

Production of Scandium and Al-Sc Alloy by Metallothermic Reduction

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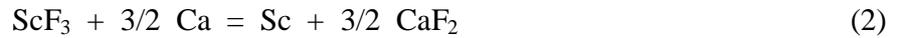
Abstract

A fundamental study was conducted on a new process for producing scandium (Sc) metal or aluminum-scandium (Al-Sc) alloy by the calciothermic reduction of scandium oxide (Sc_2O_3). In this study, aluminum (Al) and calcium chloride (CaCl_2) were used as the collector metal and flux for the reduction, respectively. A mixture of Sc_2O_3 , Al, and CaCl_2 in a tantalum crucible was placed inside a stainless steel reaction container, and the feed mixture was reacted with calcium (Ca) vapor at 1273 K for 6 h. After the reduction experiment, the reaction product (CaO), CaCl_2 flux, and excess Ca reductant were removed from the obtained alloy sample by leaching with an aqueous solution. The formation of Al_3Sc in the Al matrix phase of the alloy was confirmed by X-ray diffraction (XRD) and electron microprobe analysis (EPMA). This result indicates that Sc_2O_3 was successfully reduced to metallic Sc and alloyed in situ to form liquid Al-Sc alloy during the reduction. When Al was not used in the reduction experiment, a complex oxide (CaSc_2O_4) was formed, and the reduction was incomplete. This study demonstrates that the Al-Sc alloy can be directly produced by calciothermic reduction using CaCl_2 flux and Al collector metal.

Introduction

Scandium is classified along with yttrium (Y) and other lanthanides as a rare earth element (RE). Scandium is the 31st most abundant element in the earth's crust, with a crustal abundance of 22 ppm. Scandium is more abundant than some well-known metals such as tin (Sn, 14 ppm, 36th) and lead (Pb, 2.3 ppm, 51st) [1]. Although some very rare scandium minerals such as thortveitite (chemical composition: $(\text{Sc}, \text{Y})_2\text{Si}_2\text{O}_7$) containing large amounts of scandium (25–37 mass%) exist, such minerals are not commercially used as a source ore for scandium production because of their scarcity [2]. At present, scandium is produced in the form of an oxide (Sc_2O_3) as a byproduct of uranium (U), tungsten (W), or tantalum (Ta) smelting. The production volume of scandium as a byproduct is very small, and scandium and its compounds are extremely expensive. In recent times, nickel (Ni) smelting has been changing from a pyrometallurgical to a hydrometallurgical process that can recover nickel even from a low-grade laterite ore, and it is reported that scandium can also be efficiently recovered using this nickel smelting process. When a hydrometallurgical process for extracting nickel from low-grade ores containing scandium is established, nickel ore will become a new scandium resource [3].

Currently, metallic scandium is commercially produced by the following reactions:



In this process, Sc_2O_3 is first converted to ScF_3 by reacting Sc_2O_3 with hydrogen fluoride (HF) gas at 973 K because Sc_2O_3 is thermodynamically stable and it is difficult to reduce it to metallic scandium even by metallic calcium. The oxide feed is then converted to fluoride, and ScF_3 is reduced by using calcium at 1873 K [4]. Scandium metal with low oxide impurities can be definitely produced by this process; however, the production cost of this process is high because an expensive reaction apparatus is required for handling the fluorides. Furthermore, contamination of the produced metal by the reactor material and reductant is a serious technical problem because the reduction is based on a reduction reaction at high temperature.

Scandium and its compounds are presently applied in high intensity halide lamps, catalysts, laser crystals, and alloying elements [4]. In particular, the application of scandium as an alloying element for an aluminum alloy is gaining importance in the field of high-performance lightweight structural alloys. There are several advantages of adding trace amounts of scandium in aluminum alloys. Currently, aluminum containing 0.2 mass%Sc is commercially produced for application on bicycle frames, baseball bats, handguns, lacrosse sticks, and tent-poles. The representative effects of the addition of scandium are as follows: (1) the grain size of an alloy is reduced to a very fine size after casting, (2) the matrix of an alloy is strengthened by the precipitation of Al_3Sc , (3) recrystallization is prevented, and (4) superplastic properties are realized [5].

