Production of Scandium and Al-Sc alloy by Metallothermic Reduction

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Production of Scandium and Al-Sc alloy by Metallothermic reduction

1. Introduction

2. Experimental Procedure

3. Experimental result

4. Summary
What is scandium?

Scandium is classified as a rare earth element (RE).
### Physical properties of Sc

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic number, ( Z )</th>
<th>Atomic weight, ( M )</th>
<th>Density at 20 °C, ( \rho ) g cm(^{-3} )</th>
<th>Melting point, ( T_m ) / °C</th>
<th>Boiling point, ( T_b ) / °C</th>
<th>Ionic radius, ( r_i ) / Å</th>
<th>Crystal structure at 25 °C</th>
<th>Electro negativity</th>
<th>Price* ($ / kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>21</td>
<td>44.96</td>
<td>2.99</td>
<td>1540</td>
<td>2832</td>
<td>0.75</td>
<td>hcp</td>
<td>1.20</td>
<td>18000.00</td>
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<tr>
<td>Y</td>
<td>39</td>
<td>88.91</td>
<td>4.47</td>
<td>1525</td>
<td>3337</td>
<td>0.90</td>
<td>hcp</td>
<td>1.11</td>
<td>450.00</td>
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<tr>
<td>La</td>
<td>57</td>
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<td>6.15</td>
<td>920</td>
<td>3457</td>
<td>1.03</td>
<td>hcp</td>
<td>1.08</td>
<td>350.00</td>
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<tr>
<td>Ce</td>
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<td>140.12</td>
<td>6.77</td>
<td>798</td>
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<td>1.01</td>
<td>fcc</td>
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<td>350.00</td>
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<tr>
<td>Nd</td>
<td>60</td>
<td>144.24</td>
<td>7.01</td>
<td>1016</td>
<td>3067</td>
<td>0.98</td>
<td>hcp</td>
<td>1.07</td>
<td>450.00</td>
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<tr>
<td>Sm</td>
<td>62</td>
<td>150.40</td>
<td>7.54</td>
<td>1073</td>
<td>1791</td>
<td>0.96</td>
<td>hcp</td>
<td>1.07</td>
<td>300.00</td>
</tr>
<tr>
<td>Fe</td>
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<td>55.85</td>
<td>7.87</td>
<td>1536</td>
<td>2863</td>
<td>0.55</td>
<td>bcc</td>
<td>1.64</td>
<td>0.03</td>
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<tr>
<td>Al</td>
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<td>26.98</td>
<td>2.70</td>
<td>660</td>
<td>2520</td>
<td>0.53</td>
<td>fcc</td>
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<td>1.44</td>
</tr>
<tr>
<td>Ti</td>
<td>22</td>
<td>47.87</td>
<td>4.54</td>
<td>1666</td>
<td>3289</td>
<td>0.61</td>
<td>hcp</td>
<td>1.32</td>
<td>9.66</td>
</tr>
</tbody>
</table>

*Price of metals

- Low density
- High chemical reactivity
- One of the most stable oxides on earth
- High price
### Crustal abundance of Sc

<table>
<thead>
<tr>
<th>Rank</th>
<th>Atomic number, Z</th>
<th>Element</th>
<th>Content of earth crust (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>O</td>
<td>46.60</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
<td>Si</td>
<td>27.72</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
<td>Al</td>
<td>8.13</td>
</tr>
<tr>
<td>4</td>
<td>26</td>
<td>Fe</td>
<td>5.00</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>Ca</td>
<td>3.63</td>
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<tr>
<td>6</td>
<td>11</td>
<td>Na</td>
<td>2.83</td>
</tr>
<tr>
<td>7</td>
<td>19</td>
<td>K</td>
<td>2.59</td>
</tr>
<tr>
<td>8</td>
<td>12</td>
<td>Mg</td>
<td>2.09</td>
</tr>
<tr>
<td>9</td>
<td>22</td>
<td>Ti</td>
<td>0.44</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>H</td>
<td>0.14</td>
</tr>
<tr>
<td>11</td>
<td>15</td>
<td>P</td>
<td>0.105</td>
</tr>
<tr>
<td>12</td>
<td>25</td>
<td>Mn</td>
<td>0.095</td>
</tr>
<tr>
<td>13</td>
<td>9</td>
<td>F</td>
<td>0.0625</td>
</tr>
</tbody>
</table>

Scandium is the 31\textsuperscript{st} most abundant element in the earth’s crust.

![Image of a table showing the abundance of various elements in the Earth's crust, with Scandium highlighted as the 31\textsuperscript{st} most abundant element.]

