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Mechanism and kinetics of the $BaMgAl_{10}O_{17}:Eu^{2+}$ alkaline fusion reaction

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Abstract: Knowledge of the kinetics and mechanism of $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) fusion with sodium hydroxide will benefit recycling rare earth elements (REEs) from the waste phosphors. The reaction temperature range of 290–375 °C and the reaction mechanism were determined using X-ray diffraction, scanning electron microscopy and differential scanning calorimetry. Activation energy was determined by the four model-free methods, and calculated results showed that the Kissinger method value of 579.5 KJ/mol was close to the average value of the Kissinger-Akahira-Sunose (KAS) and the Flynn-Wall-Ozawa (FWO) methods of 563.5 kJ/mol. The calculated activation energy variation tendency versus conversion factor agreed with the proposed mechanism.

Keywords: $BaMgAl_{10}O_{17}:Eu^{2+}$; alkaline fusion; thermo-kinetic analysis; reaction mechanism; rare earths

Waste phosphor has been gaining more attention due to large amounts of rear earth elements (REEs) in it, which can be recycled[1,2]. In 2010, the U.S. Department of Energy assessed six rare earth metals: dysprosium, neodymium, terbium, europium and yttrium, along with indium, as most critical in the short term. Eu^{2+} activated barium magnesium aluminate blue phosphor ($BaMgAl_{10}O_{17}:Eu^{2+}$, BAM) is widely used for plasma display panels and fluorescent lamps due to its high efficiency and excellent color characteristics[3]. The waste phosphor containing BAM has been an important focus in the field of renewable rare earth resources[4]. The alkaline fusion of waste phosphors as a pretreatment process makes it possible to increase the leaching rate of REEs in manufacturing[5,6]. Hence, the knowledge of kinetics and mechanisms of BAM and pure phosphor extraction via fusion with sodium hydroxide will be beneficial for recycling REEs from waste phosphors. However, the reaction mechanisms of BAM alkaline fusion currently remain unknown.

Analytical techniques, such as differential scanning calorimetry (DSC) can be used to determine kinetic parameters of the alkaline fusion reaction[7]. Kinetic parameters are obtained from the DSC data by using either model-fitting or model-free methods. When the reaction mechanism of the alkaline fusion cannot be determined, model-free methods offer a simple and powerful tool to estimate the activation energy by using the data from a series of experiments at different heating rates[8]. The use of the iso-conversion methods is a trustworthy way of obtaining reliable and consistent kinetic information from both non-isothermal and isothermal data. It can also help revealing the complexity of multiple reactions due to the relationship between the activation energy and the conversion factor[9,10].

In this study, a series of alkaline fusion of BAM was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and DSC, and the reaction characteristics were studied under inert conditions at different heating rates of 3, 10, 20, and 30 ºC/min. The purpose of the study was to elucidate the reaction mechanism and reaction kinetics of the alkaline fusion of BAM. Kinetic parameters of the alkaline fusion could be obtained via the four model-free methods, i.e., the Kissinger, the Kissinger-Akahira-Sunose (KAS), the Flynn-Wall-Ozawa (FWO), and the Friedman methods.

1 Materials and methods

1.1 $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) alkaline fusion

BAM powder used in this study was obtained from the Dalian Luminglight Co. in Liaoning Province, China. The powder has a particle size of 2–4 μm. BAM powder was mixed with sodium hydroxide following the NaOH/BAM mass ratio of 1:1 by ball-milling.

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The mixtures were placed into 200 mL nickel crucibles, and then fusion was performed in a furnace at 150, 200, 250, 300, 325, 350 and 375 ℃ for 2 h. After the reaction the crucibles were immediately placed in water to cool the products. Then the fusion products obtained at 300, 325, 350 and 375 ℃ were cleaned with deionized water several times at 60 ℃ under stirring (200 r/min) for 20 min. After filtration, the products were dried, and ground to a size smaller than 52 μm (270 mesh) for XRD (Philips APD-10 X-ray diffractometer) and SEM (FEI-Quanta250, USA) analysis.

In order to understand the isothermal reaction mechanism, the fusion of the mixtures was performed at 375 ℃ for 30, 60, 90, 120 min, respectively. The products were processed using the same procedure as mentioned above for the XRD and SEM.

