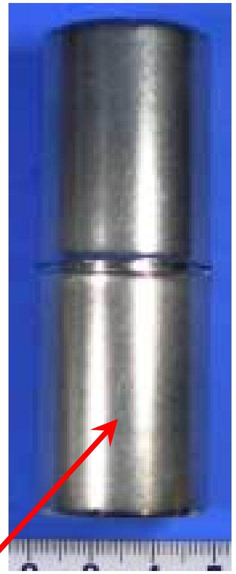
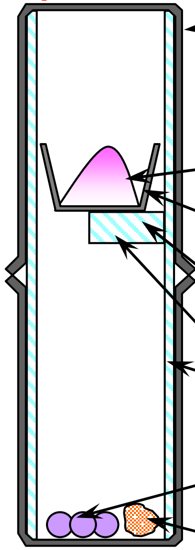
Experimental apparatus

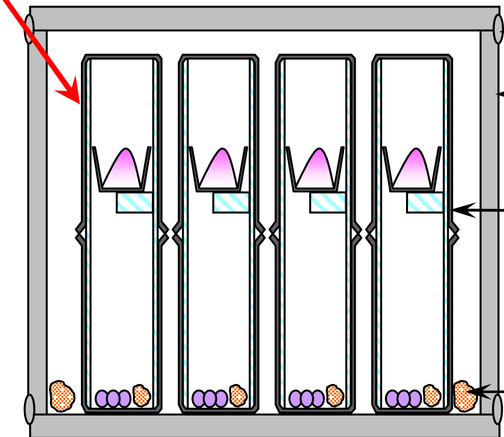
Components of reaction capsule

Reaction capsule





Reaction capsule



Stainless steel reaction chamber

Experimental condition

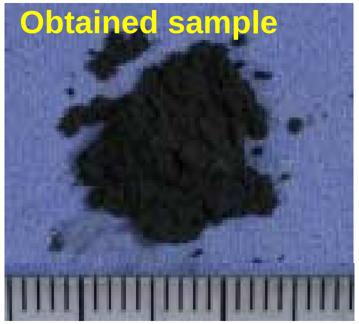
Exp. no.	Mass of sample, w_i /g					Excess reductant ratio R_{Ca} *	Calculated nominal composition of Al-Sc alloy
	Feed		Collector metal	Flux	Reductant		
	Sc_2O_3	ScF_3	Al	$CaCl_2$	Ca		
A	0.690	-	-	-	1.200	2	-
B	-	0.51	-	-	0.600	2	-
C	0.150	-	0.96	0	0.260	2	Al-9mass%Sc
D	-	0.22	0.96	0	0.260	2	Al-9mass%Sc
E	0.150	-	0.96	1.27	0.260	2	Al-9mass%Sc
F	0.100	-	0.96	1.24	0.170	2	Al-6mass%Sc
G	0.075	-	0.96	1.06	0.098	1.5	Al-5mass%Sc
H	0.075	-	0.96	1.06	0.081	1.25	Al-5mass%Sc
I	0.075	-	0.96	1.06	0.065	1	Al-5mass%Sc
J	0.075	-	0.96	1.06	0.049	0.75	Al-5mass%Sc

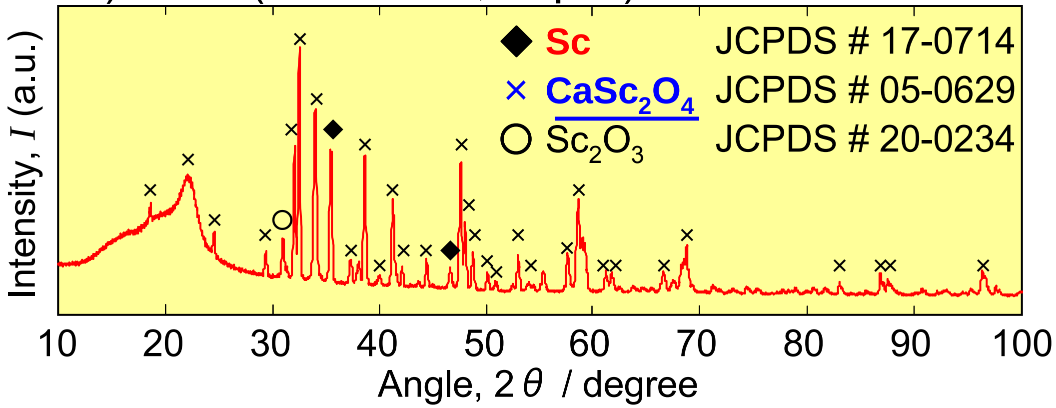
* Excess reductant ratio $R_{Ca} = w_{Ca} / w_{Ca}^{theo.}$, w_{Ca} : Mass of reductant Ca, $w_{Ca}^{theo.}$: Stoichiometic mass of reductant Ca necessary for reduction (=$0.87*w_{Sc_2O_3}$, $0.22*w_{ScF_3}$)

Result (1) Sc_2O_3 (or ScF_3) + Ca

Reduction experiment in the absence of a collector metal

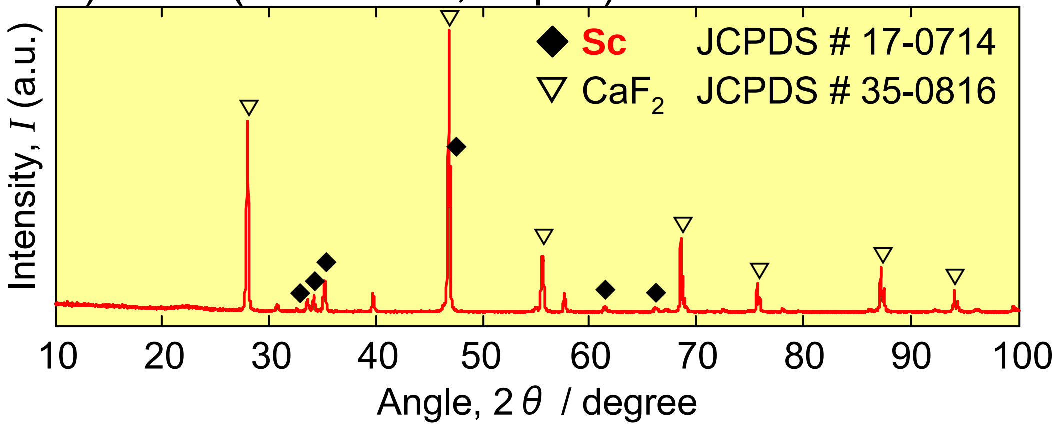
Exp. A: Sc_2O_3 (0.005 mol) + Ca (0.030 mol, vapor)





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

Exp. B: ScF_3 (0.005 mol) + Ca (0.015 mol, vapor)



➡ ScF_3 was successfully reduced to metallic Sc.

