ELSEVIER

Journal of Alloys and Compounds 217 (1995) 218–225

Journal of
ALLOYS
AND COMPOUNDS

Recovery of rare metals from scrap of rare earth intermetallic material by chemical vapour transport

Kuniaki Murase, Ken-ichi Machida, Gin-ya Adachi *

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan

Received 28 April 1994; in final form 30 June 1994

Abstract

A dry process for recovery of rare metals from sludges of Sm_2Co_{17}, $Nd_2Fe_{14}B$ and $LaNi_5$ intermetallic compounds was investigated using chemical vapour transport along a given temperature gradient. Chlorine and aluminium chloride were used as a chlorinating agent and a transporting agent respectively, and the rare metal chlorides were chemically transported as vapour complexes, e.g. RAl_nCl_{3+3n} (R = rare earth), MAl_nCl_{2+3n} (M = Co, Ni). Rare earth chlorides were concentrated in the deposits in the higher temperature zone (800–900 °C) while cobalt and nickel chlorides were in the lower temperature zone (500–700 °C). Purity of each of the recovered chlorides was more than 99%. Chlorides of other metals, such as iron, copper, zirconium, and aluminium, were condensed at the outlet of the reactor (below 350 °C) without any contamination for the recoveries. After transport reaction for 6 h, yields of nickel and cobalt were more than 99%, whereas those of lanthanum, samarium, neodymium and dysprosium were lower, i.e. 27%, 39%, 59% and 68%, owing to the relatively low formation rate of RAl_nCl_{3+3n} complexes. If the transport reaction lasts for a longer time, the yields of rare earths can be improved.

Keywords: Recovery; Vapour complexes; Rare earths; Chlorination

1. Introduction

In recent years, a number of new intermetallic materials, in which rare earth or rare metal elements play an important role, have been rapidly advanced. Some compounds, i.e. $SmCo_5$, Sm_2Co_{17}, and $Nd_2Fe_{14}B$, have been well investigated for high performance permanent magnet materials and already produced industrially for uses in portable motors and so on. Hydrogen storage alloys of RNi_5 (R = rare earth) have come into use as cathode materials for a nickel–metal hydride secondary battery as a substitute for Ni–Cd battery because cadmium is harmful to the environment. In many cases, however, the resources of these rare metals (i.e. R, Co, and Ni) are limited and unevenly distributed to some particular regions in the world and, hence, their cost and supply have strongly depended on political circumstances. This results in a repeated shortage of supply and a sudden rise in cost for the rare metals. Consequently, it becomes necessary to recover these rare metals from the scrap of the intermetallic materials by profitable methods and to recycle them for further production of the materials.

For the sintered intermetallic compounds for the use of permanent magnet materials, a large amount of their sludge is produced in shaping and grinding processes to commercially demanded forms. The total volume of the sludge sometimes becomes greater than that of the commercial products. Hence the recovery from the sludge is significant, and solvent extraction and precipitation methods are currently being developed in order to recover the rare metals from scrap [1]. However, a new simple and easy method is desired, since current methods consist of a series of complicated processes such as dissolution of the scrap in solutions, filtering off insoluble constituents, concentration of filtrates, addition of precipitant, and drying and calcination of precipitates, which are characteristic of the so-called wet processes.

Meanwhile, many kinds of metal halides including rare earth halides form halogen-bridged vapour complexes with other volatile metal halides called complex formers [2–14]. Some formation schemes are expressed as follows:

$$RCl_3(s) + (n/2)Al_2Cl_6(g) \rightleftharpoons RAl_nCl_{3+3n}(g) \quad (n = 1\text{–}4) \qquad (1)$$

$$CoCl_2(s) + Al_2Cl_6(g) \rightleftharpoons CoAl_2Cl_8(g) \qquad (2)$$

---

* Corresponding author.

SSDI 0925-8388(94)01316-A

Table 1
Composition of scrap of rare earth intermetallic compounds used for raw materials for chemical vapour transport reaction

	La	Nd	Sm	Dy	Fe	Co	Ni	Cu	Zr	Al	B	Nb, Mo
Sm_2Co_{17} sludge	–	–	22	–	15	51	–	5.2	1.8	–	–	–
$Nd_2Fe_{14}B$ sludge	–	26	–	2.2	56	3.3	–	–	–	1.0	1.0	Trace
Mixture [a]	–	13	11	1.1	36	27	–	2.6	0.9	0.5	0.5	Trace
$LaNi_5$ powder	30	–	–	–	–	–	64	–	–	–	–	–

[a] Mixture of Sm_2Co_{17} and $Nd_2Fe_{14}B$ sludges.

$$NiCl_2(s) + Al_2Cl_6(g) \rightleftharpoons NiAl_2Cl_8(g) \qquad (3)$$

In general, the volatility of metal halides is appreciably enhanced by this reversible formation of the vapour complexes. The volatility enhancements, namely the factors of increase in the volatility due to the complexation in the presence of 1 atm of $Al_2Cl_6(g)$ as one of the typical complex formers, have been calculated as follows: 10^{13} for $NdCl_3$ (at 600 K), 10^{10} for $CoCl_2$ (700 K), and 1.2×10^8 for $NiCl_2$ (600 K) [7]. Metal iodide and bromide vapour complexes have been mainly studied in terms of the luminescent materials for metal halide lamps [3].

It is noteworthy that the vapour complexation with some complex formers renders it possible to transport the non-volatile rare earth chlorides through a reactor with a temperature gradient and to condense the chlorides along the gradient according to the reverse process of the complexation [15,16]. This chemical vapour transport (CVT) reaction has been investigated principally in the fields of preparation chemistry and separation chemistry: a method to obtain anhydrous RCl_3 on a laboratory scale [17,18], a gas–solid chromatograph system for mutual separation of radioactive RCl_3 tracers [19], and purification technique for niobium contaminated by tantalum [20].

