Production of Scandium and Al-Sc Alloy

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Production of Scandium and Al-Sc Alloy

1. Introduction
2. Metallothermic reduction
3. Molten salt electrolysis
4. Summary

Scandium?

- One of the rare earth elements
- Low density (2.99 g / cm^3)
- High chemical reactivity
- High price (10,000~ yen / g)

Bicycle frame

Crustal abundance of scandium

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Rank.	Atomic number, Z	Element	Content of earth crust (%)
1	8	O	46.60
2	14	Si	27.72
3	13	Al	8.13
4	26	Fe	5.00
5	20	Ca	3.63
6	11	Na	2.83
7	19	K	2.59
8	12	Mg	2.09
9	22	Ti	0.44
10	1	H	0.14
11	15	P	0.105
12	25	Mn	0.095
13	9	F	0.0625
…	…	…	…
16	16	S	0.026
17	6	C	0.020
…	…	…	…
20	17	Cl	0.013
…	…	…	…
23	28	Ni	7.5×10^{-3}

Rank	Atomic number, Z	Element	Content of earth crust (%)
24	30	Zn	7.0×10^{-3}
25	58	Ce	6.0×10^{-3}
26	29	Cu	5.5×10^{-3}
27	39	Y	3.3×10^{-3}
28	57	La	3.0×10^{-3}
29	60	Nd	2.8×10^{-3}
30	27	Co	2.5×10^{-3}
31	**21**	**Sc**	$\mathbf{2.2\times10^{-3}}$
…	…	…	….
33	7	N	2.0×10^{-3}
34	41	Nb	2.0×10^{-3}
35	31	Ga	1.5×10^{-3}
36	82	Pb	1.3×10^{-3}
37	5	B	1.0×10^{-3}
38	59	Pr	8.2×10^{-4}
…	…	…	…
40	62	Sm	6.0×10^{-4}
41	64	Gd	5.4×10^{-4}
42	66	Dy	4.8×10^{-4}
43	70	Yb	3.0×10^{-4}

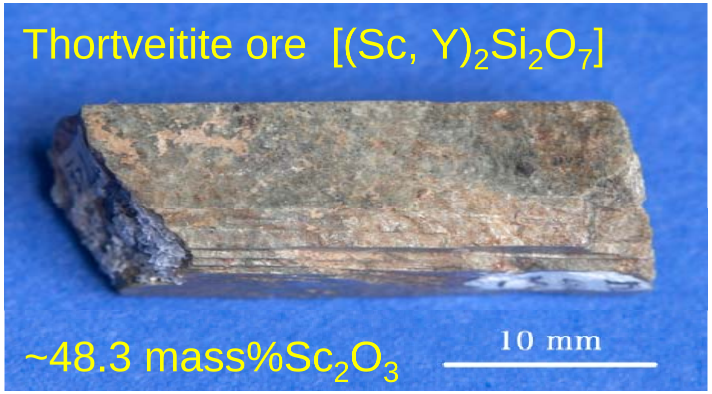
Rank.	Atomic number, Z	Element	Content of earth crust (%)
…	…	…	…
46	68	Er	2.8×10^{-4}
49	50	Sn	2.0×10^{-4}
50	73	Ta	2.0×10^{-4}
51	[illegible]	[illegible]	[illegible]
…	[illegible]	[illegible]	…
55	[illegible]	[illegible]	[illegible]
56	63	Eu	1.2×10^{-4}
57	67	Ho	1.2×10^{-4}
58	65	Tb	8×10^{-5}
59	53	I	5×10^{-5}
60	69	Tm	5×10^{-5}
61	71	Lu	5×10^{-5}
…	…	…	…
67	80	Hg	8×10^{-6}
68	47	Ag	7×10^{-6}
…	…	…	…
73	78	Pt	1×10^{-6}
74	45	Rh	5×10^{-7}
75	79	Au	4×10^{-7}

31st abundant

Scandium is the 31st most abundant element in the earth crust.

Scandium-containing minerals

Form	Mineral name	Content of Sc_2O_3 (mass%)
Silicates	Thortveitite	25.0~48.3
	Zircon	0.005~0.3
	Beryl	0.0005~1.2
	Garnet	0.02~0.4
	Olivine	0.0003~0.02
	Pyroxene	~0.04
Phosphates	Xenotime	0.0015~1.5
	Monazite	0.002~0.5
	Apatite	0.0003~0.08
Oxides	Davidite	0.02
	Columbite	0.01~0.8
	Uraninite	0.15~0.2
	Wolframite	0.005~1.3
	Magnetite	0.001~0.04
	Hematite	~0.15
	Titanomagnetit	0.0002~0.02
	Ilmenite	0.0015~0.15
	Rutile	0.005~0.16
	Laterite	0.003~0.03

