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γ'-Fe_4N, a new soft magnetic material for inductors and motors

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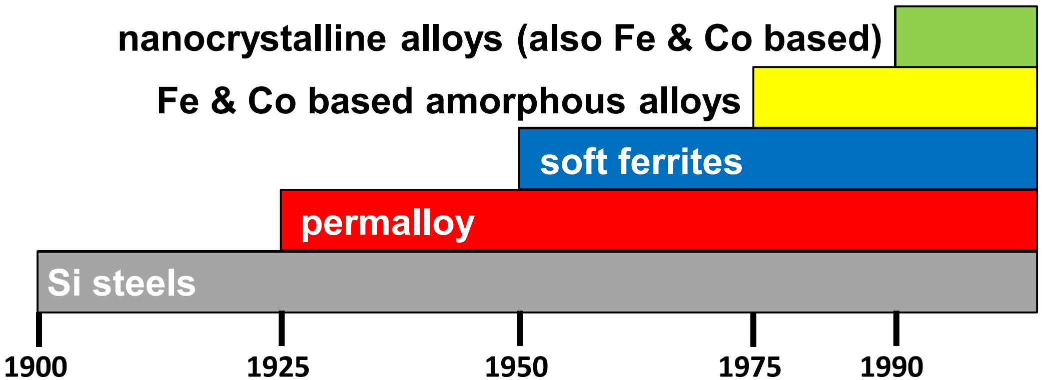
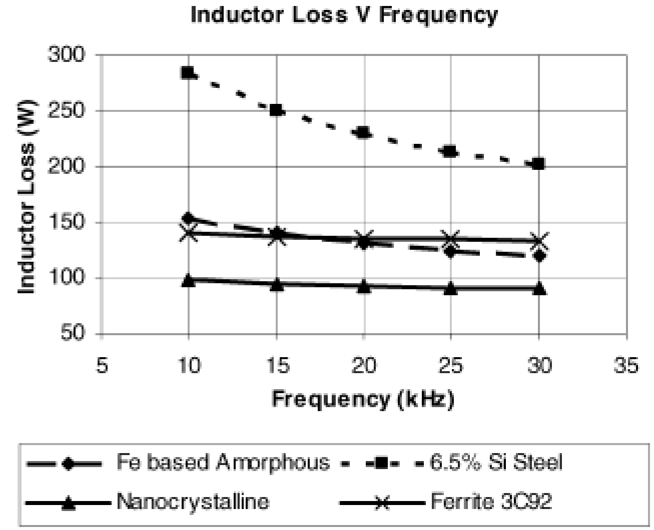
The authors acknowledge support for this work from Dr. Imre Gyuk and the Energy Storage Program in the Office of Electricity Delivery and Energy Reliability at the US Department of Energy

Soft Magnetic Material Development



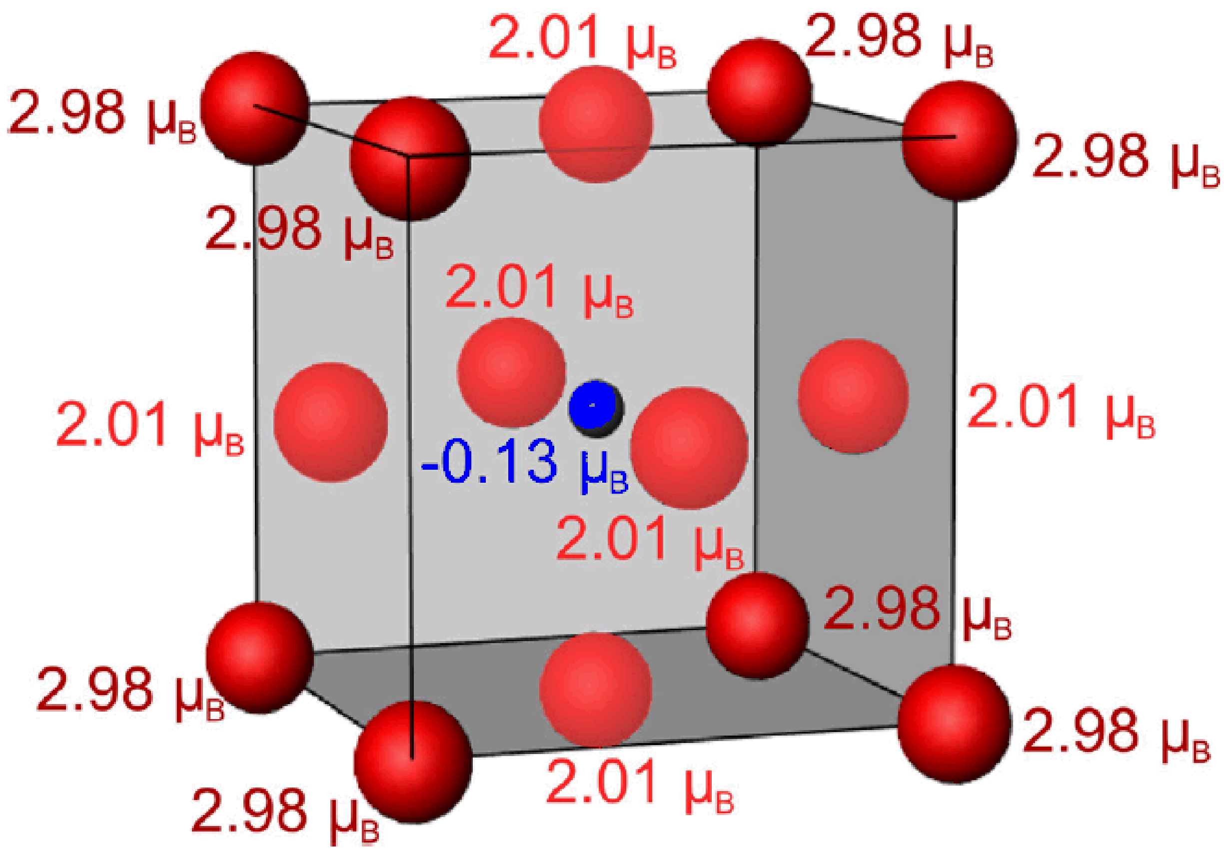
Adapted from: L.A. Dobrzański, M. Drak, B. Ziębowicz, Materials with specific magnetic properties, Journal of Achievements in Materials and Manufacturing Eng., 17, 37 (2006).



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)	$\rho(\mu\Omega\cdot m)$	Cost
VITROPERM (Vacuumschmelze)	1.20	1.15	High
Metglas 2605SC	1.60	1.37	High
Ferrite (Fexxocube)	0.52	$5x10^6$	Low
Si steel	1.87	0.05	Low
γ'-Fe_4N	1.89	> 200	Low

γ'-Fe_4N Unit Cell



fcc γFe structure stabilized by interstitial nitrogen in the body center

G. Scheunert, et al., A review of high magnetic moment thin films for microscale and nanotechnology Applications, Appl. Phys. Rev., 3, 011301 (2016).

J.M.D. Coey, *Magnetism and Magnetic Materials* (Cambridge University Press, Cambridge, UK, 2012).

Previous Syntheses of γ'-Fe_4N

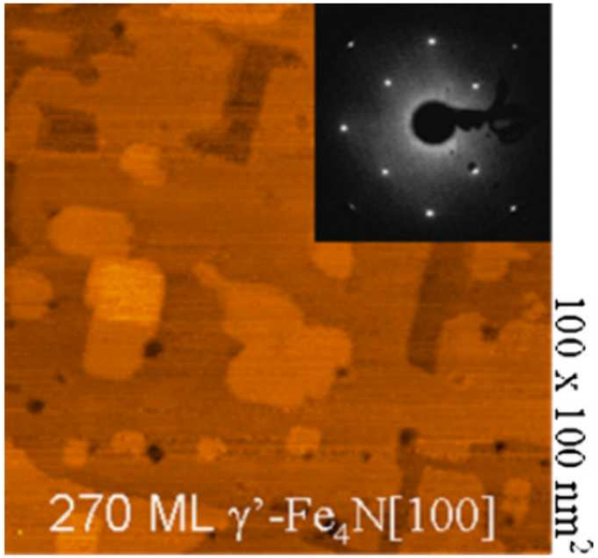
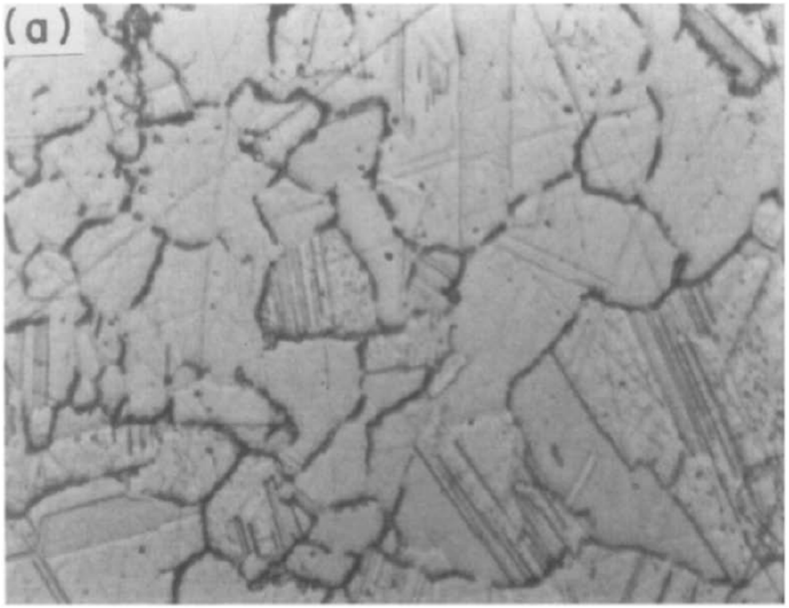


Fig. 1. STM image of a 270 monolayers (ML) thick γ'-Fe_4N film grown on Cu(1 0 0). The inset shows the corresponding LEED pattern (110 eV).

D. Ecija, et. al., "Magnetization reversal of epitaxial films of γ'-Fe_4N on Cu(100)", J. Magn. Mag. Mat., 316, 321 (2007).

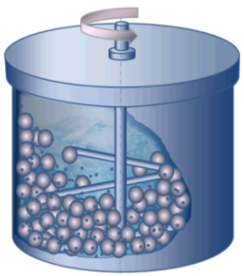


S.K. Chen, et. al., "Synthesis and magnetic properties of Fe_4N and $(Fe, Ni)_4N$ sheets", J. Magn. Mag. Mat., 110, 65 (1991).

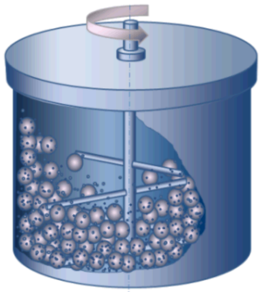
γ'-Fe_4N Synthesis and Processing

U.S. Patent Filed January 2015 (#62/105,918)

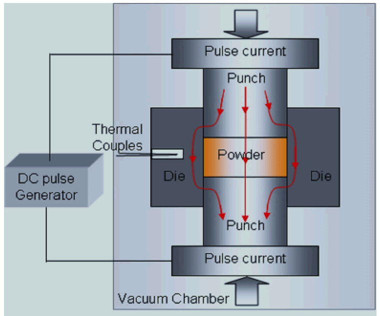
Synthesis of dense nanocrystalline iron nitrides using a two-step reactive milling and high pressure spark plasma sintering (SPS).



