

## The Extraction of Sm from Sm–Co alloys by the Glass Slag Method\*

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The use of the glass slag method in the extraction of Sm from Sm–Co alloys was studied. The magnetic SmCo<sub>5</sub> phase decomposed into Sm oxide phase and Co phases by the glass slag method. The Sm oxide phase was extracted by the surrounding molten glass slag materials in the glass slag method. The resultant alloys consisted of neither SmCo<sub>5</sub> phase nor Sm oxide phase. In the glass slag method, the Sm–Co alloys were separated into Sm-containing glass slag material and a Co–B alloy. The glass slag method was suitable for the extraction of samarium from the Sm–Co alloys as was the case for the extraction of neodymium from the Nd–Fe–B alloys.

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### 1. Introduction

The production of rare earth magnets has significantly increased mainly due to their superior maximum energy products. These magnets have been widely used for various electromechanical and electronic devices.<sup>1)</sup> On the other hand, large amounts of scrap from the rare earth magnets are being stockpiled due to the lack of a cost-effective recycling process. Thus, it is crucial to develop a recycling process for the rare earth magnets.

Several attempts to recycle the rare earth magnets (Sm–Co and Nd–Fe–B magnets) have been made.<sup>2–4)</sup> In the Nd–Fe–B magnets, the best separation of rare-earth metal from the Nd–Fe–B magnets is obtained by sulfuric acid dissolution followed by precipitation of recyclable rare-earth salts.<sup>2)</sup> However, this process produces large amounts of wastewater including dangerous solutions. Recently, Xu *et al.* have proposed a new dry recycling process for Nd–Fe–B magnets.<sup>5)</sup> This technique involves using molten magnesium metal to remove Nd from the Nd–Fe–B magnets. Although the Nd has been extracted from the Nd–Fe–B magnets by using the liquid metal, this technique may not be applied to extract the Nd from the scrap that contains several percentages of oxygen.<sup>6)</sup> Another dry process, the so-called glass slag method, has been applied to produce bulk materials with fine grains.<sup>7,8)</sup> In the glass slag method, bulk materials that melted and solidified in a molten glass slag materials experience a large undercooling before solidification. In some cases, a reaction between the bulk liquid material and the molten slag material may take place. Recently, we have succeeded in the recovery of Nd from Nd–Fe–B magnets by the reaction between the molten Nd–Fe–B materials and the molten glass slag materials.<sup>9)</sup>

In this study, the use of the glass slag method in the extraction of Sm from the Sm–Co magnets, which have become renewed interests as the high temperature permanent magnets.<sup>10,11)</sup> The degree of the extraction of Sm from the Sm–Co alloys is evaluated by chemical and microstructural analyses of the Sm–Co alloys processed by the glass slag method.

### 2. Experimental

Samarium and cobalt metals were placed in a quartz crucible with an orifice of 0.6 mm at the bottom. These metals were induction melted in an argon atmosphere and then ejected through the orifice with an argon gas into a water-cooled copper mold. The resultant Sm–Co master alloy with the composition of SmCo<sub>5</sub> had a cylindrical shape with 5 mm in diameter and 50 mm in length. A small amount of the Sm–Co master alloy was placed in a BN crucible together with pieces of boron trioxide. The alloy was preheated slowly to just above the melting temperature of the slag material and then cooled down to room temperature in the furnace that had been evacuated and backfilled with argon. The resultant alloy was encapsulated in the boron trioxide. The alloy was melted and superheated to 1673 K (about 100 K above the equilibrium liquidus temperature) and then was cooled down to room temperature in an argon atmosphere. The experimental set-up for the glass slag method has been described in detail elsewhere.<sup>12)</sup>

The specimens were removed from the slag material and the cut by a low speed diamond wheel for microstructural studies. The phases in the specimens were identified by X-ray diffraction (XRD) using Cu K $\alpha$  radiation. After polishing, the microstructures of the specimens were examined under an optical microscope (OM) and a scanning electron microscope (SEM) equipped with an electron probe microanalyzer (EPMA). The composition of the specimens was determined by chemical analyses.