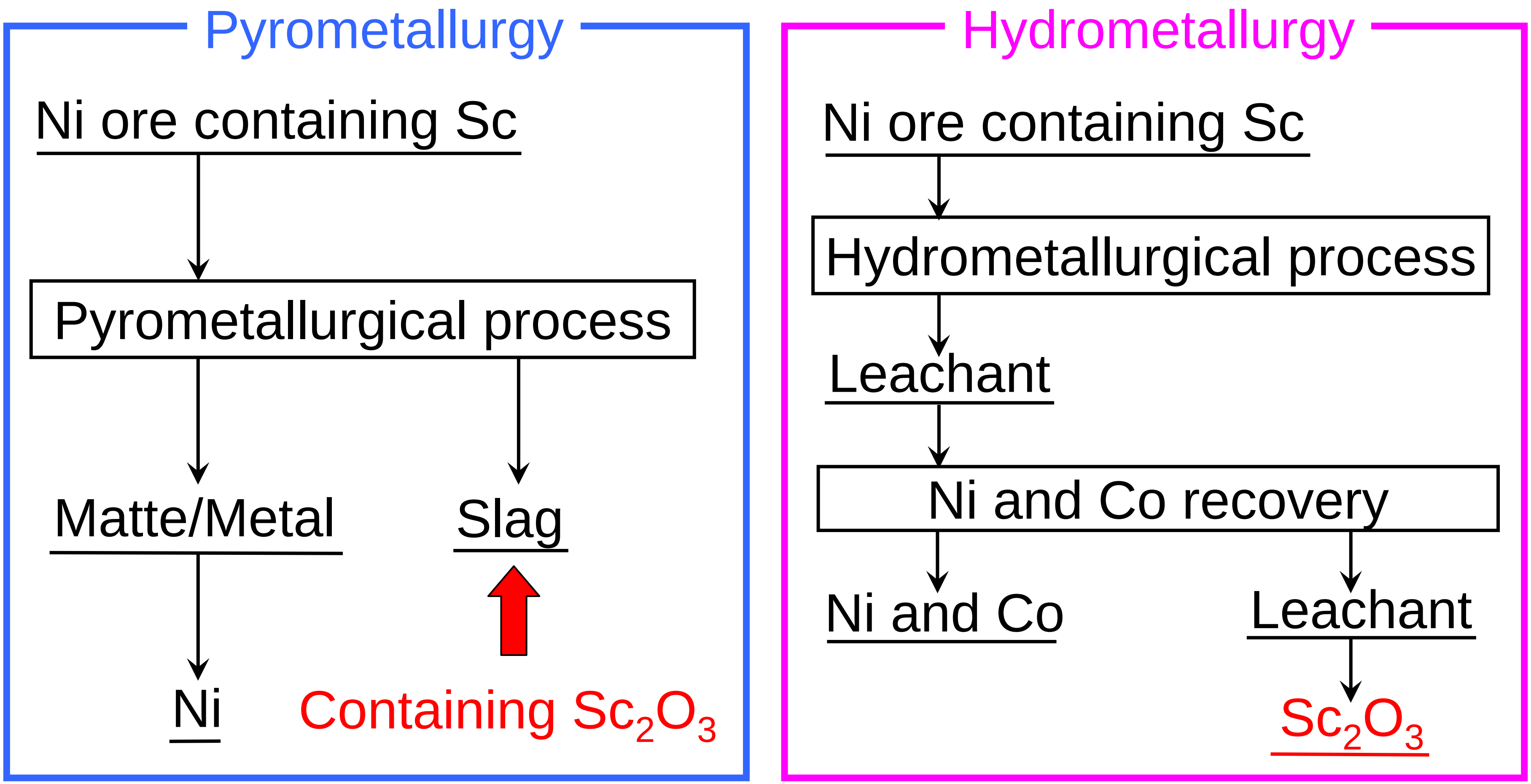


Currently, Sc is recovered from rare earth ores or as a by-product from uranium mill tailings.

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

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

Possibility of recovering scandium from nickel ore



Sc_2O_3 in a slag can not be recovered.

Sc_2O_3 in leachant can be recovered at a low cost.

Purpose of this study

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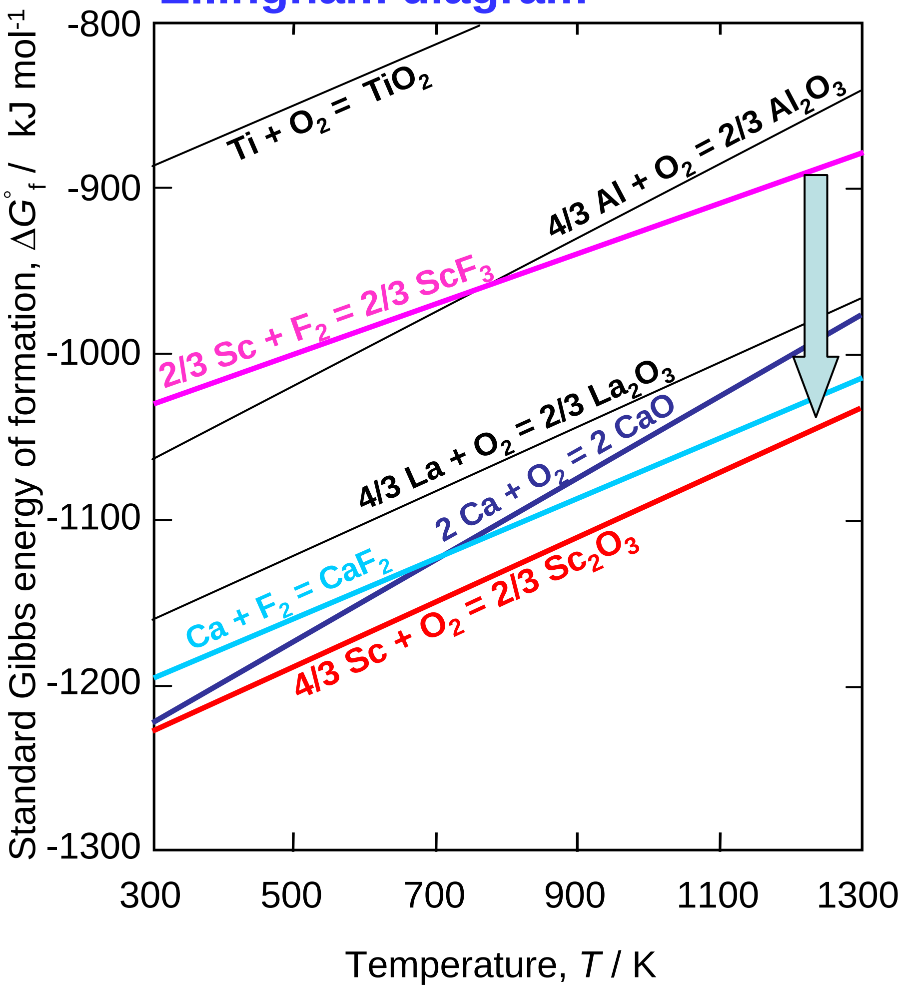
Ellingham diagram



