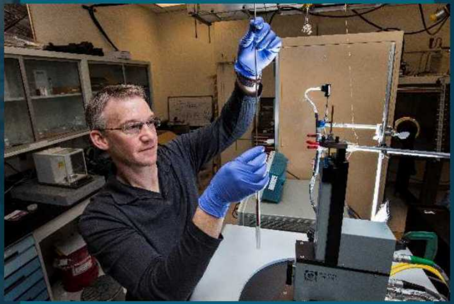
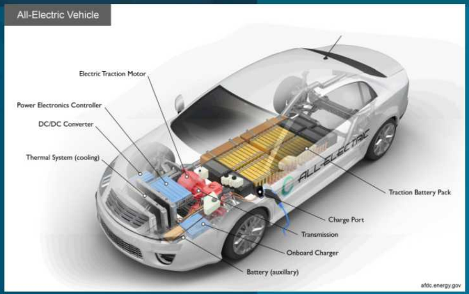
SAND2019-7239C

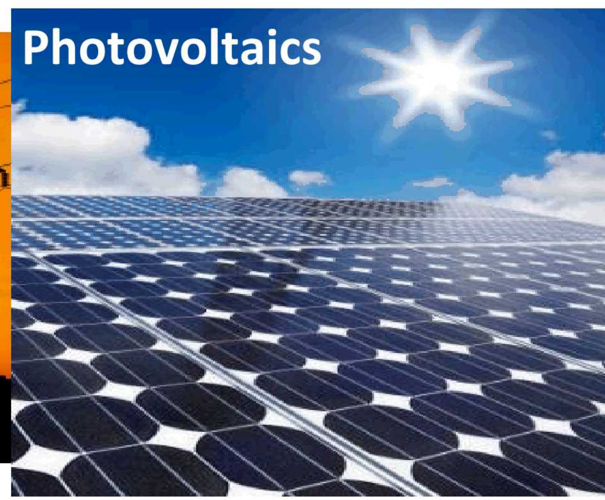
Next Generation Soft Magnetic Materials





Todd C. Monson, Tyler E. Stevens, Charles J. Pearce, Mark A. Rodriguez, Stanley Atcitty

Soft magnetic materials are ubiquitous

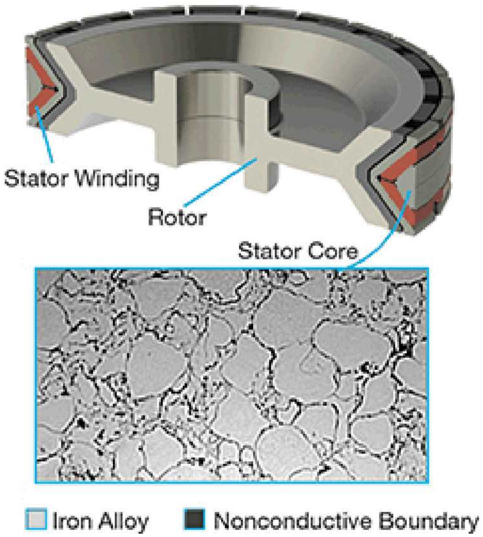


Courtesy of Bob Kaplar

Soft Magnetic Materials and Energy

Inductor cores

Transformer cores

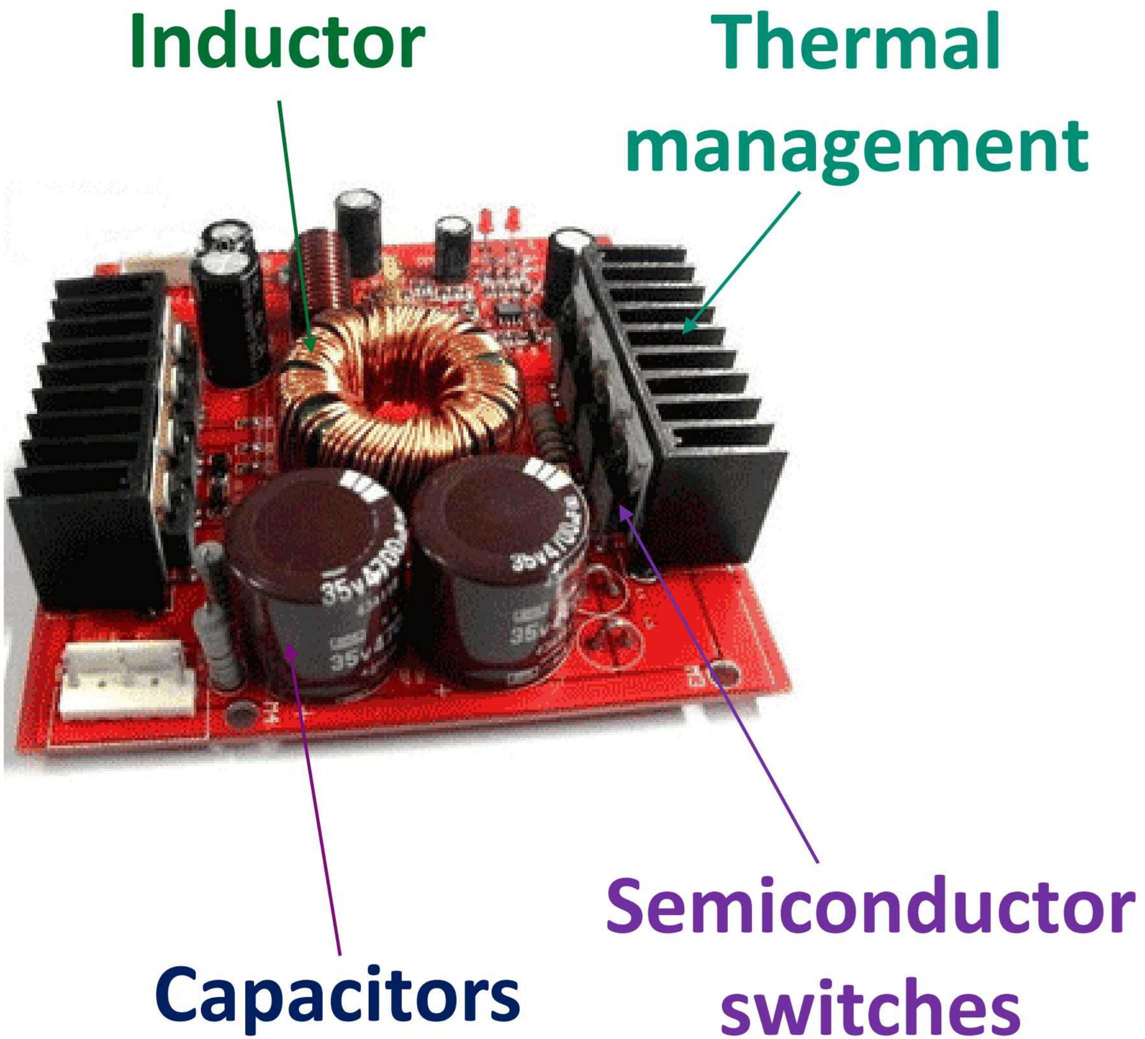


Electrical machines (motors & generators)

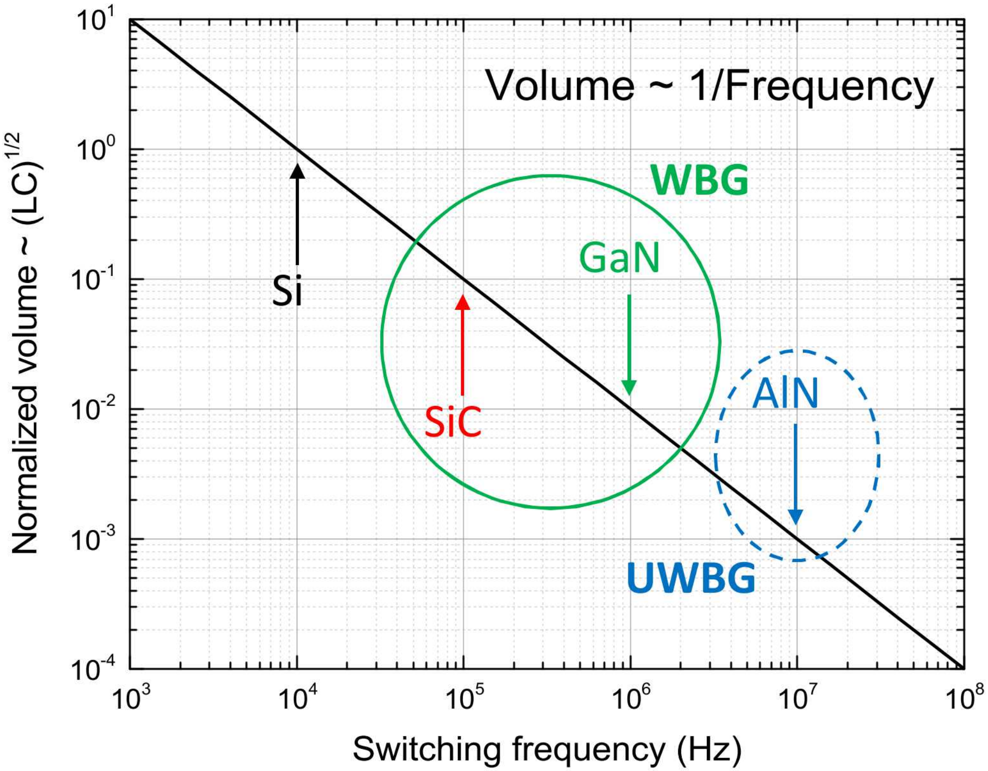
Magnetics Impact Power System Volume and Weight

