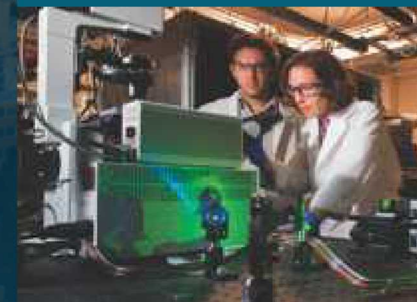
SAND2019-3592C

Synthesis and Magnetic Properties of Iron Nitrides



Tyler E. Stevens, Riley E. Lewis, Charles J. Pearce, Mark A. Rodriguez, Sara Dickens, Bonnie B. McKenzie, Stanley Atcitty, & Todd C. Monson

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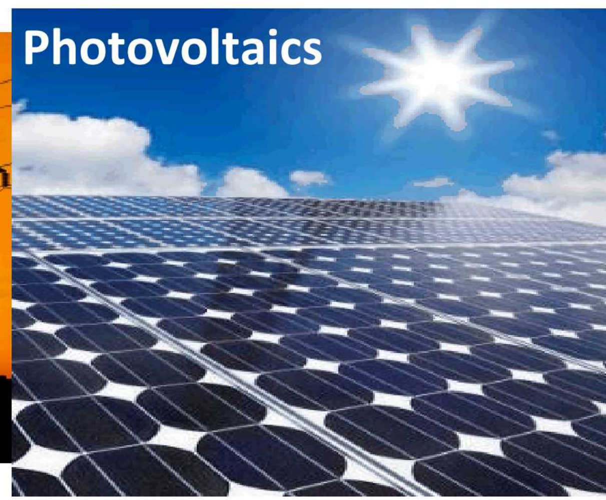
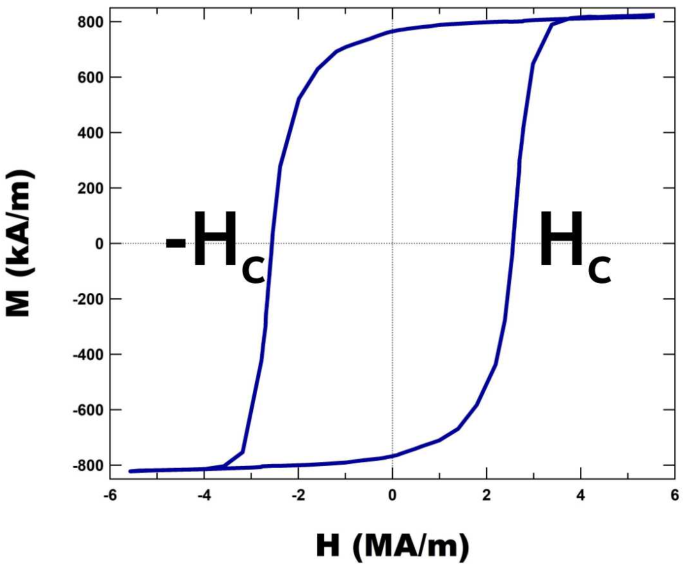
Soft magnetic materials have numerous applications

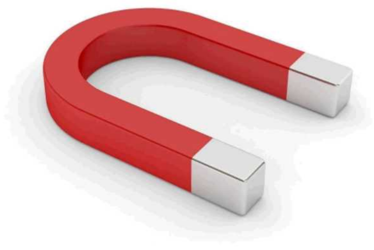


Courtesy of Bob Kaplar

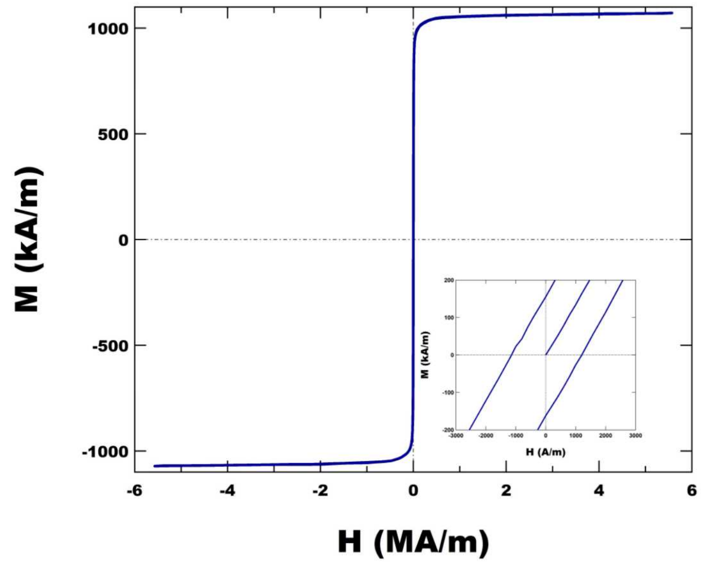
A brief magnetics overview- hard vs. soft magnets