The demand for scandium as an alloying element in an aluminum alloy is expected to increase in the future, and it is important to develop a new production process for scandium metal or Al-Sc alloy at a low cost. Based on the above background, the production process for scandium metal or Al-Sc alloy by a calciothermic reduction of Sc_2O_3 at a temperature lower than that in the conventional process was investigated in this study.

Experimental

The form and purity of the starting materials used in this study are listed in Table I. Sc_2O_3 powder (average particle size: 13.7 μm) was mainly used as a feed material, and scandium fluoride (ScF_3) powder (average particle size: 14.3 μm) was also used in the comparison experiment. Calcium (Ca) shot was used as a reductant, and it was supplied to the feed material through a gas phase. Sc_2O_3 or ScF_3 powder was reduced to scandium metal by calcium vapor. By utilizing calcium vapor for feeding the reductant, contamination from the reductant can be effectively prevented, and a high-purity metal can be obtained. In some experiments, aluminum powder (53–106 μm) and CaCl_2 powder were also used as the collector metal and flux for the reduction, respectively. The amount of chemicals used in the reduction experiment was adjusted to form an Al-Sc alloy containing less than 10 mass% scandium when the reaction was completed. This is because the solubility of scandium in aluminum is approximately 10 mass% at 1273 K, based on the phase diagram for the Al-Sc binary system [6].

Table I. Starting materials used in this study.

Materials	Form	Purity (%)	Supplier
Sc ₂ O ₃	Powder	99.9 up	Pacific Metals Co., Ltd.
	Powder	99.9 up	Shin-etsu Chemical Co., Ltd
ScF ₃	Powder	99.9 up	Pacific Metals Co., Ltd.
Ca	Shot	98.0 up	Osaka Tokushu Goukin Co., Ltd.
CaCl ₂	Powder	99.5 up	Kanto Chemicals Co., Inc.
Al	Powder	99.9 up	Koujundo Chemical Lab Co., Ltd

Figure 1 is a schematic illustration of the experimental apparatus used for producing Sc metal or Al-Sc alloy by the calciothermic reduction of Sc₂O₃ or ScF₃. Some representative experimental conditions for the production of Sc metal or Al-Sc alloy are summarized in Table II. In the table, excess reductant ratio $R_{Ca} = w_{Ca} / w_{Ca}^{theo.}$, where w_{Ca} is the mass of the calcium reductant used in the experiment and $w_{Ca}^{theo.}$ is the stoichiometric mass of the calcium reductant necessary for reducing all Sc₂O₃ or ScF₃ to metallic scandium, is calculated and listed. Sc₂O₃ or ScF₃ feed powder (0.075–0.096 g) was mixed with aluminum or CaCl₂ powder and placed in a tantalum crucible in a stainless steel reaction container (O.D. ϕ 25 mm, height 76 mm). Calcium shots (0.049–1.29 g) were placed at the bottom of the reaction container along with a titanium sponge getter. Calcium was physically isolated from the feed materials, and during the reduction experiment, its vapor was supplied to the feed at unit activity through the gas phase. As shown in Figure 1, four stainless steel reaction containers were installed in a thick-walled stainless steel chamber (O. D. ϕ 76.2 mm, 110 mm height); a titanium sponge was also placed at the bottom of the chamber for getting nitrogen gas in the system. After the installation of the reaction containers, the chamber was sealed by tungsten insert gas (TIG) welding and then maintained at 1273 K in an electric furnace. The vapor pressure of calcium was calculated to be at 1.5×10^{-2} atm at 1273 K [7]; therefore, the feed was reacted with calcium vapor. After 6 h of reaction, the chamber was removed from the furnace and quenched in water. The samples in the tantalum crucible were mechanically recovered at room temperature, and in some cases, the recovered samples were rinsed with distilled water, alcohol, and acetone to remove the reaction product (CaO), CaCl₂ flux, and excess calcium reductant; the samples were then dried in vacuum.