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**2006/08/29 Sohn International Symposium**
### Some minerals containing Sc

<table>
<thead>
<tr>
<th>Form</th>
<th>Mineral name</th>
<th>Content of Sc$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicates</td>
<td>Thortveitite</td>
<td>25.0~48.3</td>
</tr>
<tr>
<td></td>
<td>Zircon</td>
<td>0.005~0.3</td>
</tr>
<tr>
<td></td>
<td>Beryll</td>
<td>0.0005~1.2</td>
</tr>
<tr>
<td></td>
<td>Garnet</td>
<td>0.02~0.4</td>
</tr>
<tr>
<td></td>
<td>Olivine</td>
<td>0.0003~0.02</td>
</tr>
<tr>
<td></td>
<td>Pyroxene</td>
<td>~0.04</td>
</tr>
<tr>
<td>Phosphates</td>
<td>Xenotime</td>
<td>0.0015~1.5</td>
</tr>
<tr>
<td></td>
<td>Monazite</td>
<td>0.002~0.5</td>
</tr>
<tr>
<td></td>
<td>Apatite</td>
<td>0.0003~0.08</td>
</tr>
<tr>
<td>Oxides</td>
<td>Davidite</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Columbite</td>
<td>0.01~0.8</td>
</tr>
<tr>
<td></td>
<td>Uraninite</td>
<td>0.15~0.2</td>
</tr>
<tr>
<td></td>
<td>Wolframite</td>
<td>0.005~1.3</td>
</tr>
<tr>
<td></td>
<td>Magnetite</td>
<td>0.001~0.04</td>
</tr>
<tr>
<td></td>
<td>Hematite</td>
<td>~0.15</td>
</tr>
<tr>
<td></td>
<td>Titanomagnetit</td>
<td>0.0002~0.02</td>
</tr>
<tr>
<td></td>
<td>Ilmenite</td>
<td>0.0015~0.15</td>
</tr>
<tr>
<td></td>
<td>Rutile</td>
<td>0.005~0.16</td>
</tr>
<tr>
<td></td>
<td>Laterite</td>
<td>0.003~0.03</td>
</tr>
</tbody>
</table>

Thortveitite ore \([(Sc, Y)_{2}Si_{2}O_{7}]\) contains ~48.3 mass% Sc$_2$O$_3$.

Currently, Sc is recovered from rare earth ores or as a by-product from uranium mill tailings.

Sc is distributed very widely among 800 different earthly species of minerals.

Recently, possibility of recovering Sc from Ni laterite ore is focused.
Ni laterite smelting

**Pyrometallurgy**
- Smelting
  - Laterite ore
  - Drying
  - Calcine & Reduction
  - Smelting
  - Refining or Converting
    - Fe-Ni or Matte

**Hydrometallurgy**
- Caron
  - Laterite ore
  - Drying
  - Calcine & Reduction
  - Ammonical leaching
  - Purification and Recovery
    - Ni and Co
- HPAL
  - Laterite ore
  - High Pressure leaching
  - CCD & Neutralization
  - Precipitation & Redesolution
  - Purification and Recovery
    - Ni and Co

Production volume:
- 372 kt
- 100 kt
- 80 kt

Minimum grade of ore:
- 1.7% Ni
- 1.5% Ni
- 1.3% Ni

Changing due to de-grading of Ni ore

Sc is leached out with Ni and Co into the solution, and Sc in the leachant can be effectively recovered at low cost.

Possibility of recovering Sc from Ni ore

- **Pyrometallurgy**
  - Ni ore containing Sc
  - Pyrometallurgical process
  - Matte/Metal
  - Slag
  - Ni
  - Containing Sc$_2$O$_3$

  Sc$_2$O$_3$ in a slag can not be recovered.

- **Hydrometallurgy**
  - Ni ore containing Sc
  - Hydrometallurgical process
  - Leachant
  - Ni and Co recovery
  - Ni and Co
  - Leachant
  - Sc$_2$O$_3$

  Sc$_2$O$_3$ in leachant can be recovered at a low cost.
Possibility of recovering Sc from Ni ore

Ni laterite ore (1.5%Ni, 0.005%Sc₂O₃)

Present

Ni production 40000 t/year

Sc₂O₃ production ~100 t/year

Future

Great amount of Sc₂O₃ can be recovered from Ni smelting

Ni laterite ore has a great potential for Sc resource.
Currently, Sc is mainly used as an alloying element for Al alloy.
Feature of Al-Sc alloy

- Grain refinement during casting or welding
- Increased strength from Al$_3$Sc precipitates
- Increased resistance to recrystallization
- Enhanced superplastic properties

It is expected that Al-Sc alloy will be applied as structural materials for aircraft or other high spec application in the future.
Purpose of this study

Conventional process

Fluorination: \( \text{Sc}_2\text{O}_3 (s) + 6 \text{HF} (g) \rightarrow 2 \text{ScF}_3 (s) + 3 \text{H}_2\text{O} (g) \)

Reduction: \( 2 \text{ScF}_3 (l) + 3 \text{Ca} (l) \rightarrow 2 \text{Sc} (l) + 3 \text{CaF}_2 (s) \)

Disadvantage

- The production cost is high because an expensive reaction apparatus is required for handling fluorides.
- Contamination from the crucible cannot be prevented due to the high temperature reaction.