Particularly, we have also recently reported that the mutual separation of rare earth chlorides is satisfactorily conducted by a CVT reaction along various well-controlled temperature gradients via formation of vapour complexes using $AlCl_3$ and/or ACl (A = alkaline metal) as complex formers [16,21–24]. In addition, the recovery of samarium and cobalt from the sludge of Sm_2Co_{17} alloy has been found to be effectively performed by the same method [25]. Since the method is based on differences in the temperature dependences of formation–decomposition equilibria of the vapour complexes it is free from the above-mentioned complicated treatments characteristic of the wet process.

In the present work, the recovery of rare metals from the intermetallic compounds Sm_2Co_{17}, $Nd_2Fe_{14}B$, and $LaNi_5$ was studied by the CVT technique using $AlCl_3$ as the complex former.

2. Experimental details

The sludges of Sm_2Co_{17} and $Nd_2Fe_{14}B$ intermetallic compounds were supplied by Shin-Etsu Chemical Co. Ltd. and used without any pretreatment except for drying overnight in vacuo at ambient temperature. The ground scrap of $LaNi_5$ alloy provided by Santoku Metal Industry was used without any pretreatment. Compositions of the metallic elements, including boron in $Nd_2Fe_{14}B$, summarized in Table 1 were determined by means of X-ray fluorometry. The Sm_2Co_{17} sludge contains some additives (Fe, Cu, and Zr) and also the $Nd_2Fe_{14}B$ (Dy, Co, Al, Nb, and Mo) in order to improve magnetic properties such as saturation magnetization, coercive force, and Curie temperature. These scraps were oxidized to a certain degree since these contain metallic R, Fe, and Ni which are easily oxidized in the presence of oxygen or water. Abundances of the oxides in the sludge were 18% (Sm_2Co_{17} sludge), 35% ($Nd_2Fe_{14}B$ sludge), and 28% ($LaNi_5$ alloy). (In the case of Sm_2Co_{17} scrap, for example, 0.0290 g of the dried sludge was weighed and analysed for the contents of five component metals, i.e. Sm, Co, Fe, Cu, and Zr. If these component metals had been fully oxidized with the most usual oxidation numbers, Sm_2O_3, Co_2O_3, Fe_2O_3, CuO, and ZrO_2, in the raw sludge, then the sum of the masses of these oxides corresponding to the determined molar quantities would be 0.0367 g. On the contrary, if all of the components had been wholly metallic, then the sum would be 0.0273 g. Therefore the abundance of the oxides in the Sm_2Co_{17} sludge was calculated as 18%, the ratio of 0.0290 g − 0.0273 g to 0.0367 g − 0.0273 g.)

Details of the apparatus employed for the CVT reaction have been reported elsewhere [16]. The apparatus includes two tubular electric furnaces A and B (Fig. 1). The heating element in furnace B was divided into eight separate heating zones, with every

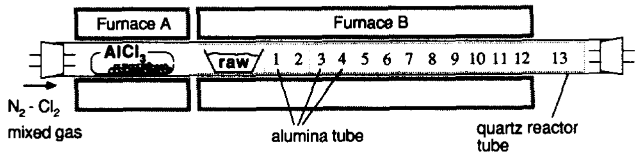

Fig. 1. Assembly of electric furnaces for CVT reaction. Numbers in furnace B denote fraction number of separation.

zone controlled differently by a thermoregulator so as to produce various temperature gradients along the quartz tube reactor. The thermoregulators were connected with thermocouples placed on the inner wall of the furnace. On setting the temperature gradient, the temperature of every zone was roughly set first on the thermoregulators and, further, the real temperatures along the central axis of the tube reactor were measured with a thermocouple inserted from the right-hand end in order to adjust the gradient precisely to the desired temperatures.

Aluminium chloride (10.0 g), the complex former, was sealed in a Pyrex ampoule (inner diameter, 14 mm; length, 10 cm) and loaded into furnace A. The ampoule has a small orifice (diameter, 0.5 mm) in order to generate gaseous aluminium chloride slowly when furnace A is heated. The scrap was weighed, put on a small carbon or alumina boat (length, ca. 8 cm), and placed at the summit of the temperature gradient (about 1050 °C) in furnace B. A mixed N_2 and Cl_2 gas (N_2, 30 ml min^{-1}; Cl_2, 5 ml min^{-1}) was flowed through the reactor as a carrier gas and a chlorinating agent respectively. After the desired temperature gradient was attained by operating furnace B, furnace A was heated over the temperature range 80–200 °C in order to generate the gaseous aluminium chloride, $Al_2Cl_6(g)$, the complex former.

The scrap on the boat was heated and directly chlorinated by Cl_2 gas. The resulting metal chloride mixture vaporizes according to a simple sublimation which sometimes accompanies the formation of aggregates such as dimers ($n=2$) or trimers ($n=3$); i.e.

$$n\mathrm{MCl}_x(\mathrm{s,\,l}) \rightleftharpoons \mathrm{M}_n\mathrm{Cl}_{nx}(\mathrm{g}) \qquad (4)$$

or vapour complexation with the $Al_2Cl_6(g)$ introduced from furnace A to B by the carrier gas:

$$n\mathrm{MCl}_x(\mathrm{s,\,l}) + (m/2)\mathrm{Al}_2\mathrm{Cl}_6(\mathrm{g}) \rightleftharpoons \mathrm{M}_n\mathrm{Al}_m\mathrm{Cl}_{nx+3m}(\mathrm{g}) \qquad (5)$$

(In practice, although a part of the $Al_2Cl_6(g)$ is decomposed into monomeric $AlCl_3(g)$ at high temperatures [26], the gaseous aluminium chloride in the present paper is described as $Al_2Cl_6(g)$ for the sake of convenience.) The resulting gas phase species were driven with the carrier gas along the temperature gradient and the metal chlorides (MCl_x) were deposited at different places in the reactor tube corresponding to the sublimation and decomposition temperatures of the reverse reaction of Eqs. (4) and (5) respectively.

