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Kinetics of AlOOH dissolving in caustic solution studied by high-pressure DSC

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Abstract: Mechanism functions and kinetic parameters of AlOOH (boehmite or diaspore) dissolving in sodium hydroxide solution were researched. The mixture of boehmite or diaspore and caustic solution was scanned by high-pressure differential scanning calorimetry (DSC) instrument with heating rate of 10 °C/min, and differential equation method was used to analyse the DSC curves, combining with iterative method and linear least square method. The most probable mechanism functions for both boehmite or diaspore and caustic solution reactions were logically selected from 30 types of non-isothermal kinetics differential equations, according to the calculated results obtained by Matlab program. The most probable differential mechanism function of boehmite dissolving in caustic solution is $f(\alpha)=1-\alpha$, which reveals the first-order reaction with apparent activation energy of 79.178 kJ/mol and the preexponential constant 1.031×10^8 s^{-1}. The function, $f(\alpha)=2(1-\alpha)^{3/2}$, can describe the dissolution of diaspore sample in sodium hydroxide solution. The calculated results of kinetic parameters are apparent activation energy of 73.858 kJ/mol, preexponential constant of 5.752×10^7 s^{-1} and reaction order of 1.5.

Key words: differential mechanism function; boehmite; diaspore; apparent activation energy; preexponential constant

1 Introduction

Boehmite, α-AlOOH, and diaspore, γ-AlOOH, which are natural heterogeneous ores and primarily consist of one aluminium hydroxide mineral, are the bauxite used to produce alumina. Bayer process is the most popular method for alumina producing all over the world. Digestion as one of the key steps of the Bayer process aims at dissolving the utmost aluminium available in the ore into caustic solution. The chemical reaction between boehmite or diaspore and sodium hydroxide solution is heterogeneous reaction, the main form of metallurgical reaction can be presented as[1]:

$$Al_2O_3\cdot H_2O + 2NaOH + 2H_2O = 2Na[Al(OH)_4] \quad (1)$$

Despite of many open reports on kinetic modelling of bauxite digestion, there is not a consensus. The basic models, $-\ln(1-\alpha)=kt$ and $1-(1-\alpha)^{1/3}=kt$ were directly employed to investigate the kinetics of leaching gibbsite and low-quality boehmite bauxite with hydrochloric acid by REDDY et al[2] and ZIVKOVSC et al[3]. Based on the shrinking core model, PEREIRA et al[4] presented four models for dissolution of gibbsite in NaOH solution controlled by chemical reaction. Some semi empirical kinetic models were developed by ZAFAR[5] for dissolution of low-grade bauxite ore with sulphuric acid. BRITTAN[6] presented a variable activation energy model postulating that the rate-limiting factors can be lumped together as an overall resistance to reaction equivalent to an activation energy barrier. GU et al[7−8] developed a mathematical model of leaching diaspore on the basis of kinetic steady-state principle, while BI et al[9] presented that the model for leaching diaspore should not be the shrinking unreacted-core model and proposed the models for three leaching temperature stages theoretically. BORNTRAG et al[10] measured the change regulation of solution conductivity to get the kinetic model of gibbsite leaching in alkali solution, while LI et al[11] employed isothermal calorimetric method and YIN et al[12] used non-isothermal analysis with differential scanning calorimetry (DSC) technology. No matter what method the authors above used, all the developed models were on the base of hypothesis simple models.

DSC is a thermoanalytical technique in which the

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difference in the amount of heat required to increase the temperature of a sample is measured as a function of temperature. The whole reaction process at a certain temperature range could be detected with the help of DSC, and thus it is much convenient to assess the kinetics of reacting process compared with the conventional method. In this work, in order to study the kinetics of dissolving in caustic solution, the high-pressure DSC technique is employed to obtain the non-isothermal kinetics for boehmite and diaspore. The differential equation method is used to analyse the sets of curve data. Finally, the most probable mechanism functions for boehmite and diaspore are selected logically.

