Estimation of Extraction Rate of Yttrium from Fluorescent Powder by Ball Milling

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Red fluorescent powder containing yttrium (Y) which is one of the rare earth elements (REEs), was milled in air using a small-scale planetary ball mill to investigate the relation between the extraction rate of Y and the impact energy of the balls calculated from computer simulation based on the Discrete Element Method (DEM) under various conditions. Milling improves the extraction yield, and extraction rate increases with an increase in mill rotational speed, whereas the rate is independent of ball diameter. The same trend is observed in the relation between the specific normal impact energy of the balls and rotational speed. The relation between the extraction rate and the specific normal impact energy can be expressed as a straight line, irrespective of the milling conditions, and it is applicable to estimation of the extraction rate using a large-scale planetary ball mill. Therefore, the extraction rate of Y would be estimated by the specific normal impact energy of the balls calculated from the computer simulation.

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1. Introduction

Much attention has been paid to rare earth elements (REEs) in the manufacture of fine ceramics and functional materials such as high intensity magnets, electrical assemblies and fluorescent materials. The waste products from these materials are important resources for the recovery of REEs.1–5 One of these waste products is a three-wave-length lamp coated with a fluorescent powder containing five REEs: yttrium (Y), europium (Eu), lanthanum (La), cerium (Ce) and terbium (Tb). Recovery of REEs from used lamps is an attractive technology in terms of energy conservation in the refining of REEs from minerals. It is also important economically for those countries that are deficient in rare earth resources. Since the REEs in the fluorescent powder exist as oxides, high temperature leaching using high concentrated solution is normally required to extract high yields from the powder.6 Zhang et al.7,8 have proposed a novel process for acid extraction of REEs from powder activated by mechanical milling, and they have confirmed that extraction yield is dependent on the milling condition. Previously, there have been several reports on the mechanical milling effect in relation to experimental milling conditions9–11 and, although these have provided much useful information, the general principle requires clarification in order to facilitate scaling of optimum yield conditions for different sized mills. It is possible to determine the optimum conditions experimentally, but this may be time and energy consuming. In order to provide general information, computer simulation techniques are a useful tool. The authors have found out the correlation between the grinding rate of gibbsite powder and the specific impact energy of the balls calculated from computer simulation based on the DEM (Discrete Element Method).12–16 However, the authors have not yet confirmed that this simulation method would be useful for estimating the mechanical milling process.

Firstly it is reported that the results of an experiment on red fluorescent powder (Y2O3:Eu3+) was milled using a small-scale planetary ball mill to investigate the relation between the extraction rate of yttrium and the impact energy of balls calculated from computer simulation based on DEM under various conditions. Secondly, it is discussed that the applicability of the relation obtained from small-scale mill to estimate the extraction rate using a large-scale planetary ball mill.

2. Experiments

The Y2O3:Eu3+ (YOX) powder sample used in this research was supplied from Tokyo Chemical Research Co., Ltd (Sagamihara, Kanagawa, Japan). Mean particle size of the starting sample is 4.8 μm. Milling of the YOX sample was conducted in air using two kinds of planetary ball mills with different volume pots. Each mill has two pots on a rotating disk, and the pots and the disk are simultaneously and separately rotated in counter direction at the same rotational speed, as shown in Fig. 1. One is a small-scale mill (Pulversette-7, Fritsch (Germany)), with pots made of zirconia and an inner diameter, di, of 40 mm and 38 mm, respectively. Zirconia mono-size balls having different diameters, d90, of 5, 8, 10 and 15 mm were used as milling media. The

Fig. 1 Schematic diagram of the planetary ball mill.

