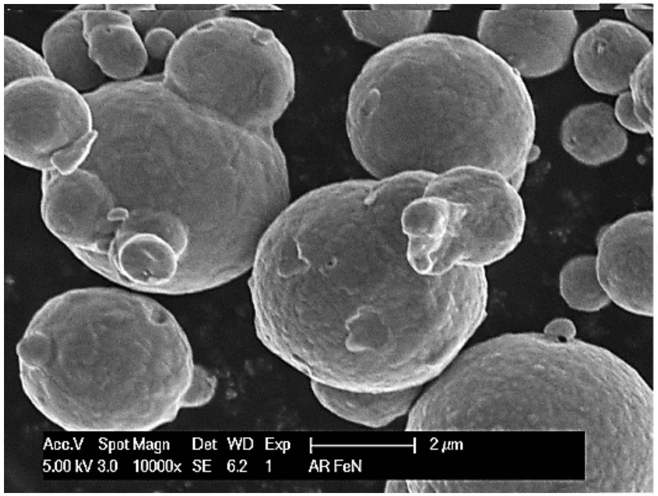
B.J. Lyons, J.G. Hayes, M.G. Egan, Magnetic Material Comparisons for High-Current Inductors in Low-Medium Frequency DC-DC Converters, IEEE, 71 (2007).

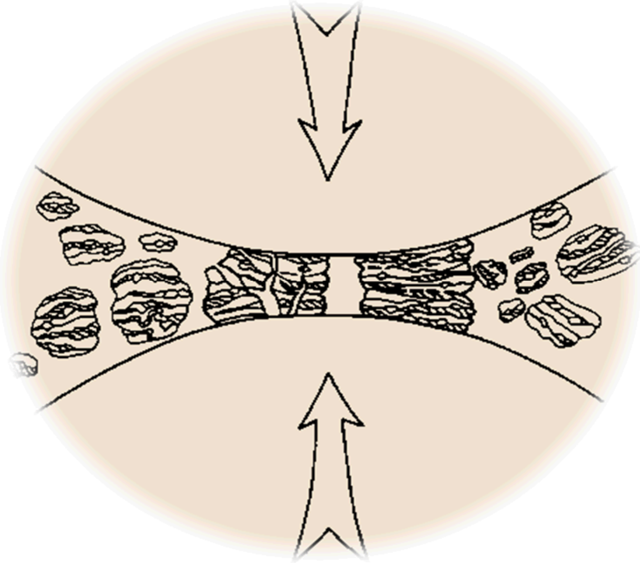
Magnetic Material	J_s (T)	$\rho(\mu\Omega\cdot m)$
Metglas 2605SC	1.60	1.37
VITROPERM (Vacuumschmelze)	1.20	1.15
Ferrite (Fexxocube)	0.52	5×10^6
Si steel	1.87	0.05
γ'-Fe_4N	1.89	~200

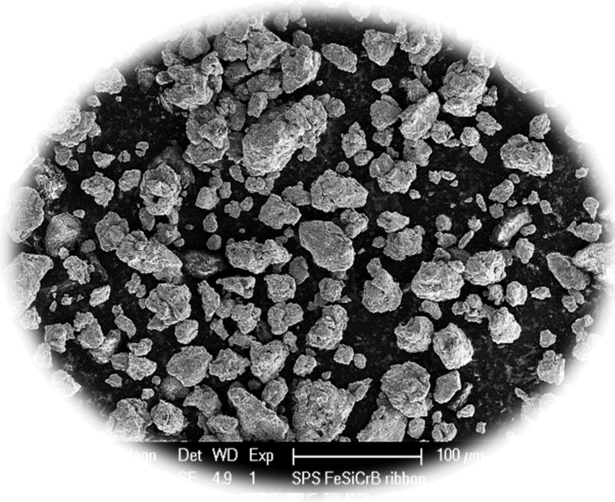
- **Little or no development of new magnetic materials since the early 1990s!**
- **Nanocrystalline alloys low loss but magnetizations low when compared to bulk iron ($P_{max} \sim f\cdot\Delta B\cdot A_{core}\cdot A_{Cu}\cdot I_{sat}$ $I_{sat} = B_{sat}\cdot l_m/\mu\cdot n$ $E_{rms} = 4.44\cdot f\cdot n\cdot A\cdot B_{sat}$)**

*** ΔB and I_{max} also limited by ΔT (max temp. rise)**

Materials Pre-Processing





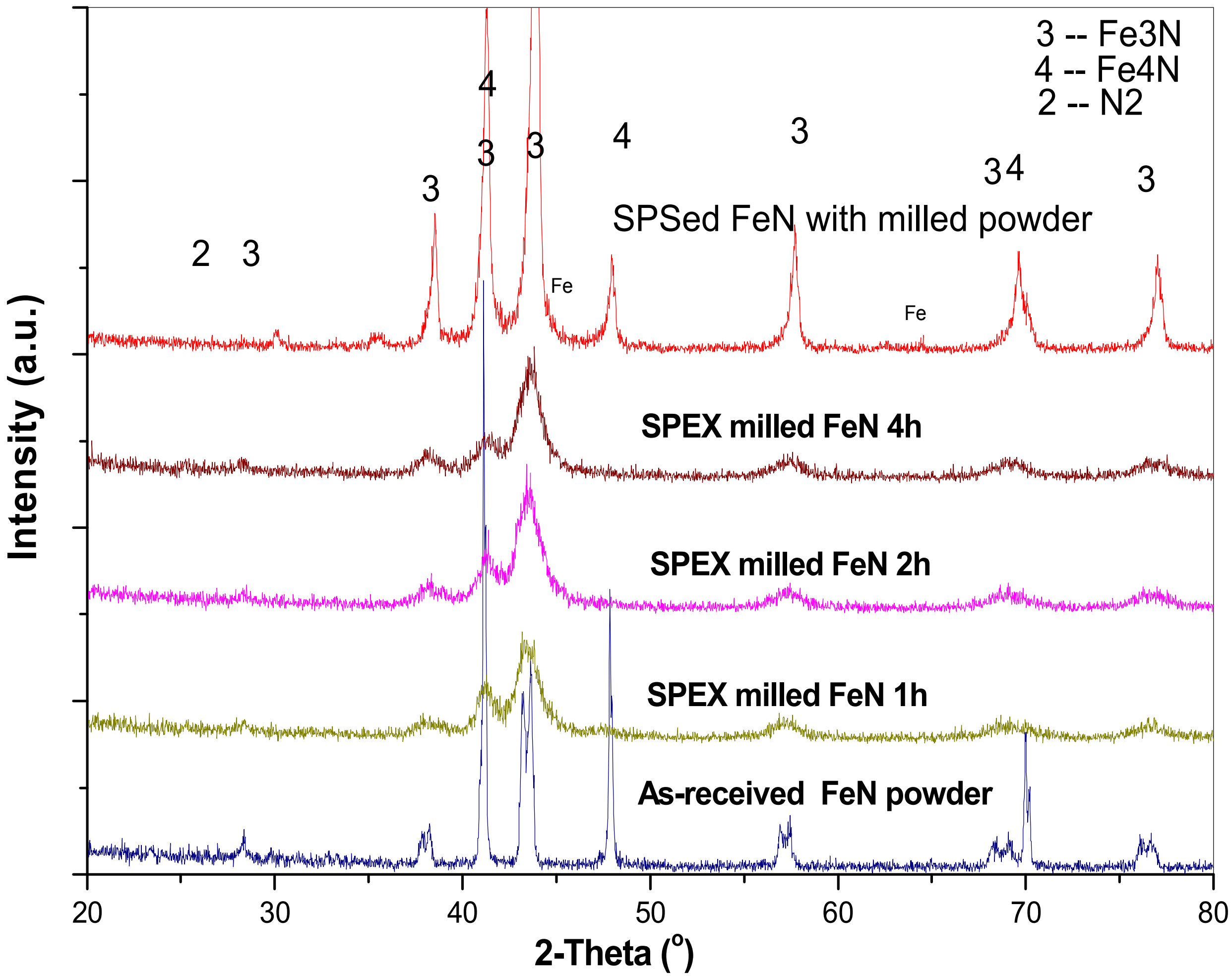


Starting FeN Powder

Mechanical Milling

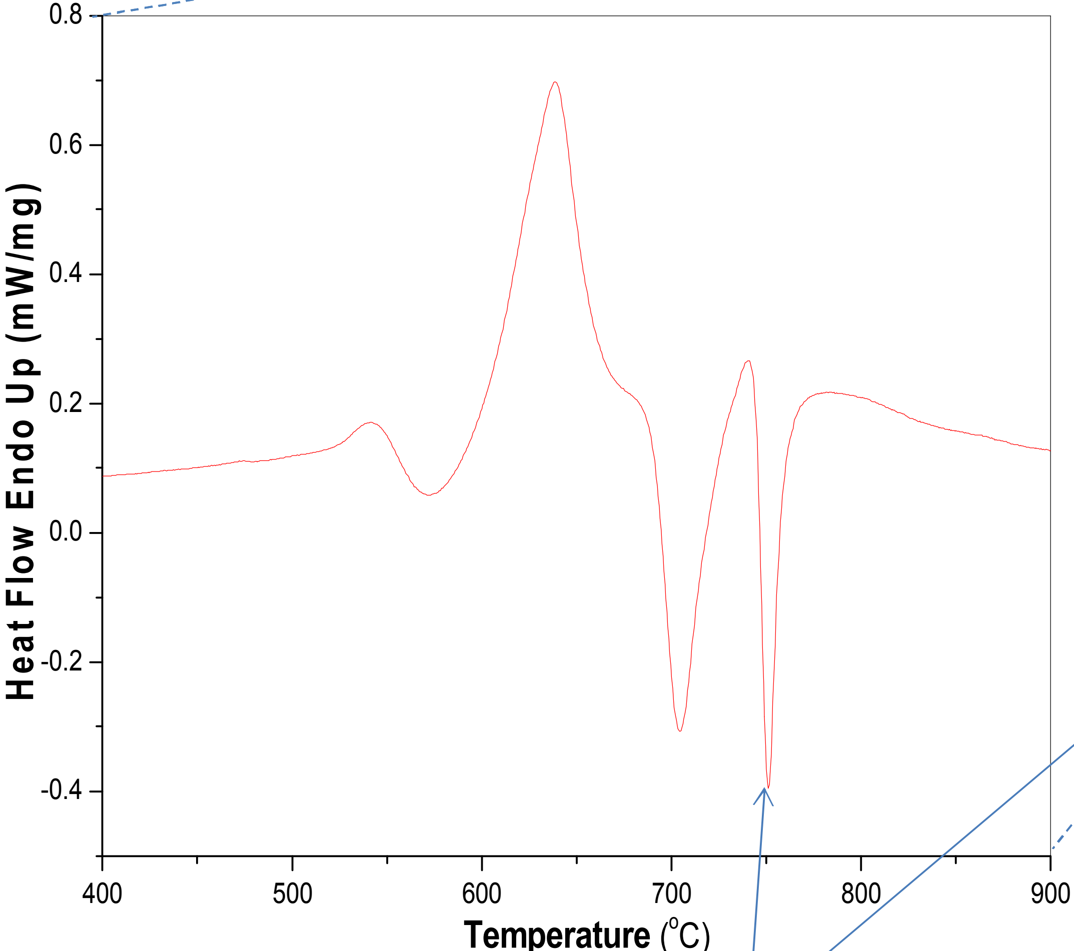
Milled FeN Powder

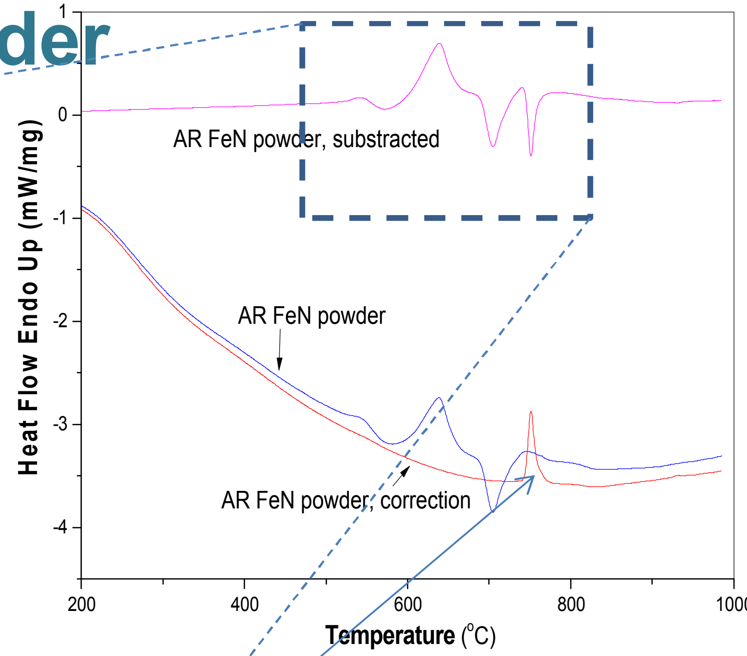
High Energy Mechanically Milled FeN



- **XRD peaks broaden after milling, indicating grain refinement**
- **Peak intensity increases after SPS (550°C, 100MPa), indicating growth**

