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Decomposition process and kinetics of waste rare earth polishing powder TG–DTA–FTIR studies

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Abstract The decomposition reaction process of waste rare earth (RE) polishing powder was monitored in real time by the thermogravimetry–differential thermal analysis (TG–DTA) and Fourier transform infrared spectroscopy (FTIR). The results showed that the reaction was divided into two stages, and the thermal weight losses got to stable when the temperature was more than 400 °C. The releasing gas mainly contained H_2O and SiF_4, and the reaction kinetics during decomposition process was studied by the methods of Freeman-Carroll and Kissinger.

Keywords Waste RE polishing powder · Thermogravimetry–differential thermal analysis · Fourier transform infrared spectroscopy · Decomposing reaction kinetics

Introduction

The rare earth (RE) elements play an important role in many fields of advanced materials science. Waste RE polishing powder is failure or unqualified product during its application and production. The content of REO (total rare earth oxide) is between 40 and 90% and cerium oxide is the main composition in waste RE polishing powder. Thousands tons of waste RE polishing powder is produced in China every year [1, 2], and most of them are disposed and land-filled as industrial solid waste.

Rare earth resource in China has decreased gradually because of the unrestrained exploitation [3] and the resource recovery of the solid waste is a development trend. In industry, weight ratio of RE concentrate and concentrated sulfuric acid was about 1.1–1.7, the decomposition temperature was from 600 to 800 °C. While the weight ratio in our study was about 1.8, decomposition reaction can be carried out in the temperature of 300 °C. Despite the extracting costs were similar with RE concentrate, this process was more economic and significant because the raw material was the solid waste. So it is very significant to recycle waste RE polishing powder as renewable RE resource [4–6]. By now the research about the recycle of waste RE polishing powder has been seldom reported, and all of the studies are in experimental stage [7–9].

In our study, the waste RE polishing powder was decomposed by concentrated sulfuric acid to become RE sulfate, and the recovery yield was above 95%. RE sulfate could be extracted directly, then obtain single high-purity products. RE sulfate also could be used in producing chlorinated RE products after precipitated by ammonium bicarbonate. The reaction controlling step could be confirmed by studying the decomposition reaction kinetics, and it would be helpful to increase the reaction rate and optimize the process conditions. Dynamic thermal analysis was widely used in investigating reaction kinetics when the changes in weight and enthalpy during reaction were obvious [10–15].

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Table 1 The composition of waste rare earth polishing powder

Composition	REO	La_2O_3/REO	CeO_2/REO	Pr_6O_{11}/REO	Nd_2O_3/REO	Fe_2O_3	CaO	Al_2O_3	MgO	F	SiO_2
Content/wt%	41.91	42.27	53.67	3.37	0.49	0.22	9.27	11.53	3.65	1.77	0.14

REO = total rare earth oxide

In this paper, the thermogravimetry–differential thermal analysis (TG–DTA) and Fourier transform infrared spectroscopy (FTIR) were used to real time monitor the reaction process of waste RE polishing powder decomposed by concentrated sulfuric acid, and the methods of Freeman-Carroll and Kissinger were applied to investigate the reaction kinetics. It could provide an important theoretical basis for recycling the waste RE polishing powder.

Experimental

Raw materials and chemical reagent

Waste RE polishing powder was supplied by Baotou Rare Earth High Technology Ltd. The composition was listed in Table 1. Concentrated sulfuric acid from Beijing Chemical Plant was analytical reagent.

Experimental method and instrument

The pretreated waste RE polishing powder and concentrated sulfuric acid were mixed proportionally and uniformly. The mixture of 54 mg was taken every time. The sample was heated and cooled in the furnace during the decomposition process. Dynamic thermal analytical test was carried out on STA409C TG-DTA analyzer and FTIR made by NETZSCH Co in German. The atmosphere in the furnace was air and the heating rate was 5, 10, 15 K min^{-1}, respectively.