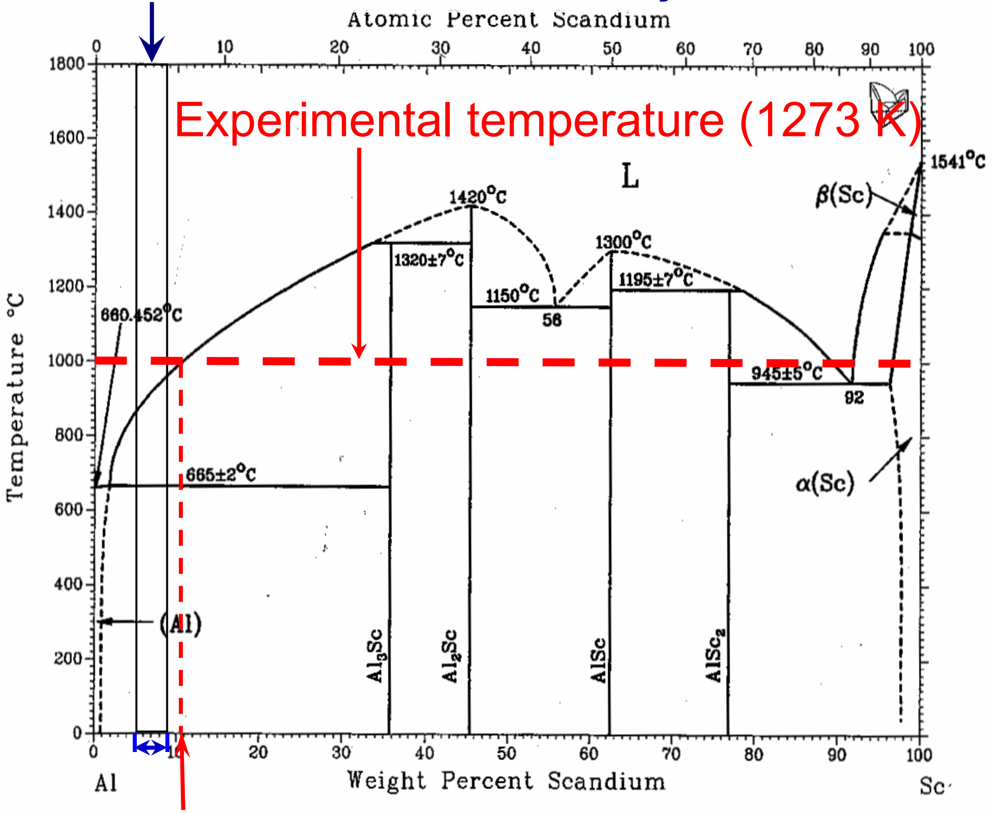
Phase diagram for the Al-Sc system

Reduction experiment using a collector metal

$$Sc_2O_3 + 6\,Al + 3\,Ca \rightarrow 2\,Al_3Sc + 3\,CaO$$

$$2\,ScF_3 + 6\,Al + 3\,Ca \rightarrow 2\,Al_3Sc + 3\,CaF_2$$

Nominal alloy composition in this study: 5–9 mass%Sc in this study



Max. sol. 11 mass%Sc at 1273 K

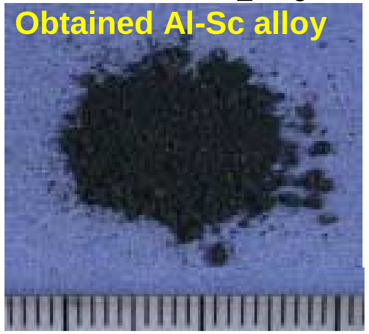
The amount of a feed material and a collector metal were adjusted to obtain the Al alloy containing 5-9 mass%Sc when the reduction was assumed to be complete.

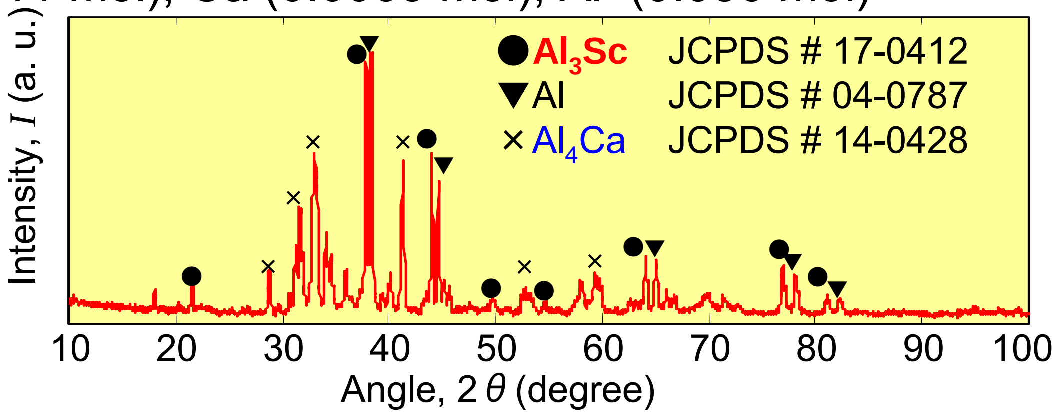
T. B. Massalski, Binary alloy phase diagrams, (Metals Park, ASM International, 1990), 162

Result (2) Sc_2O_3 (or ScF_3) + Al + Ca

Reduction experiment using a collector metal

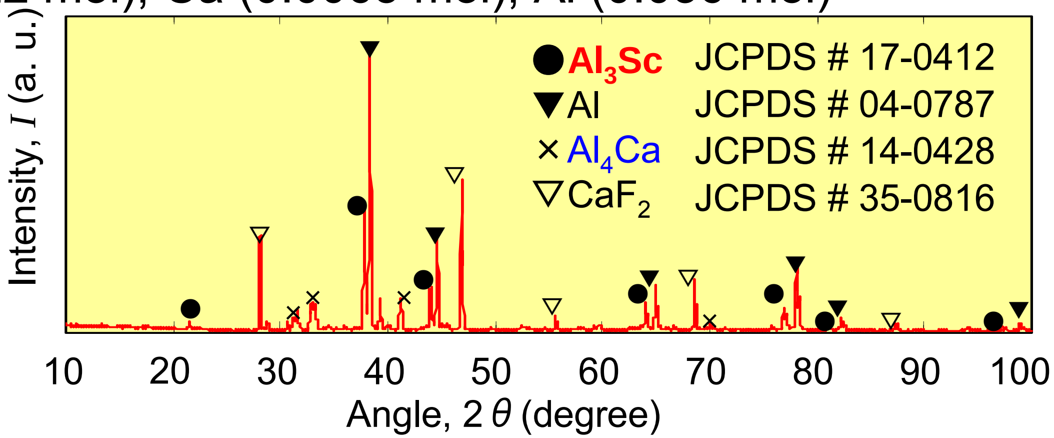
Exp. C: Sc_2O_3 (0.0011 mol), Ca (0.0065 mol), Al (0.036 mol)





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

Exp. D: ScF_3 (0.0022 mol), Ca (0.0065 mol), Al (0.036 mol)

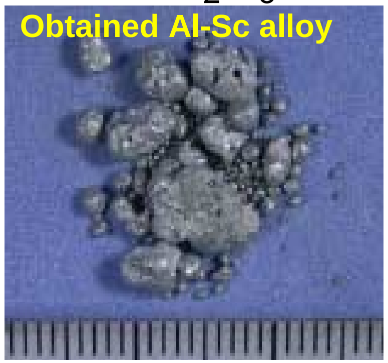


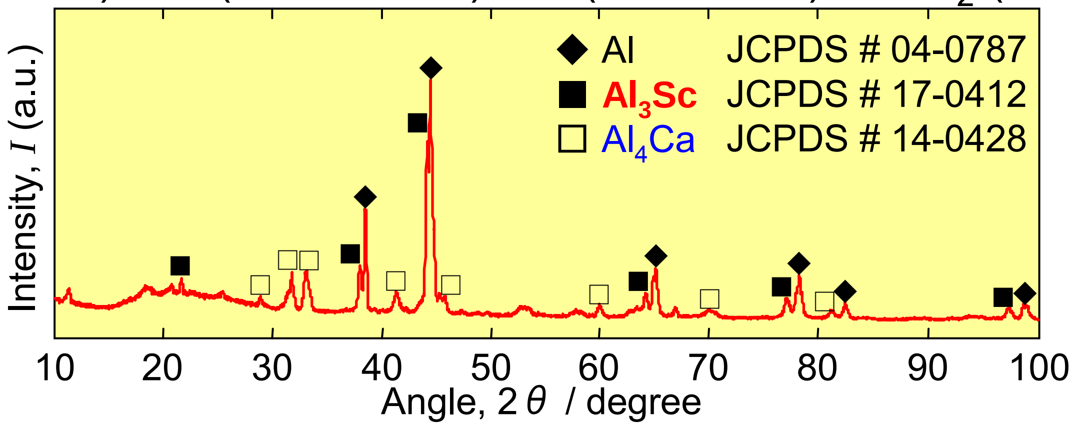
➡ ScF_3 was successfully reduced to metallic Sc and alloyed in situ to form liquid Al-Sc alloy.