DSC of as-received FeN powder





Caused by FCC-Fe transformation to BCC-Fe

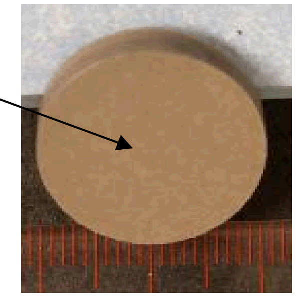
- **Decomposition of FeN powder begins at ~550°C.**
- **This limits SPS temp. in order to avoid decomposition.**

Spark Plasma Sintering (SPS)

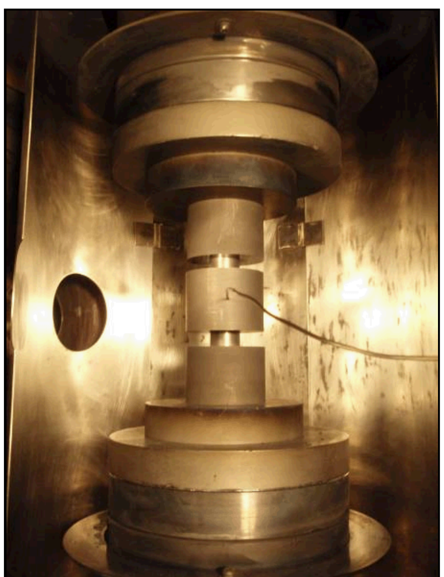
SPS Model: SPS-825S Dr. Sinter® at UCD

Starting Powder in Die

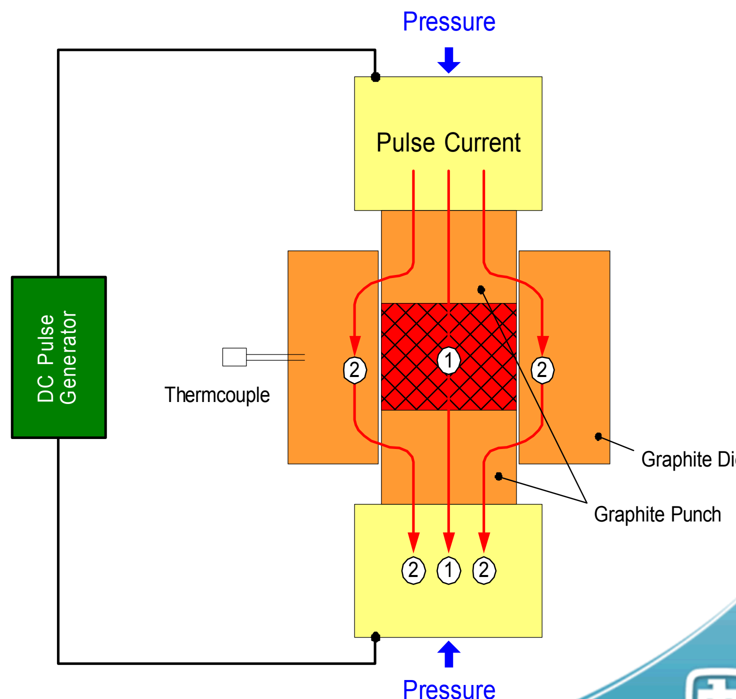
End Product



SPS Synthesis Chamber

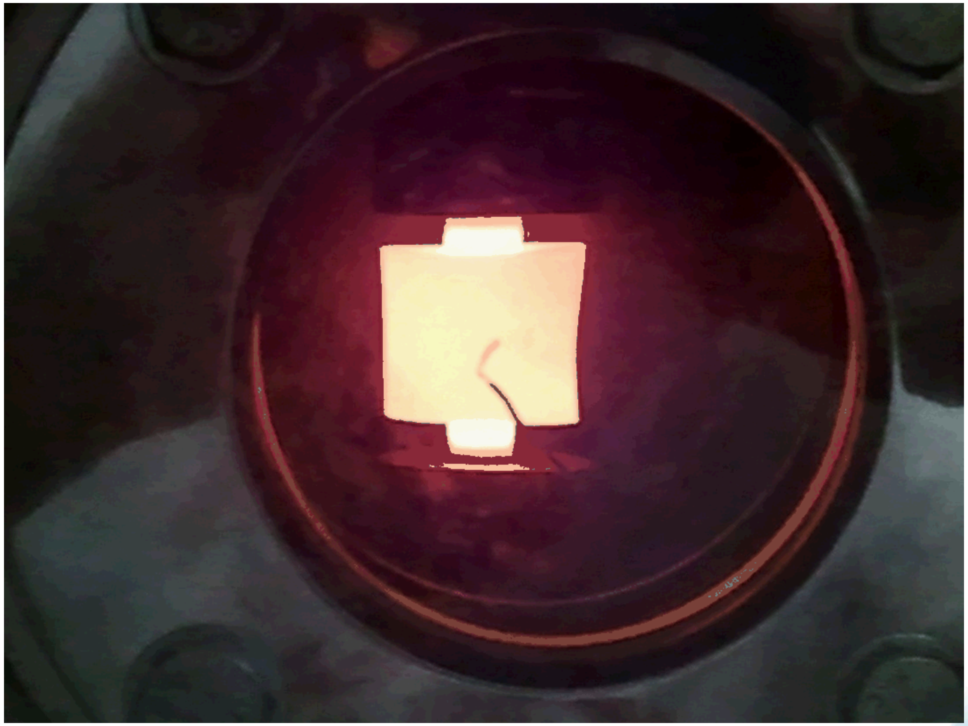


Schematic



Spark Plasma Sintering (SPS)

- DC current
  - ON(1-99 ms)/OFF(1-9 ms) pulse
- Surface activation
  - Electromigration
- Short time
  - 5~30 min
  - Max. heating rate ~ 400 ˚C/min
- SPS-825S
  - Max. force: 250 kN
  - Max. current: 8000 A
  - Sample dimension: Φ80 mm



- **Offers the ability to fine tune grain size in sintered devices**

FAST for Manufacturing Ceramics

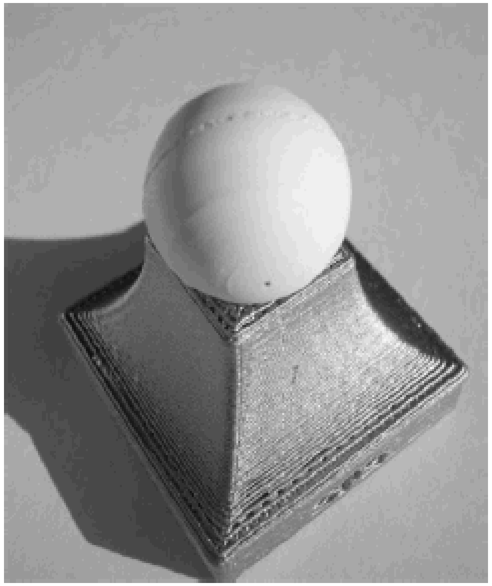


Fig. 9. Al_2O_3 sphere obtained in one single step by SPS.[63]

J. Galy, Private Communication, 2007.

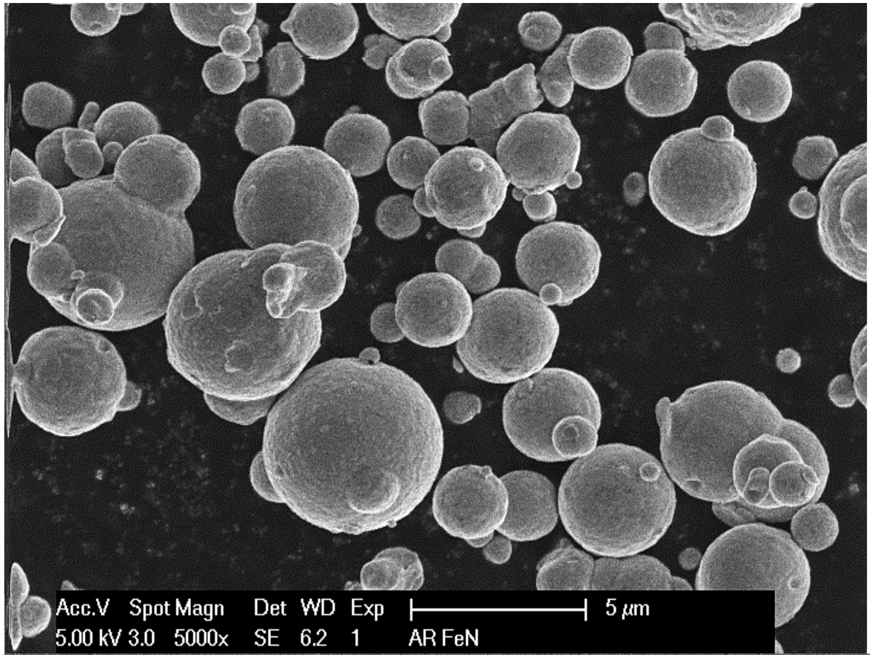
Hungría et. al., Adv. Eng. Mater. Vol. 11 (2009) 616
DOI: 10.1002/adem.200900052

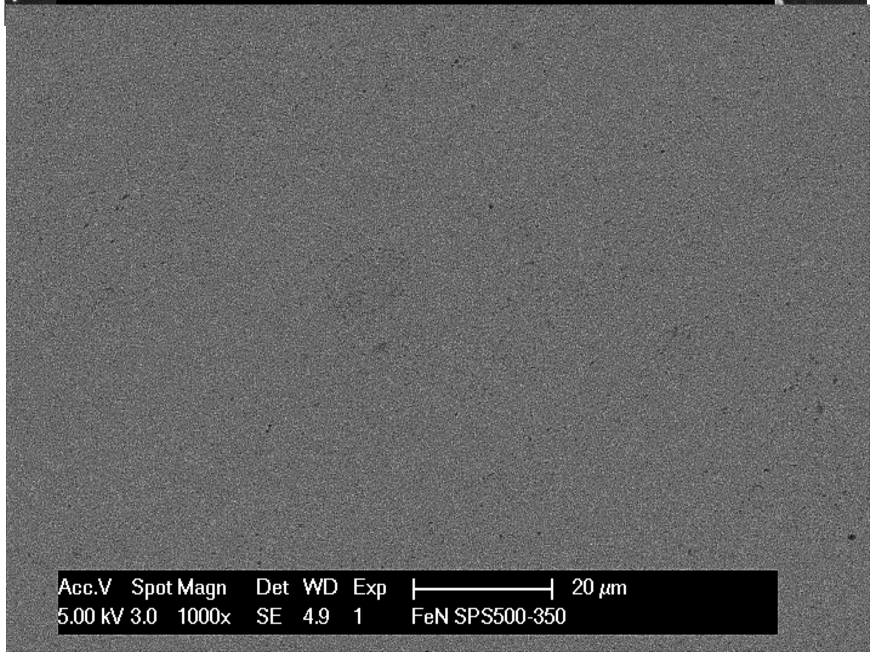
FAST System Manufacturers:

