R&D of Bulk Anisotropic Nanograin Composite Rare Earth Magnets

The project was sponsored by the US DARPA, AFRL, ONR, and DoE

Presented in Beijing, China, August, 2006

Motivation

Develop technologies

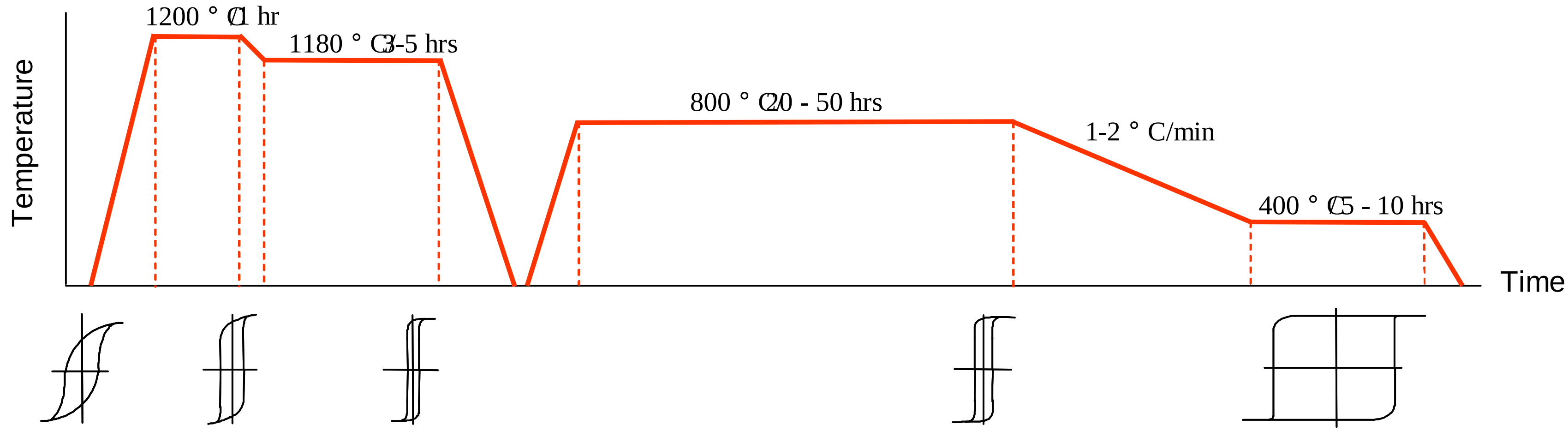
- ***To retain nanostructure in a bulk fully dense composite magnet***
- ***To create the desired nanograin alignment***
- ***To obtain an ideal microstructure, in which a fine and highly dispersed magnetically soft phase is uniformly distributed in a nanograin magnetically hard matrix phase***

Early Nanocomposite Magnets

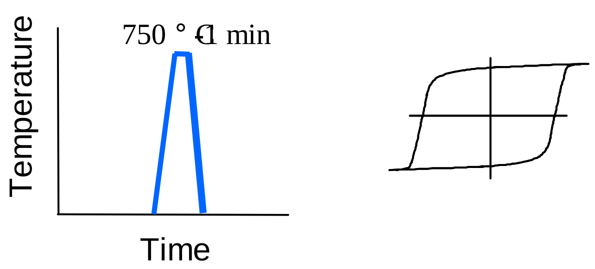
- ***in 1988, the Philips group observed $_MH_c \approx 3$ kOe in an annealed melt-spun $Nd_2Fe_{14}B/Fe_3B$ alloy powder***
- ***Extensive R&D followed worldwide in 1990s***
- ***Principal technical difficulties***
  - *How to make nanocomposite powders into a bulk magnet with full density and, at the same time, retain the nanograin structure*
  - *How to create desired grain alignment and, obtain a high-performance nanocomposite magnet*

Effect of Nanograin Structure

Conventional micron grain Sm(Co,Fe,Cu,Zr)$_{\sim 7.3}$



Nanograin structured Sm_2Co_{17}

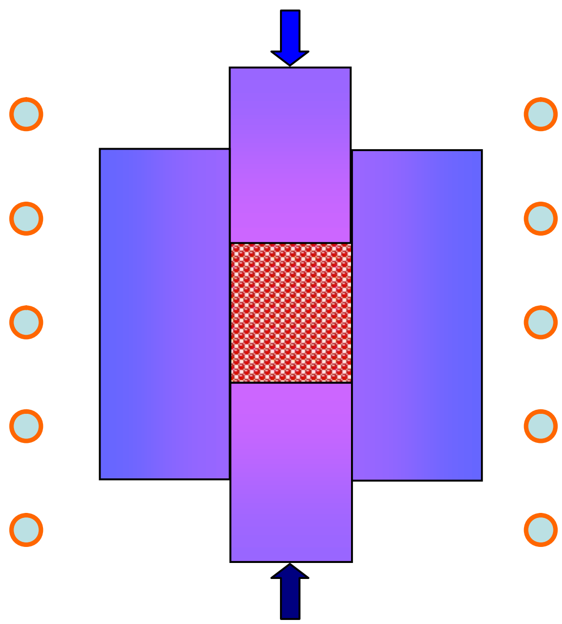


- **In 1991, J. Wecker, et al. obtained 6 kOe after annealing a mechanically alloyed stoichiometric Sm_2Co_{17} alloy powder at 700 °C for 30 minutes.**
- **In 1996, S.K. Chen, et al. obtained 4 kOe after annealing a mechanically alloyed $SmCo_{10}$ alloy powder at 750 °C for 20 minutes**
- **a high coercivity of 15.6 kOe was accomplished at the University of Dayton Magnetics Laboratory after annealing a mechanically alloyed Sm_2Co_{17} specimen at 750 °C for only 1 minute**

New Concepts of Consolidation

- ***Consolidation does not have to be performed at very high temperature***
  - *Not 1080 – 1200 ° C*
  - *But 600 – 800 ° C (Crystallization temperature)*
- ***Consolidation does not have to be performed for a long period of time***
  - *Not hours*
  - *But a few minutes*
- ***If a new consolidation technology with relatively low temperature and very short time can be developed, then nanocomposite powder can be bulk nanocomposite magnets***

Inductive Hot Compaction



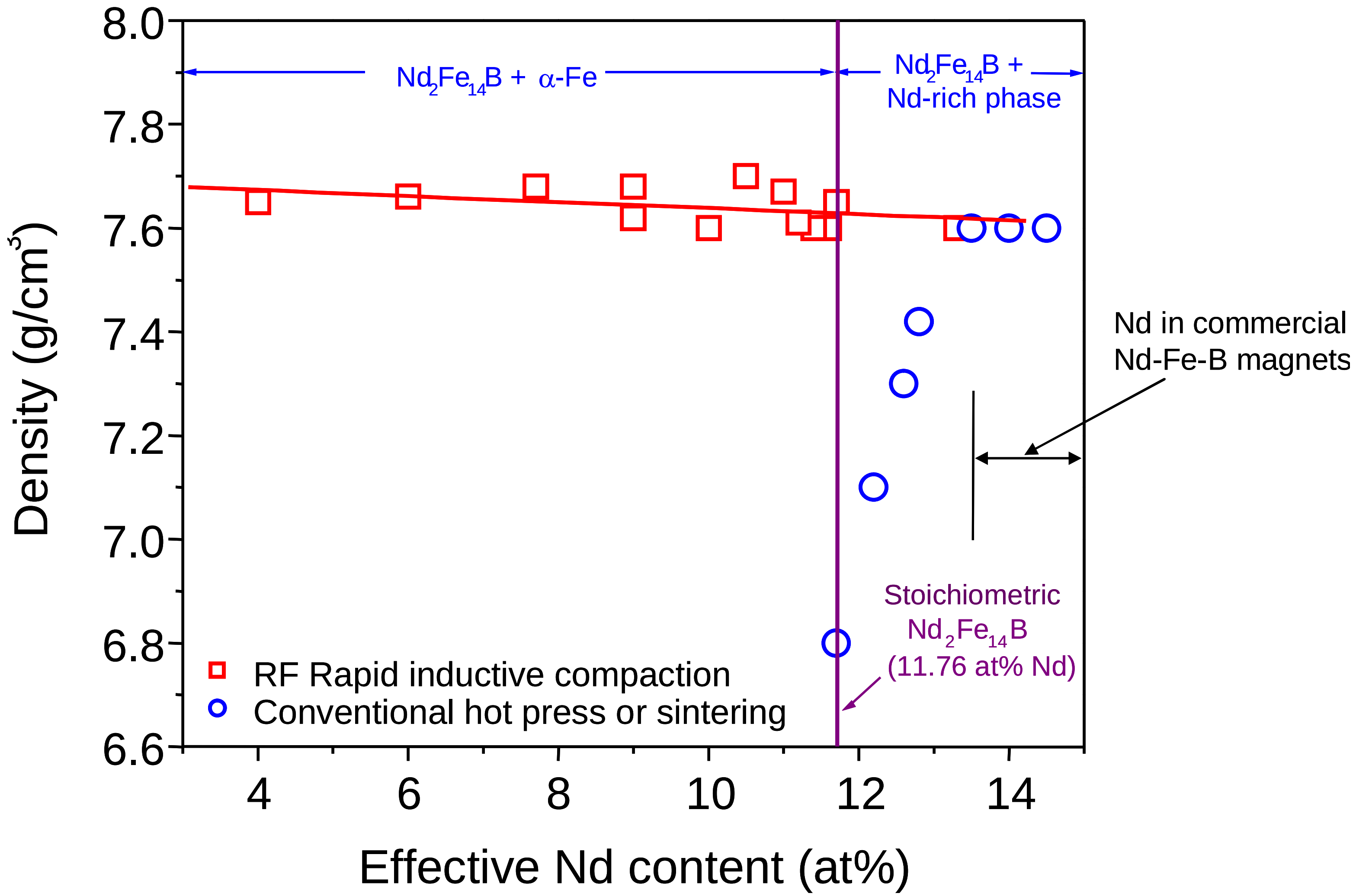
- **Relatively low temperature: 600 - 700℃**
- **Very short compaction time: ~ 2 minutes**
  - Heating from ~20℃ to the compaction temperature (around 700 ℃)
  - Performing hot compaction
  - Cooling to ~300℃
- **Relatively low pressure: 10^8 Pa**
- **Near full density can be obtained after the compaction**
- **Excessive grain growth can be avoided**
- **Low cost**

Nature of Hot Compaction

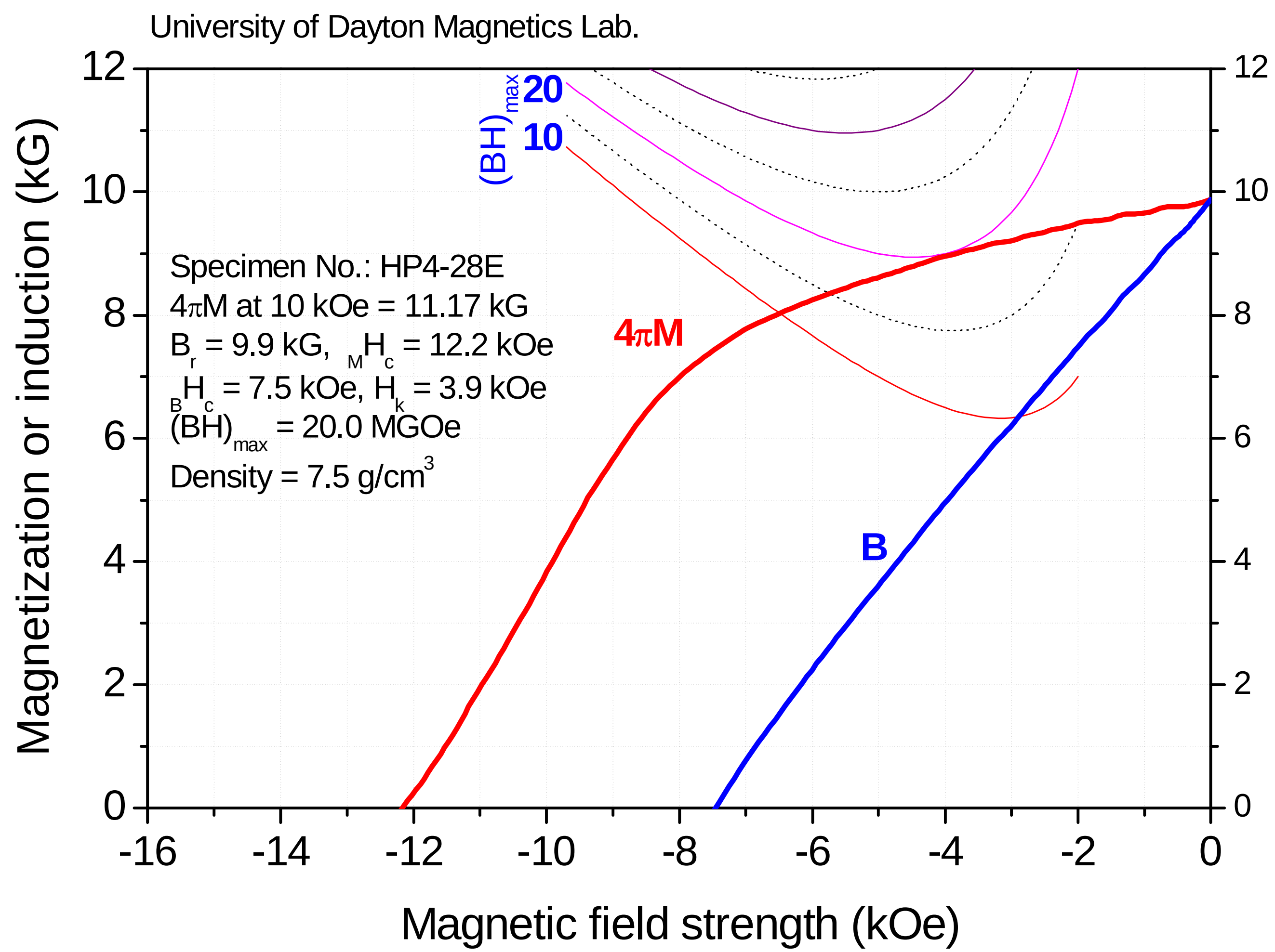
- ***A process of consolidation from powder to bulk material with near full density***

