Grain boundary restructuring of sintered Nd-Fe-B magnets

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Outline

➢ A brief introduction
  Development of Nd-Fe-B alloys

➢ Major concerns
  poor corrosion resistance
  low coercivity
  poor mechanical properties

➢ Grain boundary restructuring
  Mechanism and results
A brief introduction

Nd-Fe-B magnets: widely used in modern industries
A brief introduction

Developments of Nd-Fe-B alloys
A brief introduction

Energy density records for Nd-Fe-B magnets

2012, Hono et al.

\[ \text{H}_{cj} = 1.38 \text{T} \]

\( (BH)_{max} = 486 \text{kJ/m}^3 \)

Hirosawa, BM Symposium, 2005

Rare earth in China:

- China is the largest rare earth consumer in the world (~60%)

- Rare earth mainly exists in Inner Mongolia, Sichuan, Shandong and Jiangxi
A brief introduction

Annual output of sintered Nd-Fe-B magnet (tons)
A brief introduction

- **Japan:** 3 companies  
  (NEOMAX, TDK, Shin-Etsu Chemical)
- **Europe:** 2 companies  
  (NEOREM, VAC)
- **USA:** 0 company  
  (All closed)
- **China:** ~200 companies

NdFeB industrial pattern changed due to the development of Chinese companies
Approaches to improve corrosion resistance

Element alloying: including Dy, Co, Al, Cu, Zn, Ga, Nb, Zr, etc

Disadvantages:
- Limited improvement of corrosion resistance
- Decrease of magnetic properties
- High production cost

Approaches to improve corrosion resistance

Surface coating through chemical/electrochemical processing
Electroplating, Electroless plating and Electrophoresis etc.

Adhesion strength of Ni-P coating

Cross-sectional micrographs

Approaches to improve corrosion resistance

Effect of Yb$^{3+}$ content on $E_{\text{corr}}$

Disadvantages:

- Environmental pollution
- Inadequate adhesion between magnets and coatings

Coatings obtained from the bath with different Yb$^{3+}$ concentrations:
(a) 0 g·L$^{-1}$ (b) 0.05 g·L$^{-1}$ (c) 0.10 g·L$^{-1}$ (d) 0.15 g·L$^{-1}$ (e) 0.20 g·L$^{-1}$

Approaches to improve coercivity

Alloying with HRE elements (Dy or Tb)

The $H_{cj}$ and $B_r$ of NdFeB sintered magnets alloying with Tb element

High Dy-content for high application temperatures

Disadvantages:

- Over consuming of HRE elements
- Serious decrease of $B_r$ and $(BH)_{max}$

Approaches to improve coercivity

Grain boundary diffusion of HRE elements

**HRE sources:** Dy/Tb, (Dy/Tb)F$_3$ or Dy-alloys  
**Methods:** Coating, sputtering or vapor deposition  
**Heat treatment:** 700-1000 °C for several hours

Demagnetization curves of magnets before and after the GBD treatment  
BSE images of (a) untreated sample, (b) GBD sample  
$\Delta H_{cj}$ by GBD treatments against the sample thickness.

**Disadvantages:**  
- Only suitable for thin magnets (< 5mm)  
- Energy consuming  
- Complex process

Grain boundary restructuring

Aid alloy: $\text{Al}_{85}\text{Cu}_{15}$

Mass loss of magnets measured in $120^\circ\text{C}$, 2 atm and 100% relative humidity atmosphere for different time


SEM back-scattered images of $\text{Al}_{85}\text{Cu}_{15}$ doped magnet and EDS results of the concentration distribution of Al and Cu

Grain boundary restructuring

Aid alloy: \((\text{Pr,Nd})\text{FeCu}\)

Mass loss in hot & humid atmosphere for \((\text{Pr,Nd})_{32.5}\text{Fe}_{62.0}\text{Cu}_{5.5}\) doped magnets

Polarization curves in 0.005 M H\(_2\)SO\(_4\) and SEM micrographs of corroded surfaces before and after doping

Yan et al, Mater. Lett., 75 (2012) 1
Yan et al, Chinese Patent, ZL 200810060843.5
Grain boundary restructuring

Aid alloy: \((\text{Pr},\text{Nd})\text{FeCu}\)

HREM image of magnet with \((\text{Pr},\text{Nd})\text{FeCu}\) addition
Significant enhancement of coercivity

Only slight decrease in remanence

Grain boundary restructuring

Master alloy: \((\text{Pr},\text{Nd})_{27.73}\text{Fe}_{\text{bal}}\text{B}_{1.03}\) (wt. %)