Conventional process

Fluorination:

$$Sc_2O_3\ (s) + 6\ HF\ (g) \xrightarrow{973\ K} 2\ ScF_3\ (s) + 3\ H_2O\ (g)$$

Reduction:

$$2\ ScF_3\ (l) + 3\ Ca\ (g) \xrightarrow{\sim 1873\ K} 2\ Sc\ (l) + 3\ CaF_2\ (l)$$

Disadvantage

·The production cost is high because an expensive reaction apparatus is required for handling fluorides.

·Contamination from the crucible can not 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 Sc_2O_3 at low temperatures (~1273 K).

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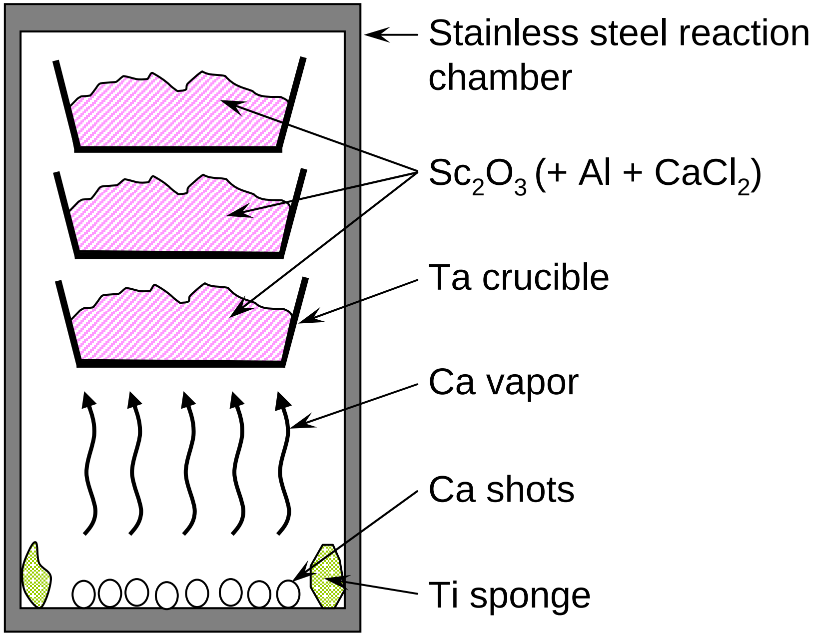
Metallothermic reduction

Reduction:

$$4\ Sc_2O_3\ (s) + 3\ Ca\ (g) \rightarrow 2\ Sc\ (s) + 3\ CaSc_2O_4\ (s)$$

Reduction and alloying:

$$Sc_2O_3\ (s) + Al\ (l) + 3\ Ca\ (g) \rightarrow \text{Al-Sc alloy}\ (l) + 3\ CaO\ (s)$$



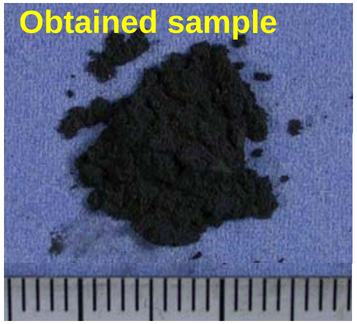
Temperature, T_{red} = 1273 K

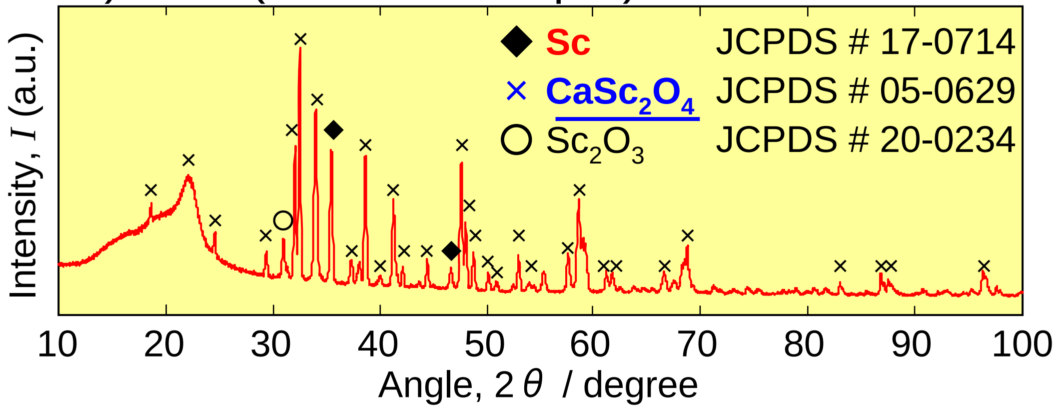
Time: t'_{red} = 6 h

Result (1) Sc_2O_3 (+ Al) + Ca

Reduction experiment in the absence of a collector metal

Exp. A: Sc_2O_3 (0.005 mol) + Ca (0.030 mol, vapor)