- ***A process of crystallization of an amorphous alloy and formation of a nanograin material***

Comparison of density values obtained using Inductive Hot Compaction and Conventional Consolidation



Isotropic Nanocomposite $Nd_{6.7}Pr_{4.3}Fe_{77.7}Co_{5.5}Ga_{0.2}Nb_{0.1}B_{5.5}$ Magnets

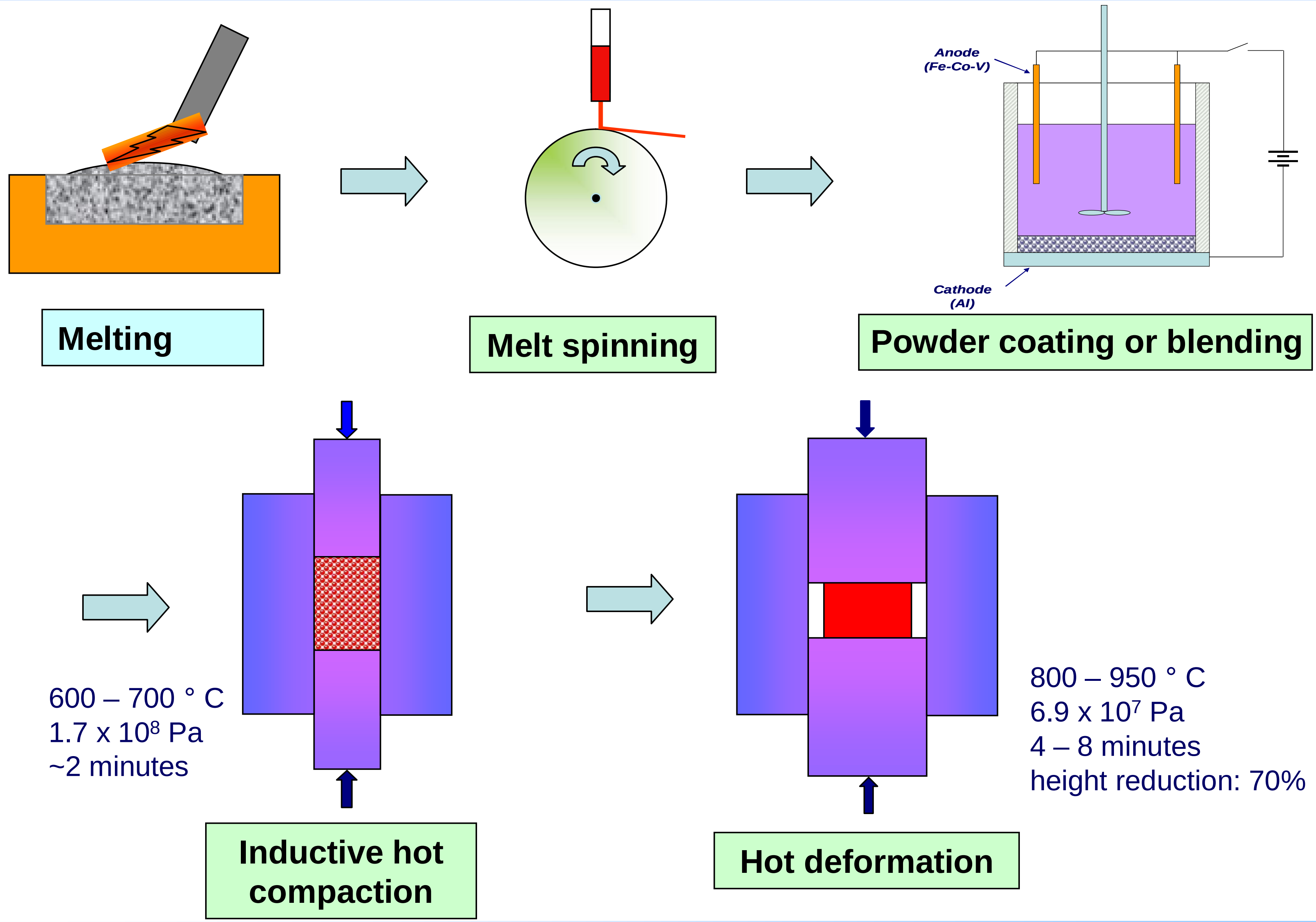


Technologies of Synthesizing Anisotropic Nanograin Composite Nd-Fe-B/Fe Magnets

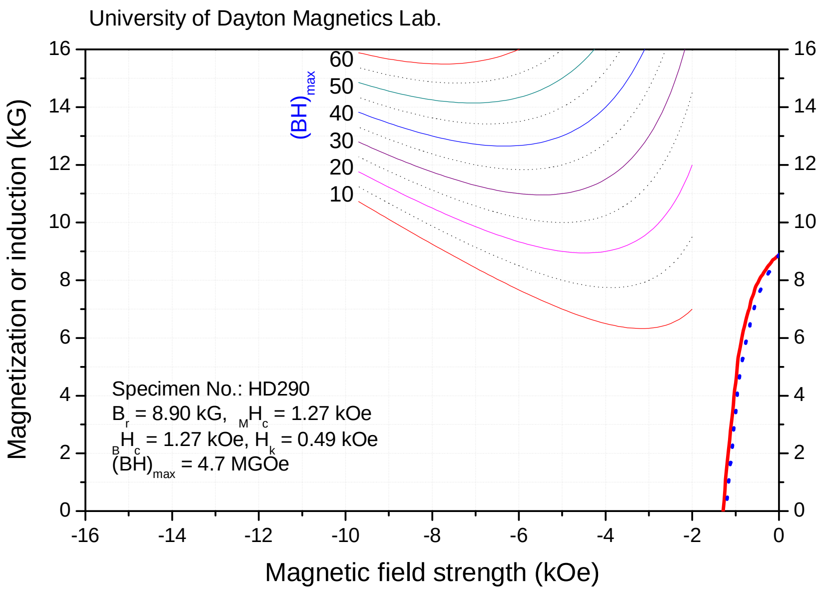
Hot compaction and hot deformation of

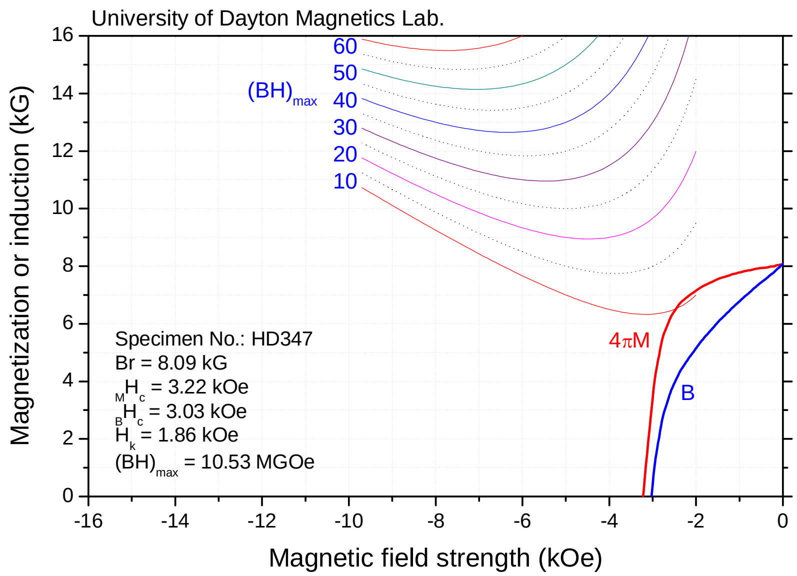
- ***A single Nd-poor Nd-Fe-B powder (Nd < 11.76 at%)***
- ***A powder mixture of a Nd-poor Nd-Fe-B powder (Nd < 11.76 at%) and a Nd-rich Nd-Fe-B powder (Nd > 11.76 at%)***
- ***A powder mixture of a Nd-rich Nd-Fe-B powder (Nd > 11.76 at%) and an α-Fe or Fe-Co powder***
- ***A Nd-rich Nd-Fe-B powder particles (Nd > 11.76 at%) coated with α-Fe or Fe-Co layers***

Processing


Anode
(Fe-Co-V)
Cathode
(Al)
Melting
Melt spinning
Powder coating or blending
600 – 700 ° C
1.7 x 10^8 Pa
~2 minutes
Inductive hot compaction
800 – 950 ° C
6.9 x 10^7 Pa
4 – 8 minutes
height reduction: 70%
Hot deformation

Processing a Single Nd-poor Nd-Fe-B Powder



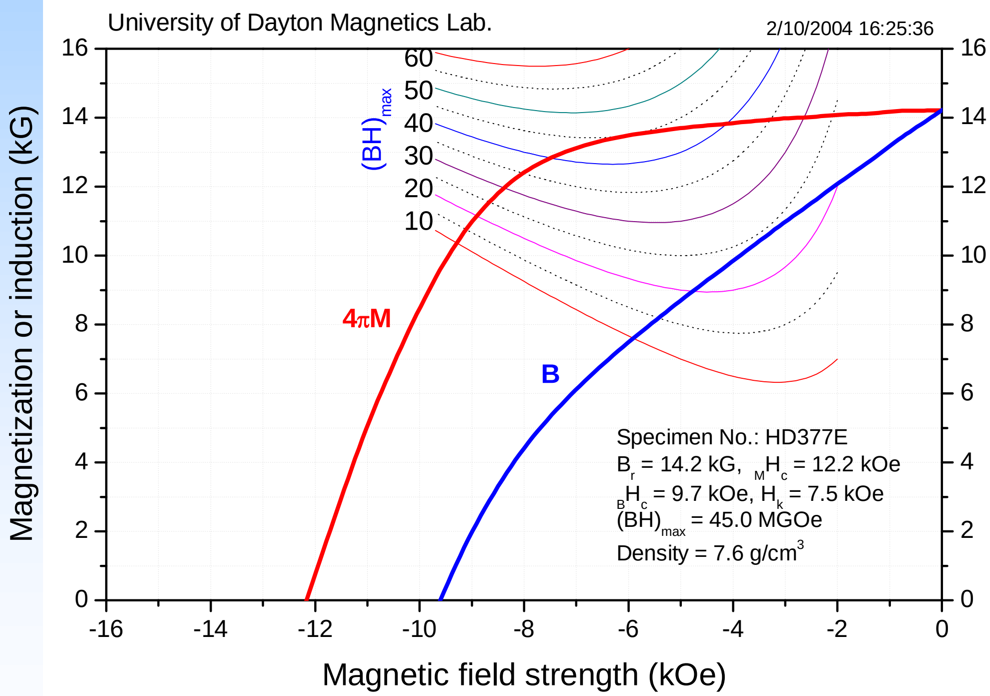


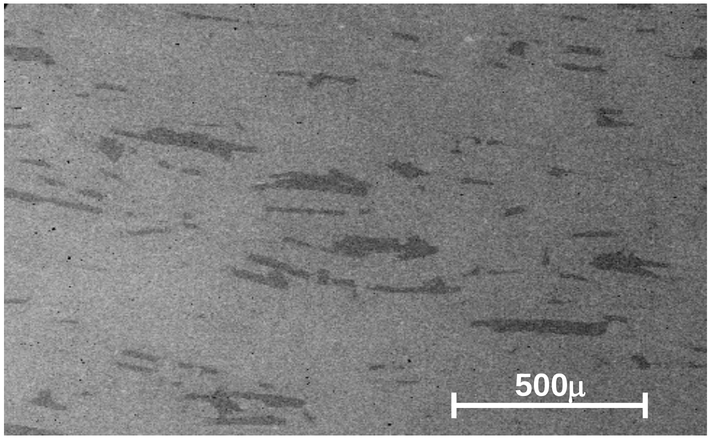
$Nd_{10.8}Pr_{0.6}Dy_{0.2}Fe_{76.3}Co_{6.3}Ga_{0.2}B_{5.6}$