Purpose of this study

Development of a new process which can produce Sc metal or Al-Sc alloy directly from \( \text{Sc}_2\text{O}_3 \) at low temperatures (1273 K).
Production of Scandium and Al-Sc alloy by Metallothermic reduction

1. Introduction

2. Experimental Procedure

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4. Summary
Experimental procedure

Metallothermic reduction

Reduction:
\[ \text{Sc}_2\text{O}_3 (s) + 3 \text{ Ca} (g) \rightarrow 2 \text{ Sc} (s) + 3 \text{ CaO} (s) \]
\[ 2 \text{ ScF}_3 (s) + 3 \text{ Ca} (g) \rightarrow 2 \text{ Sc} (s) + 3 \text{ CaF}_2 (s) \]

Reduction and alloying:
\[ \text{Sc}_2\text{O}_3 (s) + \text{ Al} (l) + 3 \text{ Ca} (g) \rightarrow \text{Al-Sc alloy} (l) + 3 \text{ CaO} (s) \]
\[ 2 \text{ ScF}_3 (s) + \text{ Al} (l) + 3 \text{ Ca} (g) \rightarrow \text{Al-Sc alloy} (l) + 3 \text{ CaF}_2 (s) \]

Experiment condition

Reduction temperature: \( T_{\text{red.}} = 1273 \text{ K} \)
Holding time : \( t'_{\text{red.}} = 6 \text{ hr} \)
Experimental apparatus

Components of reaction capsule

- Ta crucible
- Stainless steel foil

Reaction capsule

- Stainless steel reaction capsule
- Sc$_2$O$_3$ or ScF$_3$(+Al+CaCl$_2$)
- Ta crucible
- Crucible stage
- Stainless steel sheet
- Ca shot
- Ti sponge

Stainless steel reaction chamber

- TIG weld
- Stainless steel reaction chamber
- Stainless steel reaction capsule containing feed material and reductant
- Ti sponge
Production of Scandium and Al-Sc alloy by Metallothermic reduction

1. Introduction
2. Experimental Procedure
3. Experimental result
   3-1. Reduction experiment in the absence of collector metal
   3-2. Reduction experiment using a collector metal
   3-3. Reduction experiment using a collector metal and flux
   3-4. Reduction experiment changing amount of reductant
4. Summary
Result (1)  \( \text{Sc}_2\text{O}_3 \) (or \( \text{ScF}_3 \)) + Ca

Reduction experiment in the absence of a collector metal

Exp. A: \( \text{Sc}_2\text{O}_3 \) (0.005 mol) + Ca (0.030 mol, vapor)

A complex oxide (\( \text{CaSc}_2\text{O}_4 \)) was formed and reduction was incomplete.

Exp. B: \( \text{ScF}_3 \) (0.005 mol) + Ca (0.015 mol, vapor)

\( \text{ScF}_3 \) was successfully reduced to metallic Sc.
Ellingham diagrams

**Oxides**

- $\frac{4}{3} \text{Sc} + \text{O}_2 = \frac{2}{3} \text{Sc}_2\text{O}_3$
- $\frac{4}{3} \text{Y} + \text{O}_2 = \frac{2}{3} \text{Y}_2\text{O}_3$
- $\frac{3}{2} \text{Fe} + \text{O}_2 = \frac{1}{2} \text{Fe}_3\text{O}_4$
- $\text{Ti} + \text{O}_2 = \text{TiO}_2$

**Fluorides**

- $\frac{2}{3} \text{Sc} + \text{F}_2 = \frac{2}{3} \text{ScF}_3$
- $\frac{2}{3} \text{La} + \text{F}_2 = \frac{2}{3} \text{LaF}_3$
- $\frac{2}{3} \text{Y} + \text{F}_2 = \frac{2}{3} \text{YF}_3$
- $\text{Ca} + \text{F}_2 = \text{CaF}_2$

**Equations**

- $4 \text{Sc}_2\text{O}_3 + 3 \text{Ca} \rightarrow 2 \text{Sc} + 3 \text{CaSc}_2\text{O}_4$
- $2 \text{ScF}_3 + 3 \text{Ca} \rightarrow 2 \text{Sc} + 3 \text{CaF}_2$