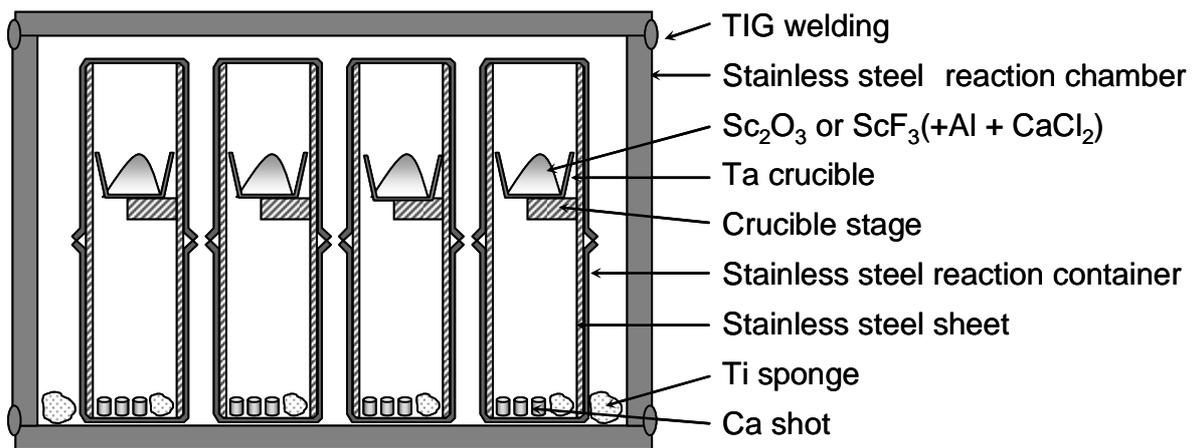


Figure 1. Schematic illustration of the experimental apparatus for the reduction experiment.

Table II Experimental condition for production of Sc metal or Al-Sc alloy by the calciothermic reduction experiment.

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 ₂ O 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, $w_{Ca}^{theo.}$: stoichiometric mass of reductant Ca necessary for reduction ($w_{Ca}^{theo.} = 0.87 \times w_{Sc_2O_3} + 0.22 \times w_{ScF_3}$)

The phases in the samples were identified by X-ray diffraction analysis (XRD, Rigaku, Rint 2000). The cross-sectional surface of the sample was observed by an electron microprobe analyzer (EPMA, JEOL, JXA8800RL), and elemental analysis was carried out. The composition of the samples was determined by X-ray fluorescence analysis (XRF, JEOL, JSX-3210).

Results and discussion

The reduction experiment in the absence of a collector metal

Figure 2(a) shows the XRD pattern of the sample obtained after the reduction experiment at 1273 K for 6 h using Sc₂O₃ as a feed material (Exp. A). In addition to scandium and Sc₂O₃, a complex oxide (i.e., CaSc₂O₄) was found in the sample. This result shows that reduction at 1273 K was incomplete; thus, it was difficult to produce scandium metal with a high yield under this experimental condition. This is because Sc₂O₃ is not only thermodynamically stable but also has a high affinity for CaO. Figure 2(b) shows the XRD pattern of the sample obtained after reduction at 1273 K for 6 h using ScF₃ as a feed material (Exp. B). When the fluoride feed was used, only scandium metal and the CaF₂ phase were identified in the obtained sample, and the reaction was complete. However, it was difficult to separate metallic scandium from the reaction product CaF₂. Scandium powder cannot be recovered by the conventional leaching process since scandium metal is chemically reactive even at room temperature and easily dissolves in water and acid.

The reduction experiment using aluminum as a collector metal

It was found that the reduction of Sc₂O₃ to metallic scandium by reaction only with calcium vapor is difficult. Hence, aluminum was added to the feed material as a collector metal for the scandium produced during the reduction. The amounts of feed material and aluminum collector metal were adjusted to obtain an aluminum alloy containing 9 mass% scandium when the reduction was assumed to be complete; all the scandium metal produced during reduction was

transferred to the aluminum phase. Figure 3(a) shows the XRD pattern of the sample obtained after the reduction experiment at 1273 K for 6 h using Sc_2O_3 as a feed material, in which aluminum was added as a collector metal (Exp. C). In the sample obtained after the experiment, Al, Al_3Sc , and Al_4Ca phases were identified. This result indicates that Sc_2O_3 was successfully reduced to metallic scandium and alloyed in situ to form liquid Al-Sc alloy without forming complex oxides such as CaSc_2O_4 . However, an intermetallic compound Al_4Ca was also formed in the alloy. Figure 3(b) shows the XRD pattern of the sample obtained after the reduction experiment at 1273 K for 6 h using ScF_3 as a starting material, in which aluminum was added as a collector metal (Exp. D). Al, Al_3Sc , Al_4Ca , and CaF_2 phases were identified, and the Al-Sc alloy was successfully produced. It was difficult to separate the metal phase from the salt phase that remained due to the experimental conditions employed in this study.