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

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



Higher Frequencies Decrease Inductance Requirements, However…

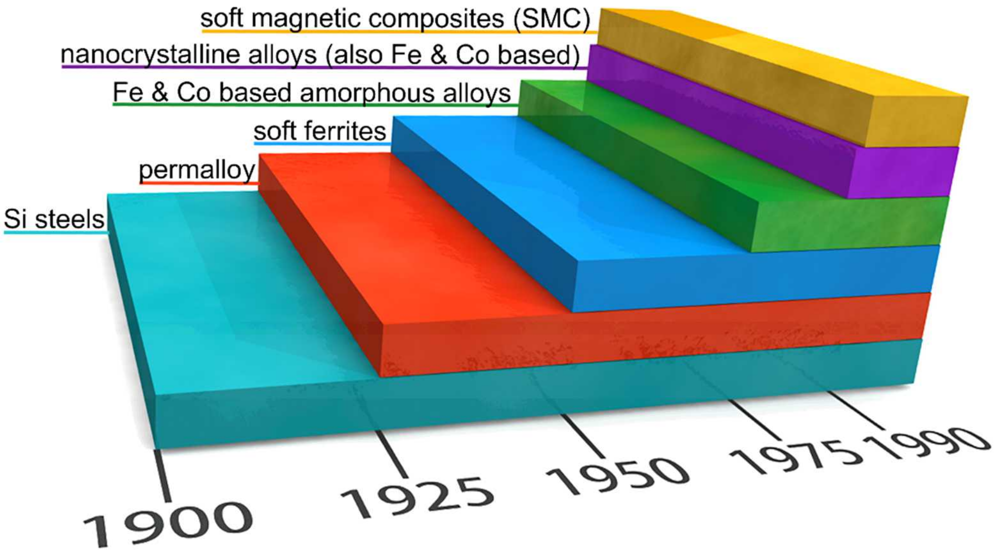


- **Higher switching frequency is enabled by scaling properties of WBG/UWBG materials**
- **Ideal 1/f SWaP dependence (true dependence likely weaker $1/f^n$ with $n < 1$ due to nonidealities)**
- **Other benefits of WBG/UWBG exist, e.g. higher voltage without series stacking of devices, and higher temperature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

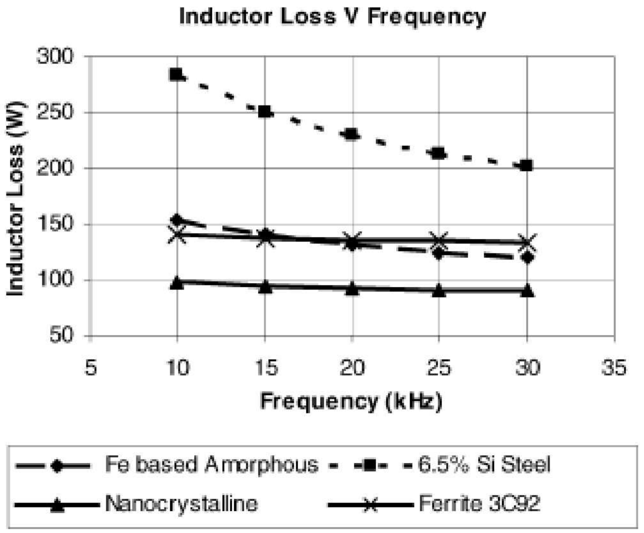
Inductive core materials have essentially been an afterthought and new magnetic materials are needed

Adapted from Bob Kaplar

Soft magnetic material development



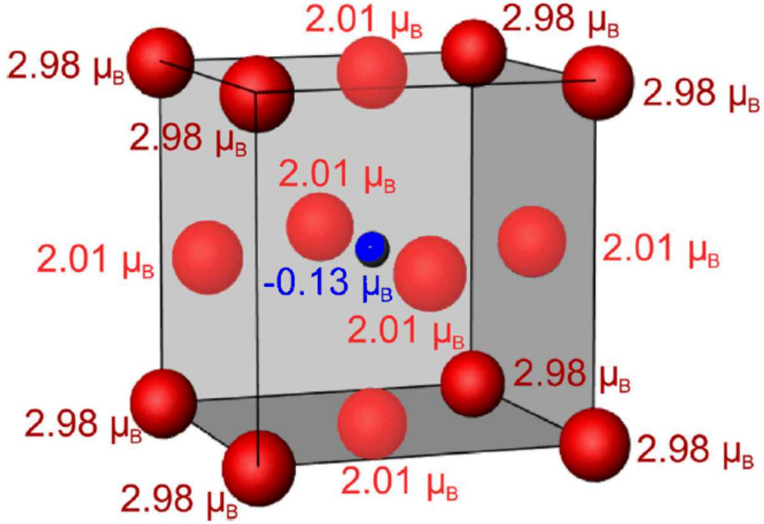
Adapted from: L.A. Dobrzański, M. Drak, B. Ziębowicz, Materials with specific magnetic properties, Journal of Achievements in Materials and Manufacturing Eng., 17, 37 (2006).

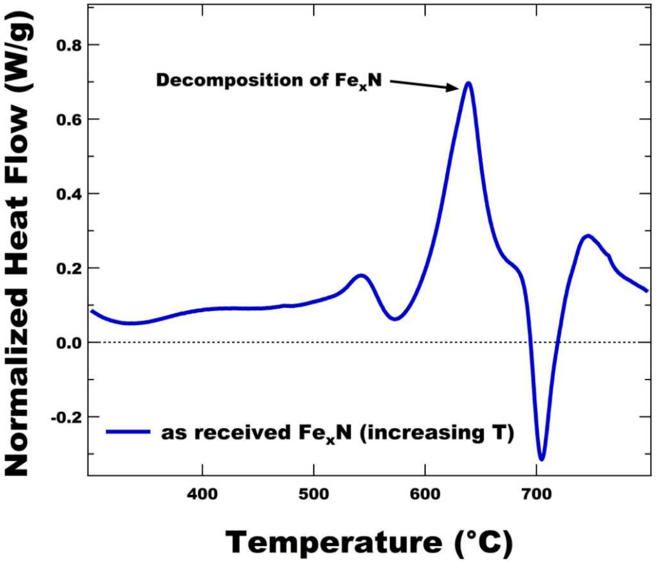


B.J. Lyons, J.G. Hayes, M.G. Egan, Magnetic Material Comparisons for High-Current Inductors in Low-Medium Frequency DC-DC Converters, IEEE, 71 (2007).

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 (Ferroxcube)	0.52	$5x10^6$	Low
Si steel	1.87	0.05	Low
CoFeV (Supermendur)	2.40	0.08	Med
γ'-Fe_4N	1.89	> 200	Low
CoFeP	~2.30	> 100	Med

γ′-Fe_4N



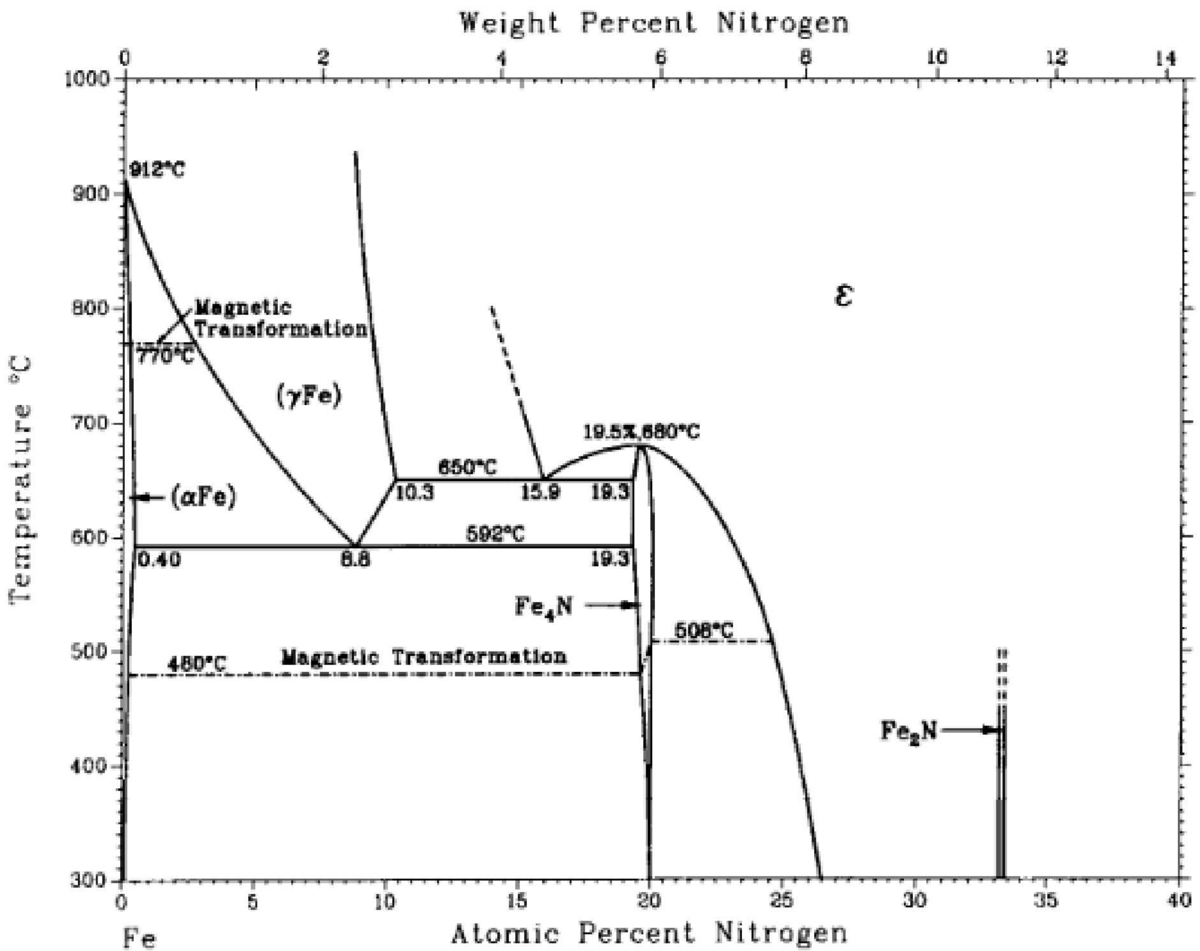


fcc γFe structure stabilized by interstitial nitrogen in the body center

Relatively low thermal decomposition limits consolidation & fabrication methods

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).