I. Barin, Thermochemical data of pure substance, 3rd edition, (Weinheim: Germany, VCH Publisher Inc., 1995).
Phase diagram for the Al-Sc system

Reduction experiment using a collector metal

\[
\text{Sc}_2\text{O}_3 + 6 \text{ Al} + 3 \text{ Ca} \\
\rightarrow 2 \text{ Al}_3\text{Sc} + 3 \text{ CaO}
\]

\[
2 \text{ ScF}_3 + 6 \text{ Al} + 3 \text{ Ca} \\
\rightarrow 2 \text{ Al}_3\text{Sc} + 3 \text{ CaF}_2
\]

The amount of a feed material and a collector metal were adjusted to obtain the Al alloy containing 5-9 mass%Sc when the reduction was assumed to be complete.

T. B. Massalski, Binary alloy phase diagrams, (Metals Park, ASM International, 1990), 162
Result (2)  
\[ \text{Sc}_2\text{O}_3 \text{ (or ScF}_3\text{) + Al + Ca} \]

**Reduction experiment using a collector metal**

Exp. C: \(\text{Sc}_2\text{O}_3\) (0.0011 mol), \(\text{Ca}\) (0.0065 mol), \(\text{Al}\) (0.036 mol)

- \(\text{Al}_3\text{Sc}\) JCPDS # 17-0412
- \(\text{Al}\) JCPDS # 04-0787
- \(\text{Al}_4\text{Ca}\) JCPDS # 14-0428

\[10 \quad 20 \quad 30 \quad 40 \quad 50 \quad 60 \quad 70 \quad 80 \quad 90 \quad 100\]

Angle, \(2\theta\) (degree)

\[\text{Intensity, } I \text{ (a. u.)}\]

\(\text{Sc}_2\text{O}_3\) was successfully reduced to metallic Sc and alloyed in situ to form liquid Al-Sc alloy without forming \(\text{CaSc}_2\text{O}_4\).

Exp. D: \(\text{ScF}_3\) (0.0022 mol), \(\text{Ca}\) (0.0065 mol), \(\text{Al}\) (0.036 mol)

- \(\text{Al}_3\text{Sc}\) JCPDS # 17-0412
- \(\text{Al}\) JCPDS # 04-0787
- \(\text{Al}_4\text{Ca}\) JCPDS # 14-0428
- \(\text{CaF}_2\) JCPDS # 35-0816

\[10 \quad 20 \quad 30 \quad 40 \quad 50 \quad 60 \quad 70 \quad 80 \quad 90 \quad 100\]

Angle, \(2\theta\) (degree)

\[\text{Intensity, } I \text{ (a. u.)}\]

\(\text{ScF}_3\) was successfully reduced to metallic Sc and alloyed in situ to form liquid Al-Sc alloy.
Reduction experiment using a collector metal and flux

Exp. E: Sc$_2$O$_3$ (0.0011 mol), Ca (0.0065 mol), Al (0.036 mol), CaCl$_2$ (0.0095 mol)

Metallic phase was easily separated from slag phase.

**EPMA analysis**

(a) Aluminum

(b) Scandium

(c) Calcium

![Obtained Al-Sc alloy](image)
Result (4) \( \text{Sc}_2\text{O}_3 + \text{Al} + \text{Ca} + \text{CaCl}_2 \)

Reduction experiment changing amount of calcium reductant

(a) \( R_{\text{Ca}} = 1.5 \) (Exp. G)

(b) \( R_{\text{Ca}} = 1.25 \) (Exp. H)

(c) \( R_{\text{Ca}} = 1 \) (Exp. I)

(d) \( R_{\text{Ca}} = 0.75 \) (Exp. J)

\[ R_{\text{Ca}} = \frac{w_{\text{Ca}}}{w_{\text{Ca}}^{\text{theo.}}} \]

- \( w_{\text{Ca}} \): The mass of the calcium reductant used in the experiment
- \( w_{\text{Ca}}^{\text{theo.}} \): The stoichiometric mass of the calcium reductant necessary for reducing all \( \text{Sc}_2\text{O}_3 \) to metallic scandium

It is thermodynamically difficult to completely prevent calcium accumulation in the alloy by controlling the amount of calcium reductant.
Summary

Fundamental study was conducted on a new production process for Sc and Al-Sc alloy by calciothermic reduction of Sc$_2$O$_3$ or ScF$_3$.

1. When Al was not used as a collector metal for the reduction of Sc$_2$O$_3$, a complex oxide (CaSc$_2$O$_4$) was formed, and the reduction was incomplete.

2. When Al was used as a collector metal for the reduction of Sc$_2$O$_3$, metallic Sc was successfully obtained directly from Sc$_2$O$_3$ and alloyed in situ to form liquid Al-Sc alloy.