XRD test was carried out on high-power X diffractometer made by MAC Science Co. Ltd in Japan. Cu Ka radiation was adopted, and the peak position and intensity of the sample in Fig. 1 were compared with data of diffraction peak in JPPDS standard card to affirm the phase composition.

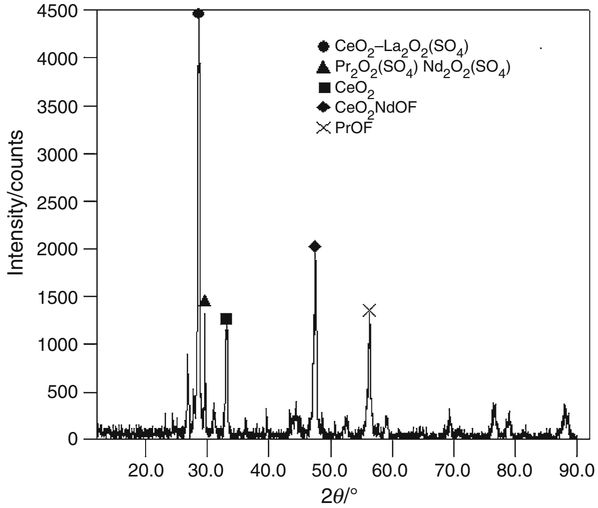


Fig. 1 XRD spectra of waste RE polishing powder

Methodology and kinetic analysis

The reaction kinetics was investigated by thermal analytical technology [16], formula (1) was fundamental equation,

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}(1-\alpha)^n \tag{1}$$

where α was the reaction percent conversion, A was the frequency factor in s^{-1} mol^{-1}, E was the activation energy in J mol^{-1}, n was the reaction order, and R was the molar gas constant in 8.314 J mol^{-1} K^{-1}.

TG calculation of the kinetic parameter by derivative method

In the TG curves, α in formula (2) meant the ratio of weight loss

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \tag{2}$$

wherein, m_0 was the original mass in mg, m_∞ was the final mass after reaction in mg, and m was the mass at time t in mg.

The non-isothermal derivative method, i.e., Freeman-Carroll method, was used to take logarithms to both sides of formula (1) and subtractive forms were given as formulas (3) and (4).

$$d\log\left(\frac{d\alpha}{dt}\right) = -\frac{E}{2.303R}d(1/T) + n\,d\log(1-\alpha) \tag{3}$$

$$\frac{\Delta\log\left(\frac{d\alpha}{dt}\right)}{\Delta\log(1-\alpha)} = -\frac{E}{2.303R}\frac{\Delta(1/T)}{\Delta\log(1-\alpha)} + n \tag{4}$$

A linear curve was drawn by $\Delta(1/T)/\Delta\log(1-\alpha)$ vs. $\Delta\log(\frac{d\alpha}{dt})/\Delta\log(1-\alpha)$, and its slope was $-E/2.303R$. So activation energy could be calculated, and the intercept of the linear curve was reaction order n.

DTA calculation of the kinetic parameter by Kissinger method

According to the Kissinger method [17], the influence of heating rate β ($\beta = \mathrm{d}T/\mathrm{d}t$) on peak temperature T_p in DTA curves could be shown as formulas (5), (6), and (7). $T_{\mathrm{p}1}$, $T_{\mathrm{p}2}$, … was relative peak temperature in K, respectively.

$$\mathrm{d}[\ln(\frac{\beta}{T_\mathrm{p}^2})]/\mathrm{d}(\frac{1}{T_\mathrm{p}}) = -\frac{E}{R} \tag{5}$$

$$\ln(\frac{\beta_1}{T_{\mathrm{p}1}^2}) + \frac{E}{RT_{\mathrm{p}1}} = \ln(\frac{\beta_2}{T_{\mathrm{p}2}^2}) + \frac{E}{RT_{\mathrm{p}2}} = \ldots \tag{6}$$

$$\ln(\frac{\beta}{T_\mathrm{p}^2}) = -\frac{E}{RT_\mathrm{p}} + n \tag{7}$$

$\ln(\frac{\beta}{T_\mathrm{p}^2})$ was taken as vertical coordinate and $1/T_\mathrm{p}$ as horizontal coordinate to make a linear curve, and activation energy E could be calculated according to its slope.