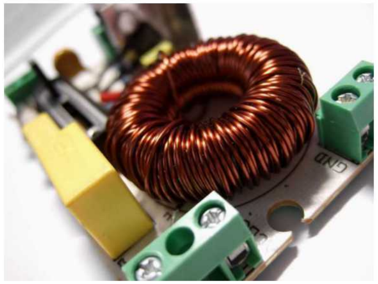
Hard (permanent)magnet



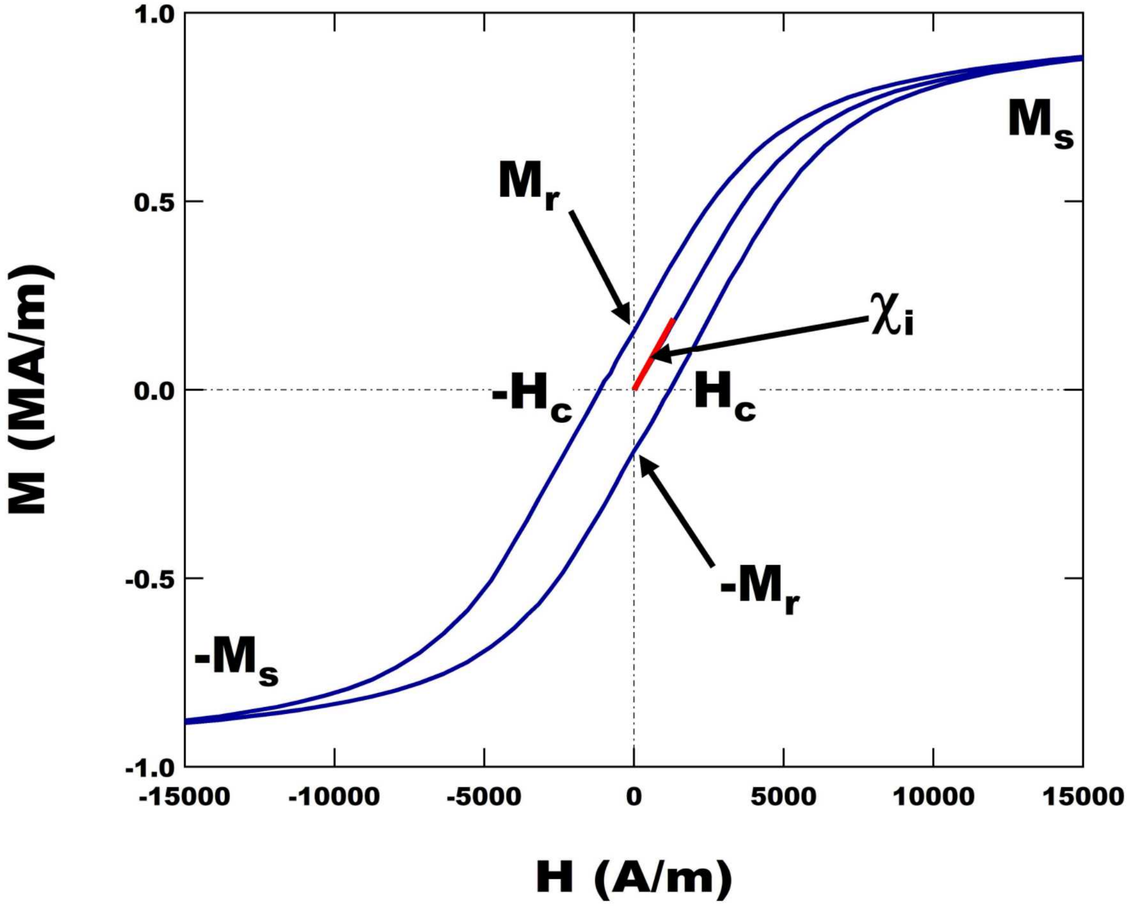


Soft magnet





Magnetic properties



M_s = saturation magnetization

M_r = magnetic remnance

H_c = coercivity

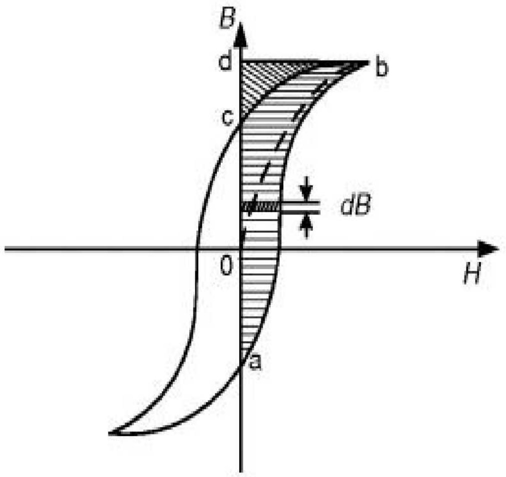
χ_i = initial susceptibility

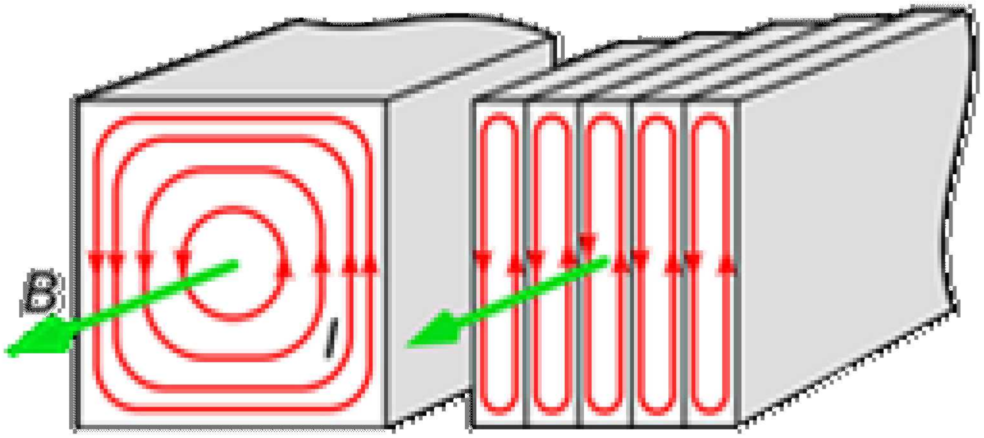
μ = permeability

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

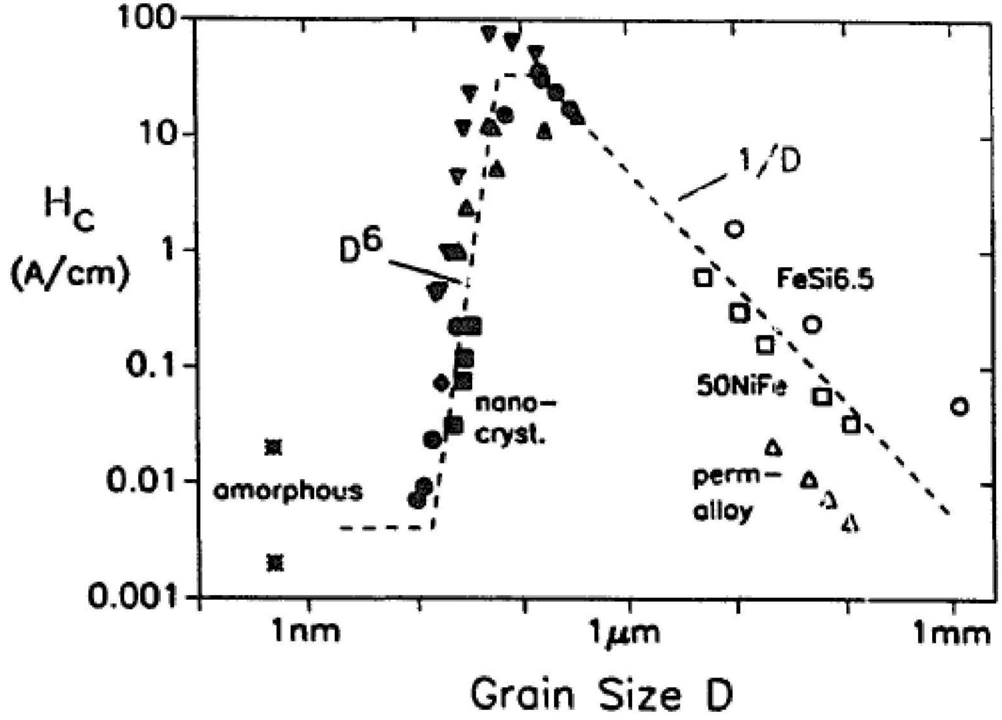


Fig. 2. Coercivity H_c vs. grain size for various soft magnetic metallic alloys. The data of the nanocrystalline material refer to (▲) FeNbSiB and (●) FeCuNbSiB [14], (◆) FeCuVSiB [15], (■) FeZrB [4] and (▼) FeCoZr [16].

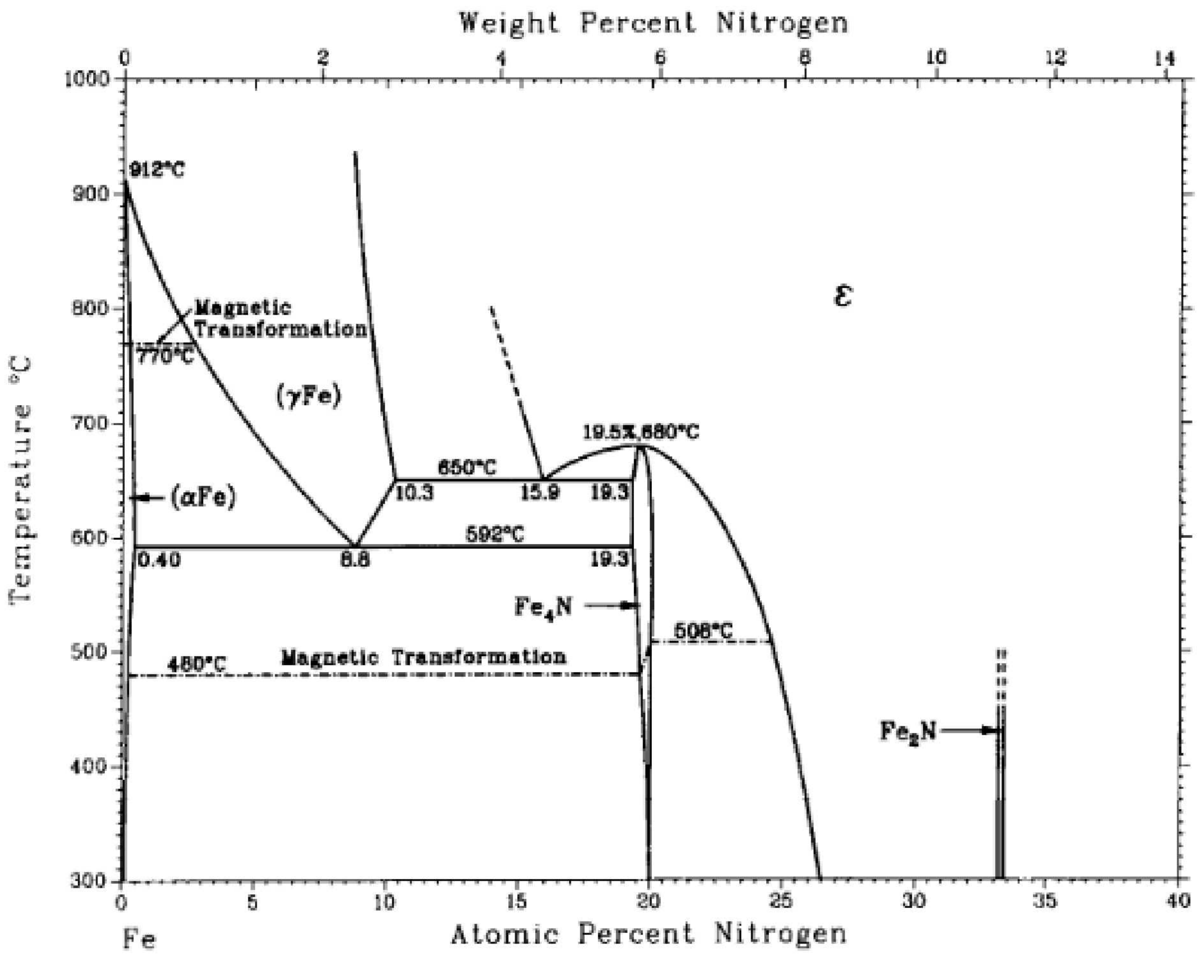
G. Herzer, Nanocrystalline Soft Magnetic Materials, J. Magn. Mag. Mat., 112, 258 (1992).

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

Synthesis of iron nitride is challenging



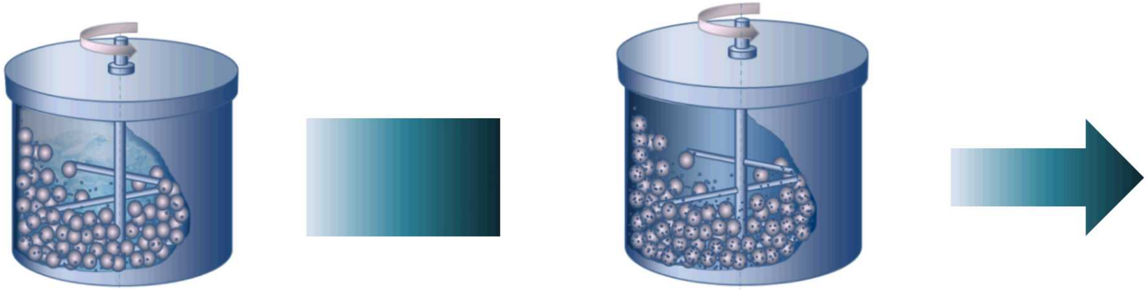
H.A. Wriedt, N.A. Gokcen, and R.H. Nafziger, 1987.

