

Recovery of samarium from cobalt–samarium solution using phosphoric acid



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ABSTRACT

Cobalt–samarium alloys are generally used for producing magnets. Samarium falls under the class of rare earth elements, which are precious and expensive, because of which they are often recovered by recycling processes to save cost. There are a few reported processes for the recycling of rare earth elements; however, these processes have disadvantages, including the requirement for high temperatures and use of harmful gases. In this paper, a novel technique to recover samarium without encountering the difficulties reported in previous methods is presented. Because rare earth phosphates are the main components of rare earth ore, a novel phosphate process is suggested in this work. The cobalt–samarium solution was mixed with phosphoric acid solution and then adjusted to several pH with sodium hydroxide solution and nitric acid. The precipitates were filtered and dried. The ratio of samarium and cobalt in the precipitates and filtered solutions was estimated by the ICP (inductively coupled plasma) method. As an ideal phenomenon, samarium phosphate was filtered off, so that the filtrate contained the cationic cobalt species. The Sm/Co and P/(Co+Sm) ratios; concentrations of samarium, cobalt, and phosphoric acid; and pH were varied to study the precipitation of samarium compounds. In this work, over 99% of samarium cation was recovered from the cobalt–samarium solution using phosphoric acid. This novel process was observed to be useful for the recovery of samarium, and it may find applications in the recycling and recovery of other rare earth elements of interest.

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1. Introduction

Samarium–cobalt permanent magnets have large magnetic energy, high Curie temperature, good thermal stability, and corrosion resistance [1]. Currently, samarium–cobalt permanent magnets are used in magnetic coupling, motors, and actuators in car, etc [2,3]. During the production of samarium–cobalt magnets, a notable amount of scrap is generated in the cutting and milling processes. Samarium tends to coexist with other rare earth elements in natural ores [4]. Separation of samarium from other rare earth elements requires energy-consuming procedures; therefore, there is an industrial demand for the recycling of samarium from scrap to save time and energy [5].

Rare earths are potential candidates for various functional materials, although there are several difficulties related to the supply of these elements to industries [6,7]. Rare earth ores tend to be localized, and often include radioactive elements [8]. Since the mining of rare earth ores leads to environmental issues, recycling

of rare earth elements from scrap may be a suitable alternative [9]. There are some reported processes for the recycling of rare earth elements. For example, transition metals were removed from rare earths by solvent extraction with an undiluted ionic liquid [10,11]. This process needs high concentration of acid and particular reagents. As another method, samarium was recovered from the sludge of samarium–cobalt magnetic alloy by a chemical vapor transporting method [12,13]. This method needs high temperature and especial apparatus. These processes have several disadvantages. Therefore, the development of a novel technique to improve the current recycling methods is preferred.

Rare earth phosphates are the main components of rare earth ore, and they are known to be stable in acidic and basic solutions [14]. However, there are very few reports on recycling processes using phosphoric acid. Precipitation is one of the most useful techniques for the separation of the target metals from other metal matrix [15,16]. Precipitation using inorganic reagents is particularly convenient because harmful organic solvents are not employed and treatment of the wastewater generated during the process is relatively simple. Generally, metal hydroxides are used in the precipitation technique because they allow for the efficient recovery of a large amount of metal cations [17,18].

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However, metal hydroxides have weak selectivity to form precipitates in the presence of the precipitant. In a previous study, a novel recycling process in which neodymium phosphate was recovered with phosphoric acid from iron–neodymium solution was reported [19]. This process was relatively simple and did not require the use of harmful organic solvents. In the present work, a recycling process with phosphoric acid was employed to recover samarium phosphate from cobalt–samarium solution.

2. Experimental

A 280 mL portion of cobalt–samarium solution (Co, 0.09 mol/L; Sm, 0.01 mol/L), prepared from cobalt nitrate and samarium nitrate, was mixed with 140 mL of phosphoric acid (P, 0.2 mol/L). This standard cobalt–samarium ratio, Co/Sm = 9, was determined with reference to the permanent magnet composition, Sm₂Co₁₇. The mixed solution (pH 1.27) was adjusted to pH 1–5 with a highly concentrated sodium hydroxide solution or nitric acid. The precipitates were then filtered off and dried at room temperature over 3 d.

To determine the optimum conditions for samarium recovery, the concentrations of cobalt and phosphoric acid were varied (Co: 0.045, 0.19, 0.29 mol/L; H₃PO₄: 0.02, 0.1, 0.3, 0.4 mol/L). The Co/Sm ratio in original solution was from 4.5 to 29, the P/(Co + Sm) ratio in mixing process was from 0.1 to 2. Further, to separate with small amount of water, condensed solution (3, 5, 7, and 10 times) were also estimated with high concentrations of phosphoric acid (Co: 0.27, 0.45, 0.63, 0.9 mol/L; Sm: 0.03, 0.05, 0.07, 0.1 mol/L; H₃PO₄: 0.6, 1.0, 1.4, 2.0 mol/L).