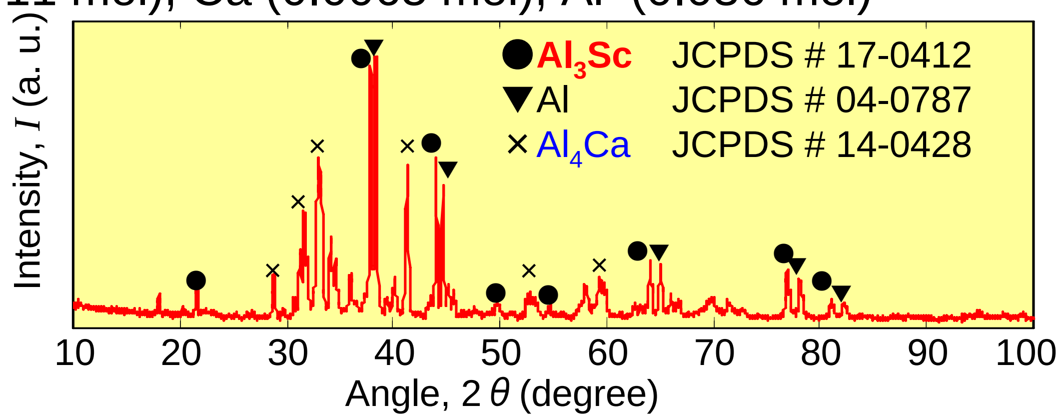




➡ A complex oxide ($CaSc_2O_4$) was formed and reduction was incomplete.

Reduction experiment using a collector metal

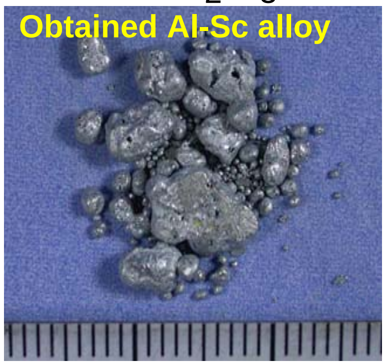
Exp. B: Sc_2O_3 (0.0011 mol), Ca (0.0065 mol), Al (0.036 mol)

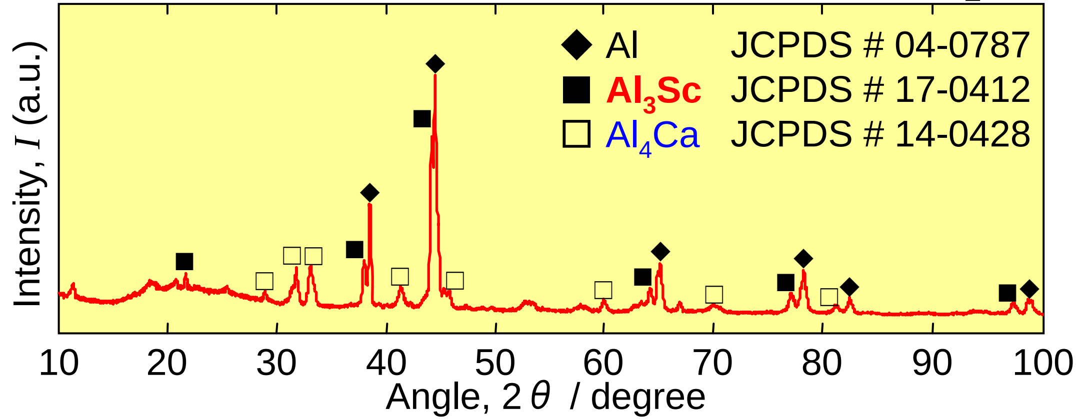


➡ Sc_2O_3 was successfully reduced to metallic Sc and alloyed in situ to form liquid Al-Sc alloy without forming $CaSc_2O_4$.

Reduction experiment using a collector metal and flux

Exp. C: Sc_2O_3 (0.0011 mol), Ca (0.0065 mol), Al (0.036 mol), $CaCl_2$ (0.0095 mol)

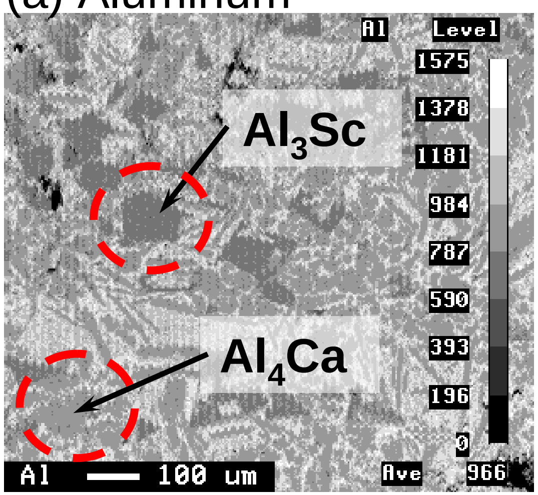




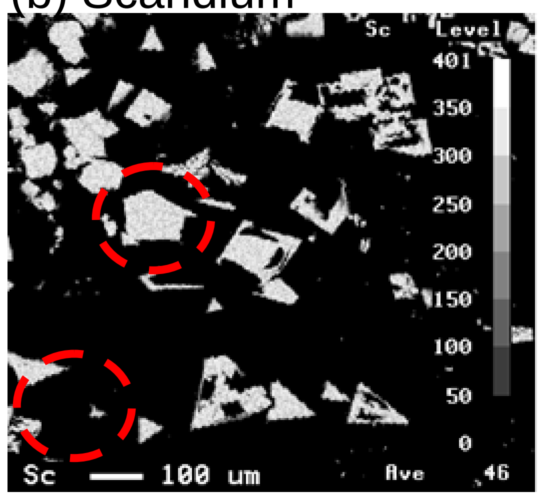
➡ Metallic phase was easily separated from slag phase.