$Nd_5Pr_5Dy_1Fe_{73}Co_6B_{10}$

Processing a Powder Mixture of a Nd-poor Nd-Fe-B Powder and a Nd-rich Nd-Fe-B Powder

$Nd_{10.8}Pr_{0.6}Dy_{0.2}Fe_{76.1}Co_{6.3}Ga_{0.2}Al_{0.2}B_{5.6}$ RE: 11 at% + 13.5 at% → 11.6 at%
Hot compaction：650 ℃—2 min，25 kpsi
Hot dformation：880 ℃ - 6 min, 10 kpsi , height reduction: 63%

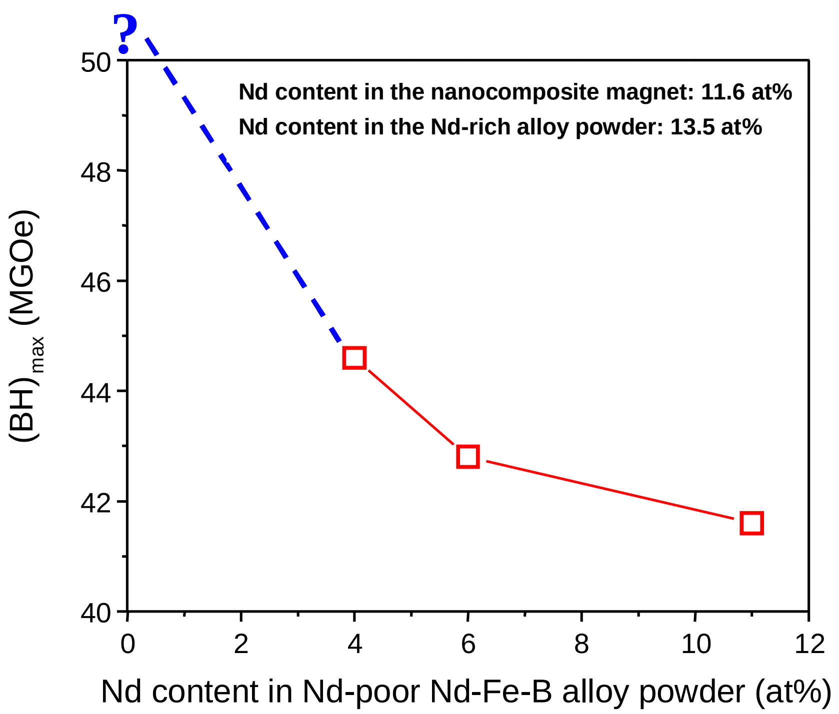


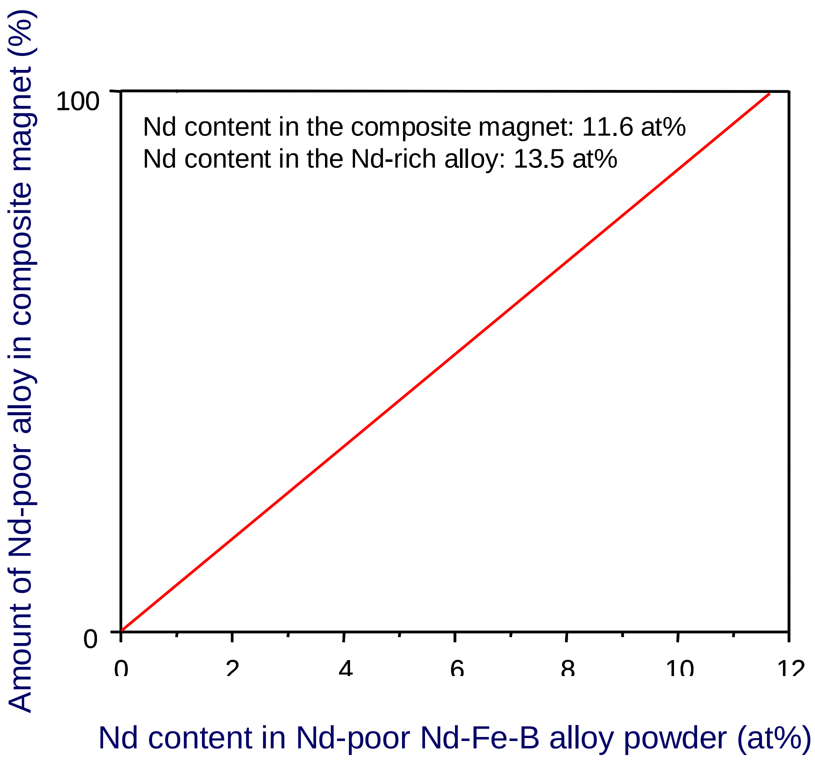


Dark gray phase: Nd-poor Nd-Fe-B: isotropic
Light gray phase: Nd-rich Nd-Fe-B: anisotropic

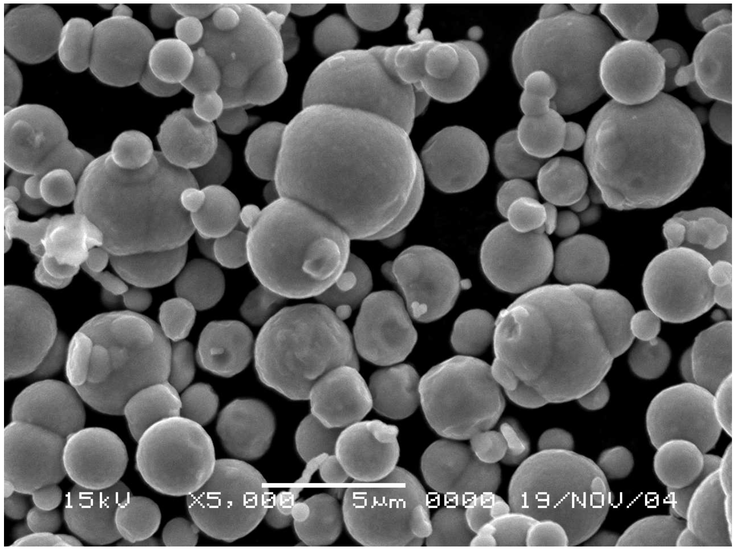
Effect of Nd Content in the Nd-Poor Nd-Fe-B Powder

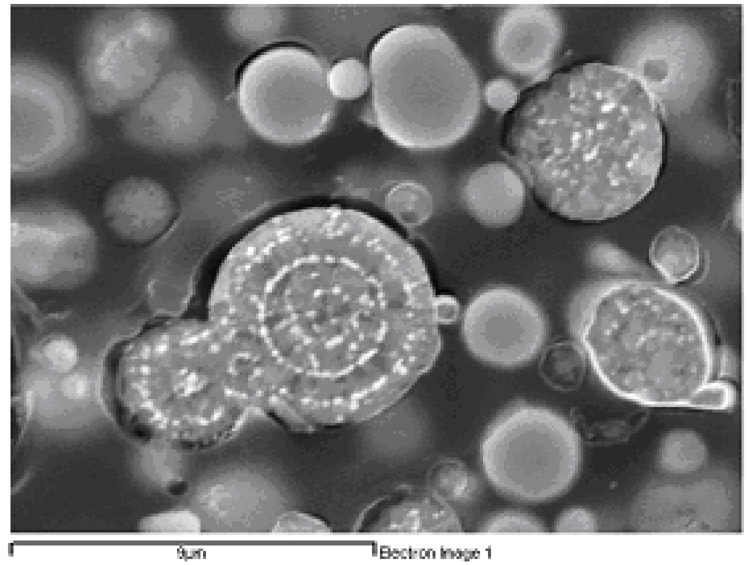
13.5 at% + 11 at% → 11.6 at%
13.5 at% + 6 at% → 11.6 at%
13.5 at% + 4 at% → 11.6 at%