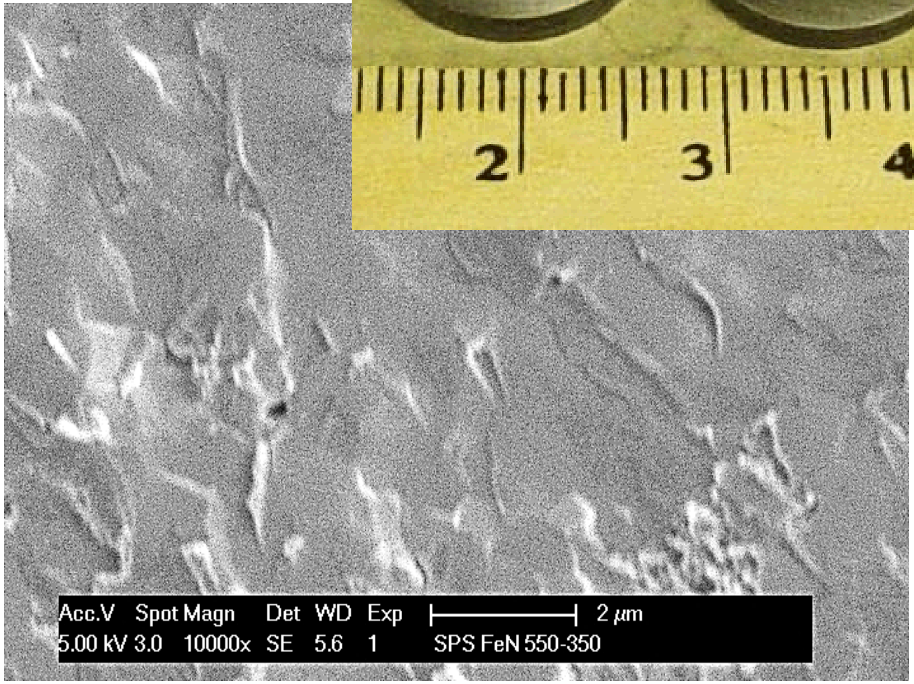
- **Fuji Electronic Industrial Co. (Japan)**
- **FCT Systeme GmbH (Germany)**
  - **Can make components up to 500 mm (~20") in diameter**
- **Thermal Technology LLC (Santa Rosa, CA)**

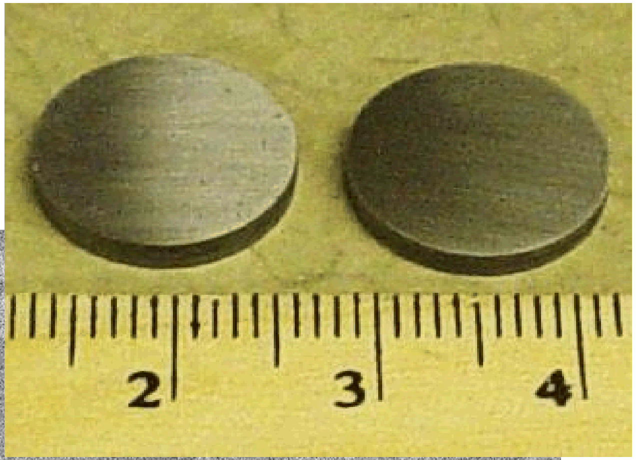
- **Size of equipment increasing to accommodate commercial needs**
- **Technology for continuous FAST under development**
- **A large number of companies have acquired FAST but often request this info to not be made public to maintain a competitive advantage**

Materials Processing









- **As-received (AR) FeN powder**
- **SPS sintering: 550°C, 350 MPa, 3 min.**
- **Close-fully densification was achieved in the SPSed iron nitride samples**

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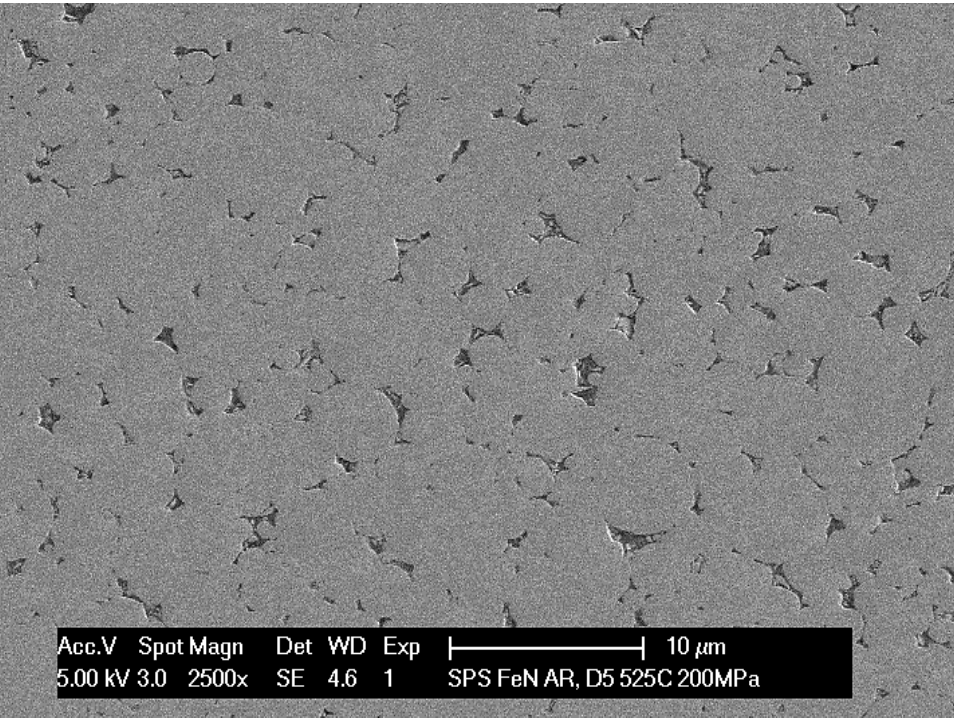
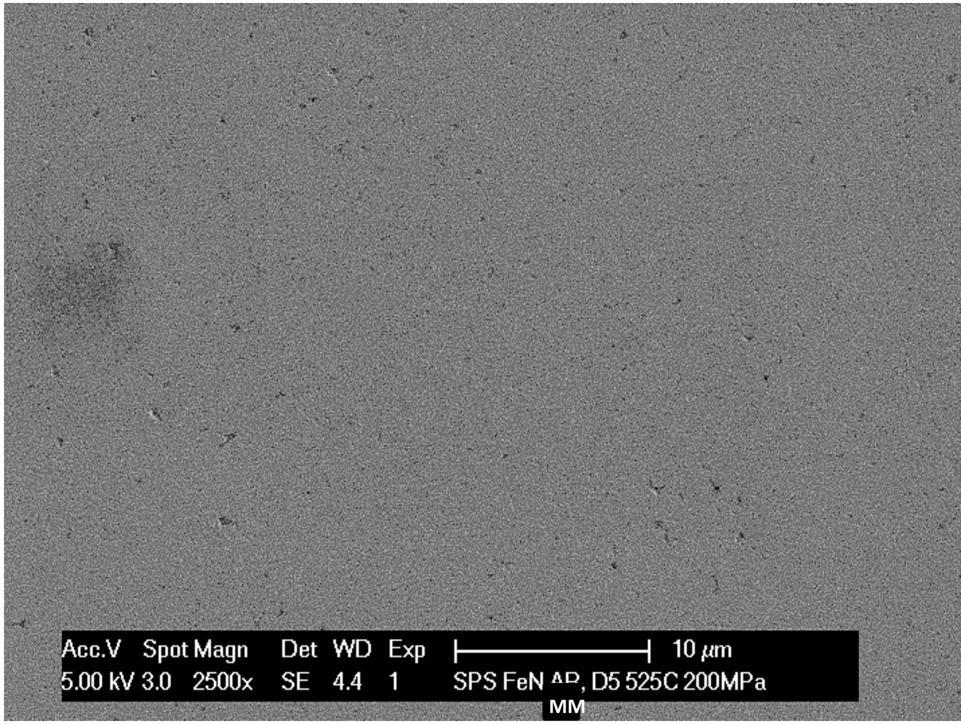
SEM of SPSed FeN samples, (Ø5mm, 525°C, 200MPa)

W/ as-received FeN powder



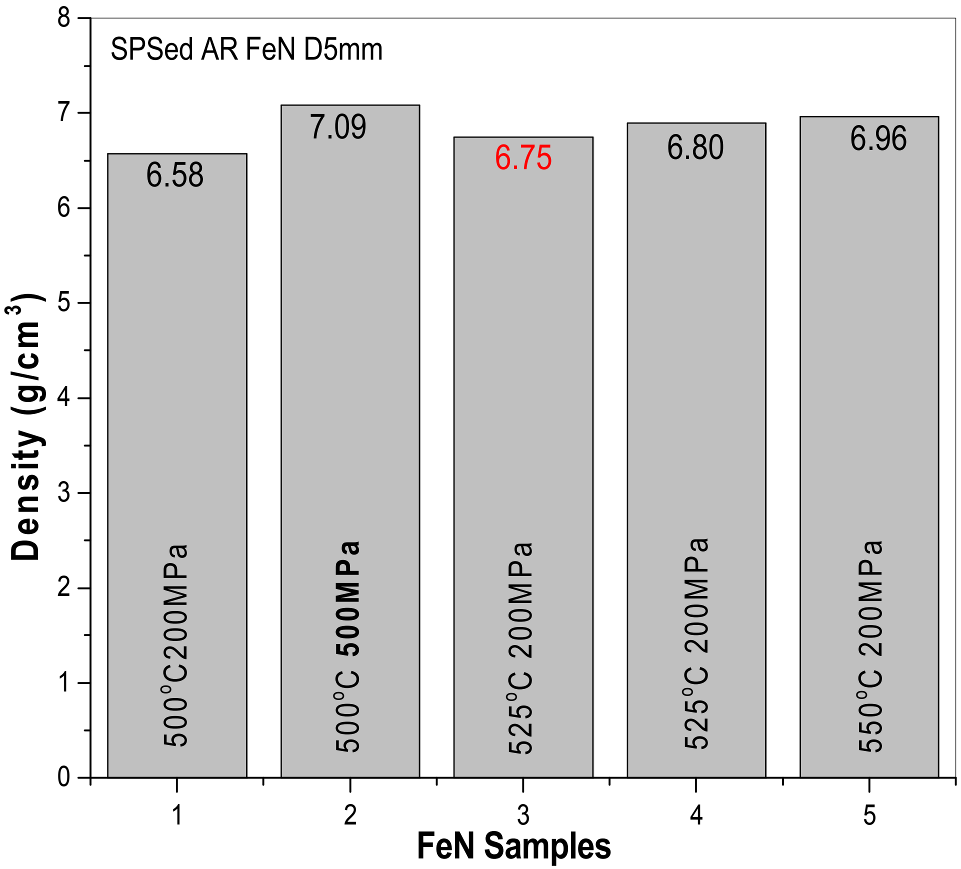
W/ milled FeN powder



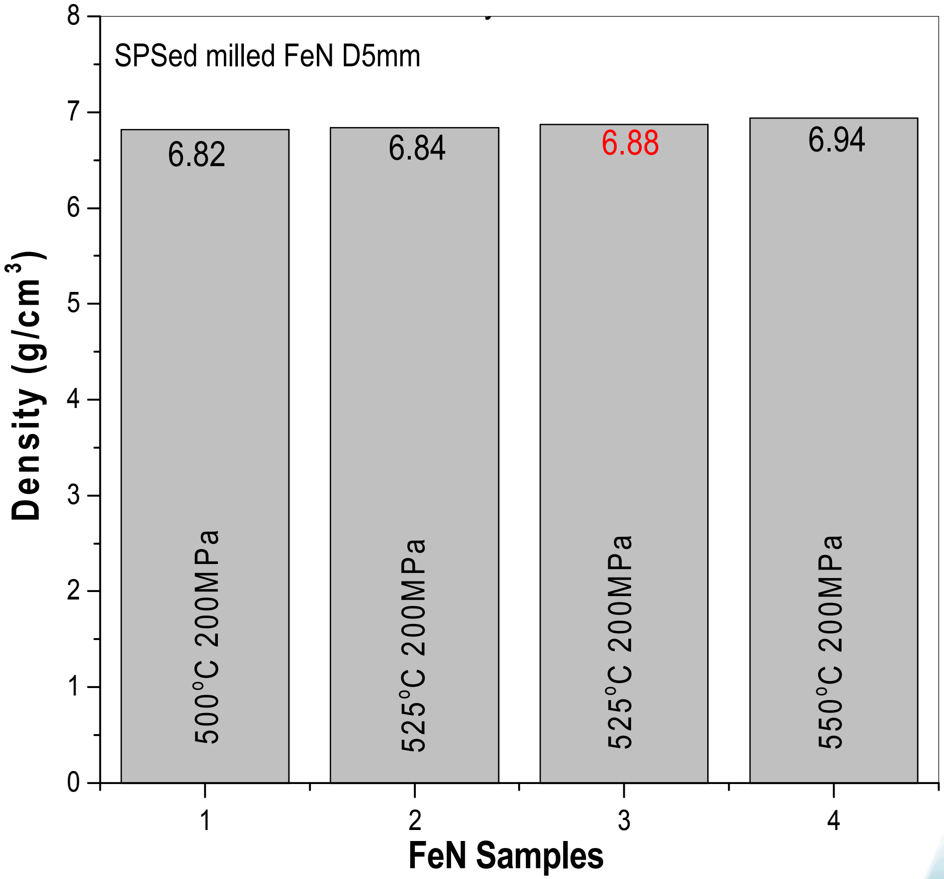
- **Milled FeN powder produces more uniform and dense SPSed billets**
  - **Higher packing density with smaller particle size**
  - **Increased diffusion ability with smaller grain size of milled powder**