Iron nitride phase diagram



H.A. Wriedt, N.A. Gokcen, and R.H. Nafziger, 1987.

Commercial synthesis yields mixture of Fe_3N and Fe_4N

Previous Syntheses of γ'-Fe_4N

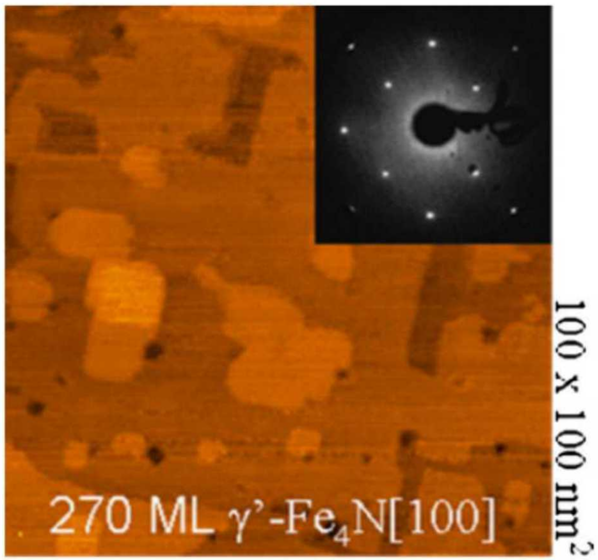
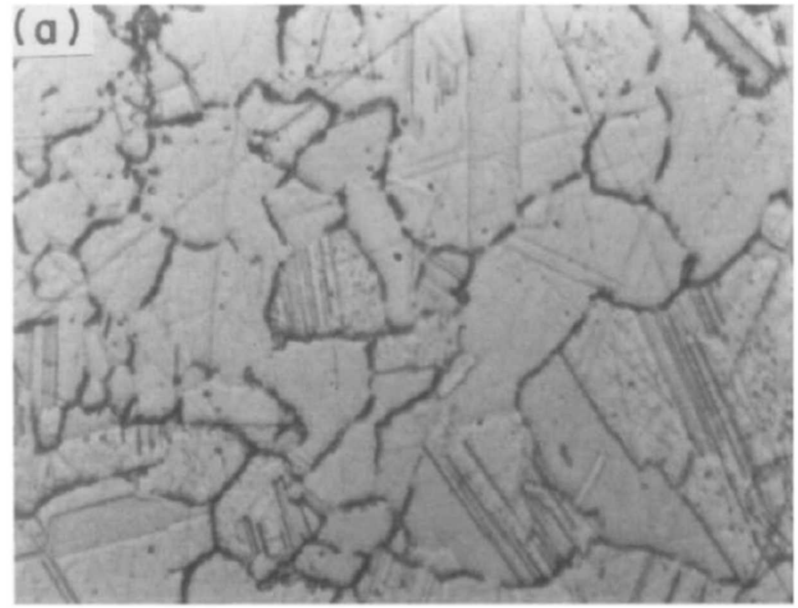


Fig. 1. STM image of a 270 monolayers (ML) thick γ'-Fe_4N film grown on Cu(1 0 0). The inset shows the corresponding LEED pattern (110 eV).

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

Up to 50 nm thick



S.K. Chen, et. al., "Synthesis and magnetic properties of Fe_4N and (Fe, Ni)$_4$N sheets", J. Magn. Mag. Mat., 110, 65 (1991).

25 μm foils

γ’-Fe_4N synthesis and processing

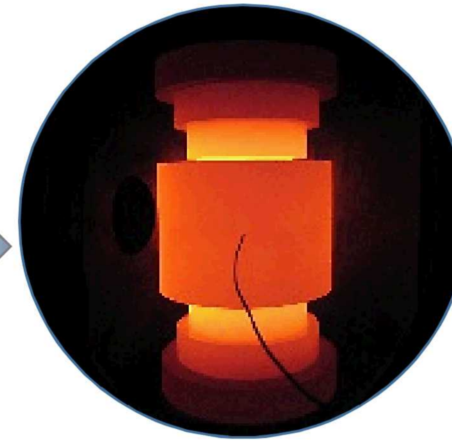
U.S. Patent # 9,963,344

Atomization of powder

Cryomilling
Severe Plastic deformation

Fluidized Bed Furnace

SPS Consolidation

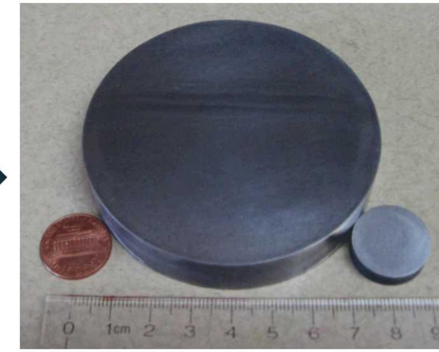


Spark Plasma Sintering
Fast sintering

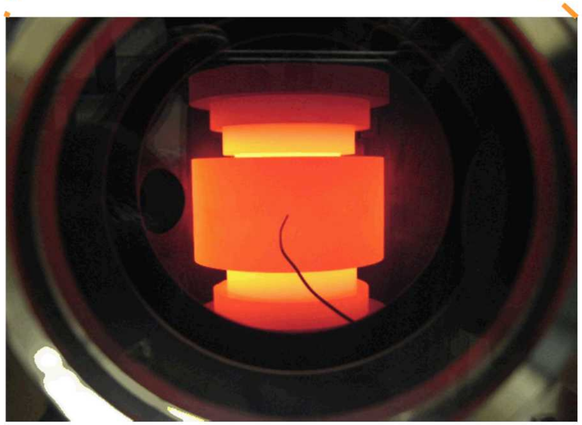
- **Pressure and pulsed current assisted sintering process**
- **Precision control over heat, pressure, and time**
- **Restrain grain growth**
- **Full densification**

Spark plasma sintering (SPS)