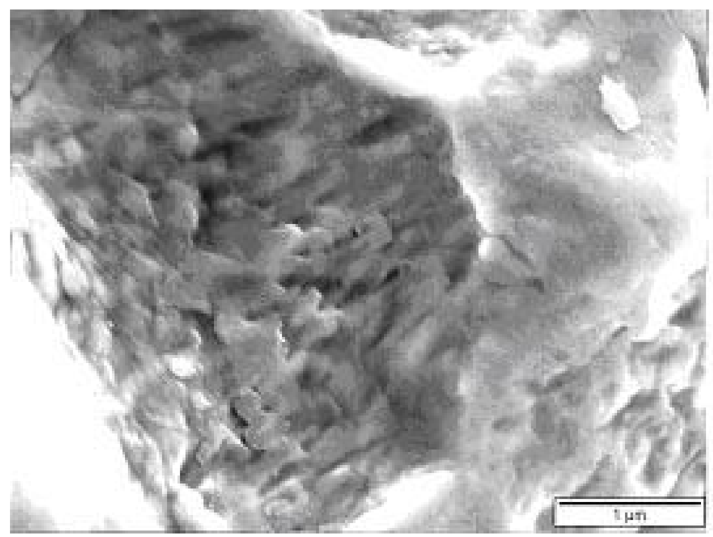


α-Fe and Fe-Co Powders Used



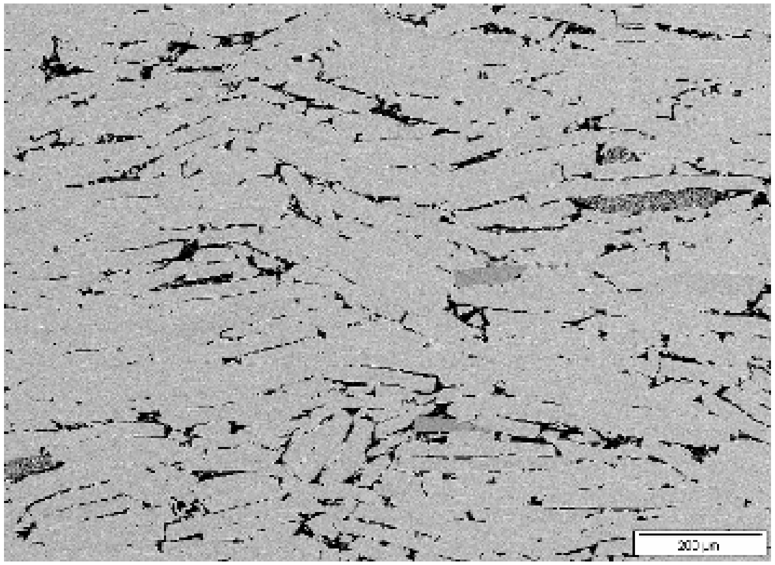


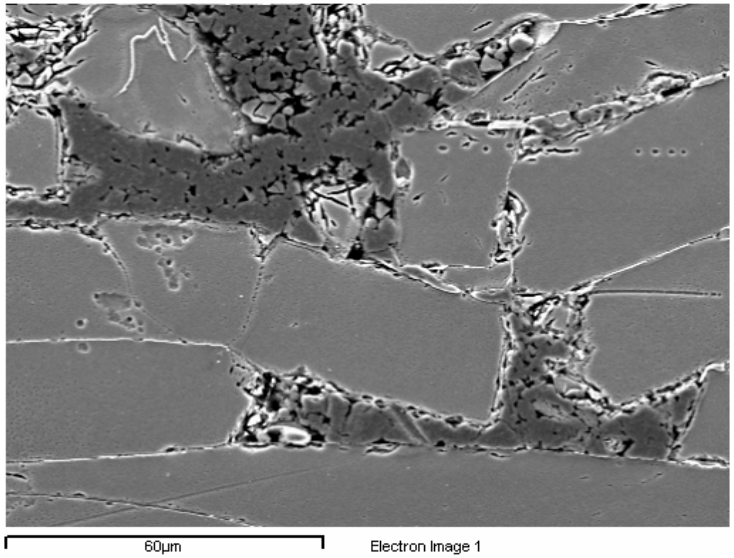
α-Fe



Fe-Co

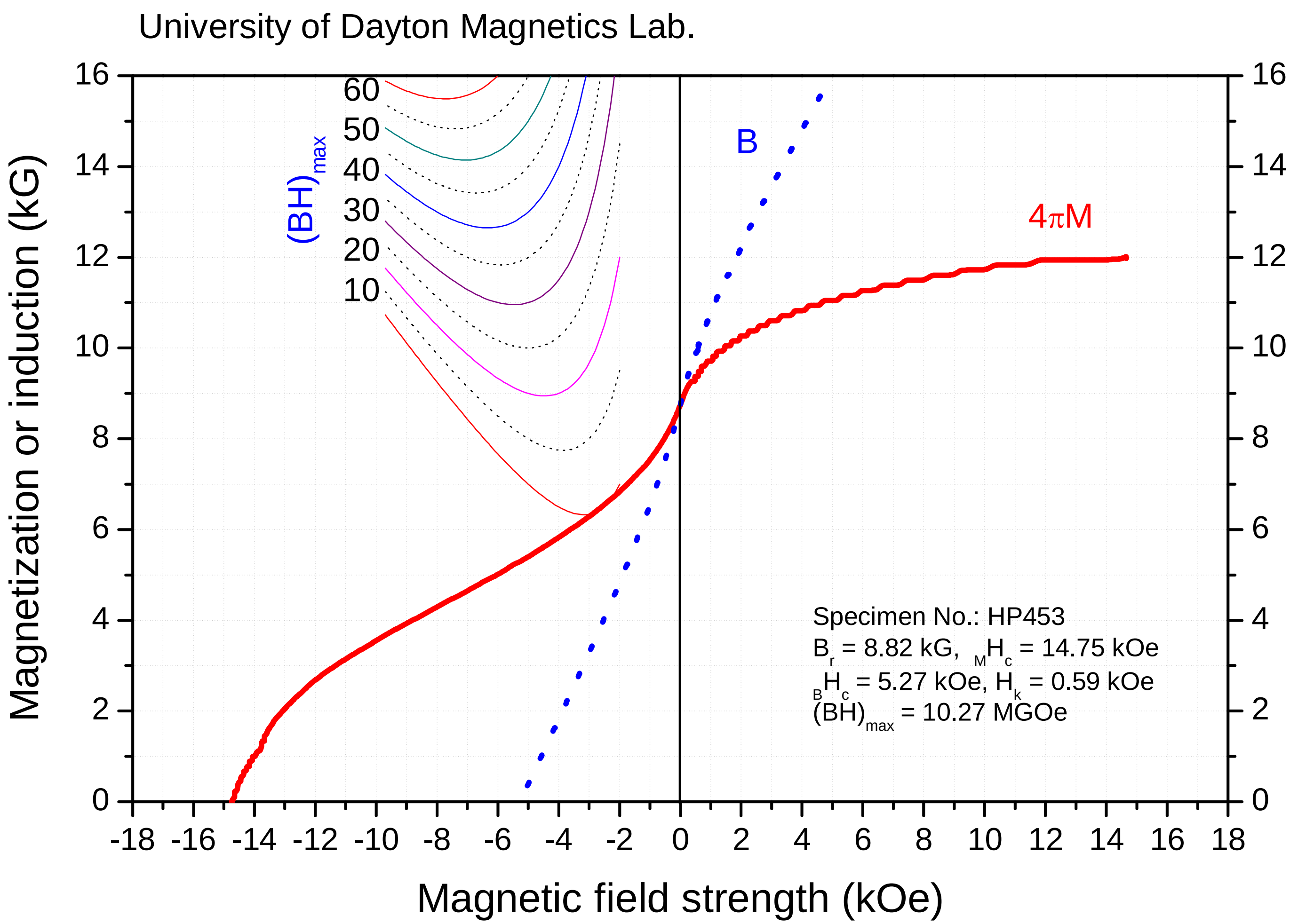
SEM Microstructure after Hot Compaction



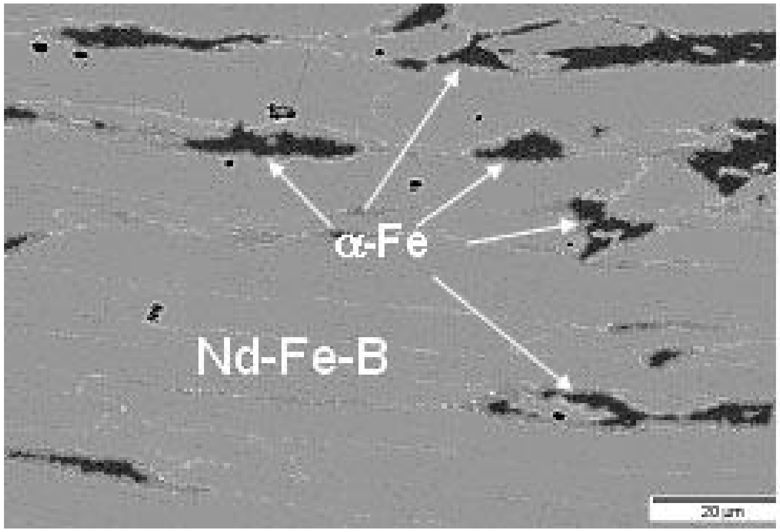


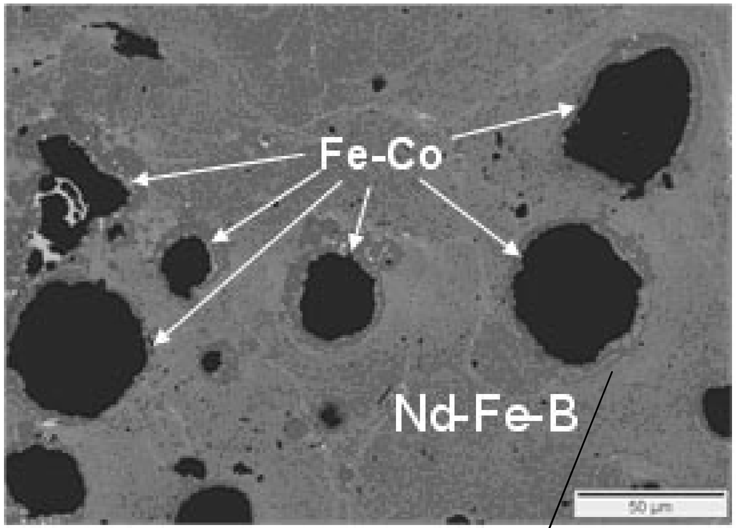
8 wt% α-Fe

Demagnetization Curve of Hot Compacted $Nd_{13.5}Fe_{80}Ga_{0.5}B_6$/ α -Fe (91.7%/8.3%)

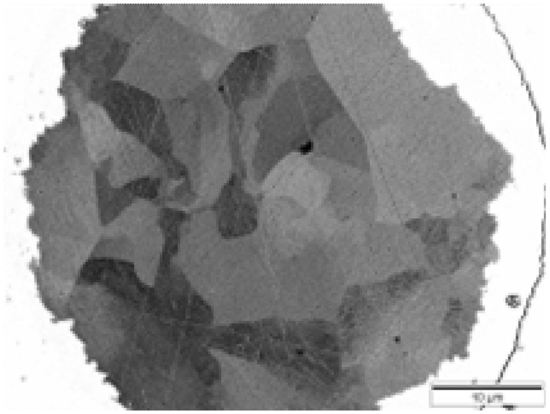


Microstructure of Nanograin Composite Nd-Fe-B/α-Fe and Nd-Fe-B/Fe-Co Magnets

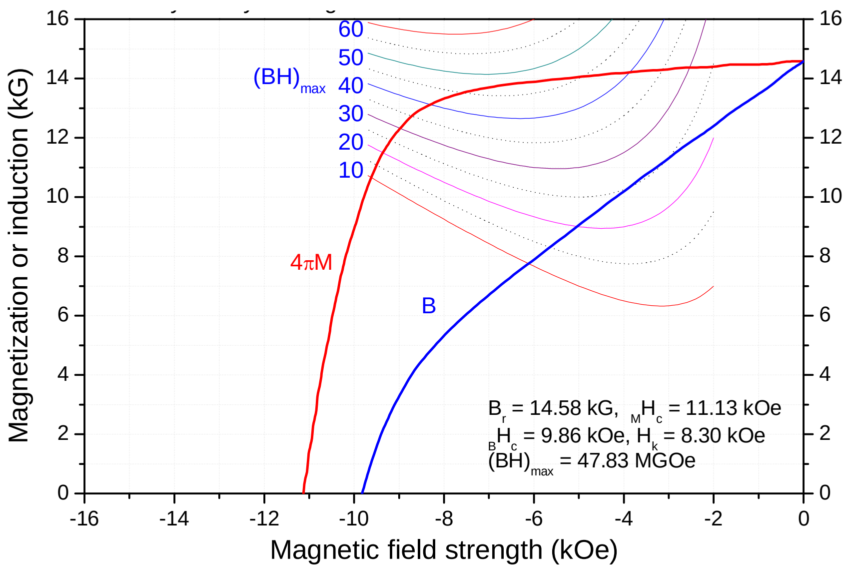


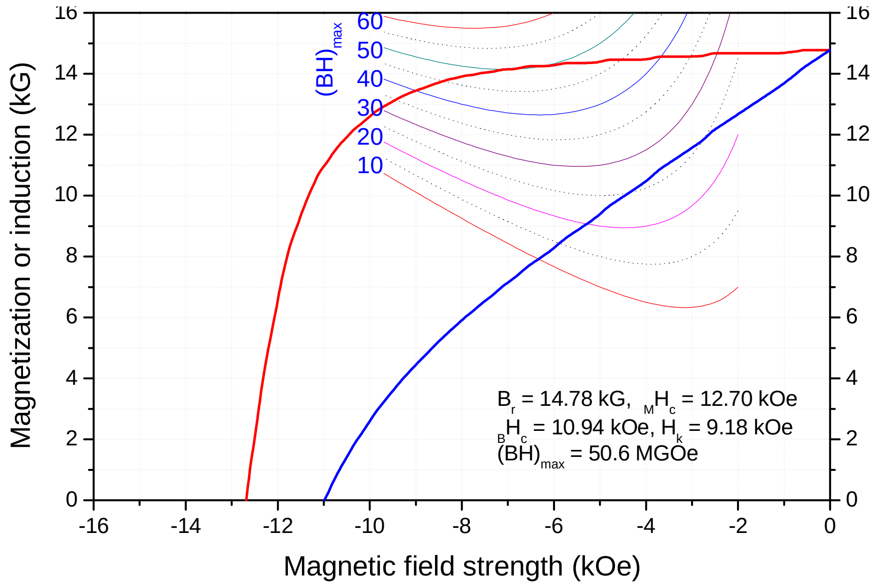


- **α-Fe powder**
  - Tend to be agglomerated
  - Form large soft phase
    - Length: 10 – 30 microns
    - thickness: 5 – 10 microns
- **Fe-Co powder**
  - Size of soft phase: 5 – 40 microns



Demagnetization Curves of Hot Deformed Composite Magnets

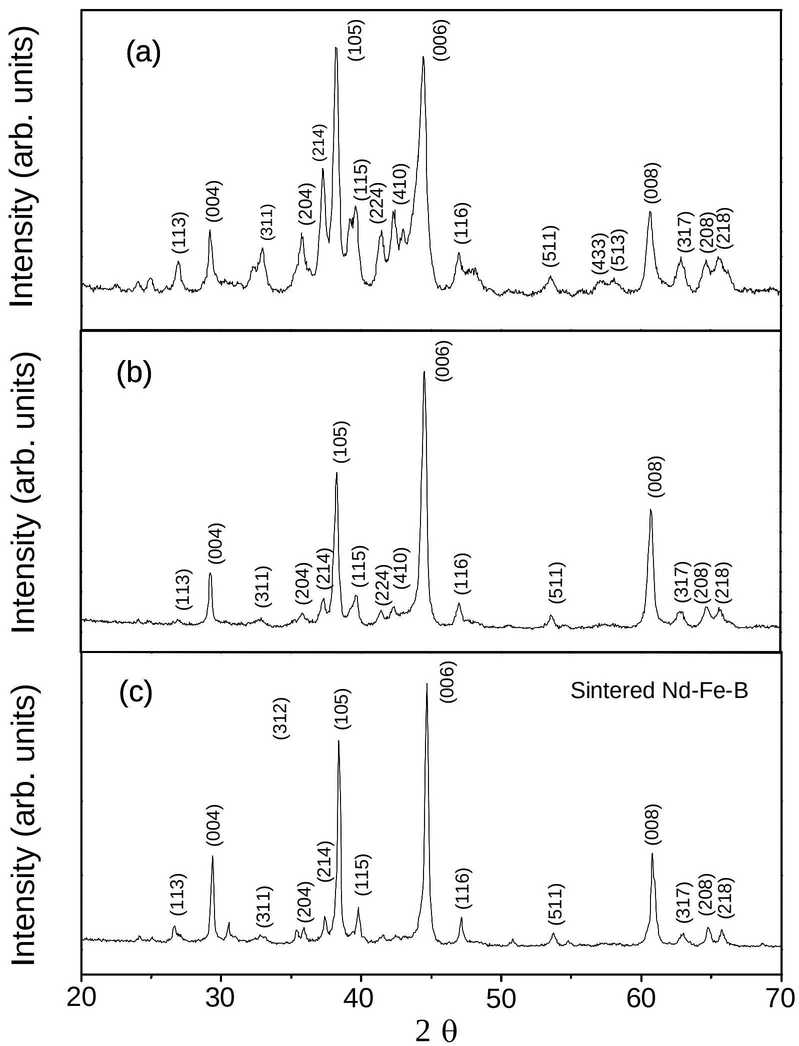




$Nd_{13.5}Fe_{80}Ga_{0.5}B_6/\alpha$-Fe (95 wt%/5 wt%)

