THE RATE OF TEMPERATURE INCREASE AND THE KINETICS OF PbS AND PbO IRRADIATED WITH MICROWAVE[①]

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ABSTRACT

The rate of temperature increase and the kinetics of PbS and PbO, irradiated with microwaves, have been studied. According to the experimental data, the interaction between PbS and PbO is nonisothermal, and the activation energy becomes lower and the rate of interaction becomes faster with microwave irradiation than with conventional heating.

Key words: Microwave irradiation PbS PbO nonisothermal kinetics

1 INTRODUCTION

Although the interaction kinetics between PbS and PbO with conventional heating have been studied in detail[1,2], the kinetics with microwave irradiation have scarecely been reported. In this paper, the rate of temperature increase and the kinetics of the interaction between PbS and PbO were investigated for the purpose of utilizing the advantageous characteristics of microwave heating and improving the techniques for extraction of lead.

2 EXPERIMENT

In order to compare the experimental results of microwave irradiation with those of conventional heating, all samples, the expression of the reaction rate and the method of measuring SO_2 were the same as Ref[2]. The weight of each sample was 50 g. A refitted commercial microwave oven, with a power of 650 W and a frequency of 2,450 MHz, was used to irradiate the sample, the method of measuring temperature was similar to Ref.[3,4]. All the experiments were carried out under an inert atmosphere.

3 RESULTS AND DISCUSSION

3.1 *The Rising Rate of Temperature of* PbS *and* PbO *with Microwave Irradiation*

As shown in Fig. 1, the rate of temperature increase of PbS irradiated with microwaves is greater than that increase of PbO, e.g, during the first 30 seconds of irradiation the temperature of PbS rose from ambient temperature to 1,000 K whereas PbO only rose to 420 K.

In addition, the $T-t$ curve of both PbS and PbO are divided into two stages. At the initial stage the temperature (T) increased rapidly with increasing irradiation time (t) because the samples absorbed microwave energy rapidly. At the later stage, the rate of temperature increase decreased and finally approached to zero when thermal equilibrium was reached.

The thermal equilibrium equation of a unit volume, inside a solid body exposed to electromagnetic energy, can be represented by

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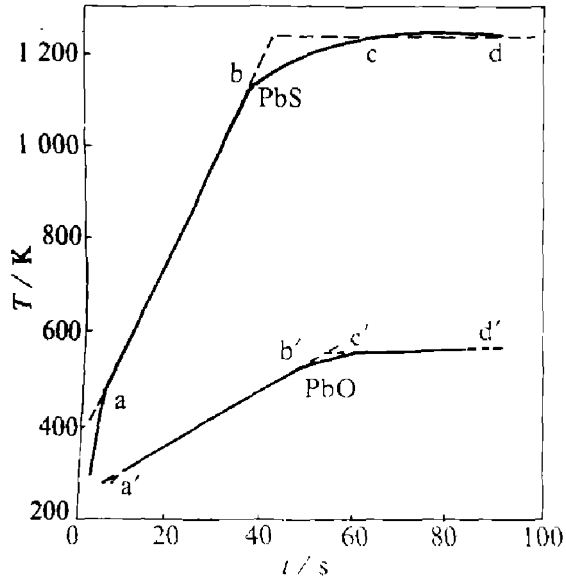

Fig. 1 Rate of temperature (T) increase of PbS and PbO irradiated with microwave at different times (t)

(Solid line—experimental data; dotted line—calculated data)

$$\operatorname{div} q = Q - C\partial T / \partial t \quad (1)$$

Where q is density of heat flux. According to Fourier's Law, the density of heat flux is proportional to the temperature gradient in the reverse direction, that is

$$q = -\lambda \operatorname{grad} T; \quad (2)$$

Q is a source term including the effective microwave power (P) and the effective heat of the chemical reaction (W), namely,

$$Q = P + W \quad (3)$$

where $P = 2\pi f F^2 \varepsilon_r \operatorname{tg}\delta$ (4)

