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Synthesis of bulk iron nitride soft magnetic materials

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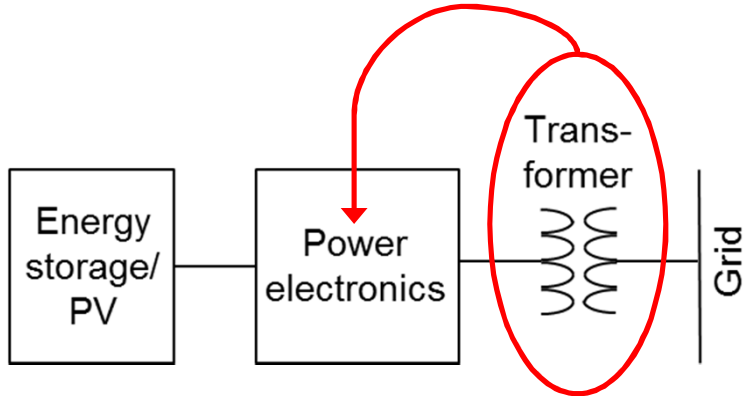
The authors acknowledge support for this work from Dr. Imre Gyuk and the Energy Storage Program in the Office of Electricity Delivery and Energy Reliability at the US Department of Energy



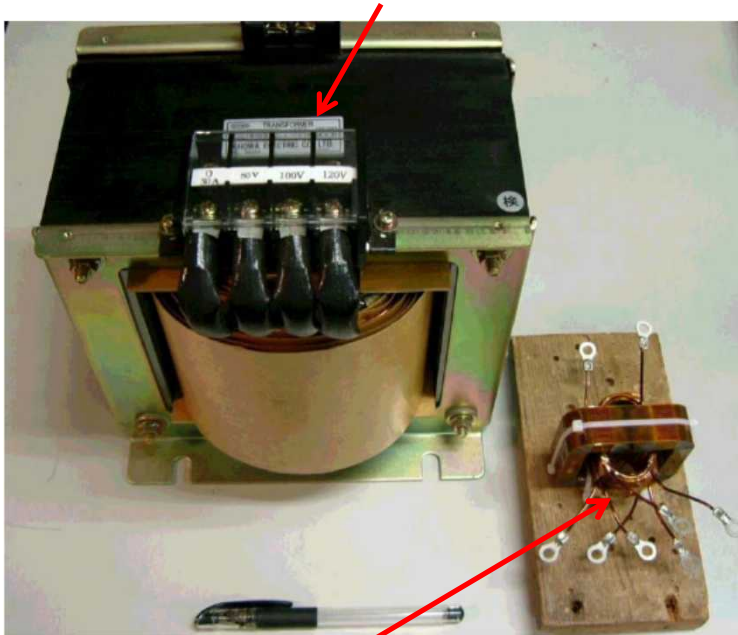
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Benefits of a High Frequency Transformer



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)

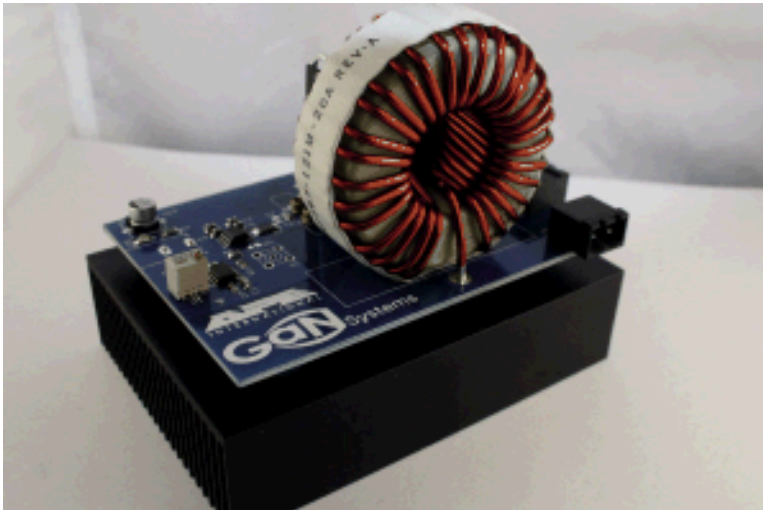
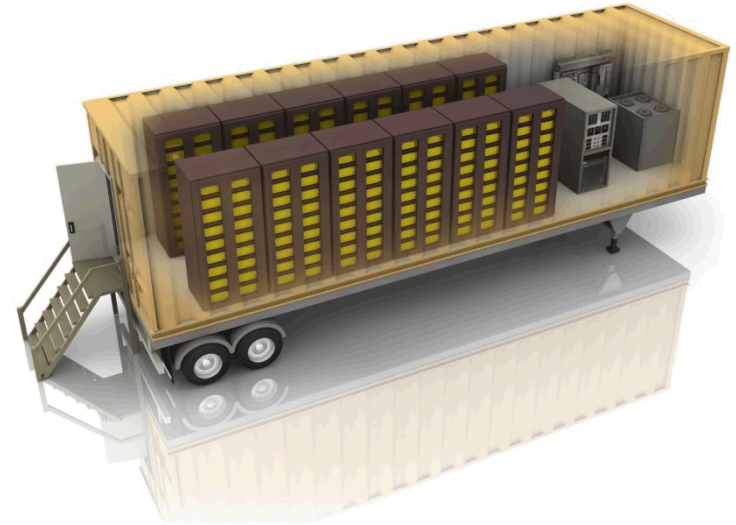
Material requirements:

- Low loss in 10-200 kHz frequency range
- High permeability (low coercivity)
- High saturation magnetizations
- Low magnetostriction
- High temperature performance
- Scalable & affordable

Transportable Energy Storage and Power Conversion Systems (PCS)

Benefits of Energy Storage:

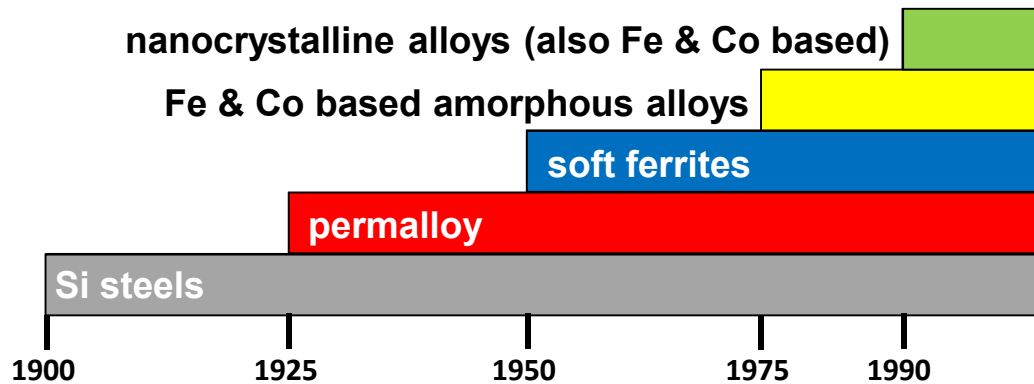
- **Maintain power quality and reliability**
 - Improve stability and defer upgrades
 - Enhanced agility and control (load leveling, power factor control, frequency and voltage regulation)
- **Increase deployment of renewable generation**



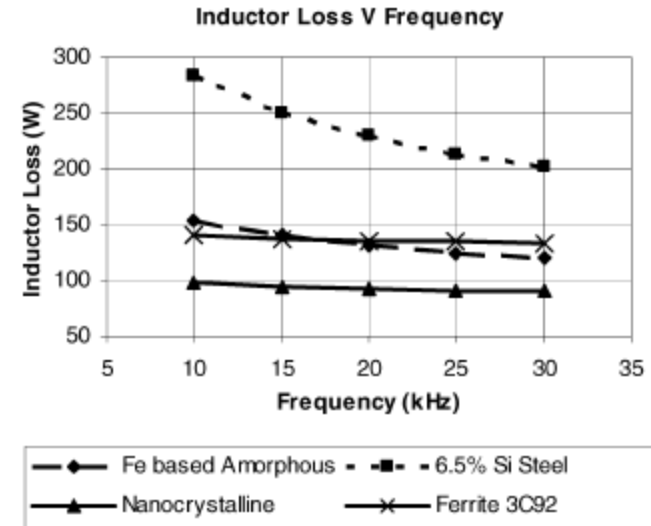
Benefits of Transportable Systems:

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

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).

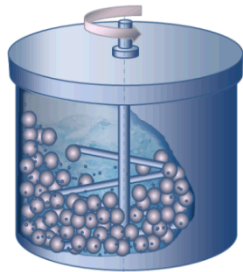
Magnetic Material	J_s (T)	ρ ($\mu\Omega\cdot m$)	Cost
VITROPERM (Vacuumschmelze)	1.20	1.15	High
Metglas 2605SC	1.60	1.37	High
Ferrite (Fexxocube)	0.52	5×10^6	Low
Si steel	1.87	0.05	Low
γ' -Fe ₄ N	1.89	~200	?

γ' -Fe₄N can meet all requirements of high frequency power electronics

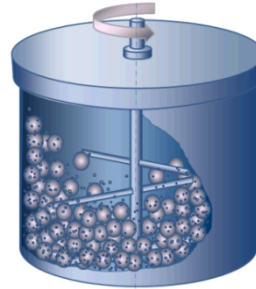
γ' -Fe₄N Synthesis and Processing

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

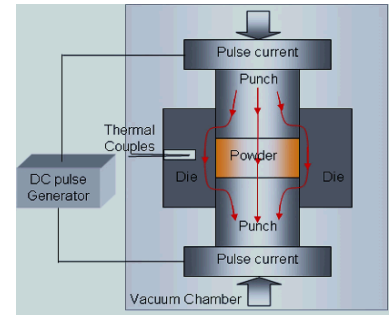
Synthesis of dense nanocrystalline iron nitrides using a two-step reactive milling and high pressure spark plasma sintering (SPS).