EPMA analysis

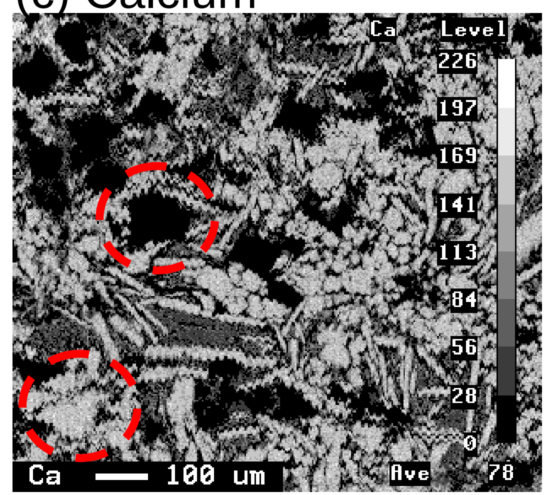
(a) Aluminum



(b) Scandium



(c) Calcium



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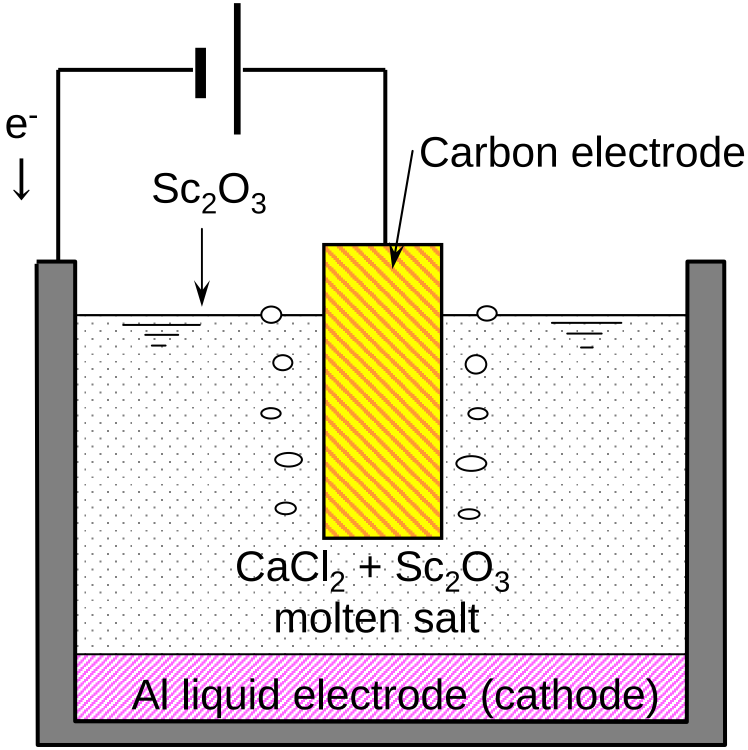
Electrolysis

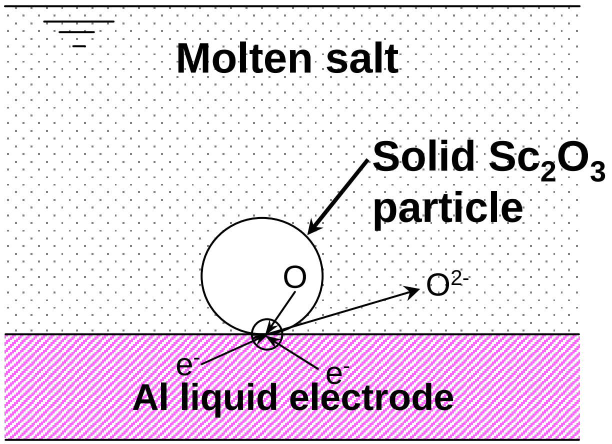
Cathodic reaction : Sc^{3+} (in salt) + 3 e^- → Sc (*l*, in Al)

Anodic reaction : C (*s*) + x O^{2-} (in salt) → CO_x (*g*) + 2x e^-

Overall reaction : Sc_2O_3 (in salt) + C (*s*) → 2 Sc (in Al)+ CO_x (*g*)

