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Recovery of Rare Metals from the Sludge of Samarium-Cobalt Magnetic Alloy by a Chemical Vapor Transporting Method

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A dry process using chemical vapor transporting technique along temperature gradient was investigated for the recovery and recycling of rare metals from the sludge of Sm-Co binary alloys. For the permanent magnetic alloy sludge of Sm_2Co_{17}, the Sm and Co elements were effectively separated in the form of anhydrous chlorides with the purity higher than 99%.

Many fields of materials science using rare earth elements were rapidly advanced in recent years. Particularly, rare earth permanent magnetic materials such as $SmCo_5$, Sm_2Co_{17}, and $Nd_2Fe_{14}B$ have been well investigated and already produced industrially. However, a large amount of sludge is produced from the sintered rare earth magnetic alloys in the shaping process to commercially demanded forms. Therefore, whether the rare metals such as rare earth and cobalt elements are recovered and recycled from the scraps by a profitable method or not is one of significant problems from the viewpoint of the effective utilization of limited resources.

For the recovery of Sm and Co elements from the scrap of Sm-Co binary alloy, solvent extraction1a,b) and precipitation1c) methods are currently employed. However, since these consist of a series of complicated processes such as dissolution of the scrap with mineral acid, concentration of filtrates, and drying or calcination of precipitates, new simple and easy method is desired.

It is well known that many metal halide molecules form gas phase halogen-bridged complexes at elevated temperatures2) and some metals are chemically transported in the presence of halogenating agents and complex formers.3) By the formation of the vapor complexes, the volatility of rare earth chlorides, which is very low even at high temperatures, is appreciably enhanced, and a fractional chemical vapor transporting (CVT) along a well-controlled temperature gradient becomes possible. For example, the partial pressure of $SmAl_3Cl_{12}$ complex is about $6x10^{-3}$ atm at 800 K in the presence of Al_2Cl_6 vapor (1 atm)5b) while the vapor pressure of $SmCl_3$ itself is $6x10^{-6}$ atm at the same temperature.6) We have already reported the mutual

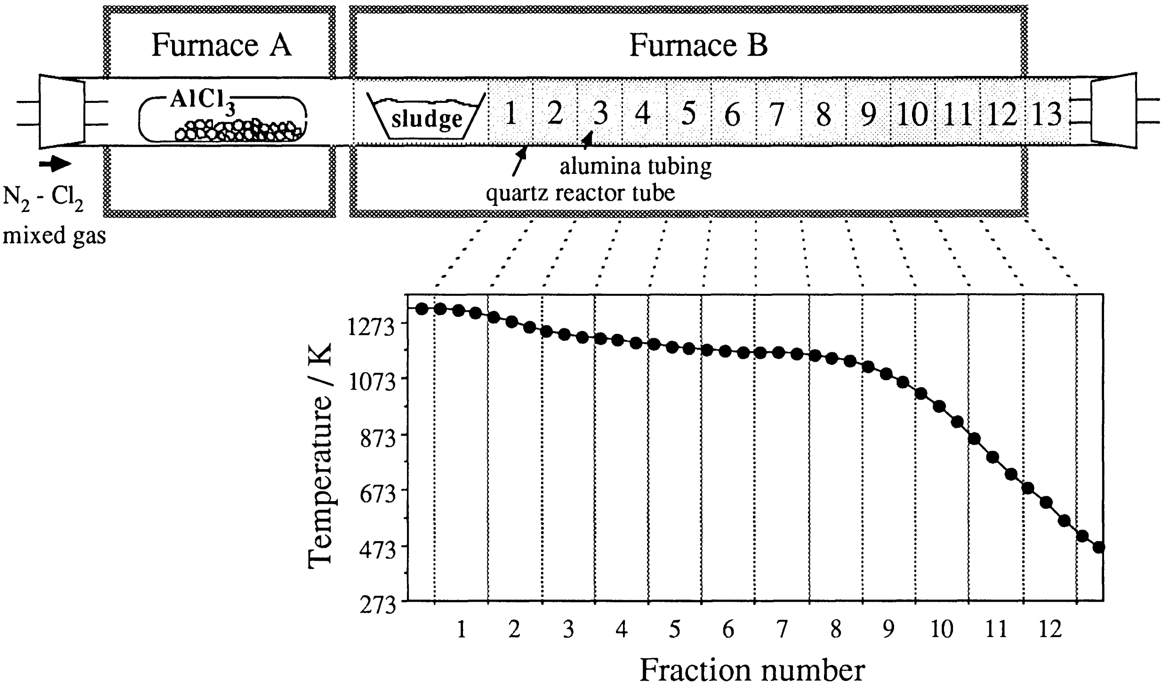

Fig.1. Assembly of electrical furnaces and temperature gradient for the CVT reaction. Numbers in furnace B denote fraction number (FN) of deposits.