- Commercial synthesis yields mixture of Fe_3N and Fe_4N

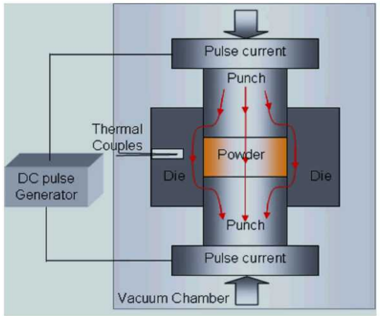
γ'-Fe_4N synthesis and processing

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**

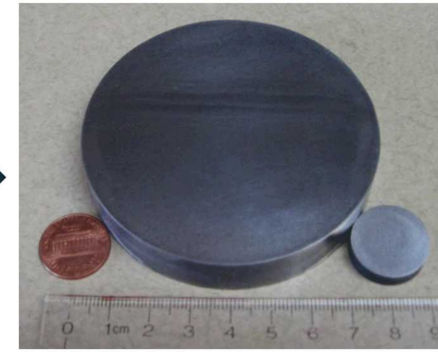


Spark Plasma Sintering (SPS)

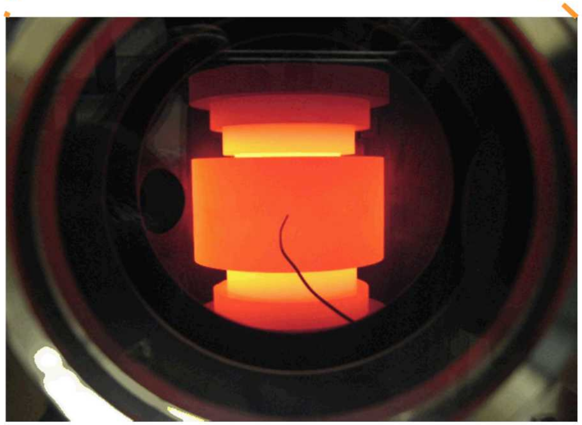
- **Cryomilling creates nanocrystalline Fe powder with large amounts of vacancies, grain boundaries, and dislocations**
- **Defects serve as fast diffusion pathways for nitrogen atoms from NH_3**
- **SPS quickly consolidates raw powders with a low sintering temperature**
  - **Excellent control over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

Spark plasma sintering (SPS)

