Replacement and Original Magnet Engineering Options

Spomenka Kobe, Paul McGuiness, Michael Coey
The consortium groups:

- the best European academic expertise in permanent magnetism
- with the leading European magnet manufacturer and
- the group of European companies who are eager to exploit the new magnets.
### The strongest R/D Groups in Europe active in the field

<table>
<thead>
<tr>
<th>Organization</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leibniz Institute for Solid State and Materials Research, Dresden, DE</td>
<td>DE</td>
</tr>
<tr>
<td>Institut Néel, Grenoble, FR</td>
<td>FR</td>
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<tr>
<td>Trinity College, Dublin, IE</td>
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<tr>
<td>St. Pölten University of Applied Sciences, AT</td>
<td>AT</td>
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<tr>
<td>Vienna University of Technology, AT</td>
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<tr>
<td>Jožef Stefan Institute, Ljubljana, SI</td>
<td>SI</td>
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<tr>
<td>Vacuumschmelz, GmbH, DE</td>
<td>DE</td>
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<tr>
<td>KOLEKOTOR Worldwide, SI</td>
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</tr>
<tr>
<td>SIEMENS, GmbH, DE</td>
<td>DE</td>
</tr>
<tr>
<td>DAIMLER, DE</td>
<td>DE</td>
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<tr>
<td>VALEO, FR</td>
<td>FR</td>
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</table>
Outline

- Current situation and foreseen solutions
- Grain Boundary Engineering
  - EPD – preliminary results
Current situation and foreseen solutions
Permanent magnets through the century

PM based on RE are increasingly important in **environmentally critical** technologies:
- for wind turbines
- hybrid and
- pure electric vehicles
  (HEVs and EVs).

Improving magnetic properties in the past 100 years.
Effect of temperature on magnetic properties for a variety of magnetic materials
Supply risk and economic importance of 14 critical raw materials
US and Japan Actions

The main goal of those projects is to lead to > 2000 kA/m coercivity values, which is a vital requirement for magnets to be used in EVs, HEVs and large wind turbines.

<table>
<thead>
<tr>
<th>AGENCY</th>
<th>PROJECT</th>
<th>INSTITUTION</th>
<th>VALUE</th>
<th>SUBJECT</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARPA-E (US)</td>
<td>High Energy Permanent Magnets for Hybrid Vehicles and Alternative Energy</td>
<td>Univ of Delaware</td>
<td>$4.5m</td>
<td>Magnets based on Fe-, Co- or Mn-rich materials.</td>
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<tr>
<td>US DoE</td>
<td>Transformational Permanent Magnet Materials</td>
<td>GE</td>
<td>$5m</td>
<td>80 MGOe and 80% less rare-earth mineral content</td>
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<tr>
<td>US DoE</td>
<td>Replacement of RE in Permanent Magnets</td>
<td>Iowa State Univ</td>
<td>Not disclosed</td>
<td>Not disclosed</td>
</tr>
<tr>
<td>Japan Gov</td>
<td>New generation magnets based on FeN</td>
<td>Tohoku Univ</td>
<td>Not disclosed (Large project)</td>
<td>Gas-phase-modified TM materials</td>
</tr>
<tr>
<td>Japan Gov</td>
<td>Permanent Magnets based on FeNi</td>
<td>Tohoku Univ</td>
<td>Not disclosed</td>
<td>FeNi phases with the L10 structure</td>
</tr>
</tbody>
</table>
European Actions

Raw Materials Initiative (2008), identify neodymium in its role in high-performance magnets, as being vital for hybrid cars as part of the EU’s attempt to reduce the problem of future energy supply.

In June 2010 the European Commission published a list of 14 critical metals or groups of metals – with specific reference to the rare earths – that are important for Europe's economy.

According to Antonio Tajani, the Industry and Entrepreneurship Commissioner, action by Europe in terms of these critical materials must include more efficient recycling.
There are ideas and reasonable believes that we can progressively remove Rare Earth’s from RE-Permanent Magnets by:

1. substituting RE at the grain boundaries and

2. substituting the main magnetic hard phase with the new one – new RE free magnets

New magnets without RE & equivalent properties to existing?
Remove the need for HREs

- by developing a nanostructured material with a Grain Boundary Engineering approach – **Goal 1**
Microstructure of Nd-Fe-B Permanent Magnets

Total amount of Rare-Earth is 32 – 34 wt.%
RE-rich phase at grain boundaries (4-10 wt.% )
Develop a completely RE-free

- medium-grade permanent-magnet material with properties between Nd-Fe-B and ferrite magnets –

**Goal 2**
...independent, or at least less dependent, on critical raw materials....

- **Goal 1.**
  High-coercivity, high-performance Nd$_2$Fe$_{14}$B magnets with zero or drastically-reduced heavy rare-earth content (Dy or Tb),

- **Goal 2.**
  Oriented dense magnets with properties intermediate between sintered ferrite and sintered Nd-Fe-B with NO rare-earth content.
Goal 2

- New materials with suitable Curie temperature and magnetization, which contain no critical materials, will be sought with uniaxial structures such as D0$_{22}$.