Result (3) Sc_2O_3 + Al + Ca + $CaCl_2$

Reduction experiment using a collector metal and flux

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

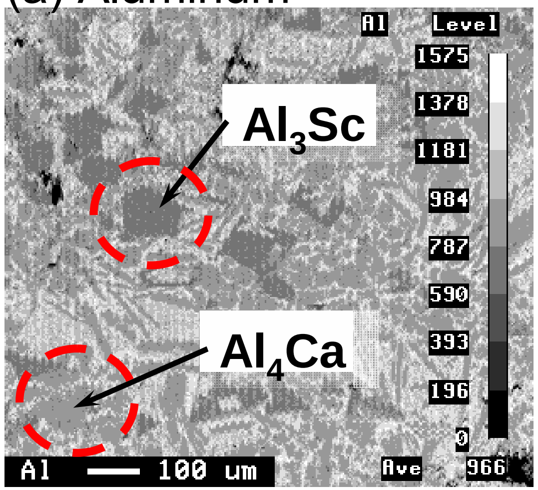




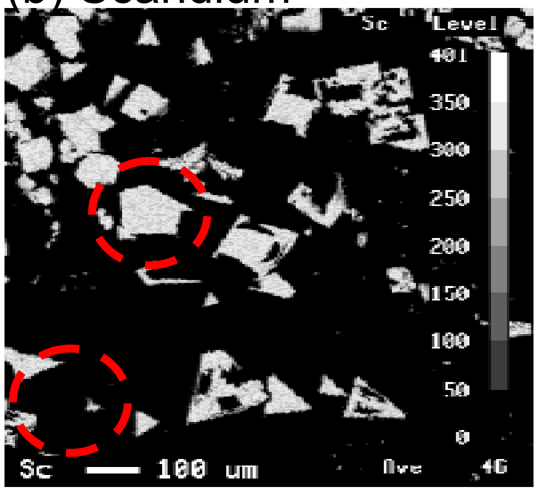
➡ Metallic phase was easily separated from slag phase.

EPMA analysis

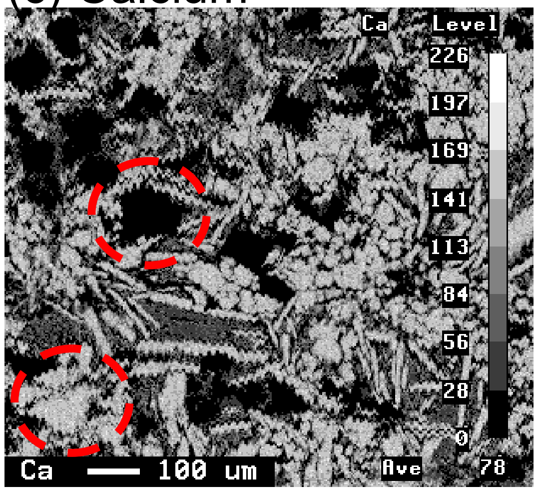
(a) Aluminum



(b) Scandium



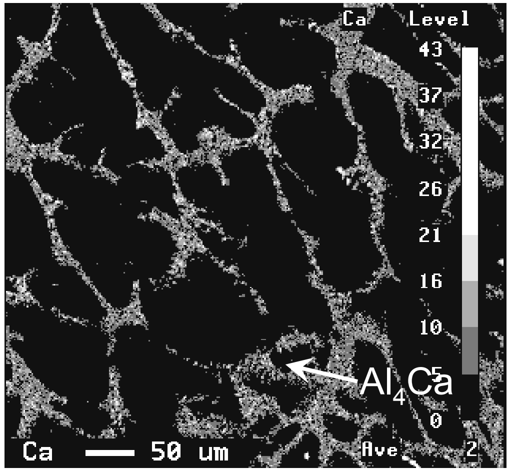
(c) Calcium



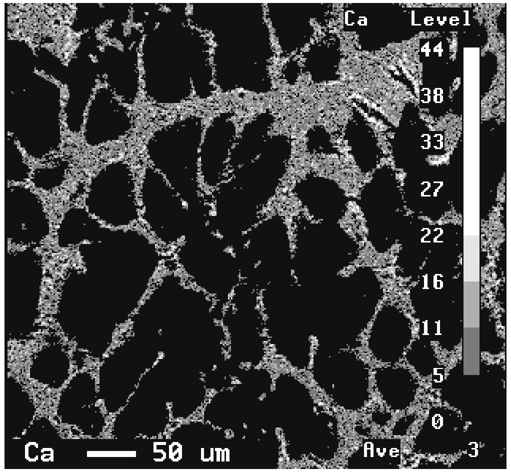
Result (4) Sc_2O_3 + Al + Ca + $CaCl_2$

Reduction experiment changing amount of calcium reductant

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



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

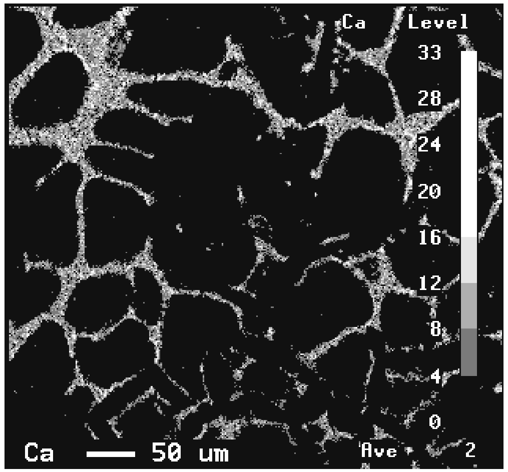


$R_{Ca} = w_{Ca} / w_{Ca}^{theo.}$

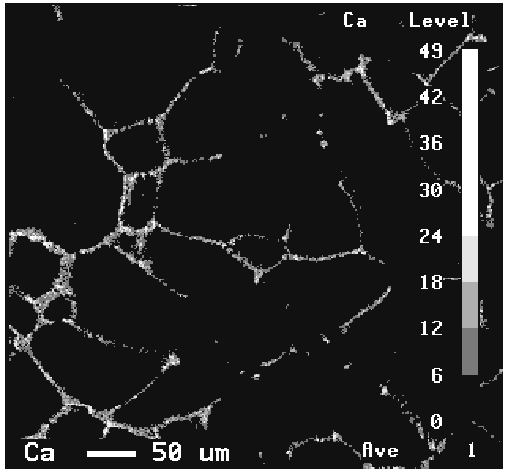
w_{Ca} : The mass of the calcium reductant used in the experiment

$w_{Ca}^{theo.}$: The stoichiometric mass of the calcium reductant necessary for reducing all Sc_2O_3 to metallic scandium

