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STUDY ON THE SEPARATION AND EXTRACTION OF RARE-EARTH ELEMENTS FROM THE PHOSPHOR RECOVERED FROM END OF LIFE FLUORESCENT LAMPS

BADANIE SEPARACJI I EKSTRAKCJI METALI ZIEM RZADKICH Z FOSFORU ZE ZUŻYTYCH ŚWIETŁÓWEK

In this study, recovered phosphor from end of life three-wavelength fluorescent lamp was selected for reuse rare earth elements in the phosphor. The effect of a type of acid, concentration, and time was investigated as solubility of rare earth elements. In addition, precipitate heat-treated was investigated as possibility of reusable phosphor. The results showed that the amount of the rare earth elements was different values depending on the type of acid, and it was investigated with concentration of acid and reaction time. After precipitation reaction, the precipitate was sintered in electric furnace in order to reuse rare earth elements as phosphor. It was confirmed that yttrium, europium, oxygen, and carbon through X-ray diffraction and inductively coupled plasma analysis. Following the results, it can assume that rare earth oxide reuse the phosphor as three-wavelength fluorescent lamp.

Keywords: recycle, yttrium, phosphor, end of life

1. Introduction

Rare earth elements consist of yttrium, scandium, lanthanide that comprise the fifteen metallic chemical elements with atomic numbers 57 through 63, from lanthanum through europium (LREE: Light rare earth elements) and 64 through 71, from gadolinium through lutetium (HREE: Heavy rare earth elements) [1]. They are very chemically stable and have good optical, electrical, magnetic properties [2]. Yttrium is used as the phosphor, addition agent of ceramic, superconductor. Scandium is also used as the addition agent of ceramic and laser. LREE is mainly used as the permanent magnet, phosphor, catalyst, and HREE is used as the laser, superconductor, crystal manufacturing. Thus, the rare earth elements are used throughout the industry [3]. They are concentrated in certain areas. China has about 48 percent of the total reserves of rare earth elements and produces over 97% of them. However, specific rare earth elements has occurred imbalance of supply and demand due to changes in export policy of China [4,9]. Therefore, some developed countries have steadily taken the method of supplying the rare earth elements continuously.

An alternative way is to develop a process cycle for recovery of resources and reuse to recyclable resource from used product. This method relieves not only economic but also environmental benefits. Furthermore, it has a high utility that the efficient use of resources. Imbalance of supply and demand and a shortage of rare earth mineral resources are serious. The three-band fluorescent lamps that require high efficiency use the rare earth mineral such as yttrium. This fluorescent lamp has a characteristic of circulation cycle is short. Therefore, the three-band fluorescent lamps used in a short period were chosen to recovery rare earth mineral for circulation usage [1]. The three-band fluorescent lamps use three kind of phosphor red, blue, and green with yttrium, terbium, europium, etc.

The rare earth elements in recovered phosphor from end of life fluorescent lamps are recovered using rare earth elements refinement from their raw materials [5]. The precipitated rare earth salt forms so that this recovery is typical after dissolve through acid and alkali solvent [6,7,8]. Using this method, First step is that phosphor powder is recovered after physical separation in order to recover rare earth elements from end of life fluorescent lamps. The next step is chemical separation using many kinds of acid. The experiment was driven separate and recovery rare earth elements using a chemical separation process and physical separation.

2. Experimental

In this study, phosphor powder was obtained by physical separation method. Spent fluorescent lamps metal caps were removed, and phosphor recovered by spraying high pressure air into the lamps tube. Recovered phosphor usually has mercury, which was removed by active carbon [10]. The presence of mercury was confirmed by X-ray diffraction (Smart Lab, Rigaku, XRD). Recovered phosphor powder was analyzed for shape and composition by scanning electron microscope (SU-8010, Hitachi, SEM) and electronic data sys-

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tem (EDS). Solvent such as sulfuric acid, nitric acid, and hydrofluoric-nitric acid mixed solution was used to extract rare earth elements from the recovered phosphor [1]. Concentration of solvent was changed to 0.5, 1, 2, 5 vol. %. Condition of temperature and time was controlled to 80°C and every 30 minutes. At this time, Degree of dissolution of rare earth elements was investigated by the type of solvent, concentration of solvent, and over time. The solution dissolved rare earth was investigated by inductively coupled plasma (PerkinElmer OPTIMA7300DV, ICP-OES).

The solution dissolved rare earth elements was reacted to deposit insoluble rare earth compounds through a commitment to oxalic acid [10]. The insoluble compounds were reacted to create rare earth oxide in a tube furnace atmosphere with heating rate of 4°C/min, 1000°C, and lasting time in 60 minutes. After the reaction of extracting rare earth elements, component of phosphor residue and rare earth oxide was investigated by X-ray diffraction (Smart Lab, Rigaku, XRD) and electronic data system (EDS). Powder shape was confirmed by scanning electron microscope (SU-8010, Hitachi, SEM).