DSC was performed using a NETZSH STA 409 C/CD thermal analyzer. The reference material was α-Al_2O_3 powder. Non-isothermal experiments were carried out at heating rates of 3, 10, 20 and 30 ℃/min with the temperature ranging from ambient to 700 ℃.

1.2 Kinetic evaluation using the model-free methods

The general non-isothermal decomposition reaction rate is:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = f(T)\cdot f(\alpha) \tag{1}$$

where α is the conversion factor; t is the reaction time; T is the absolute temperature; $f(\alpha)$ is a differential form of the reaction model, which is a function of α:

$$\alpha = \frac{H_T}{H_S} \tag{2}$$

H_T is the absolute integral area of the DSC curve from the reaction start to temperature T and H_S is the absolute integral area of the DSC curve for the whole selected reaction temperature range.

According to the Arrhenius equation, $f(T)$ is:

$$f(T) = Ae^{-\frac{E}{RT}} \tag{3}$$

where A is the frequency factor, E is the activation energy and R is the universal gas constant. $g(\alpha)$ is the integral form of the reaction model:

$$g(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(a)} \tag{4}$$

Model-free methods allow evaluating kinetic parameters without preselecting a reaction model. In this study, the Kissinger, KAS, FWO, and the Friedman methods were selected because they have been successfully applied previously to study solid decomposition[11].

The Kissinger equation can be expressed as Eq. (5)[12]. According to the Kissinger method, the activation energy, E can be obtained from the slope of the plot of $\ln(\beta/T_p^2)$ against $1/T_p$ at different heating rates for a series of experiments, in which T_p is the peak temperature of the DSC curve in the reaction range, and β is the heating rate:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_p} \tag{5}$$

The KAS equation can be expressed as Eq. (6)[13]. The activation energy, E, can be obtained from a plot of $\ln(\beta/T^2)$ against $1/T$ for a given value of α:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{Eg(\alpha)}\right) - \frac{E}{RT} \tag{6}$$

The FWO equation can be expressed as Eq. (7)[14,15]. The activation energy, E, can be obtained from a plot of $\lg\beta$ against $1/T$ for a given value of α:

$$\lg\beta = \lg\left(\frac{AE}{Rg(\alpha)}\right) - 2.315 - 0.4567\frac{E}{RT} \tag{7}$$

The Friedman equation can be expressed as Eq. (8)[16]. The activation energy, E, can be obtained from a plot of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ against $1/T$ for a given value of α:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln A + \ln f(\alpha) - \frac{E}{RT} \tag{8}$$

2 Results and discussion

2.1 Reaction mechanism

The overall chemical reaction, which takes place during the alkaline fusion of BAM can be described by the following reaction[5]:

$$Ba_{0.9}MgAl_{10}O_{17}:Eu^{2+}_{0.1} + 10NaOH + 0.9CO_2 + 0.025O_2 \rightarrow 10NaAlO_2 + MgO + 0.9BaCO_3 + 0.05Eu_2O_3 + 5H_2O \tag{i}$$

2.1.1 Non-isothermal reaction mechanism

DSC curves of the alkaline fusion at different heating rates are shown in Fig. 1. There were two obvious endothermic peaks before 290 ℃, mainly due to moisture and CO_2 absorbed in NaOH. The first endothermic peak before 100 ℃ was due to the evaporation of water, which was absorbed by NaOH. Similar DSC peaks from water evaporation were often observed in many other endothermic reactions, such as alkaline hydrolysis and ther-

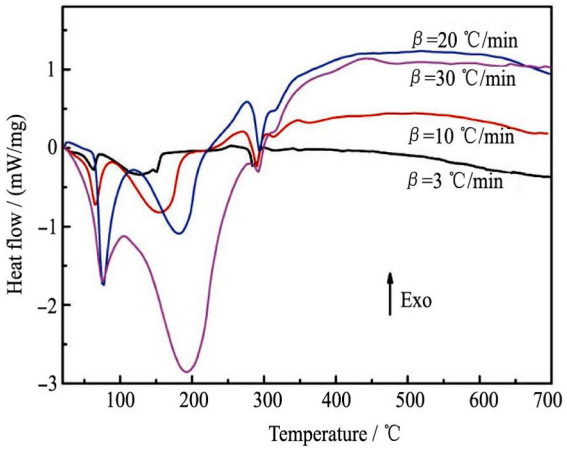

Fig. 1 DSC curves of BAM alkaline fusion reaction at different heating rates