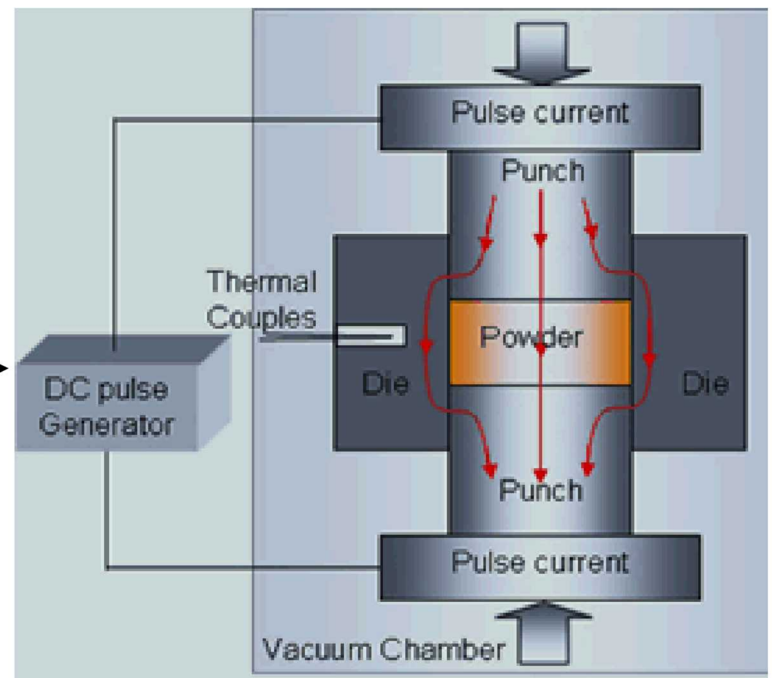
Starting Powder in Die



End Product

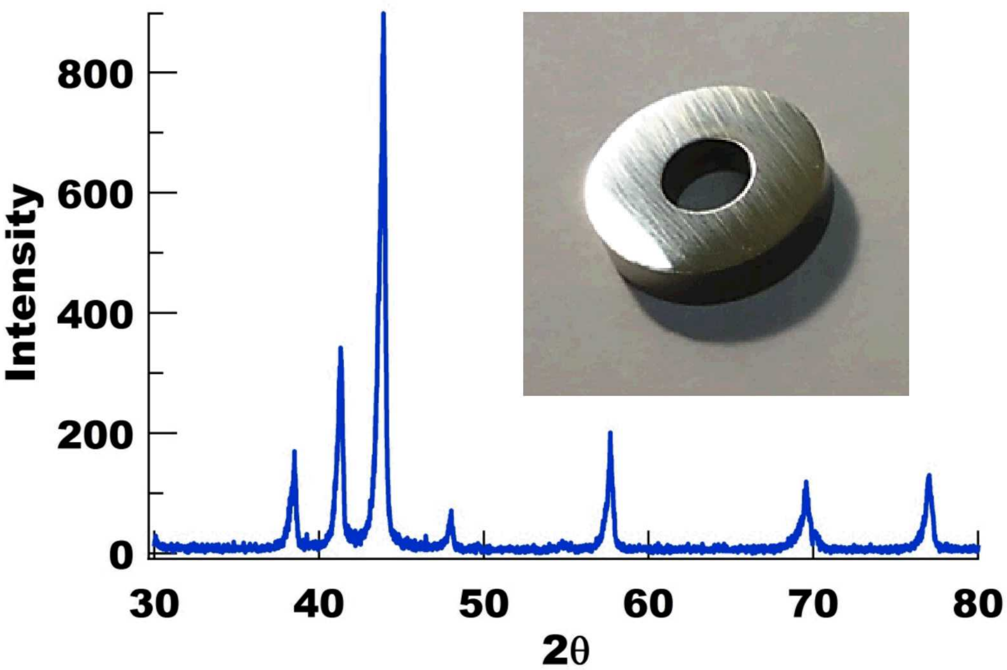


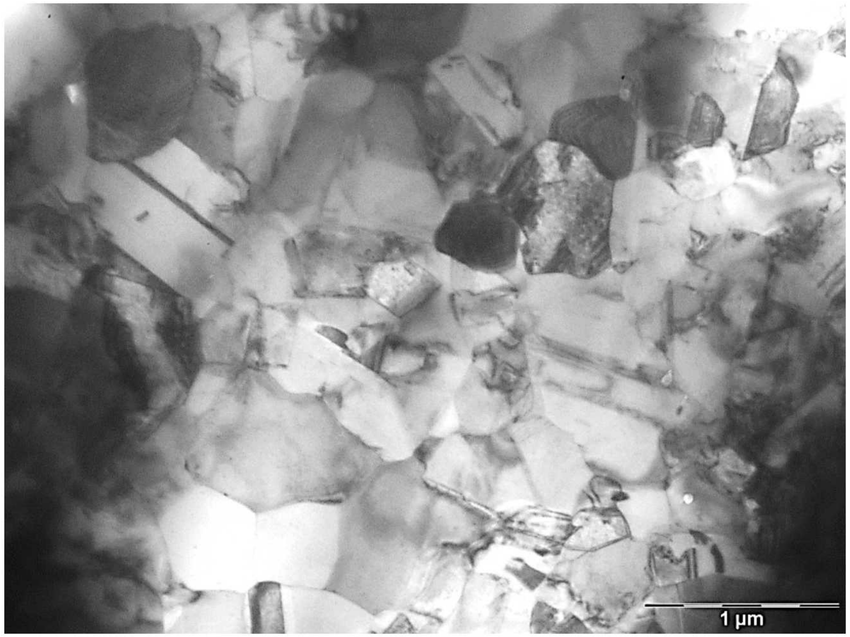
SPS
Chamber



SPS consolidated iron nitride

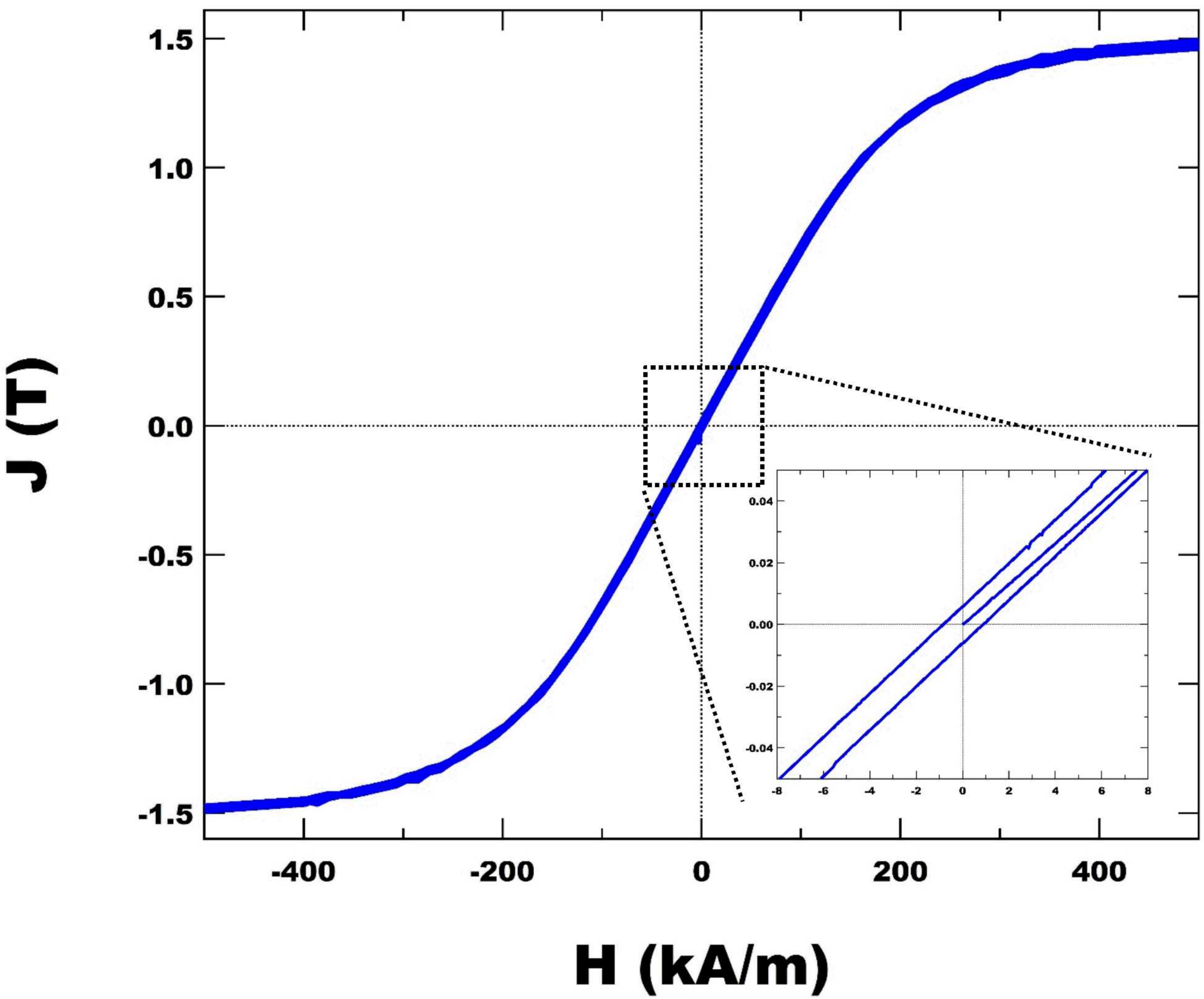
First ever bulk γ'-Fe_4N!





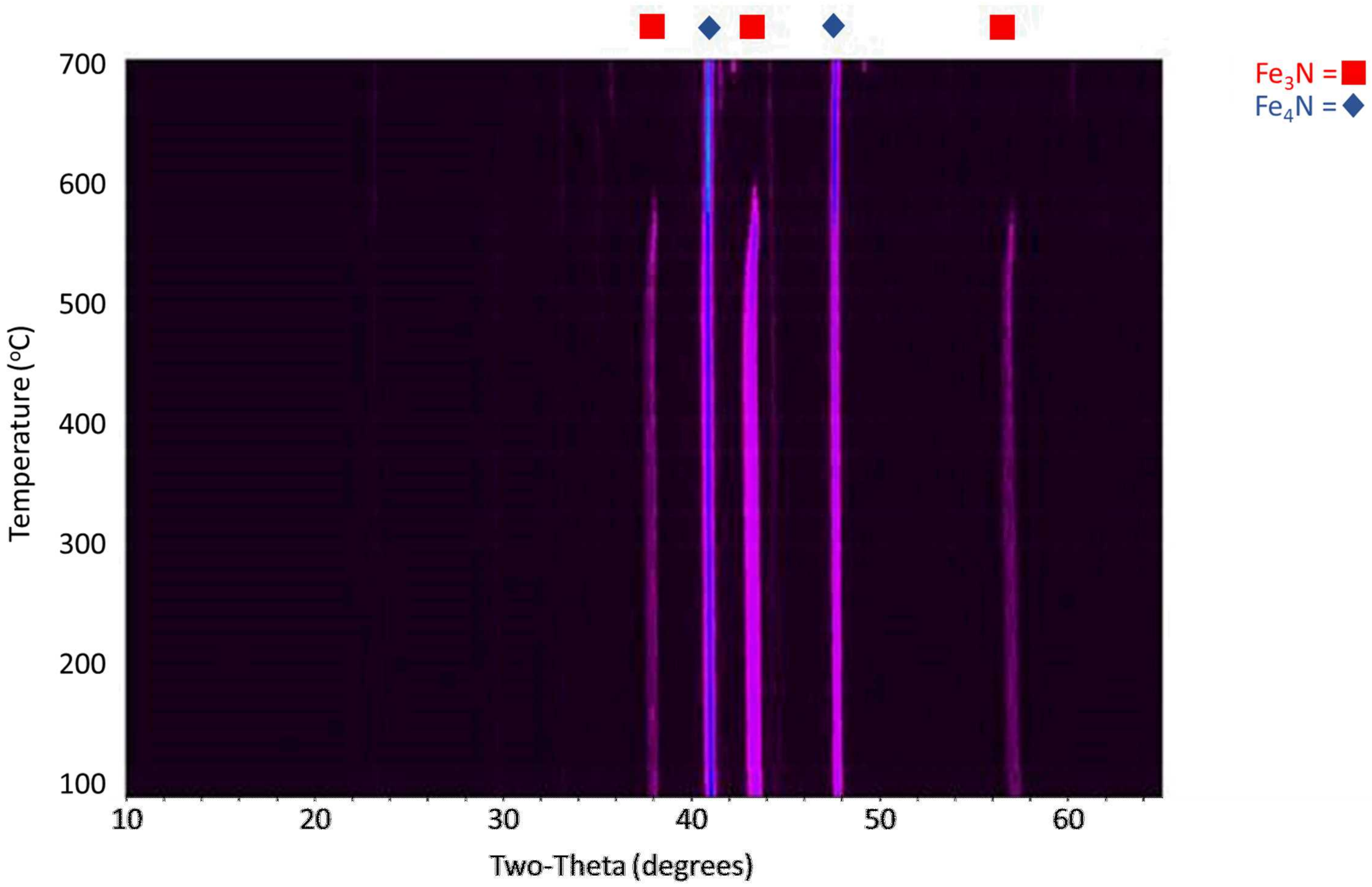
- **Fe nitride powders well consolidated with little porosity**
- **Grain sizes 200 nm – 1 µm → fine grain size = low loss**
- **γ'-Fe_4N primary phase**
- **Fe_3N secondary phase from mixed phase starting material**

Magnetic characterization



- SPSed at 550°C and 100 MPa
- J_s = 1.62 T
- Theoretical J_s = 1.89 T (SiFe is 1.87 T)
- H_c < 1000 A/m