Liquid N_2



NH_3



Spark Plasma Sintering (SPS)

- **Cryomilling creates nanocrystalline Fe powder with large amounts of vacancies, grain boundaries, and dislocations**
- **Defects serve as fast diffusion pathways for nitrogen atoms from NH_3**
- **SPS quickly consolidates raw powders with a low sintering temperature**
  - **Excellent control over grain growth**
  - **Result: Improved magnetic properties**

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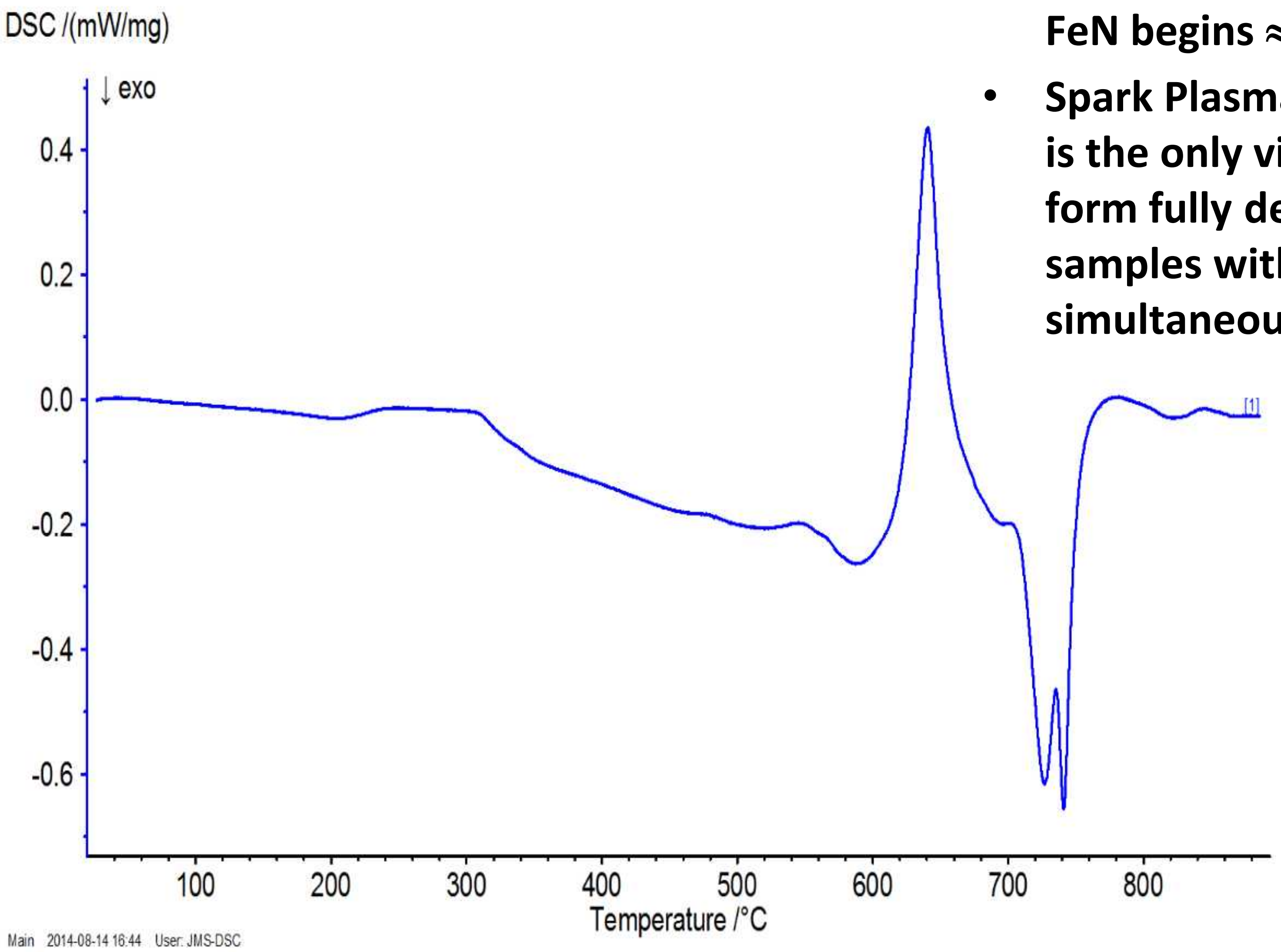
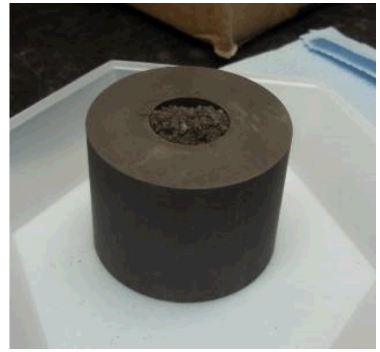
Differential Scanning Calorimetry (DSC) of Fe_4N



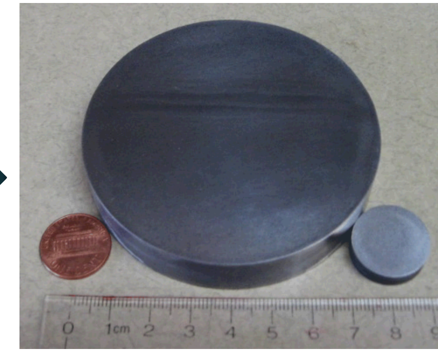
- **Decomposition of sintered FeN begins ≈ 600°C**
- **Spark Plasma Sintering (SPS) is the only viable route to form fully dense bulk Fe_4N samples without simultaneous decomposition**

Spark Plasma Sintering (SPS)

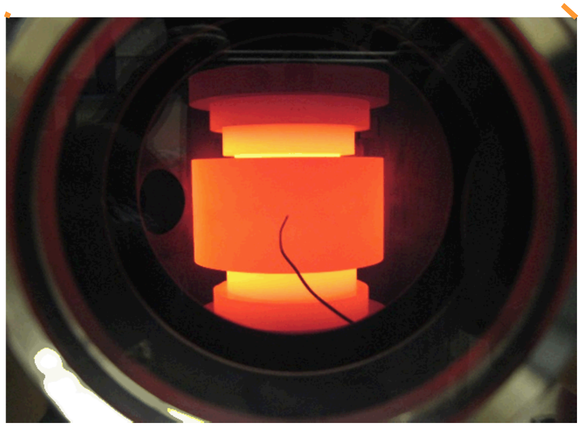
SPS Model: SPS-825S Dr. Sinter® at UC Irvine



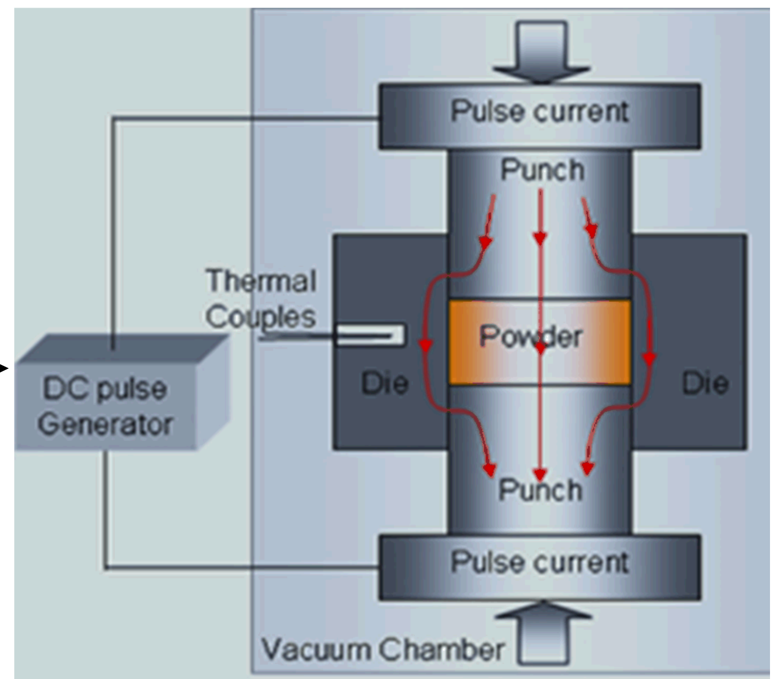
Starting Powder in Die



End Product

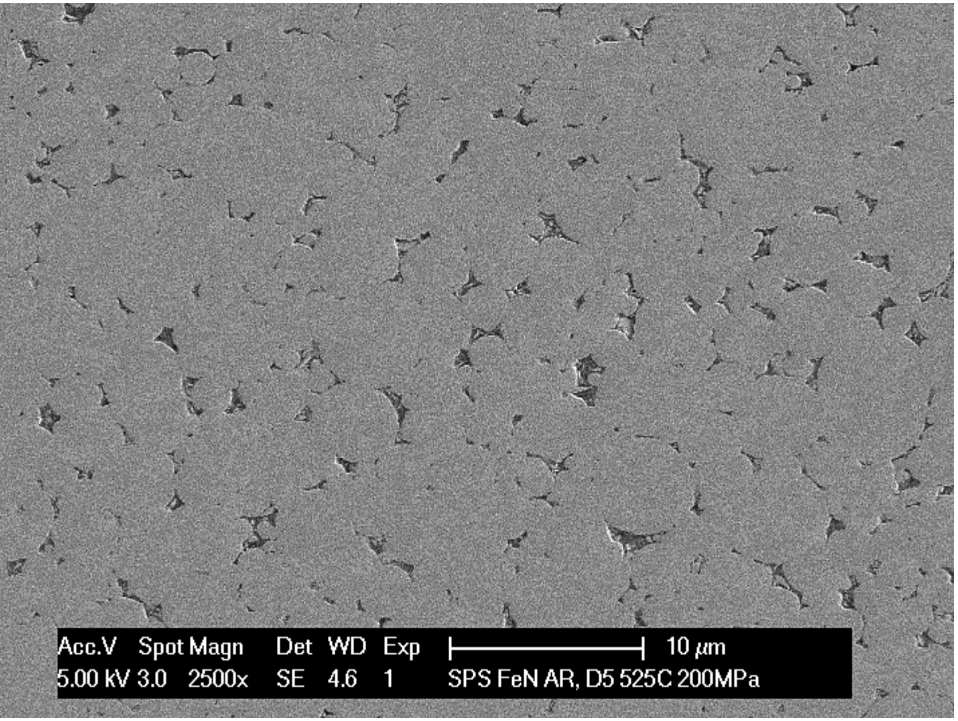


SPS Chamber

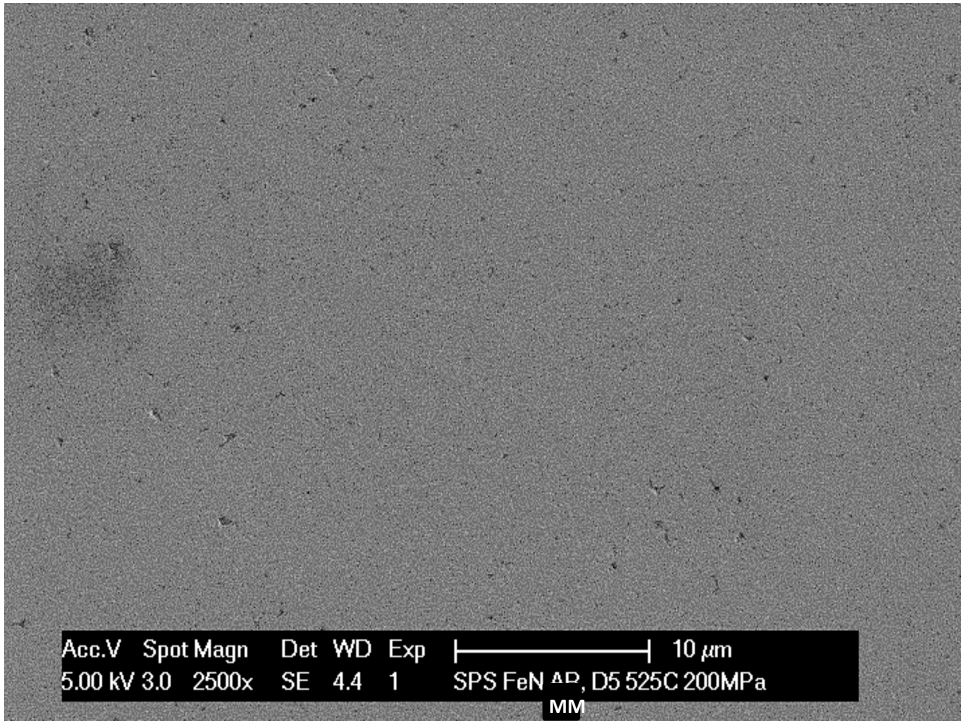


SEM of SPSed FeN samples, (Ø5mm, 525^{o}C, 200MPa)

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**

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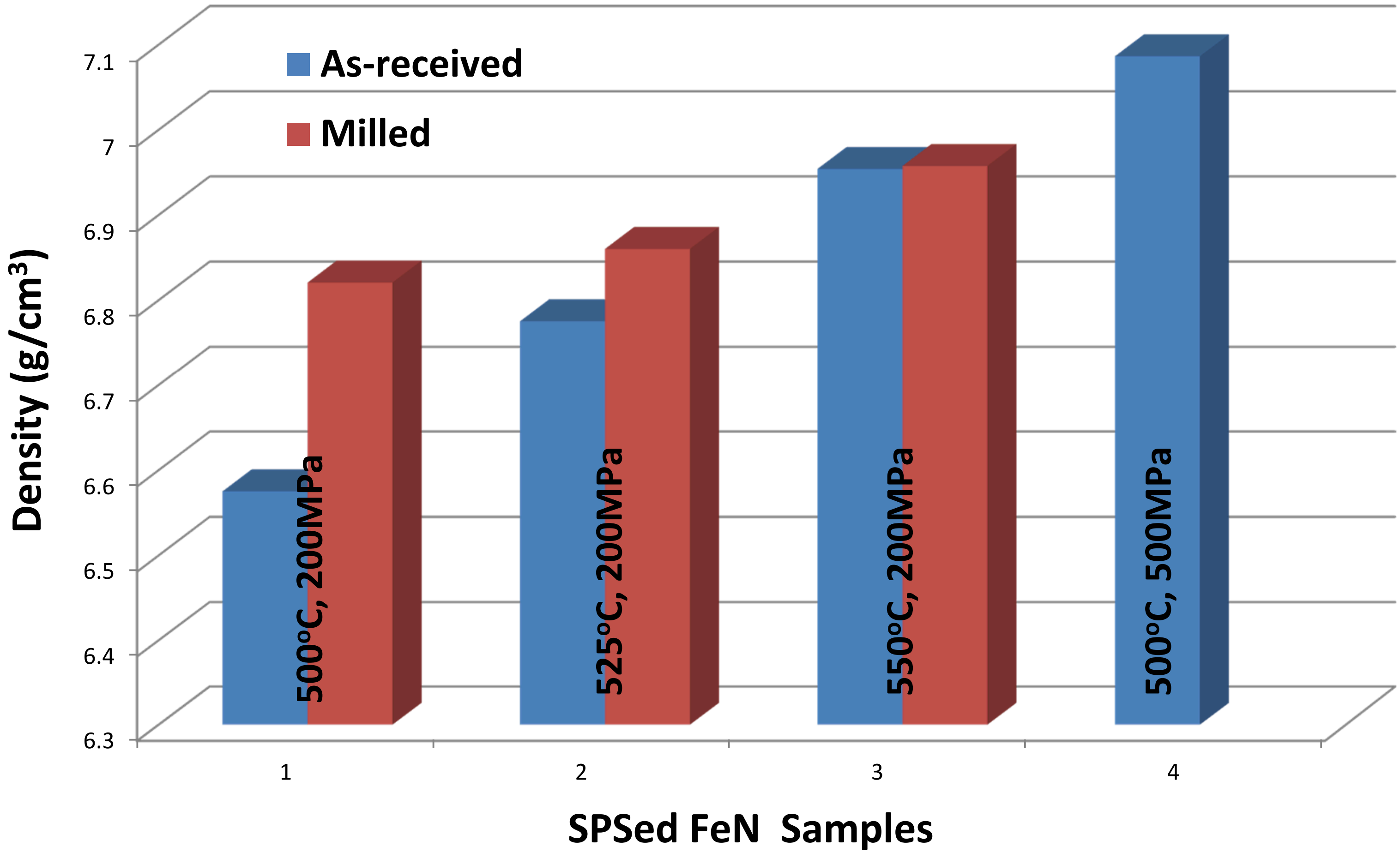
Density of SPSed Fe_4N samples