Density of SPSed FeN samples

W/ as-received FeN powder



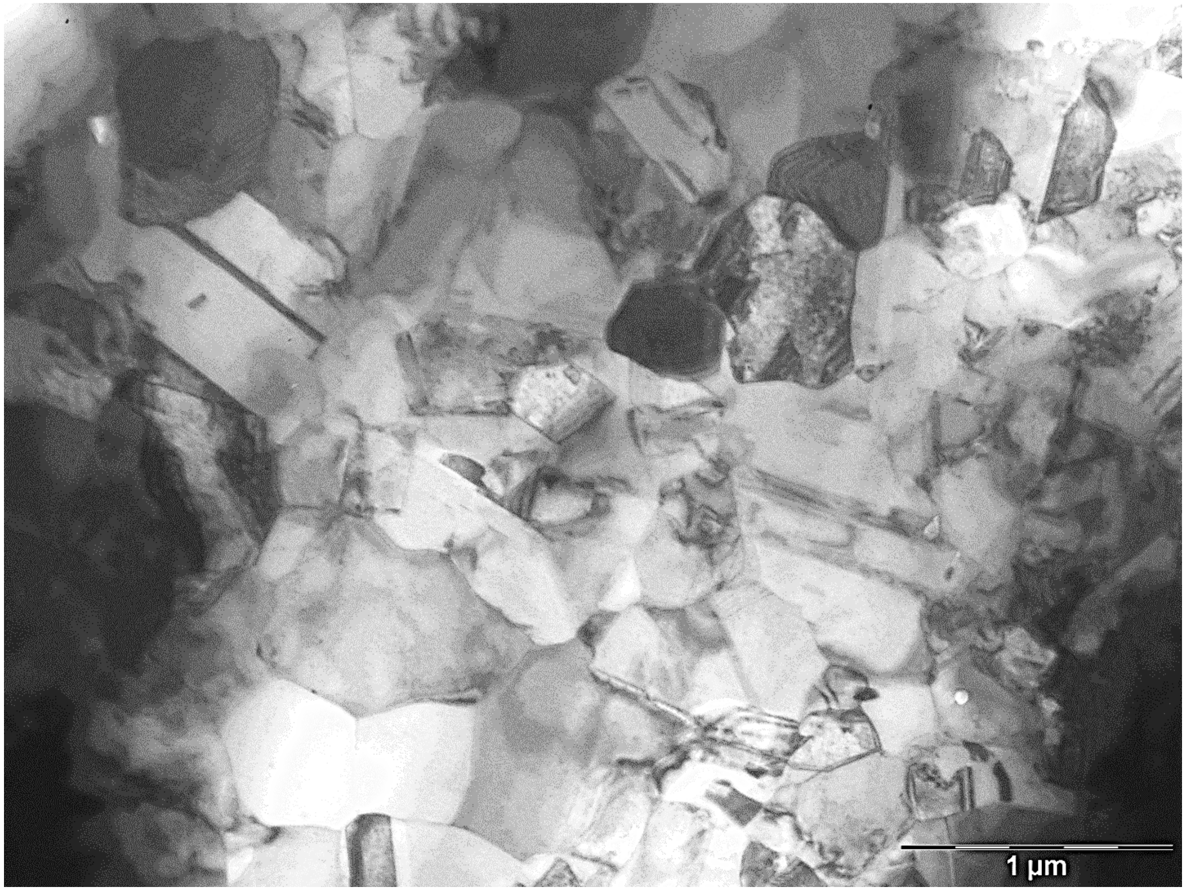
W/ milled FeN powder

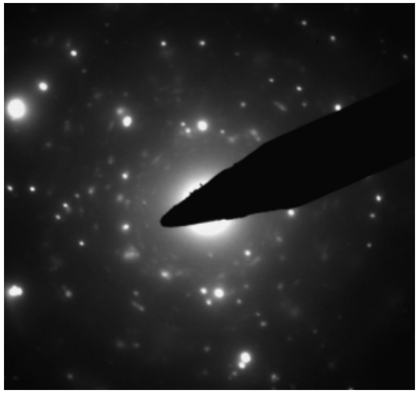


- **Density increases with increasing SPS temperature and pressure;**
- **Higher degree of variation in the density of the SPSed FeN with as-received powder**
- **Milling can improve density and uniformity of the consolidated FeN from powder**

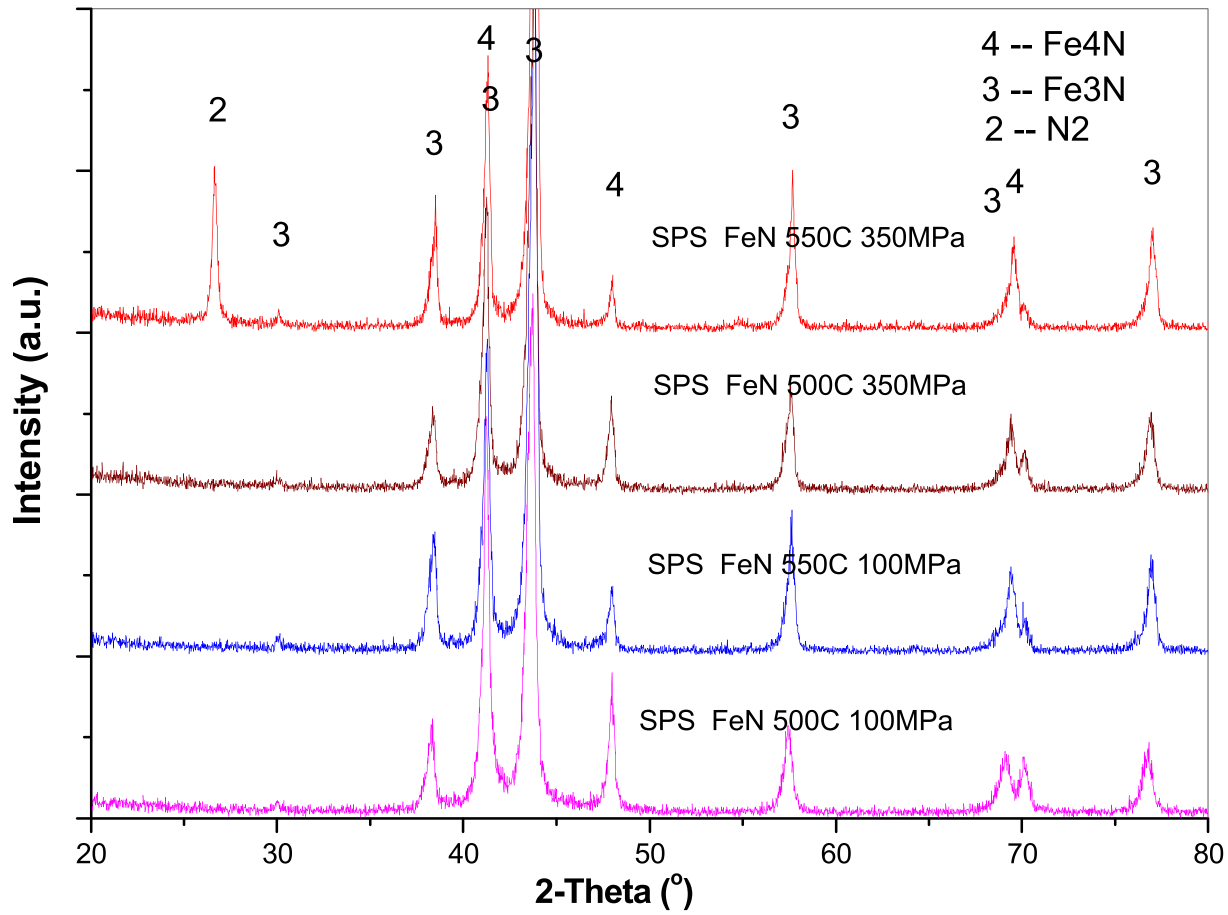
TEM of SPSed FeN

- FeN particles were well consolidated with little porosity
- The grain size of SPSed FeN ranged from 200 nm to 1 µm.



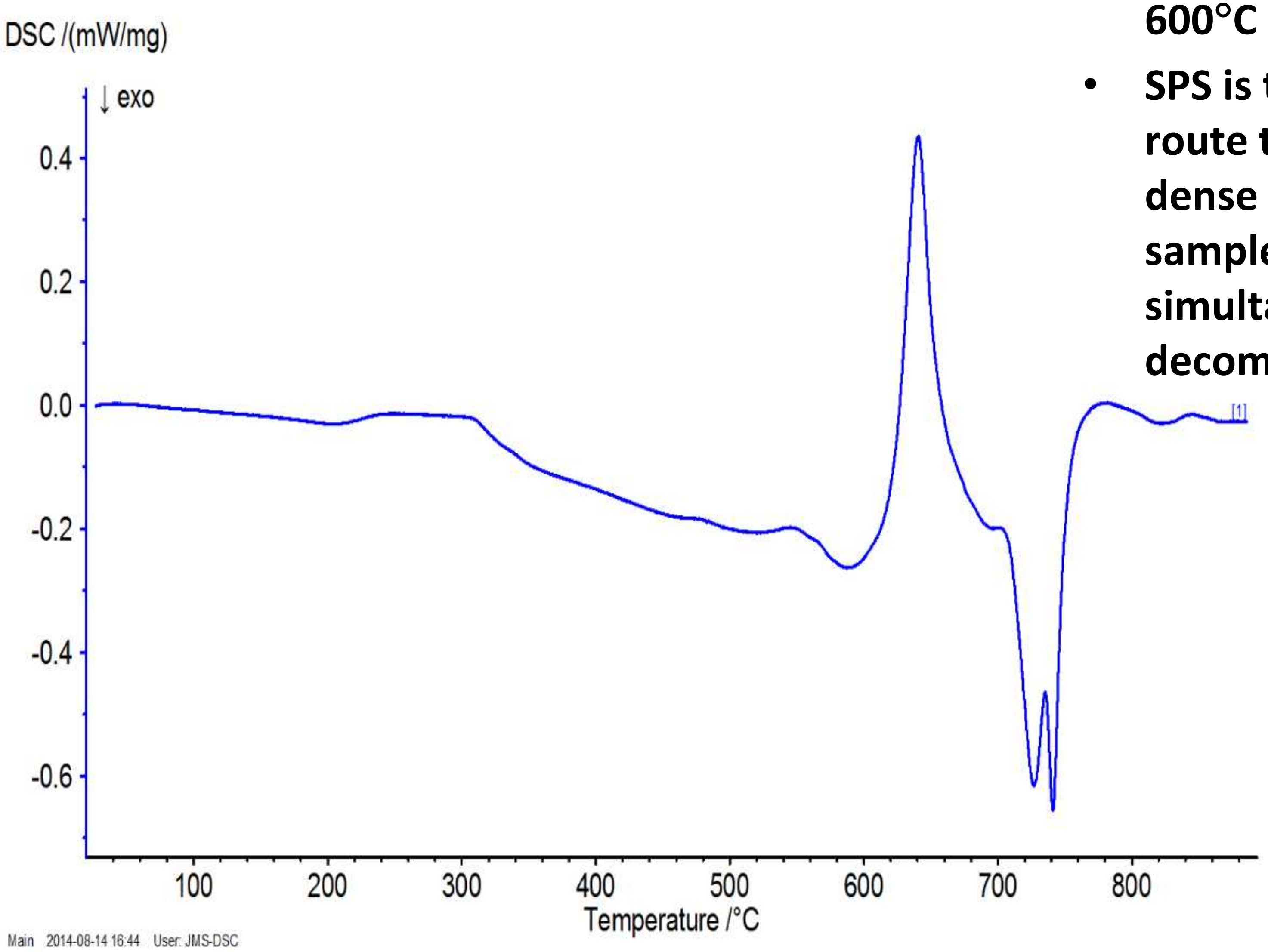


XRD of SPSed FeN



- **XRD of SPSed FeN samples produced at different conditions**
- **Most FeN samples did not show the peak around a 2-theta value of 26°**