3. The separation of metallic phase from the slag phase was improved by utilizing CaCl$_2$ as flux.

4. When aluminum was used as a collector metal, excess calcium remained in the alloy sample in the form of Al$_4$Ca.
Future works

Molten salt electrolysis

- **Anode**: $C + xO^{2-} \rightarrow CO_x + 2x e^-$
- **Cathode**: $Sc_2O_3 + 6e^- \rightarrow 2Sc + 3O^{2-}$
- **Overall reaction**: $Sc_2O_3 + C \rightarrow 2Sc + CO_x$

**Feature**

Ca contamination to Al-Sc alloy could be prevented by controlling a potential.
Electrolysis of CaCl$_2$-Y$_2$O$_3$ molten salt

(Anode: C, Cathode: Ag, Crucible: Ni, Current: 1 A, Time: 3600 s, Temperature: 1173 K)

Before Exp.

After Exp.

Remained at about 1.7 V.

Theoretical decomposition voltage

Y$_2$O$_3$(s) + 3 C(s) $\rightarrow$ 2 Y(s) + 3 CO(g) \hspace{1cm} \Delta E^0 = 1.65 V

CaCl$_2$ (l) $\rightarrow$ Ca(l) + Cl$_2$ (g) \hspace{1cm} \Delta E^0 = 3.26 V
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\textsuperscript{1}Institute of Industrial Science, The University of Tokyo, Tokyo, Japan
\textsuperscript{2}Chiba Institute of Technology, Chiba, Japan
\textsuperscript{3}Pacific Metals CO., LTD., Aomori, Japan
Supply and demand of Sc

Production from rare earth ore (China), or byproduct of U ore (Ukraine), or byproduct of P ore (Russia).

Stock release (Russia, Kazakhstan, Ukraine)

Demand for Sc will increase when Al-Sc alloy produced by low cost
### Table  Starting materials used in this study.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Form</th>
<th>Purity or conc.(%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$_2$O$_3$</td>
<td>Powder</td>
<td>99.9 up</td>
<td>Pacific Metals Co., Ltd.</td>
</tr>
<tr>
<td>ScF$_3$</td>
<td>Powder</td>
<td>99.9 up</td>
<td>Pacific Metals Co., Ltd.</td>
</tr>
<tr>
<td>Ca</td>
<td>Shot</td>
<td>98.0 up</td>
<td>Osaka Special Alloy Co., Ltd.</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>Powder</td>
<td>95.0 up</td>
<td>Kanto Chemicals Co., Inc.</td>
</tr>
<tr>
<td>Al</td>
<td>Powder, 53~106 µm</td>
<td>99.9</td>
<td>Koujundo Chemical Lab. Co., Ltd.</td>
</tr>
<tr>
<td>Ti</td>
<td>Sponge</td>
<td>98.0 up</td>
<td>Toho Titanium Co., Ltd.</td>
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<tr>
<td>2-Propanol</td>
<td>Liquid</td>
<td>99.5 up</td>
<td>Wako Pure Chemical Industries, Ltd.</td>
</tr>
<tr>
<td>Acetone</td>
<td>Liquid</td>
<td>99.0 up</td>
<td>Wako Pure Chemical Industries, Ltd.</td>
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</table>
### Experimental condition

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Mass of sample, $w_i$/g</th>
<th>Excess reductant ratio $R_{Ca}^*$</th>
<th>Calculated nominal composition of Al-Sc alloy</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Collector metal</td>
<td>Flux</td>
</tr>
<tr>
<td></td>
<td>Sc$_2$O$_3$</td>
<td>ScF$_3$</td>
<td>Al</td>
</tr>
<tr>
<td>A</td>
<td>0.690</td>
<td>-</td>
<td>-</td>
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<tr>
<td>B</td>
<td>-</td>
<td>0.51</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>0.150</td>
<td>-</td>
<td>0.96</td>
</tr>
<tr>
<td>D</td>
<td>-</td>
<td>0.22</td>
<td>0.96</td>
</tr>
<tr>
<td>E</td>
<td>0.150</td>
<td>-</td>
<td>0.96</td>
</tr>
<tr>
<td>F</td>
<td>0.100</td>
<td>-</td>
<td>0.96</td>
</tr>
<tr>
<td>G</td>
<td>0.075</td>
<td>-</td>
<td>0.96</td>
</tr>
<tr>
<td>H</td>
<td>0.075</td>
<td>-</td>
<td>0.96</td>
</tr>
<tr>
<td>I</td>
<td>0.075</td>
<td>-</td>
<td>0.96</td>
</tr>
<tr>
<td>J</td>
<td>0.075</td>
<td>-</td>
<td>0.96</td>
</tr>
</tbody>
</table>

