Recovery of Nd and Dy from Magnet Scrap by Utilizing Molten Salt

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Nd–Fe–B magnet

Nd–Fe–B rare earth magnet is the strongest permanent magnet.

- Applications:
  - Hard Disk Drive (HDD)
  - Motors for air conditioner generator
  - Electric vehicle

Large amount of magnet scrap will be produced in the future.
Supply of REE

- Worlds’ 97% supply is dominated by China.
- Prices of REE are escalating especially for Dy.
- Dy is very scarce and limited.

Fig. World share in supply of REE in 2006.
(USGS Mineral Commodity Summaries (2007))

Fig. Change in prices of Nd and Dy.
(Industrial rare metals (2007): Arum Ltd.)

Development of new recycling process is important
Aim of this study

Development of effective recovery process by utilizing molten salt as a rare earth extracting agent.
Flowchart of recycling of the magnet scrap

**Step 1: Extraction**

- **Dy-containing Nd–Fe–B magnet scrap**
- **Nd and Dy extraction by molten MXₙ**
  
  \[ \text{NdX}_n'(s, l) + \text{DyX}_n''(s, l) + \text{M}(l) + \text{MX}_n(l) + \text{Fe–B}(s) \]

- **Solid / liquid separation**
  
  - L
  - S

**Step 2: Separation**

- **Vacuum distillation / separation**
  
  \[ \text{NdX}_n'(s, l) + \text{DyX}_n''(l) + \text{M}(l) + \text{MX}_n(l) \]

- **Refining / reduction**

  - **Nd(s)**
  - **Dy(s)**

- **MXₙ(l)**

  \( \text{MX}_n : \text{MgCl}_2, \text{ZnI}_2 \)
Experimental procedure (extraction)

- Selective extraction of Nd and Dy by immersing the magnet alloy into molten salt

<table>
<thead>
<tr>
<th>Extracting agent</th>
<th>MgCl$_2$</th>
<th>ZnI$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction temp.</td>
<td>1273 K</td>
<td>740 K</td>
</tr>
<tr>
<td>Reaction time</td>
<td>3 ~ 12 h</td>
<td>12 h</td>
</tr>
</tbody>
</table>

Fig. Schematic illustration of experimental setup for the extraction experiments.
Experimental procedure (separation)

- Separation and recovery of rare earth compounds by vacuum distillation

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<tbody>
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<td>Reaction temp.</td>
<td>1273 K</td>
<td>1073 K</td>
</tr>
<tr>
<td>Reaction time</td>
<td>6 h</td>
<td>1 h</td>
</tr>
</tbody>
</table>

Fig. Schematic illustration of experimental setup for the separation experiments.
Development of novel recovery process

- Recovery of Nd and Dy by utilizing molten MgCl$_2$.
- Recovery of Nd and Dy by utilizing molten ZnI$_2$.

\[
2 \text{ Nd (in magnet alloy, s)} + 3 \text{ MgCl}_2(\ell) \rightarrow 2 \text{ NdCl}_3(\ell) + 3 \text{ Mg(\ell)} \\
\text{Dy (in magnet alloy, s)} + \text{ MgCl}_2(\ell) \rightarrow \text{ DyCl}_2(\ell) + \text{ Mg(\ell)}
\]
Results (extraction)

Composition analysis:

**Extraction ratio**,

\[ R_i = \frac{w_{i, \text{salt}}}{w_{i, \text{Nd-Fe-B}}} \times 100 \% \]

\( w_{i, \text{salt}} \) : mass of element \( i \) in salt after exp.
\( w_{i, \text{Nd-Fe-B}} \) : initial mass of element \( i \) in alloy

XRD analysis:

**Salt obtained after exp. (1273 K, 6 h)**

\[ 2 \text{Nd}(s) + 3 \text{MgCl}_2(l) \rightarrow 2 \text{NdCl}_3(l) + 3 \text{Mg}(l) \]

\( \Delta G^\circ = -151.7 \text{ kJ at 1273 K} \)

\( \text{Nd and Dy were selectively extracted into molten MgCl}_2. \)
Results (vacuum distillation)

- Deposition of samples after vacuum distillation

![Diagram showing deposition and temperature distribution](image)

**Deposit obtained after exp.**
- 1-(A)
- 1-(B)
- 1-(C)

**Remained sample in the crucible**

**Sample** : Temperature during exp.
- 1-(A) : 500 K ~ 900 K
- 1-(B) : 1050 K
- 1-(C) : 1273 K

- Distance from the open end of quartz tube, \( L \) / mm
- Temperature, \( T \) / K
Results (vacuum distillation)

Fig. XRD patterns of the samples obtained after vacuum distillation.