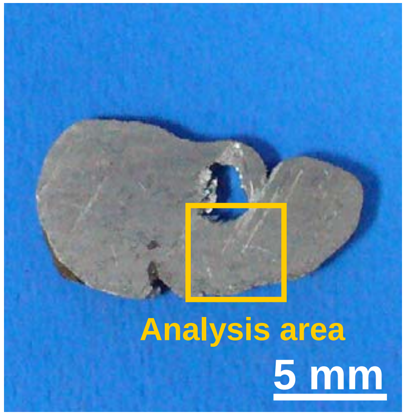


T = 1173 K

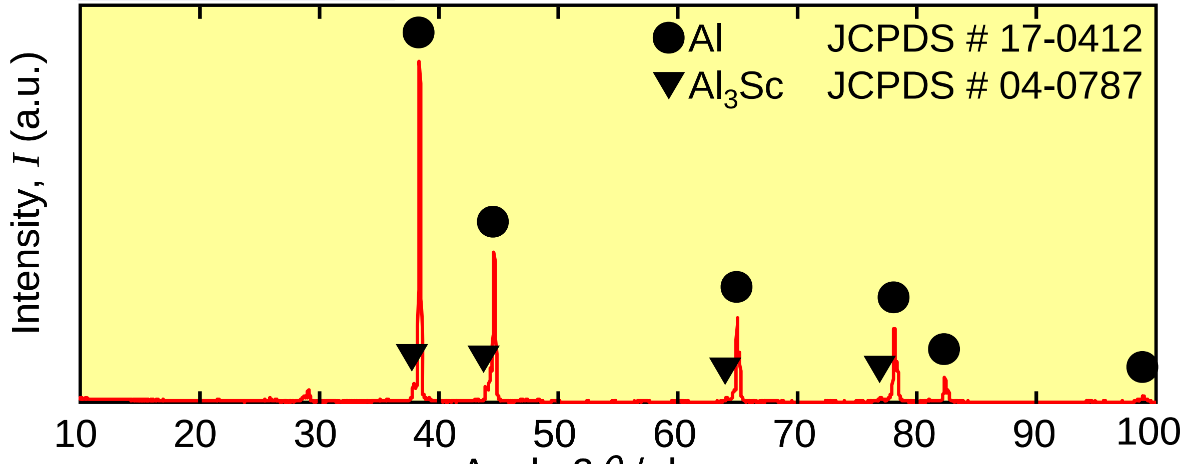


Molten salt electrolysis (XRD, EPMA)

Sectioned sample

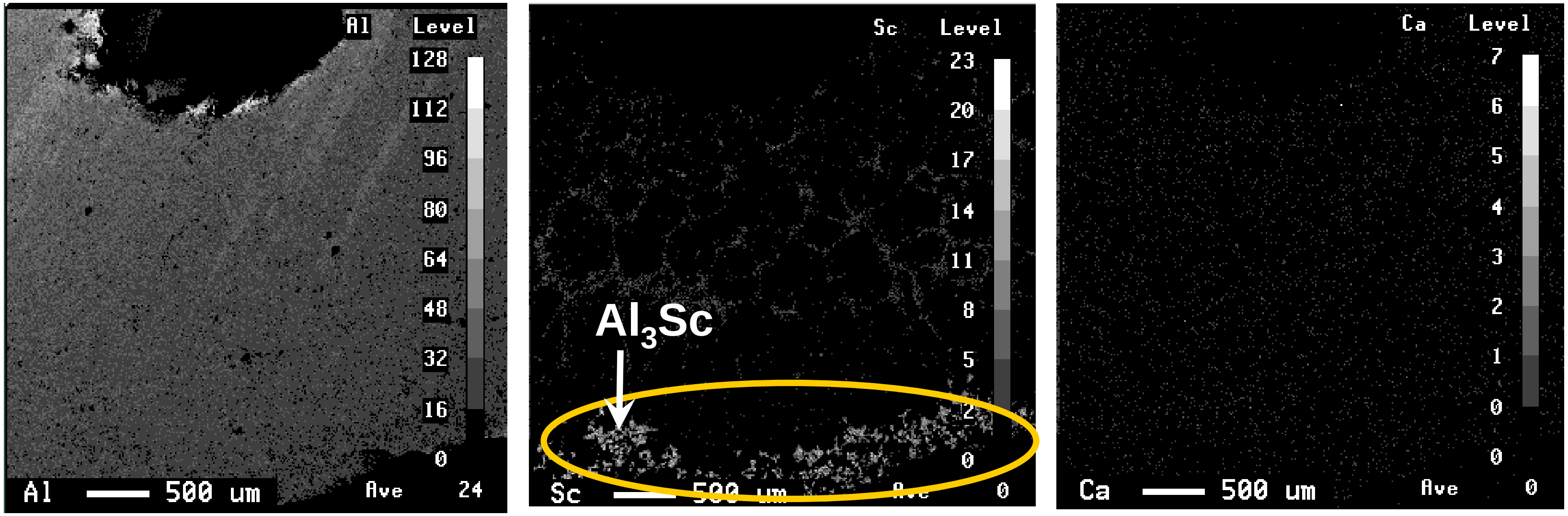


XRD analysis



EPMA analysis

(a) Aluminum (b) Scandium (c) Calcium



Sc segregated at the surface of the sample.

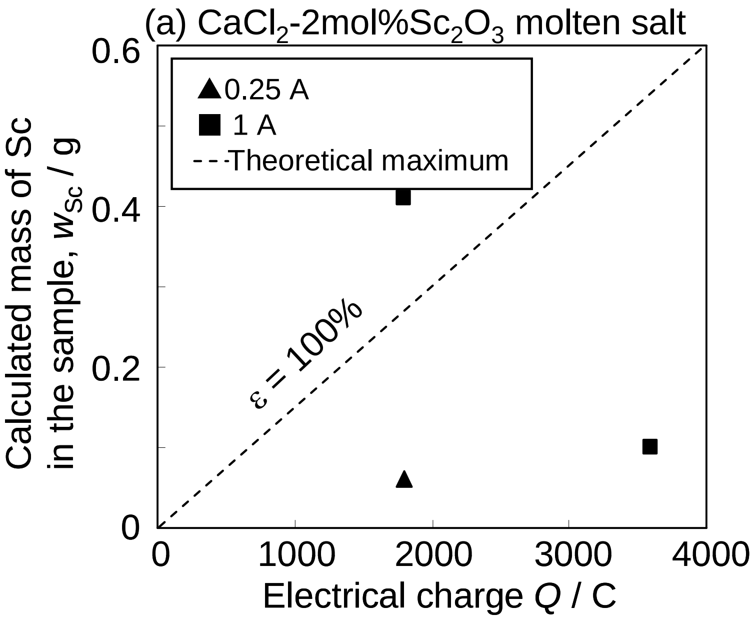
XRF results of the samples obtained after the electrolysis.