Results and discussion

Reaction procedure decided by TG–DTA and FTIR

Figure 1 was XRD spectra of waste RE polishing powder, which showed that the RE phase composition consisted of oxide, oxy-fluoride, and sulfate. Figure 2 was TG–DTA results of waste RE polishing powder decomposed by concentrated sulfuric acid at the heating rate of 5 K min^{-1}. There were two obvious endothermic peaks nearby 250 and 300 °C in DTA curve, which meant acute reactions occurred. During the first reaction stage at the temperature of 240–280 °C, the peak temperature was 276.5 °C, the extension starting temperature was 247.6 °C, and the ending temperature was 280.7 °C, and the weight loss of related TG curve was 22.97%. Figure 3 was infrared spectra of releasing gas detected in real time by TG–DTA and FTIR. 1541.46 and 3740.98 cm^{-1} was the absorption peak of H_2O, showing that decomposition reaction

Fig. 2 TG–DTA curve of decomposition reaction (β = 5 K min^{-1})

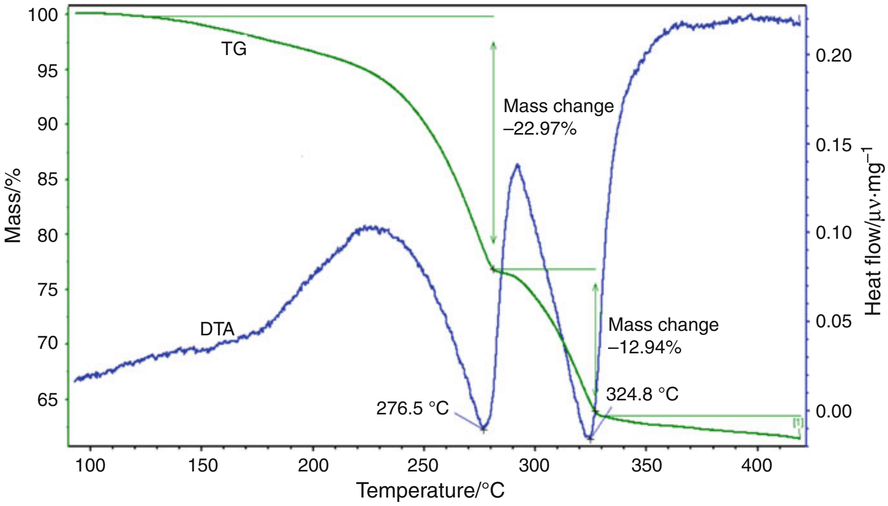
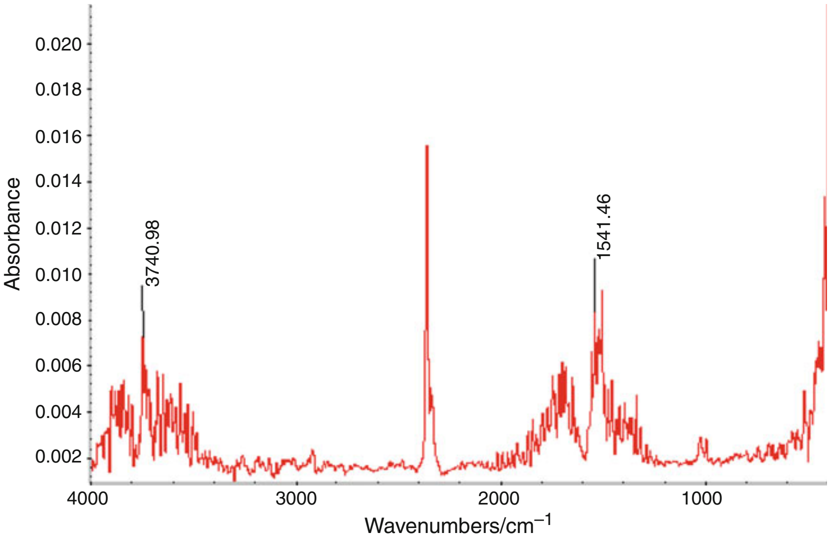


Fig. 3 Infrared spectra of produced gas at the first stage



occurred between REO and sulfuric acid during the first reaction stage. It was also proved by practical experiment that waste RE polishing powder was decomposed into dissoluble RE sulfate by concentrated sulfuric acid at 250 °C.