2 Experimental

2.1 Preparation of AlOOH

The boehmite sample used was synthesized by hydrothermal synthesis method[13] and the diaspore sample was the diaspore flotation concentrate[14−16].

The material for preparing boehmite was pure gibbsite with the diaspore flotation concentrate as crystal seed, and the reaction media was sodium hydroxide solution with the concentration of 1mol/L. The mixture of materials in proportion reacted in autoclave under the conditions of temperature of 400 °C, stirring speed of 200 r/min and pressure of 17 MPa. Keeping reaction for 25 d, the new sample was washed to be neutral by distilled water, and then dried in oven at 60 °C. Figure 1 shows the XRD pattern of the dried sample, indicating that the sample is boehmite.

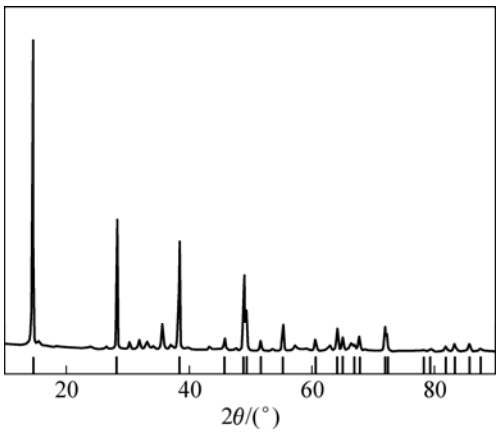


Fig.1 XRD pattern of sample prepared by hydrothermal synthesis method and JCPDS pattern of boehmite

The diaspore from Tiandong, Guangxi Province of China, concentrated for 5 times by direct flotation method, was used as the sample. Sodium oleate was taken as the flotation agent, sodium hexamet aphosphate as the regulator, pine oil as the foaming agent and sodium carbonate as the pH regulator. The results of chemical analysis showed that Al_2O_3 content in the diaspore concentrate was 74%, while the theoretical content in pure diaspore is 85%.

2.2 DSC experiment

The DSC experiment was carried out on 204HP differential scanning analyzer made by NETZSCH Instrument Manufacture Co. Ltd., Germany. A gold crucible with the stainless steel cap was used as the reactor to enduring high pressure. The mixture of solid sample and sodium hydroxide solution was sealed in the gold crucible. Since the leaching condition of boehmite was different from that of diaspore, the caustic concentration of solution for boehmite sample and diaspore sample were 220 and 240 g/L, respectively. The setting parameters of DSC experiment were different as well. For boehmite, the range of scanning temperature was 20−250 °C, while the range for diaspore sample was 20−300 °C. The heating rate was 10 °C/min for both samples. Proteus software developed by NETZSCH was used to collect and process the differential thermal signals.

2.3 Differential equation method

Differential equation method was employed to analyse the DSC curve to research the reaction kinetics. The model of differential equation for non-isothermal kinetics is[17]

$$\ln\left\{\frac{\frac{\mathrm{d}\alpha}{\mathrm{d}T}}{f(\alpha)\left[\frac{E(T-T_0)}{RT^2}+1\right]}\right\}=\ln\frac{A}{\beta}-\frac{E}{RT} \tag{1}$$

where $f(\alpha)$ is the reaction differential mechanism function, α is the reaction fraction, T is the scanning temperature, T_0 is the initial reaction temperature on non-isothermal kinetic curve at which DSC curve deviates from the baseline, E is the apparent activation energy of reaction, A is the preexponential constant, β is the linear heating rate and R is the gas constant. Thus, $T=T_0+\beta t$, where t is the scanning time.

There are 30 mechanism functions of differential equation[17], shown as Table 1.