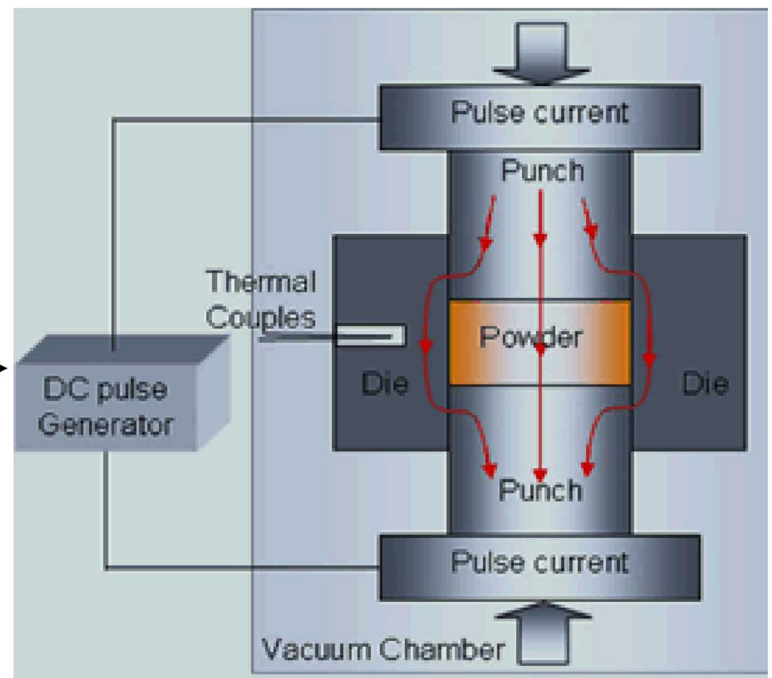
Starting Powder in Die



End Product

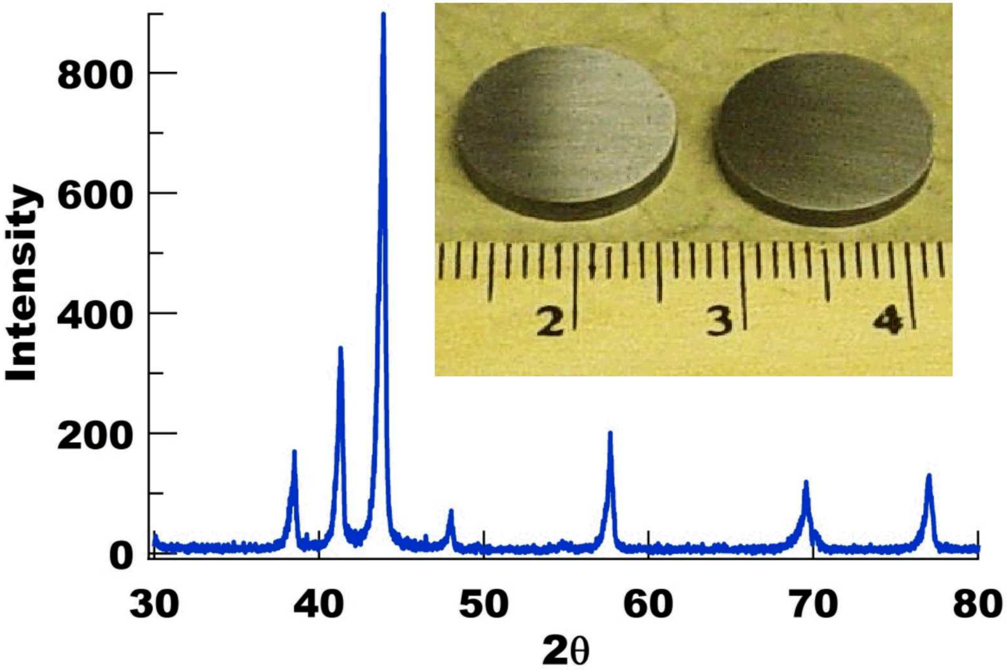


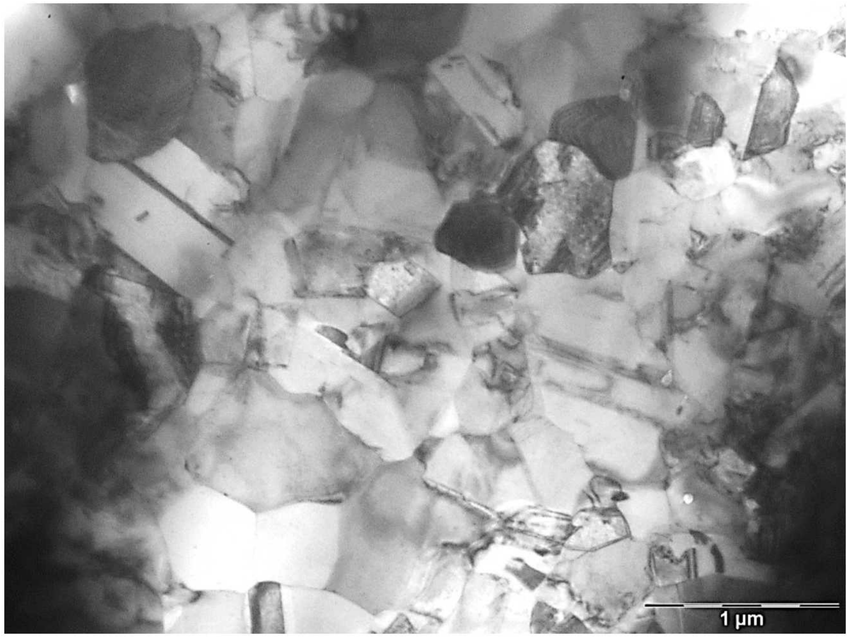
SPS
Chamber



SPS consolidated iron nitride

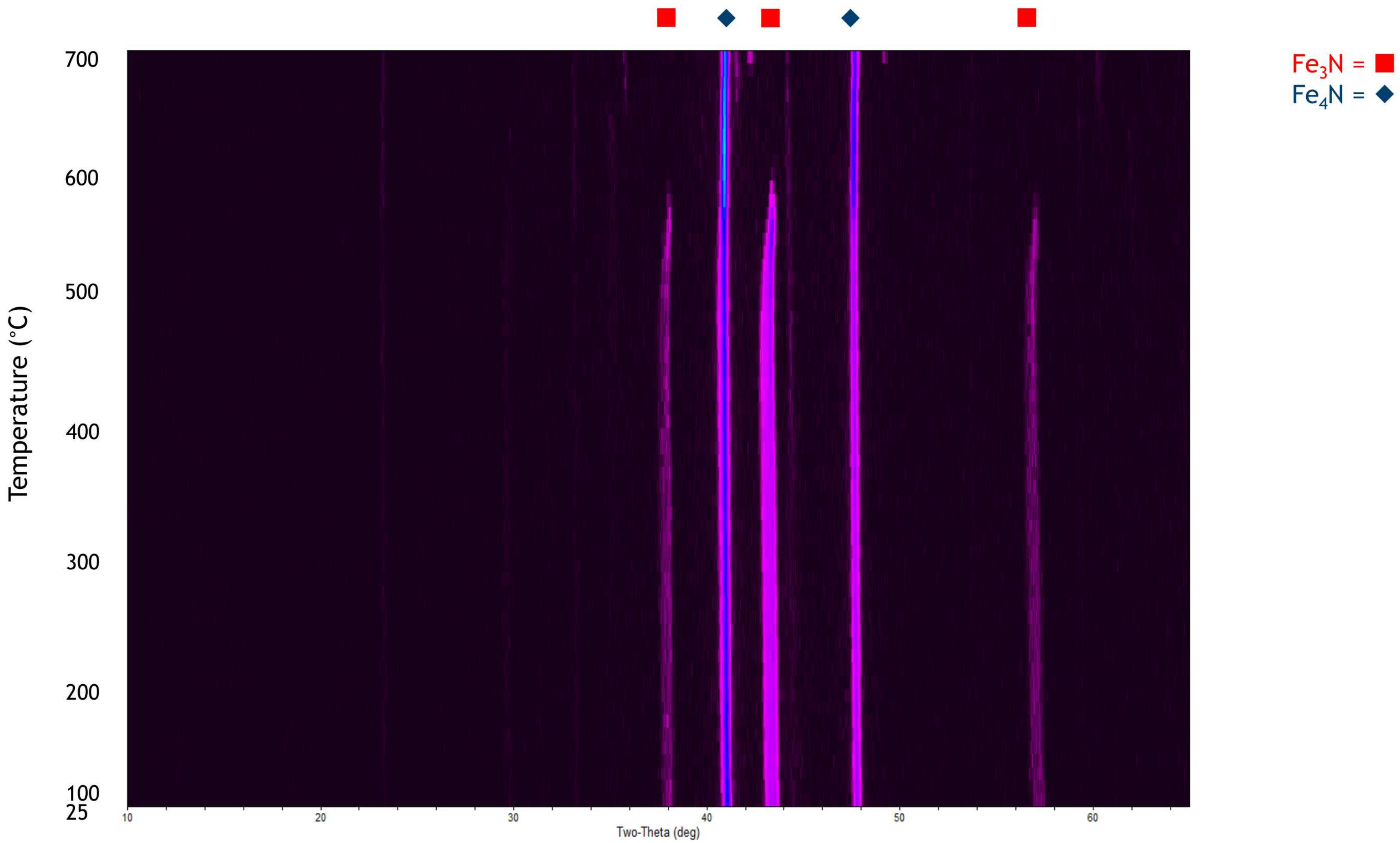
First ever bulk γ'-Fe_4N!





- 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

Continued efforts to improve phase purity



Powder XRD, mixed phase iron nitride

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.

Metathesis- methods to facilitate for late metals

$$FeCl_3 + Li_3N \longrightarrow ?$$

- Other methods to facilitate reaction?
  - Perform reaction in high boiling point solvent
    - Solvent acts also as a "heat sink"
- Non-oxidizing solvent
  - Oleylamine

$$FeCl_3 + Li_3N \xrightarrow[\text{oleylamine}\\ \text{-LiCl}]{350\ °C} \text{mixture of } Fe_2N/\ Fe_3N$$

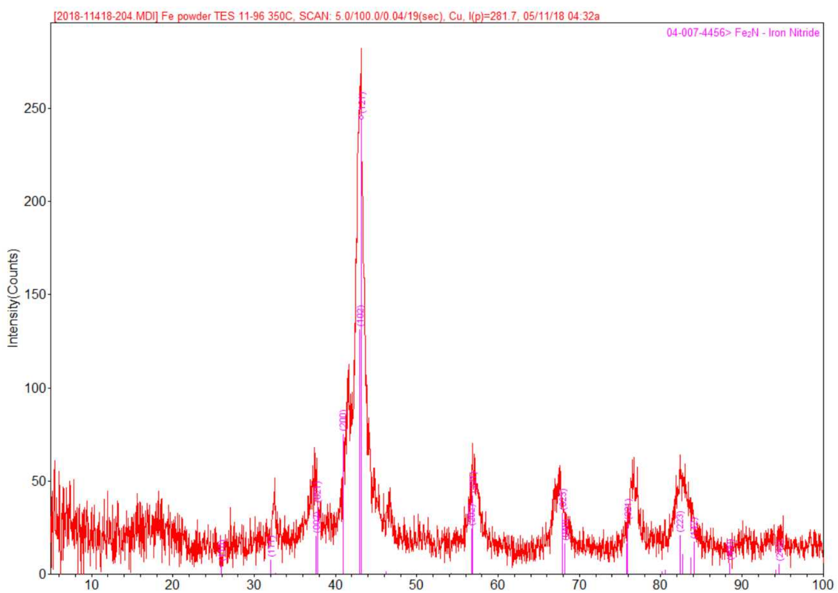
- LiCl and Fe_2N/ Fe_3N confirmed by XRD
- Can reaction conditions be tuned to favor one product?

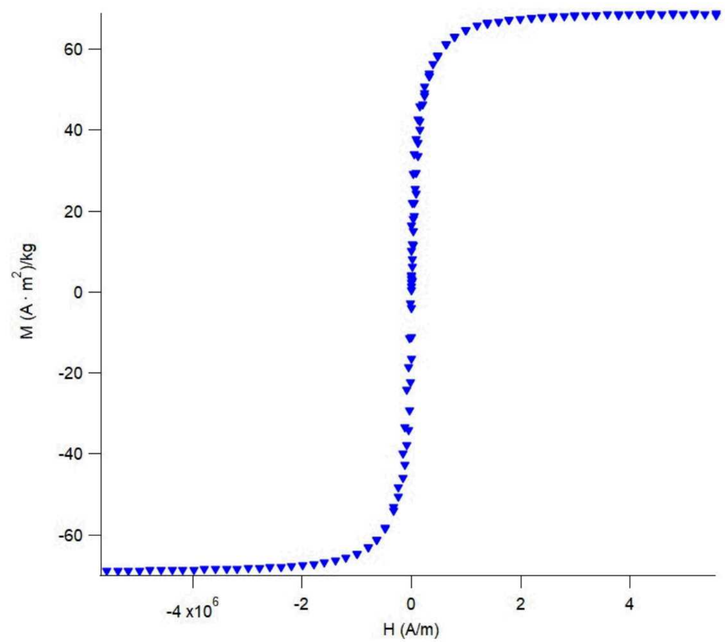
Slow addition of $FeCl_3$ results in phase pure Fe_2N

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

-LiCl

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





Fe_2N is generally not observed in isolation

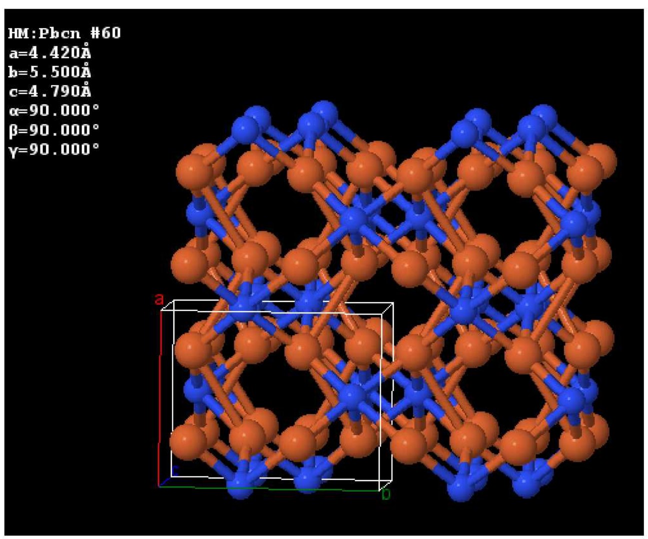
ELSEVIER
Science and Technology of Advanced Materials 5 (2004) 83–87
SCIENCE AND TECHNOLOGY OF ADVANCED MATERIALS
www.elsevier.com/locate/stam

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

$FeCl_3$ decomposes to $FeCl_2$ at >316 °C

$$FeCl_2 + Li_3N \xrightarrow[\text{oleylamine, -LiCl}]{350\ °C} Fe_3N$$

- 0.124 M $FeCl_2$ oleylamine
- Injected at 80 µL/min
- 4 hour reaction time

- Fe(III) precursor results in lower Fe concentration

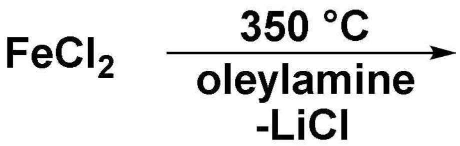
Iron chloride appears to be required for iron nitride formation

$$Fe(acac)_3 + Li_3N \xrightarrow[\text{oleylamine}]{350\ ^\circ C} ?$$

- 0.124 M $Fe(acac)_3$ oleylamine
- Injected at 80 μL/min
- 4 hour reaction time

- Intractable products (XRD)
- No evidence of any iron nitrides

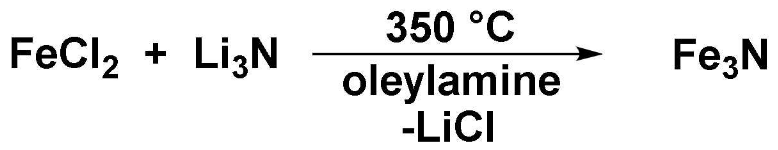
Li_3N is equally important for iron nitride formation