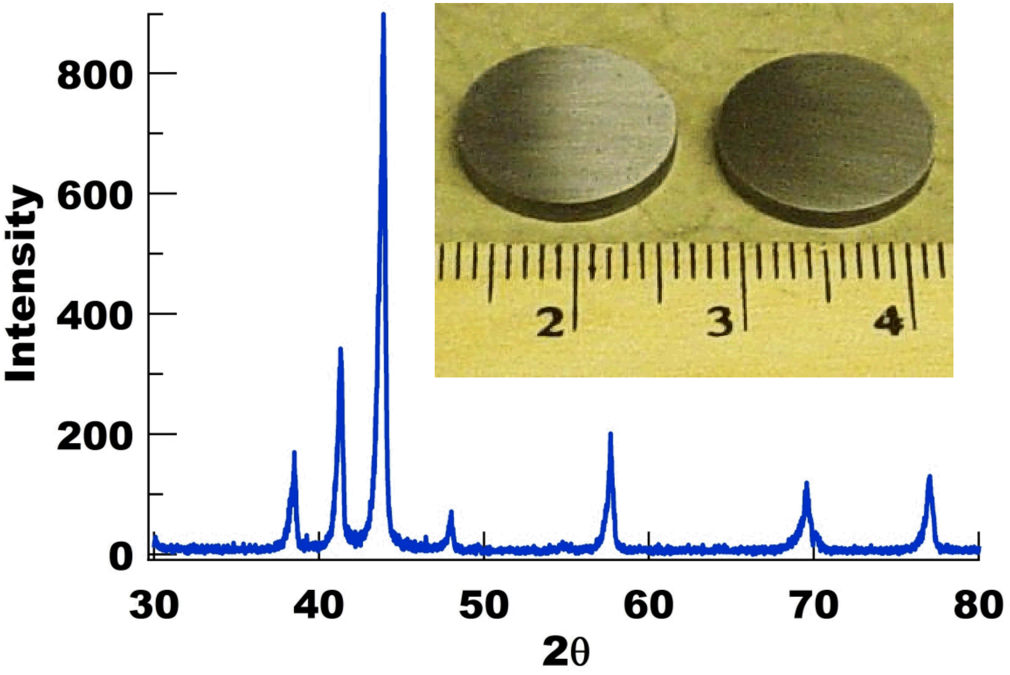
ρ_{theory} = 7.212 g/cm^3

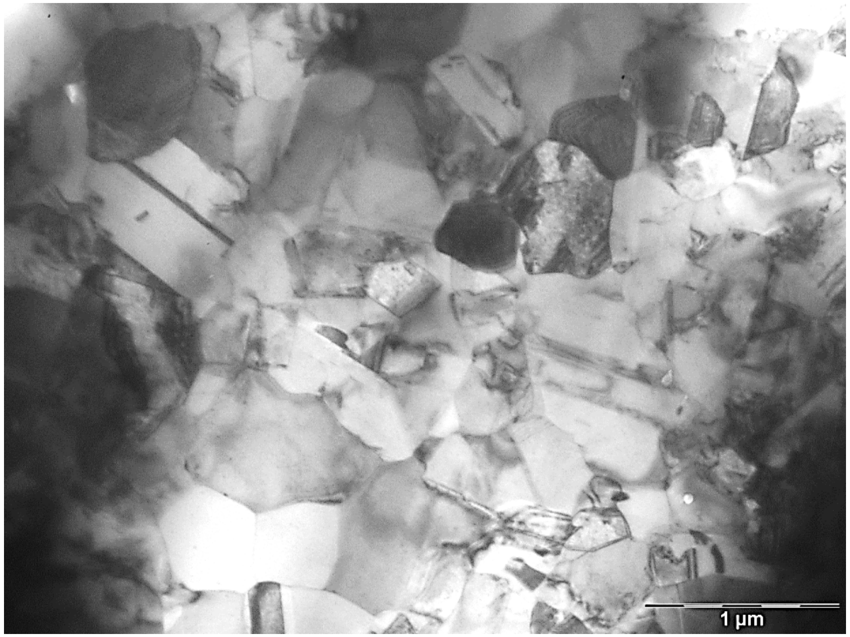


- Density increases with increasing SPS temperature and pressure
- Higher degree of variation in SPSed samples using as-received powder
- Milling improves density and uniformity

SPS consolidated Iron Nitride

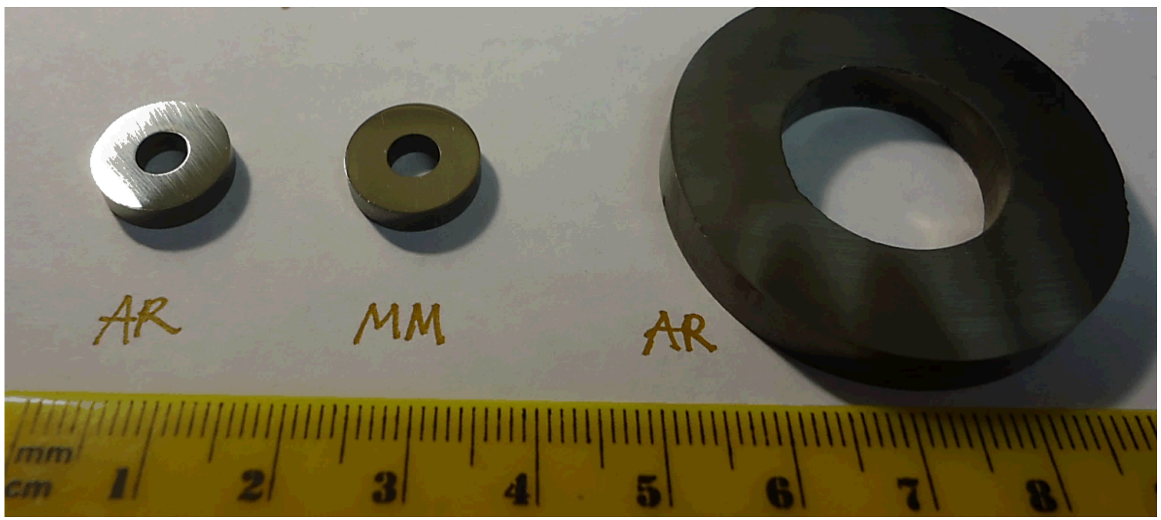
First ever bulk γ'-Fe_4N!





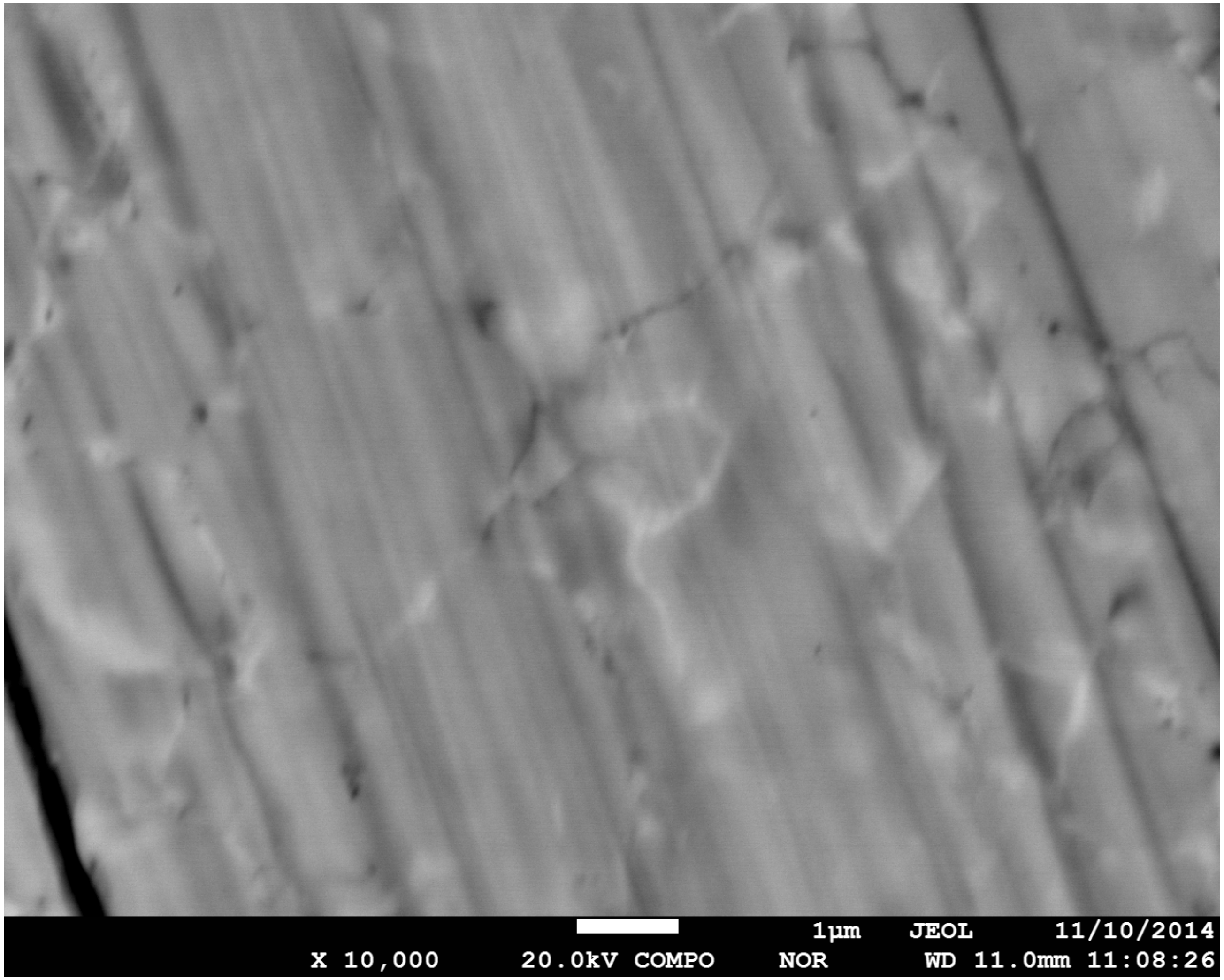
- Fe nitride powders well consolidated with little porosity
- Grain sizes 200 nm – 1 µm $\rightarrow$ fine grain size = low loss
- γ'-Fe_4N primary phase
- Fe_3N secondary phase from mixed phase starting material

Net-Shaping of Transformer Cores



- **Can sinter toroids and other shapes directly (net-shaping)**
- **Eliminates the need for machining**
- **Toroids will be wound and tested soon**