Liquid N₂



NH₃

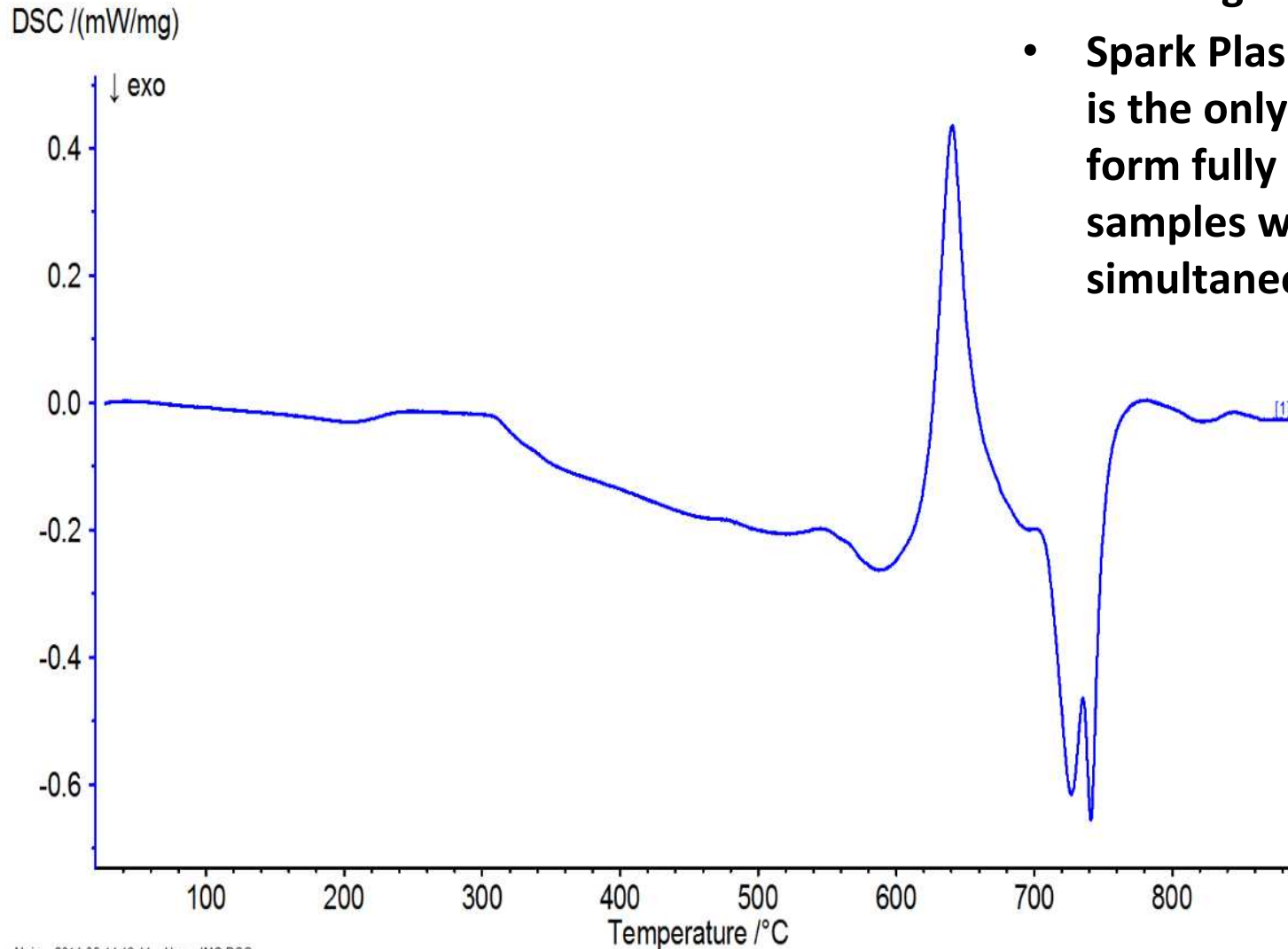


Spark Plasma
Sintering (SPS)

- Cryomilling creates nanocrystalline Fe powder with large amounts of vacancies, grain boundaries, and dislocations
- Defects serve as fast diffusion pathways for nitrogen atoms from NH₃
- SPS quickly consolidates raw powders with a low sintering temperature
 - Excellent control over grain growth
 - Result: Improved magnetic properties

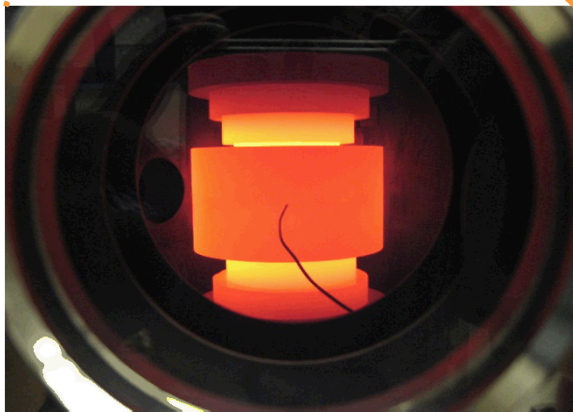
Differential Scanning Calorimetry (DSC) of Fe_4N

- Decomposition of sintered FeN begins $\approx 600^\circ\text{C}$
- Spark Plasma Sintering (SPS) is the only viable route to form fully dense bulk Fe_4N samples without simultaneous decomposition

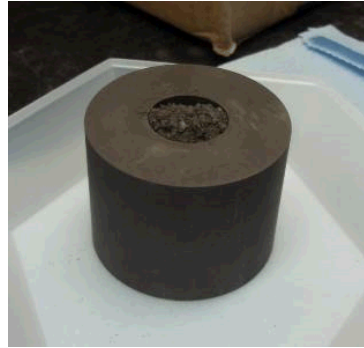


Spark Plasma Sintering (SPS)

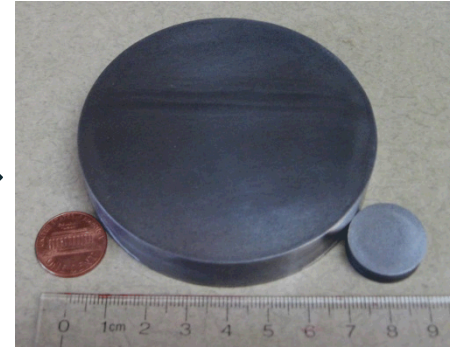
SPS Model: SPS-825S Dr. Sinter® at UC Irvine



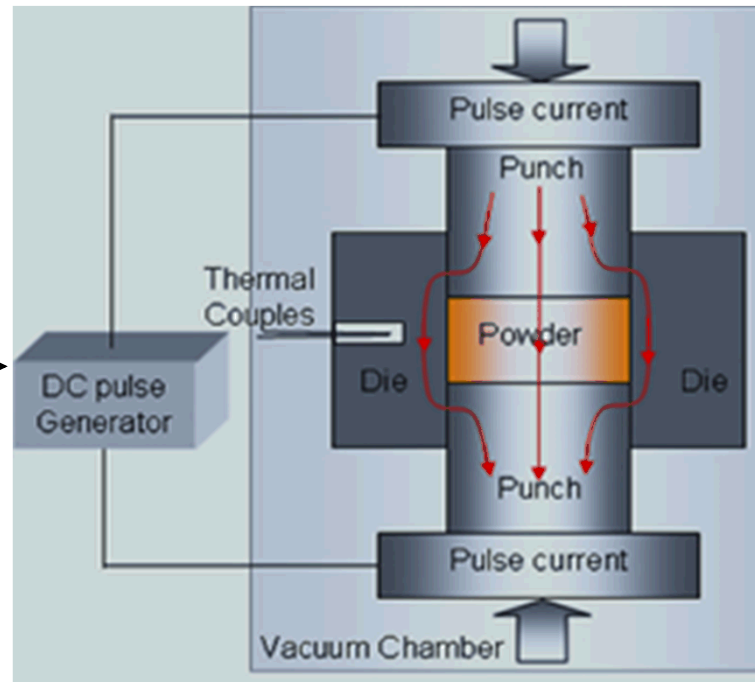
**SPS
Chamber**



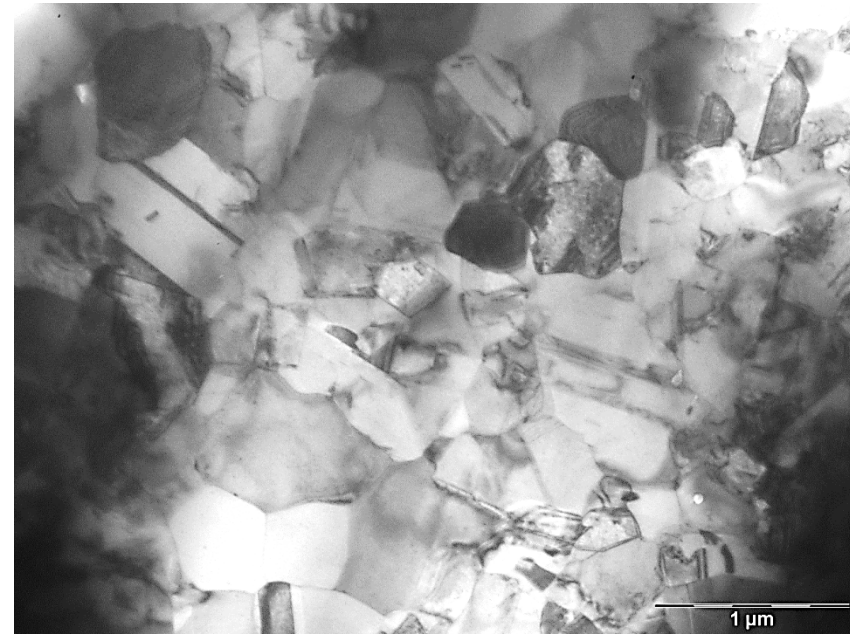
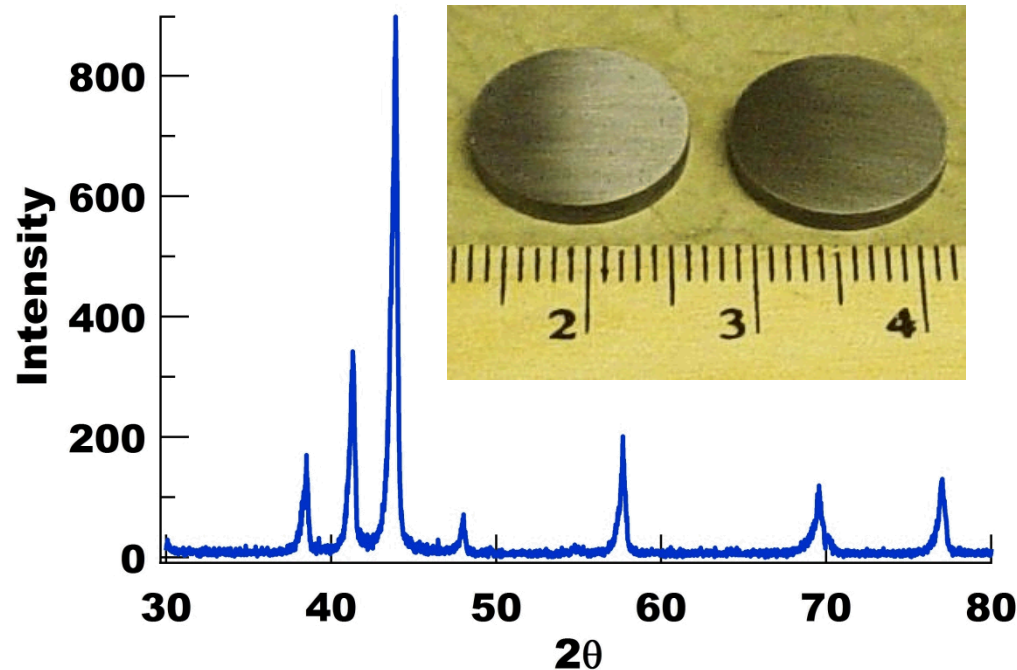
Starting Powder in Die