For the first stage, the equation was as following:

$$RE_2O_3 + 3H_2SO_4 \Rightarrow RE_2(SO_4)_3 + 3H_2O$$

Because the reaction degree was not only related to the temperature, but also affected by acidity and reaction time, so the reaction weakened along with the acid being consumed, and the weight loss and endothermic phenomenon were not obvious.

As the temperature increased, the decomposition reaction was strengthened and the second obvious endothermic peak at temperature of 300–330 °C appeared on DTA curve. The peak temperature was 324.8 °C, the extension starting temperature was 302.7 °C, and the ending temperature was 327.3 °C. The weight loss amounts to 12.94% on related TG curve. Figure 4 was infrared spectra of releasing gas. 1528.29 and 3740.98 cm^{-1} was the absorption peak of H_2O, and 1023.41 cm^{-1} was the absorption peak of SiF_4. It showed the RE oxy-fluoride also reacted with sulfuric acid. For the second stage, the equation is as following:

$$RE_2O_3 + 3H_2SO_4 \Rightarrow RE_2(SO_4)_3 + 3H_2O$$

$$2REOF + 3H_2SO_4 \Rightarrow RE_2(SO_4)_3 + 2HF + 2H_2O$$

$$SiO_2 + 4HF \Rightarrow SiF_4 + 2H_2O$$

Dynamic thermal analytical test had also been carried out at the heating rate of 10 and 15 K/min, and the result showed that the temperature ranges of reaction stage were in agreement with 5 K/min, and the temperature difference was between 10 and 20 °C.

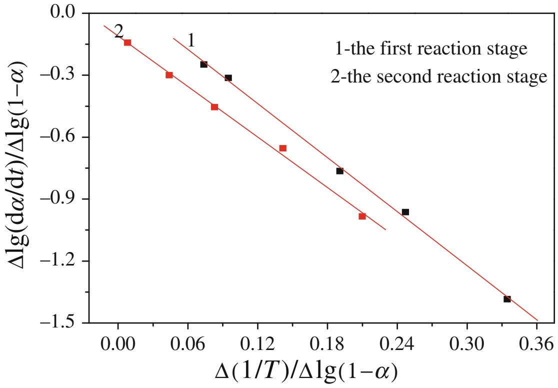


Fig. 5 Calculated results of TG kinetics

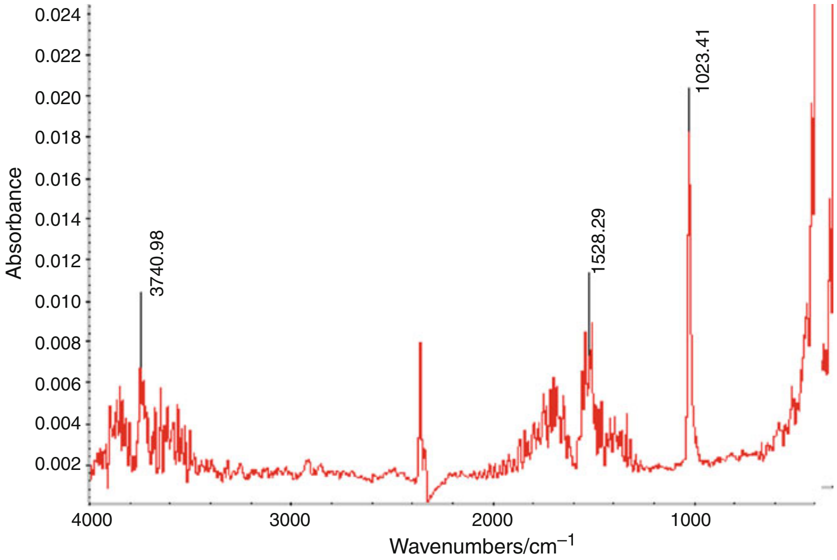
Calculated results of reaction kinetics

(1) The rate of weight loss related to different temperatures could be obtained from DTG curve. A linear relation could be gained by the method of Freeman-Carroll, as seen in Fig. 5.