3 Results and discussion

3.1 Mechanism function of boehmite dissolution

The DSC curve of boehmite and caustic solution scanning from 20 °C to 250 °C is shown in Fig.2. It is seen that an endothermic peak appears at 118 °C. The reaction between boehmite and solution happens around 90 °C, and ends at 180 °C. Besides, the curve between 170 °C and 250 °C tends to a straight line, because the

Table 1 30 mechanism functions of differential equation

No.	Differential mechanism function, $f(\alpha)$
1	$\alpha^{-1}/2$
2	$-[\ln(1-\alpha)]^{-1}$
3	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$
4−5	$(3/n)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-(n-1)}$ (n=2,1/2)
6	$4(1-\alpha)^{1/2}[1-(1-\alpha)^{1/2}]^{1/2}$
7	$(3/2)(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$
8	$(3/2)(1-\alpha)^{4/3}[(1+\alpha)^{-1/3}-1]^{-1}$
9	$1-\alpha$
10−16	$(1/n)(1-\alpha)[-\ln(1-\alpha)]^{-(n-1)}$ (n=2/3, 1/2, 1/3, 4, 1/4, 2, 3)
17−22	$(1/n)(1-\alpha)^{-(n-1)}$ (n=1/2, 3, 2, 4, 1/3, 1/4)
23−27	$(1/n)\alpha(1/2)^{-(n-1)}$($n$=1, 3/2, 1/2, 1/3, 1/4)
28	$(1-\alpha)^2$
29	$(1-\alpha)^2$
30	$2(1-\alpha)^{3/2}$

reaction rate, α, at 170 °C reaches 99.998%. Therefore, the temperature of starting reaction, T_0, is taken as 363.5 K, and the range of T was from 364.5 K to 443.5 K. According to thermal analysis kinetics, the reaction fraction, α, equals the ratio of the heat absorbed at a transient time, t, to the total absorbed heat of reaction. The total absorbed heat is equivalent to the whole peak area above the baseline of DSC curve, H, while the heat absorbed is the part peak area before a transient time, H_t. Proteus software gives a set of values of reaction fraction and the rate of endotherm at time t, dH/dt, at the temperature from 364.5 K to 443.5 K. From $\alpha=H_t/H$ and $T=T_0+\beta t$, it is easy to express dα/ dT as

$$\frac{\mathrm{d}H_t}{\mathrm{d}t}=H\beta\frac{\mathrm{d}\alpha_t}{\mathrm{d}T} \tag{2}$$

Thus, a set of corresponding value of dα/dT can be got.

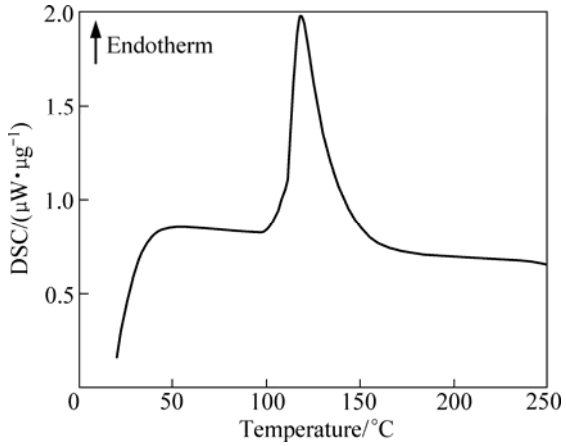


Fig.2 DSC curve of boehmite and caustic solution scanning from 20 to 250 °C with heating rate of 10 °C/min

Since there is a linear relationship between the left side of Eq.(2) and 1/T, Eq.(2) can be solved by iterative method. Giving E any positive value, the linear least square method could be carried out to obtain new values of E from the slope of straight line and A from the intercept. Considering the new value of E as initial value and performing iterative calculation again, another new value of E would be gained. After several times of iteration, reasonable values of E and A can be got. Using Matlab software[18] to process data, the difference value of two adjacent E less than 10^{-6} was set as iterating termination condition. If iteration times was more than 500, the corresponding E was set as 0. Each differential mechanism function $f(\alpha)$ in Table 1 is taken into Eq.(2) and processed by the procedures above and the one with the highest correlation coefficient, r, and the least residual variance Q may be chosen as the proper function. The expressions of r and Q are as follows:

$$r=\frac{\left|L\cdot\sum_{i=1}^{L}\frac{1}{T_i}Z_i-\sum_{i=1}^{L}\frac{1}{T_i}\cdot\sum_{i=1}^{L}Z_i\right|}{\sqrt{\left[L\cdot\sum_{i=1}^{L}\left(\frac{1}{T_i}\right)^2-\left(\sum_{i=2}^{L}\frac{1}{T_i}\right)^2\right]\left[L\cdot\sum_{i=1}^{L}{Z_i}^2-\left(\sum_{i=2}^{L}Z_i\right)^2\right]}} \tag{3}$$

$$Q=\sum_{i=1}^{L}\left[Z_i-\left(\ln\frac{A_{\mathrm{last}}}{\beta}+\frac{E_{\mathrm{last}}}{RT_i}\right)\right]^2 \tag{4}$$

where $Z_i=\ln\left\{\frac{\mathrm{d}\alpha_i/\mathrm{d}T}{f(\alpha_i)\left[E_{\mathrm{last}}(T_i-T_0)/RT_i^2+1\right]}\right\}$, L is the number of the data, and A_{last} and E_{last} are the values of A and E got by the last iteration, respectively.

Using 30 points on the DSC curve of boehmite sample dissolving in sodium hydroxide solution to analyse the 30 differential functions, the analysis results are shown in Table 2. It is noted that the boehmite or diaspore dissolves in caustic solution is a type of reaction between ions and neutral molecules, shown as Eq.(1). According to transition state theory[19] and numbers of empirical values, the value of preexponential constant A in Arrhenius equation for the reaction between ions and neutral molecules is in the range of 10^6 to 10^{13}. In this case, only four functions, namely No.1, No.2, No.9 and No.22 may be suitable for the reaction process. However, the function No.9, $f(\alpha)=1-\alpha$, shows the highest correlation (0.985 6) and the lowest variance (0.237 5) among the four, which thus is considered the most proper expression to describe the kinetics of boehmite dissolving in sodium hydroxide solution. After 8 times of iteration, the obtained apparent activation energy, E, is

Table 2 Kinetic parameters obtained by iterative method of 30 differential mechanism functions using data of DSC curve of boehmite sample dissolving in caustic solution