End Product

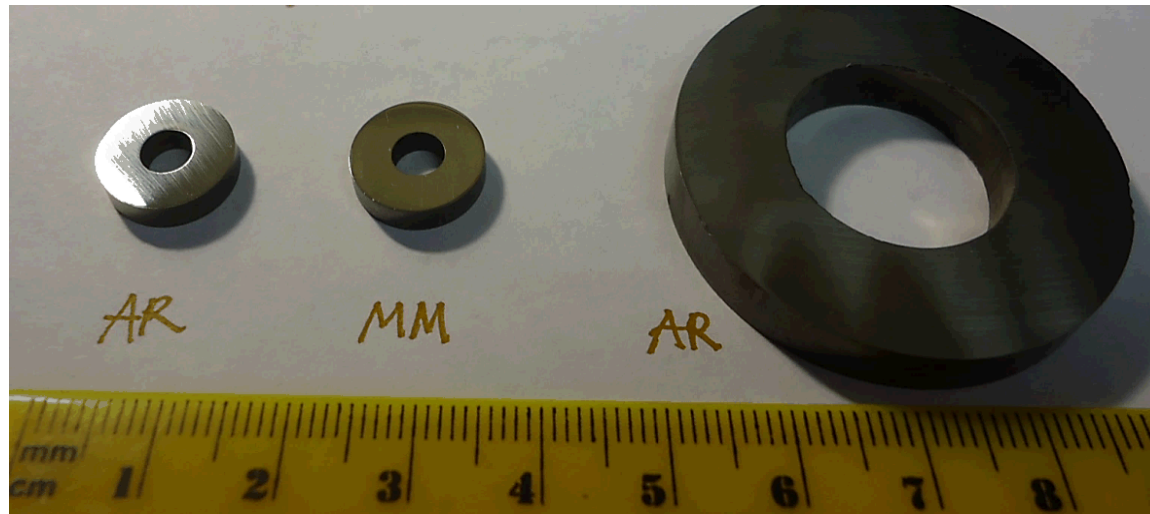


SPS consolidated Iron Nitride



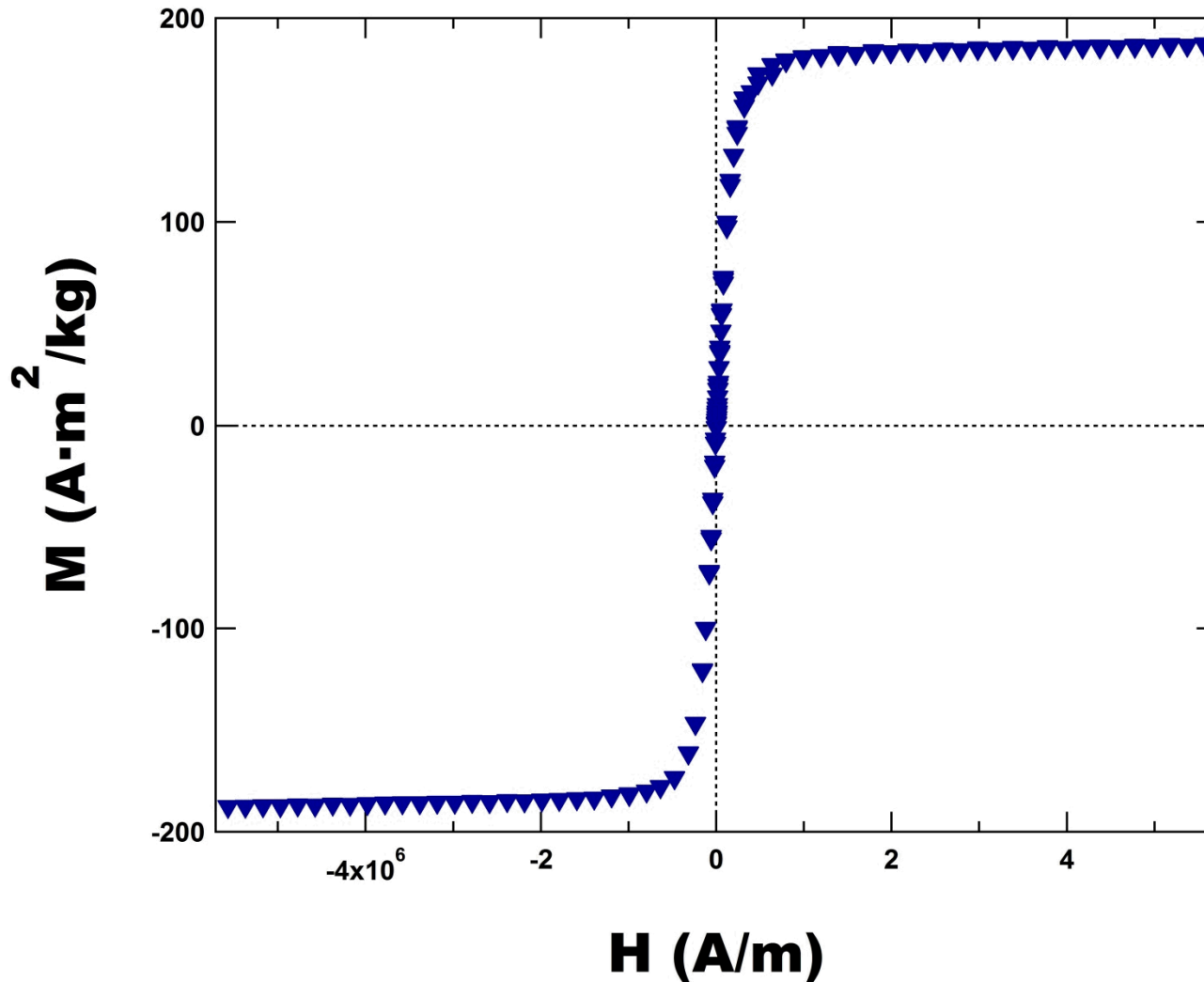
- Fe nitride powders well consolidated with little porosity
- Grain sizes 200 nm – 1 μm → fine grain size = low loss
- γ' -Fe₄N primary phase
- Fe₃N secondary phase from mixed phase starting material

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 in 2016

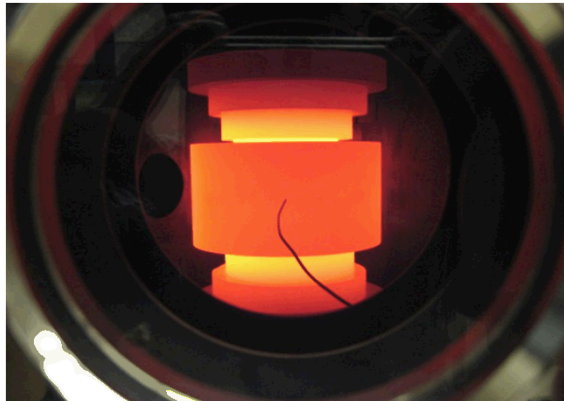
Magnetic Characterization



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

Conclusions

- γ' -Fe₄N has the potential to serve as a new low cost, high performance transformer core material
 - $M_{\text{sat}} > \text{Si steel}$
 - 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' -Fe₄N using SPS has been demonstrated
 - SPS can consolidate iron nitrides without material decomposition
 - Parts can be fabricated directly using net-shaping