The linear regression was analyzed by Least Square method. For the first stage, it could be obtained as $Y = -4.430 \times 10^3 X + 0.078$, the correlation coefficient $r = 0.998$, the activation energy $E = 84.82$ kJ mol^{-1}, and the reaction order $n = 0.078$. When the peak temperature $T = 549$ K, the frequency factor $A = 36.274 \times 10^6$ and the reaction rate constant $K = 0.27$.

For the second stage, it could be obtained as $Y = -4.364 \times 10^3 X - 0.094$, the correlation coefficient $r =$

Fig. 4 Infrared spectra of produced gas at the second stage



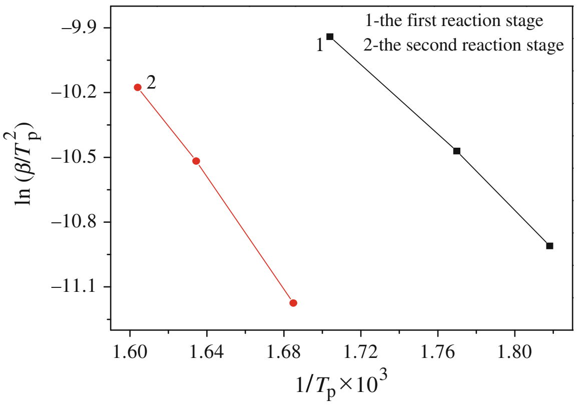


Fig. 6 Calculated results of DTA kinetics

0.999, and the activation energy $E = 83.55$ kJ mol^{-1}, and the reaction order $n = 0.094$. When the peak temperature $T = 597$ K, the frequency factor $A = 5.322 \times 10^6$ and the reaction rate constant $K = 0.2469$.

The results showed that activation energy was 84.82 and 83.55 kJ mol^{-1}, respectively at two stages, and reaction processes at two stages were both controlled by reaction kinetics because activation energy was between 40 and 300 kJ mol^{-1}. Because the content of REO in waste RE polishing powder was higher than that of RE oxy-fluoride, REO was decomposed at the first stage. The reaction order at every stage was 0.078 and 0.094, respectively, which was less than 1 and meant that the reactant concentration had a little influence on reaction rate. The influence of temperature on reaction was higher than that of reactant concentration.

(2) The heating rate in experiment was 5, 10, and 15 K/min, respectively, and three DTA curves were obtained. Two linear relations could be gained by processing two peak temperatures of each curve with Kissinger method, as seen in Fig. 6.

The linear regression was analyzed by Least Square method. For the first stage, it could be obtained as $Y = -9.3180 \times 10^3 X + 4.4192$, the correlation coefficient $r = 0.999$, and the activation energy $E = 77.47$ kJ mol^{-1}.

For the second stage, it could be obtained as $Y = -10.256 \times 10^3 X - 6.037$, the correlation coefficient $r = 0.998$, and the activation energy $E = 85.26$ kJ mol^{-1}.

It showed that the activation energies at two stages obtained by Kissinger method were in agreement with that by Freeman-Carroll method.

Conclusions

The TG–DTA and FTIR were used to real time monitor the reaction process of waste RE polishing powder decomposed by concentrated sulfuric acid. The results showed that the process was mainly divided into two stages. The reaction of REO decomposition occurred at about 250 °C at the first stage, and REO and RE oxy-fluoride were decomposed by sulfuric acid at about 300 °C at the second stage. The results were in agreement with that in practical experiment, in which the waste RE polishing powder could be decomposed at 250 °C.