### 3. Results and Discussion

Figure 1 shows the XRD patterns of the Sm–Co alloys produced by the glass slag method together with the Sm–Co master alloys. The XRD pattern of the Sm–Co master alloys is indexed to the SmCo<sub>5</sub> phase and Sm<sub>2</sub>Co<sub>7</sub> phase. It is known that the magnetic SmCo<sub>5</sub> phase decomposes into the Sm<sub>2</sub>Co<sub>7</sub> and Sm<sub>2</sub>Co<sub>17</sub> phases below about 1073 K.<sup>13)</sup> In order to prevent the decomposition of the SmCo<sub>5</sub> phase, the Sm–Co alloy was produced by the metallic mold casting in this experiment. No Sm<sub>2</sub>Co<sub>17</sub> phase is seen in the XRD pattern, suggesting that the decomposition of the SmCo<sub>5</sub> phase is

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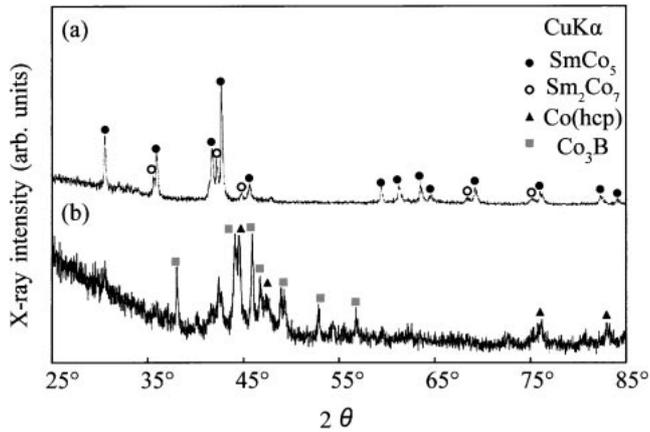


Fig. 1 XRD patterns of (a) the Sm–Co master alloy and (b) the alloy produced by the glass slag method.

suppressed. However, the  $\text{Sm}_2\text{Co}_7$  phase is found in the XRD pattern. This implies that the Sm–Co master alloys produced by the metallic mold casting are slightly off-stoichiometric composition of  $\text{SmCo}_5$ . On the other hand, no diffraction peaks of the  $\text{SmCo}_5$  phase are found in the XRD pattern of the Sm–Co alloys produced by the glass slag method. The diffraction peaks are well indexed to the Co and  $\text{Co}_3\text{B}$  phases in the XRD pattern, suggesting that the Sm–Co alloys produced by the glass slag method consist of Co and  $\text{Co}_3\text{B}$  phases. It has been reported that the magnetic  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase decomposes into the mixtures of Nd-containing phase,  $\alpha\text{-Fe}$  and  $\text{Fe}_2\text{B}$  phases and that the Nd-containing phase is extracted by the surrounding molten boron trioxide in the glass slag method.<sup>7)</sup> By the same token, the Sm–Co alloys decomposes into the mixtures of Sm-containing phase and Co phases and the Sm-containing phase might have been extracted by the surrounding molten boron trioxide during the melting and solidification of the Sm–Co alloy.

Figure 2 shows the cross-sectional microstructures of the Sm–Co alloy produced by the glass slag method together with the Sm–Co master alloy. The Sm–Co master alloy has fine grains. This is due to the relatively high solidification rate of the metallic mold casting.<sup>14)</sup> On the other hand, large dendrites are seen in the microstructure of the Sm–Co alloy produced by the glass slag method. In order to examine the differences in the microstructure, detailed microstructural studies of both the Sm–Co master alloy and the Sm–Co alloy produced by the glass slag method were made by EPMA.

Figure 3 shows the SEM micrograph of the Sm–Co master alloy and the corresponding X-ray mappings of samarium, cobalt, and boron. Although the Sm–Co master alloy does not contain boron, the X-ray mapping of boron has been taken for the comparison. Samarium and cobalt have been detected in the microstructure, as expected for the Sm–Co alloys. Samarium is slightly enriched in the boundary, indicating that the boundary is the  $\text{Sm}_2\text{Co}_7$  (42.2 mass%Sm) phase and the matrix is the  $\text{SmCo}_5$  (33.8 mass%Sm) phase.