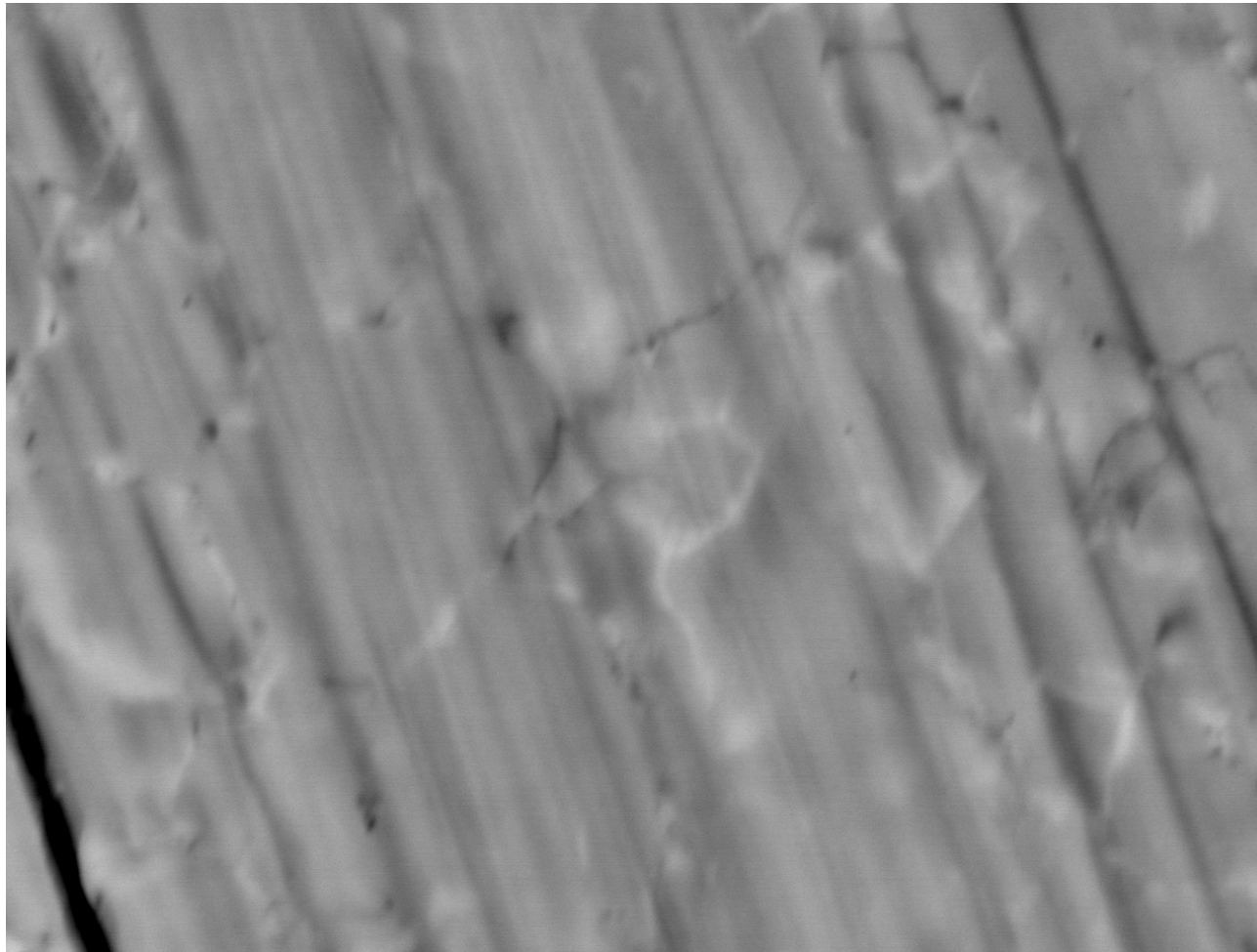
Acknowledgements

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

Toroid Surface SEM and EDS



- Small variation in composition between grain boundary and center
- Grain center stoichiometry $\approx \text{Fe}_4\text{N}$
- Grain boundary is ≈ 3 Atomic% richer in iron

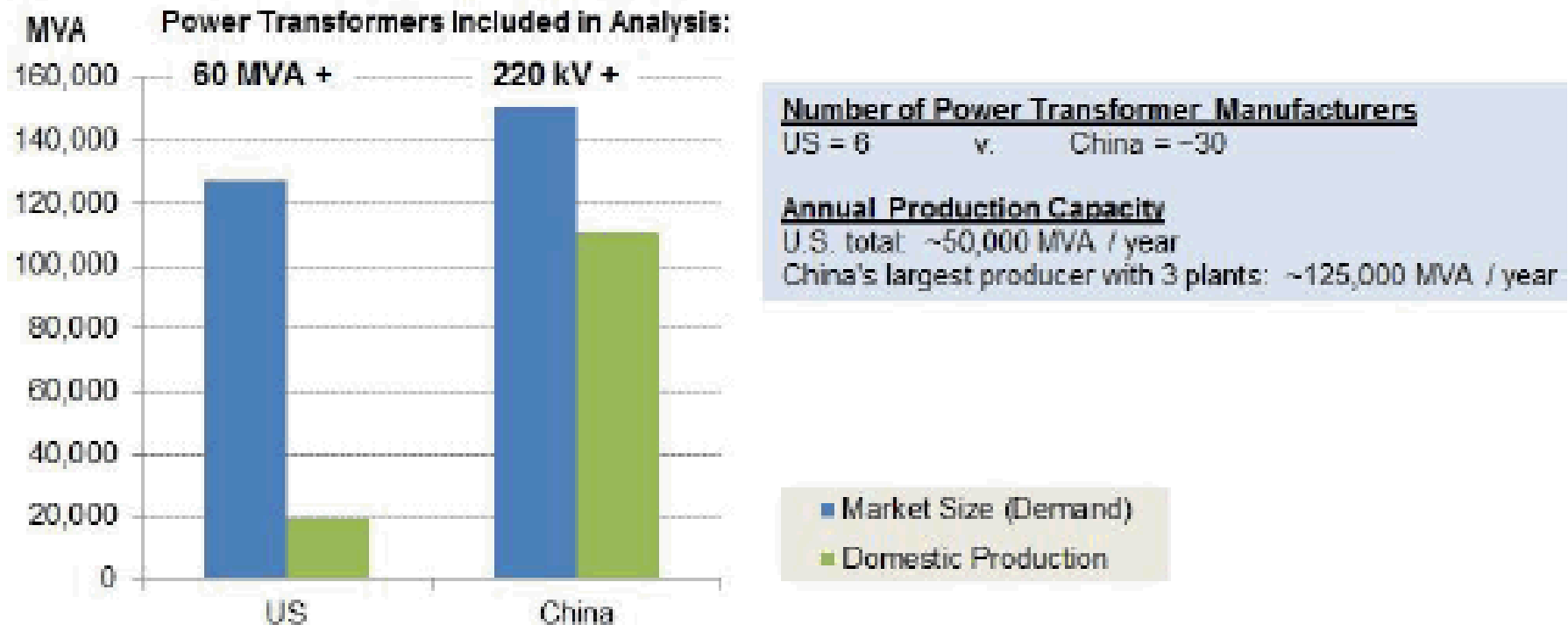
*SEM/EDS analysis completed by Dick Grant (SNL)

X 10,000 20.0kV COMPO 1μm JEOL 11/10/2014
WD 11.0mm 11:08:26

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

Power Transformer Market Analysis

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



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



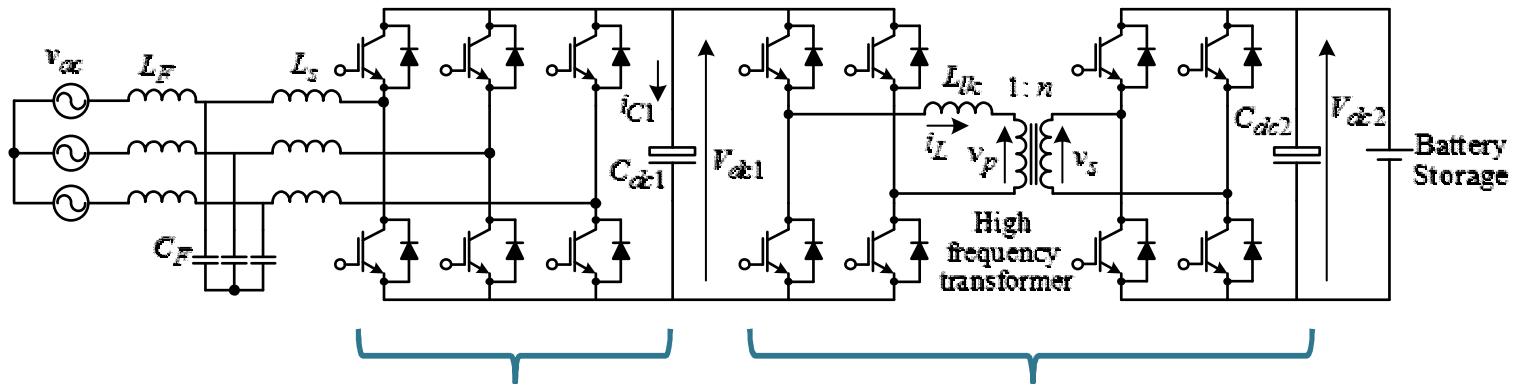
- **Geomagnetic storms couple very efficiently to long transmission lines**
- **Transformer can be driven to saturation, creating harmonics and reactive power**
- **Enough heat generated to melt copper windings**
- **Transformers the grid component that is hardest to replace**



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

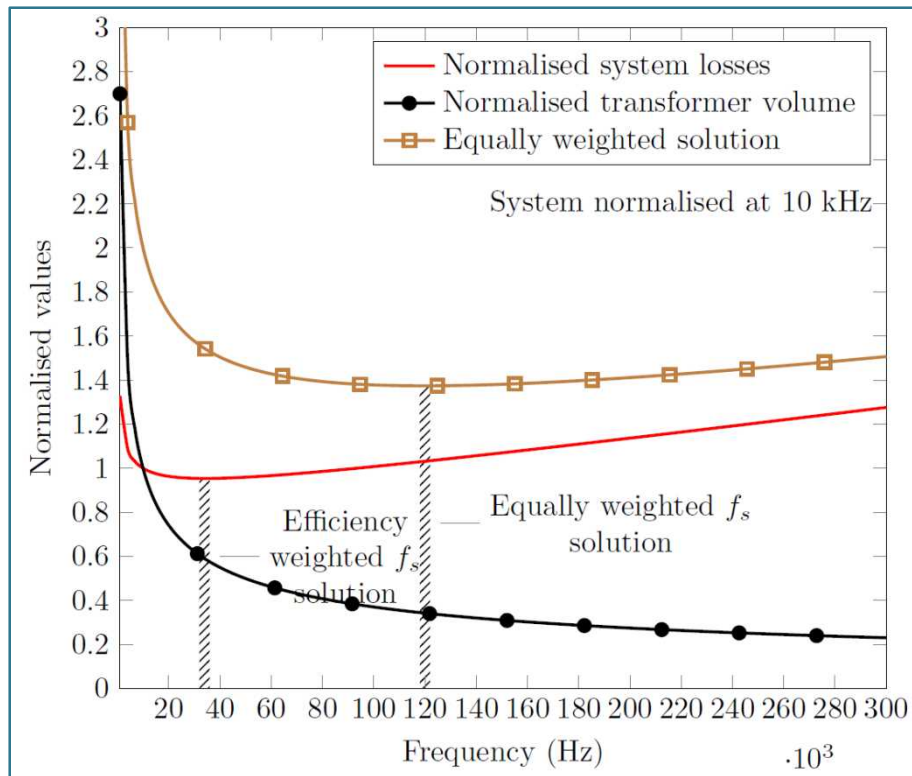
High Frequency Link Power Conversion System Configuration