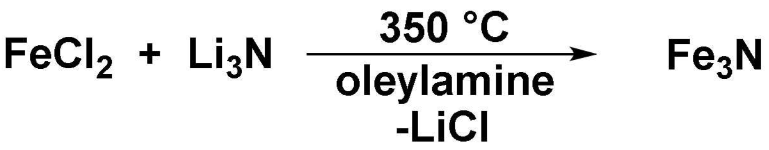
Production of phase pure γ'-Fe_4N powder

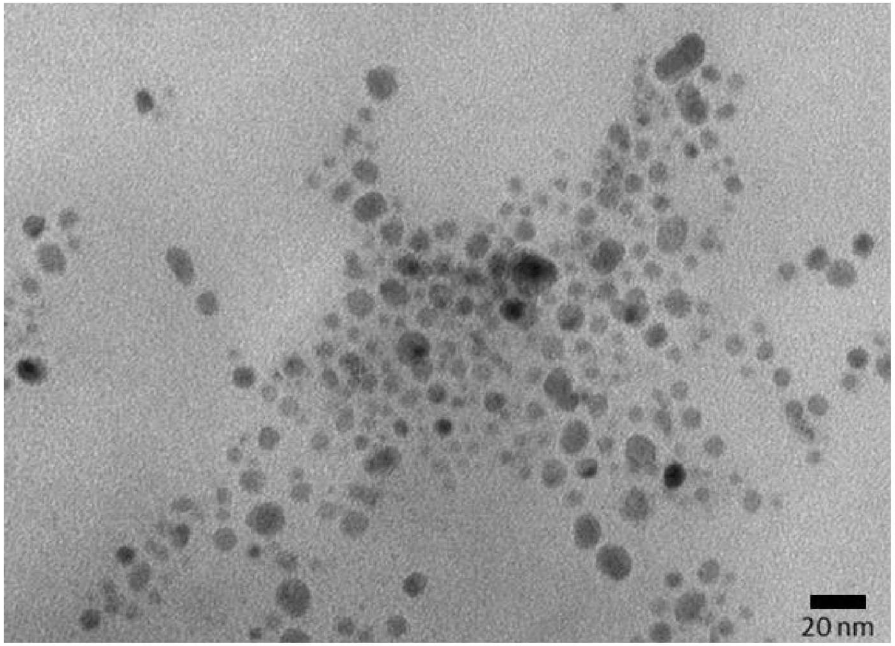


- Simple heat treatment converts mixed phase commercial powder
- Only phase pure γ'-Fe_4N remains

An example of other routes to iron nitrides

Reaction of $FeCl_2$ with Li_3N results in Fe_3N



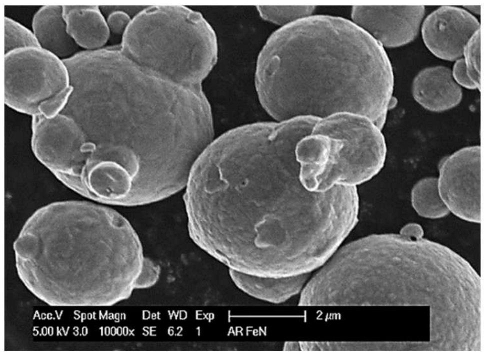


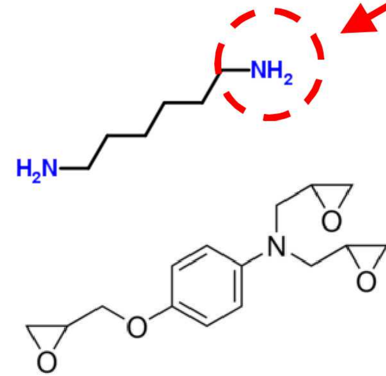
- 0.124 M $FeCl_2$ oleylamine
- Injected at 80 µL/min
- 4 hour reaction time
- Improvements to size distribution possible

Iron Nitride/Epoxy Composites

Diamines will bond directly to Fe_4N surface and epoxy matrix for enhanced mechanical robustness and particle electrical isolation

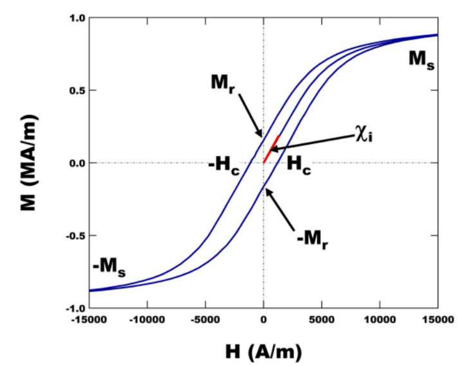
Convert commercial Fe_xN powder to phase pure Fe_4N





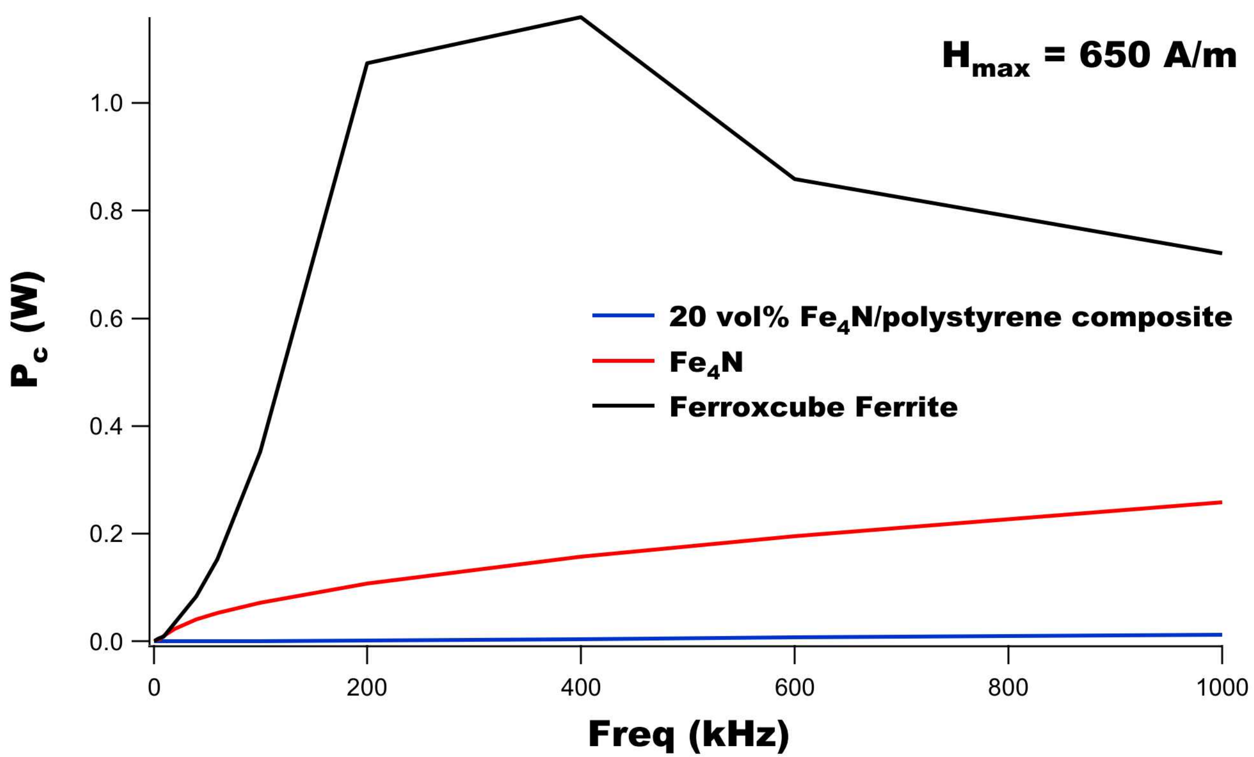
Coat Fe_4N and mix with epoxy monomers

- Pour into 3D printed mold and cure into stator/rotor part
- Press if necessary to increase density and loading factor
- Results in a net-shaped part (no machining required)



Evaluate and test

Preliminary γ'-Fe_4N composite results



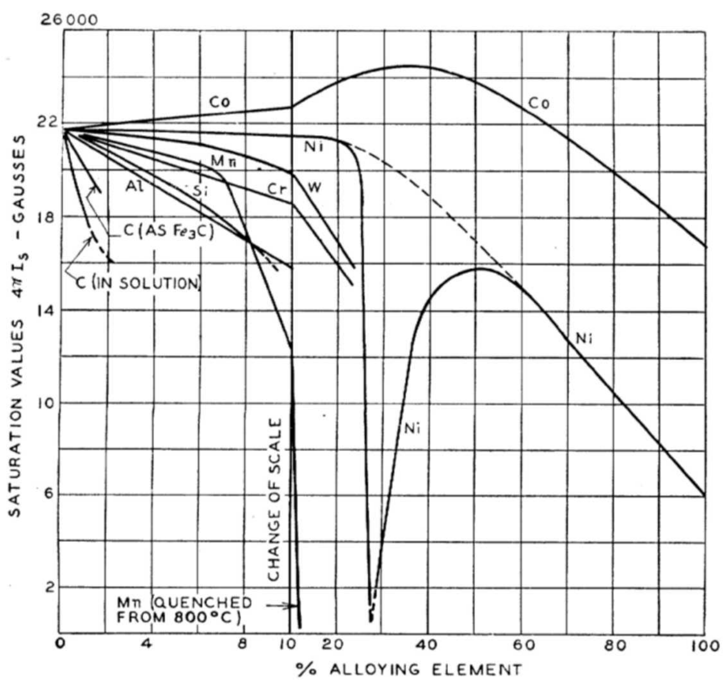
- Significantly lower core losses in Fe_4N composites when compared to both bulk Fe_4N and COTS ferrites
- Much higher volume loadings of Fe_4N still possible
- Transitioning to epoxy matrix will exceed temperature and mechanical strength requirements