DSC of SPSed FeN



- Decomposition of sintered FeN begins ~ 600°C
- SPS is the only viable route to form fully dense bulk FeN samples without simultaneous decomposition

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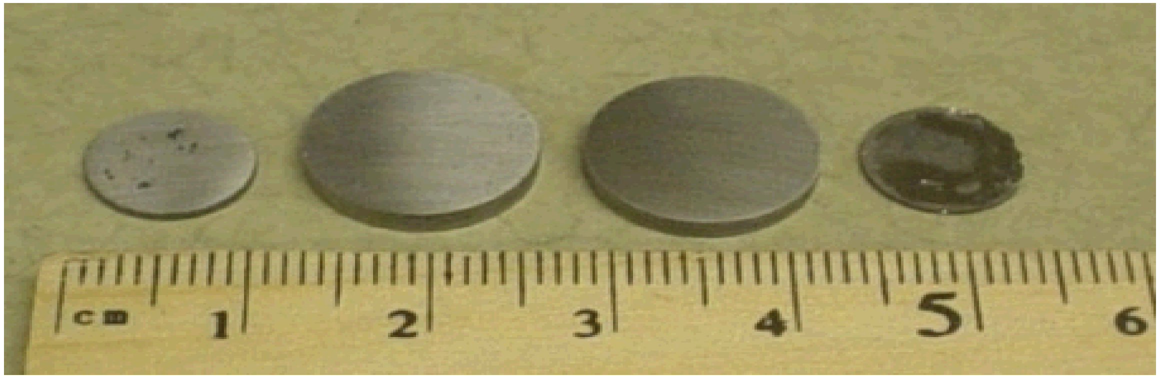
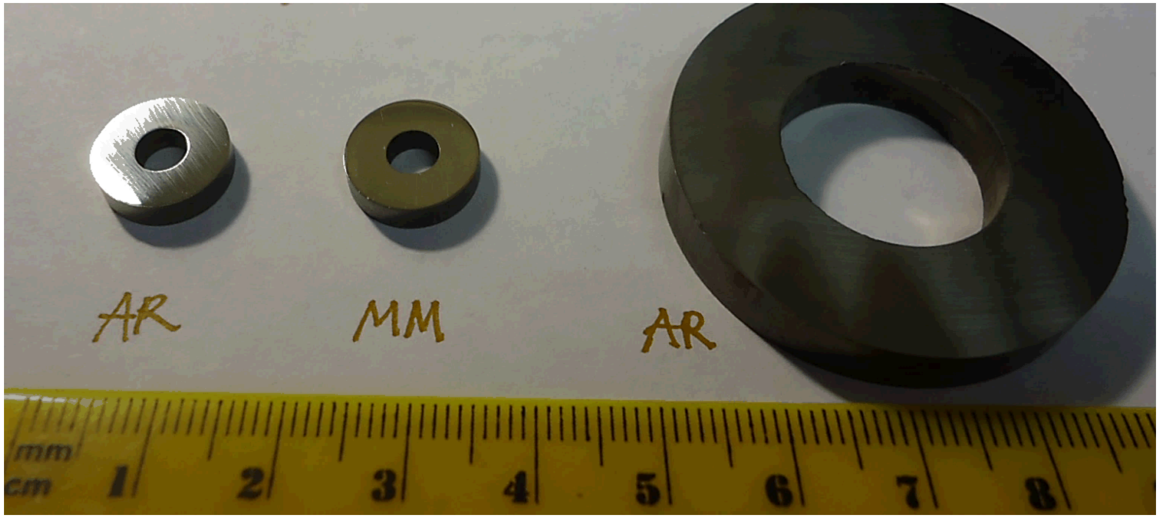
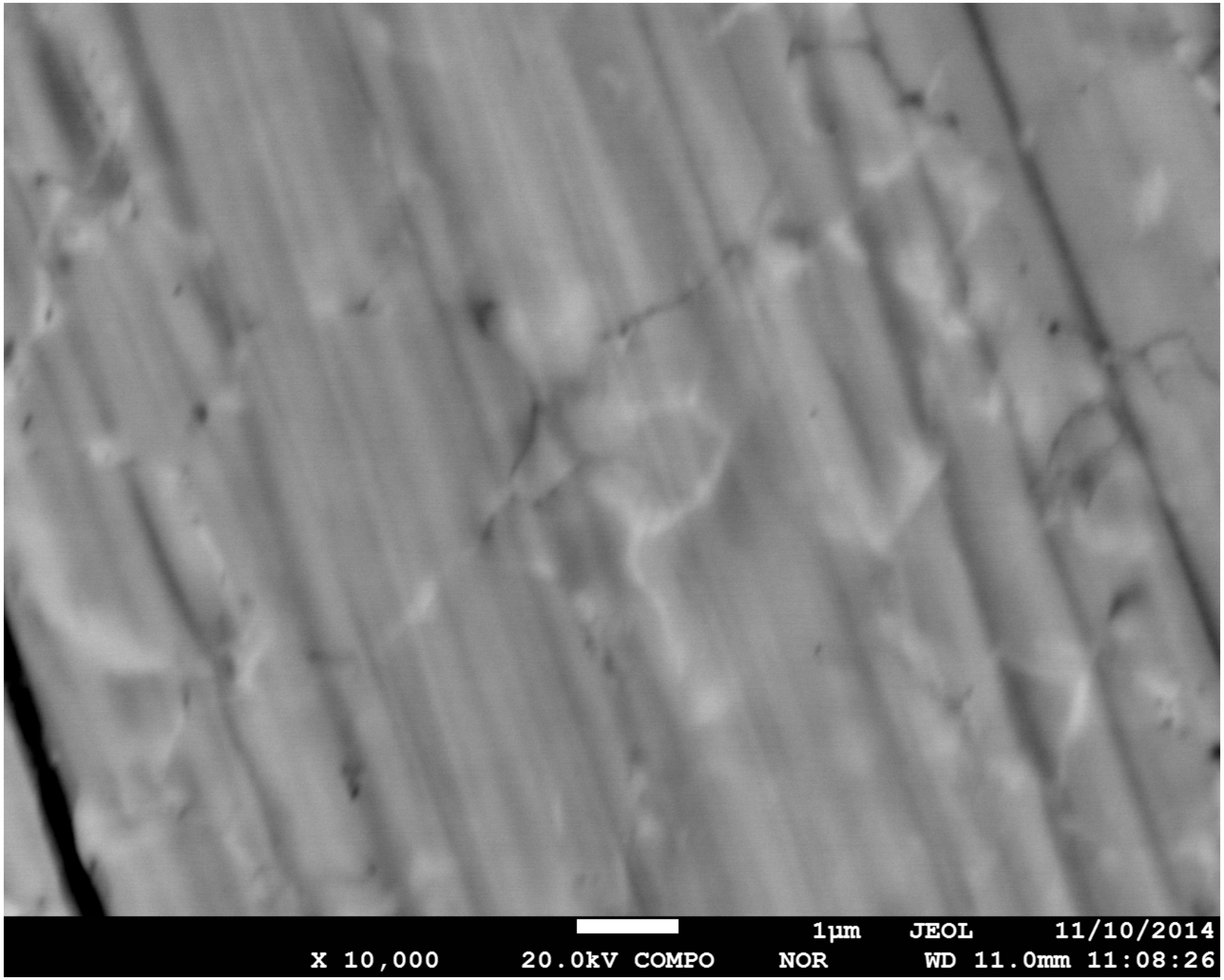
SPSed Samples and Net-Shaping





- **Can sinter toroids and other complex shapes directly (net-shaping), eliminating the need for machining**
- **Toroids will be wound and tested under this fiscal year's effort**

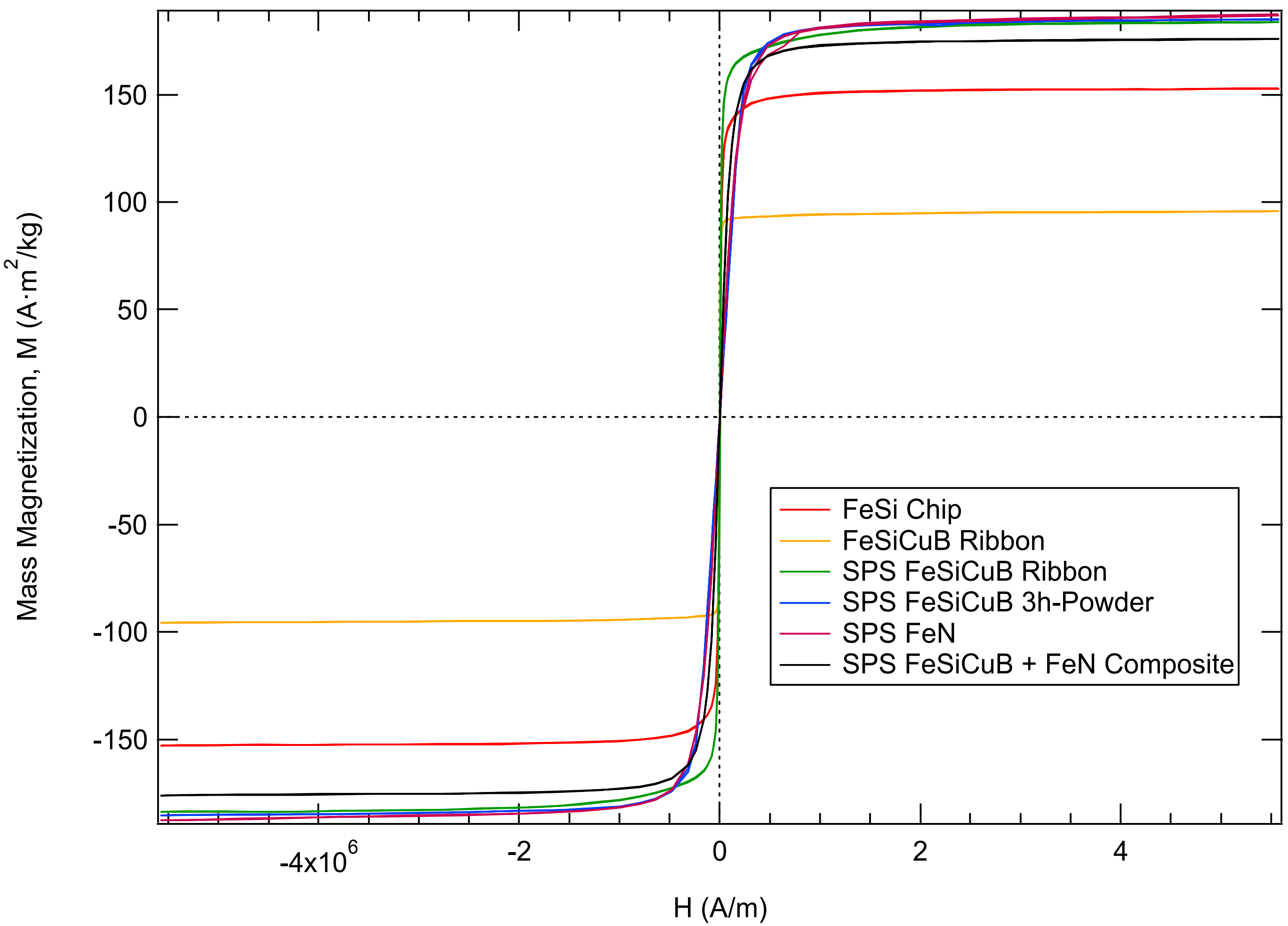
Toroid Surface SEM and EDS



- Small variation in composition between grain boundary and center
- Grain center stoichiometry ~ Fe_4N
- Grain boundary is ~ 3 Atomic% richer in iron