- Optimal switching frequency based on the losses at this stage

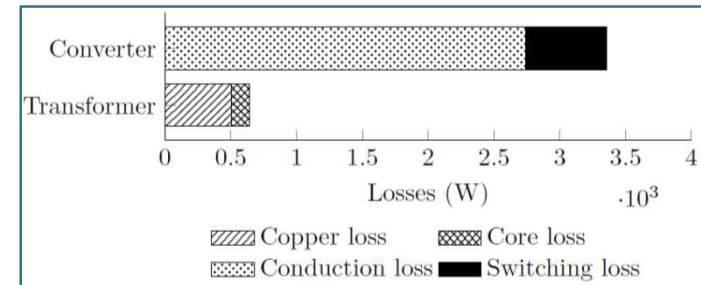
Volume occupied by heat sinks and non-magnetic components were not considered !!

- Optimal switching frequency based on:
- Switching and conduction losses in the switch
- Volume of the transformer
- Losses in the transformer
 - Copper losses in transformer windings
 - Core losses of the transformer



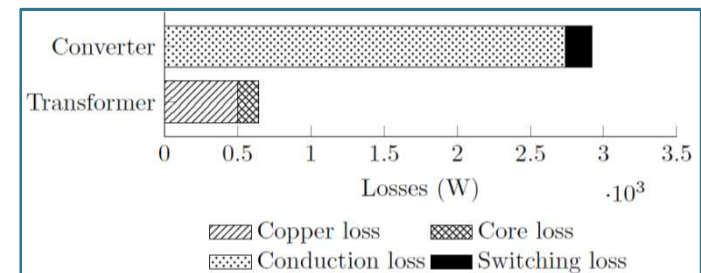
Equally weighted solution:

The converter has optimal solution at a frequency of **120 kHz** with equal weights on volume and losses



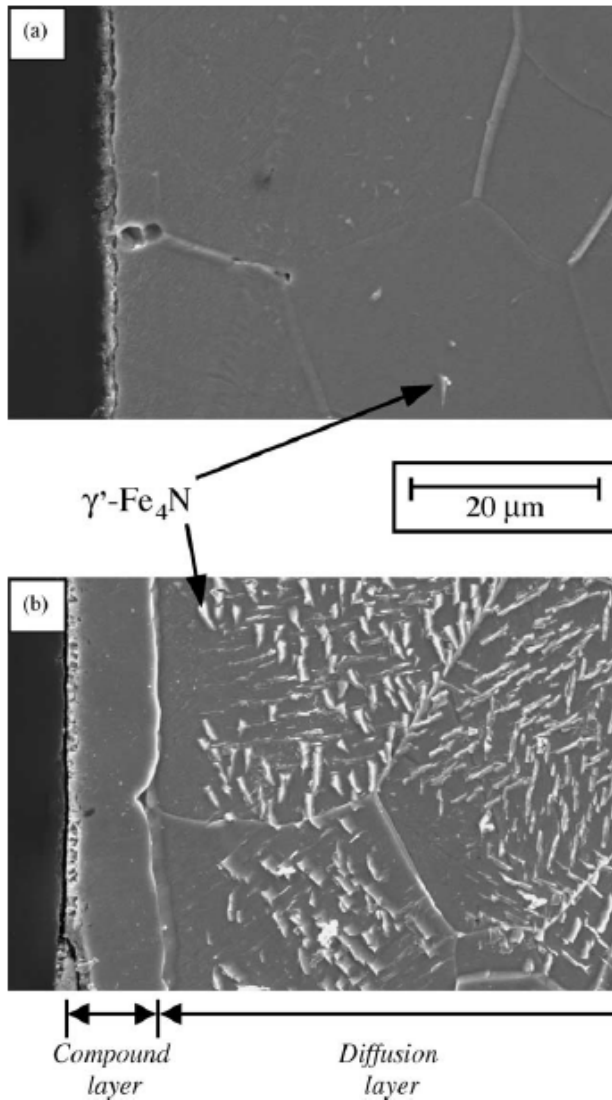
Efficiency driven solution:

The optimal solution for minimum loss condition is **35 kHz**



In House Synthesis of Raw Materials:

Electrochemical Nitriding of Iron



- Growth of γ' -Fe₄N demonstrated by Japanese electrochemists
- Formed γ' -Fe₄N at the surface of Fe(0) electrode using Li₃N as nitride source
- Demonstrates electrochemical synthesis of iron nitride possible
- Our goal is to demonstrate autonucleation of iron nitride with flowing N₂

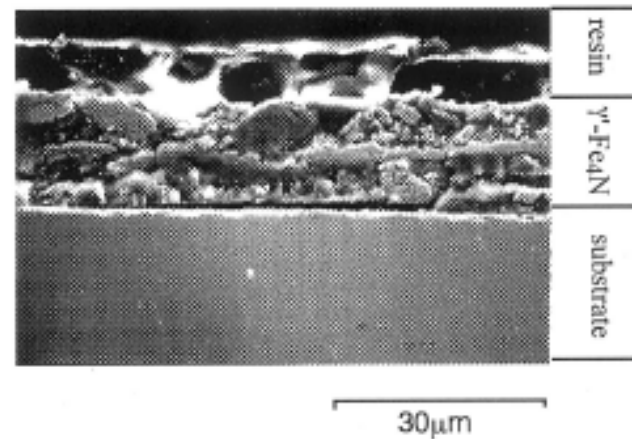
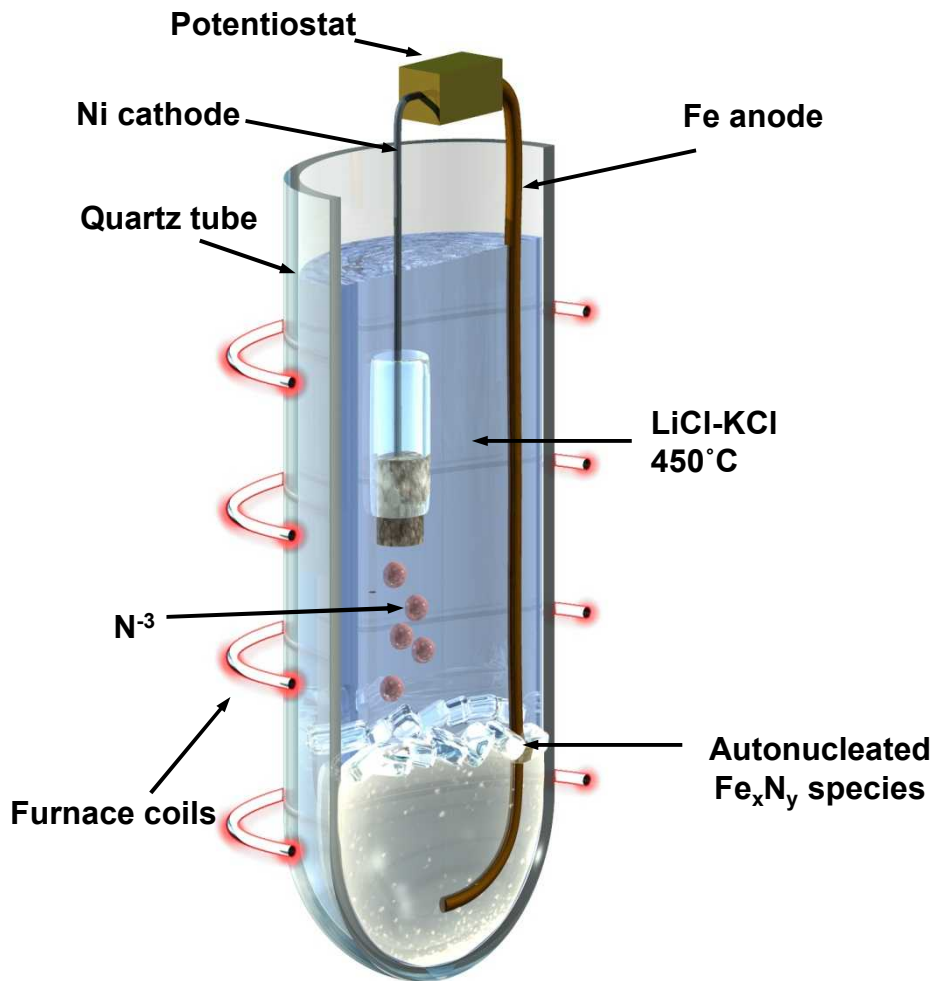


Fig. 10. Cross-sectional SEM image of iron electrode after potential pulse electrolysis for 1 h.