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



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

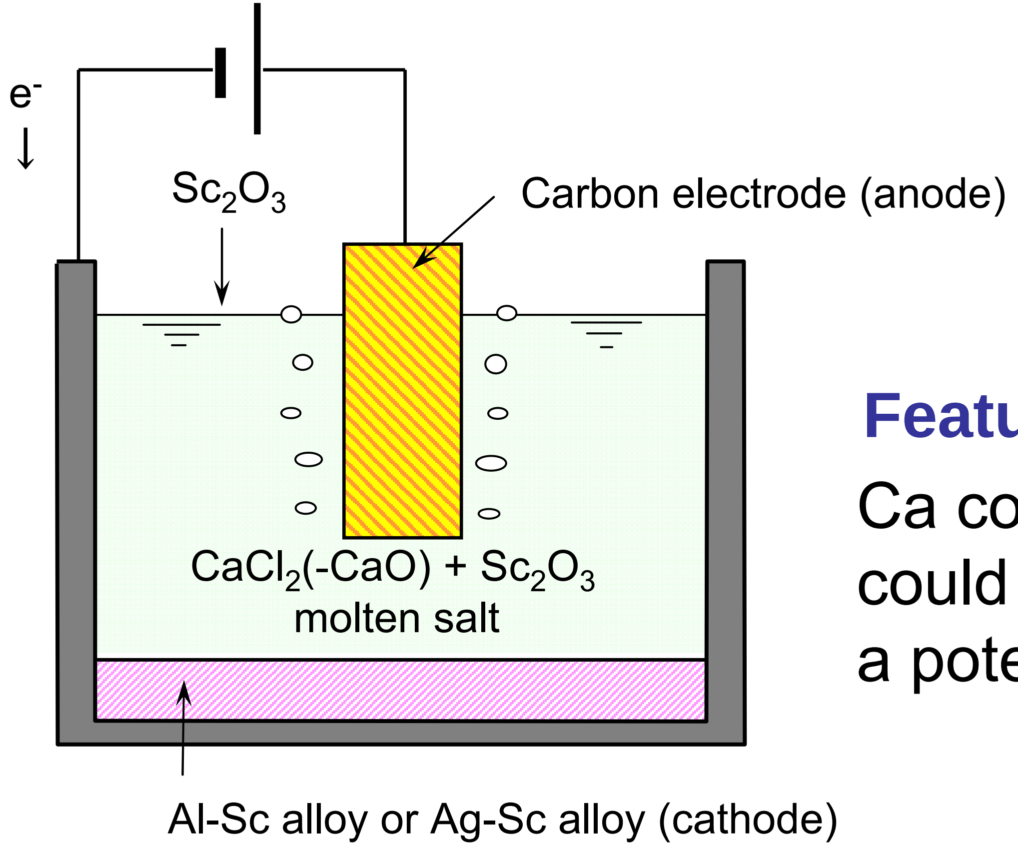


It is thermodynamically difficult to completely prevent calcium accumulation in the alloy by controlling the amount of calcium reductant.

Experimental apparatus

Molten salt electrolysis

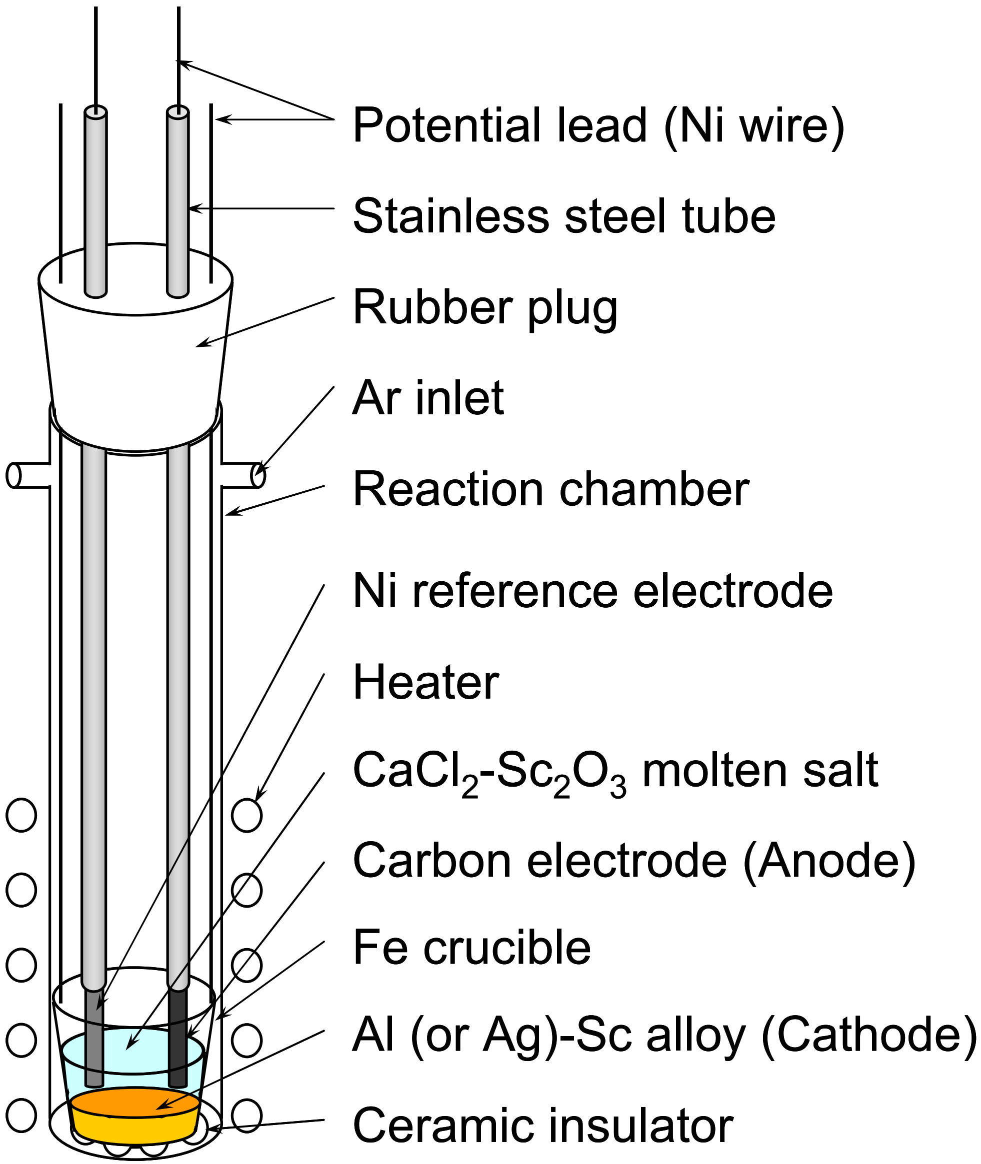
・Anode	$C + x\,O^{2-}$	→	$CO_x + 2x\,e^-$
・Cathode	$Sc_2O_3 + 6\,e^-$	→	$2\,Sc + 3\,O^{2-}$
・Overall reaction	$Sc_2O_3 + C$	→	$2\,Sc + CO_x$