$Nd_{13.5}Fe_{80}Ga_{0.5}B_6$/Fe-Co (95 wt%/5 wt%)

Comparison of XRD Patterns



(a) ***A magnet made by blending a Nd-poor Nd-Fe-B and a Nd-rich Nd-Fe-B with $(BH)_{max} \approx 40$ MGOe***

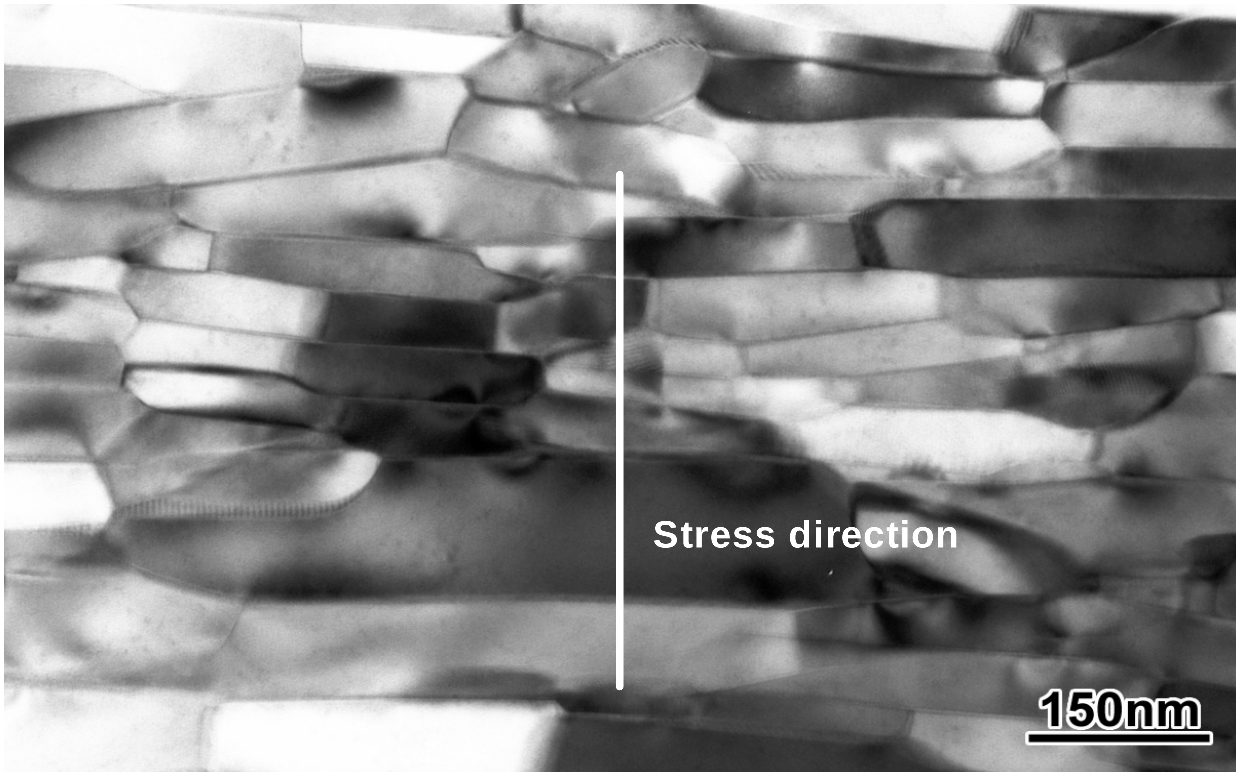
(b) ***A magnets made by blending a Nd-poor Nd-Fe-B with a commercial a-Fe powder with $(BH)_{max} \approx 50$ MGOe***

(c) ***A sintered Nd-Fe-B magnet with $(BH)_{max} \approx 40$ MGOe***

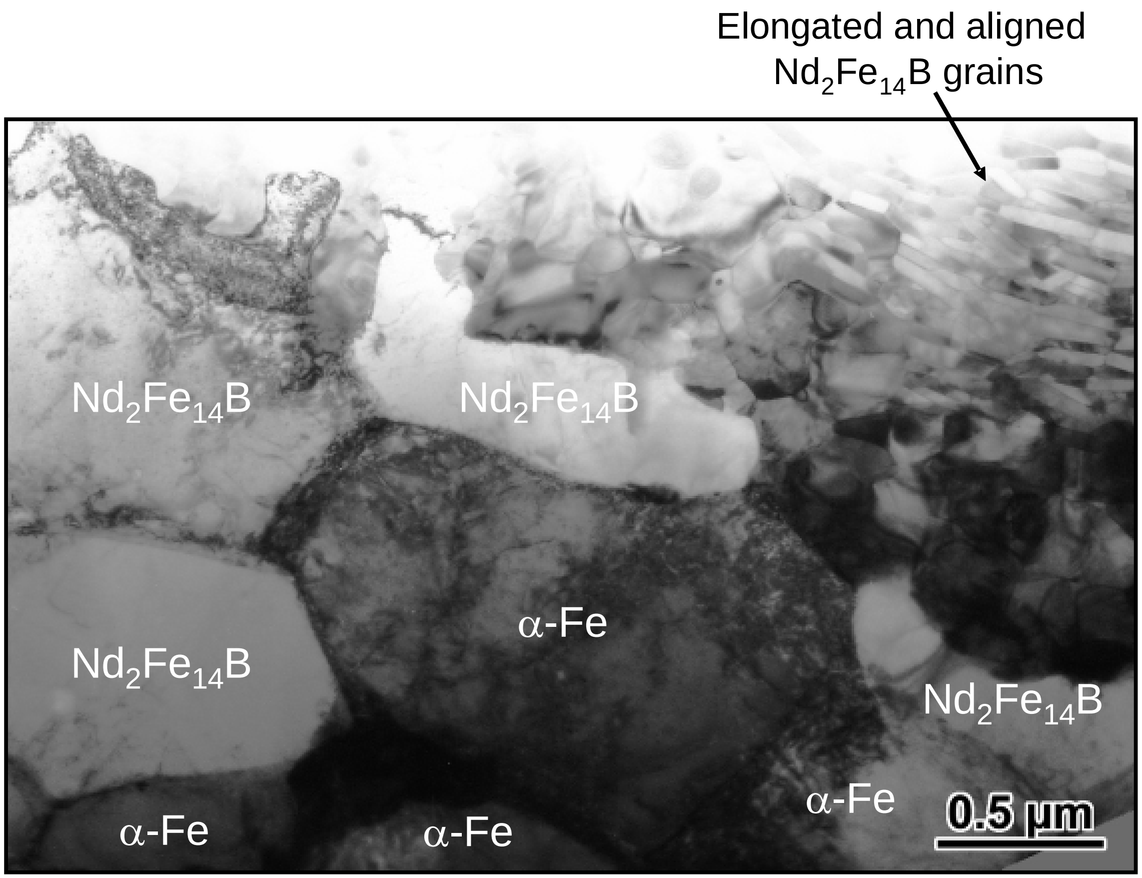
Better grain alignment:

- ***Enhanced (004), (006), and (008) intensity***
- ***Greater than 1 (006)/(105) ratio***

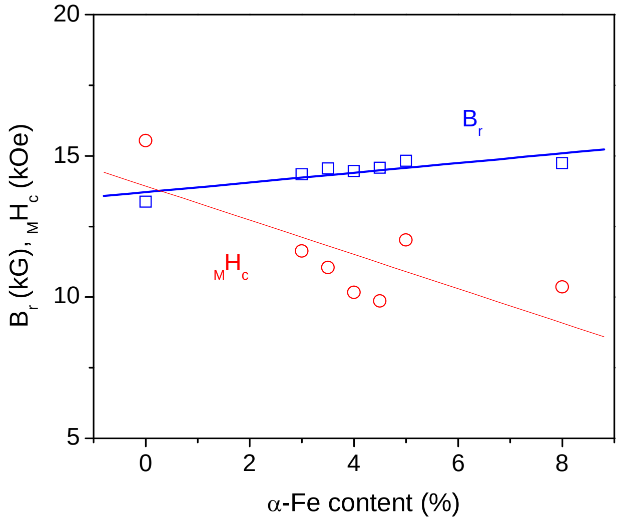
TEM Micrograph of $Nd_{13.5}Fe_{80}Ga_{0.5}B_6$/ α -Fe (95%/5%) Composite Magnet

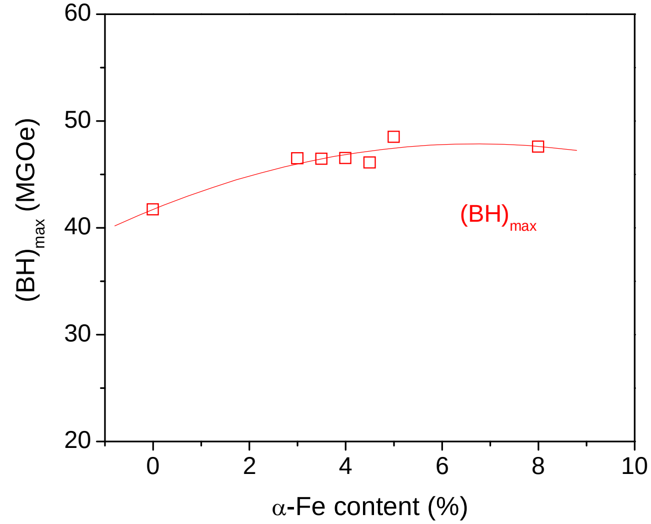


Hard/Soft Interface of $Nd_{13.5}Fe_{80}Ga_{0.5}B_6$/ α -Fe (95%/5%) Composite Magnet

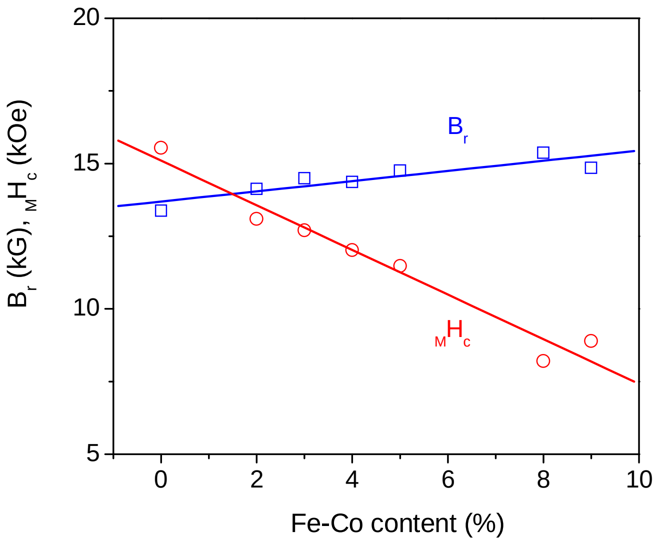


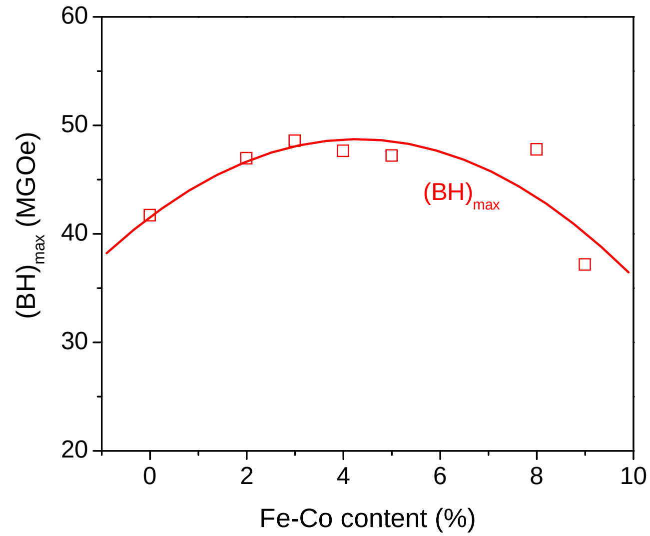
Effect of Amount of Soft Phase





Nd-Fe-B/ α-Fe





Nd-Fe-B/ Fe-Co

Comparison of three Types of Composite Magnets

- **Type I:**

A single *Nd-Fe-B* alloy ---------→ Isotropic

$(BH)_{max}$ = ~10 MGOe

- **Type II:**

Nd-rich *Nd-Fe-B* alloy ---------→ Anisotropic

\+

Nd-poor *Nd-Fe-B* alloy ---------→ Isotropic

(Anisotropic + Isotropic) → Mixture

$(BH)_{max}$ = 35 - 45 MGOe

- **Type III:**

Nd-rich *Nd-Fe-B* alloy ---------→ Anisotropic

\+

α-Fe or Fe-Co: Does not have to be aligned

May improve grain alignment
of the hard phase under certain conditions

$(BH)_{max}$ = 45 - 55 MGOe

Significance of this Technology

- ***The upper limit of the soft phase predicted by the current model of interface exchange coupling is around 20 – 30 nm***
- ***The size of the soft phase can be 1000 times larger than this dimension***
- ***This technology is very cost effective***
- ***This technology leads to a new type of nanograin composite magnets***