Electrochemical Solution Growth of Magnetic Nitrides



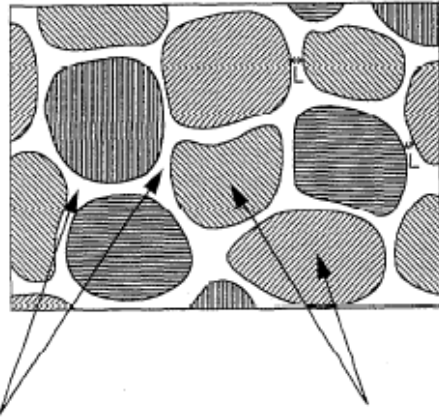
- **Not electroplating!!!!**
- Molten salt solution growth of GaN developed and patented at Sandia
- Create ionic precursors electrochemically
- Use salt transport to deliver precursors
- Increase growth rate through flux of reactants (increase currents, N₂ flow also has an effect)
- Can control oxidation state of transition metal
- Produces high quality material



Precursors can be replenished as they are consumed
Advantage: Continuous, isothermal or steady-state growth

U.S. Patent Filed November 2014

Nanocrystalline Alloy Materials & Manufacturing

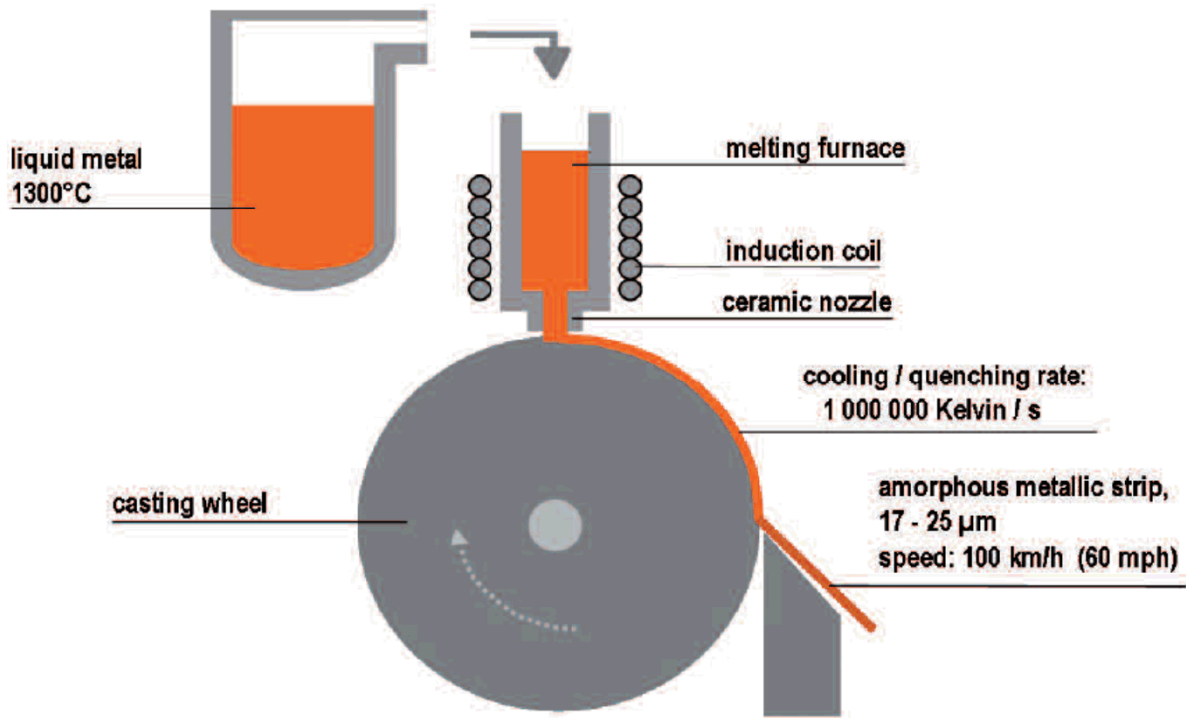


Intergranular amorphous phase with high T_c and high thermal stability due to large amounts of M and B elements.

Nano-scale α -Fe grains with small λ due to small amounts of M and B elements.

"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)

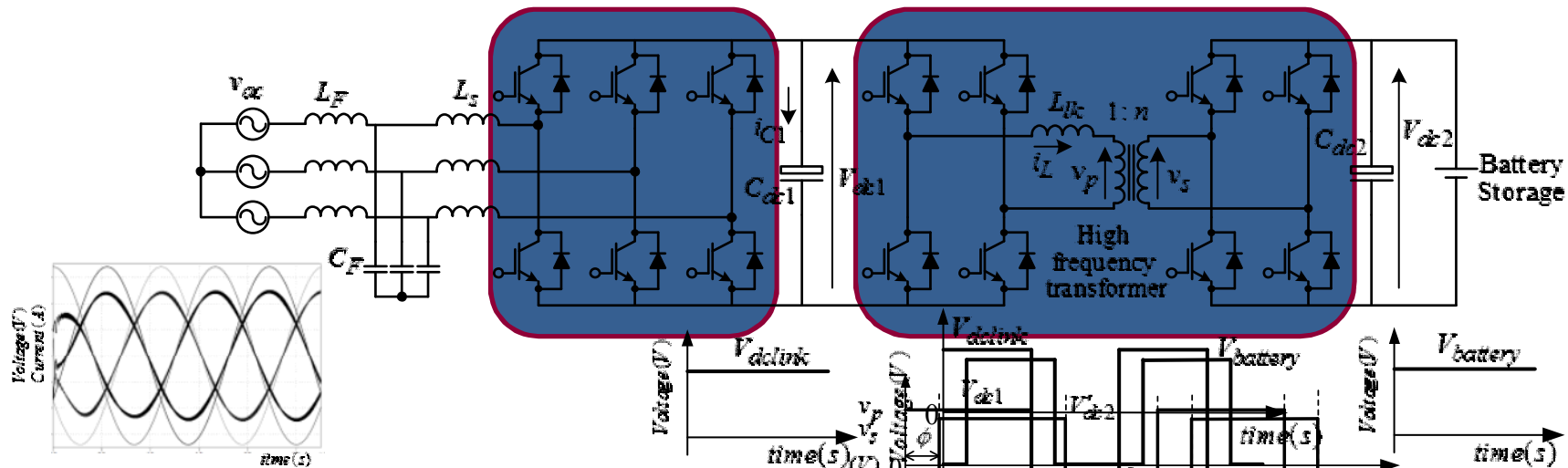
- Complex stoichiometries including Fe, Co, and other inactive elements such as B, Zr, Hf, Nb, Cu, Mo, Si, C
- Time consuming and high temperature processing → costly!
- Substantial inactive material to form a low loss nanocrystalline structure and limit eddy current loss
- Material produced in tapes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

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 ₄ N	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 ₄ N 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

System Configuration



Parameters

Power Level

Maximum RMS current

Maximum voltage

Transformer core material

Transformer turns ratio

Transformer leakage inductance

Snubber capacitance

DC Capacitor (Input/ Output)

Specifications

250 kW

370 A

1100 V \pm 10 %

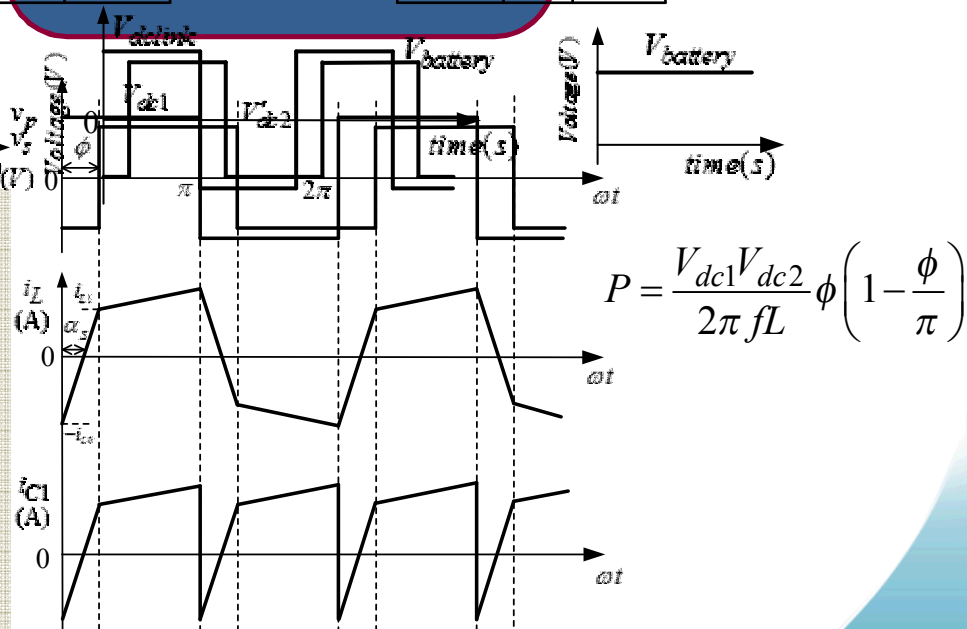
Ferrite

1:1

18 μ F

20 nF

4.4 mF



$$P = \frac{V_{dc1} V_{dc2}}{2\pi f L} \phi \left(1 - \frac{\phi}{\pi} \right)$$

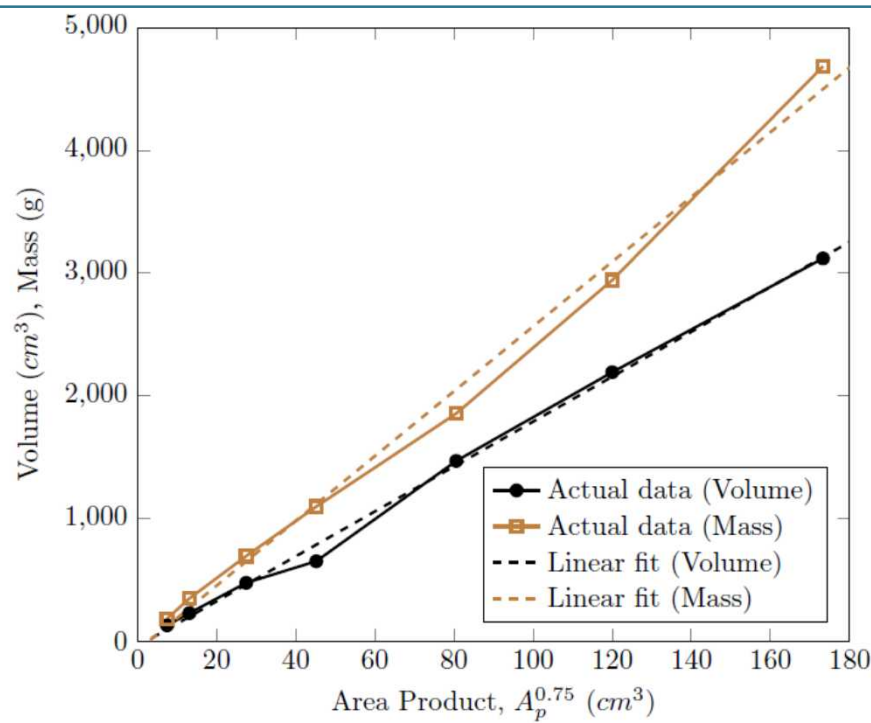
Loss and Volume Estimation

Transformer Volume Estimation:

Power handling capacity of the cores are identified by Area product, A_p (cm^4)

$$A_p = \frac{S}{k_w J_{max} \Delta B_{max} f}$$

Area Product vs Volume, Mass



A_c = Area of the core

A_w = Window area

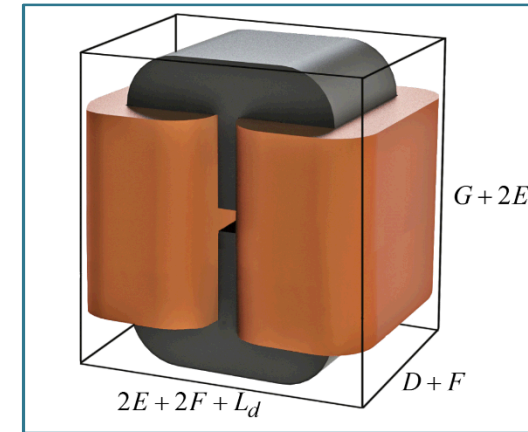
S = Total volt-amp rating of the transformer (VA)

k_w = window utilization factor

J_{max} = Current density (A/cm^2)

ΔB_{max} = flux density (T)

f = switching frequency (Hz)



$$\text{Volume} = K_v A_p^{0.75}; K_v = 18.302$$

$$\text{Mass} = K_p A_p^{0.75}; K_p = 26.41$$

$$\text{Volume} = \frac{8.328 \times 10^6}{\Delta B^{0.75} f^{0.75}} \text{cm}^3$$

Transformer Losses

Transformer copper loss:

$$P_{cu} = 2K_r \frac{N_{pri} \rho l}{A_{cond}} I_{rms}^2$$

$$N_{pri} = \frac{V_{pri}}{\Delta B_{max} A_c f}$$

$$P_{cu} = \frac{288475.68}{\Delta B^{0.75} f^{0.75}} W$$

Mean turns length :

$$l = 2 (E + D) + \pi F/2$$

where,

$$N_{pri} = \frac{1703.1}{\Delta B^{0.5} f^{0.5}}; R_{dc} = \frac{1.0536}{\Delta B^{0.75} f^{0.75}}$$

Transformer Iron loss:

$$P_{fe} = (k f_{eq}^{\alpha-1} \hat{B}^\beta) f$$

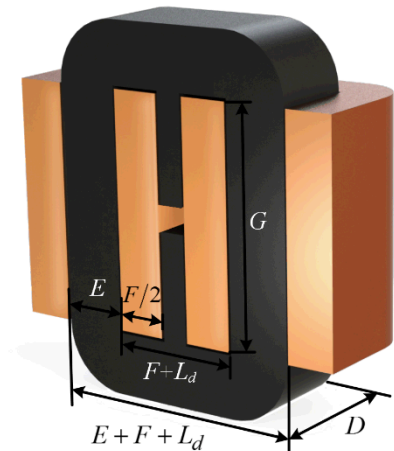


Modified Steinmetz equation

$$f_{eq} = \frac{2}{\Delta B^2 \pi^2} \int_0^T \left(\frac{dB}{dt} \right)^2 dt$$

The total iron losses in a 3C93 ferrite core is

$$P_{fe} = 4.77 f^{0.6} \Delta B^{2.45}$$



Optimal flux density

$$\begin{aligned} P_T &= P_{cu} + P_{fe} \\ &= \frac{288475.68}{\Delta B^{0.75} f^{0.75}} + 4.77 f^{0.6} \Delta B^{2.45} \end{aligned}$$

$$\frac{dP_T}{dB} (f = \text{const}) = 0$$

$$B_{opt} = \frac{21.557}{f^{0.425}}$$

Two applications of high frequency high power transformers (HFHPTs)

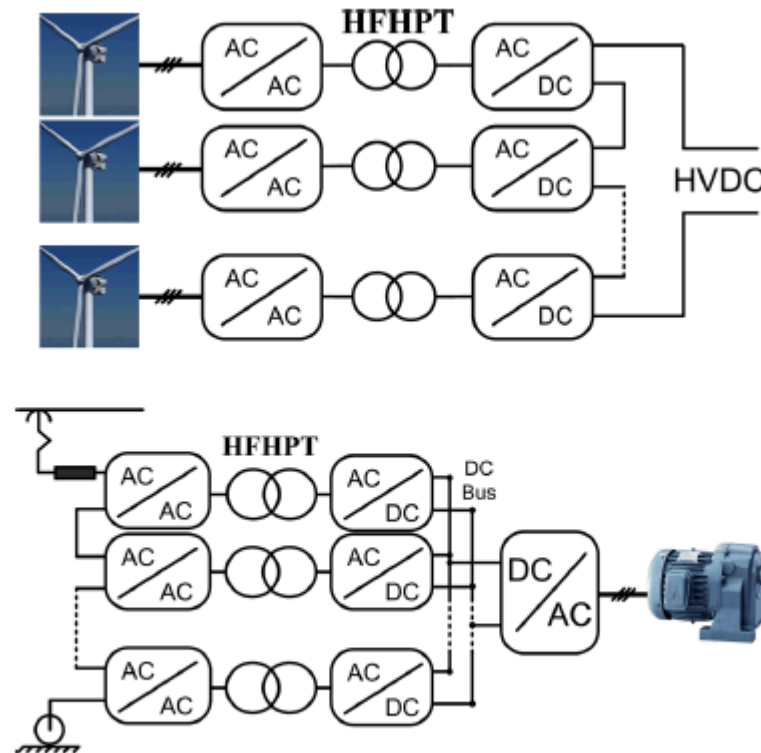


FIG. 1. Two main applications of high power converters with HFHPTs, (top) offshore wind farm and (bottom) traction converter.

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).

Grid-connected inverter with high-frequency DC link

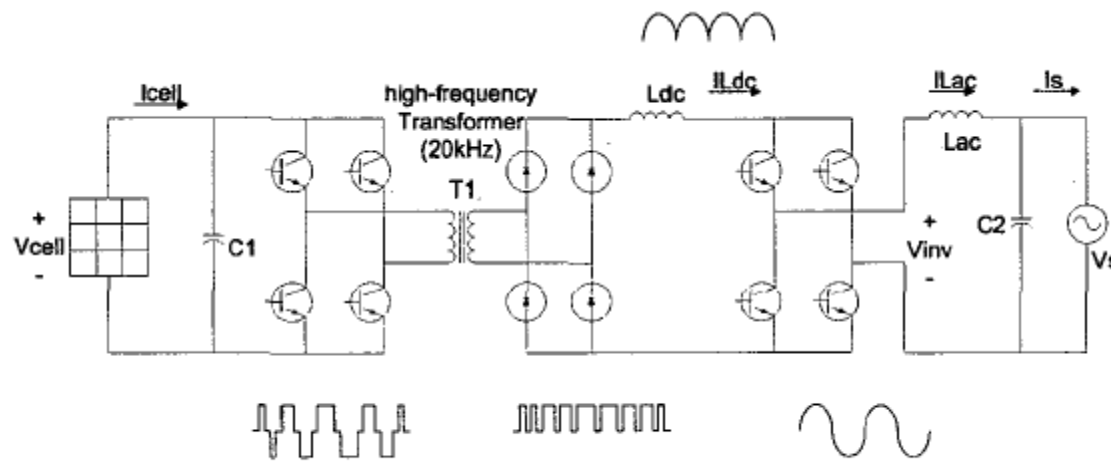


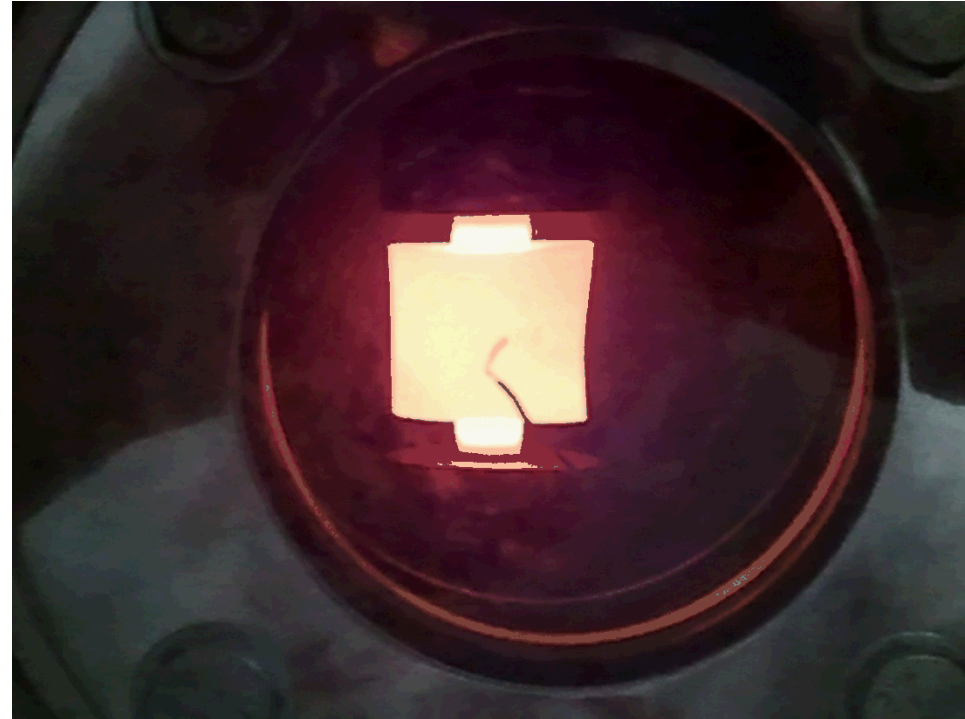
Fig. 1. Grid-connected inverter with high-frequency DC link.