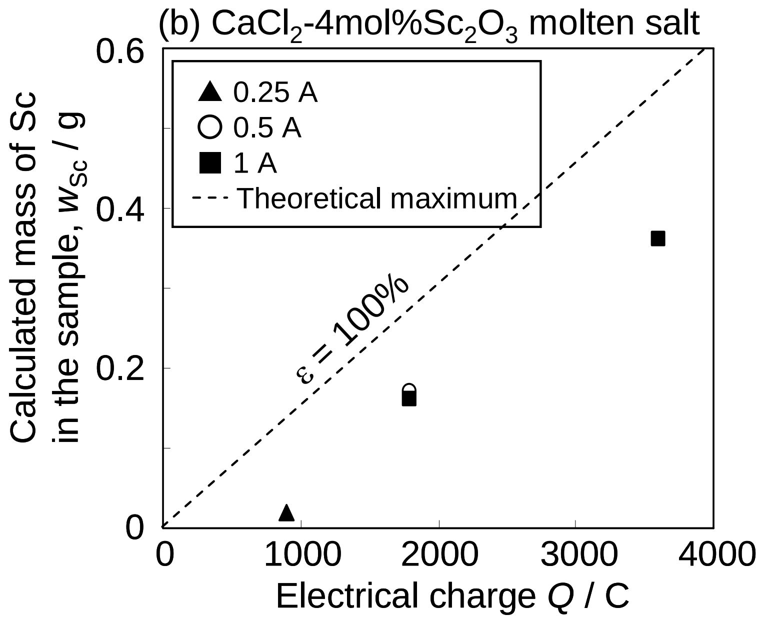
Exp. #	Molten salt system	Current, *i* /A	Time, *t* /s	Al	Sc	Ca	Fe
d-1[1]	$CaCl_2$-1.37mol%Sc_2O_3	1	1800	88.3	11.5	0.14	<0.01
d-1[2]	$CaCl_2$-1.37mol%Sc_2O_3	1	1800	96.9	3.1	<0.01	<0.01
d-2[1]	$CaCl_2$-2mol%Sc_2O_3	0.25	7200	97.4	2.2	0.21	0.26
d-3[1]	$CaCl_2$-2mol%Sc_2O_3	1	1800	83.3	16.3	0.28	0.19
d-4[1]	$CaCl_2$-2mol%Sc_2O_3	1	3600	95.6	3.9	0.46	<0.01
d-5[1]	$CaCl_2$-4mol%Sc_2O_3	0.25	3600	98.9	0.8	0.08	0.21
d-6[1]	$CaCl_2$-4mol%Sc_2O_3	0.5	3600	92.4	6.7	0.45	0.47
d-7[1]	$CaCl_2$-4mol%Sc_2O_3	1	1800	93.2	6.2	0.35	0.25
d-8[1]	$CaCl_2$-4mol%Sc_2O_3	1	3600	85.7	13.8	0.39	0.09
d-9[1]	$CaCl_2$-8mol%Sc_2O_3	0.25	3600	67.0	32.3	0.65	<0.01
d-9[2]	$CaCl_2$-8mol%Sc_2O_3	0.25	3600	83.1	16.5	0.10	0.27
d-10[1]	$CaCl_2$-8mol%Sc_2O_3	0.25	7200	89.4	9.6	0.39	0.60

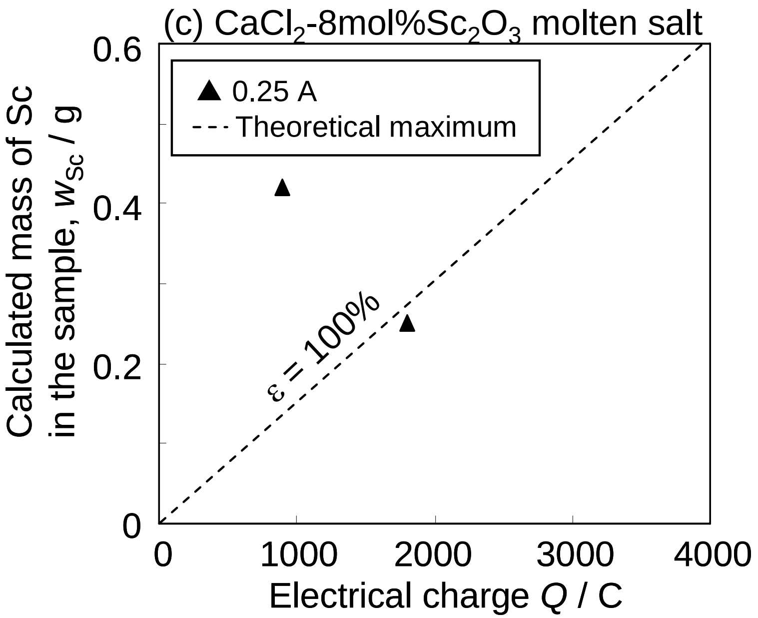
[1] Surface of the sample was analyzed.
[2] Section of the sample was analyzed.