Toroid Surface SEM and EDS

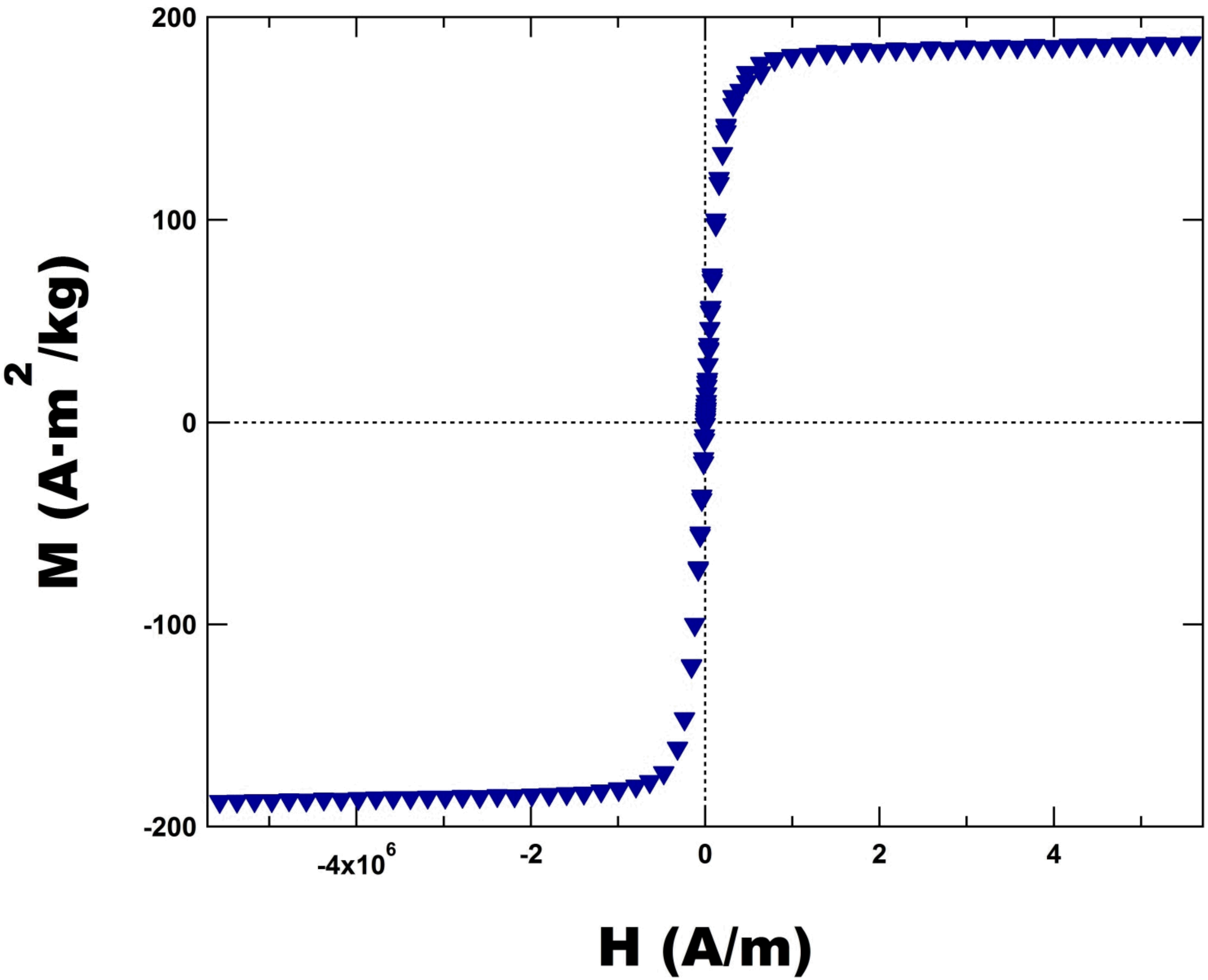


- **Small variation in composition between grain boundary and center**
- **Grain center stoichiometry ≈ Fe_4N**
- **Grain boundary is ≈ 3 Atomic% richer in iron**

*SEM/EDS analysis completed by Dick Grant (SNL)

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

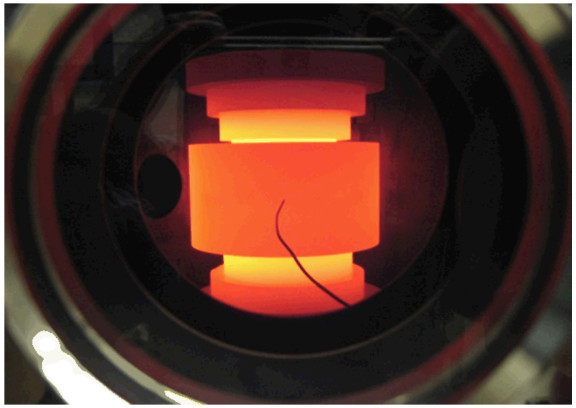
Magnetic Characterization



- Fe_4N SPSed at 550°C and 100 MPa achieved an M_{sat} of 188 $A{\cdot}m^2/kg$.
- Predicted M_{sat} of bulk γ'-Fe_4N is 209 $A{\cdot}m^2/kg$ (Fe is 217 $A{\cdot}m^2/kg$)
- Negligible coercivity

Conclusions

- γ'-Fe_4N has the potential to serve as a new low cost, high performance transformer core material
  - M_{sat} > Si steel
  - Increased current and field (and therefore power) carrying capability
  - Resistivity 200X greater than nanocrystalline and amorphous alloys
  - Only requires low cost and abundant elements (Fe & N)
  - High temperature (T) operation complementing Sandia development of high T capacitors and WBG semiconductors
- The fabrication of bulk γ'-Fe_4N using SPS has been demonstrated
  - SPS can consolidate iron nitrides without material decomposition
  - Parts can be fabricated directly using net-shaping



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2017 Spring MRS Symposium

Symposium ES12: Soft magnetic materials for next generation power electronics

Increased demand for energy efficiency, dynamic and resilient electrical grids, and more renewable energy is driving a revolution in power electronics. This revolution is being driven in part through the development and adoption of wide bandgap (WBG) semiconductors and the implementation of new power electronic topologies that leverage WBG semiconductors' fast switching speed, high voltage operation, and high temperature operation. Higher operating frequencies (approximately 1 – 100 kHz) decrease inductive requirements in power electronics but demand soft magnetic materials that can minimize electrical losses in this regime. At the present time, losses in transformers account for roughly 3.5% of the world's total energy consumption. The magnetic materials community is being challenged to drive down energy losses in transformers and inductors and keep up with advanced power electronics systems.

In order to successfully address this challenge, materials scientists, physicists, and electrical engineers from both academia and industry will need to work together to push the limits of the current soft magnetic materials and seek out new high performance material that can both minimize losses to eddy currents and support high magnetic flux densities. Furthermore, any soft magnets will need to gain widespread adoption by power systems designers and therefore manufacturing cost will be an important consideration.

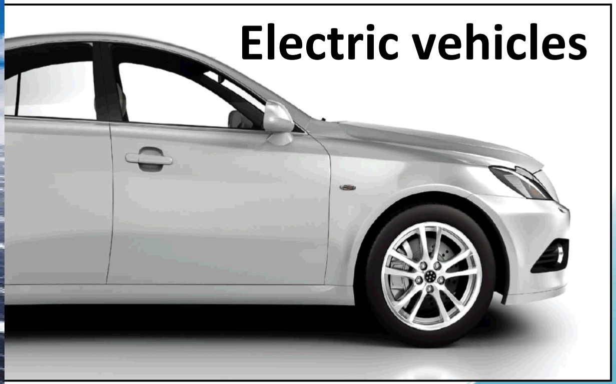
This proposed symposium intends to bring together the broad interdisciplinary mix of engineers and materials scientists necessary to accelerate research, development, and implementation of soft magnetic materials in the next generation of power electronics. Invited talks will cover the gamut of researchers and stakeholders in enhanced soft magnetic materials in order to provide all attendees with both in depth knowledge and breadth. This approach will foster collaboration and accelerate the understanding and development of enhanced soft magnetic materials.

Acknowledgements

- γ'-Fe_4N R&D supported by Dr. Imre Gyuk and the Energy Storage Program in the Office of Electricity Delivery and Energy Reliability at the US Department of Energy
- We thank Robert Delaney (El Dorado High School) for his assistance with magnetic data fitting and analysis

Extra Slides

Power Electronics (and Therefore Inductive Elements) are Ubiquitous



Courtesy of Bob Kaplar

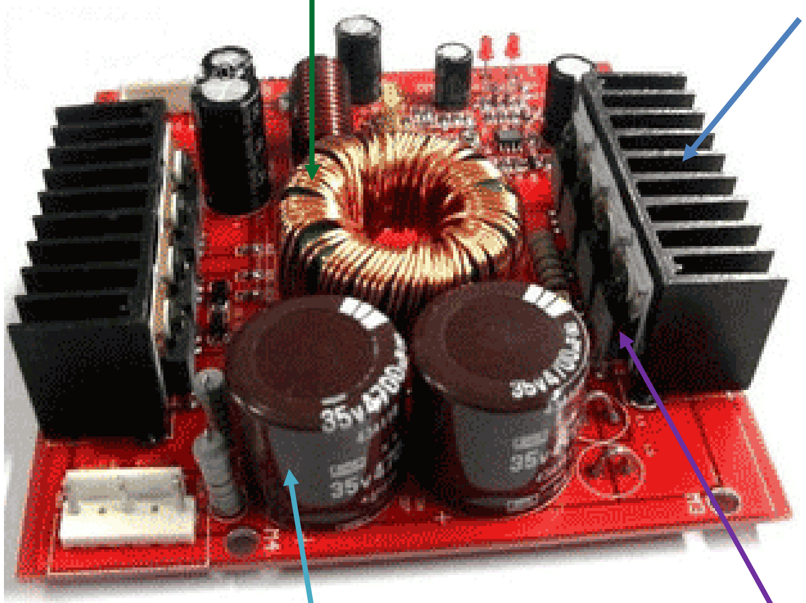
Magnetic Devices Impact Power System Volume and Weight

Passive elements and thermal management comprise the bulk of the volume and mass of a power converter

WBG/UWBG materials enable higher switching frequency and better thermal management

Magnetics

Thermal management

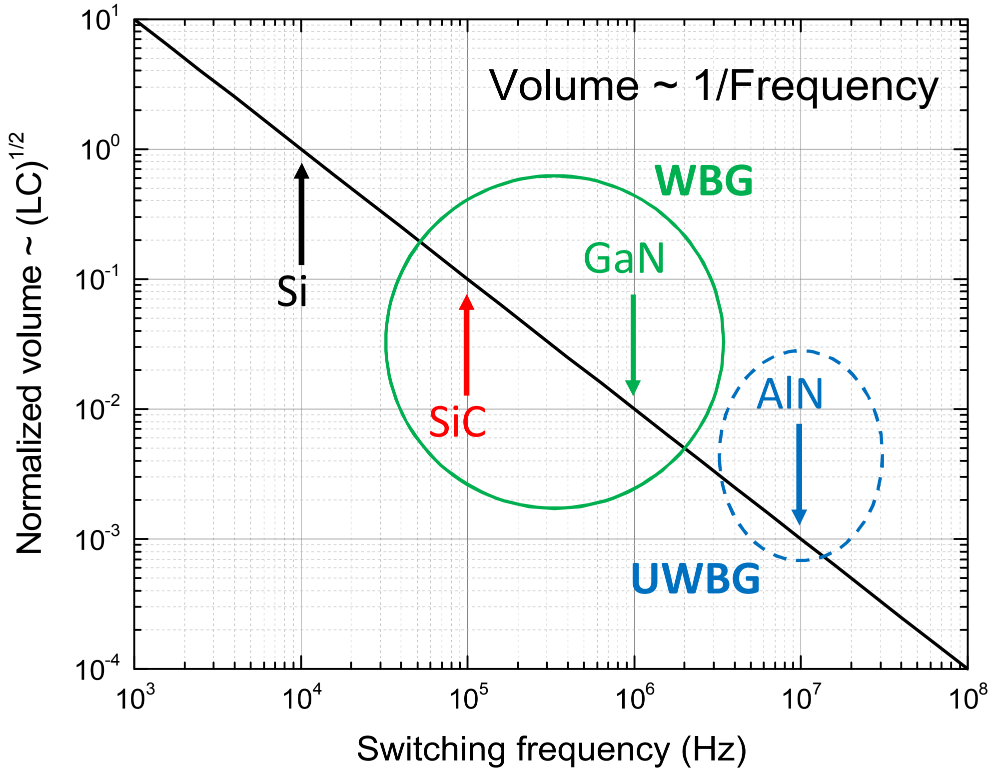


Capacitors

Semiconductor switches

J. Neely, J. Flicker, B. Kaplar

Higher Frequencies Decrease Inductance Requirements, However…



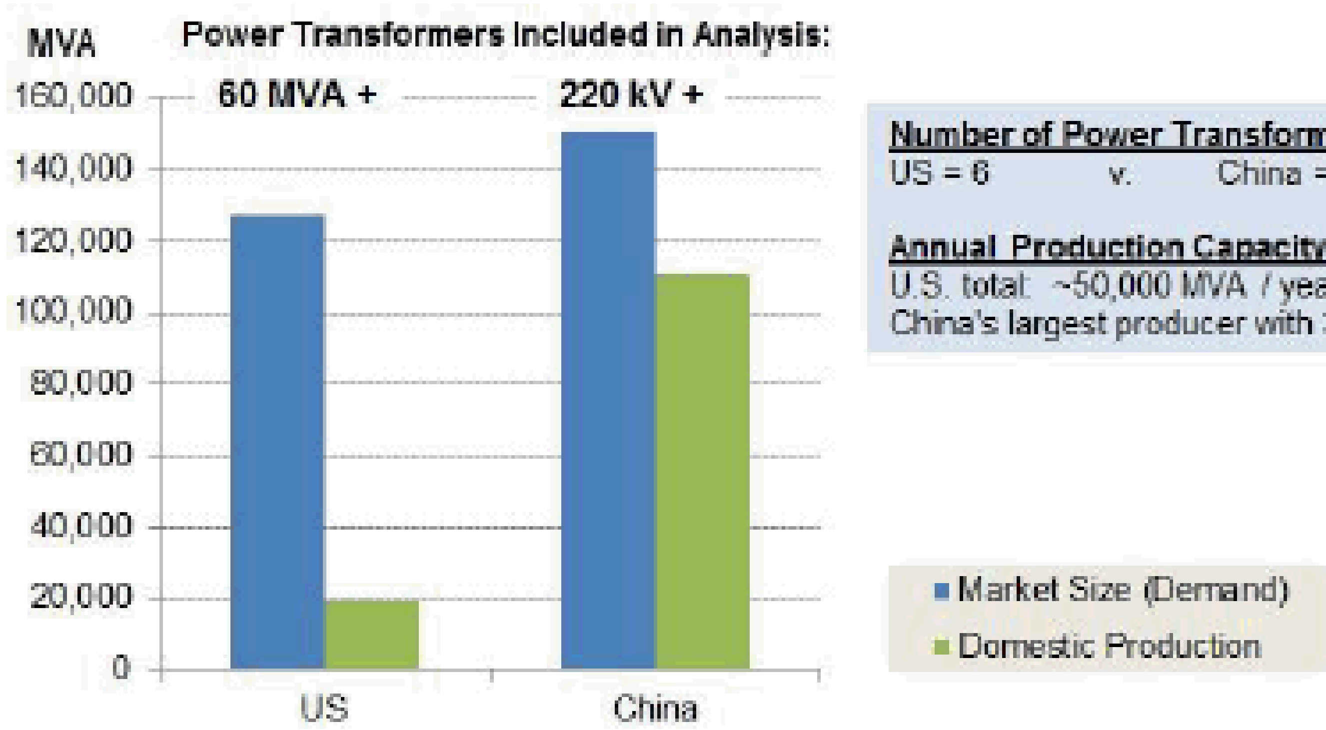
- **Higher switching frequency is enabled by scaling properties of WBG/UWBG materials**
- **Ideal 1/f SWaP dependence (true dependence likely weaker $1/f^n$ with $n < 1$ due to nonidealities)**
- **Other benefits exist, e.g. higher voltage without series stacking of devices, and higher temperature operation**
- ***UWBGs may be required for specialized applications such as pulsed power***