After the CVT reaction had lasted for 6 h, the deposits were collected by removing the 13 pieces of alumina inner tubing [16]. The deposits were then dissolved individually into deionized water to determine the compositions of metal chlorides for every portion (fraction number FN) with a wavelength-dispersive type of X-ray fluorescent spectrometer (Rigaku System 3270A) using Zn^{2+} as an internal standard substance. When the sludge of $Nd_2Fe_{14}B$ was used as raw material, the boron content of every fraction was determined with an atomic absorption spectrometer (Nippon Jarrel-Ash AA-8500 mark II) using the absolute calibration method.

3. Results and discussion

3.1. Recovery from Sm_2Co_{17} sludge

3.1.1. Transport conditions

Among the five metal chlorides produced by chlorination of the Sm_2Co_{17} sludge, $SmCl_3$ is most difficult to transport chemically owing to the low volatility of rare earth chlorides. The CVT reactions under various conditions were tested using the Sm_2Co_{17} sludge (1.0 g) as a raw material. Six conditions attempted are listed in Table 2. The transported amounts of $SmCl_3$ under these conditions were compared with one another in terms of boat materials, a chlorinating agent, and a complex former.

First, an alumina boat was utilized to load the sludge. Under condition (i), without using any complex former, the total amount of transported $SmCl_3$ portion was quite small, while most other metal chlorides were effectively transported. On the contrary, under condition (iii), using $AlCl_3$ as the complex former, the amount of transported $SmCl_3$ was increased by a factor of 30 (4.0×10^{-4} mol). This demonstrates the effectiveness of using $AlCl_3$ as the complex former for the CVT of non-volatile $SmCl_3$.

The CVT reaction under condition (i) produced white residue on the alumina boat, which was analysed by means of powder X-ray diffractometry. The obtained diffraction pattern coincided with the diffraction pattern for SmOCl [27]. This suggests either that samarium species (Sm and Sm_2O_3) in the sludge are not fully chlorinated into $SmCl_3$ but into SmOCl in the presence of Cl_2 gas, i.e.

$$2\mathrm{Sm}_2\mathrm{O}_3(\mathrm{s}) + 2\mathrm{Sm}(\mathrm{s}) + 3\mathrm{Cl}_2(\mathrm{g}) \longrightarrow 6\mathrm{SmOCl}(\mathrm{s}) \qquad (6)$$

Table 2
Amount of transported $SmCl_3$ under various reaction conditions

Transport condition	Boat material	Chlorinating agent	Complex former	Transported amount ($\times 10^{-4}$ mol)
(i)	Alumina	Cl_2	–	0.13
(ii)	Alumina	–	$AlCl_3$ [a]	1.8
(iii)	Alumina	Cl_2	$AlCl_3$	4.0
(iv)	C	Cl_2	–	2.0
(v)	C	Cl_2	$AlCl_3$	5.6
(vi)	Alumina [b]	Cl_2	$AlCl_3$	4.2

[a] Aluminium chloride also acts as chlorinating agent; see text.
[b] Active carbon powder (0.2 g) was added to the raw material.

or that, even if chlorinated into $SmCl_3$, the $SmCl_3$ immediately reacts with Al_2O_3, the boat material, and forms SmOCl:

$$SmCl_3(s, l) + Al_2O_3(s) \longrightarrow SmOCl(s) + AlOCl(s) \quad (7)$$

although X-ray diffraction pattern did not show the existence of AlOCl. On the contrary, SmOCl can react with $Al_2Cl_6(g)$ to directly form the vapour complex without the formation of $SmCl_3$ as an intermediate, i.e.

$$2SmOCl(s) + (n+1)Al_2Cl_6(g) \longrightarrow 2SmAl_nCl_{3+3n}(g) + 2AlOCl(s) \quad (8)$$

and, hence, the transported reaction took place under condition (iii). In this case, therefore, the $Al_2Cl_6(g)$ functions also as chlorinating agent. This is supported by the fact that the transport reaction more or less takes place under condition (ii), in the absence of Cl_2 gas flow.

In conclusion, the increase in the amount of transported $SmCl_3$ portion was attributed not only to a volatility enhancement due to the vapour complexation with $Al_2Cl_6(g)$ but also to effective chlorination of SmOCl by the $Al_2Cl_6(g)$. Halogenation by gaseous aluminium halides is applied to the preparation of anhydrous metal halides from corresponding oxides on a laboratory scale [17,18]. For example, the chlorination of R_2O_3 is expressed as

$$2R_2O_3(s) + 3Al_2Cl_6(g) \longrightarrow 4RCl_3(s) + 6AlOCl(s) \quad (9)$$

$$R_2O_3(s) + Al_2Cl_6(g) \longrightarrow 2RCl_3(s) + Al_2O_3(s) \quad (10)$$

According to Eqs. (8)–(10) the $Al_2Cl_6(g)$ which acts as a chlorinating agent is converted to AlOCl or Al_2O_3. The formation of these inert substances against vapour complexation reduces the effective amount of $Al_2Cl_6(g)$ as a complex former. In order to depress the formation of SmOCl and the consumption of $Al_2Cl_6(g)$ as chlorinating agent, a carbon boat was used instead of that of alumina. The carbon boat which itself acts as a deoxidant via the reactions

$$Sm_2O_3(s) + 3C(s) + 3Cl_2(g) \longrightarrow 2SmCl_3(s, l) + 3CO(g) \quad (11)$$

$$SmOCl(s) + C(s) + Cl_2(g) \longrightarrow SmCl_3(s, l) + CO(g) \quad (12)$$

promotes the chlorination of Sm_2O_3 (or SmOCl) by Cl_2. In this case, carbon oxide (CO), carbon tetrachloride (CCl_4), or thionyl chloride ($SOCl_2$) indeed seem to be effective deoxidizing agents in attacking oxide and oxychloride, but these are not suitable in view of economy. The carbon boat is gradually corroded away according to Eqs. (11) and (12) with the progress of the CVT reaction. From the industrial aspect, however, the use of an exchangeable reactor made of carbon is economically advantageous rather than the use of expensive materials such as alumina and mullite.