*Excess reductant ratio $R_{Ca}^* = w_{Ca}/w_{Ca}^{theo.}$, $w_{Ca}^{theo.}$: Stoichiometric mass of reductant Ca necessary for reduction ($=0.87\times w_{Sc$_2$O$_3$} + 0.22\times w_{ScF$_3$}$)
### Analytical results by XRF

Table. Analytical results of the samples obtained after the reduction experiment.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Nominal composition of Al-Sc alloy&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Excess reductant ratio, $R_{Ca}^a$</th>
<th>Mass of flux $w_{flux/g}$</th>
<th>Concentration of element $i$, $C_i$ (mass%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>C</td>
<td>Al-9mass%Sc</td>
<td>2</td>
<td>0.00</td>
<td>58.32</td>
</tr>
<tr>
<td>D</td>
<td>Al-9mass%Sc</td>
<td>2</td>
<td>0.00</td>
<td>63.67</td>
</tr>
<tr>
<td>E</td>
<td>Al-9mass%Sc</td>
<td>2</td>
<td>1.27</td>
<td>61.14</td>
</tr>
<tr>
<td>F</td>
<td>Al-6mass%Sc</td>
<td>2</td>
<td>1.24</td>
<td>70.02</td>
</tr>
<tr>
<td>G</td>
<td>Al-5mass%Sc</td>
<td>1.5</td>
<td>1.06</td>
<td>73.87</td>
</tr>
<tr>
<td>H</td>
<td>Al-5mass%Sc</td>
<td>1.25</td>
<td>1.06</td>
<td>76.67</td>
</tr>
<tr>
<td>I</td>
<td>Al-5mass%Sc</td>
<td>1</td>
<td>1.06</td>
<td>82.44</td>
</tr>
<tr>
<td>J</td>
<td>Al-5mass%Sc</td>
<td>0.75</td>
<td>1.06</td>
<td>84.67</td>
</tr>
</tbody>
</table>

<sup>a</sup> Excess reductant ratio $R_{Ca} = w_{Ca} / w_{Ca}^{theo.}$, $w_{Ca}$ : Mass of reductant Ca, $w_{Ca}^{theo.}$ : Stoichiometric mass of reductant Ca necessary for reduction ($=0.87 \times w_{Sc_2O_3}$ or $0.22 \times w_{ScF_3}$)

<sup>b</sup>Determined by X-ray fluorescence analysis.
Starting materials used in the reduction experiment

(a) Sc$_2$O$_3$ powder
(b) ScF$_3$ powder
(c) Ca shot

Fig. Starting materials used in the reduction experiment.
(a) Sc$_2$O$_3$ powder produced by Pacific Metals Co., Ltd.
(b) ScF$_3$ powder produced by Pacific Metals Co., Ltd.
(c) Ca shot produced by Osaka Special Alloy Co., Ltd.
Al-Sc alloy obtained after the reduction experiment varying the amount of flux

(a) $R_{\text{flux}} / \text{Al-Sc} = 1.2$

(b) $R_{\text{flux}} / \text{Al-Sc} = 0.75$

(c) $R_{\text{flux}} / \text{Al-Sc} = 0.25$

(d) $R_{\text{flux}} / \text{Al-Sc} = 0.125$

$R_{\text{flux}} / \text{Al-Sc} = \frac{w_{\text{CaCl}_2}}{w_{\text{Al-Sc}}}$

- $w_{\text{CaCl}_2}$: The mass of CaCl$_2$ used in this study
- $w_{\text{Al-Sc}}$: The mass of the sample obtained after the reduction experiment when the reduction assumed to be complete
### Minerals containing a large amount of Sc