3. Results and discussion

Recovered phosphor powder contains usually mercury from end of life fluorescent lamps. Thus, mercury had to be removed before the rare earth dissolved. Fig. 2 shows the result of X-ray diffraction of the phosphor powder. As shown in this figure, there was no mercury in the recovered phosphor powder. Fig. 3 shows the shape and component of the recovered phosphor powder. Powder shape was very irregular and particle size was between 5 and 20 µm respectively. In addition, the phosphor powder was composed of the elements such as yttrium, europium, terbium, lanthanum, barium, aluminum, and calcium. But different elements were contained unlike XRD analysis. In this case, it could estimate that some elements; carbon, silicon, copper; were mixed in the physical separation process, which were very small.

![Fig. 2. X-ray diffraction analysis of recovered phosphor from spent fluorescent lamps](image)

![Fig. 3. Surface scanning electron microscope (SEM) and electronic data system (EDS) of recovered phosphor powder from spent fluorescent lamps](image)
vent was controlled with 100ml of volume, 30 vol. % of concentration, and 5g of the phosphor powder at 80°C in 120 minutes. Table 1 lists the concentration of cerium, lanthanum, barium, terbium, europium, and yttrium in solution with three kinds of acid. HNO₃, it was confirmed that barium, terbium, europium were dissolved. In case of H₂SO₄, it was similar to the case of HNO₃, but yttrium was discovered by inductively coupled plasma analysis and amount of yttrium was the biggest in solution. Barium was the biggest in solution when HF-HNO₃ solvent was used. In conclusion, it was confirmed that sulfuric acid was suited to extract yttrium and europium which want to recover.

| Concentration of rare earth elements in solution after the reaction | Ce | La | Ba | Tb | Eu | Y |
|---------------------------------------------------------------|----|----|----|----|----|---|
| [Unit : ppm] | HNO₃ | 0 | 0 | 0.3 | 6.7 | 2.92 | 0 |
| H₂SO₄ | 0 | 0 | 0.04 | 0.28 | 76.06 | 1166.8 |
| HF-HNO₃ | 0 | 0 | 38.08 | 6.88 | 0 | 0 |

The proper concentration to experiment was 2 vol. % of sulfuric acid. The next step, it was investigated that change of amount of dissolved the rare earth elements according to reacting time. Thus, concentration was identified at an interval of 30-minutes. Fig. 5 shows the concentration of yttrium and europium according to time progress. Yttrium was confirmed that progress of dissolution was made rapidly in 60 minutes, decreased after 60 minutes. Finally, there were little rare-earth elements in 120 minutes. In case of europium, there was little change of amount of rare earth elements, decreased rapidly after 60 minutes. It was same like yttrium in 120 minutes. In conclusion, it could be assumed that yttrium and europium in the recovered phosphor powder was dissolved completely in 120 minutes. The reaction time was thought to be able to secure the economy and efficiency.

Recovered rare earth elements in solution need to be produced a type of rare earth oxalate for using the recovered phosphor powder as phosphor. Oxalic acid is one such oxidizing method [10]. The following chemical reaction formula is necessary to make the insoluble oxide from the resulting sulfuric acid reacts with the soluble rare earth sulfide.

\[ RE_2(SO_4)_3 + 3H_2C_2O_4 + nH_2O \rightarrow RE_2(C_2O_4)_3 \cdot nH_2O + 3H_2SO_4 \]  

(1)

\[ Y_2O_3 : Eu^{3+} + 6H^+ \rightarrow 2Y^{3+} + Eu^{3+} + 3H_2O \]  

(2)

\[ 2Y^{3+} + 3H_2C_2O_4 \rightarrow Y_2(C_2O_4)_3 + 6H^+ \]  

(3)

The making red phosphor reaction is Eq. (2) and (3). According to these formulas, yttrium and europium is ionized to trivalent cation. When oxalic acid is added, yttrium and europium becomes oxide like Eq. (1) and (3)[1,10]. Thus, an oxidation experiments was conducted to add the oxalic acid same the weight of phosphor powder in solution condition of 2 vol. % sulfuric acid at 80°C in 30 minutes. The resulting precipitate was sintered at 1000°C, which was treated in air atmosphere with a temperature speed of 4°C/min in lasting time 60 minutes. Fig. 6 shows component of powder which was yttrium oxide and europium [11]. In order to get more accurate results, the component was investigated through EDS analysis. It was confirmed that the component of powder after the reaction was yttrium, europium, and carbon through Fig. 7. The shape of the powder was distributed in a regular shape generally.
4. Conclusions

In this study, solubility of rare earth elements in the end of life fluorescent lamps was investigated for use recovered phosphor powder as the separation and recovery process of the rare earth elements. In conclusion, possibility of the rare earth oxide was confirmed to use as the phosphor.

1. Mercury in recovered phosphor powder was removed completely.
2. It was assumed that rare earth elements such as yttrium and europium were dissolved completely when sulfuric acid of concentration of 2 vol.% was used in above 120 minutes.
3. Oxalic acid was added to the solution of rare earth for create the rare earth sulfide, and the rare earth oxide was produced through heat treatment.
4. The rare earth oxide was synthesized as a phosphor for reuse, and it was confirm that possibility of reuse the produced phosphor.

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