With the carbon boat (condition (v)) the amount of transported $SmCl_3$ portion increased 45 times over the amount transported in condition (i). Furthermore, about 2.0×10^{-4} mol of $SmCl_3$, 15 times as large as that under condition (i), was transported even in the absence of complex former $AlCl_3$ (condition (iv)). On the contrary, addition of active carbon (0.2 g) in the alumina boat instead of using the carbon boat (condition (vi)) is also effective in chlorinating the sludge. These results suggest that the use of the alumina boat reduces the transported amount of $SmCl_3$, owing presumably to the reaction of $SmCl_3$ with Al_2O_3 as Eq. (7). Based on the results, condition (v) was adopted as the transport condition for further investigation of the recovery characteristics unless otherwise indicated.

3.1.2. *Recovery of samarium and cobalt*

Fig. 2 shows deposition profiles for transported $SmCl_3$ and $CoCl_2$ portions against the fraction number FN, together with the operated temperature gradient. Temperature ranges of each fraction are summarized in Table 3. The amount of $SmCl_3$ deposit peaked at FN = 3 (approximate temperature range, 960–1000 °C), while $CoCl_2$ peaked at FN = 11 (520–700 °C). The $CoCl_2$ was obtained as anhydrous blue plates.

The CVT reaction lasted for 6 h and the transportation rate of $CoCl_2$ was more than 99.9% whereas that of $SmCl_3$ was 59%. This is attributed to the fact that the formation reaction of vapour complexes RAl_nCl_{3+3n} is generally slow to equilibrate [28]. Fig. 2(c) shows the profiles of purities of $SmCl_3$ and $CoCl_2$ represented in molar per cent against the sum of the molar quantities of deposited elements, i.e. Sm, Co, Fe, Cu, and Zr. The chlorides $SmCl_3$ and $CoCl_2$ were concentrated up to 99.5 mol.% and 99.1 mol.% at FN = 3 and FN = 11 respectively.

Table 3
Temperature range of each fraction

FN	Temperature (°C)
1	1050–1043
2	1043–1003
3	1003–957
4	957–935
5	935–914
6	914–897
7	897–891
8	891–873
9	873–815
10	815–699
11	699–518
12	518–353
13	below 353

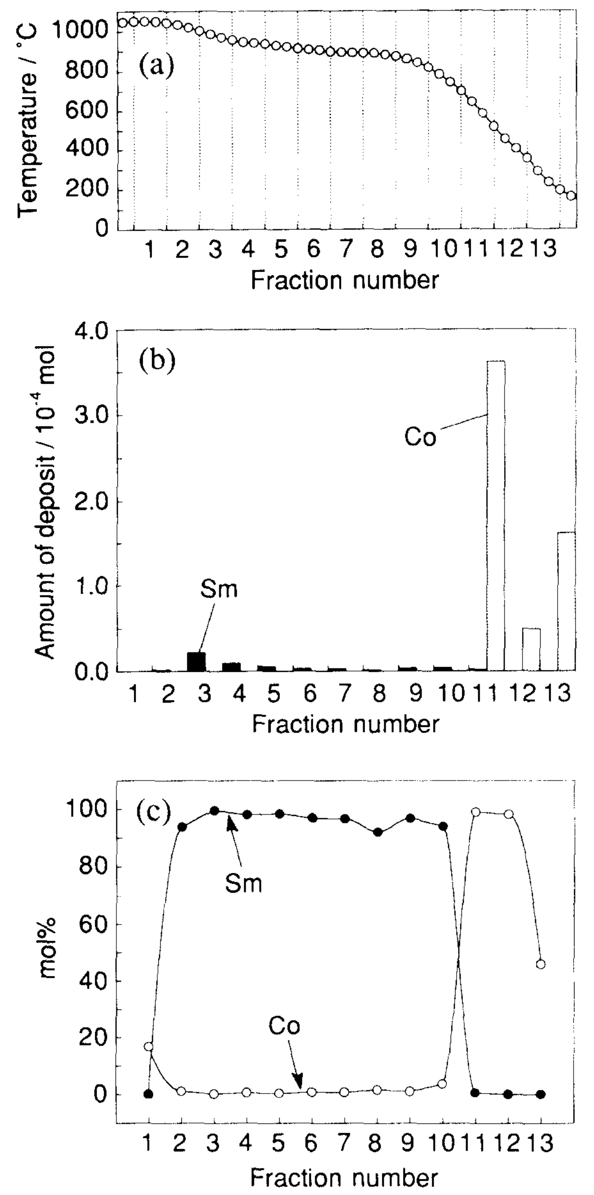

Fig. 2. (a) Temperature gradient and distribution of $SmCl_3$ and $CoCl_2$ deposits; distribution profile of $SmCl_3$ and $CoCl_2$ deposits represented (b) in moles and (c) in molar per cent. Raw material was dried Sm_2Co_{17} sludge (1.0 g) containing Fe, Cu, and Zr as additives; complex former was $AlCl_3$ (10.0 g); mixed N_2 and Cl_2 gas (N_2, 30 ml min^{-1}; Cl_2, 5 ml min^{-1}) was flowed as carrier; reaction time was 6 h.