A New Type of Nanograin Composite Nd-Fe-B/α-Fe Magnets

- ***Grain size*** → ***nanocomposite***
  - *Hard phase: nanometer range*
  - *Soft phase: nanometer range*
- ***Phase size*** → ***microcomposite***
  - *Hard phase: micrometer range*
  - *Soft phase: micrometer range*
- ***The overall Nd content in a composite magnet***
  - *Can be*
    - *< 11.76 at%*
    - *= 11.76 at% (stoichiometry)*
    - *> 11.76 at%*
- ***A Nd-rich phase and an α-Fe (or Fe-Co) phase can co-exist simultaneously***
- ***Composite magnet is in a non-equilibrium condition***

Effect of Soft Phase and Ideal Microstructure

- ***Effect of adding the soft phase***
  - *Enhance magnetization*
  - *Decrease coercivity*
- ***The Coercivity drop depends on***
  - *The amount of soft phase*
  - ***The size and distribution of the soft phase***
- ***Ideal microstructure***
  - *Soft phase*
    - *Very small size*
    - *Highly dispersed*
    - *Uniformly distribution*
  - *Hard phase*
    - *Nanograins*
    - *Good grain alignment*

Current Technical Difficulties

- ***Very large soft phase***
  - *Large particle size*
  - *Particle agglomeration*

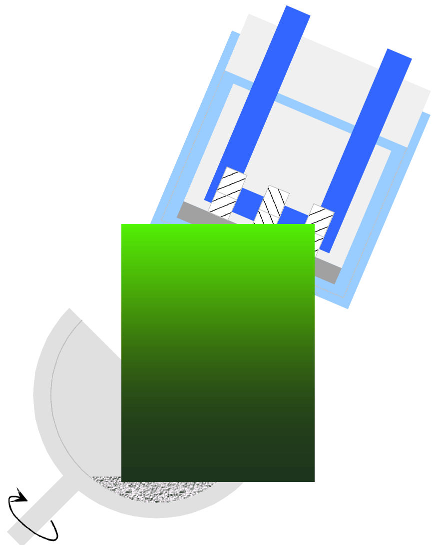
- ***Increased oxygen pickup with reducing particle size of soft phase***

- ***Increased trend of agglomeration with reducing particle size of soft phase***

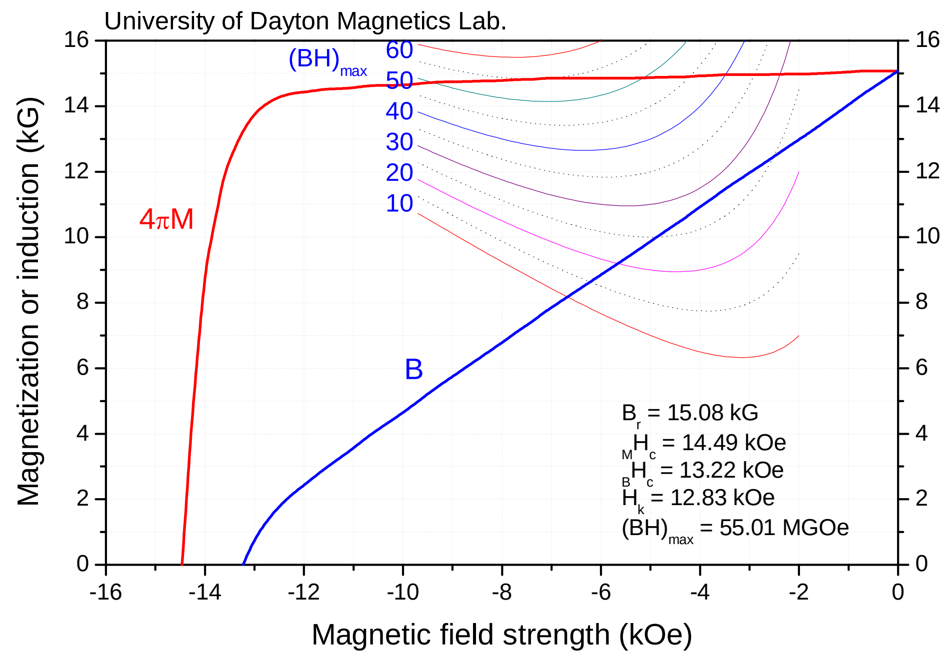
Powder Coating Technologies

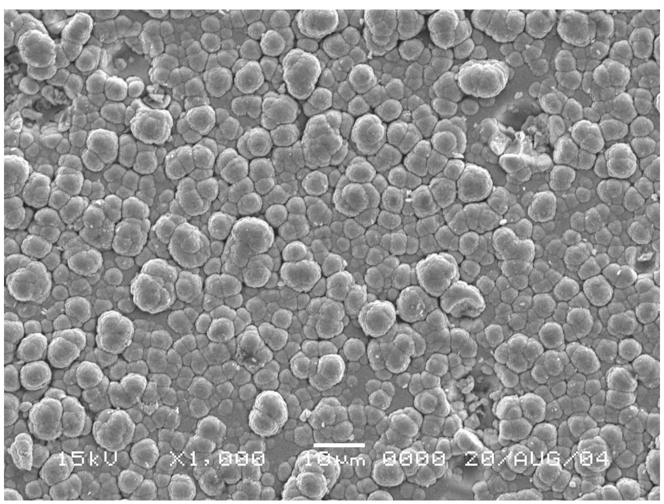
- *DC & RF sputtering*
- *Pulsed laser deposition (PLD)*
- *Chemical (electroless) coating*
- *Electrolytic coating*

Sputtering



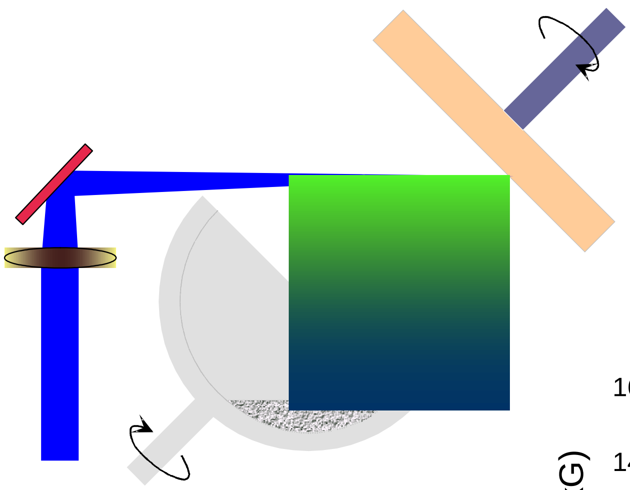
- ***Target: α-Fe, Fe-Co-V***
- ***Argon pressure: 15 mtorr***
- ***Sputtering time: 15 min to 20 hours***



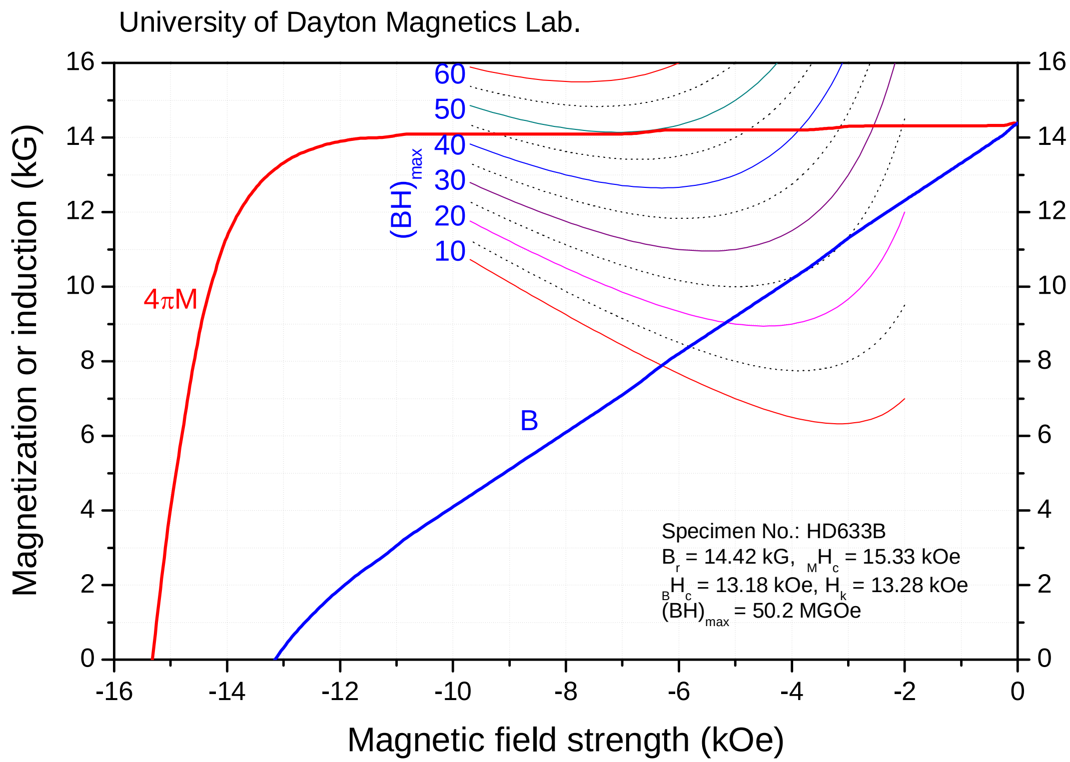


$Nd_{14}Fe_{79.5}Ga_{0.5}B_6$/ α -Fe, DC sputtering for 20 hours,
hot compacting at 630 ° C for 2 minutes,
and die upsetting at 930 ° C for 4 minutes

Pulsed Laser Deposition



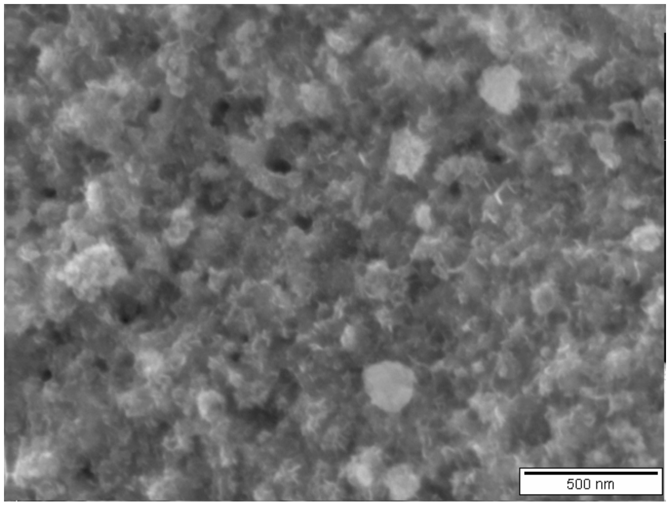
- *Target: α-Fe or Fe-Co-V*
- *Laser: Nd:$Y_3Al_5O_{12}$ (λ = 1064 nm), 340 mJ/pulse and 10 Hz*
- *Time**:** 15 min to 20 hours*