Substituting Eqs. (2)~ (4) into Eq. (1) gives

$$\operatorname{div} \operatorname{grad} T = \nabla^2 T = (C/\lambda)(\partial T/\partial t) - (2\pi f F^2 \varepsilon_r \operatorname{tg}\delta + W)/\lambda \quad (5)$$

where

$$\nabla^2 T = \partial^2 T/\partial x^2 + \partial^2 T/\partial y^2 + \partial^2 T/\partial z^2 \quad (6)$$

Because the sample is irradiated uniformly and heated to a high temperature in a short time, the internal heat transfer is significant, that is, grad $T=0$ and $\nabla^2 T = 0$. Under an inert atmosphere, the heat effect of chemical reaction can be neglected. Additionally, suppose that dielectric constants, loss factors and specific heat are constants[4], then

$$\partial T / \partial t = \text{const} \quad (7)$$

Eq. (7) shows that both the calculated and experimental results are in good agreement. Thus the following equations are obtaind.

For PbS:

$$T = 22.03t + 370.19 \quad (440\ \text{K} < T < 1{,}100\ \text{K}) \quad (8)$$

$$dT/dt = 0 \quad (T = 1{,}240.5\ \text{K}) \quad (9)$$

For PbO:

$$T = 5.22t + 267.78 \quad (320\ \text{K} < T < 510\ \text{K}) \quad (10)$$

$$dT/dt = 0 \quad (T = 561.2\ \text{K}) \quad (11)$$

The relative coefficients are 0.997,8 and 0.997,3 respectively in Eqs. (8) and (10).

3.2 *Interaction Kinetics Between* PbS *and* PbO *with Microwave Irradiation*

As shown by curve 5 in Fig. 2, the interaction between PbS and PbO with microwave irradiation is nonisothermal. From which, by functional fitting, we get the sample temperature as

$$\ln t = -a/T + b \quad (12)$$

namely, $t = c\,e^{-a/T}$ (13)

where $a = 31{,}232.21$, $b = 29.63$, $c = e^b$, and the relative coefficient is 0.999, 6.

It also can be seen from Fig. 2 that the interaction between PbS and PbO with microwave irradiation is carried out quickly at lower temperatures (1,070~ 1,170 K), and then after irradiating about 13 min, the interaction has finished over 90%. With conventional heating it has only finished 8%, 29%, 60% after the same time (13 min) and temperature (1,073 K, 1,123 K, 1,173 K) respectively.

The fraction α of SO_2 generated by the interaction against temperature (T) is shown in Fig. 3.

Supposing the chemical reaction of PbS and PbO is

$$PbS + 2PbO = 3Pb + SO_2 \quad (14)$$

the rate of SO_2 generated by the reaction is

$$d\alpha/dt = kN_s \cdot N_o \quad (15)$$

where N_S and N_O are the concentrations of sulfur and oxygen in moles.

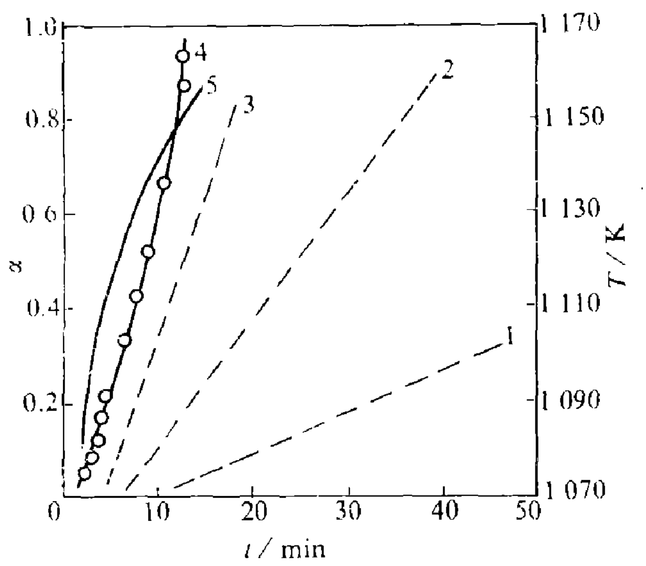

Fig. 2 Fraction α of SO_2 vs heating time (t) and temperature (T) vs time (t)