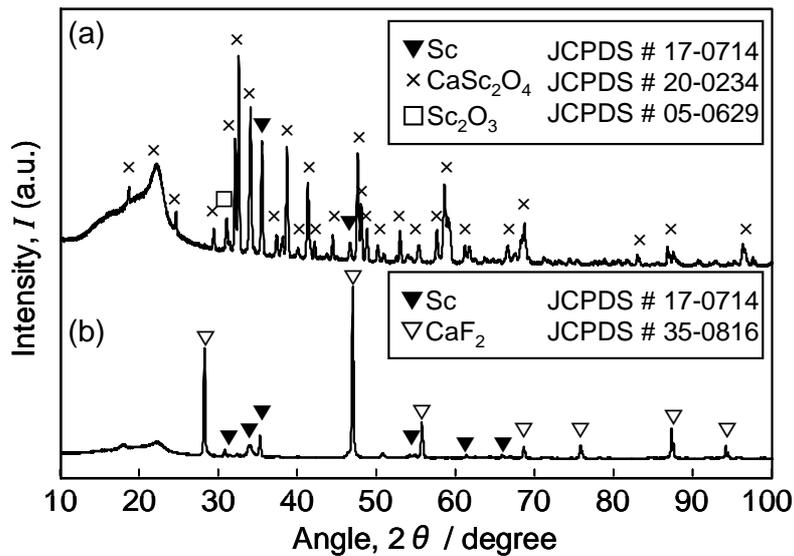


Figure 2. X-ray diffraction pattern of the samples obtained after the reduction. (Exps. A, B)
(Feed : (a) Sc_2O_3 , (b) ScF_3 , $T_{\text{red.}} = 1273$ K, $t'_{\text{red.}} = 6$ h)

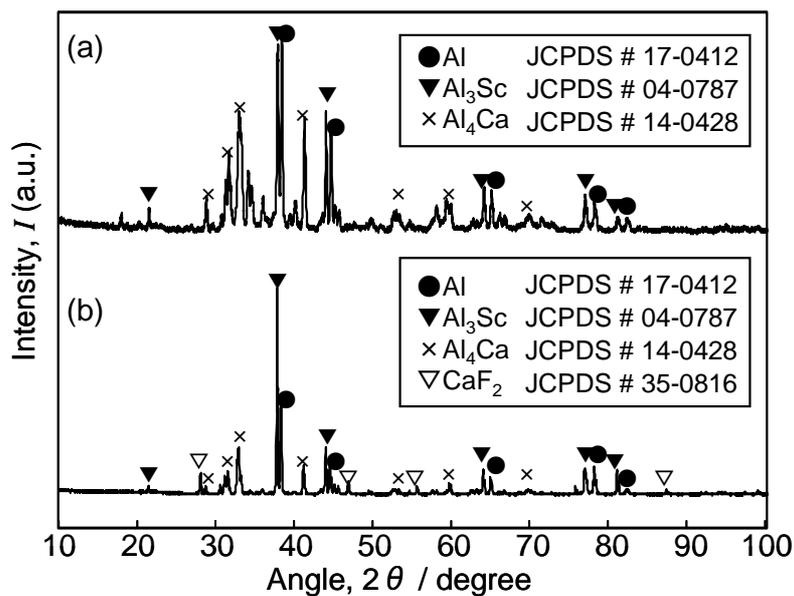


Figure 3. X-ray diffraction pattern of the samples obtained after the reduction. (Exps. C, D)
(Feed : (a) Sc_2O_3 , (b) ScF_3 , Collector metal : Al, $T_{\text{red.}} = 1273$ K, $t'_{\text{red.}} = 6$ h)

The reduction experiment using a collector metal and flux

In order to separate the metallic phase from the salt phases, flux (CaCl_2) was added to the feed materials. A metallic phase with a round shape (1–4 mm) was formed after the reduction experiment using CaCl_2 as flux; this phase was easily separated from the slug phase. Figure 4 shows the representative XRD pattern of the sample obtained after the reduction experiment using Sc_2O_3 as a starting material, in which aluminum and CaCl_2 were added as the collector metal and flux, respectively (Exp. E). Based on the XRD pattern, Al, Al_3Sc , and Al_4Ca phases were found, and the slug phase mainly consisting of CaCl_2 and CaO was successfully removed. This is because reaction product CaO dissolved in CaCl_2 and was removed along with CaCl_2 by leaching. Figure 5 shows the elemental mapping of the sectioned samples obtained after the reduction experiment (Exp. E). The Al_3Sc phase precipitated in aluminum matrix, and excess calcium also remained in the Al_4Ca phase.