The method of Freeman-Carroll was used to analyze the TG curve. The activation energies at two stages were between 40 and 300 kJ·mol^{-1}. It could be concluded that two reaction processes at two stages were controlled by reaction kinetics. The reaction order was less than 1, which showed that the reactant concentration had a little influence on reaction rate.

The method of Kissinger was used to analyze the DTG curve. The activation energy for the first reaction stage was $E = 77.47$ kJ mol^{-1}, and $E = 85.26$ kJ mol^{-1} for the second reaction stage. The result was in agreement with that analyzed by the method of Freeman-Carroll.

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References

1. Xv T, Peng HQ, Lin Zh, Lv BY. Formation cause, composition analysis and comprehensive utilization of rare earth solid wastes. Chin Rare Earths. 2010;31(2):34–9.
2. Abreu RD, Morais CA. Purification of rare earth elements from monazite sulphuric acid leach liquor and the production of high-purity ceric oxide. Miner Eng. 2010;23:536–40.
3. JZh Cheng, Che LP. Current mining situation and potential development of rare earth in China. Chin Rare Earths. 2010;31(2):65–9.
4. Hajime N, Kazuo S, Toyohiko S. Fundamental research on the preparation of recycling ceramics using industrial waste. J Electroceram. 2005;26(1):35–8.
5. Jonker A, Potgieter JH. An evaluation of selected waste resources for utilization in ceramic materials applications. J Eur Ceram Soc. 2005;25(13):3145–9.
6. Amritphale SS, Bhasin S, Chandra N. Energy efficient process for making pyrophyllite-based ceramic tiles using phosphoric acid and mineralizers. Ceram Int. 2006;32(2):181–7.
7. Xv T, Yu YH, Gao XL, Yan XJ. Research on resource characteristic of solid waste RE polishing powder. China Resour Compr Util. 2010;28(5):22–5.
8. Wang GX, Su DZ. Preparation of high performance ceramic tiles using waste tile granules and ceramic polishing powder. J Chongqing Univ Eng Ed. 2008;7(4):291–6.
9. Tesuya O, Ken-Ichi M, Gin-Ya A. Extraction and mutual separation of rare earths from used polishes by chemical vapor transport. Metall Mater Trans. 1999;30B:45–51.
10. Mojumdar SC, Madhurambal G, Saleh MT. A study on synthesis and thermal, spectral and biological properties of carboxylato-Mg(II) and carboxylate-Cu(II) complexes with bioactive ligands. J Therm Anal Calorim. 2005;81:205–10.

11. Hu YH, Qiao J, Hao XK. Study on the thermal decomposition of ammonium nitrate cerium (IV). Chin Rare Earths. 2001;22(6): 69–72.
12. Otero M, Calvo LF, Estrada B, García AI, Morán A. Thermogravimetry as a technique for establishing the stabilization progress of sludge from wastewater treatment plants. Thermochim Acta. 2002;389(1–2):121–32.
13. ZhR Lu, Yang L, Guo YJ. Thermal behavior and decomposition kinetics of six electrolyte salts by thermal analysis. J Power Sources. 2006;56(2):555–9.
14. Kalogirou M, Samaras Z. Soot oxidation kinetics from TG experiments, Can they be used reliably in diesel particulate filter modelling tools. J Therm Anal Calorim. 2010;99:1005–10.
15. Zouaoui N, Brilhac JF, Mechati F, Jeguirim M, Djellouli B, Gilot P. Study of experimental and theoretical procedures when using thermogravimetric analysis to determine kinetic parameters of carbon black oxidation. J Therm Anal Calorim. 2010;102(3): 837–49.
16. Chen JH, Li CR. Thermoanalysis and application. 1st ed. Beijing: Science Press; 1987. p. 121–7.
17. Yu BL, Jiang JD. Practical thermal analysis. 1st ed. Beijing: Textile Industry Press; 1990. p. 168–9.