#### Table Sc containing minerals.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical formula</th>
<th>Discovered year</th>
<th>Production country</th>
<th>Content of Sc$_2$O$_3$ (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thortveitite</td>
<td>(Sc, Y)$_2$Si$_2$O$_7$</td>
<td>1911</td>
<td>Norway</td>
<td>25.01</td>
</tr>
<tr>
<td>Bazzite</td>
<td>Be$_3$(Sc, Al)$_2$Si$<em>6$O$</em>{18}$</td>
<td>1915</td>
<td>Norway</td>
<td>14.50</td>
</tr>
<tr>
<td>Kolbeckite</td>
<td>ScPO$_4$$\cdot$2(H$_2$O)</td>
<td>1926</td>
<td>U.S.</td>
<td>41.30</td>
</tr>
<tr>
<td>Magbasite</td>
<td>KBa(Al, Sc)(Mg, Fe$^{2+}$)$_6$Si$<em>6$O$</em>{20}$F$_2$</td>
<td>1965</td>
<td>Russia</td>
<td>2.10</td>
</tr>
<tr>
<td>Jervisite</td>
<td>(Na, Ca, Fe$^{2+}$)(Sc, Mg, Fe$^{2+}$)Si$_2$O$_6$</td>
<td>1982</td>
<td>Italy</td>
<td>18.48</td>
</tr>
<tr>
<td>Cascandite</td>
<td>Ca(Sc, Fe$^{2+}$)Si$_3$O$_8$(OH)</td>
<td>1982</td>
<td>Italy</td>
<td>14.74</td>
</tr>
<tr>
<td>Juonniite</td>
<td>CaMgSc(PO$_4$)$_2$(OH)$\cdot$4(H$_2$O)</td>
<td>1997</td>
<td>Russia</td>
<td>17.76$^a$</td>
</tr>
<tr>
<td>Pretulite</td>
<td>ScPO$_4$</td>
<td>1998</td>
<td>Austria</td>
<td>47.38</td>
</tr>
<tr>
<td>Scandiobabingtonite</td>
<td>Ca$_2$(Fe$^{2+}$, Mn)ScSi$<em>5$O$</em>{14}$(OH)</td>
<td>1998</td>
<td>Italy</td>
<td>11.32</td>
</tr>
<tr>
<td>Kristiansenite</td>
<td>Ca$_2$ScSn(Si$_2$O$_7$)(Si$_2$O$_6$OH)</td>
<td>2002</td>
<td>Norway</td>
<td>8.11</td>
</tr>
</tbody>
</table>

$^a$: Calculated value

---


Vapor pressure

Vapor pressure of Sc and Al is substantially smaller than that of Ca.
Vapor pressure

Vapor pressure of Sc and Al is substantially smaller than that of Ca

I. Barin, Thermochemical data of pure substance, 3rd edition, (Weinheim: Germany, VCH Publisher Inc., 1995)
Phase diagram for the Al-Ca system

Experimental temperature (1273 K)

World’s Land Based Nickel Resources and Primary Nickel Production  
(Resources Distribution by Contained Nickel)

### World Ni Resource on Land

- **Laterite**: 72%
- **Sulfide**: 28%

### Primary Ni Production

- **Laterite**: 58%
- **Sulfide**: 42%

### Table: MT Resource and Ni Content

<table>
<thead>
<tr>
<th></th>
<th>MT Resource</th>
<th>% Ni</th>
<th>Mt Ni</th>
<th>% of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphide</td>
<td>10500</td>
<td>0.58</td>
<td>62</td>
<td>27.8%</td>
</tr>
<tr>
<td>Laterite</td>
<td>12600</td>
<td>1.28</td>
<td>161</td>
<td>72.2%</td>
</tr>
<tr>
<td>Total</td>
<td>23100</td>
<td>0.97%</td>
<td>223</td>
<td>100</td>
</tr>
</tbody>
</table>

### Present and Future HPAL Operations

<table>
<thead>
<tr>
<th>Country</th>
<th>Operation</th>
<th>Capacity (ktNi/year)</th>
<th>Product</th>
<th>Start Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>Murrin Murrin</td>
<td>45</td>
<td>briquettes</td>
<td>1999</td>
</tr>
<tr>
<td>Australia</td>
<td>Cawse</td>
<td>9</td>
<td>electronickel</td>
<td>1999</td>
</tr>
<tr>
<td>Australia</td>
<td>Bulong</td>
<td>7</td>
<td>electronickel</td>
<td>1999</td>
</tr>
<tr>
<td>Philippines</td>
<td>Coral Bay</td>
<td>10</td>
<td>electronickel</td>
<td>2005</td>
</tr>
<tr>
<td>New Caledonia</td>
<td>Goro</td>
<td>54</td>
<td>nickel oxide</td>
<td>2007</td>
</tr>
<tr>
<td>Australia</td>
<td></td>
<td>45</td>
<td></td>
<td>2007–2012</td>
</tr>
<tr>
<td>S. America</td>
<td></td>
<td>45</td>
<td></td>
<td>2007–2012</td>
</tr>
<tr>
<td>Africa</td>
<td></td>
<td>40</td>
<td></td>
<td>2007–2012</td>
</tr>
<tr>
<td>S. E. Asia</td>
<td></td>
<td>15</td>
<td></td>
<td>2007–2012</td>
</tr>
<tr>
<td>Caribbean</td>
<td></td>
<td>10</td>
<td></td>
<td>2007–2012</td>
</tr>
<tr>
<td>Australia</td>
<td></td>
<td>54</td>
<td></td>
<td>2012+</td>
</tr>
<tr>
<td>S. E. Asia</td>
<td></td>
<td>40</td>
<td></td>
<td>2012+</td>
</tr>
<tr>
<td>S. E. Asia</td>
<td></td>
<td>45</td>
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<td>2012+</td>
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<tr>
<td>S. E. Asia</td>
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<td>32</td>
<td></td>
<td>2012+</td>
</tr>
<tr>
<td>Caribbean</td>
<td></td>
<td>40</td>
<td></td>
<td>2012+</td>
</tr>
</tbody>
</table>
Prediction of Ni production by HPAL

The concentrations of Ni and Sc$_2$O$_3$ in laterite ore are estimated as 1.5 mass% and 0.005 mass%, respectively.