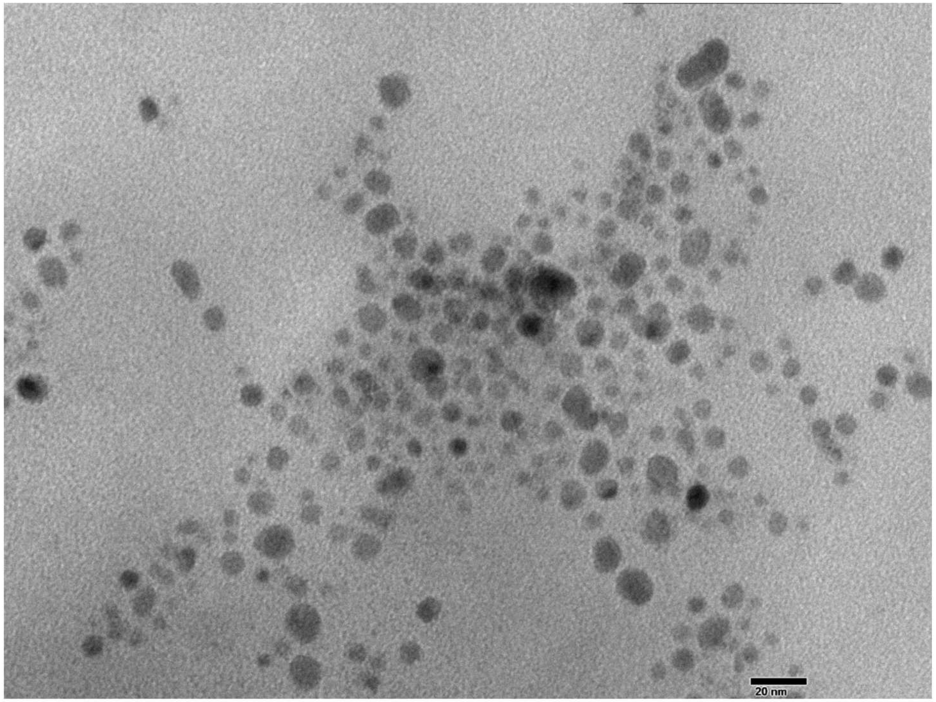
- 0.124 M $FeCl_2$ oleylamine
- Injected at 80 µL/min
- 4 hour reaction time

- No particle participated from solution

Reaction of $FeCl_2$ with Li_3N results in Fe_3N



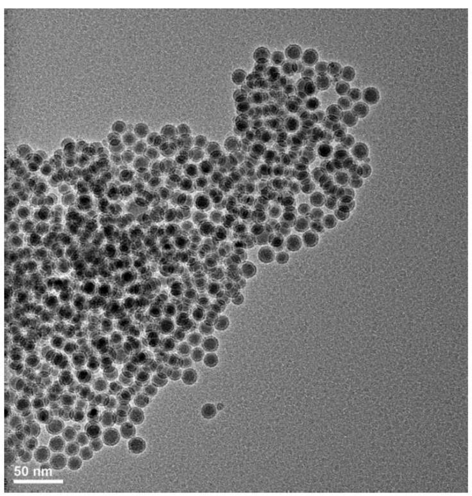
- 0.124 M $FeCl_2$ oleylamine
- Injected at 80 μL/min
- 4 hour reaction time

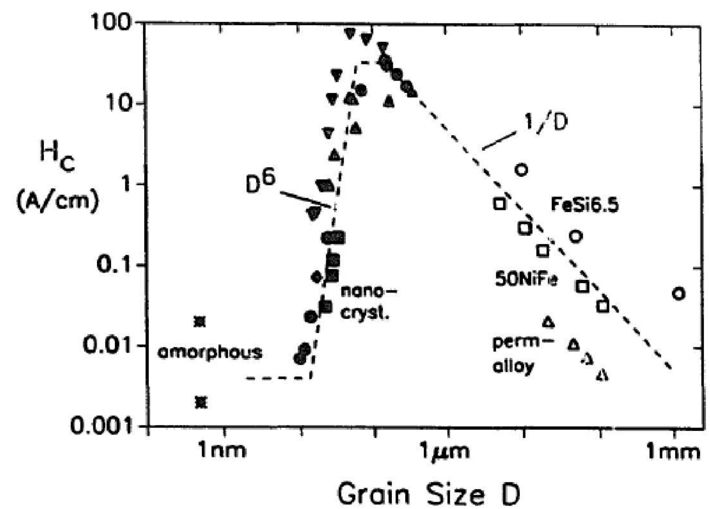


- Size distribution could be improved

Nitridation of Iron Nanoparticles

- Synthesis from well defined precursors
- Huber reported large-scale iron nanoparticle synthesis (Huber, 2011 *US Patent* #7,972,410)
  - Size control by reversible magnetic agglomeration





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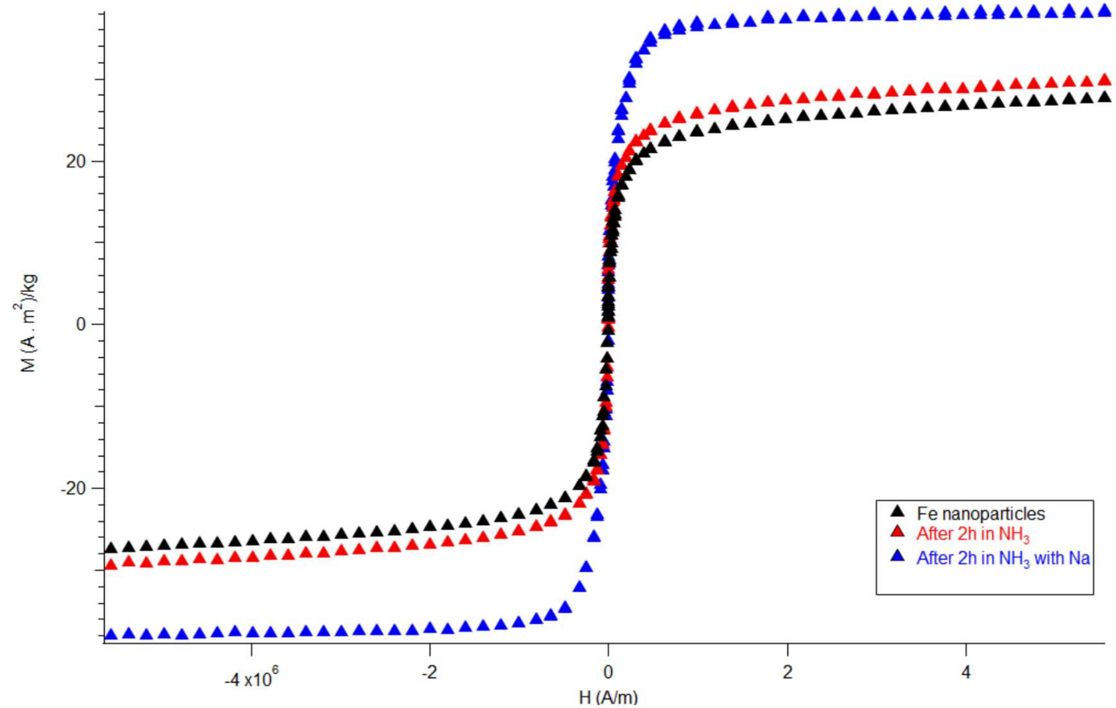
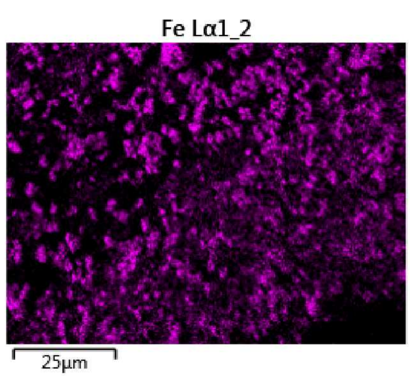
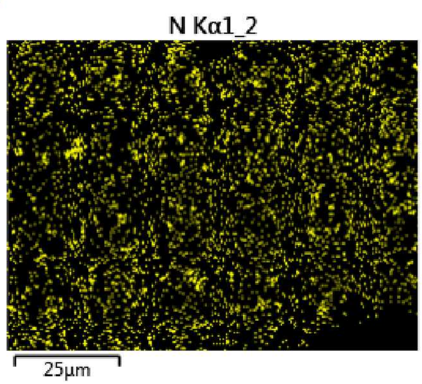
Magnetic Data Supports Formation of New Material

Fe nanoparticles $\xrightarrow{NH_3\ (l)}$ Fe_xN_y ?





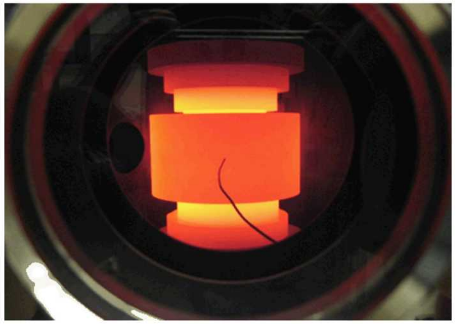


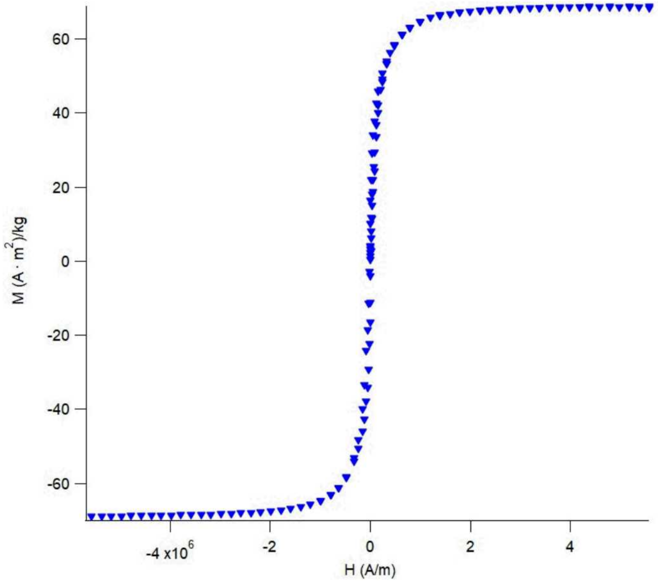
Summary

- SPS consolidation has successfully been used to fabricate bulk γ'-Fe_4N

- Metathesis
  - A simple straight forward route to iron nitride
  - Phase of iron nitride is determined by iron chloride precursor