Figure 4 shows the SEM micrograph of the Sm–Co alloy produced by the glass slag method and the corresponding X-ray mappings of samarium, cobalt, and boron. The large spherical grain examined in the SEM micrograph is a part of the dendrite seen in the optical micrograph (see Fig. 2).

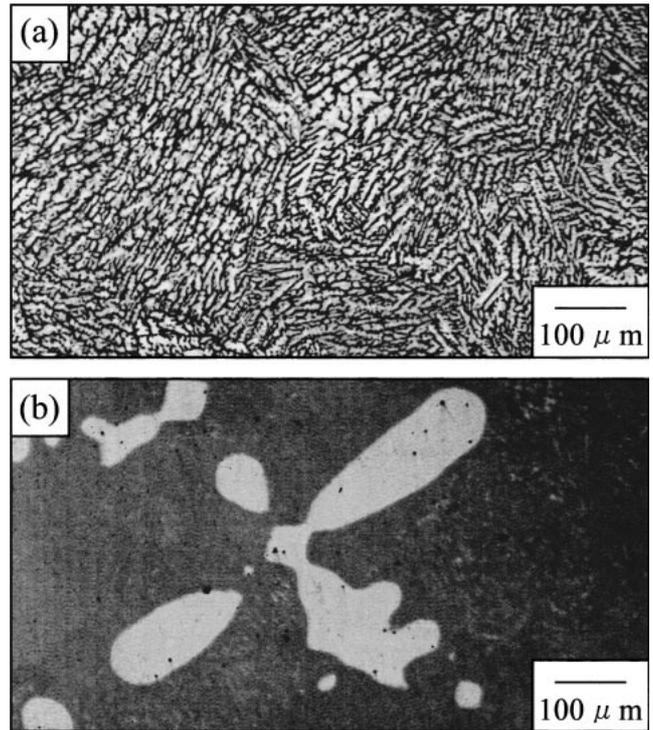


Fig. 2 Optical micrographs of (a) the Sm–Co master alloy and (b) the alloy produced by the glass slag method.

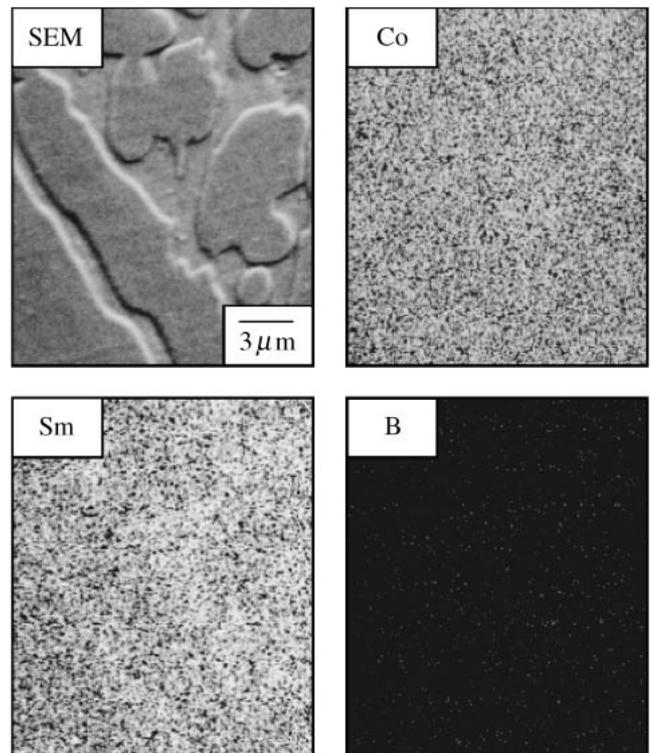


Fig. 3 Scanning electron micrograph of the Sm–Co master alloy and the corresponding X-ray mappings of samarium (Sm), cobalt (Co), and boron (B).