separation characteristics of rare earth elements by the CVT reaction.4) In the present work, the recovery of Sm and Co elements from the sludge of Sm_2Co_{17} alloy was made by using the CVT method, which is a dry process free from the above-mentioned complicated processes.

The sludge of Sm_2Co_{17} alloy supplied by Shin-Etsu Chemical Co., Ltd. was used without any pretreatment except for drying overnight at room temperature in vacuo. The sludge contains Sm (22 wt%), Co (51 wt%), and some additional metal elements in the form of metal or oxide. The apparatus employed for the CVT reaction is shown in Fig.1. Assembly of the apparatus was reported in detail in previous papers.4) The furnace A was utilized for generating the gaseous aluminium chloride Al_2Cl_6 acting as the complex former. A mixed gas of N_2 and Cl_2 was passed into the quartz reactor tube at the respective flow rates of 30 and 5 ml/min.

One gram of the sludge was weighed, put on a small alumina boat, and loaded in the furnace B (see Fig.1). The sludge was heated up to ca. 1273 K and directly chlorinated by Cl_2 in the carrier gas. The resulting metal chloride mixture vaporizes according to a simple sublimation accompanying, in certain cases, the formation of aggregates:

$$n\ MCl_x\ (s,l) \rightleftharpoons M_nCl_{nx}\ (g), \qquad (1)$$

or the complexation with the Al_2Cl_6 (g) injected from the furnace A:

$$n\ MCl_x\ (s,l) + m/2\ Al_2Cl_6\ (g) \rightleftharpoons M_nAl_mCl_{nx+3m}\ (g). \qquad (2)$$

The resulting gas phase species were driven with the carrier gas along the temperature gradient in the furnace B (see Fig.1) and the metal chlorides (MCl_x) were deposited at different places in the reactor tube according to the reverse process of above equations. After the CVT reaction for 6 h, the materials deposited in 13 pieces of alumina inner tubing were collected and dissolved in deionized water. The contents of Sm, Co, Al, and the other additional metal elements were determined by means of the X-ray fluorescence spectrometry.

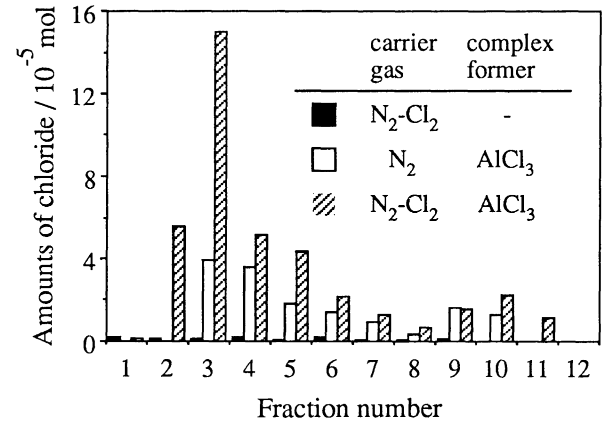

Fig.2. Distribution profiles of the $SmCl_3$ deposits transported under several conditions.

