PRODUCTION OF SCANDIUM AND Al-Sc ALLOY BY USING $CaCl_2$ MOLTEN SALT

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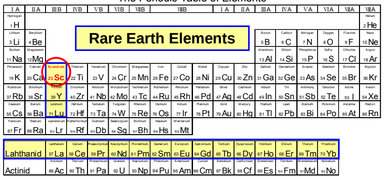
Introduction

・What is Scandium?

The Periodic Table of Elements



Sc is one of the rare earth elements (RE).

・Properties of Sc

Element	Atomic number Z	Atomic weight M	Density at 20 ℃ ρ/ g・cm^{-3}	Melting point T_m / ℃	Boiling point T_b / ℃	Ionic radius r_i / Å	Crystal structure at 25 ℃	Electro negativity	Price ($/kg)
Sc	21	44.96	2.99	1540	2832	0.75	hcp	1.20	18000.00
Y	39	88.91	4.47	1525	3337	0.90	hcp	1.11	450.00
La	57	138.91	6.15	920	3457	1.03	hcp	1.08	350.00
Ce	58	140.12	6.77	798	3427	1.01	fcc	1.08	350.00
Nd	60	144.24	7.01	1016	3067	0.98	hcp	1.07	450.00
Sm	62	150.40	7.54	1073	1791	0.96	hcp	1.07	300.00
Fe	26	55.85	7.87	1536	2863	0.55	bcc	1.64	0.03
Al	13	26.98	2.70	660	2520	0.53	fcc	1.47	1.44
Ti	22	47.87	4.54	1666	3289	0.61	hcp	1.32	9.66

・Lightweight ・Expensive
・Chemically reactive
・Sc_2O_3 is one of the most stable oxides on earth

・Resource

Sc is the 31st most abundant element in the earth's crust, with a crustal abundance of 22 ppm.

Thortveitite $(Sc,Y)_2Si_2O_7$

Minerals such as Thortveitite contain a large amount of Sc. However, such minerals are not used as a source of Sc because they are scarce.

Table Chemical composition of Thortveitite

Concentration of element *i*, C_i (wt%)*								
Al	Si	P	Sc	Mn	Fe	Y	Zr	Hf
1.33	26.25	0.21	58.13	0.55	3.45	5.99	2.39	1.69

* Determined by X-ray fluorescence analysis.

Table Minerals containing Sc

	Minerals	Sc_2O_3 content (%)		Minerals	Sc_2O_3 content (%)
Oxides	Magnetite	0.0001～0.04	Phosphates	Xenotime	0.0015～1.5
	Hematite	up to 0.15		Monazite	0.002～0.5
	Titanomagnetite	0.0002～0.02		Apatite	0.0003～0.08
	Ilmenite	0.0015～0.15	Silicates	Zircon	0.005～0.3
	Rutile	0.005～0.16		Beryl	0.0005～1.2
	Wolframite	0.005～1.3		Garnet	0.02～0.4
	Uraninite	0.15～0.2		Olivine	0.0003～0.02
	Laterite	0.003～0.03		Pyroxene	up to 0.04

Currently, Sc is produced in the form of oxide (Sc_2O_3) from rare earth ores or as a byproduct of uranium mill tailings.

Recently, Ni smelting has changed from a pyrometallurgical process to a hydrometallurgical process that can recover a large amount of Sc_2O_3 at a low cost.

・Applications

Al-Sc alloys

Metal halide lamp

Others

Catalysts, Laser crystals

Currently, Sc is mainly used as an alloying element for Al alloy.
Al-Sc alloy is expected to be used as a structural material for aircraft etc.

・Conventional process

・**Conversion into fluoride:**
$$Sc_2O_3 + 6\,HF \xrightarrow{973\,K} 2\,ScF_3 + 3\,H_2O$$

・**Reduction**
$$2\,ScF_3 + 3\,Ca \xrightarrow{1873\,K} 2\,Sc + 3\,CaF_2$$

Sc_2O_3 is converted into ScF_3 because it is thermodynamically stable. Further, it is difficult to reduce Sc_2O_3 to metallic Sc even by using Ca as a reductant.