The behavior of calcium in the sample after the reduction experiment was investigated by varying the amount of calcium reductant. Figure 6 shows the elemental mapping of the sectioned samples obtained after the reduction experiment by EPMA (Exps. G–J). The Al_4Ca phase precipitated in a dendritic structure and remained in the alloy even when $R_{\text{Ca}} = 0.75$. It is thermodynamically difficult to completely prevent calcium accumulation in the alloy by controlling the amount of calcium reductant. This is because aluminum has a strong affinity for calcium and the activity of calcium is high even when the amount of calcium reductant decreases. Currently, we are attempting to determine the concentration of scandium and calcium in the alloy and analyze the behavior of these elements under various experimental conditions. The chemical analysis of the alloys by XRF was previously carried out; however, we recently found large uncertainties in the values obtained in this analysis. If the concentration of calcium in the alloy is high, it must be reduced by an additional process such as vacuum distillation at an elevated temperature. It is important to reduce the concentration of the remaining calcium in the Al-Sc alloy products. Further investigations for optimizing the reduction process are currently in progress.

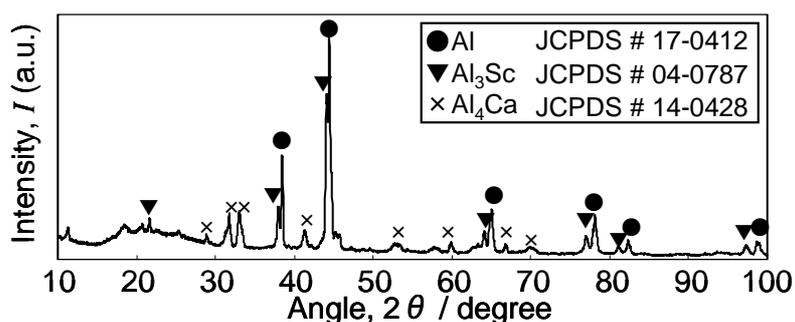


Figure 4. X-ray diffraction pattern of the samples obtained after the reduction. (Exp. E)
(Feed : Sc_2O_3 , Collector metal : Al, Flux : CaCl_2 , $T_{\text{red.}} = 1273 \text{ K}$, $t'_{\text{red.}} = 6 \text{ h}$
metal and flux, respectively (Exp. E).

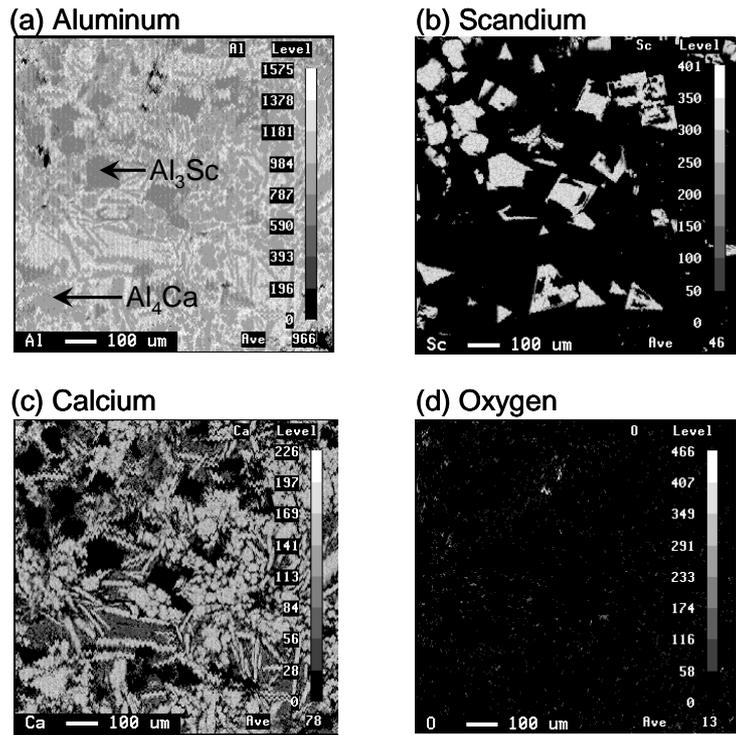


Figure 5. Elemental mapping of sectioned aluminum alloy sample obtained after the reduction experiment. (Exp. E)
 (Feed : Sc_2O_3 , Collector metal : Al, Flux : CaCl_2 , $T_{\text{red.}} = 1273 \text{ K}$, $t'_{\text{red.}} = 6 \text{ h}$)