Inductive core materials have essentially been an afterthought and new magnetic materials are needed

Adapted from Bob Kaplar

Power Transformer Market Analysis

Figure 12. Estimated Power Transformer Markets: United States v. China in 2010



Number of Power Transformer Manufacturers
US = 6 v. China = ~30

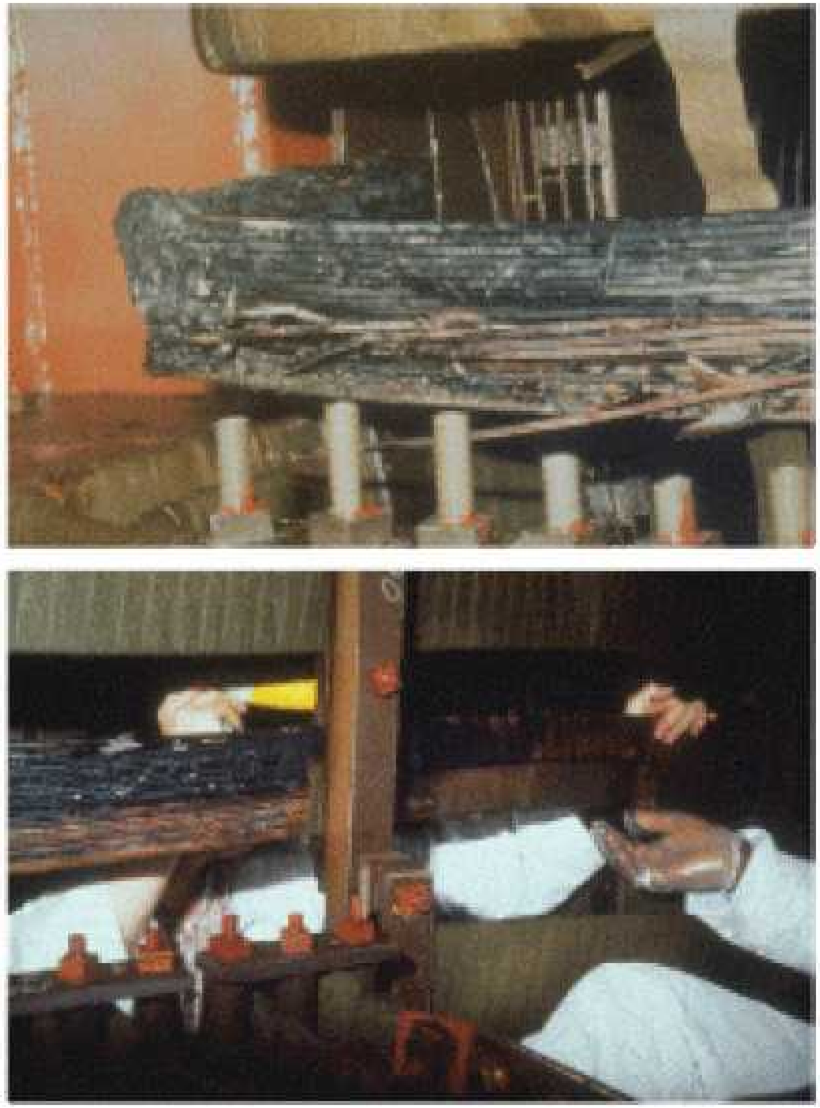
Annual Production Capacity
U.S. total: ~50,000 MVA / year
China's largest producer with 3 plants: ~125,000 MVA / year

Note: Different criteria used for the United States and China. For the United States, power transformers with capacity greater than or equal to 60 MVA are included in the data; for China, power transformers with capacity greater than or equal to 220 kV are included in the data.

Sources: USITC, 2011; China Transformer Net, 2010; China's Power Transformer Industry Report, Reuters, 2011.

"Large Power Transformers and the U.S. Electric Grid", Infrastructure Security and Energy Restoration Office of Electricity Delivery and Energy Reliability, U.S. Department of Energy, June 2012.

Transformer EMP Vulnerability

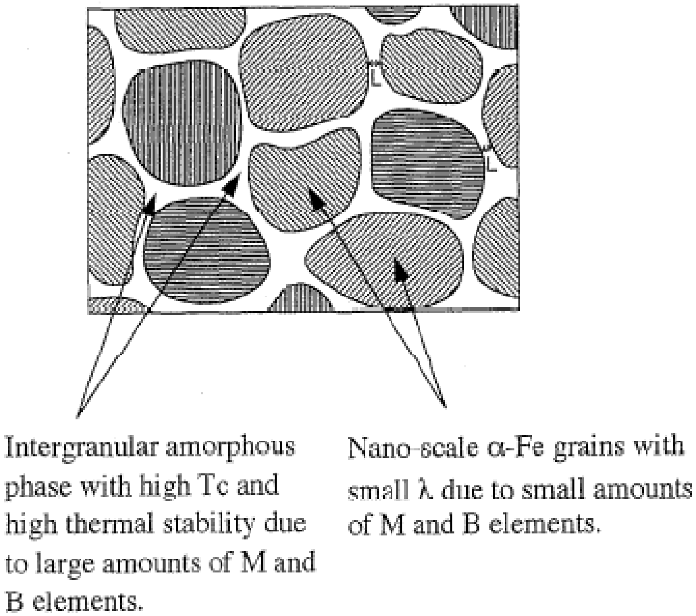


- **Geomagnetic storms couple very efficiently to long transmission lines**
- **Transformer can be driven to saturation, creating harmonics and reactive power**
- **Enough heat generated to melt copper windings**
- **Transformers the grid component that is hardest to replace**

Permanent damage to the Salem New Jersey Nuclear Plant GSU Transformer caused by the March 13, 1989 geomagnetic storm. Photos courtesy of PSE&G.

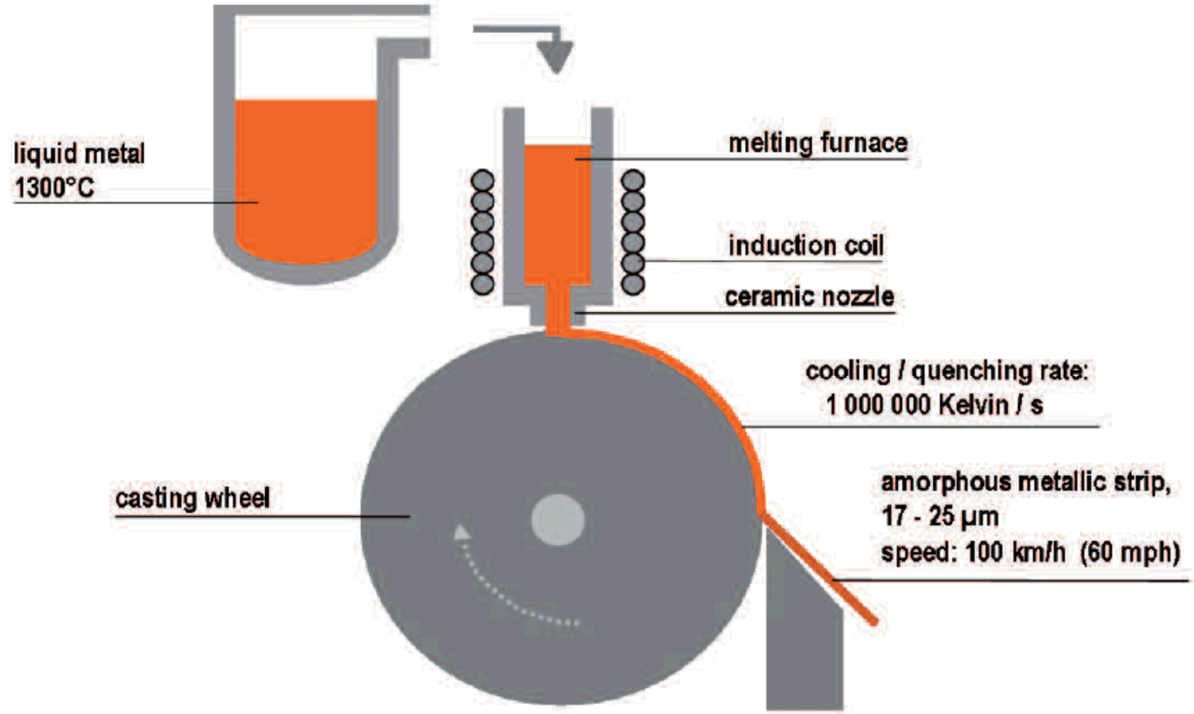
Report of the Commission to Assess the Threat to the United States from Electromagnetic Pulse (EMP) Attack, Critical National Infrastructures, April 2008

Nanocrystalline Alloy Materials & Manufacturing



“NANOPERM”

A. Makino, et. al., Nanocrystalline Soft Magnetic Fe-M-B (M = Zr, Hf, Nb) alloys and their applications, Mat. Sci, and Eng., A226-228, 594 (1997).



VITROPERM (Vacuumschmelze)

- Complex stoichiometries including Fe, Co, and other inactive elements such as B, Zr, Hf, Nb, Cu, Mo, Si, C
- Time consuming and high temperature processing → costly!
- Substantial inactive material to form a low loss nanocrystalline structure
- Material produced in tapes and often combined with plastic laminations

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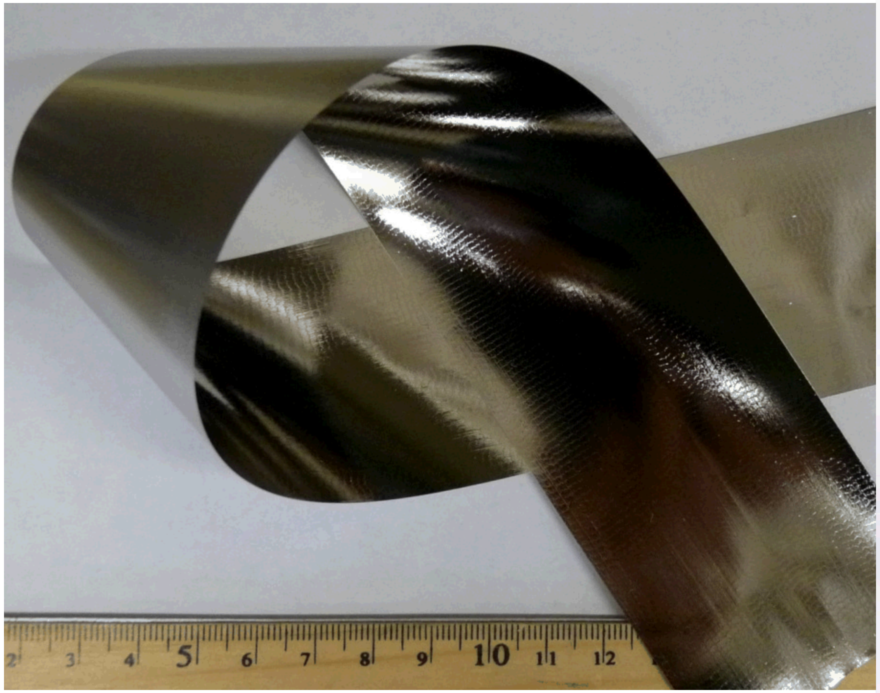
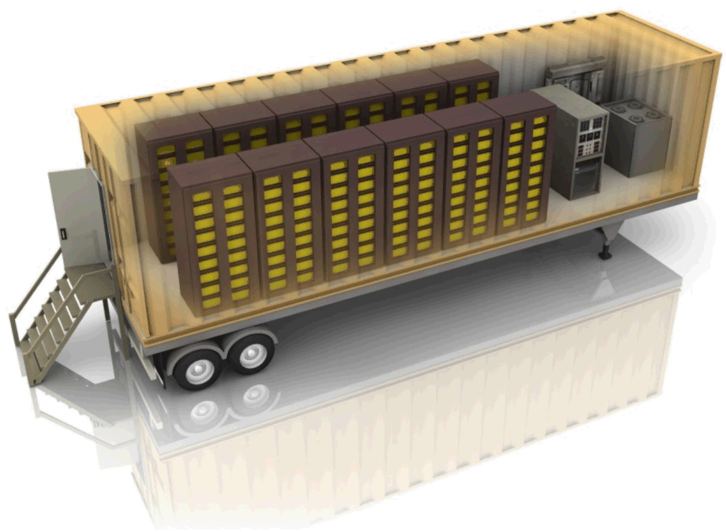
Metglas Ribbon and Laminated Motor Parts