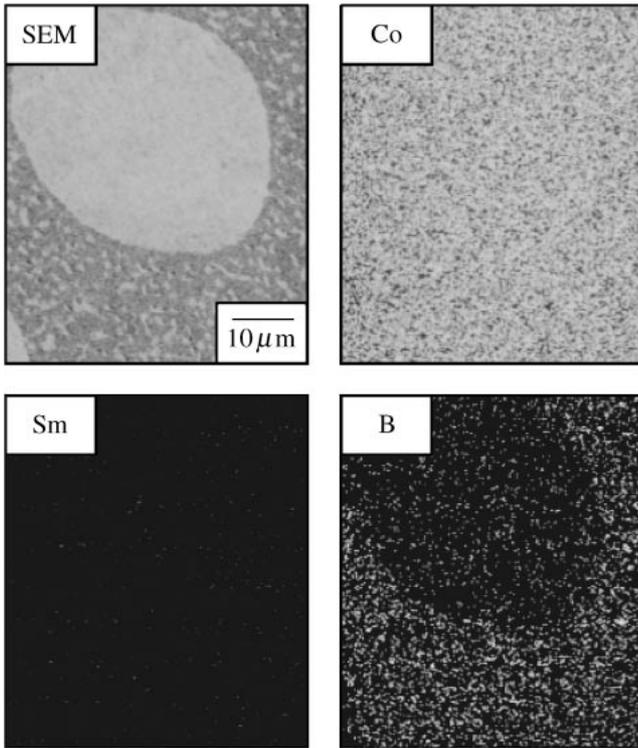


Fig. 4 Scanning electron micrograph of a Sm–Co alloy produced by the glass slag method and the corresponding X-ray mappings of samarium (Sm), cobalt (Co), and boron (B).

Cobalt is enriched in the dendrite region, suggesting that the dendrites consist of the Co phase. No samarium is detected in the microstructure of the Sm–Co alloy produced by the glass slag method. This is consistent with the results of the XRD studies, in which no Sm-containing phase has been found in the Sm–Co alloy produced by the glass slag method. Both cobalt and boron have been detected in the matrix of the latter Sm–Co alloy, suggesting that fine grains in the matrix are the eutectic of the Co and  $\text{Co}_3\text{B}$  phases.

The chemical analyses of both the Sm–Co alloy and boron trioxide were made to investigate the change in the Sm content. The results are shown in Table 1. The Sm content in the Sm–Co master alloy is larger than that of the stoichiometric composition of  $\text{SmCo}_5$  (33.8 mass%Sm). Thus, the Sm–Co master alloy contained some Sm-rich ( $\text{Sm}_2\text{Co}_7$ )

Table 1 Composition of (a) Sm–Co alloys and (b) boron trioxide. (Sm, Co, and B are given in mass percent)

(a) Sm–Co alloys			
	Sm (mass%)	Co (mass%)	B (mass%)
Sm–Co master alloys	35.39	64.30	<0.01
Sm–Co alloys after the glass slag experiment	<0.05	96.35	3.00
(b) boron trioxide			
	Sm (mass%)	Co (mass%)	B (mass%)
boron trioxide	0.01	0.02	28.12
boron trioxide after the glass slag experiment	58.28	0.38	10.67

phase. It should be noted that the Sm content in the Sm–Co alloy produced by the glass slag method was less than 0.05 mass%. This is consistent with the results of the XRD and EPMA studies. On the other hand, the Sm content in the resultant boron trioxide was more than 58 mass%. This confirms that the Sm in the Sm–Co alloy is extracted by the boron trioxide during the melting and solidification of the Sm–Co alloy. If only the Sm-containing phase would have been extracted by the boron trioxide, the resultant alloy would be the pure Co metal. The chemical analyses revealed that the boron content in the resultant alloys was 3.00 mass%B. Neither boron trioxide nor crystalline boron has been found in the XRD pattern of the resultant alloy. The only boron-containing phase found in the XRD pattern is the  $\text{Co}_3\text{B}$  phase. This suggests that the resultant alloy had absorbed boron from the boron trioxide during the melting and solidification of the Sm–Co alloys. The boron trioxide was first reduced to elemental boron and then the  $\text{Co}_3\text{B}$  phase was formed by the reaction between the elemental boron and the elemental cobalt during the melting and solidification of the Sm–Co alloy.