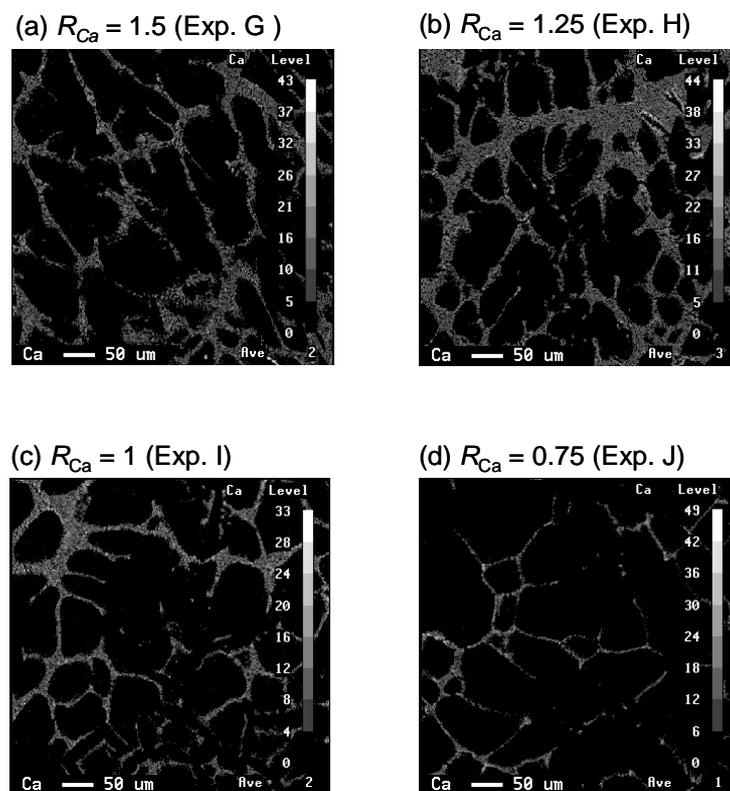


Figure 6. Calcium mapping of sectioned aluminum alloy sample obtained after the reduction experiment. (Exps. G-J)
 (Feed : Sc_2O_3 , Collector metal : Al, Flux : CaCl_2 , $T_{\text{red.}} = 1273 \text{ K}$, $t'_{\text{red.}} = 6 \text{ h}$)
 (a) $R_{\text{Ca}} = 1.5$, (b) $R_{\text{Ca}} = 1.25$, (c) $R_{\text{Ca}} = 1.0$, (d) $R_{\text{Ca}} = 0.75$, R_{Ca} is excess reductant ratio.

Conclusion and Future remarks

A fundamental study was conducted on a new production process for scandium metal or aluminum-scandium (Al-Sc) alloy by the calciothermic reduction of Sc_2O_3 or ScF_3 . When aluminum was not used as a collector metal for the reduction of Sc_2O_3 , a complex oxide (CaSc_2O_4) was formed, and the reduction was incomplete. On the contrary, when aluminum was used as a collector metal for the reduction of Sc_2O_3 , metallic scandium was successfully obtained directly from Sc_2O_3 and alloyed in situ to form liquid Al-Sc alloy. It is noteworthy that thermodynamically stable Sc_2O_3 was reduced by calcium by using aluminum as a collector metal at a temperature (1273 K) that is lower than the reaction temperature (~ 1873 K) employed in the conventional method. Furthermore, the separation of the metallic phase from the salt phase was improved by utilizing CaCl_2 as flux. The calcium contamination in the Al-Sc alloy remained an unsolved problem, especially when the amount of reductant was increased. This study demonstrated that the Al-Sc alloy can be directly produced by calciothermic reduction using CaCl_2 flux and Al collector metal. A new production process for scandium and Al-Sc alloy by molten salt electrolysis using CaCl_2 as a molten salt is also currently under investigation.

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