1-(A): 500 K ~ 900 K

Deposit obtained after exp., 1-(A)
MgCl$_2$ + NdCl$_3$

1-(B): 1050 K

Deposit obtained after exp., 1-(B)
NdCl$_3$

1-(C): 1273 K

Remained sample in the crucible, 1-(C)
NdOCl

- Deposit obtained after exp., 1-(A)
- Deposit obtained after exp., 1-(B)
- Remained sample in the crucible, 1-(C)

Intensity, $I$ (a.u.)

<table>
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<tr>
<th>Temperature Range</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 K ~ 900 K</td>
<td>MgCl$_2$ #03-0854, MgCl$_2$ #25-1156, NdCl$_3$ #12-0785, NdOCl #08-0046</td>
</tr>
<tr>
<td>1050 K</td>
<td>MgCl$_2$ + NdCl$_3$</td>
</tr>
<tr>
<td>1273 K</td>
<td>NdCl$_3$, NdOCl</td>
</tr>
</tbody>
</table>
Summary of recovery exp. by utilizing MgCl$_2$

- In the extraction step:
  - Selective extraction of Nd and Dy was experimentally demonstrated.

- In the separation step:
  - MgCl$_2$ was removed from mixed salt.
  - NdCl$_3$ were recovered by gas phase transportation.

Generation of NdOCl is probably due to the hydration of the salt during handling.
Development of novel recovery process

- Recovery of Nd and Dy by utilizing molten MgCl$_2$. 
- Recovery of Nd and Dy by utilizing molten ZnI$_2$.

\[
\begin{align*}
2 \text{Nd (in magnet alloy, s)} + 3 \text{ZnI}_2(l) & \rightarrow 2 \text{NdI}_3(l) + 3 \text{Zn}(l) \\
2 \text{Dy (in magnet alloy, s)} + 3 \text{ZnI}_2(l) & \rightarrow 2 \text{DyI}_3(l) + 3 \text{Zn}(l)
\end{align*}
\]
Results (vacuum distillation)

- Small pieces of the magnet alloy were used in the extraction experiment. (740 K, 12 h)
- Substance obtained after extraction exp. was distilled under vacuum. (1073 K, 1 h)

Sample : Temperature during exp.

- 2-(W) : 410 K ~ 640 K
- 2-(X) : 500 K ~ 700 K
- 2-(Y) : 920 K
- 2-(Z) : 1073 K
Results (vacuum distillation)

Fig. XRD patterns of the samples obtained after vacuum distillation.
Summary of recovery exp. by utilizing ZnI₂

Selective extraction of Nd and Dy by ZnI₂ is feasible.

NdI₁.₉₅ was recovered by gas phase transportation.
Conclusion

- Recovery of Nd and Dy from magnet alloy by utilizing molten MgCl₂ or ZnI₂ was investigated.

- Extraction experiment
  - By utilizing MgCl₂ and ZnI₂, selective extraction of Nd and Dy was experimentally verified.

- Separation experiment
  - Excess extracting agent was removed by vacuum distillation.
  - Gas phase transportation of rare earth compounds was experimentally verified.

Effective recovery process can be established by utilizing molten salt.
Aim of this study

Efficient recovery of rare earth compounds

Reaction with molten salt

Motor for driving (Scrap)

Discarded

Development of effective recovery process by utilizing molten salt as a rare earth extracting agent
Acknowledgement

Travel expense of the author (Sakae Shirayama) was supported by the grant from the Foundation for the Promotion of Industrial Science (FPIS).

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