Since the sublimation temperature of $CoCl_2$ is relatively low at about 500 °C, the $CoCl_2$ formed by the chlorination of the sludge was transported and condensed at FN = 11 even without the complex former, $AlCl_3$ (condition (iv)). Under this condition, however, contamination with $CuCl_2$ (or CuCl) was significant for FN = 11; the purity of $CoCl_2$ (FN = 11) was lowered at 98.4 mol.%. Consequently, the transport condition (v) is also suitable for the recovery of $CoCl_2$ as well as the case of $SmCl_3$.

3.1.3. *Deposition of other metal chlorides*

The vapour pressure of iron chloride or its complex with $AlCl_3$ is high below 350 °C. Therefore, 99.4% of transported iron chloride ($FeCl_3$ or $FeCl_2$) was condensed at FN = 13 as well as $AlCl_3$, and was not contaminated with recovered $SmCl_3$ and $CoCl_2$. Copper chloride ($CuCl_2$ or CuCl) was also condensed at FN = 13 under condition (v). However, as mentioned above, copper chloride was most concentrated at FN = 10 (700–815 °C) owing to the low volatility of copper chloride itself under condition (iv). Zirconium chloride ($ZrCl_4$) was condensed at FN = 13 under any transport condition at the sublimation temperature of 331 °C.

3.2. *Recovery from $Nd_2Fe_{14}B$ sludge*

3.2.1. *Recovery of neodymium and dysprosium*

Fig. 3 shows deposition profiles for an RCl_3 mixture (R = Nd and Dy) and $FeCl_3$ (or $FeCl_2$). The temperature gradient operated was the same as in Fig. 2(a). The recovered amounts of rare earths were maximized at FN = 3. The purity of rare earth chloride mixture in

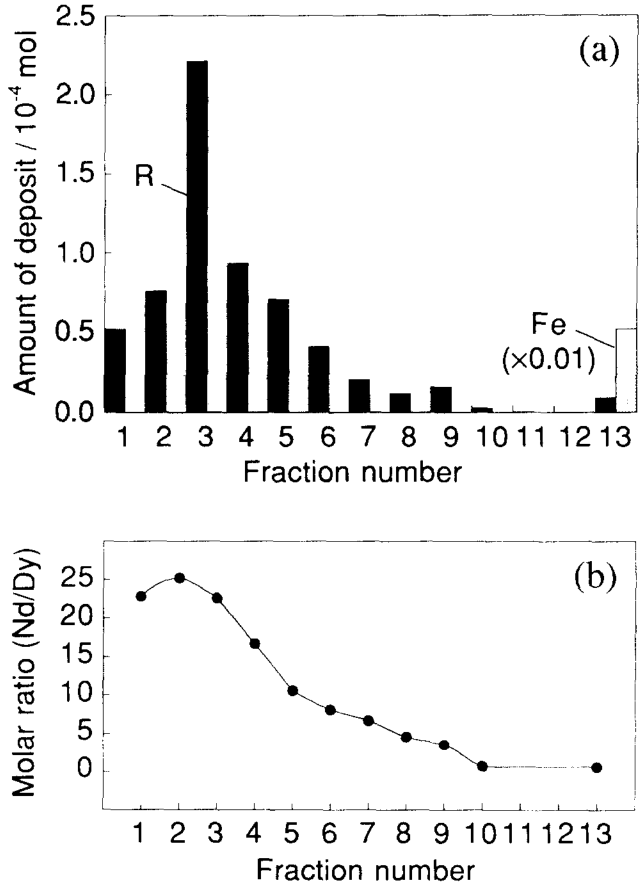

Fig. 3. (a) Distribution of RCl_3 mixture (R = Nd and Dy) and $FeCl_3$ deposits and (b) relationship between molar ratio Nd:Dy and fraction number. Raw material was dried $Nd_2Fe_{14}B$ sludge (1.0 g) containing Co, Al, Nb, and Mo as additives; complex former was $AlCl_3$ (10.0 g); mixed N_2 and Cl_2 gas (N_2, 30 ml min^{-1}; Cl_2, 5 ml min^{-1}) was flowed as carrier; reaction time was 6 h.

this fraction was 98.4 mol.%. Although $NdCl_3$ and $DyCl_3$ were recovered as the mixture, the molar ratio of Nd:Dy at each fraction increased with increase in its temperature range (see Fig. 3(b)). In other words, $NdCl_3$ is more concentrated in the fractions of higher temperatures. This is because the volatility of RAl_nCl_{3+3n} complexes with smaller rare earth ions was generally larger than those with larger rare earth ions [16] and, hence, the heavier rare earth chlorides, $DyCl_3$ in this case, tend to deposit at low temperature fractions. Application of a multiple CVT reaction employed for mutual separation of the $PrCl_3$–$SmCl_3$ [16] binary system may make it possible to improve the purity of recovered $NdCl_3$. Alternatively, if the recovered rare earths are used for the processing of the same material ($Nd_2Fe_{14}B$ in this case), the mutual separation of $NdCl_3$ and $DyCl_3$ may not be required.

Under transport condition (v) the transportation rates of $NdCl_3$ and $DyCl_3$ were 39% and 68% respectively, while under condition (iv) they were 34% and 59%. It is worth noting that the difference in the amount between the two conditions was smaller than the difference for transported $SmCl_3$ when Sm_2Co_{17} sludge was used as raw material: 28% under condition (iv) and 59% under condition (v). This means that the $FeCl_3$ formed by chlorination of $Nd_2Fe_{14}B$ sludge also acts as a complex former and that the rare earth chlorides are effectively transported in the absence of $AlCl_3$. However, purity of recovered rare earths was not so good, 91.1 mol.% (FN = 1) at the most, without $AlCl_3$.