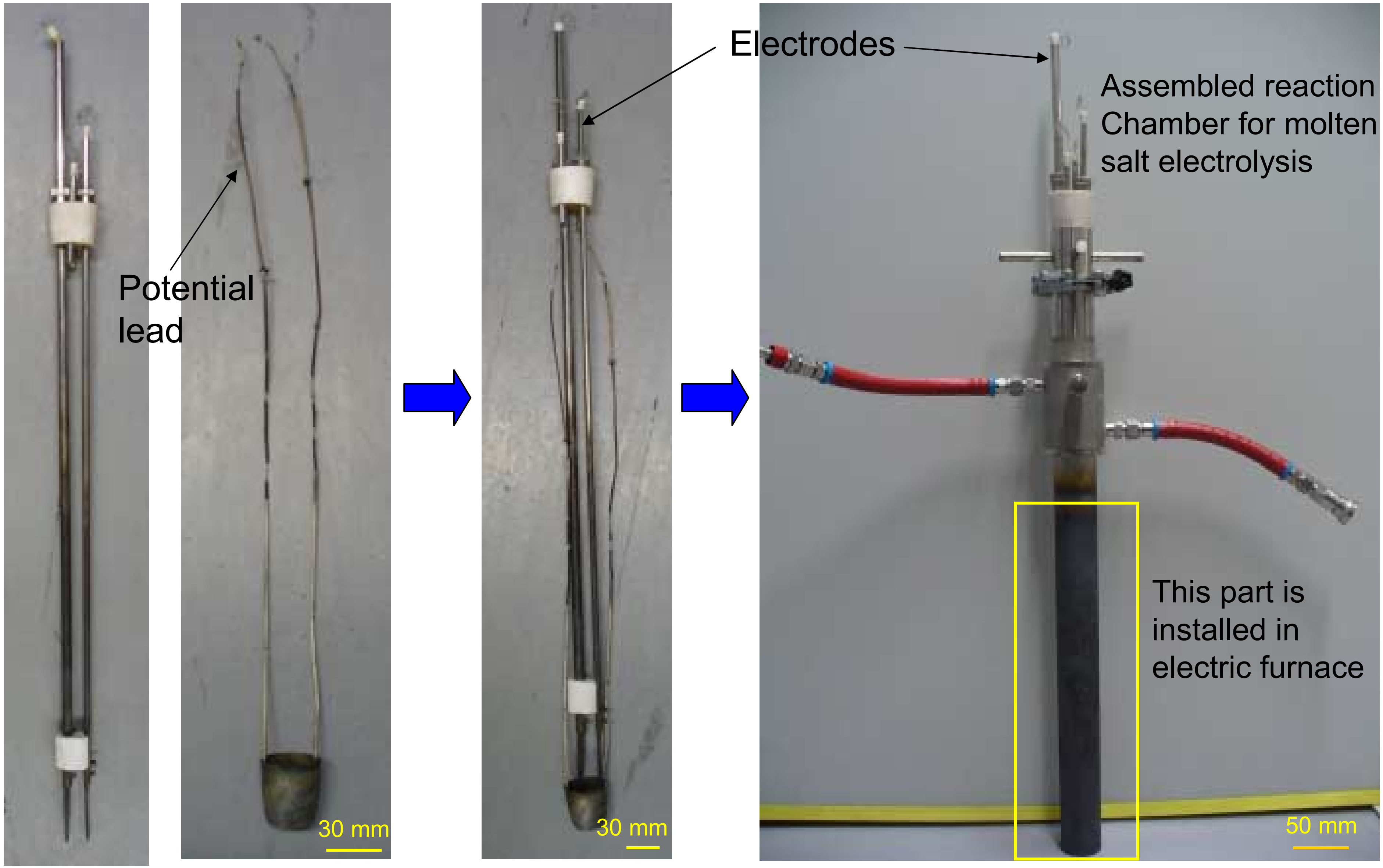
Feature

Ca contamination to Al-Sc alloy could be prevented by controlling a potential.

Experimental apparatus

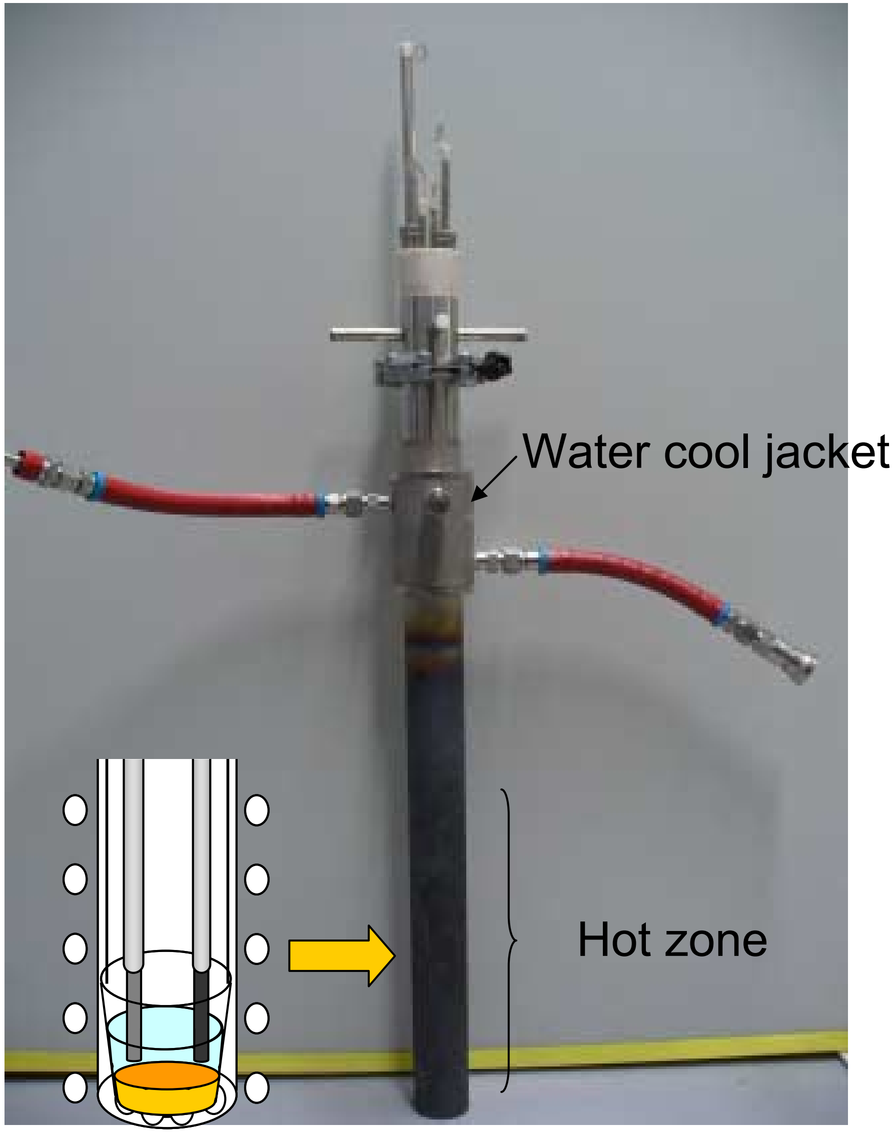


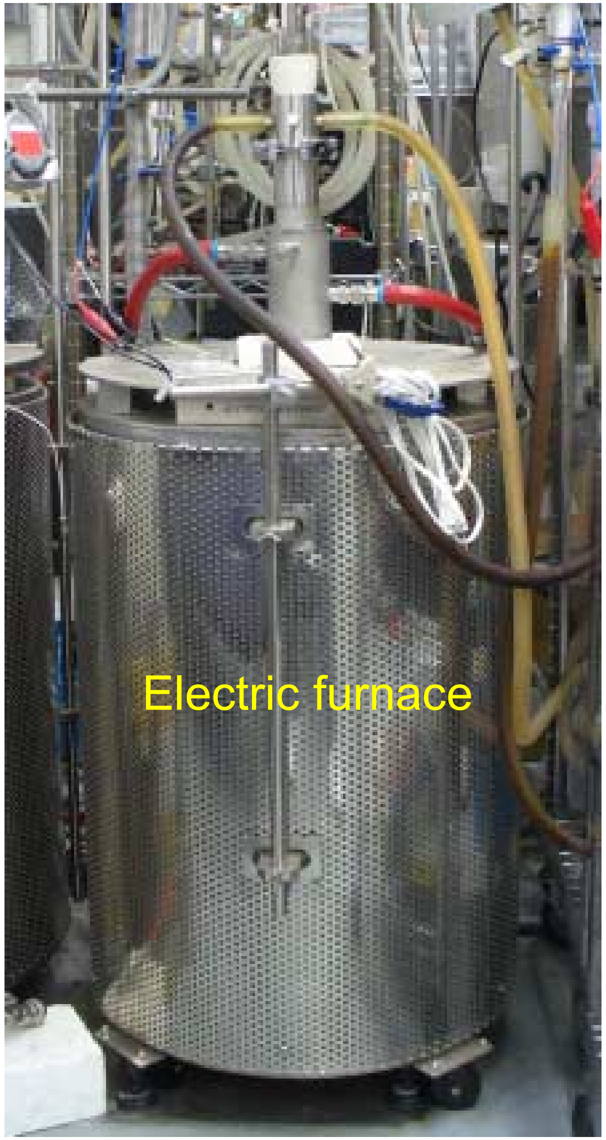
Experimental apparatus



Electrode Crucible Electrode＋Crucible

Assembled apparatus for molten salt electrolysis





Experimental condition

Exp. #	Molten salt System	Mass of samples, w_i / g					Cathode	Anode	Crucible	Electrolysis		
		Y_2O_3	Sc_2O_3	$CaCl_2$	Ag	Al				Current, i /A	Temp., T /K	Time, t '/s
A	$CaCl_2$-Y_2O_3	1.13	-	40	4.49	-	Silver	Carbon	Iron	0.5	1173	3600
B	$CaCl_2$-Y_2O_3	1.13	-	40	2.22	-	Silver	Carbon	Nickel	1.0	1173	1800
C	$CaCl_2$-Sc_2O_3	-	0.69	40	-	2.66	Aluminum	Carbon	Nickel	0.5	1173	1800