・Disadvantages

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

・Purpose of this study

To develop a new process that can produce Sc metal or Al-Sc alloy directly from Sc_2O_3 at temperatures lower than those used in the conventional process.

Metallothermic Reduction

Thermodynamic analysis

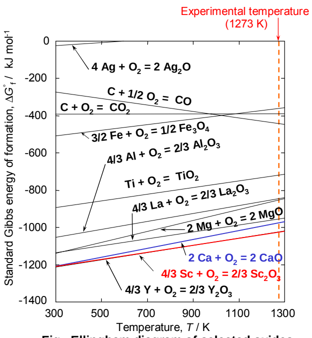


Fig. Ellingham diagram of selected oxides.

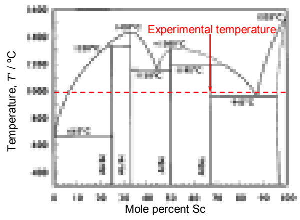


Fig. Phase diagram for the Al–Sc reaction

Experiment

・**Reduction:**
$$Sc_2O_3\,(s) + 3\,Ca\,(g) \rightarrow 2\,Sc\,(s) + 3\,CaO\,(s)$$

・**Reduction and alloying:**
$$Sc_2O_3\,(s) + Al\,(l) + 3\,Ca\,(g) \rightarrow \text{Al-Sc alloy}\,(l) + 3\,CaO\,(s)$$

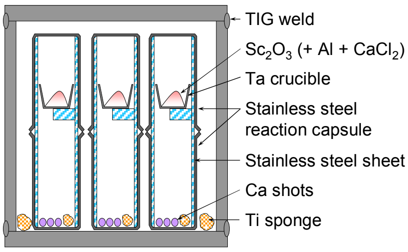


Fig. Schematic illustration of experimental apparatus for the metallothermic reduction experiment.

Table Experimental conditions for the metallothermic reduction

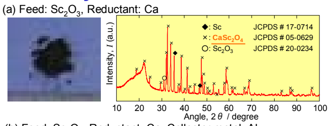
Exp. no.	Mass of sample, w_i/g: Feed	Collector metal	Flux	Reductant	Excess reductant ratio	Calculated nominal composition of Al-Sc alloy
	Sc_2O_3	Al	$CaCl_2$	Ca		
a	0.69	-	-	1.20	2	-
b	0.15	0.96	-	0.26	2	Al-6mol%Sc
c	0.15	0.96	1.27	0.26	2	Al-6mol%Sc

Reduction temperature: T = 1273 K
Holding time: t' = 6 hr

Results

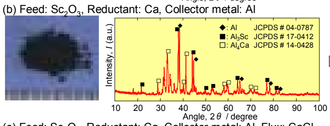
XRD analysis

(a) Feed: Sc_2O_3, Reductant: Ca



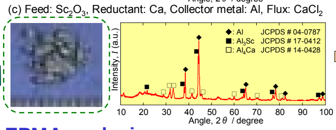
A complex oxide ($CaSc_2O_4$) was formed and reduction was incomplete.

(b) Feed: Sc_2O_3, Reductant: Ca, Collector metal: Al



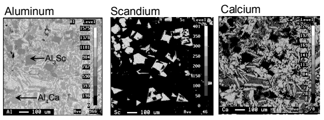
Sc_2O_3 was successfully reduced to metallic Sc and alloyed in situ to form Al-Sc liquid alloy during the reduction. It was difficult to separate the metal phase from the salt phase.

(c) Feed: Sc_2O_3, Reductant: Ca, Collector metal: Al, Flux: $CaCl_2$



Phase separation was improved by using $CaCl_2$ as a flux. However, excess Ca reductant remained in the Al_4Ca phase.

EPMA analysis



Conclusion

Al-Sc alloy was directly produced from Sc_2O_3 by using Al as the collector metal; however, excess Ca reductant remained in the alloy sample.