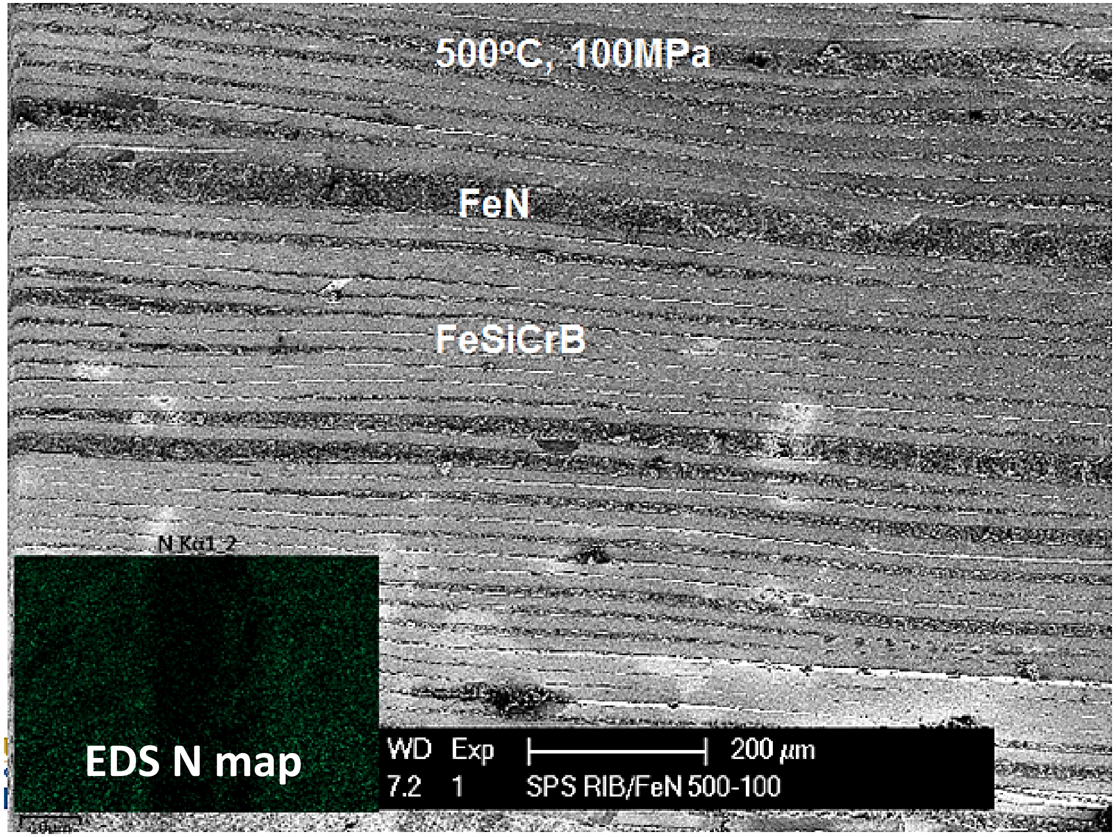
Location	Fe (Atomic %)	N (Atomic %)
Grain center	81.3	18.7
Grain boundary	84.2	15.8

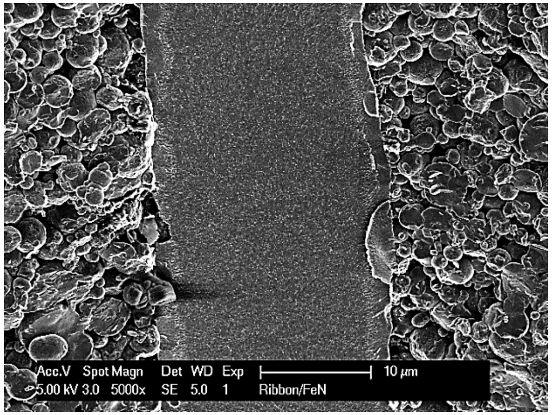
Magnetic Results

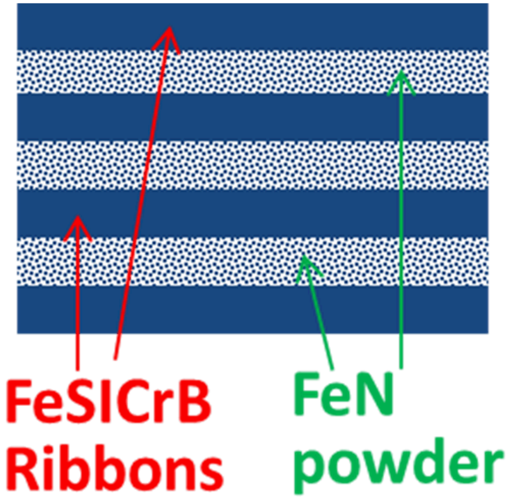


- **Magnetic hysteresis curves of SPSed FeSiCrB and FeN materials.**
- **SPSed FeN under 550°C and 100MPa achieved the highest M_{sat} of 188 A·m²/kg.**
- **Predicted M_{sat} of bulk γ'-Fe_4N is 209 A·m²/kg (Fe is 217 A·m²/kg)**

FeN/FeSiCrB (Metglas) Composite

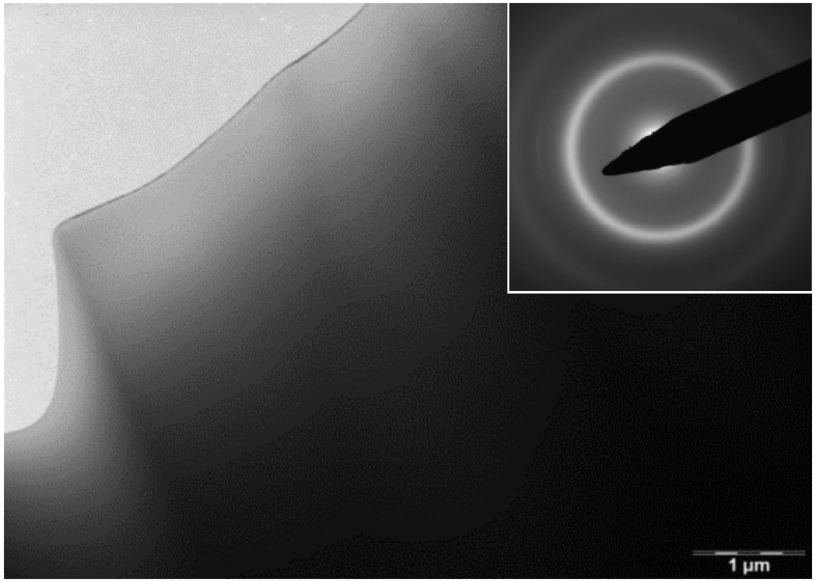


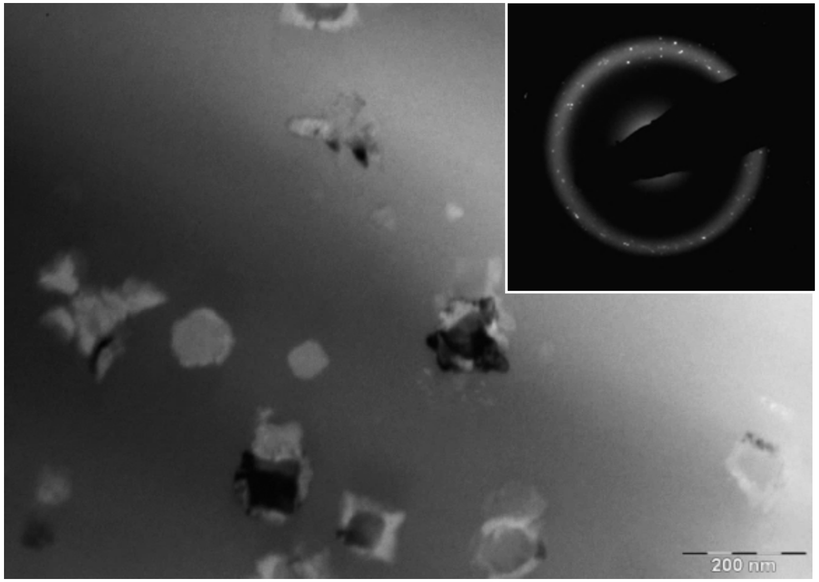




- **Difficult to sinter amorphous tapes (i.e. Metglas) into bulk material**
- **FeN powders are excellent binders**
- **FeN layer has higher electrical resistivity than FeSiCrB and can be used to reduce eddy current losses**

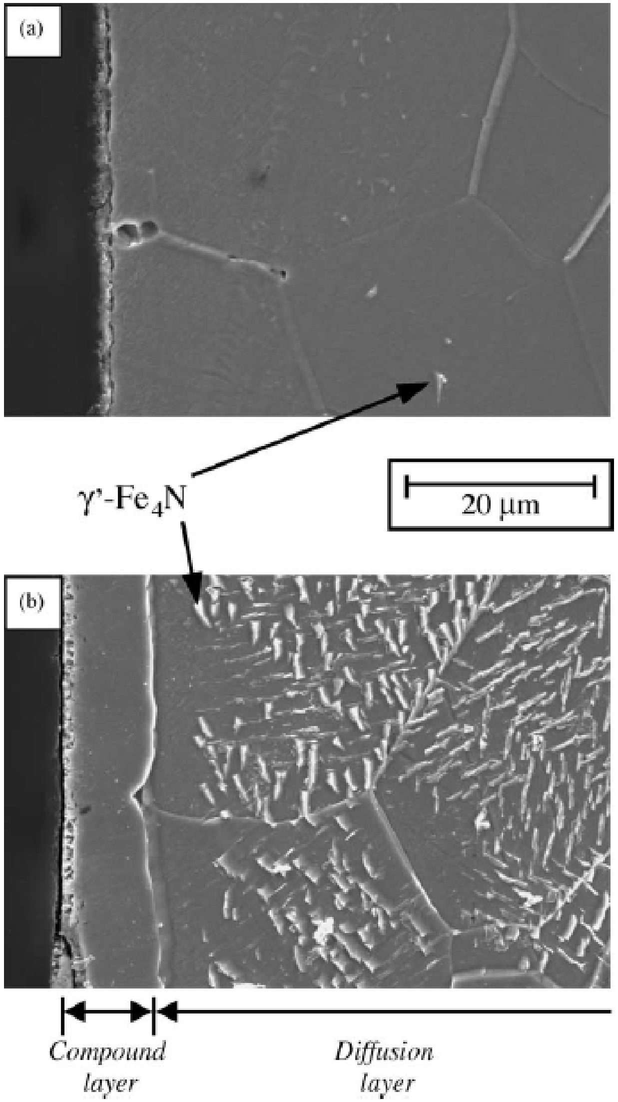
FeN/FeSiCrB (Metglas) Composite





- **Above: fully amorphous FeSiCrB ribbon (as received)**
- **Below: Nanocrystalline Fe clusters formed after SPS at 500°C**

In house Synthesis of Raw Materials: Electrochemical Nitriding of Iron



H. Tsujimura, T. Goto, Y. Ito, Journal of Alloys and Compounds, 376, 246 (2004)

- Growth of γ'-Fe_4N demonstrated by Japanese electrochemists
- Formed γ'-Fe_4N at the surface of Fe(0) electrode using Li_3N as nitride source
- Demonstrates electrochemical synthesis of iron nitride possible
- Our goal is to demonstrate autonucleation of iron nitride with flowing N_2

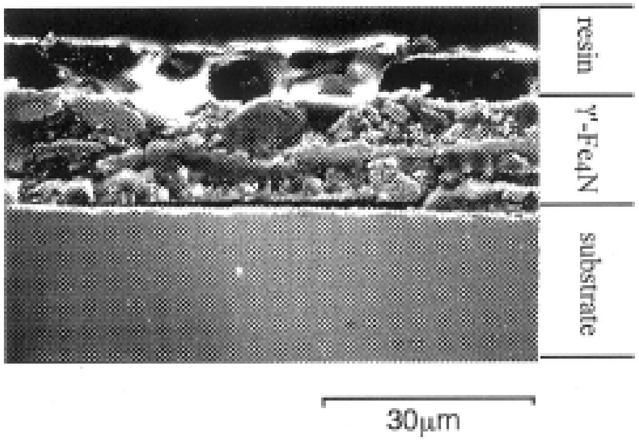
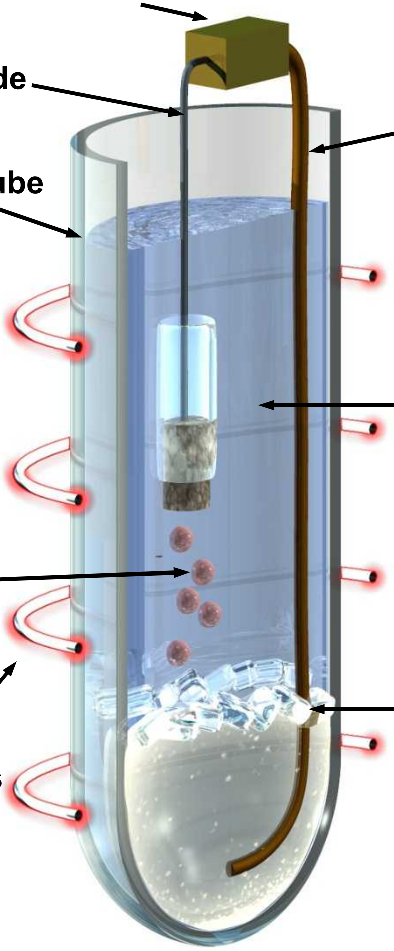


Fig. 10. Cross-sectional SEM image of iron electrode after potential pulse electrolysis for 1 h.