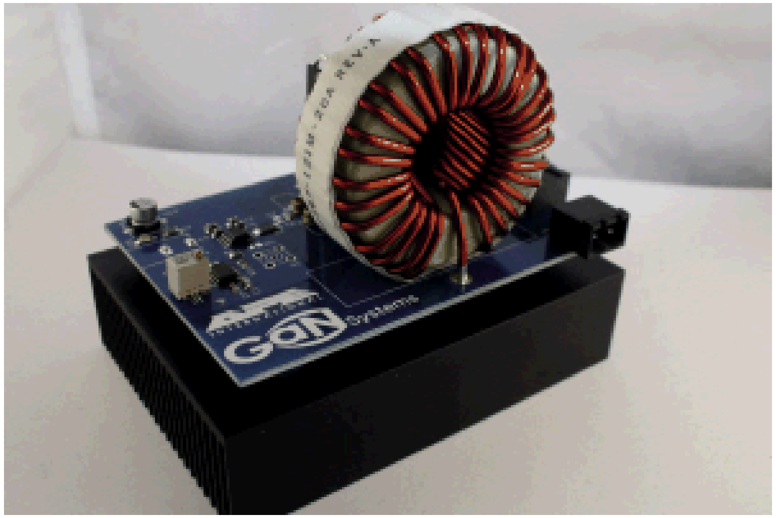


DOE/OE application: Transportable Energy Storage and Power Conversion Systems (PCS)

Benefits of Energy Storage:

- **Maintain power quality and reliability**
  - **Improve stability and defer upgrades**
  - **Enhanced agility and control (load leveling, power factor control, frequency and voltage regulation)**
- **Increase deployment of renewable generation**

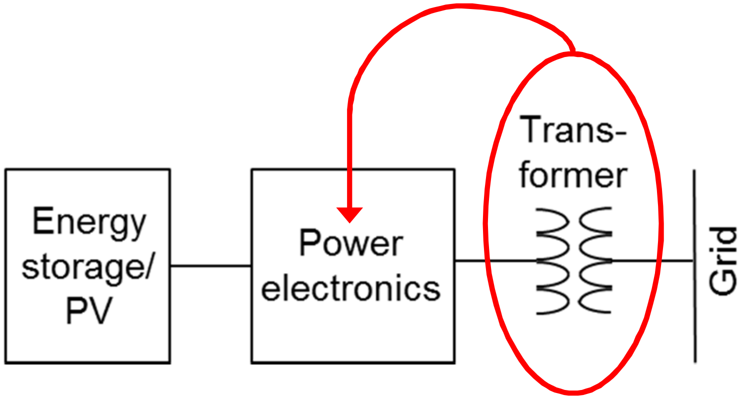




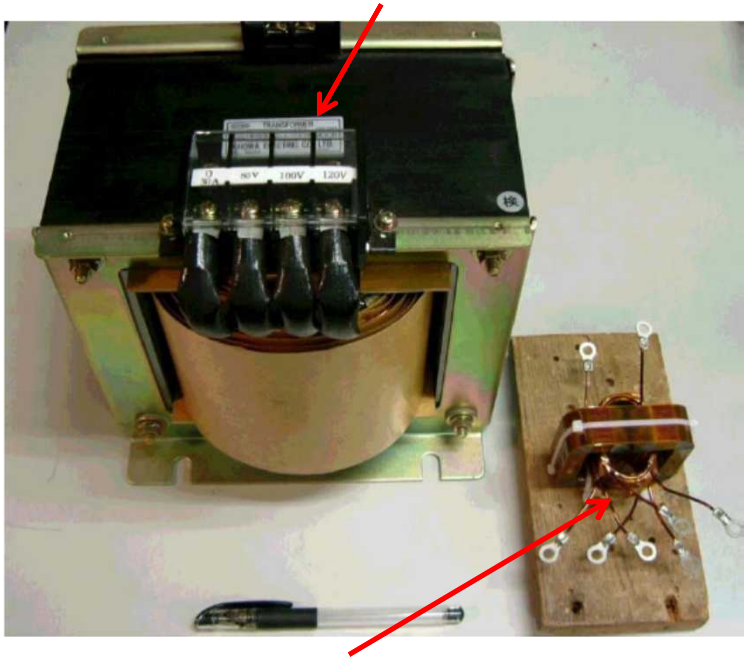
Benefits of Transportable Systems:

- **Lower cost**
- **Modular design reduces assembly and validation time**
- **Faster installation at renewable energy generation sites**

Benefits of a High Frequency Transformer



Line frequency (50 Hz) transformer



High frequency (20 kHz) transformer

- **Integrate output transformer within power conversion electronics**
- **Leverage high switching speed, voltage, and 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 10-200 kHz frequency range**
- **High permeability (low coercivity)**
- **High saturation magnetizations**
- **Low magnetostriction**
- **High temperature performance**
- **Scalable & affordable**

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

Two other applications of high frequency high power transformers (HFHPTs)

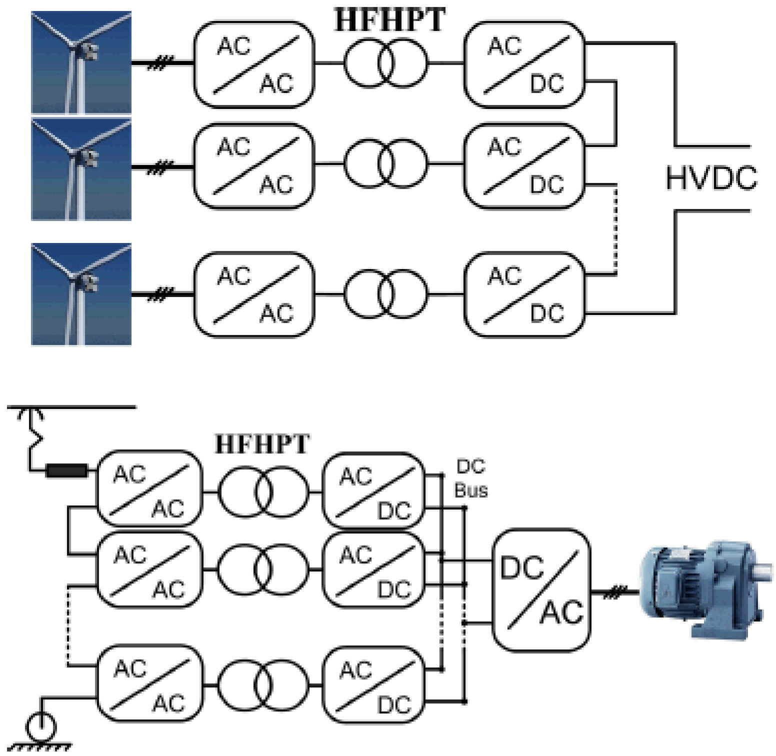


FIG. 1. Two main applications of high power converters with HFHPTs, (top) offshore wind farm and (bottom) traction converter.

E. Agheb, et. al., Core loss behavior in high frequency high power transformers-II: Arbitrary excitation, J. of Renewable and Sustainable Energy, 4, 033113 (2012).

Coercivity as a Function of Particle Size

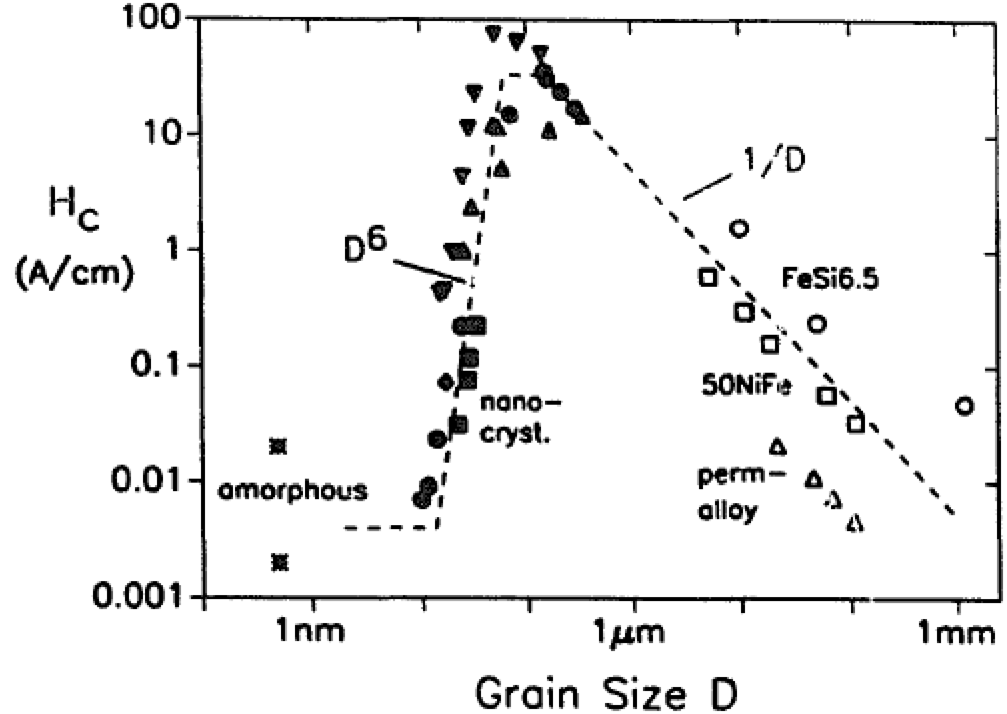
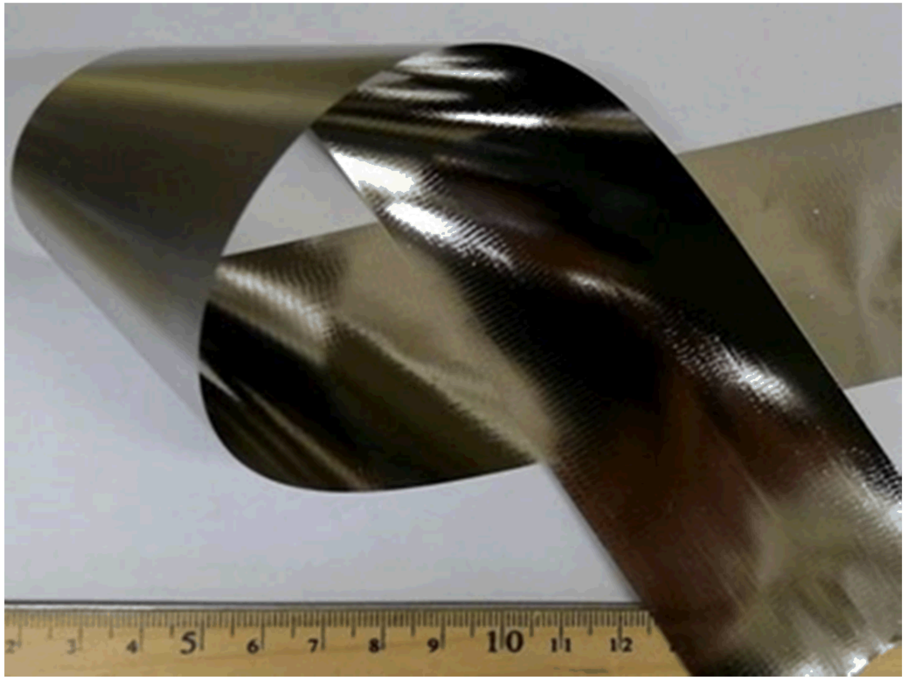


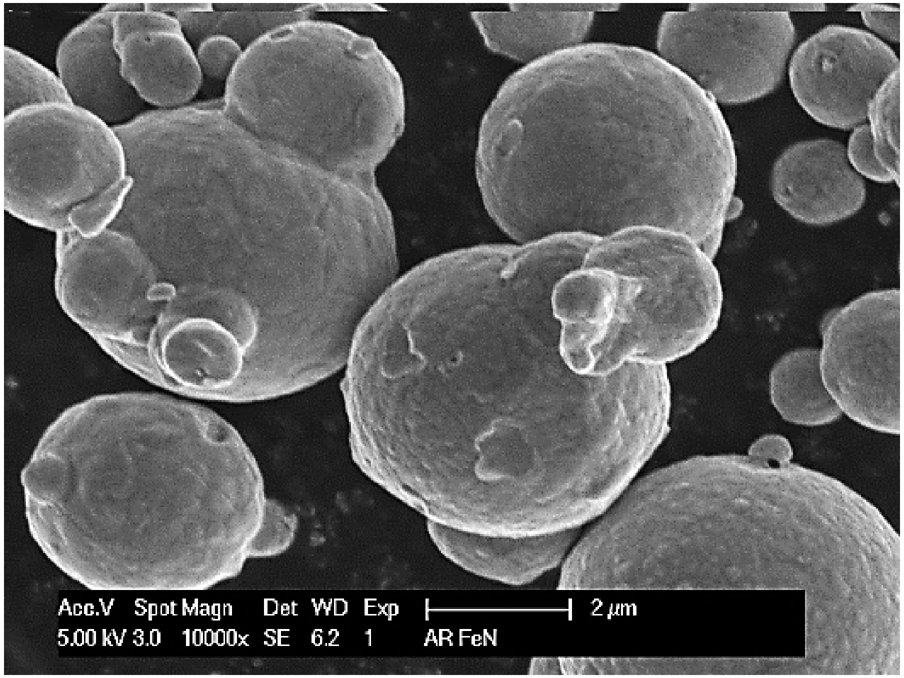
Fig. 2. Coercivity H_c vs. grain size for various soft magnetic metallic alloys. The data of the nanocrystalline material refer to (▲) FeNbSiB and (●) FeCuNbSiB [14], (◆) FeCuVSiB [15], (■) FeZrB [4] and (▼) FeCoZr [16].