- Large coercivity will be developed with the help of a thin ferromagnetic grain boundary phase, which couple antiferromagnetically with the main phase, the patented ‘superferrimagnetic’ concept.
Magnets based on the Nd$_2$Fe$_{14}$B phase have a theoretical maximum coercivity in excess of 6000 kAm$^{-1}$.

What limits Dy-free and Tb-free Nd$_2$Fe$_{14}$B-based magnets to 1500 kAm$^{-1}$, at best, is their microstructure, more specifically their imperfect grain boundaries and relatively large grain size.
Towards 100-500 nm grains...

- HDDR process offers the possibility of making sub-micron grain sizes with an **anisotropic texture**. The HDDR process is a process to break down single-crystal particles to **nanocrystals** in hydrogen at high-temperature and then re-make polycrystals by removing the hydrogen.

- By the HDDR we subtile control the reaction conditions. Most excitingly, the **grain size is about one-tenth that of conventionally neodymium sintered magnets** (~3µm), leading to a potential for coercivities that exceed those currently available (>2000 kAm⁻¹) only with HRE-containing magnets.
Grain boundary phase

- Incorporating the grain-boundary material will have to be a part of the size-reduction process, and combining these two steps will be crucial to the success of this concept.

- Once the innovative grain-boundary phase is part of the magnet, the effect of temperature on the magnetic properties will be much reduced.
Increasing coercivity with reducing grain size

- Increase the coercivity of **HRE-free magnets** by driving the grain size down towards the **nanoscale**.

- Introduce modified grain boundaries (**GBs**) in order to achieve coercivities that are much higher than >2000 kAm\(^{-1}\).

- Increased coercivity based on increased grain surface anisotropy - consequently reduced dipolar interactions.
This effect will be achieved

- by using a novel electro-deposition method for RE diffusion,
- by particle coating,
- and by hot consolidation.

At the same time we will strive to make the magnets more suitable for recycling and much more intrinsically resistant to corrosion,
The challenge of this approach

- Produce a fine grain size in a stable form,
- Incorporate the grain-boundary material,
- Induce alignment in the sample to maximise the remanence,
- Consolidate the material into fully dense magnets,
- Ensure the durability of the nanostructure and the magnetic properties under realistic conditions,
- Test the lifetime properties of newly developed materials (resistance against corrosion, high temperatures, etc.)
Japanese projects

- Hirosawa, Hitachi Metals
  High performance Anisotropic Nano Composite Permanent Magnets with Low Rare Earth Content

- Sugimoto, Tohoku University
  Development of Technology to reduce Dy use in Rare Earth Magnets

- Kato
Properties of available Nd-Fe-B magnets

![Graph showing properties of different magnet types](image)
Grain Boundary Engineering
- EPD – preliminary results
The grain-boundary diffusion process in Nd-Fe-B sintered magnets based on the electrophoreetic deposition of DyF$_3$

M. Soderžnik, K. Žužek Rožman, P. McGuiness, S. Kobe
After GBDP

Dy

GBDP

Nd$_2$Fe$_{14}$B

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Grain-boundary diffusion process

- 3D sputtering with Tb or Dy metal
- Heat treatment at 973 –1273K for 10 min to 6 h
- Annealing at 873K for 20 min in Ar
- Squareness on the demagnetization curve was improved from 79.1% to 89.0%

- EPMA images of untreated (a,b) and Tb-treated (c,d) magnets with Nd (a,c) and Tb (b,d) element mapping
- heat treated at 1173K for 6 h
- the highest remanence and coercivity among conventional rare-earth permanent magnets

D. Li et al., 2008
Grain-boundary diffusion process

- (a) the untreated magnet and the magnets treated with
- (b) Dy₂O₃,
- (c) DyF₃,
- (d) Dy₂O₃+CaH₂ and
- (e) DyF₃+CaH₂

at 1173K for 3 h

- reduction-diffusion process
- Dy₂O₃+3CaH₂→2Dy+3CaO+3H₂ @900deg

- Electron Probe Micro Analysis (EPMA) images

(D. Li et al., 2009)
Grain-boundary diffusion process

- use of Dy or Tb in a slurry
- immersing magnets in DyF₃ suspension

(Suzuki H. et al., 2009)
Grain-boundary diffusion process

- Dy-Ni-Al eutectic powder ($\text{Dy}_{73}\text{Ni}_{9.5}\text{Al}_{17.5}$) was mixed with paraffin and painted onto the surface.
- Heat-treatment at 1173 K for 3 h and aging at 773 K for 3 h in vacuum.