T. Goto, R. Obata, Y. Ito, Electrochimica Acta, 45, 3367 (2000)

Molten Salt Solution Growth of Magnetic Nitrides



- Not electroplating!!!!
- Molten salt solution growth of GaN developed and patented at Sandia
- Create ionic precursors electrochemically
- Use salt transport to deliver precursors
- Increase growth rate through flux of reactants (increase currents, N_2 flow also has an effect)
- Can control oxidation state of transition metal
- Produces high quality material

$$\tfrac{1}{2}N_2 + 3e^- \rightarrow N^{-3}$$

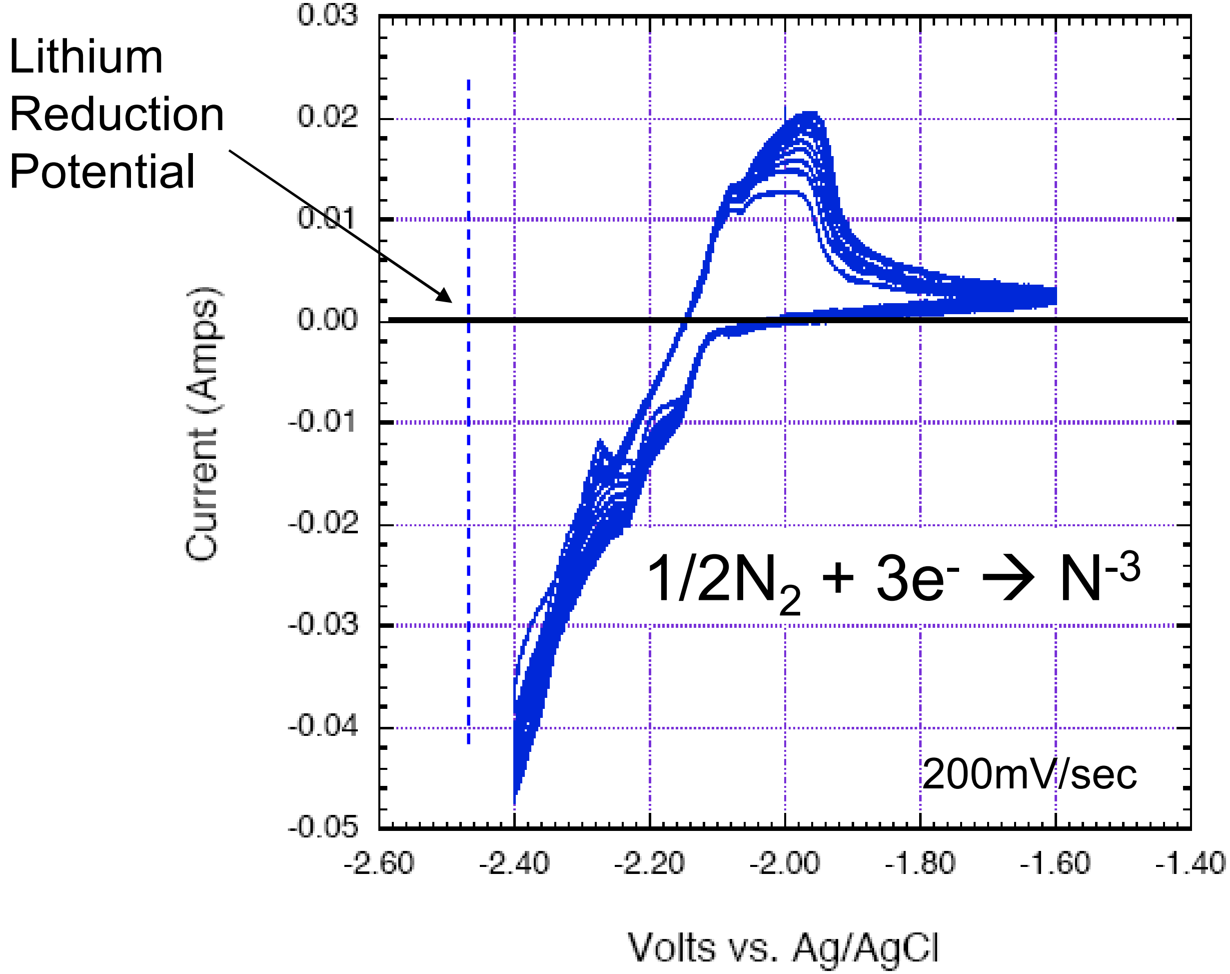
$$T \rightarrow T^{+3} + 3e^-$$

Precursors can be replenished as they are consumed

Advantage: Continuous, isothermal or steady-state growth

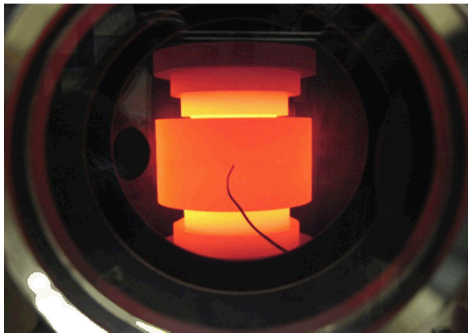
U.S. Patent Issued October 2008 (for GaN growth)

Example of Nitrogen Gas Reduction Cyclic Voltammograms



Conclusions & Future Work

- **γ'-Fe_4N has the potential to serve as a new low cost, high performance transformer core material**
  - Increased M_{sat}
  - Higher resistivity
  - Increased field and current carrying capability with less eddy current losses
  - Only requires low cost elements (Fe & N)
- **The fabrication of bulk γ'-Fe_4N through the SPS consolidation of raw materials has been demonstrated**
  - SPS can consolidate iron nitrides without material composition
  - Parts can be fabricated directly using net-shaping
- **SPS processing parameters are being modified to improve phase purity**
- **Parallel development of in house synthesis of raw materials**



Acknowledgements

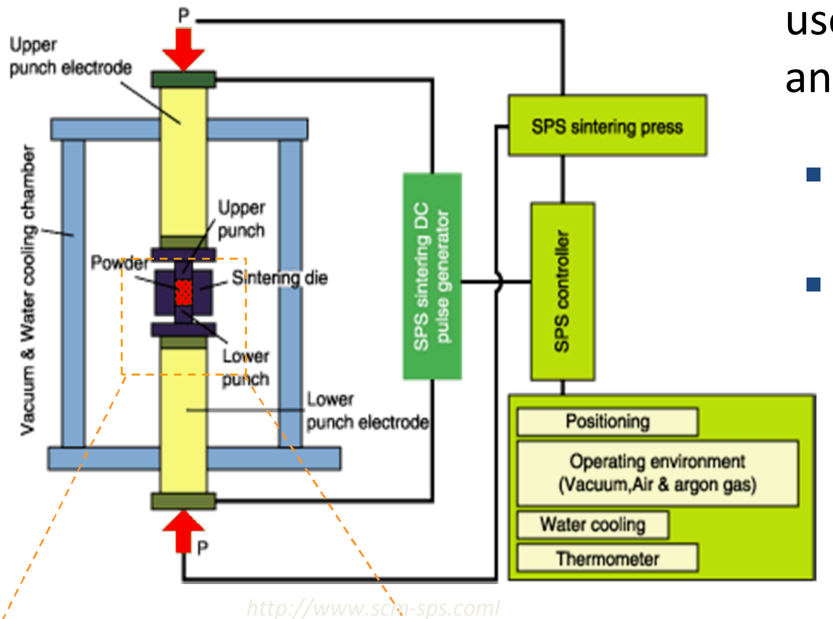
SEM/EDS: Dick Grant (SNL)

The authors acknowledge support for this work from Dr. Imre Gyuk and the Energy Storage Program in the Office of Electricity Delivery and Energy Reliability at the US Department of Energy

Extra Slides

Background

Spark plasma sintering (SPS)

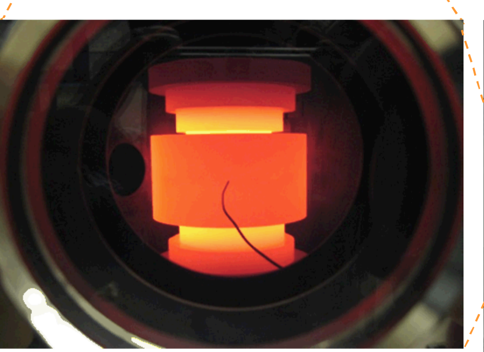


An novel and effective consolidation technique with fast heating rates and brief consolidation time, widely used for sintering nanocrystalline (NC), amorphous and composite materials.

- Pressure and pulsed current assisted sintering process;
- Pulsed DC current passes through the die and powder, heating metallic powders internally;

Advantages:

- Rapid and uniform sintering;
- Precision control heat, cooling, and pressure;
- Full density compaction;



Model: SPS-825S

- Sintering pressure: 250 kN
- Maximum diameter: 100 mm
- Open height: 250 mm
- Maximum temperature: 2400°C
- DC output: pulse 12 V, 8000 A

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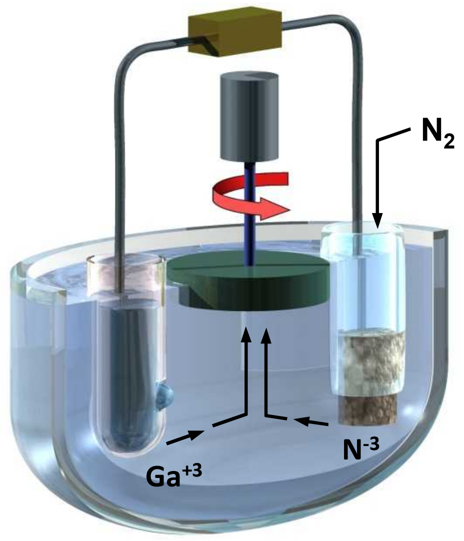
Progress in Electrochemical Solution Growth Technique Development for Nitride Materials for Power Electronics

K. Waldrip, T. Monson, S. Atcitty, Sandia National Labs



A new approach to growth of large area, high quality, low cost bulk metal nitride crystals for substrates for high efficiency, high power electronics

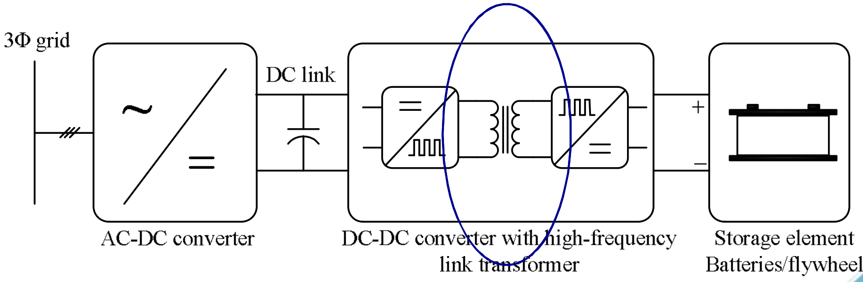
Sandia patented (Waldrip et al, 2008)

OE foundation provided opportunity for 2012 Award of Advanced Manufacturing Office's Innovative Manufacturing Initiative ($4.6M/3 yr)

Now partnered with SunEdison, Georgia Tech, and Qynergy Corp. for bulk GaN growth

Innovative electrochemical synthesis technique may enable large scale manufacturing of new, improved magnetic materials for high frequency transformer cores for dc-dc links