The recovery ratio of cobalt, samarium, and phosphoric acid was calculated from the ideal concentrations and the results of inductively coupled plasma–atomic emission spectrometry analysis (ICP–AES; Model SPS1500VR; Seiko Instruments, Inc.) performed on the filtered solutions. A part of the precipitate was dissolved in nitric acid solution. The ratios of phosphorus, cobalt, and samarium in the precipitates were also calculated based on the ICP–AES results for these solutions. The crystalline phase compositions of the precipitates were analyzed by X-ray diffraction (XRD; MiniFlex, Rigaku Corp.), using monochromated Cu K α radiation. A part of the precipitate was heated at 700 °C for 1 h in air, and the thermal products were analyzed according to their XRD patterns.

3. Results and discussion

3.1. Influence of pH

Fig. 1 shows the residual ratio of each element in solution at various pH levels (Co/Sm = 9, P/(Co + Sm) = 1). Without pH adjustment (pH 1.27), the residual ratio of samarium in solution was about 6%, and this ratio reduced to almost zero when the pH was adjusted from 2 to 5. On the other hand, the residual samarium ratio reached 21% at pH 1 because samarium phosphate dissolved at this pH. The residual ratio of cobalt in solution decreased with increasing pH because cobalt phosphate readily precipitated at higher pH. Furthermore, the residual ratio of phosphorus was comparable to that of cobalt. In this process, samarium phosphate was separated from the cobalt cations at pH 2–4.

To elucidate the mechanism underlying this precipitation, the chemical composition of the precipitates was estimated. The Co/Sm and Sm/(Sm + Co) ratios in precipitates were related with the formation of samarium phosphate and cobalt phosphate. Table 1 shows the Co/Sm and Sm/(Sm + Co) ratios in the precipitate at various pH levels. Samples prepared at pH 1–3 had a small Co/Sm ratio. This Co/Sm ratio in the precipitate exceeded 0.1 at pH 4, and dramatically increased at pH 5. When samarium phosphate formed without cobalt phosphate, this Co/Sm ratio became small. The

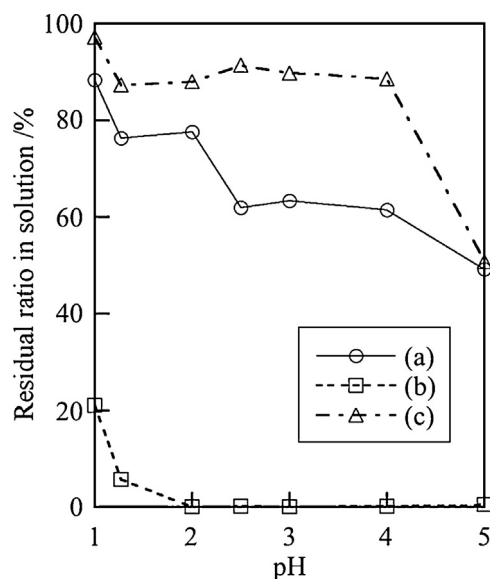


Fig. 1. Residual ratio of each element in solution at various pH levels: (a) phosphorus, (b) samarium, and (c) cobalt (Co/Sm = 9, P/(Co + Sm) = 1).

Table 1

Co/Sm and Sm/(Sm + Co) ratios in the precipitate at various pH levels (Co/Sm = 9 in original solution, P/(Co + Sm) = 1).

pH	Co/Sm	Sm/(Sm + Co)
1	0.021	0.979
1.27 ^a	0.014	0.986
2	0.018	0.981
2.5	0.045	0.957
3	0.051	0.951
4	0.197	0.835
5	3.476	0.223

^a Without pH adjustment.

formation of cobalt phosphate produced high Co/Sm ratio in precipitates. From these results, it was confirmed that samarium phosphate was separated from the cobalt cations at pH 1–3.

All the precipitates considered in this study showed weak peaks in the XRD patterns, and therefore, their crystalline phase composition was not clear. To clarify the crystalline phase composition of the precipitates, all samples were heated at 700 °C for 1 h. Fig. 2 shows the XRD patterns of the precipitates prepared at various pH levels and then heated at 700 °C. The sample prepared at pH 1 could not be estimated by XRD analysis because the amount of precipitate was insufficient. Peaks due to samarium phosphate, SmPO₄, were observed in the XRD patterns of the samples prepared without pH adjustment and at pH 2–4. On the other hand, the XRD pattern of the sample prepared at pH 5 showed peaks due to cobalt phosphate, Co₃(PO₄)₂. These XRD results were consistent with the ICP results for the filtered solution and precipitates. To sum up, the optimal pH for the separation of samarium phosphate from the cobalt cations was in the range 2–4.

3.2. Ratio of Co/Sm

To clarify the range of use in this process with phosphoric acid, the Co/Sm ratio in the original solution was varied from 4.5 to 29. Fig. 3 shows the residual ratio of each element in solution at various Co/Sm ratios (P/Sm = 10, pH 3). All the conditions indicated

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