CoFeP synthesis

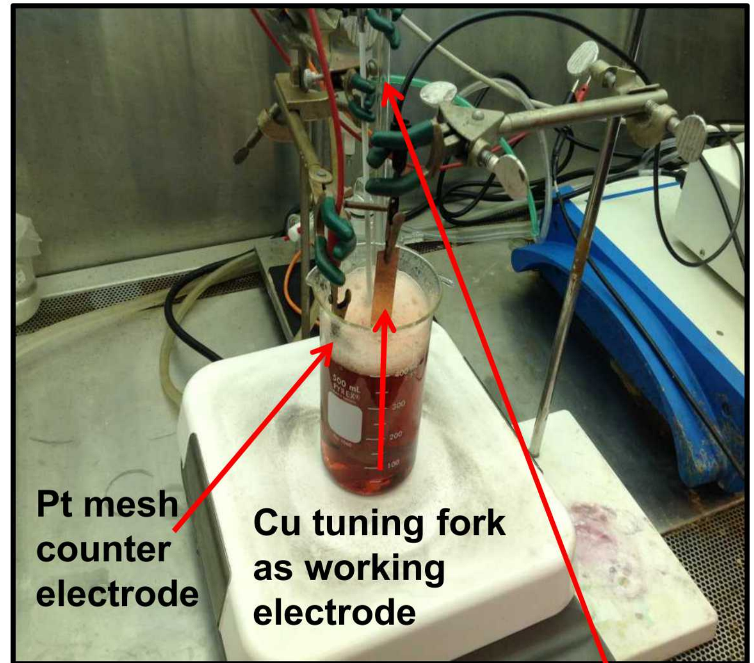
Jamin Pillars (SNL), Eric Langlois (SNL)

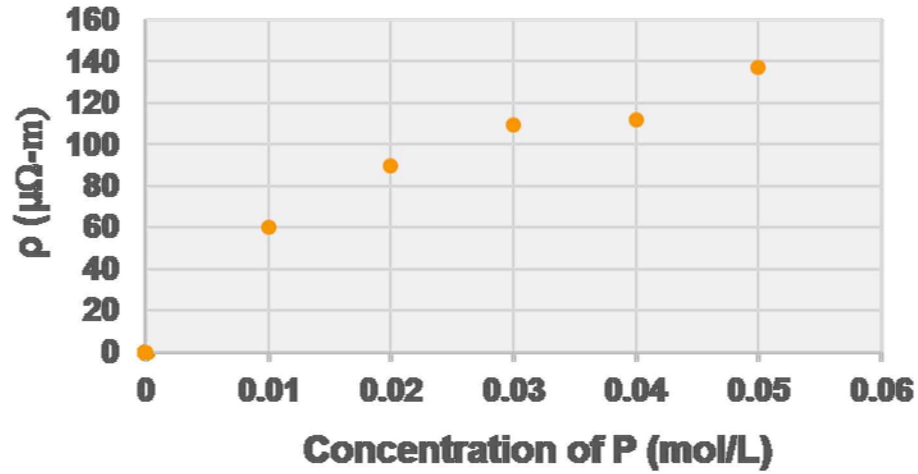
Figure 1. Effect of elements on the saturation values of iron

STANLEY is also with the
Corporation, East Pittsbur
* I_s = saturation intensity c



J.K. Stanley, T.D. Yensen, "Hiperco—A Magnetic Alloy," AIEE Transactions, 66, (1947).





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
- Additional support: DOE/VTO, SNL LDRD
- We thank Robert Delaney (Univ. of NM) for his assistance with magnetic data analysis

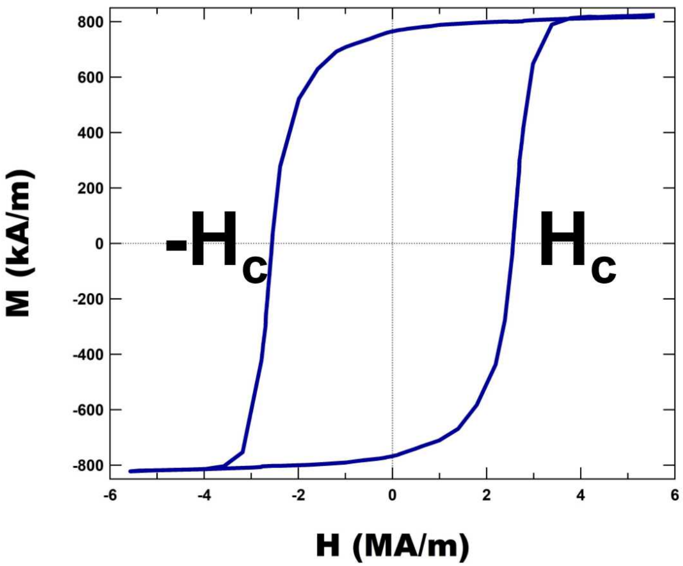
Iron nitride offers superior magnetic properties

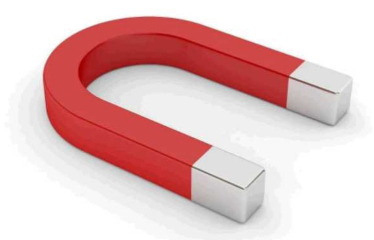
Material	σ_s (Am^2/kg)
α-Fe	218
Magnetite	80 - 103
FeN	209
Fe_2N	~70
Fe_3N	144
Fe_4N	209

- Iron nitrides offer superior magnetic properties comparted to oxides
  - Numerous applications could benefit a straight forward route to synthesis these materials, particularly in phase pure form
- Iron nitrides are metastable, therefore synthesis is challenging

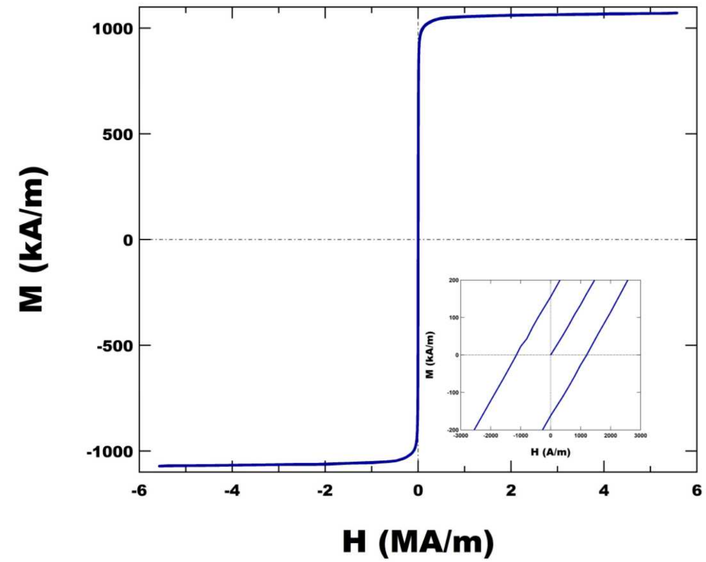
A brief magnetics overview- hard vs. soft magnets