Thus, the reaction between the boron trioxide and the Sm–Co alloys can be expressed by the following equation:



According to the above equation, the B content in the Sm–Co alloy produced by the glass slag method using the boron trioxide is calculated to be 3.54 mass%. This value is slightly higher than the experimental results of 3.00 mass%B. This is because the Sm–Co master alloy contains some Sm-rich ( $\text{Sm}_2\text{Co}_7$ ) phase as well as the  $\text{SmCo}_5$  phase. The presence of virtually no Sm content in the Sm–Co alloy produced by the glass slag method indicates that the Sm oxide phase is thoroughly extracted by the surrounding boron trioxide during the melting and solidification of the Sm–Co alloy. In the glass slag experiment, the Sm–Co alloy ingot must be immersed in the molten glass slag materials of the boron trioxide. Therefore, the boron trioxide was used twelve times as much as it was required from the above equation.

Figure 5 shows the XRD patterns of the boron trioxides before and after the glass slag experiment. The XRD pattern

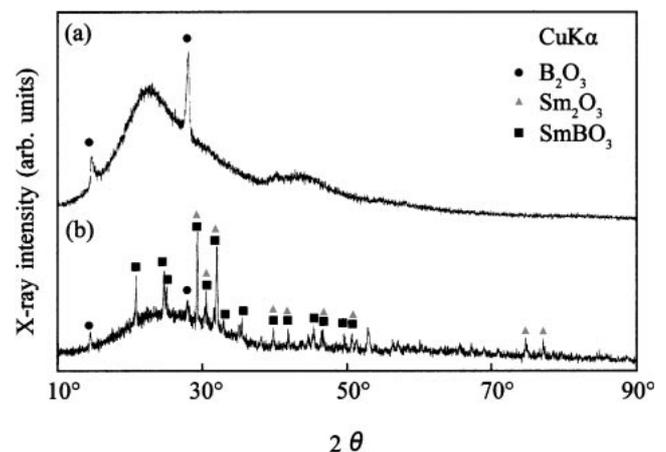


Fig. 5 XRD patterns of (a) the boron trioxide and (b) the boron trioxide after the glass slag experiment.

of the boron trioxide shows diffraction peaks of the  $B_2O_3$  phase. However, halo-like peaks are evident in the XRD pattern, suggesting that the boron trioxide contains some amorphous phase, most probably amorphous  $B_2O_3$  phase, together with the crystalline  $B_2O_3$  phase. Although the small diffraction peaks of the  $B_2O_3$  phase are seen in the XRD pattern of the boron trioxide after the glass slag experiment, the clear diffraction peaks of the  $Sm_2O_3$  and  $SmBO_3$  phases are found. The reaction between the Sm oxide phase and the excess amount of the  $B_2O_3$  phase may result in the formation of the  $SmBO_3$  phase.<sup>15)</sup> This confirms that the Sm oxide phase is extracted by the surrounding boron trioxide during the melting and solidification of the Sm–Co alloy. The Sm was successfully extracted from the Sm–Co alloys by the glass slag method by means of the boron trioxide. In other words, a Co–B alloy has been obtained from the Sm–Co alloy by the glass slag method.

#### 4. Conclusions

Co alloys were produced by the glass slag method from Sm–Co magnets using boron trioxide. The chemical analyses combined with the XRD and EPMA studies revealed that the Sm in the Sm–Co alloys was extracted by the surrounding boron trioxide. The resultant alloys had fine grains of Co and  $Co_3B$  phases together with dendrites of the Co phase. It was found that the glass slag method was suitable for the extraction of samarium from the Sm–Co alloys as was the case for the extraction of neodymium from the Nd–Fe–B alloys.

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