The deposition profiles of $SmCl_3$ under several CVT conditions are shown in Fig.2. The total amount of $SmCl_3$ deposit was quite low without using $AlCl_3$ because, as mentioned above, the vapor pressure of $SmCl_3$ itself is too low even at the elevated temperatures to be enough for the transportation according to the simple sublimation-deposition reaction (Eq.1). On the other hand, the total amount of $SmCl_3$ deposit was increased by using $AlCl_3$ as the complex former, and the peak of the deposition profile appeared at FN=3 (FN: fraction number). Under this condition, the migration via the gas phase complex (Eq.2) becomes a dominant route for the CVT reaction. The CVT reaction of $SmCl_3$ together with $AlCl_3$ took place even in the absence of Cl_2. It implies that $AlCl_3$ also functions as a chlorinating agent.$^{5)}$ However, since $AlCl_3$ acting as the chlorinating agent produces inert Al_2O_3 by the reaction with the metal oxides in the sludge, the

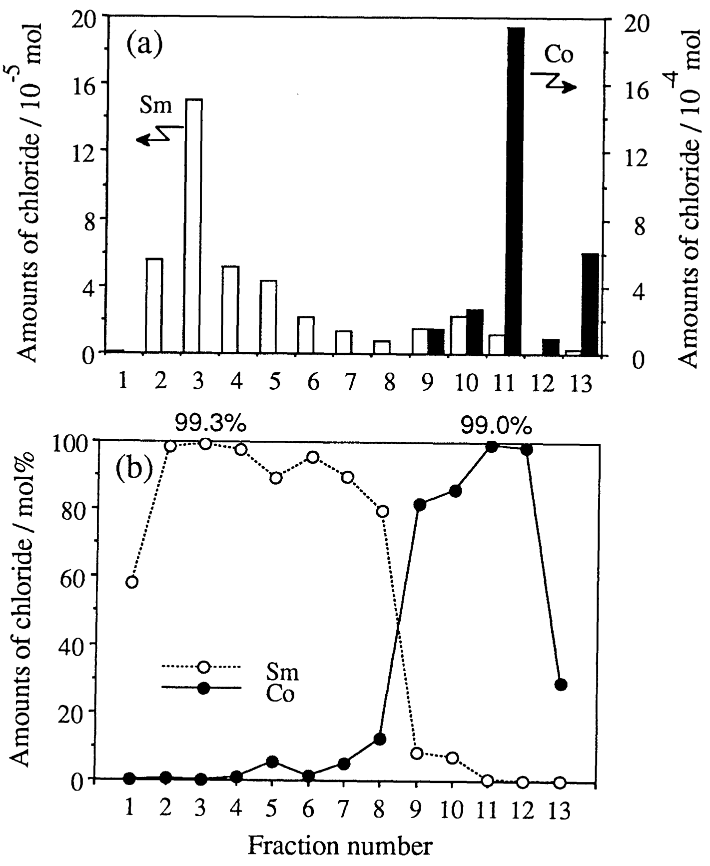

Fig.3. Distribution profiles of the $SmCl_3$ and $CoCl_2$ deposits transported.

CVT reaction without the Cl_2 flow seems unsuitable. As a result, the condition using $AlCl_3$ under the flow of Cl_2 was most appropriate for the transportation of $SmCl_3$.

A deposition profile with a peak at FN=11 was observed on the cobalt element which was also obtained as the anhydrous chloride $CoCl_2$ (see Fig.3a). Consequently, the mutual separation between Sm and Co elements was performed satisfactorily. The contamination with other additional metal chlorides was suppressed at low level, because they were predominantly accumulated at FN=13. Moreover, the complex former $AlCl_3$ also does not contaminate the recoveries ($SmCl_3$ and $CoCl_2$), due to its low sublimation temperature below 473 K.

Figure 3b shows the deposition profiles of $SmCl_3$ and $CoCl_2$ represented in mole percent. The chloride $SmCl_3$ was concentrated to 99.3 mol% at FN=3, while the $CoCl_2$ amounted to 99.0 mol% at FN=11. The deposition amounts of $SmCl_3$ and $CoCl_2$ at FN=3 and 11 were 38 and 64% of the total amounts of $SmCl_3$ and $CoCl_2$ deposits, respectively.

Concluding the above, it was found that by the application of the CVT method using $AlCl_3$ as the complex former to the sludge of Sm_2Co_{17} magnetic alloy the Sm and Co elements were independently recovered from the sludge by an all-dry process in the form of anhydrous chlorides in high purity. Moreover, the resulting anhydrous rare earth chlorides can be directly used to produce rare earth metals by thermal or electrolytic reduction, which are recycled to production of the magnetic alloys. Since this method is very simpler and easier than wet one, it seems to have a great advantage toward the recycling of component rare metals not only in the Sm-Co systems but also in other various systems including the rare earth metals.

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