G. Herzer, Nanocrystalline Soft Magnetic Materials, J. Magn. Mag. Mat., 112, 258 (1992).

FeSiCrB ribbons and Fe_xN powder



FeSiCrB ribbon



Fe_xN powder

Iron nitrides crystalline structure

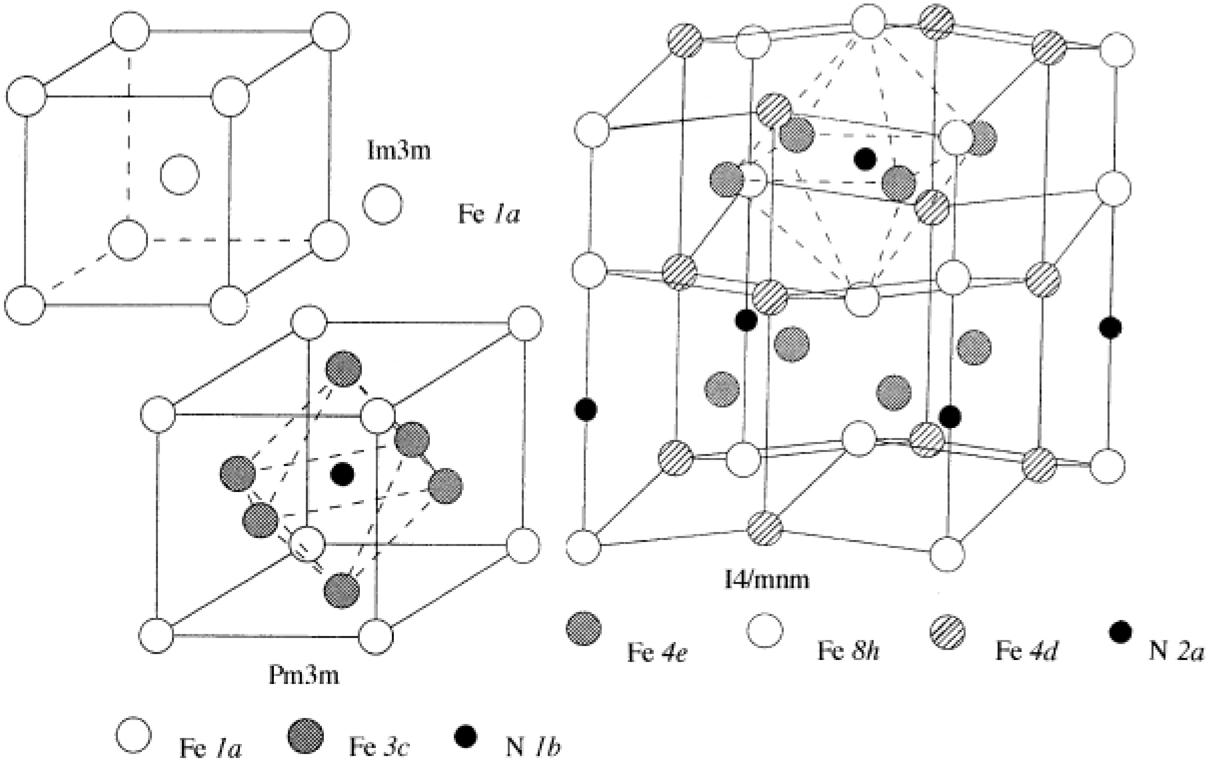


Fig. 1. Crystal structures of αFe, $\gamma'Fe_4N$ and $\alpha''Fe_{16}N_2$, drawn to scale.

J.M.D. Coey, P.A.I. Smith, Magnetic Nitrides, J. Magn. Mag. Mat., 200, 405 (1999).

Soft Magnetic Material Permeability

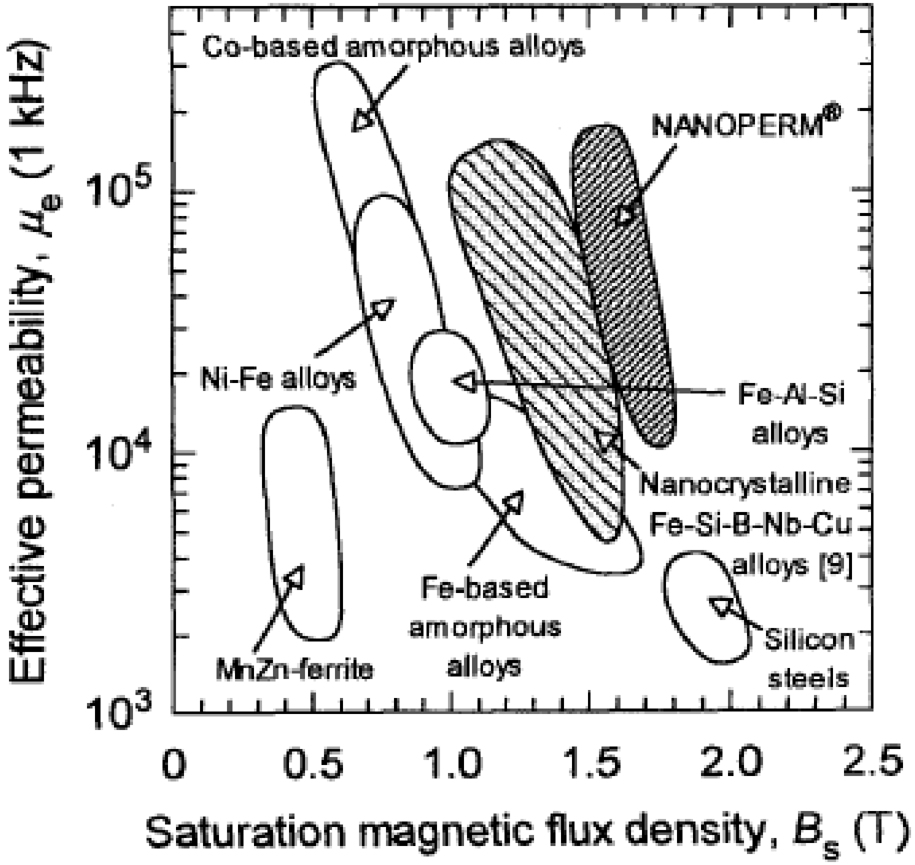


Fig. 2. Relation between B_s and μ_e at 1 kHz for NANOPERM®, the nanocrystalline Fe-Si-B-Nb-Cu alloys [9] and conventional soft magnetic materials

A. Makino, et. al., Applications of Nanocrystalline Soft Magnetic Fe-M-B (M = Zr, Nb) Alloys "NANOPERM", IEEE Trans. Magn., 33, 3793 (1997).

Magnetic Moment Variation with Nitrogen Concentration

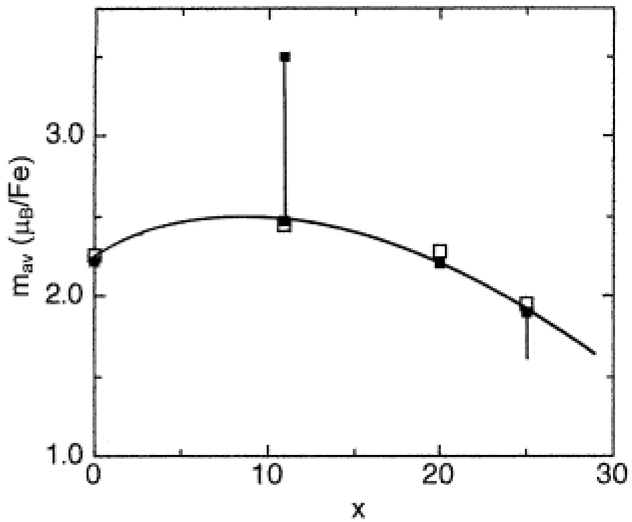
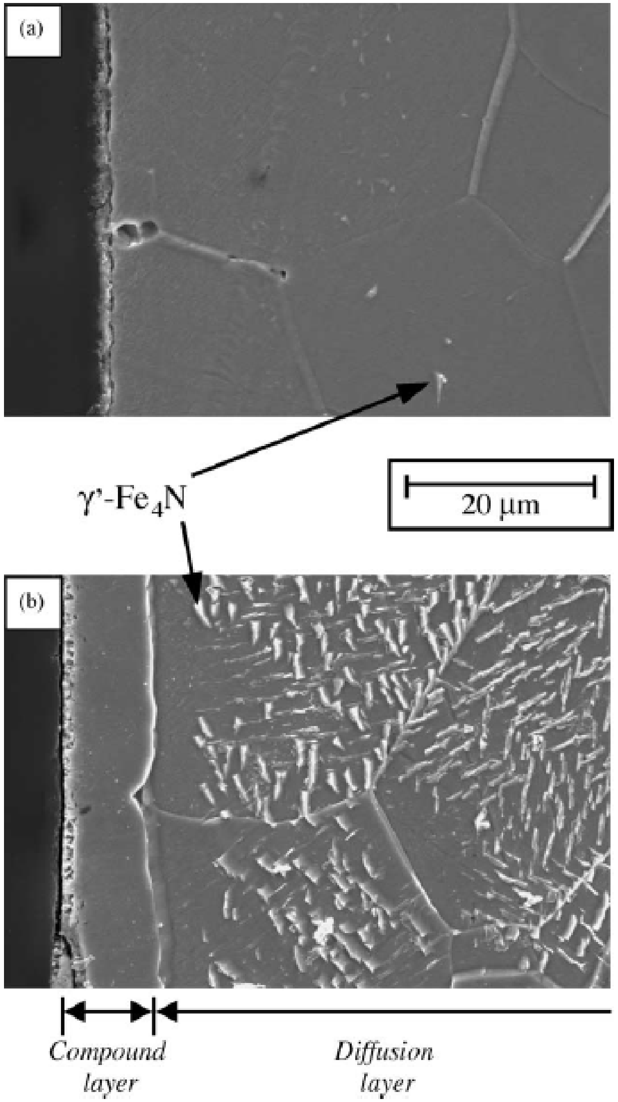


Fig. 3. Calculated (open symbol) and measured (solid symbol) average iron moments in Fe–N compounds.

J.M.D. Coey, P.A.I. Smith, Magnetic Nitrides, J. Magn. Mag. Mat., 200, 405 (1999).

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

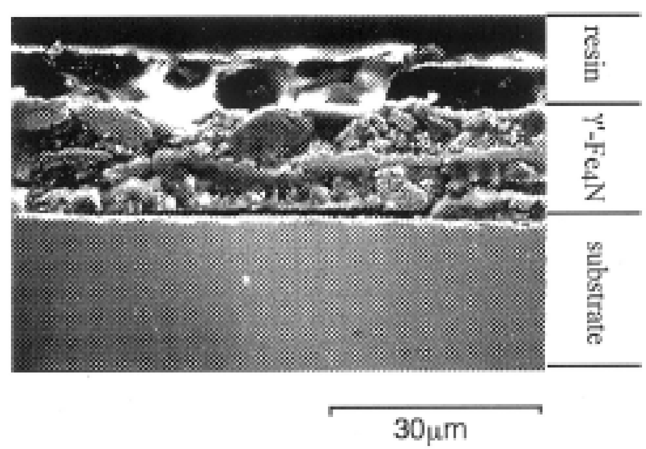
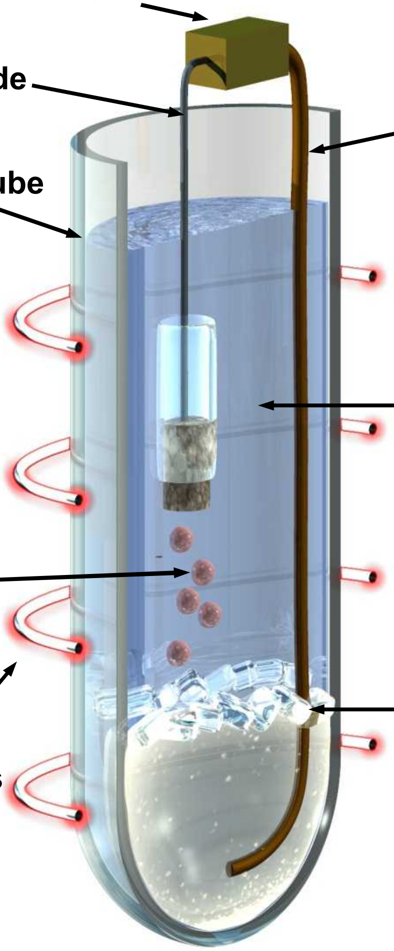


Fig. 10. Cross-sectional SEM image of iron electrode after potential pulse electrolysis for 1 h.