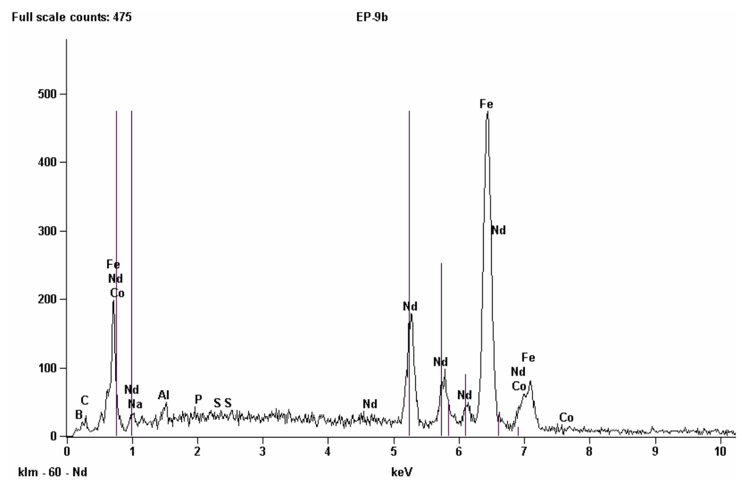


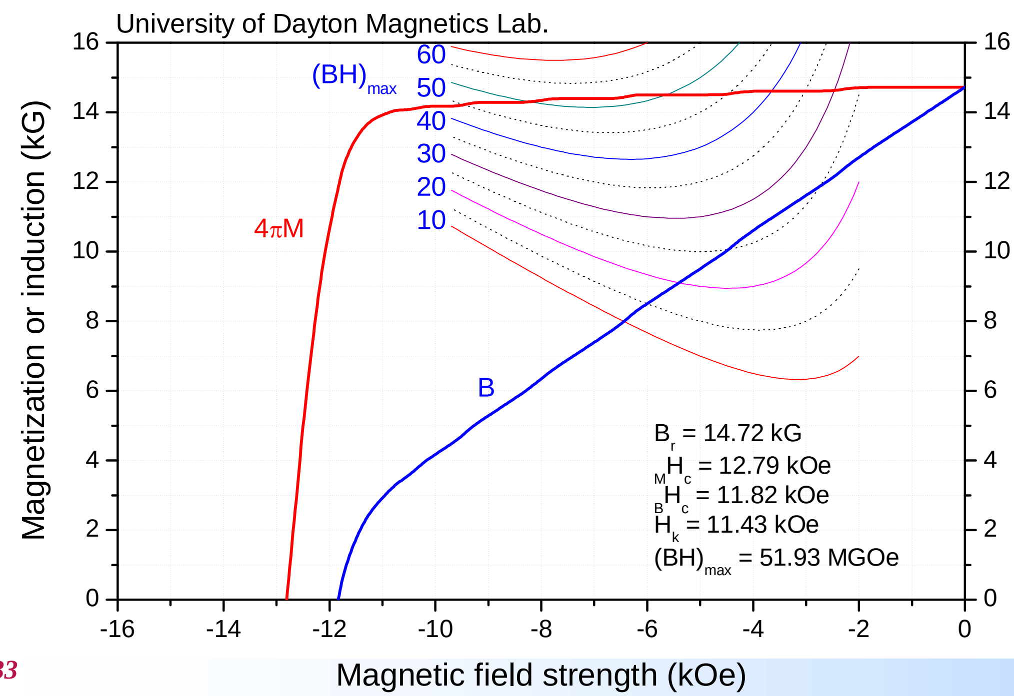
Chemical Coating

- ***Chemical coating conditions***
  - *Ion source: $FeCl_2$, $CoCl_2$, or $FeSO_4$, $CoSO_4$*
  - *Reducing agent: NaH_2PO_2*
  - *Complexing agent: $Na_3C_6H_5O_7$*
  - *pH value: 5 – 8*
  - *Temperature: 20 – 50 ° C*
  - *Time: 15 m – 3 hours*
- ***Advantage of chemical coating***
  - *Many parameters can be controlled*
  - *A short-time process*
  - *Cost effective and suitable for production*

Results of Chemical Coating

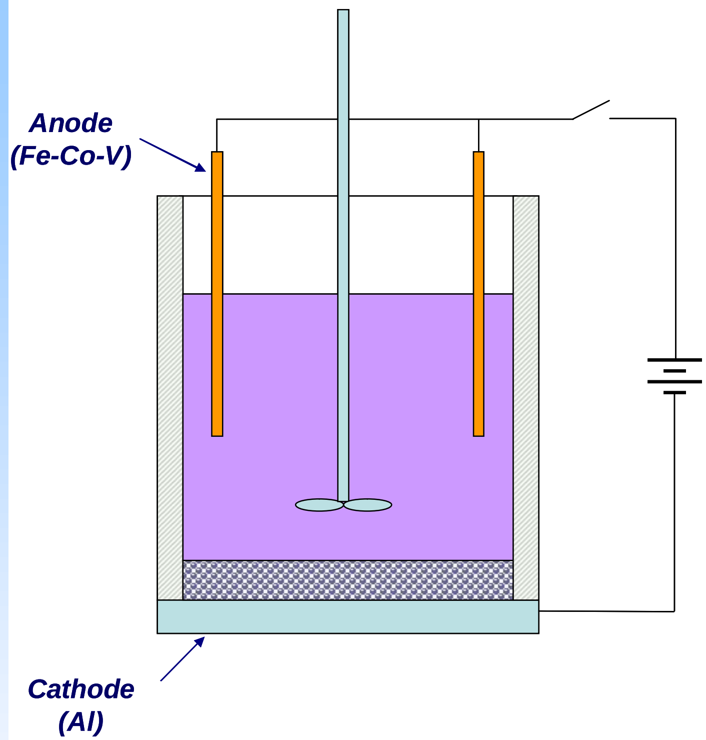






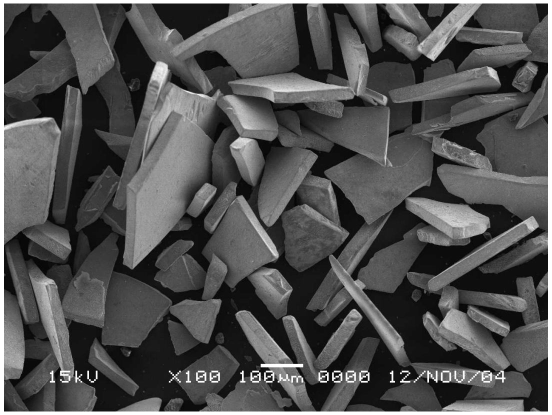
- **Low oxygen pick up**
- **Low deposition rate**
- **Only a small portion of particles could be coated**

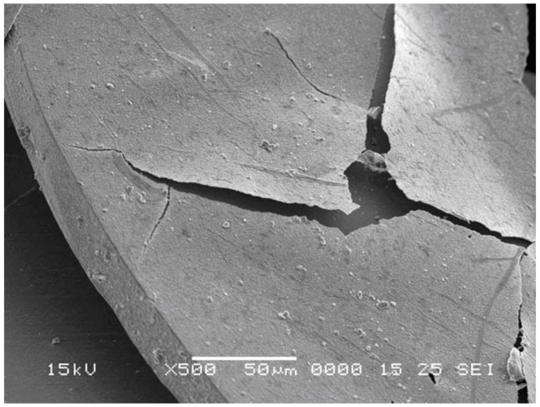
Electrolytic Coating Apparatus

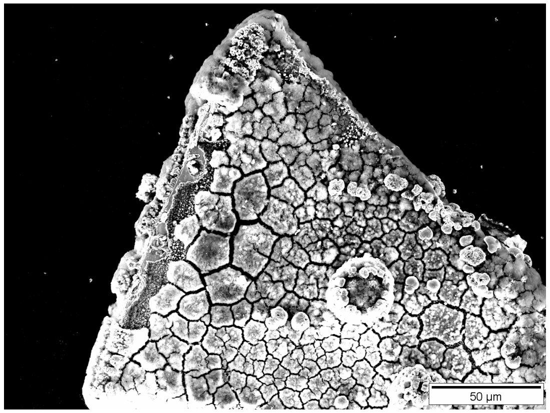


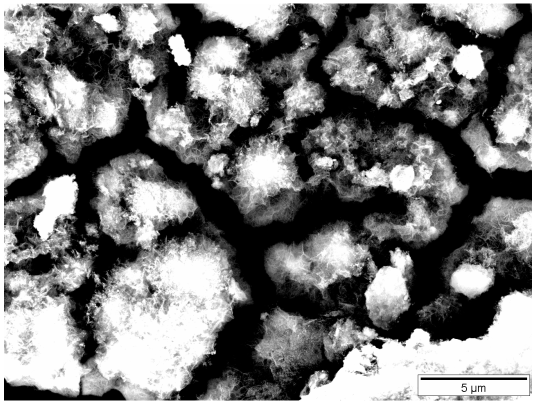
- Solution: $FeSO_4 \cdot 7H_2O$ at 0.3 mol/l with an addition of $MgSO_4 \cdot 4H_2O$ at 0.3 mol/l
- pH value: 2 – 3
- Time: 15 min – 2 hours
- Anode: α-Fe or Fe-Co-V
- Cathode: Al
- cathode current density was 0.5 to 5 A/dm^2