× 1/300

Solid Oxide Fuel Cell (SOFC)

ScSZ (scandia stabilized zirconia)

It is predicted that between 500 kg and 200 t of Sc$_2$O$_3$ will be used in SOFC.
Flowchart for recovering Sc from Ni laterite

1. **Laterite**
   - Pressure acid leaching
   - Sulfuration
   - Sc content solution

2. **Sc content solution**
   - Solvent extraction
   - Scrubbing
   - Stripping
   - Filtration
   - Sc(OH)₃

3. **Sc(OH)₃**
   - Dissolution
   - Precipitation
   - Oxalate
   - Filtration
   - Calcination
   - Sc₂O₃
Molten salt electrolysis

Experimental apparatus for molten salt electrolysis

- Potential lead (Ni wire)
- Stainless steel tube
- Rubber plug
- Ar inlet
- Reaction chamber
- Ni reference electrode
- Heater
- CaCl₂-Sc₂O₃ molten salt
- Carbon electrode (Anode)
- Fe crucible
- Al (or Ag)-Sc alloy (Cathode)
- Ceramic insulator
### Theoretical decomposition voltage

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^0$ (kJ, at 1100K)</th>
<th>$\Delta E^0$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sc}_2\text{O}_3 + \frac{3}{2} \text{C} \rightarrow 2 \text{Sc} + \frac{3}{2} \text{CO}_2$</td>
<td>991.01</td>
<td>1.71</td>
</tr>
<tr>
<td>$\text{Sc}_2\text{O}_3 + 3 \text{C} \rightarrow 2 \text{Sc} + 3 \text{CO}$</td>
<td>957.719</td>
<td>1.65</td>
</tr>
<tr>
<td>$\text{Sc}_2\text{O}_3$ $\rightarrow$ $2 \text{Sc} + \frac{3}{2} \text{O}_2$</td>
<td>1584.887</td>
<td>2.73</td>
</tr>
<tr>
<td>$\text{CaCl}_2(\ell)$ $\rightarrow$ $\text{Ca(\ell)} + \text{Cl}_2$</td>
<td>629.108</td>
<td>3.26</td>
</tr>
<tr>
<td>$\text{CaO} + \frac{1}{2} \text{C} \rightarrow \text{Ca(\ell)} + \frac{1}{2} \text{CO}_2$</td>
<td>322.825</td>
<td>1.67</td>
</tr>
<tr>
<td>$\text{CaO} + \text{C} \rightarrow \text{Ca(\ell)} + \text{CO}$</td>
<td>311.728</td>
<td>1.61</td>
</tr>
<tr>
<td>$\text{CaO} \rightarrow \text{Ca(\ell)} + \frac{1}{2} \text{O}_2$</td>
<td>520.784</td>
<td>2.7</td>
</tr>
</tbody>
</table>

### Theoretical decomposition voltage

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^0$ (at 1100K)</th>
<th>$\Delta E^0$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Y}_2\text{O}_3 + \frac{3}{2} \text{C} \rightarrow 2 \text{Y} + \frac{3}{2} \text{CO}_2$</td>
<td>992.574</td>
<td>1.71</td>
</tr>
<tr>
<td>$\text{Y}_2\text{O}_3 + 3 \text{C} \rightarrow 2 \text{Y} + 3 \text{CO}$</td>
<td>959.283</td>
<td>1.66</td>
</tr>
<tr>
<td>$\text{Y}_2\text{O}_3$ $\rightarrow$ $2 \text{Y} + \frac{3}{2} \text{O}_2$</td>
<td>1586.451</td>
<td>2.74</td>
</tr>
<tr>
<td>$\text{CaCl}_2(\ell)$ $\rightarrow$ $\text{Ca(\ell)} + \text{Cl}_2$</td>
<td>629.108</td>
<td>3.26</td>
</tr>
<tr>
<td>$\text{CaO} + \frac{1}{2} \text{C} \rightarrow \text{Ca(\ell)} + \frac{1}{2} \text{CO}_2$</td>
<td>322.825</td>
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<td>2.7</td>
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