3.2.2. Deposition of other metal chlorides

More than 99.9% of $FeCl_3$ (or $FeCl_2$) and $AlCl_3$ were deposited at FN = 13. Further, $CoCl_2$ was also condensed at FN = 13 for the most part (98.9%) while $CoCl_2$ was recovered in high purity at FN = 11 when Sm_2Co_{17} sludge was used as raw material. This difference is attributed to the "recrystallization effect" mentioned below.

The chlorides of boron and niobium were selectively deposited at FN = 13. Molybdenum was not detected from any fractions because the content in the sludge was quite small. However, the molybdenum should also deposit at FN = 13 as chloride considering the fact that the gaseous complexation between $MoCl_5$ and $AlCl_3$ does not occur [29] and that the boiling point of $MoCl_5$ is low at 268 °C.

3.3. Recovery of rare earths from a mixed sludge

Sludge is not always in a "pure" state, produced in the shaping process of a single material. It is probable that many kinds of sludges produced from various materials are mixed together. In order to demonstrate the recovery from sludge in an "impure" state, the CVT reaction of a 1:1 mixed sludge (1.0 g) of Sm_2Co_{17} and $Nd_2Fe_{14}B$ by weight was demonstrated.

Fig. 4 shows the deposition profiles of $NdCl_3$, $SmCl_3$, and $DyCl_3$ along the temperature gradient together with molar ratios of Nd:Sm, Sm:Dy, and Nd:Dy, that is the ratios of lighter and heavier rare earth element. Although the rare earth chlorides were recovered as a mixture by only one CVT operation, lighter elements of each pair were always concentrated in the fractions of the high temperature zone just as observed in the recovery from $Nd_2Fe_{14}B$ sludge. The slope of the molar ratio curves decreased in the order Nd:Dy > Sm:Dy > Nd:Sm. This indicates that the rare earth pairs for which atomic numbers are close to each other are difficult to separate mutually.

Deposition profiles of other metal chlorides were similar to the case of Sm_2Co_{17} or $Nd_2Fe_{14}B$ sludge treated independently as the raw material.

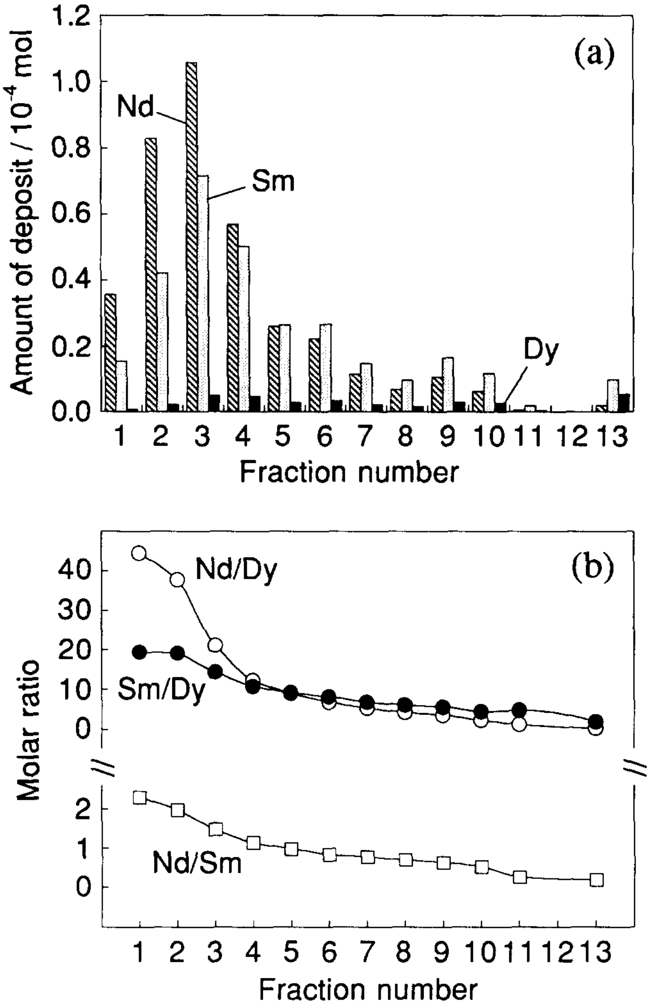

Fig. 4. (a) Distribution of $NdCl_3$, $SmCl_3$, and $DyCl_3$ deposits and (b) relationship between molar ratios of Nd:Dy, Sm:Dy, and Nd:Sm and fraction number. Raw material was mixture of dried Sm_2Co_{17} sludge (0.50 g) and $Nd_2Fe_{14}B$ sludges (0.50 g) containing some additives as in Table 1; complex former was $AlCl_3$ (10.0 g); mixed N_2 and Cl_2 gas (N_2, 30 ml min^{-1}; Cl_2, 5 ml min^{-1}) was flowed as carrier; reaction time was 6 h.

3.4. Deposition temperature of $CoCl_2$: a "recrystallization effect"

When Sm_2Co_{17} sludge was transported under condition (v), 63% of total transported $CoCl_2$ was recovered from FN = 11 (520–700 °C). However, when $Nd_2Fe_{14}B$ sludge, which contains a small amount of cobalt as an additive (see Table 1), was transported under the same conditions, 98% of the $CoCl_2$ was selectively deposited at FN = 13 (below 350 °C). This difference in deposition temperature of $CoCl_2$ is interpreted as follows.