(Oono et al. 2010)
Processing – Experimental results

- Dipping commercial magnets into the:
  - Tb oxide
  - Dy fluoride
  - Nd fluoride
  - Nd oxide

850°C/10h Ar atmosphere

500°C C/1h

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Dipping
Dipping

- GBDP
- Uncoated
- As-sintered
- GBDP effect

- 850°C/10h
- 500°C/1h
- Ar atmosphere

H[kA/m]
Electrophoretic deposition

- Low costs
- Short deposition time
- Thickness control
- Even particle distribution

Voltage: 60 V
Time for 200 µm thick coating: 40 sec
Particle size: 5 µm and 20 µm
Solvent: Ethanol
Particles: DyF$_3$
Electrophoretic Deposition

Schematically shown particle in movement towards cathode

- Particles are moving towards electrode under electrical field
- Charge of particle is determining the way of movement
Dipping vs. EPD
Starting magnets

- Starting alloy was first crushed into a powder by jet-milling in a nitrogen atmosphere to ≤5 μm
- Powder was aligned in an external magnetic field of 1500 kA/m and pressed in a parallel-configured press
- Sintering temperature was 1010°C/2h in Ar
- Composition is
  \[
  \text{Nd}_{14.25}\text{Pr}_{0.29}\text{Fe}_{75.66}\text{Co}_{3.39}\text{Ga}_{0.21}\text{Al}_{0.37}\text{Cu}_{0.15}\text{B}_{5.68}
  \]
- Different sizes of magnets can be used in the EPD process
An attempt to make an EDS analysis

**Nd$_2$Fe$_{14}$B phase**

**((Nd,Tb)$_2$Fe$_{14}$B phase**

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>K$\alpha$</td>
<td>6.398 keV</td>
</tr>
<tr>
<td>Tb</td>
<td>L$\alpha$</td>
<td>6.272 keV</td>
</tr>
</tbody>
</table>

Characteristic X-ray peaks are too close to distinguish between each other!

Overlapping !!!
**Characteristic X-rays detection**

**EDS** detector detects all the X-rays that are generated when the sample is irradiated.

**WDS** detector uses certain crystal, which covers certain energy range.

**Example:** LiF crystal covers an energy range of 3.5-12.5 keV. To detect X-rays outside of this energy range, another crystal of different $d$ value must be employed.

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WDS analysis – advantages

- Better energy resolution (5-10 eV)
- Better detection limit (≈0.01 wt%)
- Longer analysis time
- Spatial artefacts are rare
- Peak/Background sensitivity is higher
WDS analysis

WDS results

<table>
<thead>
<tr>
<th>at. %</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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</thead>
<tbody>
<tr>
<td>Fe</td>
<td>87.35</td>
<td>87.59</td>
<td>87.45</td>
<td>87.30</td>
<td>87.24</td>
<td>87.19</td>
<td>87.37</td>
<td>87.17</td>
<td>86.74</td>
<td>86.83</td>
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<tr>
<td>Tb</td>
<td>5.82</td>
<td>5.22</td>
<td>5.32</td>
<td>4.67</td>
<td>0.08</td>
<td>0.09</td>
<td>0.07</td>
<td>5.59</td>
<td>5.83</td>
<td>5.95</td>
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<tr>
<td>Nd</td>
<td>6.83</td>
<td>7.19</td>
<td>7.24</td>
<td>8.03</td>
<td>12.68</td>
<td>12.72</td>
<td>12.56</td>
<td>7.25</td>
<td>7.43</td>
<td>7.23</td>
</tr>
</tbody>
</table>
Microstructure

- Surface
- 20 µm
- 100 µm
- 200 µm

200 µm

100 µm

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Thickness effect on coercivity on first type of magnets

@25°C

230 µm
200 µm
50 µm
uncoated

H[kA/m]

B[T]

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Thickness effect on coercivity on second type of magnets

@50°C

200 μm

150 μm

60 μm

uncoated

HcI [kA/m]
Conclusions

- EPD technique is very useful for evenly coating the magnet
- With thickness of DyF₃ coating we can tailor coercivity
- It is easy to coat samples with complicated geometry
- The technique is cheap, fast and reliable
- EDS analysis could not be used for (Nd,Tb)₂Fe₁₄B
- WDS gave us ratio of Nd and Tb, which was found to be 1:1
Concerted Action Europe-Japan?

Thank you for your attention!