- Nitridation of iron nanoparticles
  - Fine control over size and morphology

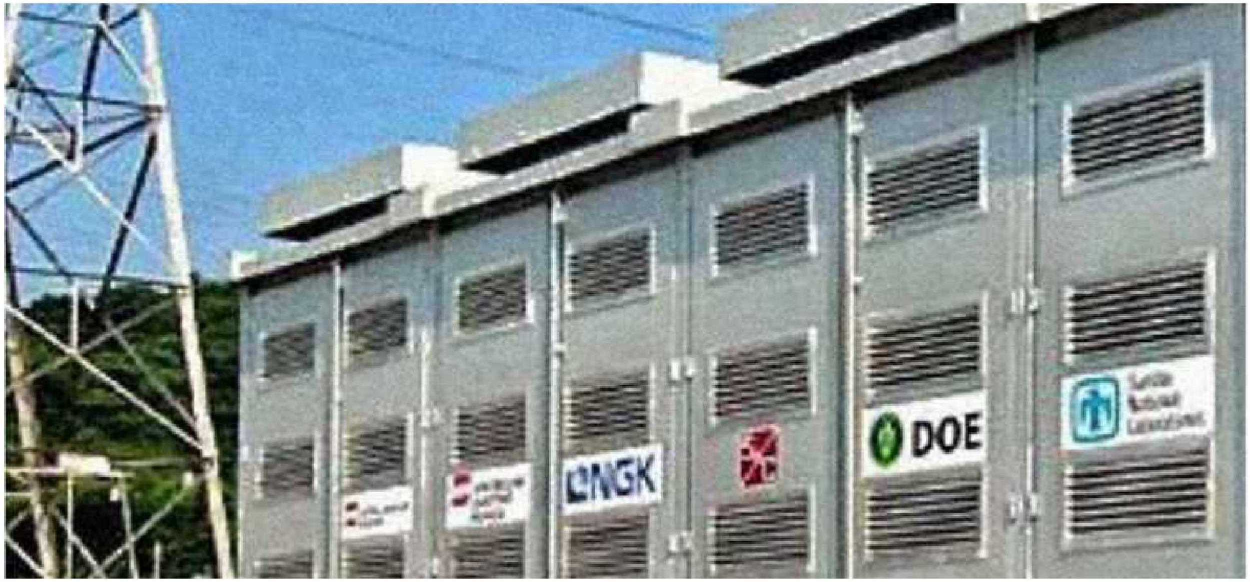




Acknowledgements

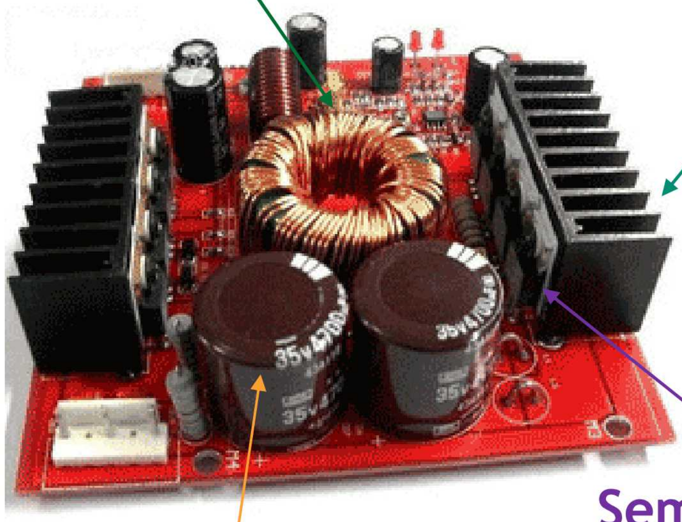
- John Watt
- Dale Huber

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



Magnetic Devices Impact Power System Volume and Weight

Power Electronics Components

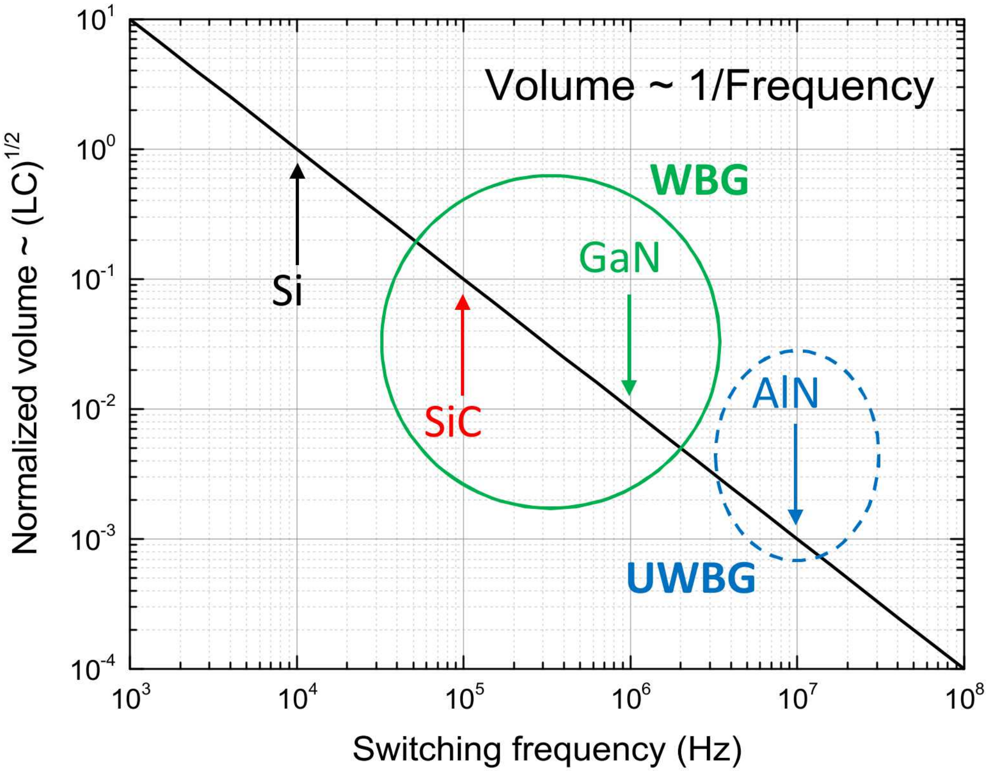


WBG/UWBG materials enable higher switching frequency and better thermal management

J. Neely, J. Flicker, B. Kaplar

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

Higher Frequencies Decrease Inductance Requirements, However…

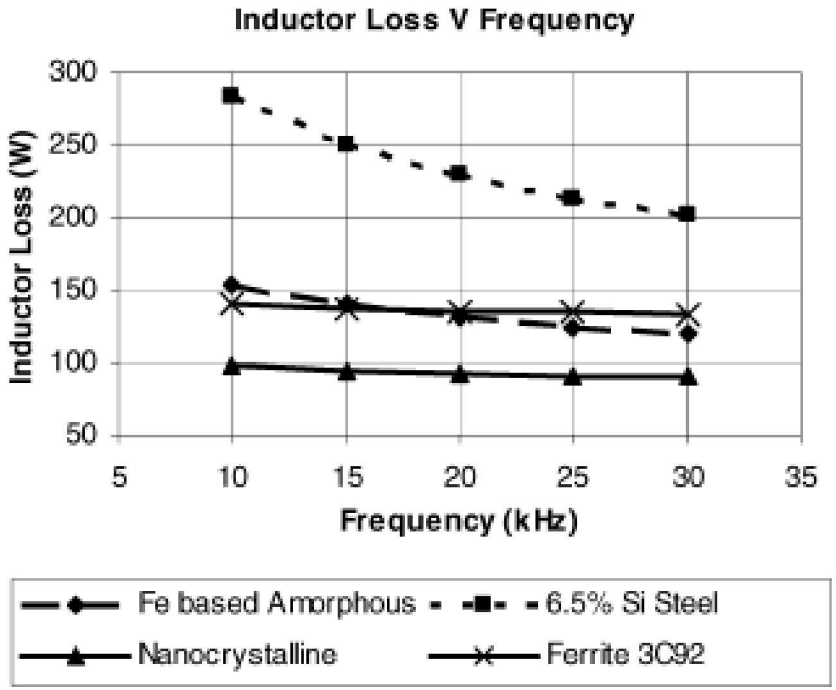


- **Higher switching frequency is enabled by scaling properties of WBG/UWBG materials**
- **Ideal 1/f SWaP dependence (true dependence likely weaker $1/f^n$ with n < 1 due to nonidealities)**
- **Other benefits of WBG/UWBG exist, e.g. higher voltage without series stacking of devices, and higher temperature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

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

Adapted from Bob Kaplar

Inductor Loss Increases with Frequency

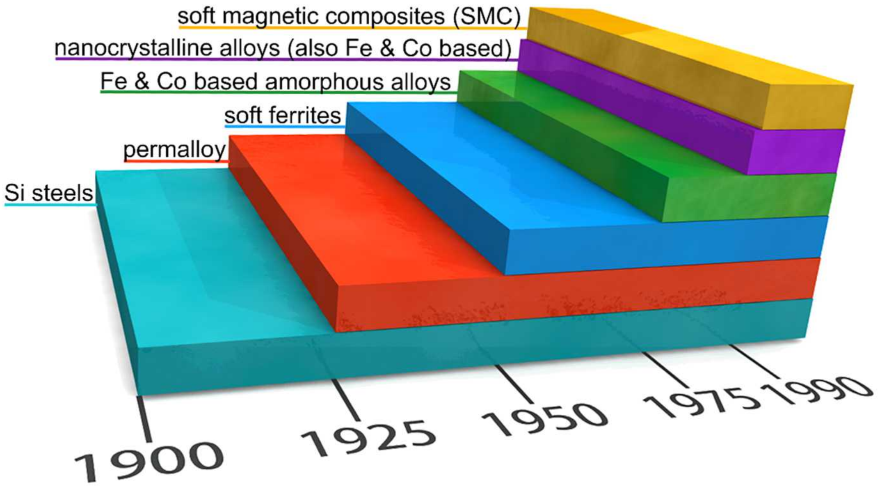


B.J. Lyons, J.G. Hayes, M.G. Egan, Magnetic Material Comparisons for High-Current Inductors in Low-Medium Frequency DC-DC Converters, *IEEE*, **2007**, 71.