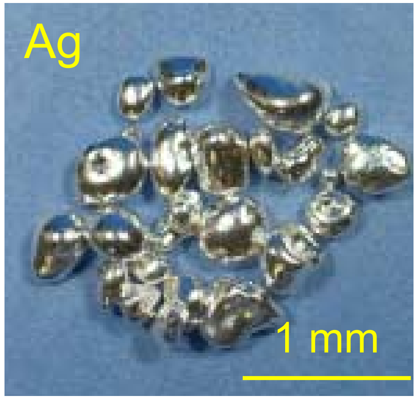
Theoretical decomposition voltage

		ΔG°(kJ, at 1100K)	ΔE°(V)
Sc_2O_3 + 3/2 C	→ 2 Sc + 3/2 CO_2	991.01	1.71
Sc_2O_3 + 3 C	→ 2 Sc + 3 CO	957.719	1.65
Sc_2O_3	→ 2 Sc + 3/2 O_2	1584.887	2.73
$CaCl_2(l)$	→ Ca(l) + Cl_2	629.108	3.26
CaO + 1/2 C	→ Ca(l) + 1/2 CO_2	322.825	1.67
CaO + C	→ Ca(l) + CO	311.728	1.61
CaO	→ Ca(l) +1/2 O_2	520.784	2.7

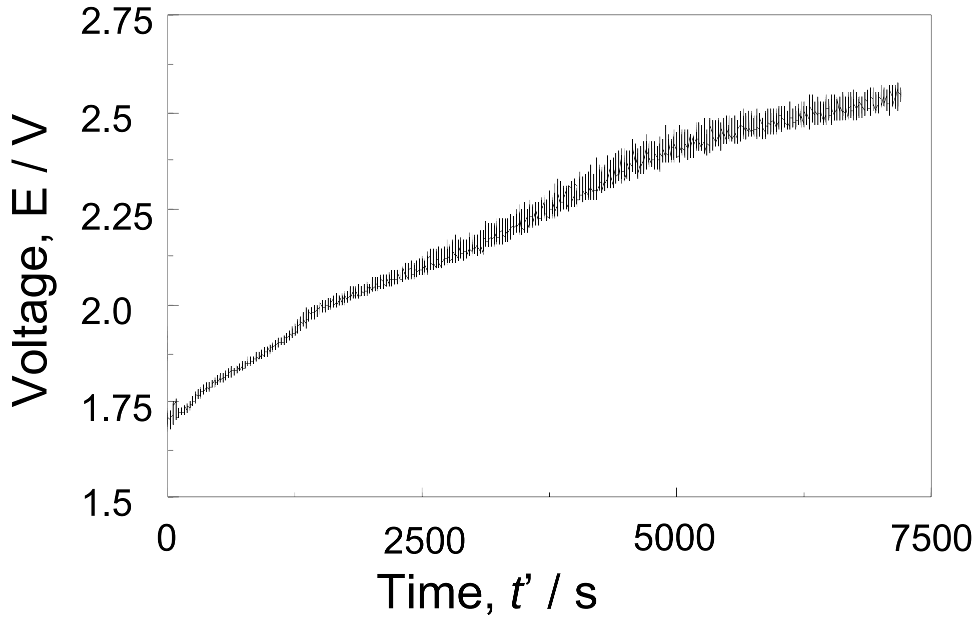
		ΔG°(at 1100K)	ΔE°(V)
Y_2O_3 + 3/2 C	→ 2 Y + 3/2 CO_2	992.574	1.71
Y_2O_3 + 3 C	→ 2 Y + 3 CO	959.283	1.66
Y_2O_3	→ 2 Y + 3/2 O_2	1586.451	2.74
$CaCl_2(l)$	→ Ca(l) + Cl_2	629.108	3.26
CaO + 1/2 C	→ Ca(l) + 1/2 CO_2	322.825	1.67
CaO + C	→ Ca(l) + CO	311.728	1.61
CaO	→ Ca(l) +1/2 O_2	520.784	2.7

Exp. A (Electrolysis of $CaCl_2$-Y_2O_3 molten salt)

(Anode: C, Cathode: Ag, Crucible: Fe, Current: 0.5 A, Time: 7200 s)



0.5 A, 7200 s



	Concentration of element *i*, C_i (mass%)[a]				
	Ag	Y	Fe	Ca	Ni
After exp.	53.93	2.90	41.83	0.79	0.56

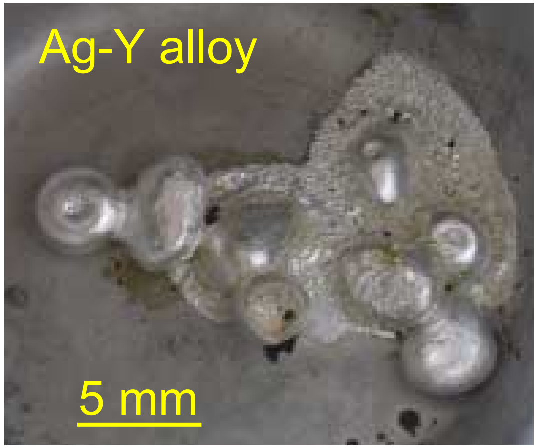
Exp. B (Electrolysis of $CaCl_2$-Y_2O_3 molten salt)

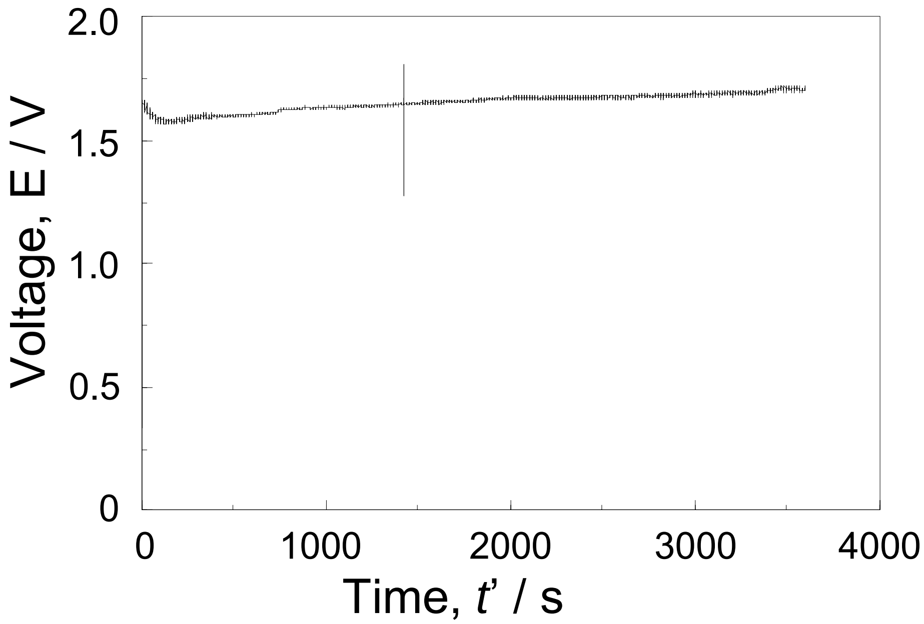
(Anode: C, Cathode: Ag, Crucible: Ni, Current: 1 A, Time: 3600 s)

Before Exp.

1 A, 3600 s

After Exp.