1, 2, 3—α—t of conventional heating with temperature 1.073 and 1.123 and 1.173 K respectively; 4— α—t of microwave irradiation in a nonisothermal state, temperature 1.070 ~ 1.170 K; 5—T—t of microwave irradiation

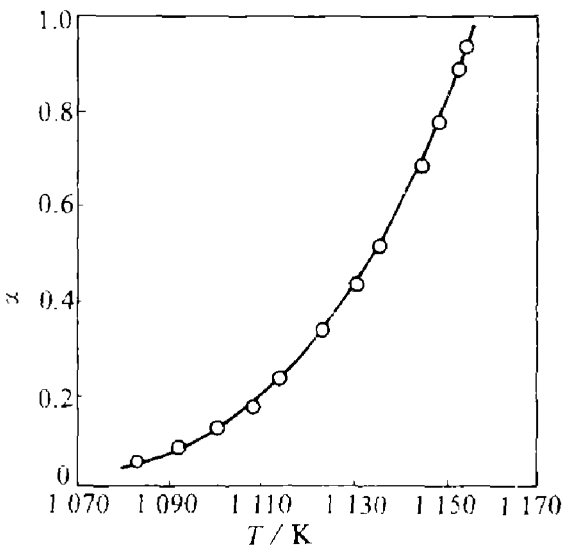

Fig. 3 Plot of α vs T with microwave irradiation

The stoicheometric ratio of PbO / PbS is 2:1, and the concentrations of both sulfur and oxygen may be considered as constants[1], then

$$d\alpha / dt = k \cdot I \qquad (16)$$

where $I = N_S \cdot N_O = \text{const}$.

$$k = A e^{-E/RT} \qquad (17)$$

$$d\alpha / dt = A \cdot I \cdot e^{-E/RT} \qquad (18)$$

Let $d\alpha / dt$ be equal to $d\alpha / dT \cdot dT / dt$, and differentiate Eq. (13) to get dt / dT, then

$$d\alpha / dT = AIce^{-(E+aR)/RT} \cdot a / T^2 \qquad (19)$$

$$d\alpha = aAIcR \times (E+aR)^{-1} \cdot e^{-(E+aR)/RT} d(-E+aR) / RT \qquad (20)$$

$$\int_o^\alpha d\alpha = \int_{T_o}^T aAIcR \times (E+aR)^{-1} \cdot e^{-(E+aR)/RT} d(-E+aR) / RT \qquad (21)$$

$$\alpha = aAIcR \cdot (E+aR)^{-1} \cdot e^{-(E+aR)/RT} \qquad (22)$$

Because $aIcR = m = \text{const}$

$$\alpha = Am \cdot (E+aR)^{-1} \cdot e^{-(E+aR)/RT} \qquad (23)$$

$$\ln \alpha = \ln (Am / E+aR) - (E+aR) / RT \qquad (24)$$

Plotting ln α against 1 / T, a straight line is obtained and the activation energy is 142.76 kJ / mol. Comparing this figure to the activation energy of conventional heating, 190 or 181 kJ / mol [1,2], the former has been decreased.

4 CONCLUSIONS

At lower temperature, the interaction between PbS and PbO can proceed rapidly with microwave irradiation, which not only increases the reaction rate and decreases the energy loss but also avoids the volatization of PbS and PbO at high temperature. Therefore the technology of extraction of Pb using microwave irradiation has positive significance for innovating conventional technology and for developing the application of microwave energy to metallurgy.

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