Al-Sc alloy with low Ca contamination (<0.65 mass%) was successfully produced by electrolysis of $CaCl_2$-Sc_2O_3 molten salt.

Evaluation of current efficiency







$w_{Sc} = w_{Al\text{-}Sc} \times C_{Sc}$

w_{Sc} : Mass of Sc in the sample.

$w_{Al\text{-}Sc}$: Mass of the sample obtained after electrolysis.

C_{Sc} : Concentration of Sc in the sample determined by XRF.

- Current efficiency of each sample varied widely.
- In some experiment, current efficiency was more than 100%.

Summary

For producing Sc and Al-Sc alloy directly from Sc_2O_3 at low temperatures, metallothermic reduction and molten salt electrolysis were conducted.

Metallothermic reduction

・When Al was used as a collector metal for the reduction of Sc_2O_3, metallic Sc was successfully obtained directly from Sc_2O_3 and alloyed in situ to form liquid Al-Sc alloy.

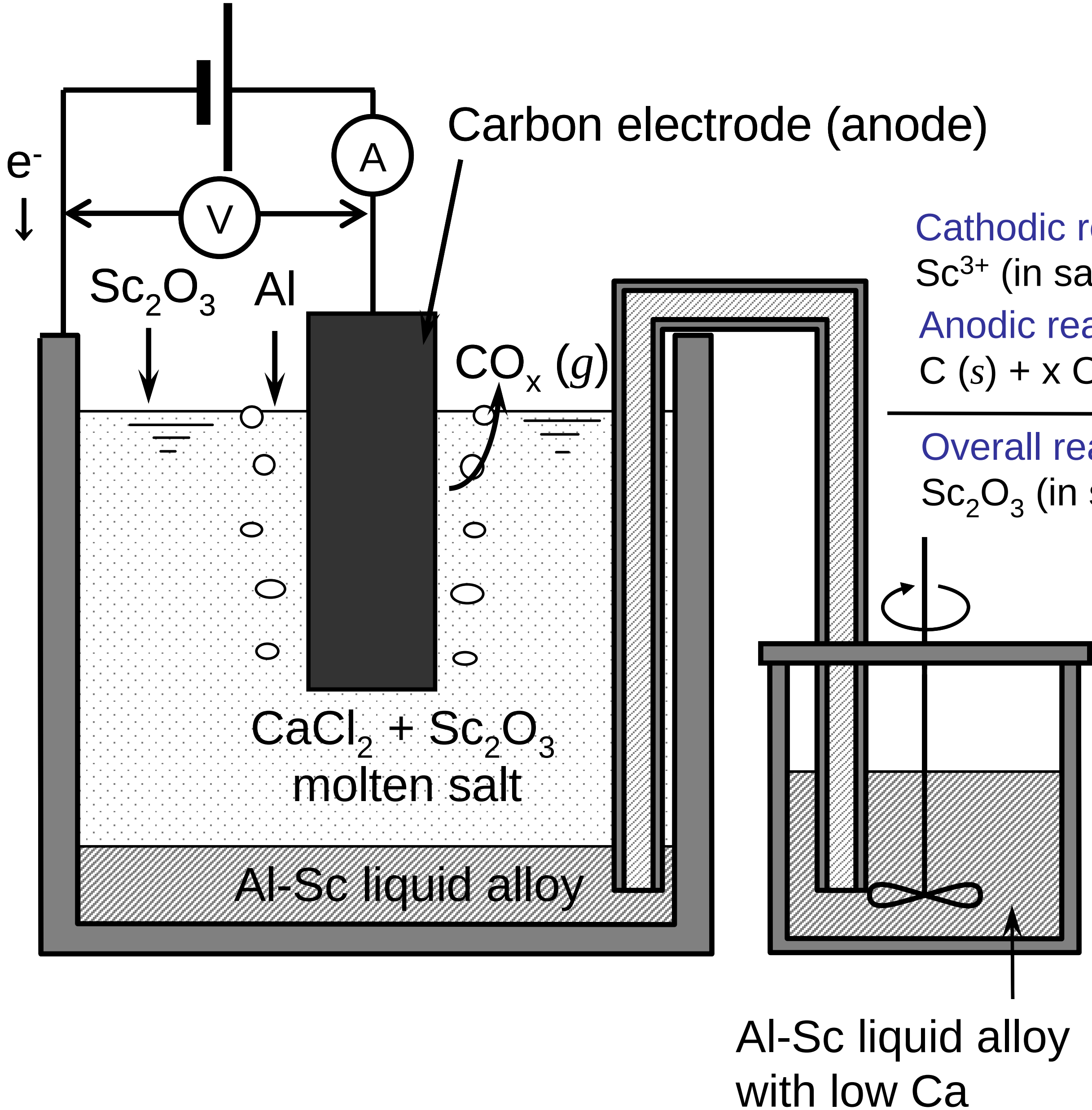
・When aluminum was used as a collector metal, excess calcium remained in the alloy sample in the form of Al_4Ca.

Molten salt electrolysis

・ It was difficult to evaluate the current efficiency of electrolysis because Sc segregated around the surface of the Al-Sc alloy sample.

・ Al-Sc alloy（0.81~32.31 mass%) with low calcium impurity(~0.69 mass%) was successfully produced by the electrolysis of $CaCl_2$-Sc_2O_3 molten salt.

Future Process of high performance Al alloy production



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→ 2 Sc (in Al)+ CO_x (*g*)