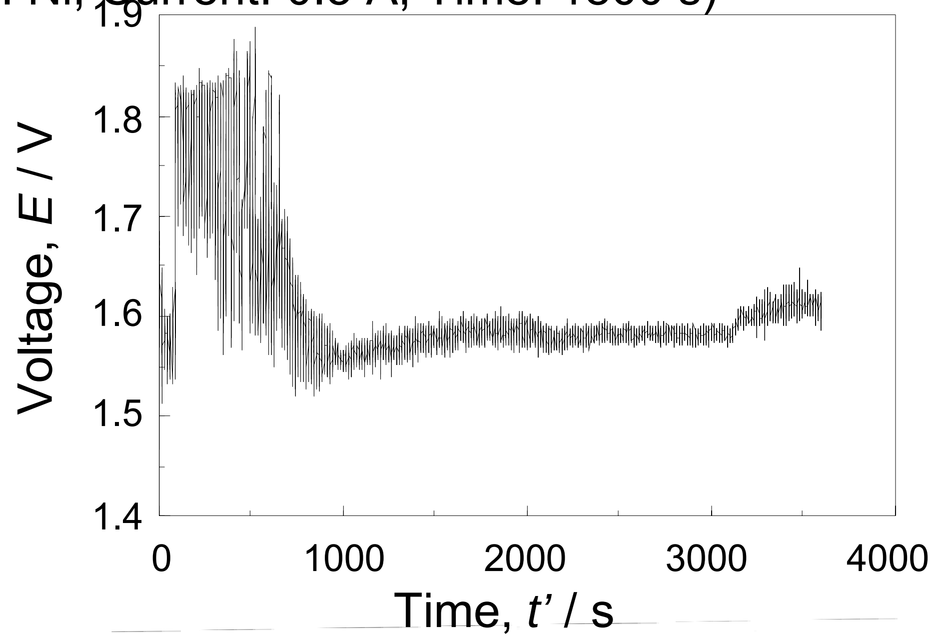


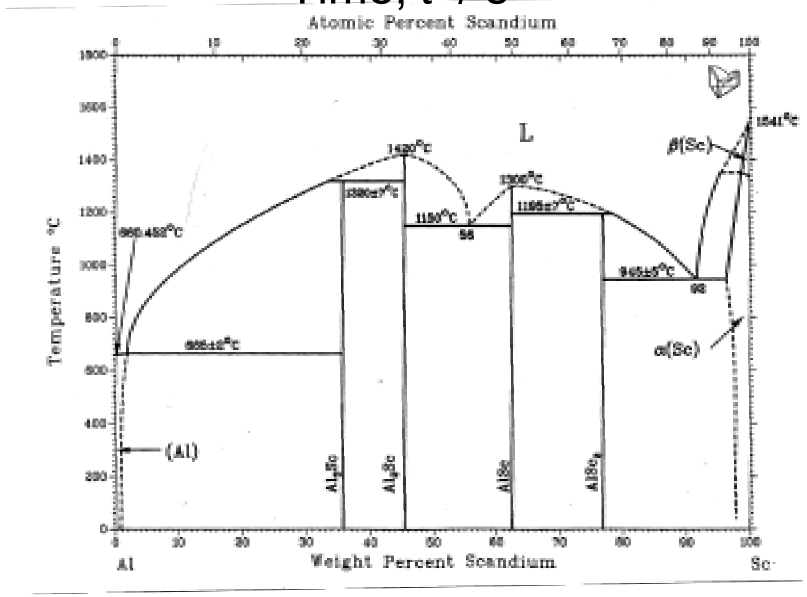
Exp. C (Electrolysis of $CaCl_2$-Sc_2O_3 molten salt)

(Anode: C, Cathode: Al, Crucible: Ni, Current: 0.5 A, Time: 1800 s)

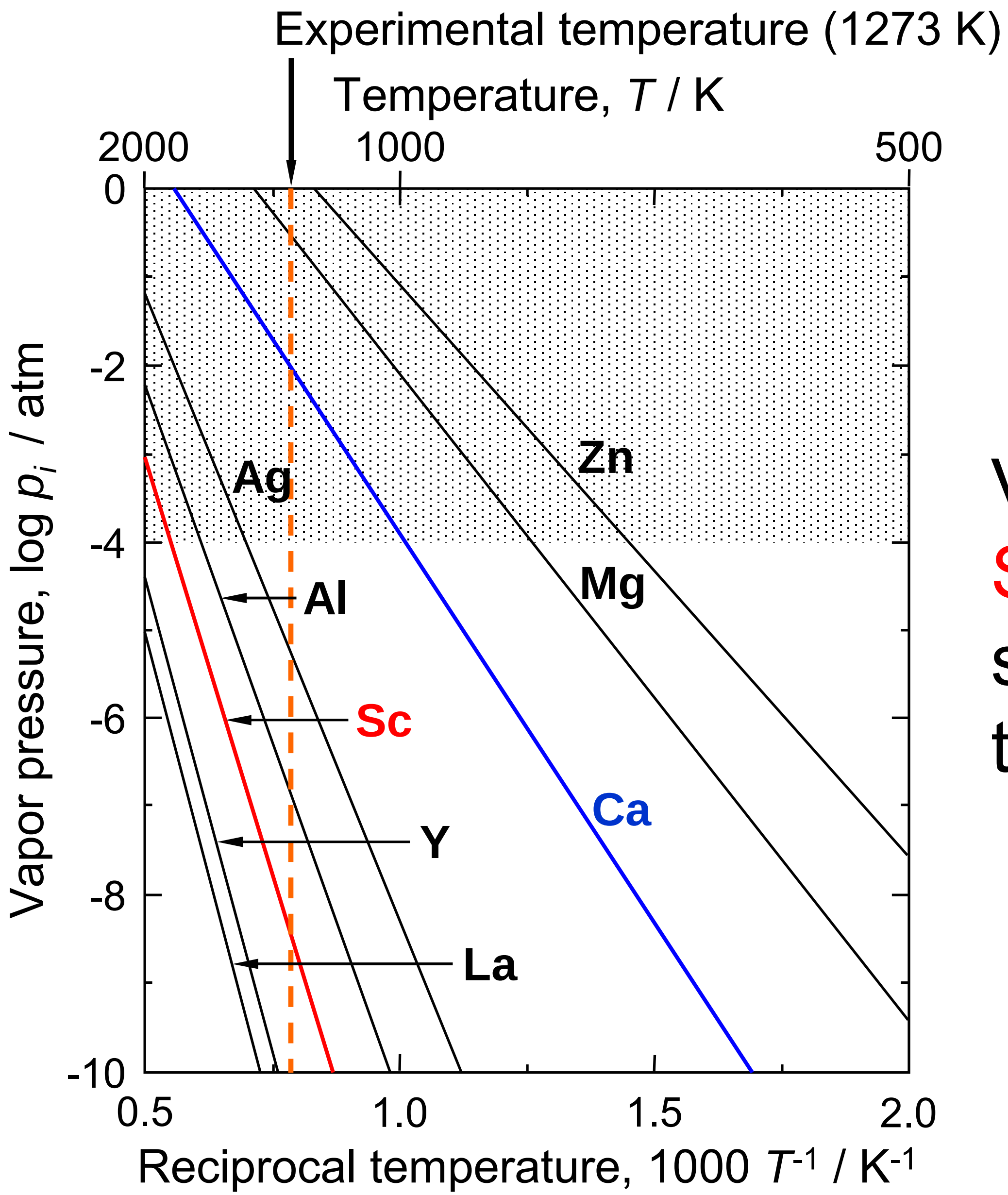
0.5 A, 3600 s

After exp.