The $CoCl_2$, whose volatility is higher than those of RCl_3, is vaporized according to a simple sublimation process expressed as

$$m\mathrm{CoCl_2(s, l)} \rightleftharpoons \mathrm{Co}_m\mathrm{Cl}_{2m}\mathrm{(g)} \qquad (13)$$

accompanying, in certain cases, the formation of aggregates ($m > 1$). On the contrary, $CoCl_2$ is known to form more volatile vapour complexes with $Al_2Cl_6(g)$ [5] as

$$\mathrm{CoCl_2(s, l, g)} + (n/2)\mathrm{Al_2Cl_6(g)} \rightleftharpoons \mathrm{CoAl}_n\mathrm{Cl}_{2+3n}\mathrm{(g)} \; (n = 1, 2, 3) \qquad (14)$$

At the temperatures around FN = 11, partial pressure of $\mathrm{CoAl}_n\mathrm{Cl}_{2+3n}(g)$ complexes is larger than that of free $\mathrm{Co}_m\mathrm{Cl}_{2m}(g)$ in the presence of excess amount of complex forming $Al_2Cl_6(g)$. When the Sm_2Co_{17} sludge was used as the raw material of the CVT reaction, cobalt species in the boat are in excess against the complex former. Therefore, a large portion of cobalt species is transported via $\mathrm{Co}_m\mathrm{Cl}_{2m}(g)$ in Eq. (13) and $CoCl_2(s)$ deposits at FN = 11 corresponding to the sublimation temperature of $CoCl_2$, ca. 500 °C. However, when $Nd_2Fe_{14}B$ is the raw material, the situation is reversed and the complex former is in excess since the content of cobalt as one of the additives in the sludge is small (3.3 wt.%; see Table 1). Hence, the majority of cobalt vapour species, $\mathrm{Co}_m\mathrm{Cl}_{2m}(g)$, which volatilize from the raw material, react with $Al_2Cl_6(g)$ vapour during the transportation by the carrier gas to form the stable vapour complex $\mathrm{CoAl}_n\mathrm{Cl}_{2+3n}(g)$ and, finally, deposit at FN = 13. In this case in particular the proportion of the condensed amount of $CoCl_2$ at FN = 13 to the total transported amount was quite high (98%) since $FeCl_3$ also acts as a complex former as mentioned above.

Table 4 summarizes amounts of $CoCl_2(s)$ deposited at FN = 11 and 13 under various CVT reactions. Total amount of complex former ($AlCl_3$ and $FeCl_3$) increases with the order (up to down) in Table 4. The proportion of $CoCl_2$ deposited at FN = 13 is increased in the same order. When Sm_2Co_{17} sludge was transported under condition (iv), for example, which is the reaction where there are scarcely any compounds acting as a complex former, the deposition at FN = 13 hardly took place.

Table 4
Amounts of deposit of $CoCl_2$ at FN = 11 and 13

Raw material (1.0 g)	Chlorinating agent	Complex former	Condensed amounts ($\times 10^{-5}$ mol)	
			FN = 11	FN = 13
Sm_2Co_{17} sludge	Cl_2	–	479	5.42
Sm_2Co_{17} sludge	Cl_2	$AlCl_3$	362	163
Mixture [a]	Cl_2	$AlCl_3$	19.2	186
$Nd_2Fe_{14}B$ sludge	Cl_2	–	2.44	9.05
$Nd_2Fe_{14}B$ sludge	Cl_2	$AlCl_3$	0.02	28.1

[a] Mixture of Sm_2Co_{17} and $Nd_2Fe_{14}B$ sludges.

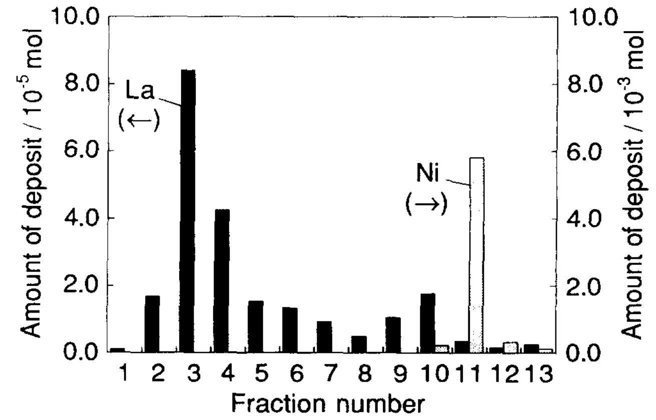

Fig. 5. Distribution of $LaCl_3$ and $NiCl_2$ deposits. Raw material was ground $LaNi_5$ alloy (0.50 g); complex former was $AlCl_3$ (10.0 g); mixed N_2 and Cl_2 gas (N_2, 30 ml min^{-1}; Cl_2 5 ml min^{-1}) was flowed as carrier; reaction time was 6 h.

We can compare this operation of removing the impurity, cobalt in this case, from rare earth by the vapour complexation with a complex former with a purification technique by means of recrystallization. The former technique is based on a gas–solid equilibrium, the latter on a liquid–solid equilibrium. If one looks on the gaseous $AlCl_3$ (or $FeCl_3$) as a "solvent" for the recrystallization technique, the formation of vapour complexes and the transportation along a temperature gradient correspond to the dissolution of a solute in a heated solvent and cooling the solution respectively, because both techniques take advantage of difference in affinity between plural chemical species: the former is between metal chlorides and a complex former and the latter solutes and a solvent.

3.5. Recovery of lanthanum and nickel from $LaNi_5$

When a powder of $LaNi_5$ alloy (0.50 g) was used as a raw material for the CVT reaction under condition (v), recovery of the two rare elements, La and Ni, was also effectively performed. As shown in Fig. 5, they were obtained as anhydrous chlorides and provided deposition profiles with peaks at FN = 3 and FN = 11. Purities of the chlorides were more than 99.9 mol.% in these fractions.

However, the transportation rate for $LaCl_3$ (27%) is lower than that for $NdCl_3$ (39%), $SmCl_3$ (59%) and $DyCl_3$ (68%) when Sm_2Co_{17} or $Nd_2Fe_{14}B$ were used as raw because the vapour complex $LaAl_nCl_{3+3n}$(g) containing the largest ionic radius element, lanthanum, among rare earths is the most difficult to form.