Materials synthesis driven by systems requirements



SunEdison Sandia National Laboratories Georgia Institute of Technology

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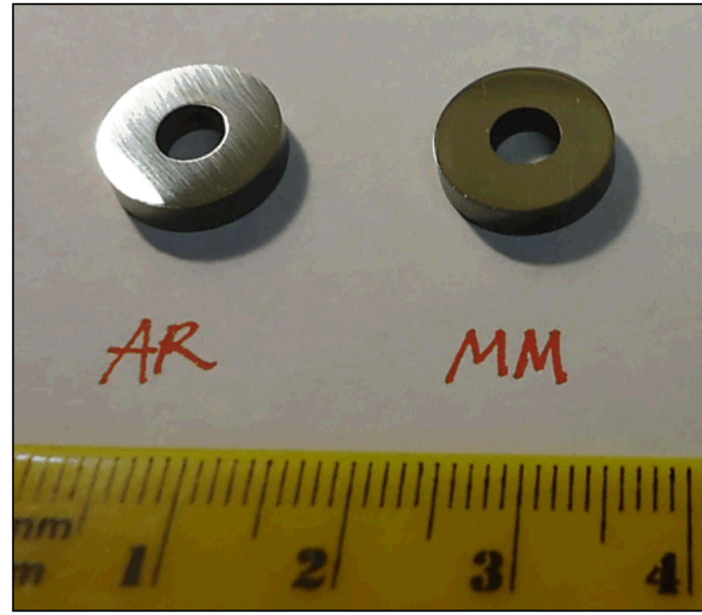
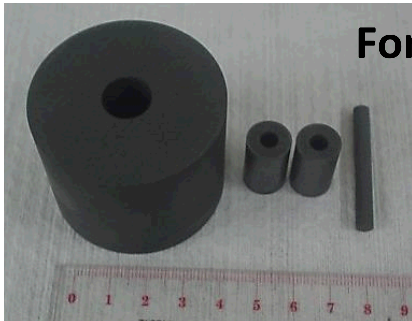
Photos of SPSed FeN, FeSiCrB, and FeSiCrB+FeN samples and parts



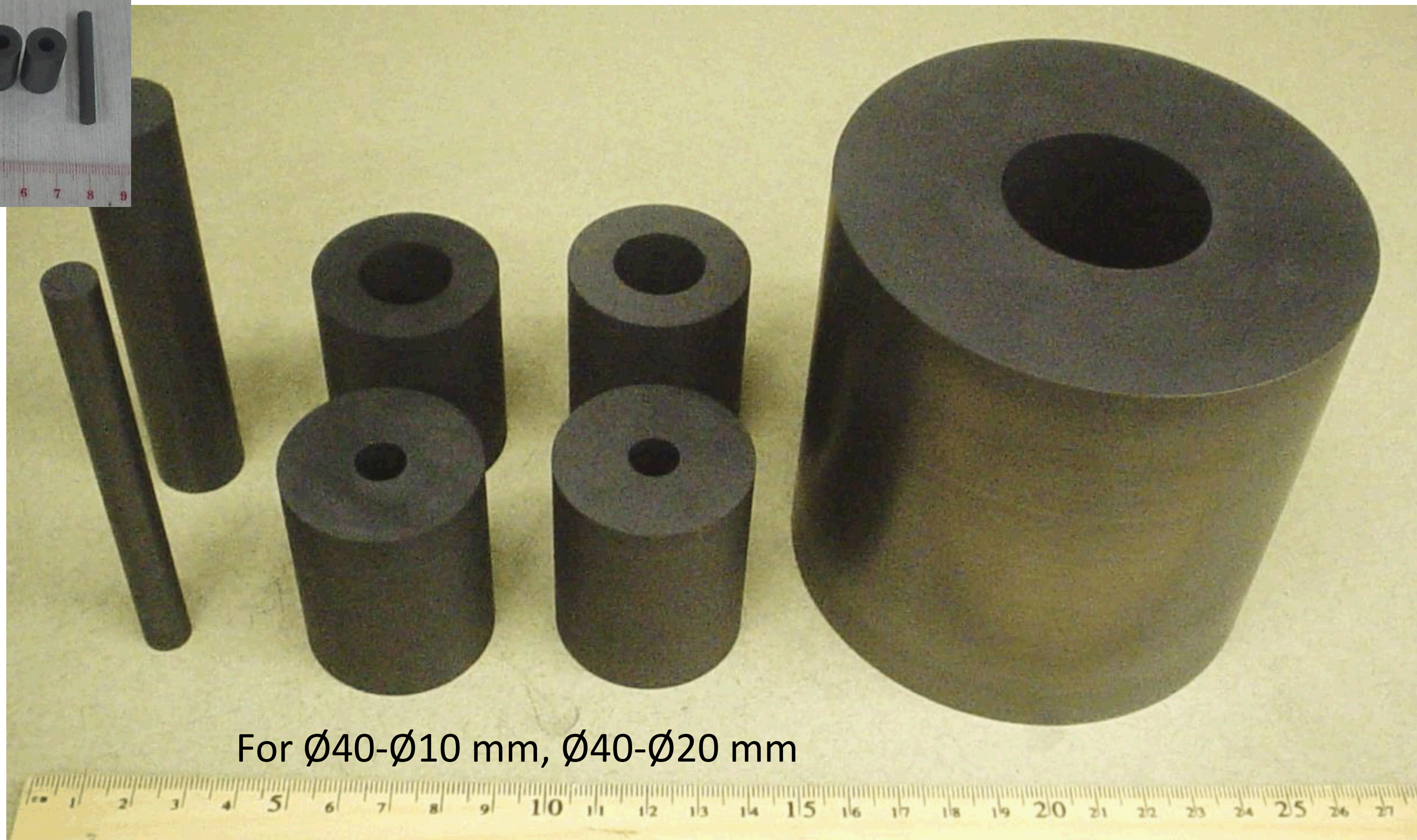
SPSed Ø12.5mm FeN parts

SPSed Ø5mm FeN, FeSiCrB, and FeSiCrB+FeN samples

Dies for SPS net-shaping of FeN components



For Ø12-Ø5x3mm



For Ø40-Ø10 mm, Ø40-Ø20 mm

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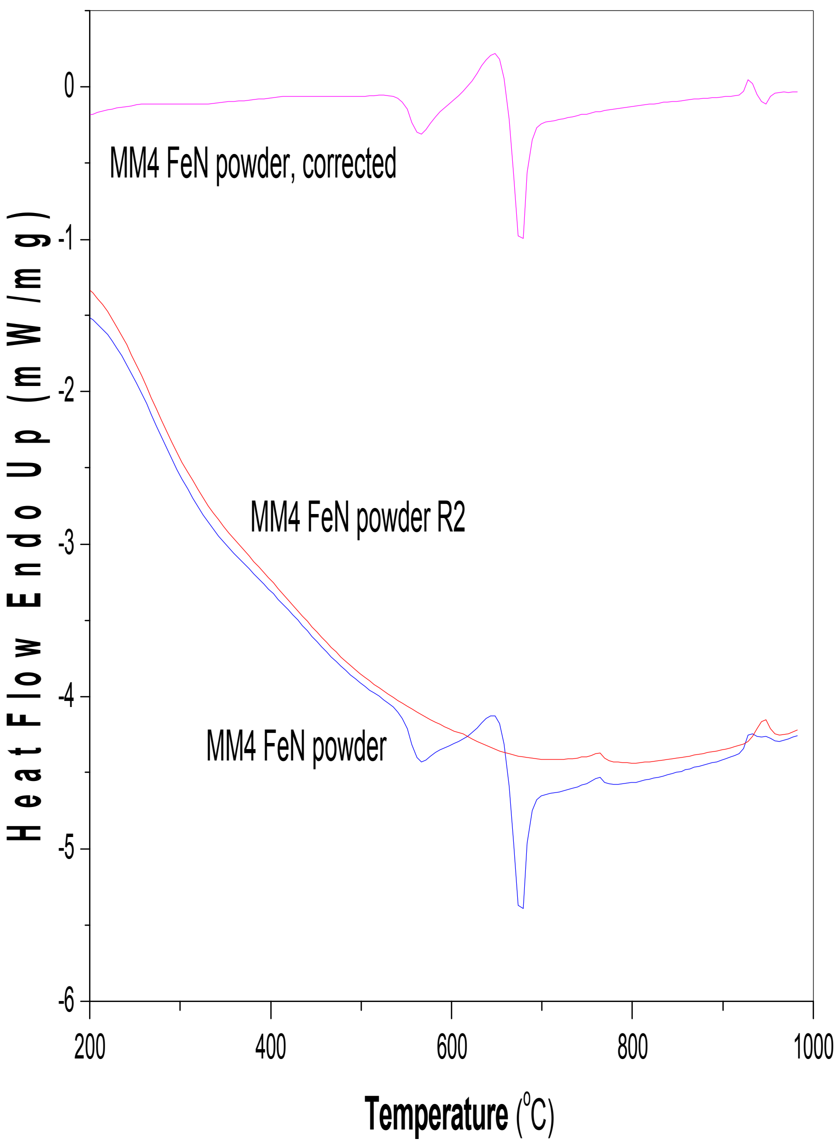
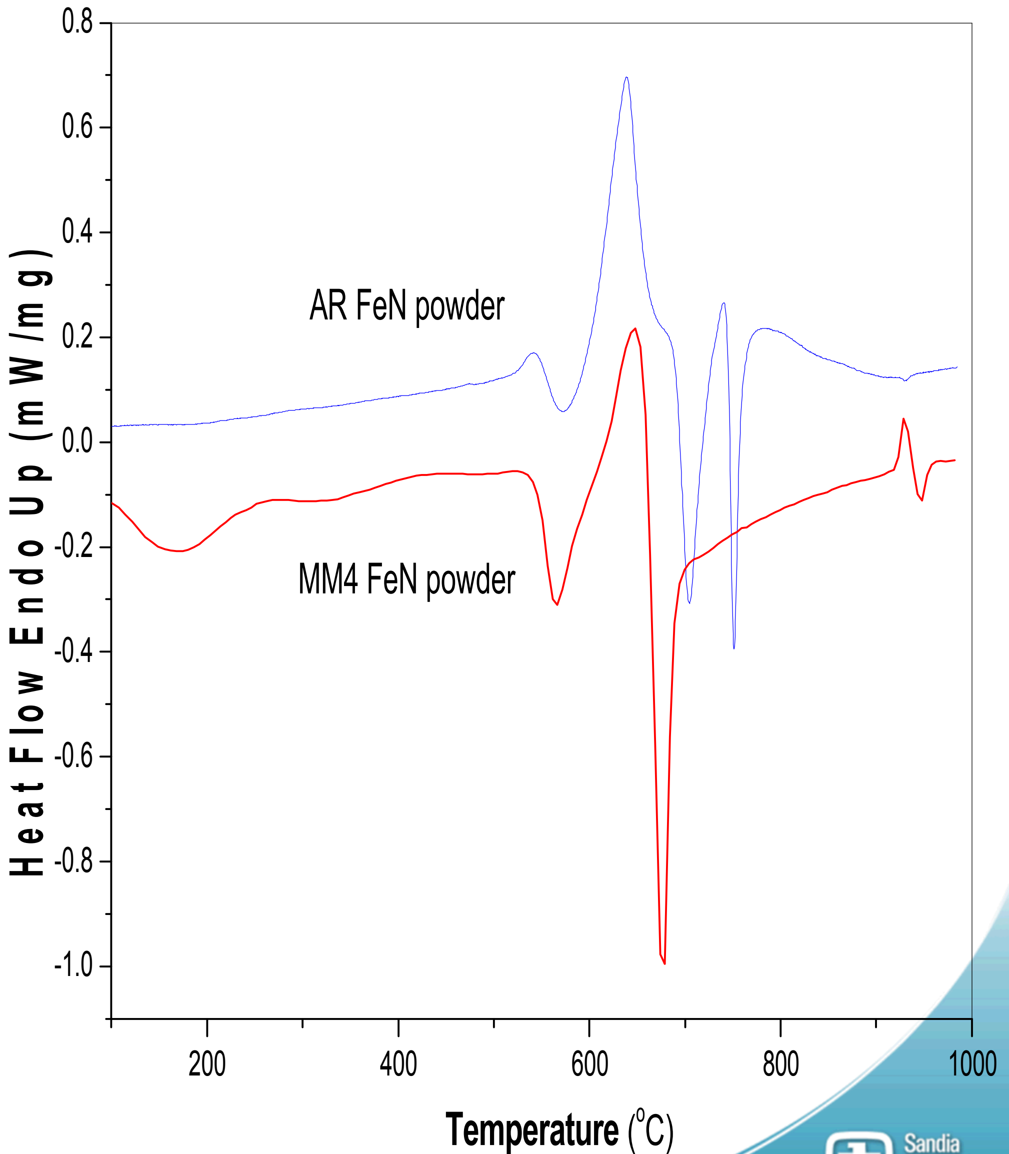
DSC of 4h milled FeN powder





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