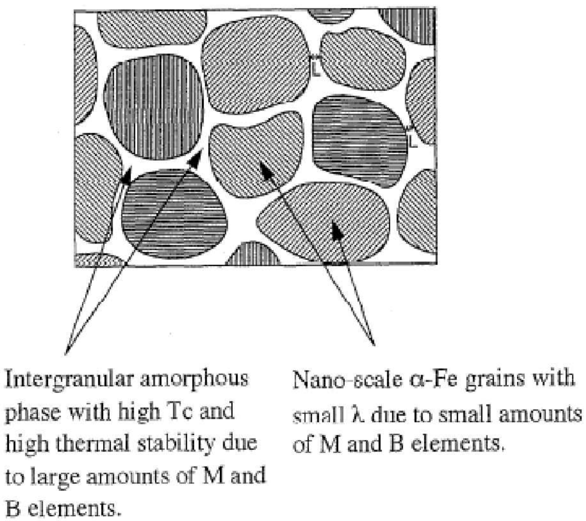
<u>Requirements for a new magnetic material</u>

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

Development of Soft Magnetic Materials

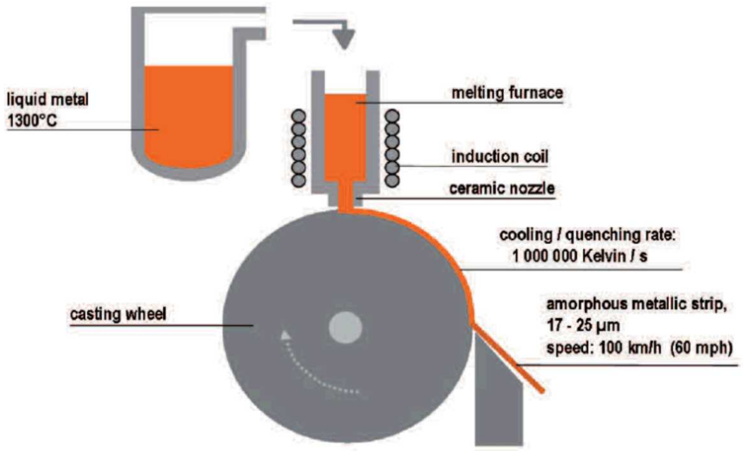


Adapted from: L.A. Dobrzański, M. Drak, B. Ziębowicz, Materials with specific magnetic properties, Journal of Achievements in Materials and Manufacturing Eng., 17, 37 (2006).



"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).



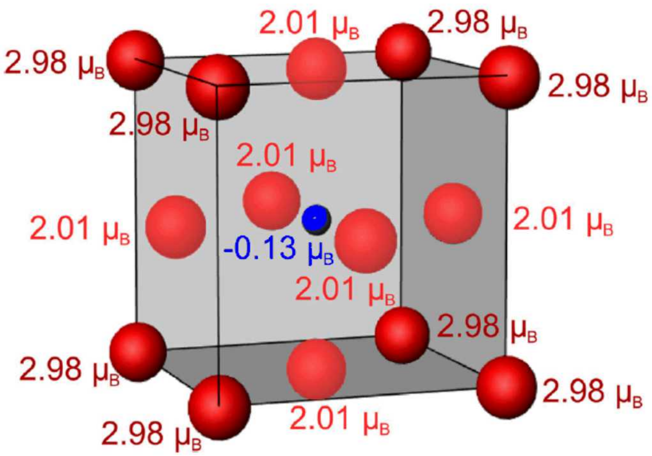
VITROPERM (Vacuumschmelze)

- **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**

γ'-Fe_4N meets all of the requirements for a new soft magnetic material

Magnetic Material	J_s (T)	ρ(μΩ·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
γ'-Fe_4N	1.89	> 200	Low

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).

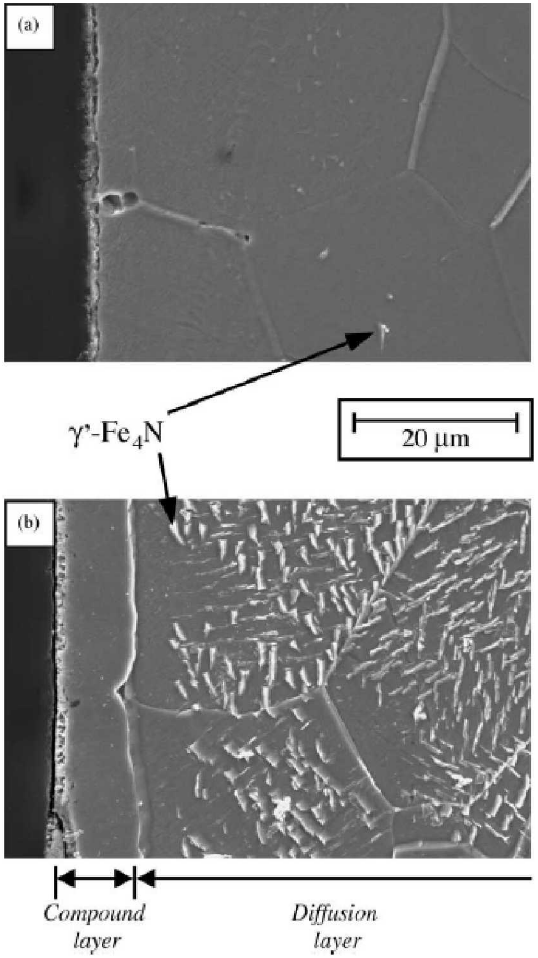
Other Magnetic Nitrides of Interest

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**

Electrochemical Nitridation of Fe(0)

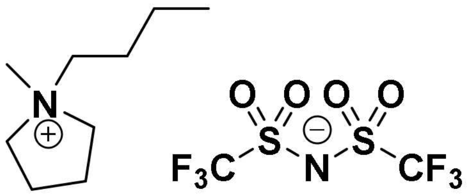
- **Growth of γ'-Fe_4N demonstrated in LiCl-KCl eutectic melt**
- **γ'-Fe_4N Formed at surface of Fe(0) electrode**
  - **Li_3N nitride source**
- **Demonstrates electrochemical synthesis of iron nitride possible**
- **Requires >700 K**
- **Is a lower temp approach possible?**

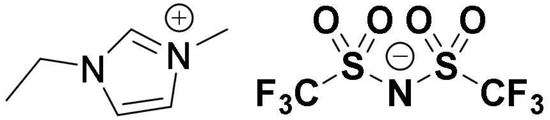


Ito *Journal of Alloys and Compounds* **2004**, *376*, 246.