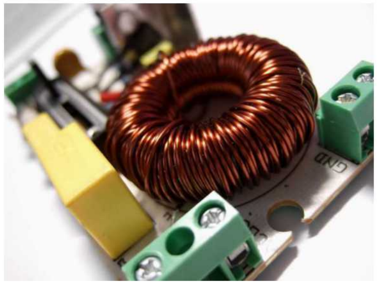
Hard (permanent)magnet



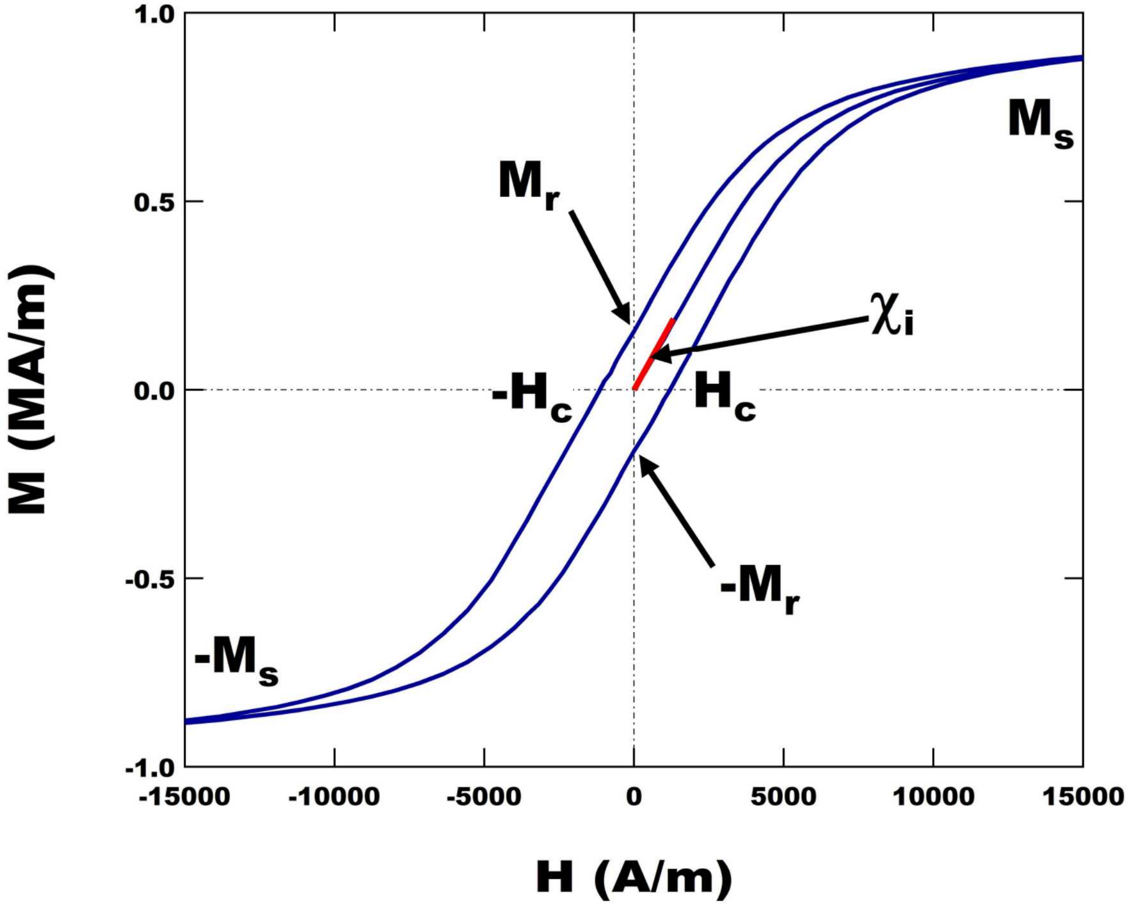


Soft magnet





Magnetic properties



M_s = saturation magnetization

M_r = magnetic remnance

H_c = coercivity

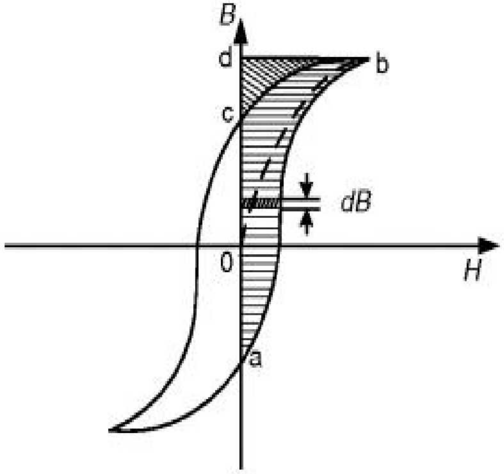
χ_i = initial susceptibility

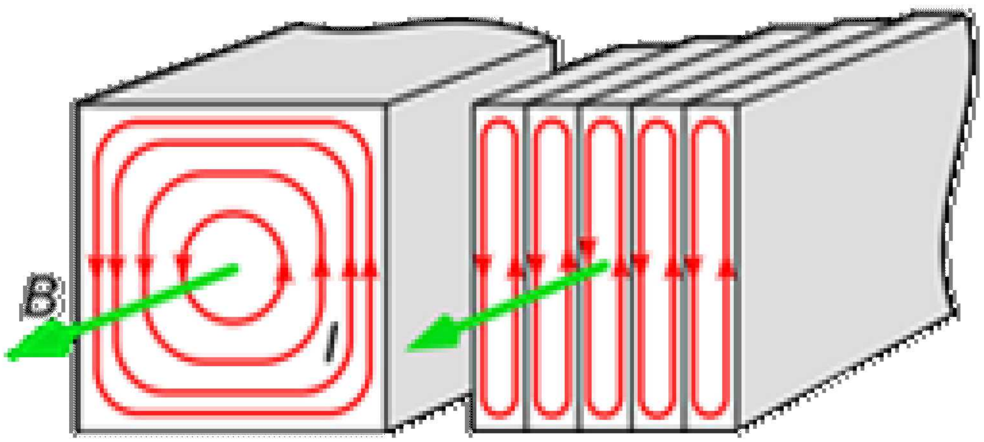
μ = permeability

μ_r = permeability

$\mu_r = \mu/\mu_0 = 1 + \chi$

Magnetic losses





$$\frac{P_{hys}}{V} = \oint H(t)dB$$

$$\frac{P_{eddy}}{V} = \frac{\omega B^2 A}{48\rho}$$

Hysteresis

Eddy Currents

Coercivity as a function of particle size

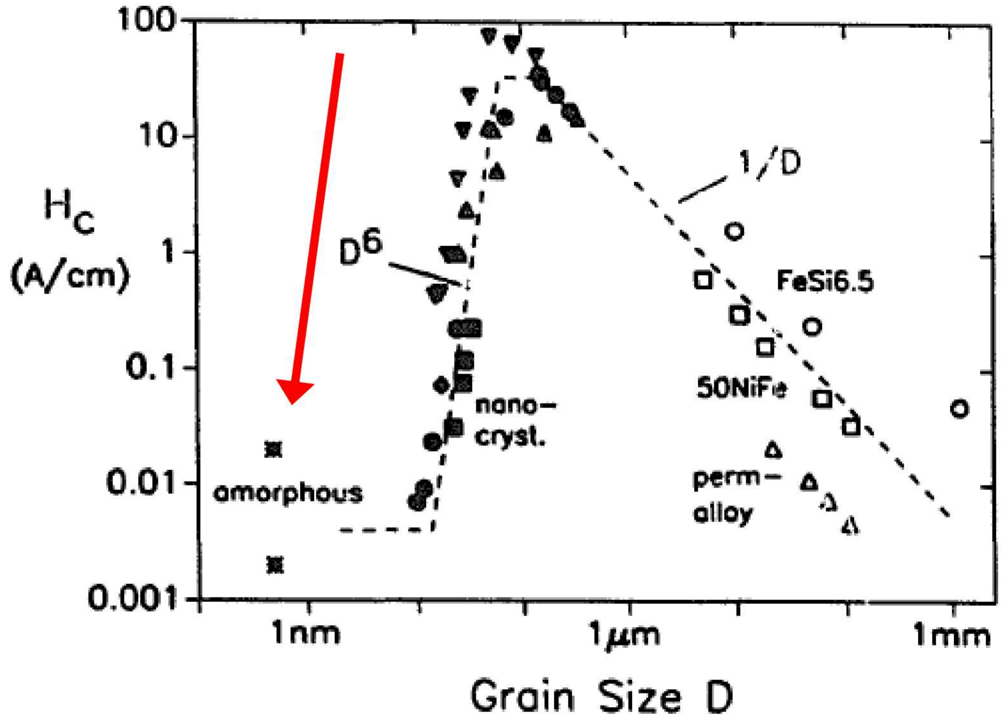
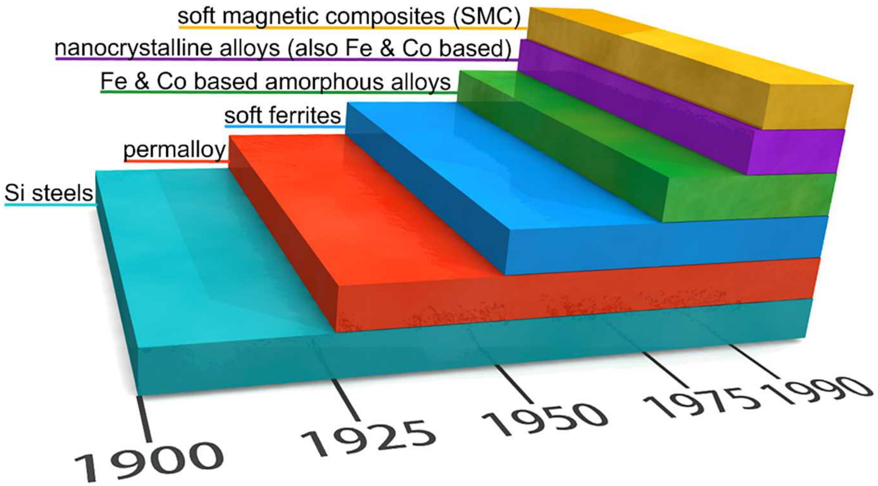


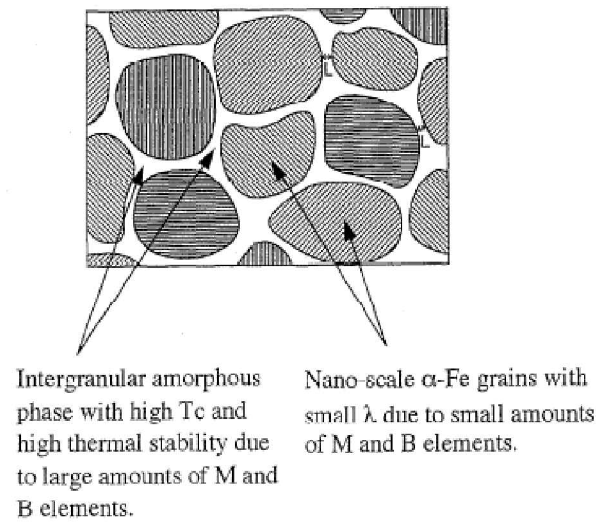
Fig. 2. Coercivity H_c vs. grain size for various soft magnetic metallic alloys. The data of the nanocrystalline material refer to (▲) FeNbSiB and (●) FeCuNbSiB [14], (◆) FeCuVSiB [15], (■) FeZrB [4] and (▼) FeCoZr [16].

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

Development of Soft Magnetic Materials

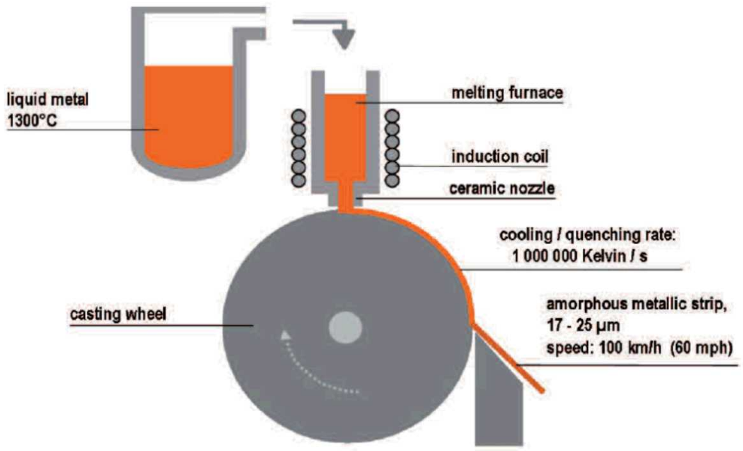


Adapted from: L.A. Dobrzański, M. Drak, B. Ziębowicz, Materials with specific magnetic properties, Journal of Achievements in Materials and Manufacturing Eng., 17, 37 (2006).