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

Electrochemical 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

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

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

Precursors can be replenished as they are consumed

Advantage: Continuous, isothermal or steady-state growth

U.S. Patent Filed November 2014

Other Magnetic Nitrides of Interest

Material	Phase	σ_s (Am^2/kg)	J_s (T), if available	T_c (K)	H_c (A/m)
FeN	rocksalt (fcc or fct)	209			
γ'-Fe_4N	antiperovskite-like	209	1.89	769	460
α''-$Fe_{16}N_2$	tetragonal	230 - 286	2.3	810	
α''-$Fe_{90}N_{10}$		230			
g-C_4N_3	graphitic	62			
MnN	rocksalt	194-308			4000
α-Fe	bcc	217	2.15	1044	70

- **Nitrides will have higher resistivities than current transformer core materials and will not require laminations of inactive material to mitigate eddy current losses**

SPS for Manufacturing Ceramics

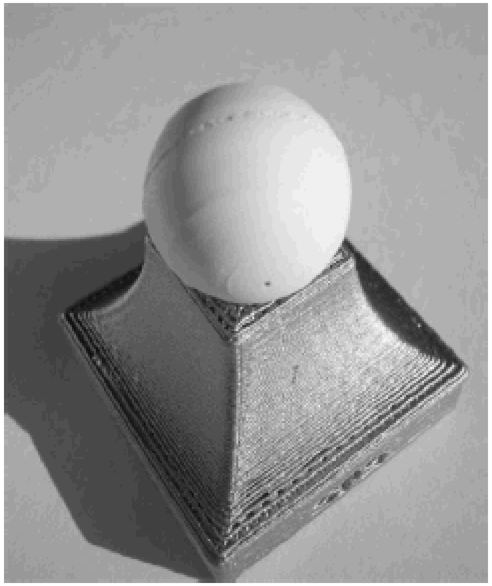


Fig. 9. Al_2O_3 sphere obtained in one single step by SPS.[63]

J. Galy, Private Communication, 2007.

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

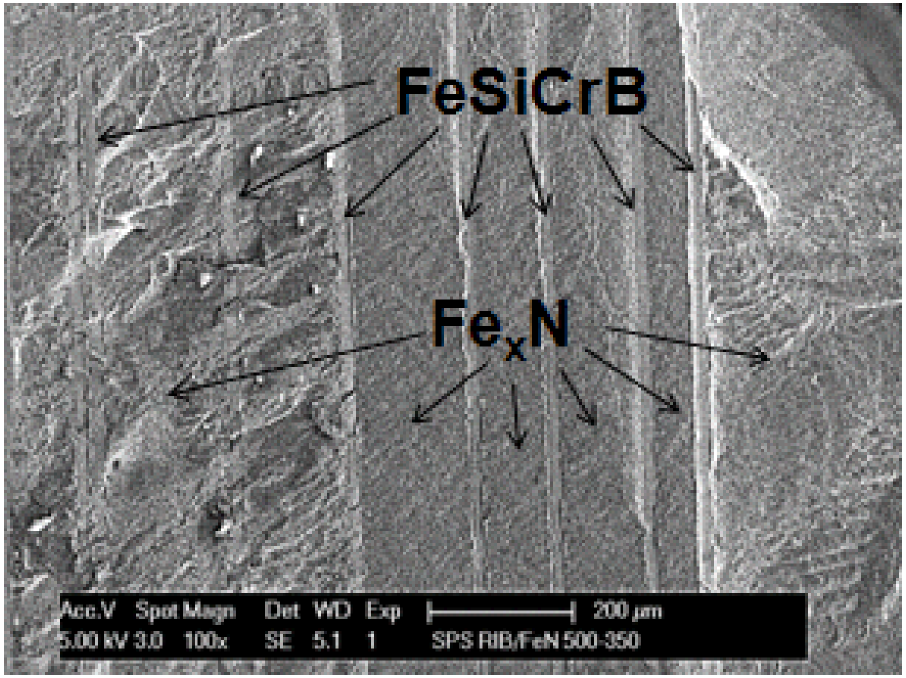
SPS System Manufacturers:

- **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)**

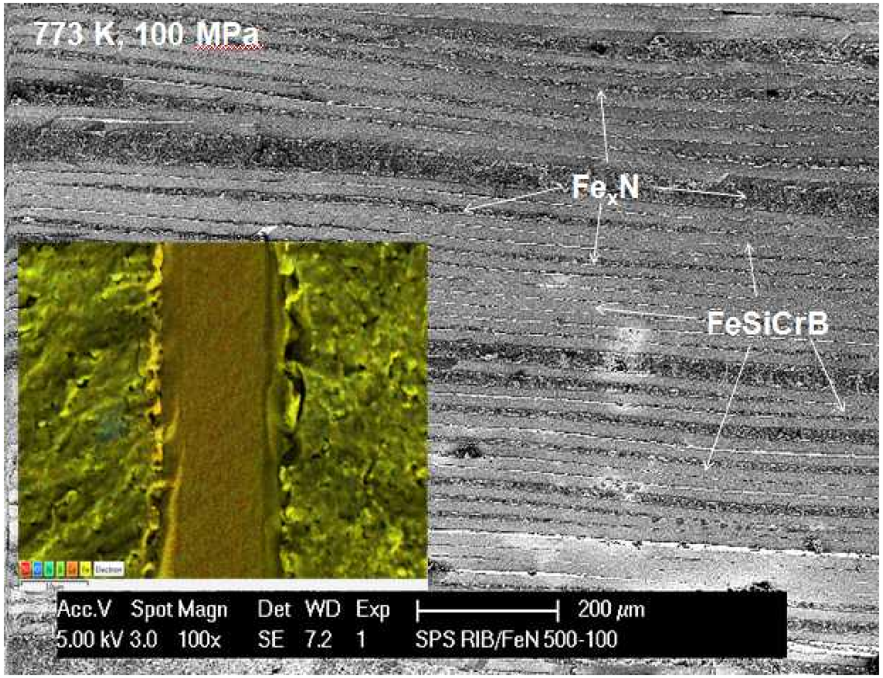
- **Size of equipment increasing to accommodate commercial needs**
- **Technology for continuous SPS under development**
- **A large number of companies have acquired SPS but often request this info to not be made public to maintain a competitive advantage**

Sandia National Laboratories

SEMs of FeSiCrB and Fe_xN composites

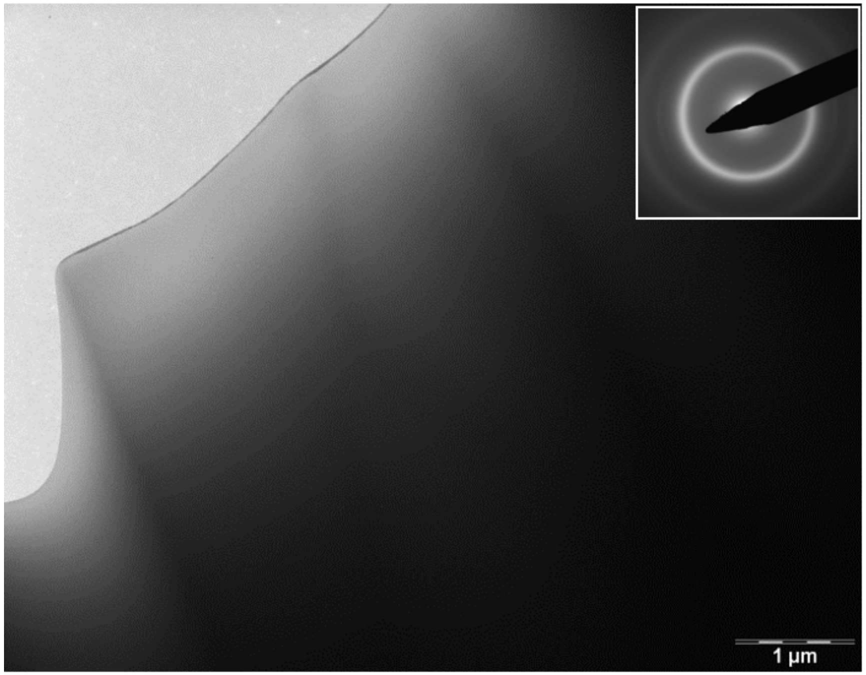


10 vol% FeSiCrB ribbon

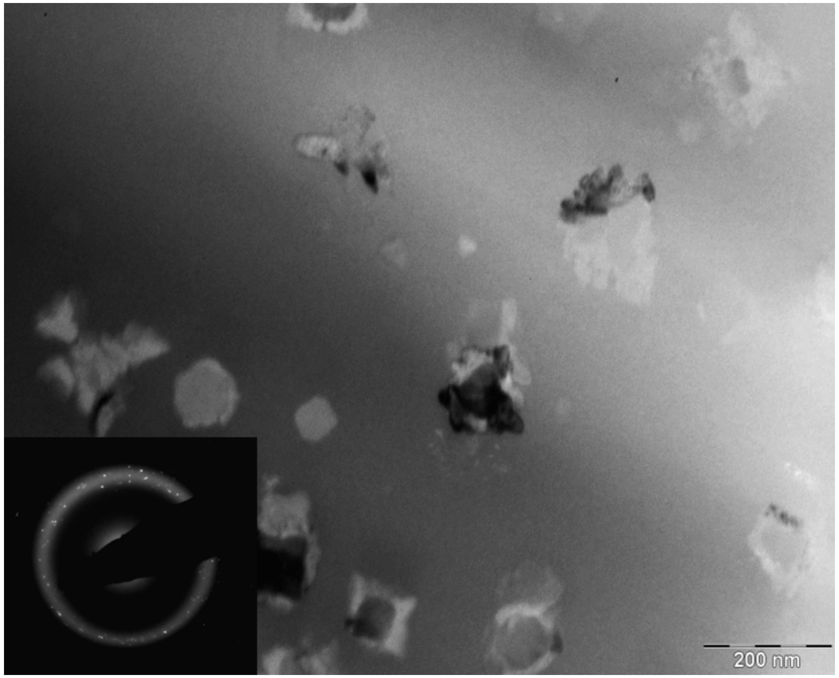


90 vol% FeSiCrB ribbon plus EDS mapping (inset)

TEMs of FeSiCrB before and after sintering

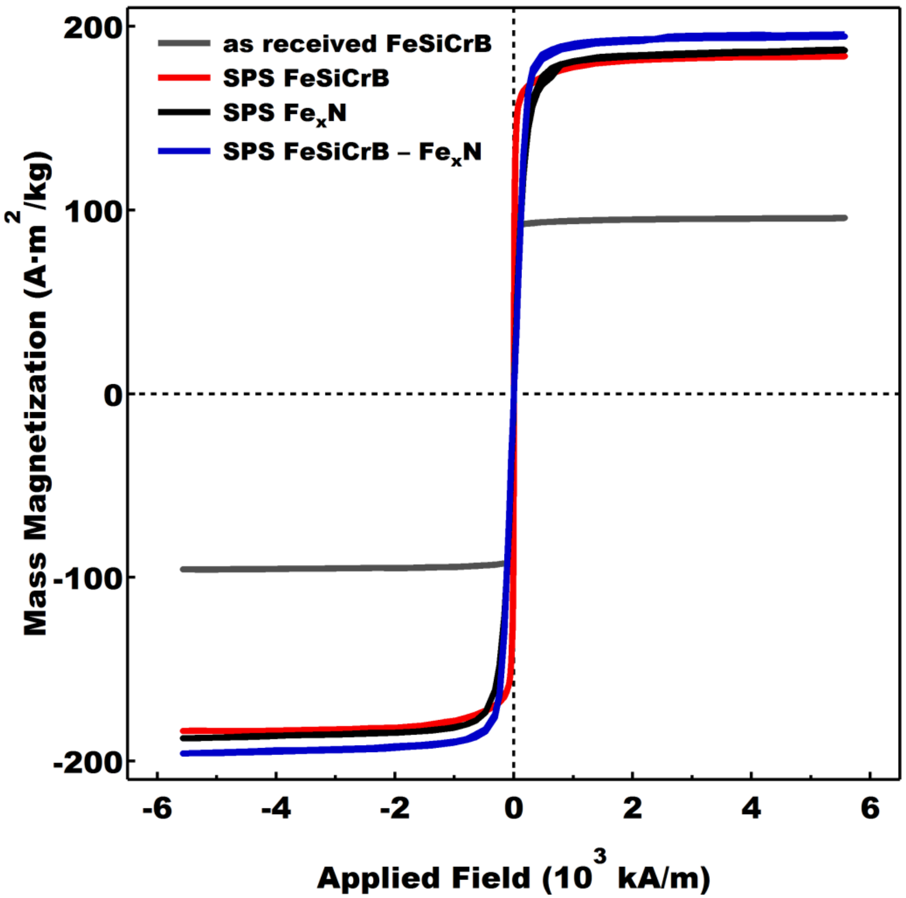


Before SPS



After SPS

Composite DC Magnetic Response



Sample	M_{sat} ($A \cdot m^2/kg$)
As received FeSiCrB ribbon	96.0
SPSed FeSiCrB ribbon	185.3
SPSed Fe_xN	188.0
SPSed FeSiCrB–Fe_xN	196.5