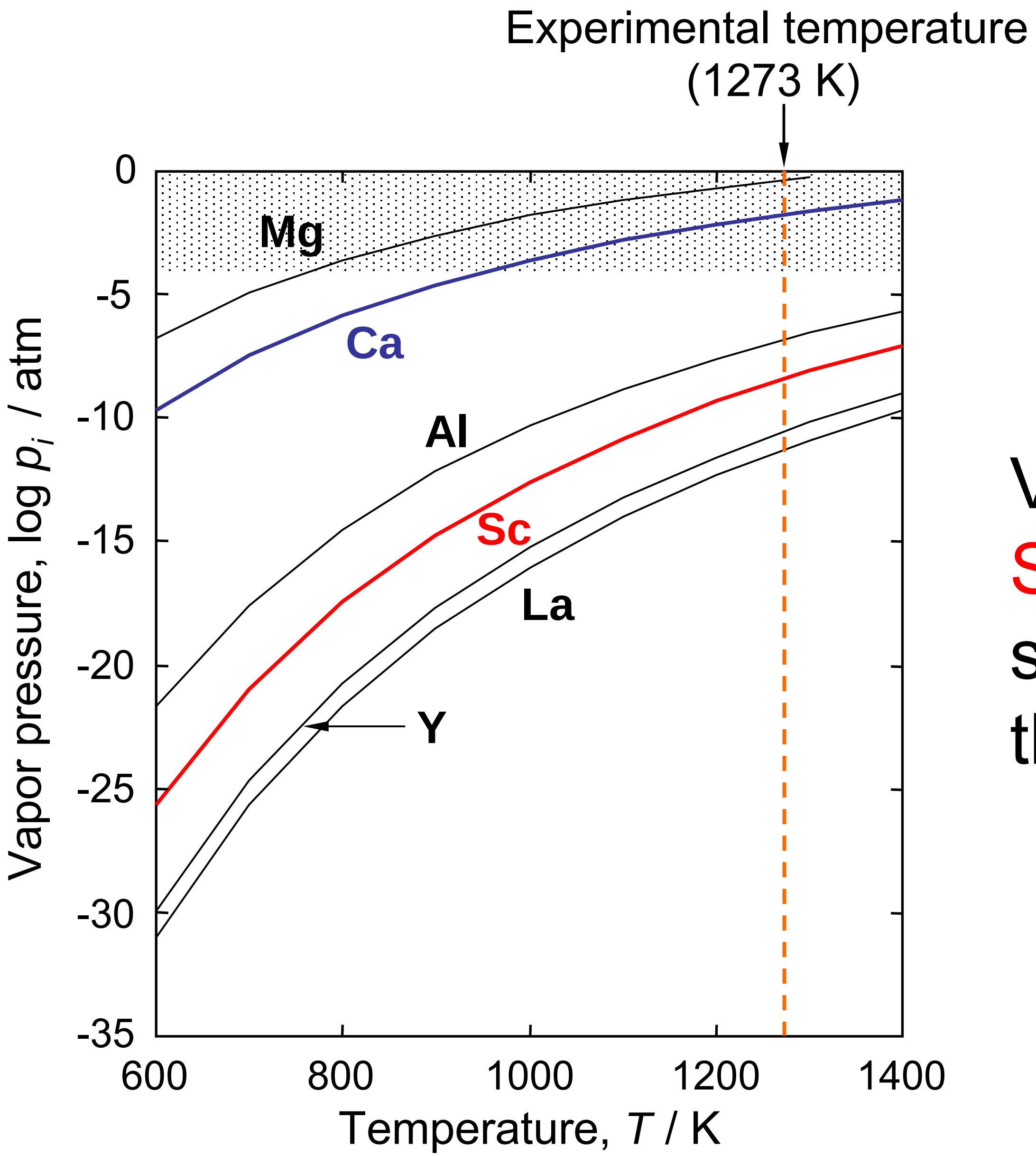


Vapor pressure



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)

Analytical results by XRF

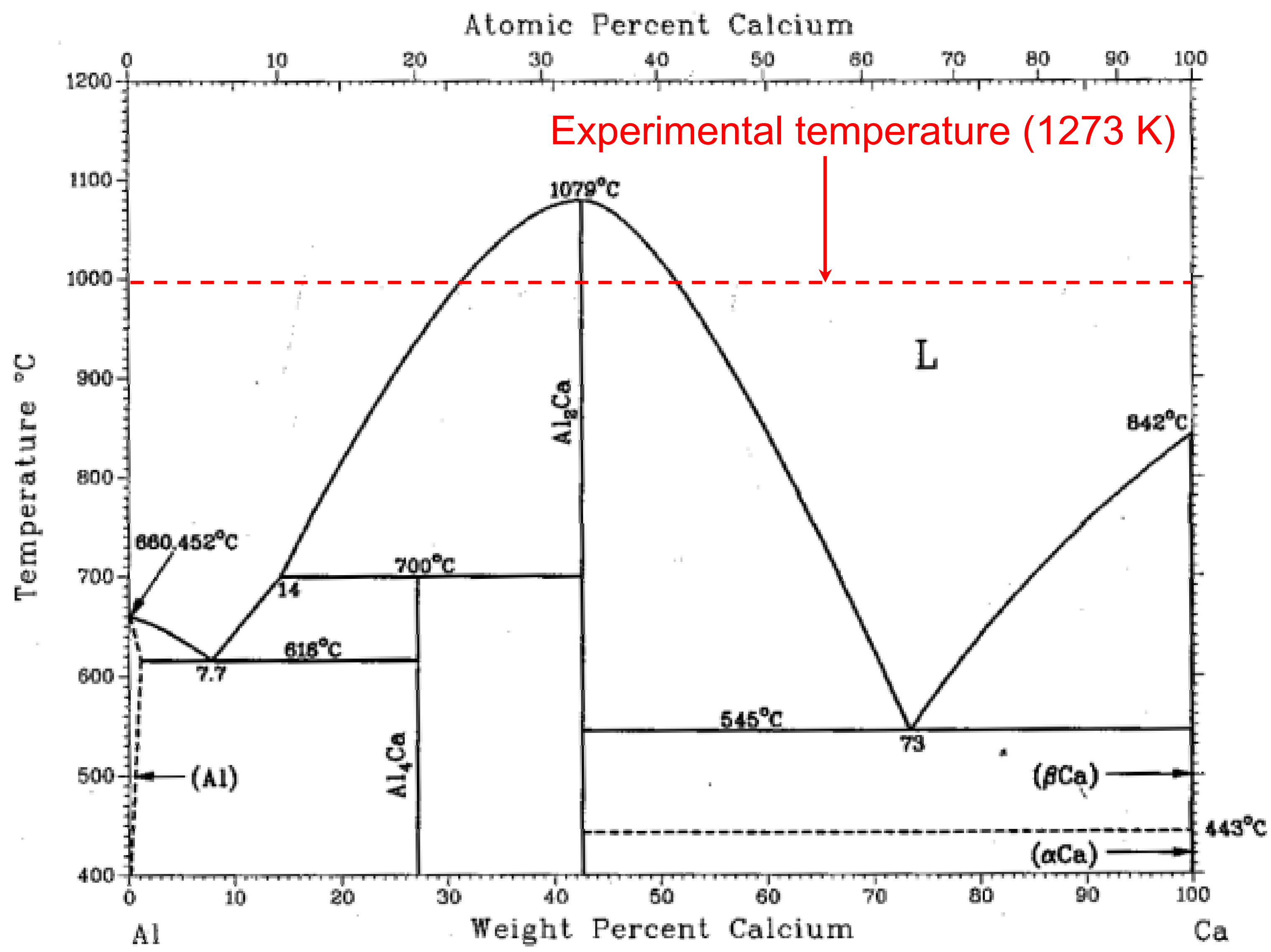
Table. Analytical results of the samples obtained after the reduction experiment.

Exp. no.	Nominal composition of Al-Sc alloy[a]	Excess reductant ratio, R_{Ca}[a]	Mass of flux w_{flux}/g	Concentration of element i, C_i (mass%)[b]					
				Al	Sc	Ca	Si	Fe	Ta
C	Al-9mass%Sc	2	0.00	58.32	19.00	22.45	< 0.01	0.14	< 0.01
D	Al-9mass%Sc	2	0.00	63.67	17.81	17.12	< 0.01	0.36	1.03
E	Al-9mass%Sc	2	1.27	61.14	21.76	14.83	< 0.01	0.41	1.85
F	Al-6mass%Sc	2	1.24	70.02	16.61	12.74	< 0.01	0.14	0.47
G	Al-5mass%Sc	1.5	1.06	73.87	13.37	10.85	0.30	0.22	1.37
H	Al-5mass%Sc	1.25	1.06	76.67	11.22	11.60	0.54	0.10	0.40
I	Al-5mass%Sc	1	1.06	82.44	9.76	5.93	< 0.01	1.16	0.68
J	Al-5mass%Sc	0.75	1.06	84.67	10.09	2.15	< 0.01	2.08	0.99

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

[b] Determined by X-ray fluorescence analysis.

Phase diagram for the Al-Ca system



T. B. Massalski, *Binary alloy phase diagrams*, (Metals Park, ASM International, 1990), 98