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Table 1 Experimental conditions.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Pulverisette-7</th>
<th>Pulverisette-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mill diameter (d_m/mm)</td>
<td>40</td>
<td>75</td>
</tr>
<tr>
<td>Mill depth (h/mm)</td>
<td>38</td>
<td>65</td>
</tr>
<tr>
<td>Mill volume (V_m/cm³)</td>
<td>48</td>
<td>290</td>
</tr>
<tr>
<td>Revolution radius (R/mm)</td>
<td>70</td>
<td>120</td>
</tr>
<tr>
<td>Ball diameter (d_b/mm)</td>
<td>5.8, 10, 15</td>
<td>15</td>
</tr>
<tr>
<td>Number of balls (n_b)</td>
<td>187, 49, 24, 7</td>
<td>50</td>
</tr>
<tr>
<td>Ball-filling ratio (%)</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Sample weight (W/g)</td>
<td>5.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Rotational speed (N/rpm)</td>
<td>300, 500, 700</td>
<td>250</td>
</tr>
</tbody>
</table>

Table 2 Material properties and physical constants for the DEM.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of balls (ρ/Mg·m⁻³)</td>
<td>6.0</td>
</tr>
<tr>
<td>Young’s modulus (E/GPa)</td>
<td>210</td>
</tr>
<tr>
<td>Poisson’s ratio (ν)</td>
<td>0.30</td>
</tr>
<tr>
<td>Frictional coefficient (μ)</td>
<td>0.71</td>
</tr>
<tr>
<td>Time step (Δt/µs)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

ball-filling ratio was kept constant at 60%. 5.0 g sample powder was introduced into each pot. The rotational speed of the mill, N, was changed at three steps, i.e., 300, 500 and 700 rpm, and the milling period of time was changed from 5 to 90 minutes. The other is a large-scale mill (Pulverisette-5, Fritsch (Germany)). Zirconia pots of d_m = 75 mm and h = 65 mm, and balls of d_b = 15 mm, were used. The milling conditions were set at 60% of ball-filling ratio and 15.0 g of sample. The rotational speed of the mill, N, was 250 rpm, and the milling period of time was changed from 10 to 30 minutes. The summary of experimental conditions are tabulated in Table 1.

0.5 g milled sample from each mill was agitated in 50 ml of 1N HCl solution for 1 hour at room temperature, then it was washed and filtered with 50 ml of distilled water three times. The yield of Y leached was analyzed using an inductively coupled plasma (ICP, Perkin Elmer, Optima-330XL) spectrophotometer.

3. Simulation of Ball Motion

3.1 Conditions of the simulation work

The three-dimensional motion of each ball during the milling was simulated using the Discrete Element Method (DEM), which takes into account the effect of the presence of the powder sample. 12) Physical properties such as Young’s modulus and Poisson’s ratio of the ball, and the time step in the simulation of the present work are tabulated in Table 2. The frictional coefficient between two balls and/or ball-wall in the simulation was assumed as 0.71, which was determined by a Parameter Fitting Method. 12) The motion of balls was reproduced from the start of the milling to 3.0 seconds in this work. Other conditions in the simulation were the same as those in the experiment.

3.2 Impact energy of balls

The colliding velocity of a ball against another ball or the mill wall can be calculated by the computer simulation. The specific impact energy of balls, E_W, can be calculated from the relative velocity between two colliding balls or a ball colliding against the mill wall, v_j = (v_jN + v_jT), v_jN: normal component, v_jT: tangential component, as given by eq. (1), where m is the mass of a milling media, n denotes number of collision within a second. W is the mass of sample charged into the mill pot.

\[ E_W = \sum_{j=1}^{n} \frac{1}{2}m v_j^2 \]  \hspace{1cm} (1)

4. Results and Discussion

4.1 Milling by a small-scale mill

Figure 2 shows the yield of Y, Y₁, extracted from milled sample as a function of milling time, t, when the d_b = 15 mm balls are used as milling media. The marked values in the figure denote experimental results. The yield increases with increasing milling time and the rotational speed. It reaches about 1.0 (100%) within 30 minutes of milling at more than 500 rpm. The solid lines are the calculated ones, obtained from an empirical equation, given by eq. (2).

\[ Y_1 = 1 - (1 - Y_0) \exp(-K_e \cdot t), \]  \hspace{1cm} (2)

where, Y_0 is the yield of the starting sample (= 0.22), and K_e is defined as the extraction rate of Y.