Low Temperature Approach- Li_3N Solubility is Poor in ILs

- Two Ionic liquids considered
  - Both have excellent electrochemical stability



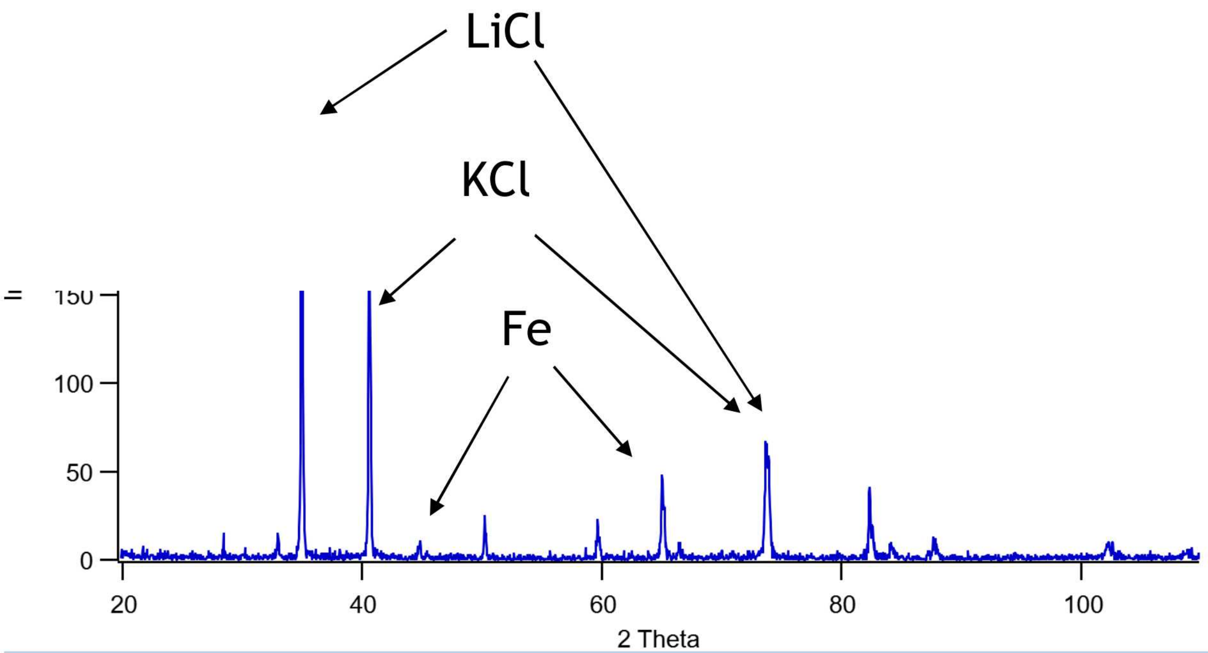


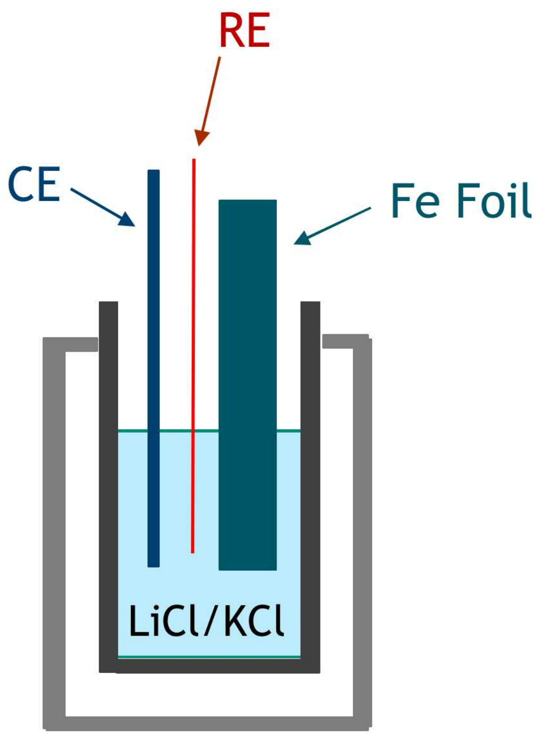
Lewandowski *Electrochemica Acta* **2006**, *51*, 5567.

- Even with the use of crown ethers, we have yet to observe solubility of Li_3N

Electrochemical Nitridation of Fe(0)- LiCl/KCl

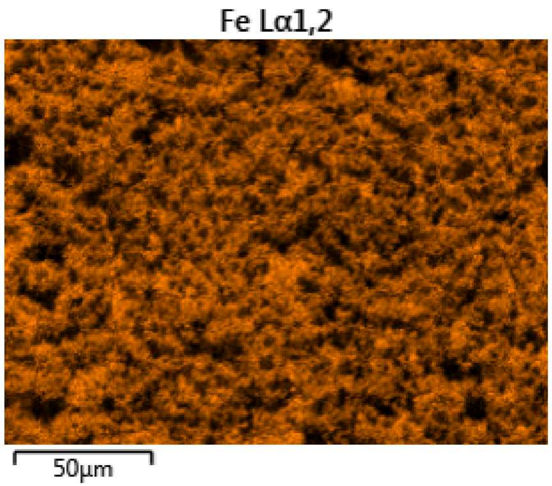
- Conditions similar to Ito
  - 450 ºC LiCl/KCl
  - 1 mol % Li_3N
    - Potential applied to oxidize N^{3-}
- Non-trivial to reproduce results
- Initial attempts did not produce nitride layer

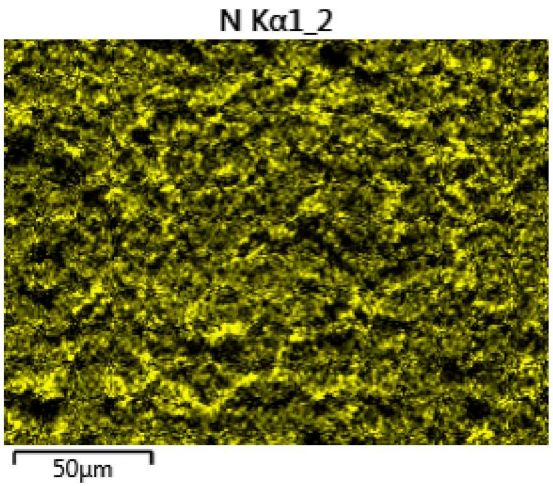


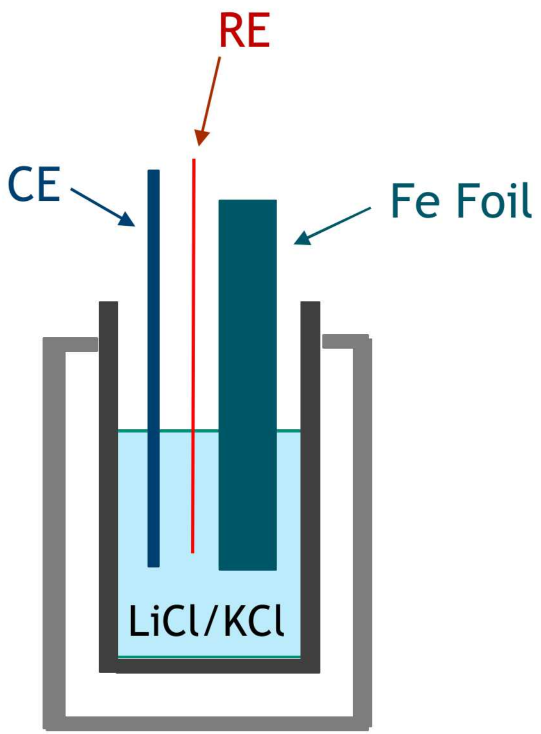


Electrochemical Nitridation of Fe(0)- LiCl/KCl

- Subsequent attempts have produced nitride layer
    - Longer reaction time
    - Addition of Li_3N in portions

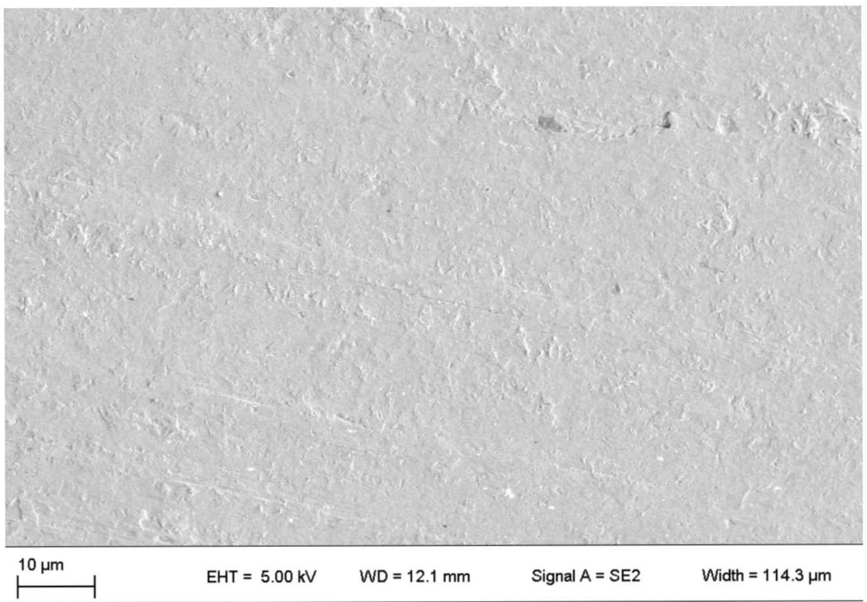


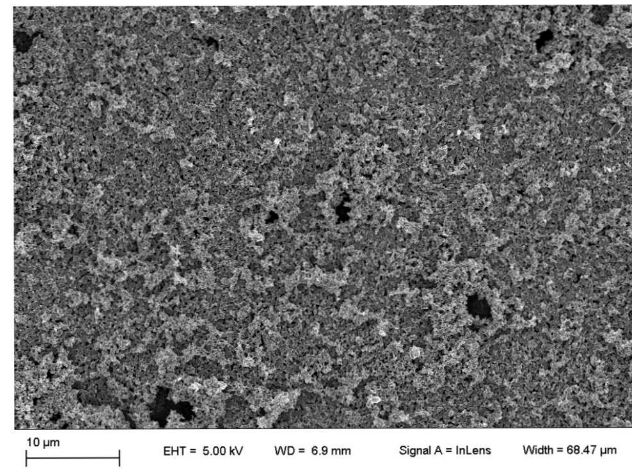


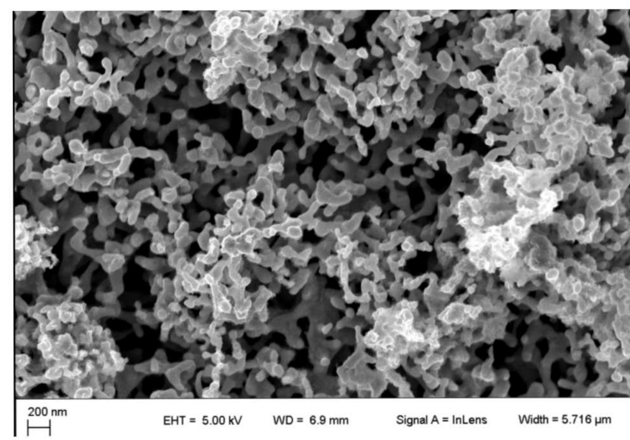


Electrochemical Nitridation of Fe(0)- LiCl/KCl

- Subsequent attempts have produced nitride layer







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