"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 stoichiometry including Fe, Co, and other inactive elements such as B, Zr, Hf, Nb, Cu, Mo, Si, C**
- **Time consuming and high temperature processing → costly!**
- **Some inactive material to form a low loss nanocrystalline structure**

Metathesis- effective for early transition metals

$$MX_n + Li_3N \longrightarrow M_yN + LiX$$

- Potentially facile route to iron nitride

Group	MX_n	Product
4	$TiCl_4$	TiN
	$ZrCl_4$	ZrN
	$HfCl_4$	HfN
5	VCl_3	VN, V_2N
6	$CrCl_3$	Cr, Cr_2N
7	MnI_2	Mn_4N, Mn
8	$FeCl_3$	Fe
10	$NiCl_2$	Ni

- Effective for the early transition metals

$$FeCl_3 + Li_3N \longrightarrow ?$$

- Reactions with late metals generate too much heat
  - Decomposition to elemental metal

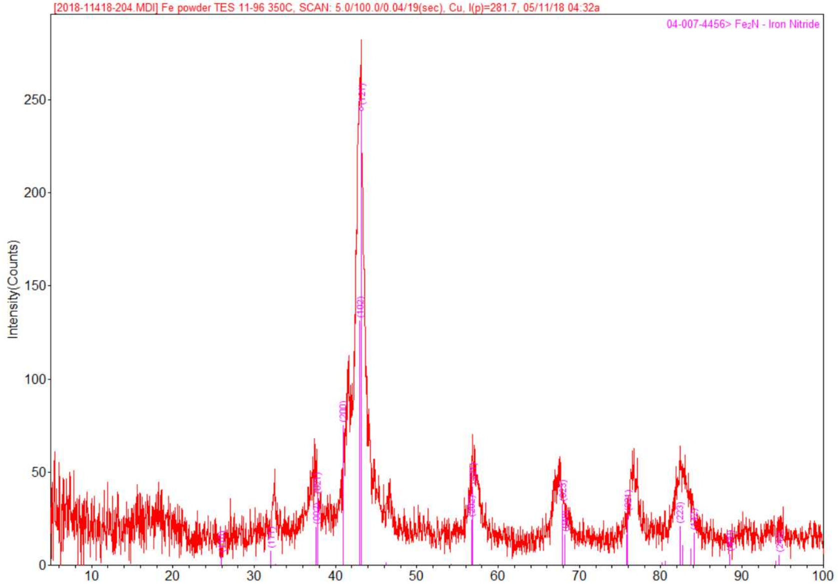
Parkin *J. Chem. Soc., Dalton Trans.* **1993**, 2435.

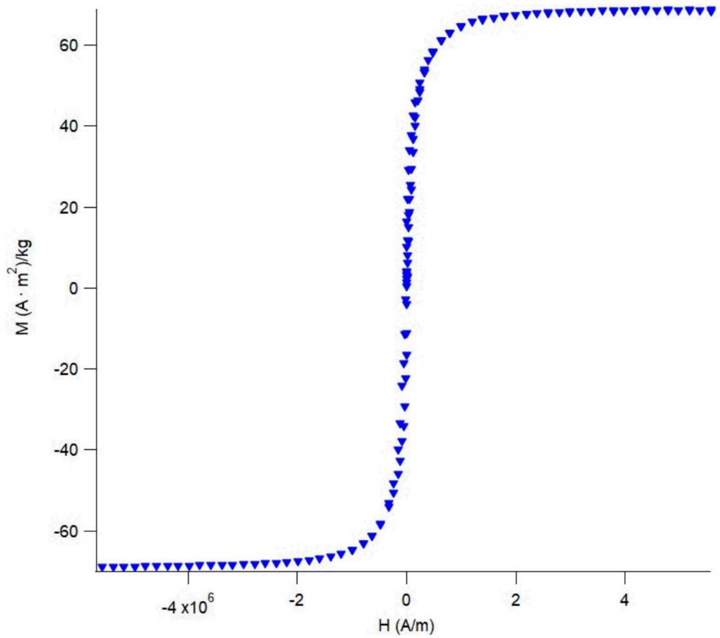
Slow addition of $FeCl_3$ results in phase pure Fe_2N

$$FeCl_3 + Li_3N \xrightarrow[\text{oleylamine}]{350\ ^\circ C} Fe_2N$$

-LiCl

- 0.124 M $FeCl_3$ oleylamine
- Injected at 80 μL/min
- 4 hour reaction time





Fe_2N is generally not observed in isolation

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Science and Technology of Advanced Materials 5 (2004) 83–87

SCIENCE AND TECHNOLOGY OF ADVANCED MATERIALS

www.elsevier.com/locate/stam

Magnetic properties of weak itinerant ferromagnetic ζ-Fe_2N film

Hiroshi Naganuma[a], Yasushi Endo[a,b], Ryoichi Nakatani[a,b,c], Yoshio Kawamura[a], Masahiko Yamamoto[a,b,*]

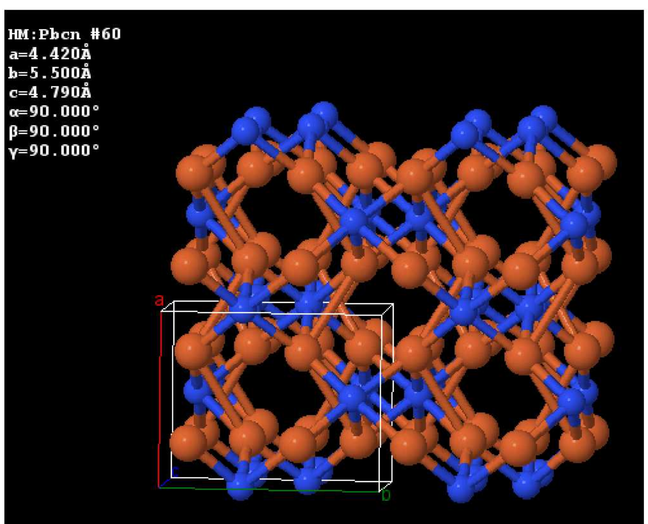
cm CHEMISTRY OF MATERIALS

Communication

Cite This: *Chem. Mater.* 2018, 30, 1830–1834

pubs.acs.org/cm

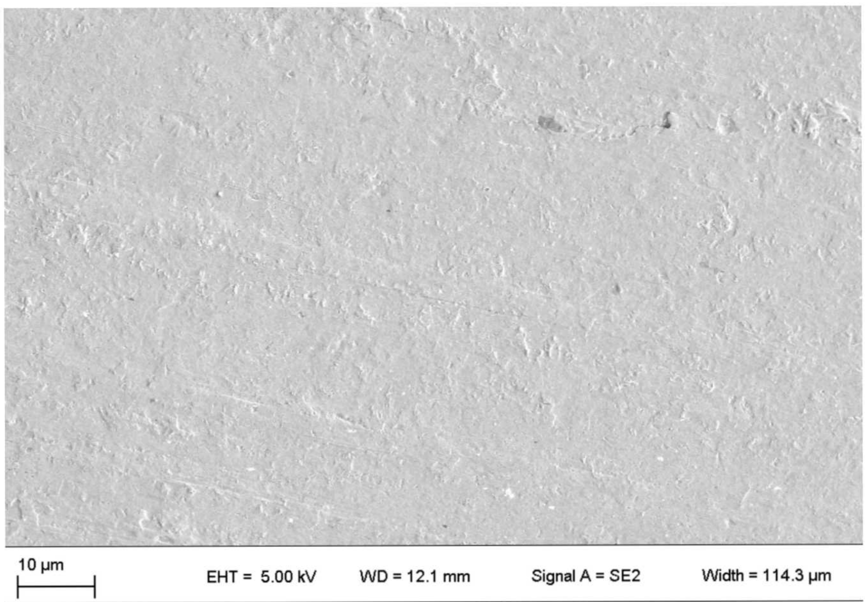
Fabrication of ε-Fe_2N Catalytic Sites in Porous Carbons Derived from an Iron–Triazolate Crystal

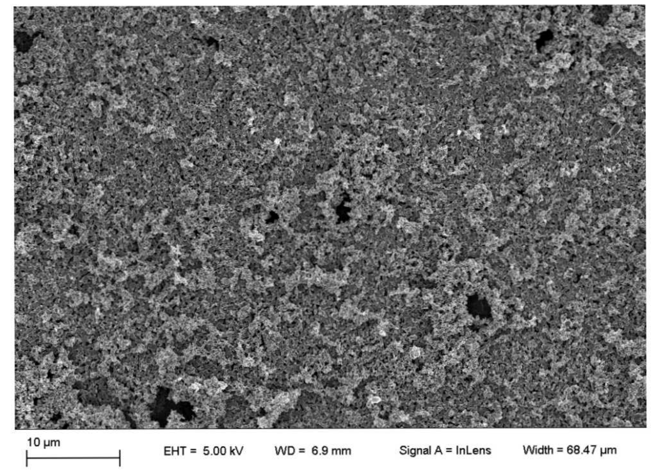


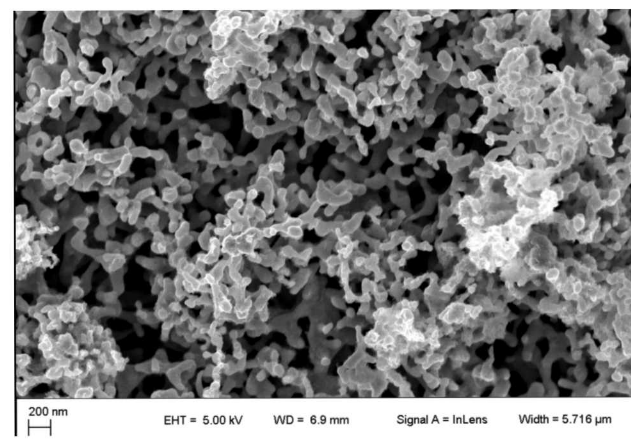
- Orthorhombic structure
- Further magnetic characterization is underway

Electrochemical Nitridation of Fe(0)- LiCl/KCl

- Subsequent attempts have produced nitride layer







- A phase evolution vs. temperature (XRD) suggests FeN is the predominant phase

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 soft magnetic materials and will not require laminations of inactive material to mitigate eddy current losses