Most of the experimental values are well fitted near the calculated lines. A similar relation was observed for other conditions of different ball diameters. This indicates that K_e is a representative value in the extraction of Y. Figure 3 shows K_e as a function of N with a parameter of the ball diameter, d_b. K_e increases with an increase in N, and it is independent of d_b except for d_b = 8 mm at N = 500 and 700 rpm. In order to
clarify this, the kinetic energy of balls within a second driven at 500 rpm was calculated from the computer simulation, and is tabulated in Table 3. The kinetic energy attains the largest value using 8 mm balls. When large balls such as \( d_B = 10 \) or 15 mm are used, the space to move for these balls in the pot becomes less due to large ratio of ball size to the mill diameter. On the other hand, smaller balls such as \( d_B = 5 \) mm have enough space to move in the pot, but the kinetic energy is small because of the lesser mass of balls. Therefore, this is one reason that \( K_e \) becomes large value using \( d_B = 8 \) mm.

Figure 4 shows the specific impact energy of the balls calculated from the simulation, (a): \( E_W \) (normal and tangential components), and the specific normal impact energy, (b): \( E_N \) (normal component), as a function of \( N \), depending on \( d_B \). It is found that \( E_W \) is dependent on \( d_B \), while \( E_N \) independent. Figure 5 shows \( K_e \) as a function of (a) \( E_W \) and (b) \( E_N \) under different conditions. The data (a) are scattered widely, while most of data (b) plot on the straight line. This indicates that \( K_e \) is better correlated with \( E_N \) than \( E_W \). Therefore, it can be concluded that the normal impact energy of balls is an important key for estimating the extraction rate of \( Y \) in this process. The extraction rate can be determined by eq. (3), and the gradient in the equation, \( A_Y = 1.19 \times 10^{-3} \text{ g/J} \) also depends on the material. This has a high potential to estimate the extraction rate of \( Y \) from eq. (3), in the case of milling YOX powder using a large mill, and this is demonstrated in the following section.

\[
K_e = A_Y \cdot E_N \tag{3}
\]

4.2 Milling by a large-scale mill

The specific normal impact energy of balls for the large mill calculated from the computer simulation was determined as \( E_N = 0.954 \text{ J/(s·g)} \) at 250 rpm. The extraction
rate of Y calculated by substituting $E_N$ for eq. (3) was $K_e = 1.14 \times 10^{-3} \text{s}^{-1}$. Figure 6 shows $Y_t$ as a function of $t$ for the large mill. The curves in this figure are obtained by substituting $K_e$ from eq. (3) into eq. (1) and plotted values are the experimental ones. It is found that the experimental values are consistent with the estimated line. This means that the extraction rate of Y for a large mill can be estimated by substituting $E_N$ in the large mill into the relation (eq. (3)) obtained for the small mill. Therefore, the extraction rate of Y by a planetary ball mill can be estimated from the relation (eq. (3)) and the DEM simulation.

5. Conclusions

Red fluorescent powder ($\text{Y}_2\text{O}_3\text{Eu}^{3+}$) was milled in air using a small-scale planetary ball mill, to investigate the extraction rate as a function of impact energy of balls simulated by the DEM under various conditions. This is applied to estimation of the extraction rate using the large-scale mill. The results are summarized as follows.

1) The extraction yield of Y proceeds as the milling progresses, and the extraction rate is improved with an increase in the mill rotational speed.

2) The extraction rate of Y is proportional to the specific normal impact energy of balls calculated from the computer simulation, irrespective of the milling conditions.

3) The relation between extraction rate and specific normal impact energy for the small-scale mill is applicable for estimating the extraction rate using the large-scale mill. This indicates that the extraction yield and its rate of Y for any large mill can be estimated by substituting the specific normal impact energy of the balls into the relation between $K_e$ and $E_N$, obtained from the small-scale mill.

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