4. Conclusions

The recovery of rare metals was conducted effectively using the CVT process mediated by vapour complexes in metal halide systems. Rare earths, cobalt and nickel of almost 100% purity, were obtained from Sm_2Co_{17}, $Nd_2Fe_{14}B$ and $LaNi_5$ scraps through only one process. The obtained anhydrous rare earth chlorides can be converted directly to corresponding rare earth metals again, which are recycled to use for further processing of rare earth intermetallic compounds.

Acknowledgements

We thank Arai Science and Technology Foundation and Kansai Research Foundation for Technology Promotion for financial support. The present work is also supported by Grants-in-Aid for Scientific Research 06241106, 06241107 (Priority Areas "New Development of Rare Earth Complexes"), 05555236, and 051298 from the Ministry of Education, Science and Culture. The authors are sincerely grateful to Shin-Etsu Chemical Co. Ltd. for gifts of sludge of Sm_2Co_{17} and $Nd_2Fe_{14}B$. The authors are also sincerely grateful to Santoku Metal Industry for providing $LaNi_5$ alloy. K.M. is in receipt of a Fellowship of the Japan Society for the Promotion of Science for Japanese Junior Scientists.

References

[1] H. Koshimura and S. Yamamoto, *Proc. Symp. on Solvent Extraction, 1983,* p. 155; *Proc. Symp. on Solvent Extraction, 1984,* p. 115; *Proc. Symp. on Solvent Extraction, 1987,* Japanese Association of Solvent Extraction, Tokyo, p. 227.

[2] K. Hilpert, Chemistry of inorganic vapors, in M.J. Clarke, J.B. Goodenough, J.A. Ibers, C.K. Jørgensen, D.M.P. Mingos, J.B. Neilands, G.A. Palmer, D. Reinen, P.J. Sadler, R. Weiss and R.J.P. Williams (eds.), *Structure and Bonding,* Vol. 73, Springer, Berlin, 1990, p. 97.

[3] K. Hilpert, *J. Electrochem. Soc., 136* (1989) 2099.

[4] D.S. McPhail, M.G. Hocking and J.H.E. Jeffes, *J. Mater. Sci., 20* (1983) 449.

[5] H. Schäfer, *Adv. Inorg. Chem. Radiochem., 26* (1983) 201.

[6] M.H. Brooker and G.N. Papatheodorou, Vibrational spectroscopy of molten salts and related glasses and vapors, in G. Mamantov (ed.), *Advances in Molten Salt Chemistry,* Vol. 5, Elsevier, New York, 1983, p. 26.

[7] G.N. Papatheodorou, Spectroscopy, structure and bonding of high-temperature metal halide vapor complexes, in E. Kaldis (ed.), *Current Topics in Materials Science,* Vol. 10, North-Holland, New York, 1982, p. 249.

[8] G.N. Papatheodorou, Vibrational spectroscopy of high temperature metal-halide vapor complexes, in J.L. Gole and W.C. Stwalley (eds.), *Metal Bonding and Interactions in High Temperature Systems,* ACS Symposium Series, Vol. 179, American Chemical Society, 1982, p. 309.

[9] H. Schäfer, *Angew. Chem., Int. Edn. Engl., 15* (1976) 713.

[10] J.W. Hastie, *High Temperature Vapors,* Academic Press, New York, 1975.

[11] J.W. Hastie, Thermodynamic studies, by mass spectrometry, of molten mixed halide systems, in J. Braunstein, G. Mamantov and G.P. Smith (eds.), *Advances in Molten Salt Chemistry,* Vol. 1, Plenum, New York, 1972, p. 225.

[12] F.P. Emmenegger, *J. Cryst. Growth, 17* (1972) 31.

[13] G.I. Novikov and F.G. Gavryuchenkov, *Russ. Chem. Rev., 36* (1967) 156.

[14] A. Büchler and J.B. Berkowitz-Mattuck, *Adv. High Temp. Chem., 1* (1967) 95.

[15] H. Schäfer, *Z. Anorg. Allg. Chem., 403* (1974) 116.

[16] K. Murase, K. Shinozaki, Y. Hirashima, K. Machida and G. Adachi, *J. Alloys Comp., 198* (1993) 31.

[17] G.N. Papatheodorou and G.H. Kucera, *Inorg. Chem., 18* (1979) 385.

[18] H. Gunsilius, W. Urland and R. Kremer, *Z. Anorg. Allg. Chem., 550* (1987) 35.

[19] T.S. Zvarova and I. Zvara, *J. Chromatogr., 44* (1969) 604.

[20] D.R. Sadoway and S.N. Flengas, *Metall. Trans. B, 11* (1980) 57.

[21] G. Adachi, K. Shinozaki, Y. Hirashima and K. Machida, *J. Less-Common Met., 169* (1991) L1.

[22] G. Adachi, K. Murase, K. Shinozaki and K. Machida, *Chem. Lett.,* (1992) 511.

[23] K. Murase, K. Shinozaki, K. Machida and G. Adachi, *Bull. Chem. Soc. Jpn., 65* (1992) 2724.

[24] K. Murase, K. Machida and G. Adachi, *Chem. Lett.,* (1994) 1297.

[25] K. Murase, K. Machida and G. Adachi, *Chem. Lett.,* (1992) 1555.

[26] G.E. Vrieland and D.R. Stull, *J. Chem. Eng. Data, 12* (1967) 532.

[27] *X-ray Powder Diffraction Standards,* ASTM, Philadelphia, PA, Card 12-790 (SmOCl).

[28] H.A. Øye and D.M. Gruen, *J. Am. Chem. Soc., 91* (1969) 2229.

[29] H. Schäfer and U. Flörke, *Z. Anorg. Allg. Chem., 479* (1981) 89.