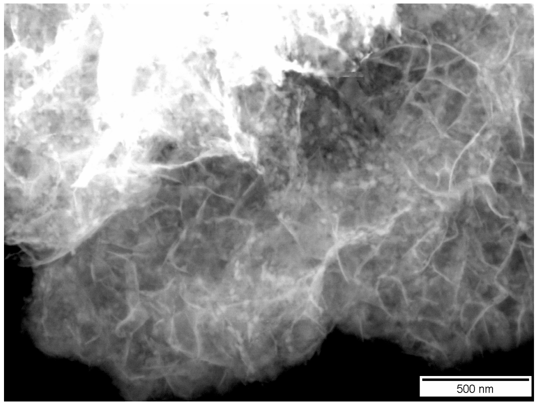
Surface Morphology of Coated Particles

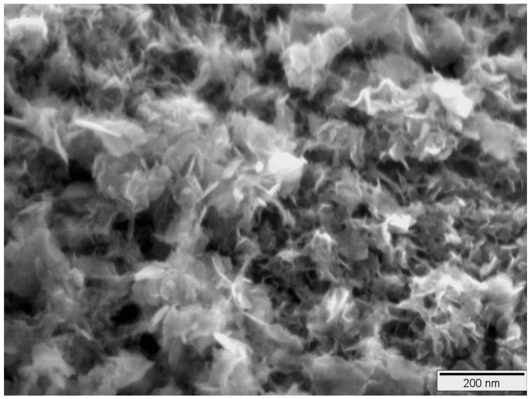




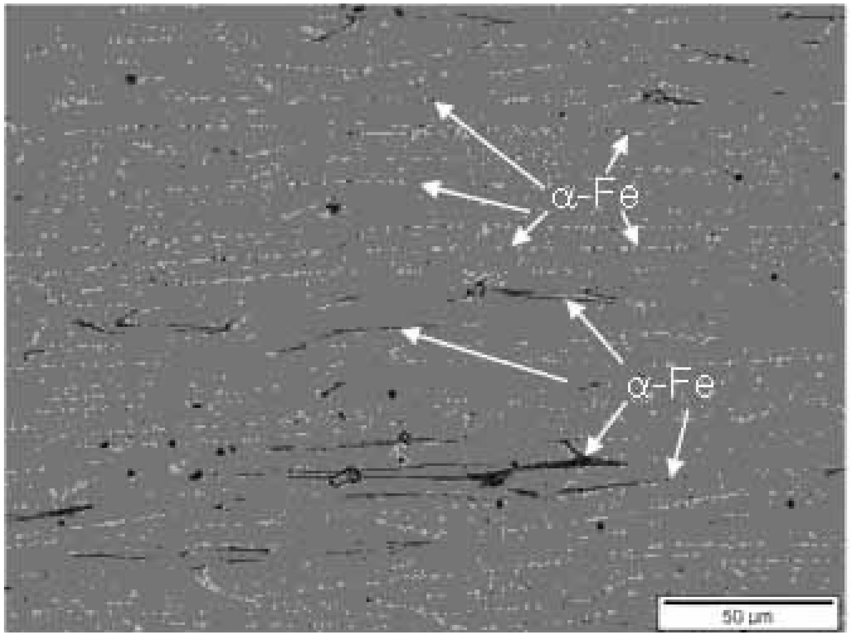


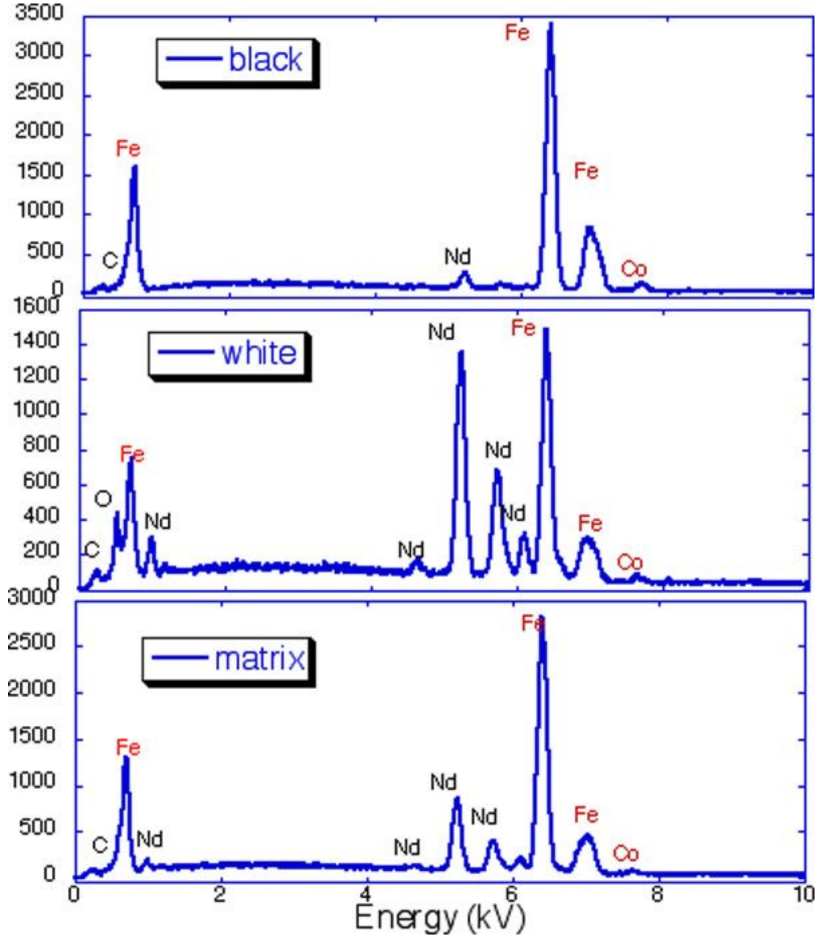




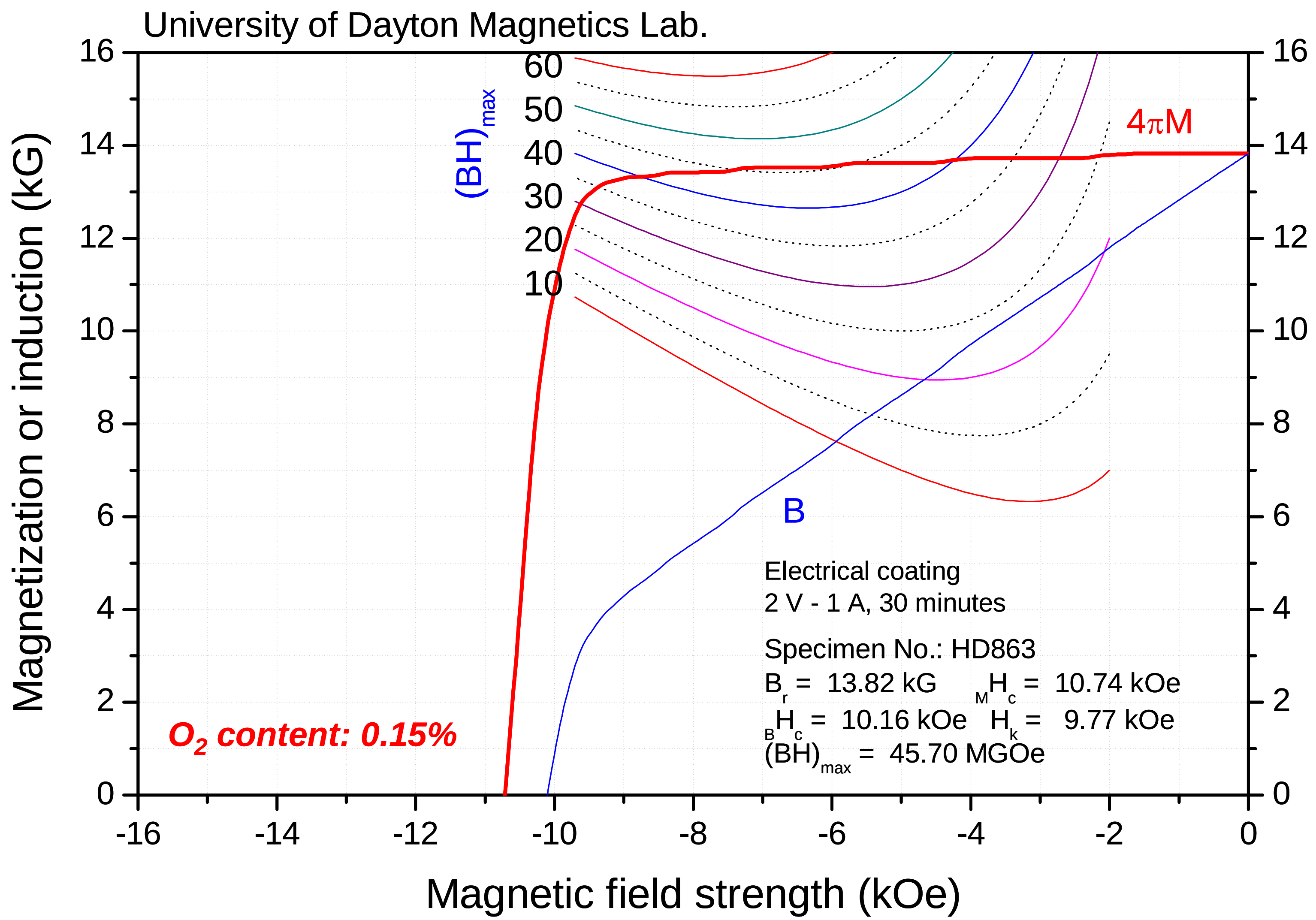


SEM/EDS Results

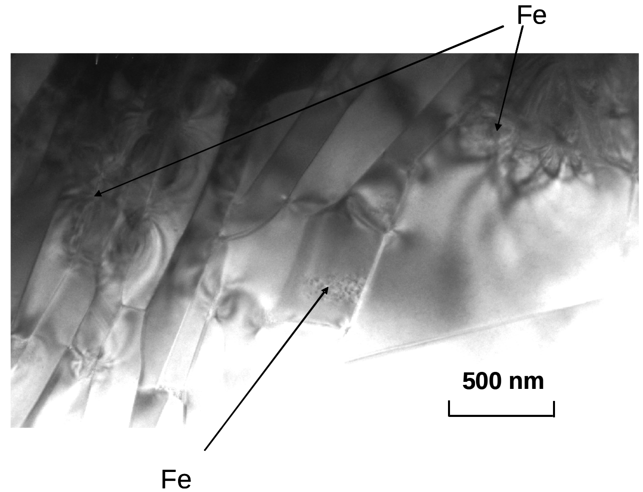


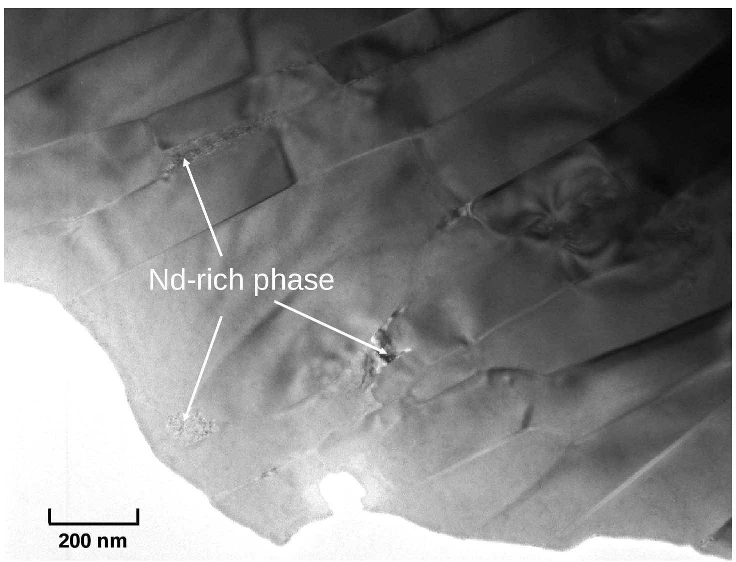


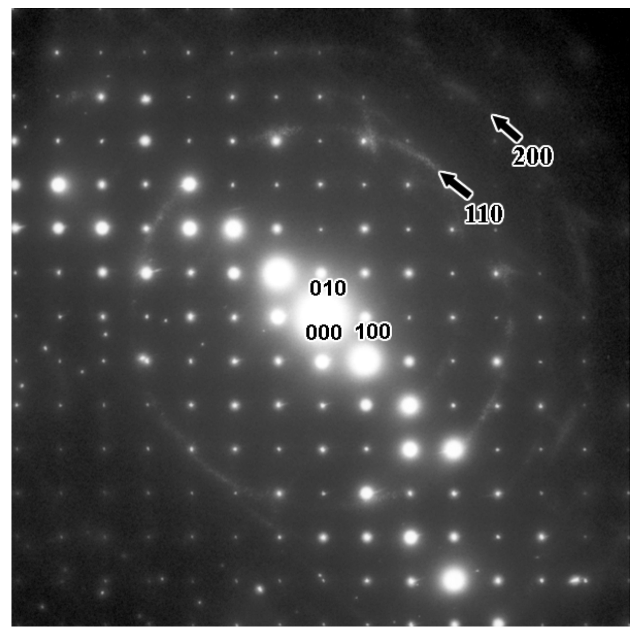
Demagnetization Curves



TEM Micrographs

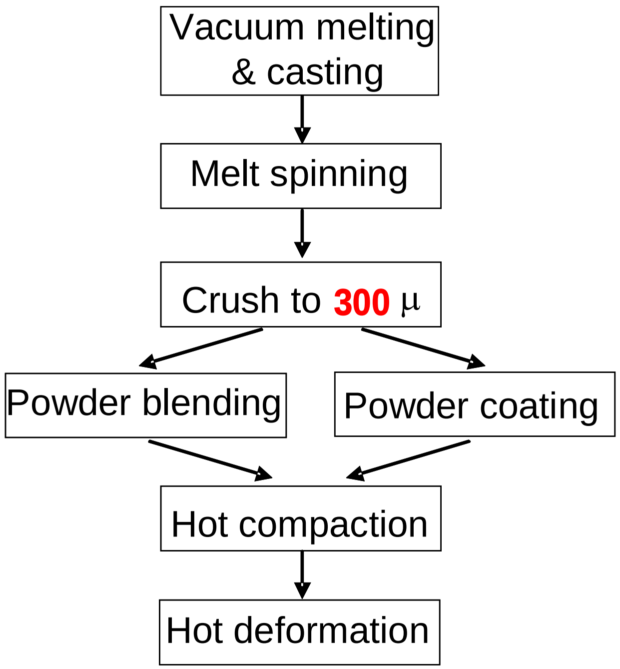




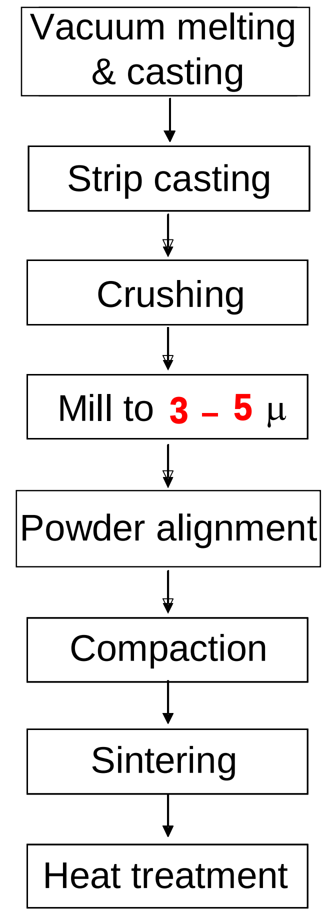


Comparison of Processes

Nanograin composite Nd-Fe-B/α-Fe magnet



Conventional sintered Nd-Fe-B magnet



Advantage of Nanograin Composite Magnets

- *Potential for higher magnetic performance*
- *Potential for lower price*
  - *Lower rare earth content*
  - *Fewer processing steps*
- *Better corrosion resistance*
  - *Lower rare earth content*
  - *Especially when Nd-Fe-B particles are coated with α-Fe or Fe-Co layers*
- *Better fracture resistance*
  - *The soft phase has relatively higher toughness*
  - *Fine nanograin structure*

Conclusions

- *Bulk nanograin composite magnets with full density can be readily obtained by using rapid inductive hot compaction*
- *Anisotropic nanograin composite magnets with very good grain alignment can be obtained by hot compaction and hot deformation of Nd-rich Nd-Fe-B powder particles coated with α-Fe or Fe-Co layers*
- *New technologies lead to a new type of nanograin composite magnets*
- *Better powder blending and coating techniques are to be established*