Aid alloy: DyFe

Magnetic properties of \((\text{Pr},\text{Nd})\text{FeB}\) magnets with aid alloy DyFe

<table>
<thead>
<tr>
<th>Samples</th>
<th>(B_r) (T)</th>
<th>(H_{cj}) (kA/m)</th>
<th>((BH)_{\text{max}}) (kJ/cm(^3))</th>
<th>Squareness factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.43</td>
<td>765.3</td>
<td>285</td>
<td>35.6</td>
</tr>
<tr>
<td>b</td>
<td>1.41</td>
<td>973.0</td>
<td>390</td>
<td>96.3</td>
</tr>
<tr>
<td>c</td>
<td>1.40</td>
<td>1153.2</td>
<td>382</td>
<td>96.4</td>
</tr>
<tr>
<td>d</td>
<td>1.33</td>
<td>1267.5</td>
<td>352</td>
<td>95.9</td>
</tr>
</tbody>
</table>

Demagnetization curves of magnets with (a) 0 (b) 1%, (c) 2% and (d) 3% aid alloy DyFe
Grain boundary restructuring

Master alloy: $\text{Nd}_{10}\text{Pr}_{19}\text{Fe}_{\text{bal}}\text{B}_1\text{Dy}_1(\text{Co, Zr, Al})_2$ (wt. %)
Aid alloy: (Nd, Dy)FeCu

<table>
<thead>
<tr>
<th>Content of Aid alloy (wt.%)</th>
<th>$H_{cj}$ (kOe)</th>
<th>$B_r$ (T)</th>
<th>$(BH)_{max}$ (MGOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17.46</td>
<td>1.354</td>
<td>45.07</td>
</tr>
<tr>
<td>2.5</td>
<td>18.49</td>
<td>1.331</td>
<td>43.63</td>
</tr>
<tr>
<td>5</td>
<td>19.33</td>
<td>1.33</td>
<td>43.46</td>
</tr>
<tr>
<td>10</td>
<td>20.69</td>
<td>1.308</td>
<td>42.26</td>
</tr>
<tr>
<td>12.5</td>
<td>22.14</td>
<td>1.296</td>
<td>41.46</td>
</tr>
</tbody>
</table>

- Coercivity and corrosion resistance are enhanced
- only slight decrease in remanence and energy product
- Low Dy content: $<$ 2%

Coercivity and corrosion resistance are enhanced

Only slight decrease in remanence

Energy product even increased at 3 wt.% addition

Master alloy:

\[(\text{Pr}, \text{Nd})_{13.05} \text{Dy}_{0.12} \text{Fe}_{\text{bal}} \text{Al}_{0.25} \text{Nb}_{0.07} \text{B}_{5.7}\] (at. %)

Aid alloy:

DyFeCu

Grain boundary restructuring
Grain boundary restructuring

Cu nanopowders modification

Schematic diagrams of NdFeB magnets with Cu nanopowders modification

Potentiokinetic polarization with additions of 0, 0.05 and 0.1 wt% Cu in 3.5wt% NaCl solution

Yan et al, Chinese patent, ZL 200710068486.2

Yan et al, Physica B, 403, 2008, 3303
Grain boundary restructuring

**SiO$_2$ nanopowders modification**

Before sintering

After sintering

$4\text{Nd} + 3\text{SiO}_2 \rightarrow 2\text{Nd}_2\text{O}_3 + 3\text{Si}$

E-V curve in NaCl solution with 0, 0.01, 0.03 and 0.05 wt% SiO$_2$ nanopowders modification


Yan et al, *Chinese patent*, ZL 200710069227.1

Magnetic properties with SiO$_2$ nanopowders modification
Grain boundary restructuring

Toughness with different amount of $(Pr,Nd)_{22.0}Fe_{71.6}Cu_{6.4}$ wt.% modification

Bending strength with different amount of $(Pr,Nd)_{22.0}Fe_{71.6}Cu_{6.4}$ wt.% modification

➢ Toughness and bending strength can be improved under some conditions

Summary

- Grain boundary restructuring has been proved to be a very effective way to improve the corrosion resistance of NdFeB magnets through decreasing the difference in electrochemical potentials between the main phase and intergranular phase.

- Grain boundary restructuring has been proved to be a very effective way to enhance the coercivity without addition a big amount of HRE in the main phase through utilization of HRE in the intergranular phase.

- Grain boundary restructuring has minimal disturbance to $B_r$ and $BH_{\text{max}}$, and is not limited by the shape and size of NdFeB magnets.

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