Molten Salt Electrolysis

Experiment

・**Anode**
$$C + x\,O^{2-} \rightarrow CO_x + 2x\,e^-$$

・**Cathode**
$$Sc_2O_3 + 6\,e^- \rightarrow 2\,Sc + 3\,O^{2-}$$

・**Overall reaction**
$$Sc_2O_3 + C \rightarrow 2\,Sc + CO_x$$

Table Theoretical decomposition voltage

Reactant	Product	ΔG°/ kJ at 1100 K	ΔE°/ V
$Sc_2O_3(s) + 3/2\,C(s)$	$\rightarrow 2\,Sc(s) + 3/2\,CO_2(g)$	991.01	1.71
$Sc_2O_3(s) + 3\,C(s)$	$\rightarrow 2\,Sc(s) + 3\,CO(g)$	957.719	1.65
$Sc_2O_3(s)$	$\rightarrow 2\,Sc(s) + 3/2\,O_2(g)$	1584.89	2.73
$Y_2O_3(s) + 3/2\,C(s)$	$\rightarrow 2\,Y(s) + 3/2\,CO_2(g)$	992.574	1.71
$Y_2O_3(s) + 3\,C(s)$	$\rightarrow 2\,Y(s) + 3\,CO(g)$	959.283	1.66
$Y_2O_3(s)$	$\rightarrow 2\,Y(s) + 3/2\,O_2(g)$	1586.45	2.74
$CaCl_2(l)$	$\rightarrow Ca(l) + Cl_2(g)$	629.108	3.26
$CaO(s) + 1/2\,C$	$\rightarrow Ca(l) + 1/2\,CO_2(g)$	322.825	1.67
$CaO(s) + C(s)$	$\rightarrow Ca(l) + CO(g)$	311.728	1.61
$CaO(s)$	$\rightarrow Ca(l) + 1/2\,O_2(g)$	520.784	2.70

Ca contamination of Al-Sc alloy could be prevented by controlling the potential between the anode and the cathode.

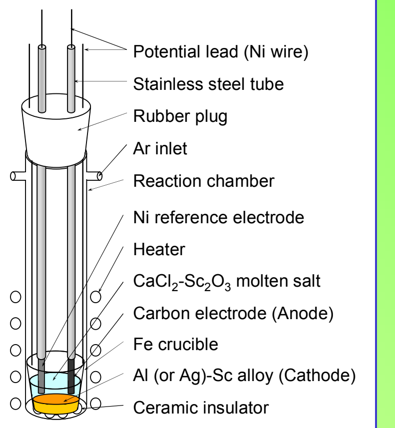
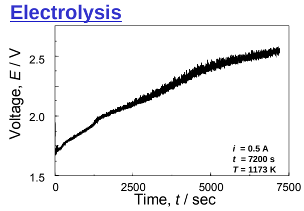


Fig. Schematic illustration of experimental apparatus for molten salt electrolysis.

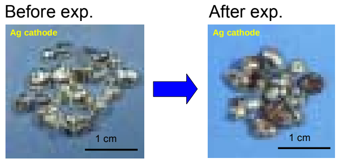
As a preliminary experiment, Y_2O_3 was used instead of Sc_2O_3, and the production of Ag-Y alloy by the electrolysis of $CaCl_2$-Y_2O_3 molten salt was investigated.

Results

Electrolysis



Before exp. After exp.



	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

[a] Determined by X-ray fluorescence analysis.

➡ Currently, Sc_2O_3 reduction is an ongoing experiment.

Conclusion

It was demonstrated that Ag-Y alloy could be produced by the electrolysis of $CaCl_2$-Y_2O_3 molten salt.
The electrolysis cell must be improved to prevent the contamination of the molten salt by Fe.

Future study

・**Metallothermic reduction**
Development of a new technique for preventing Ca contamination of Al-Sc alloy.

・**Molten salt electrolysis**
Improvement of electrolysis cell to prevent Fe contamination.
Investigation of the reaction mechanism of $CaCl_2$–Sc_2O_3 molten salt.
Development of a new direct production process of Sc or Al-Sc alloy by molten salt electrolysis.