Y. Jung, et. al., High-frequency DC link inverter for grid-connected photovoltaic system, IEEE, 1410 (2002).

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: $\Phi 80$ mm
- Offers the ability to fine tune grain size in sintered devices



SPS for Manufacturing Ceramics

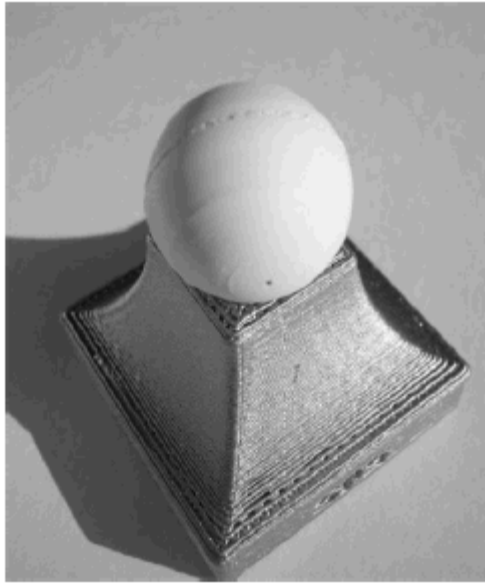


Fig. 9. Al₂O₃ sphere obtained in one single step by SPS!^{63]}

J. Galy, Private Communication, 2007.

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

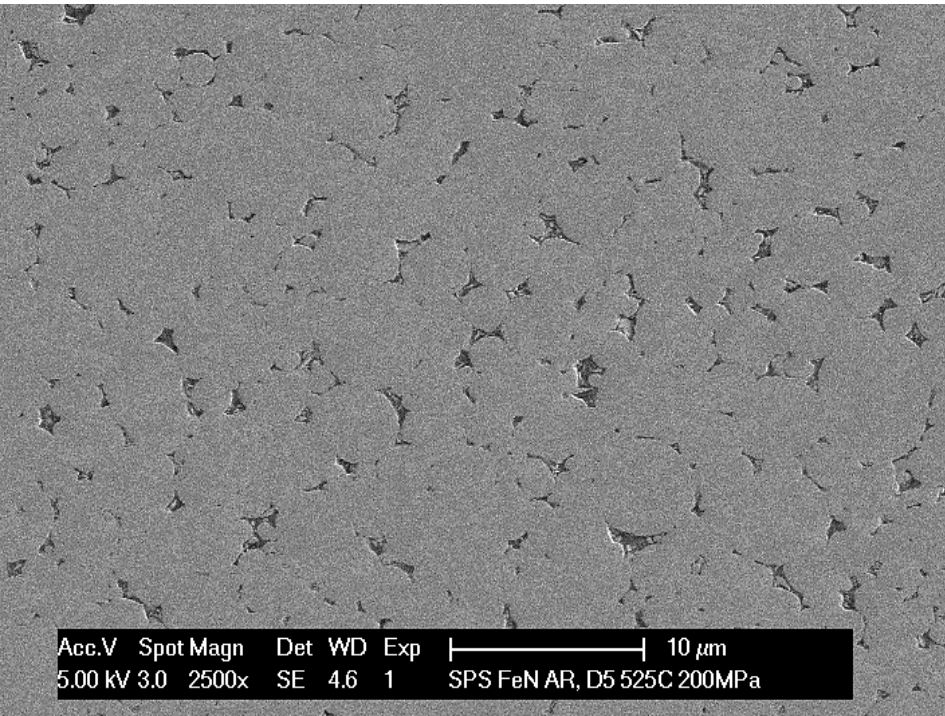
SPS System Manufacturers:

- 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)

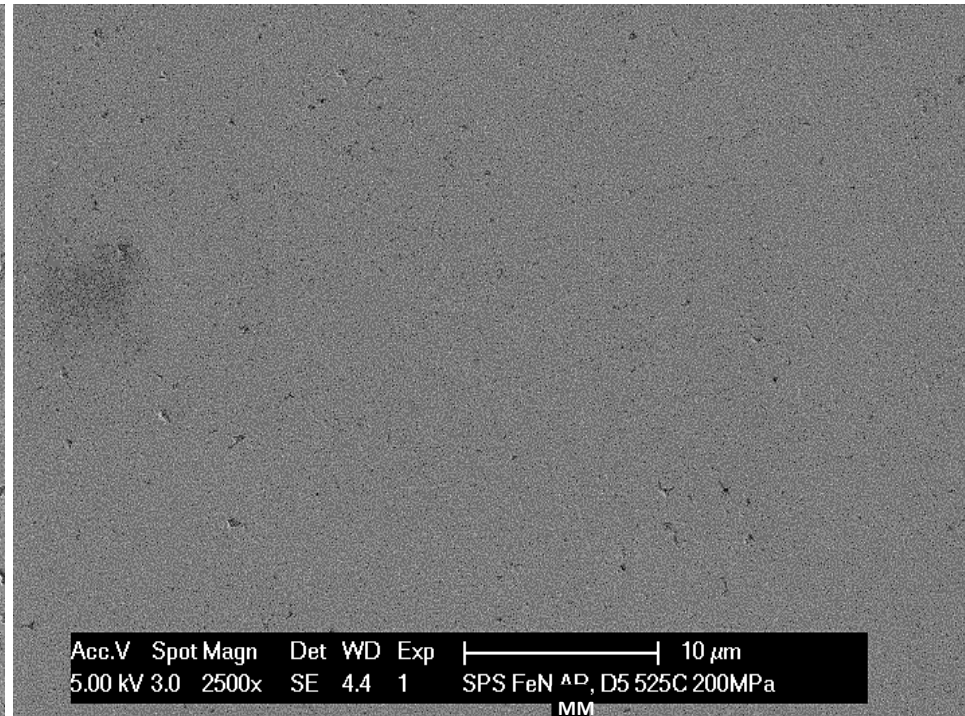
- **Size of equipment increasing to accommodate commercial needs**
- **Technology for continuous SPS under development**
- **A large number of companies have acquired SPS but often request this info to not be made public to maintain a competitive advantage**

SEM of SPSed FeN samples, (\emptyset 5mm, 525°C, 200MPa)

W/ as-received FeN powder

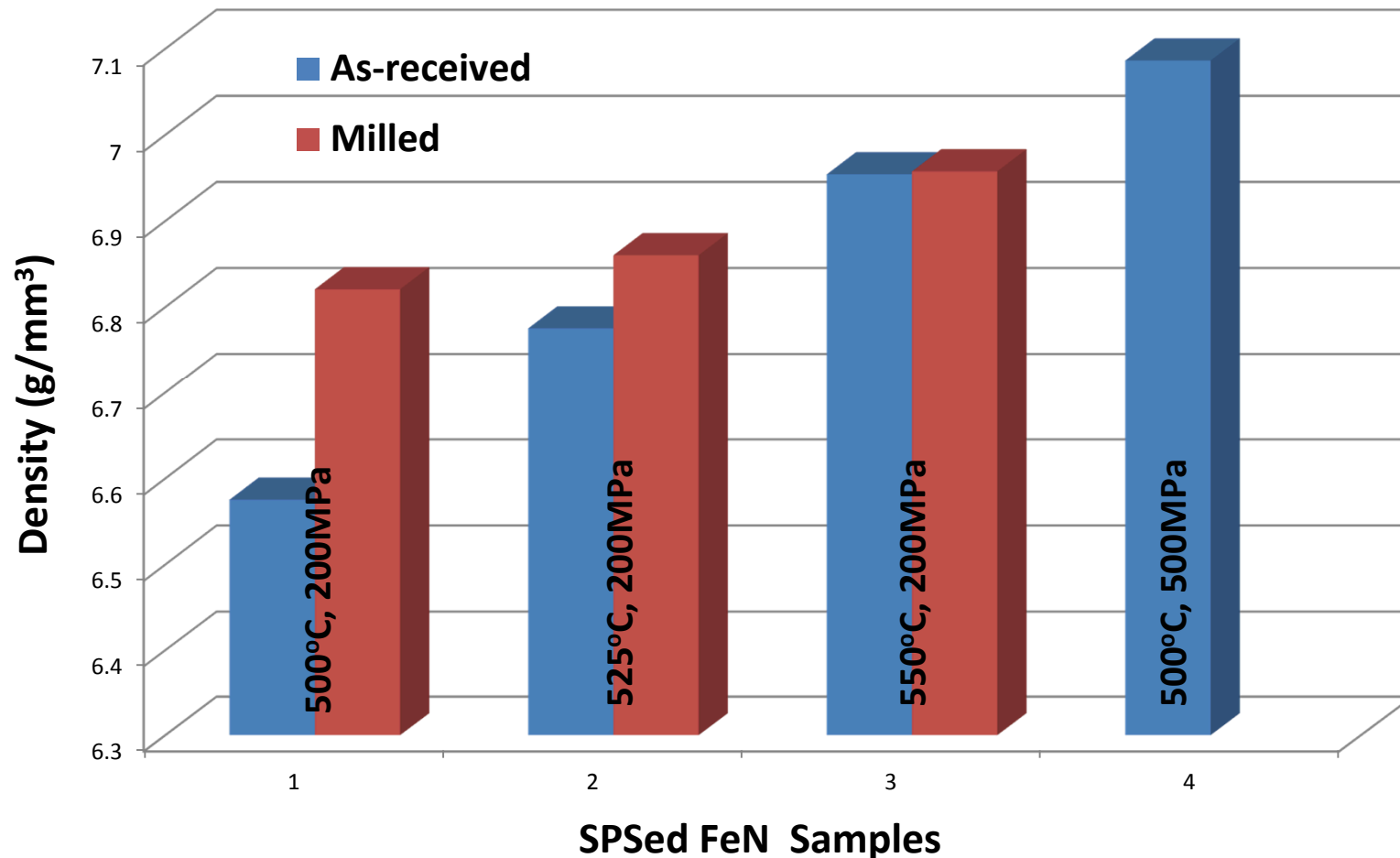


W/ milled FeN powder



- 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



- 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