No.	Apparent activation energy, E/(J·mol^{-1})	Preexponential constant, A/s^{-1}	Correlation coefficient, r	Variance, Q	Iterative times
1	$8.345\ 0\times10^{4}$	$1.136\ 8\times10^{8}$	0.757 6	6.643 2	8
2	$1.268\ 9\times10^{5}$	$3.005\ 5\times10^{13}$	0.881 4	5.944 9	7
3	$1.454\ 7\times10^{5}$	$1.906\ 4\times10^{15}$	0.912 3	5.480 5	7
4	$1.806\ 2\times10^{5}$	$8.775\ 2\times10^{19}$	0.948 0	4.725 0	7
5	$-3.399\ 7\times10^{4}$	$-2.180\ 2\times10^{-7}$	0.919 0	0.273 3	31
6	$-4.500\ 7\times10^{4}$	$-5.300\ 2\times10^{-9}$	0.961 1	0.215 1	16
7	$4.558\ 1\times10^{4}$	$1.917\ 8\times10^{2}$	0.572 0	5.491 6	9
8	$2.862\ 8\times10^{5}$	$1.073\ 8\times10^{34}$	0.986 9	2.816 6	6
9	$7.917\ 8\times10^{4}$	$1.031\ 2\times10^{8}$	0.985 6	0.237 5	8
10	$2.943\ 0\times10^{4}$	$5.039\ 9\times10^{1}$	0.928 9	0.176 9	11
11	$6.856\ 0\times10^{3}$	$8.957\ 3\times10^{-2}$	0.384 2	0.348 9	20
12	$-3.308\ 6\times10^{4}$	$-4.800\ 5\times10^{-7}$	0.811 1	0.731 9	35
13	$5.403\ 2\times10^{5}$	$5.347\ 3\times10^{67}$	0.967 2	25.848 2	5
14	$-4.300\ 7\times10^{4}$	$-1.191\ 5\times10^{-8}$	0.847 9	0.929 7	17
15	$2.323\ 9\times10^{5}$	$6.180\ 9\times10^{27}$	0.974 0	3.753 2	6
16	$3.863\ 0\times10^{5}$	$5.532\ 9\times10^{47}$	0.969 4	12.289 3	6
17	$2.795\ 3\times10^{4}$	$1.328\ 3\times10^{1}$	0.826 1	0.467 4	11
18	$-2.406\ 6\times10^{5}$	$-8.278\ 3\times10^{-36}$	0.976 9	3.566 2	6
19	$-1.352\ 9\times10^{5}$	$-1.785\ 5\times10^{-21}$	0.961 5	1.919 7	7
20	$-3.463\ 8\times10^{5}$	$-3.928\ 8\times10^{-50}$	0.981 9	5.743 1	6
21	$4.471\ 5\times10^{4}$	$1.184\ 8\times10^{3}$	0.934 2	0.375 0	9
22	$5.325\ 4\times10^{4}$	$1.111\ 4\times10^{4}$	0.957 0	0.334 8	9
23	$-3.533\ 2\times10^{4}$	$-1.826\ 3\times10^{-7}$	0.820 8	0.777 0	27
24	$2.997\ 8\times10^{4}$	$2.795\ 4\times10^{1}$	0.526 8	3.007 3	11
25	$-8.534\ 2\times10^{4}$	$-1.106\ 0\times10^{-14}$	0.993 3	0.126 0	9
26	$-1.033\ 1\times10^{5}$	$-2.992\ 3\times10^{-17}$	0.991 9	0.226 0	8
27	$-1.123\ 4\times10^{5}$	$-1.428\ 9\times10^{-18}$	0.989 8	0.337 1	8
28	$1.843\ 2\times10^{5}$	$7.852\ 5\times10^{21}$	0.997 9	0.185 7	7
29	$1.843\ 2\times10^{5}$	$7.852\ 5\times10^{21}$	0.997 9	0.185 7	7
30	$1.316\ 1\times10^{5}$	$4.036\ 2\times10^{14}$	0.996 8	0.144 6	7

79.178 kJ/mol and the preexponential constant, A, is 1.031×10^{8} s^{-1}.

3.2 Mechanism function of diaspore dissolution

Figure 3 displays the DSC curve of diaspore sample dissolving in sodium hydroxide solution with scanning temperature from 20 °C to 300 °C. On the start of the curve, there is a fluctuation before 70 °C, which is led by the error of equipment and the unstable voltage. There is a small peak appearing around 235 °C resulting from the impurities in the diaspore sample gained by flotation. Around 110 °C, a main endothermic peak turns up, and climbs up with the increase of temperature. The endothermic peak reaches the highest at 121 °C, and ends around 195 °C. The initial value of parameter in

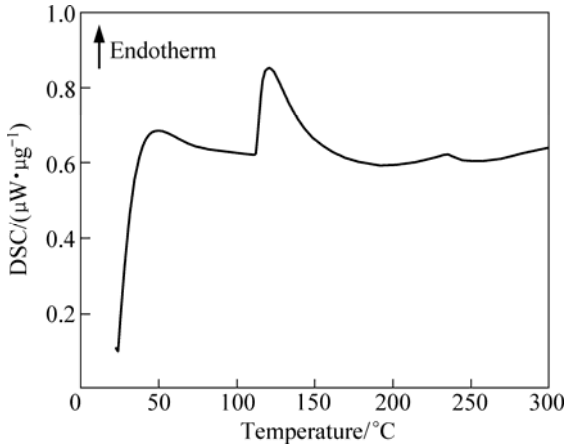


Fig.3 DSC curve of diaspore and caustic solution scanning from 20 °C to 300 °C with heating rate of 10 °C/min

Eq.(2), T_0, is set as 384.5 K. The range of T in accordance with the start and end of peaks is considered to be from 385.5 K to 465.5 K.

Iterative method and linear least square method were carried out using the data of 30 points in the temperature range of 112 °C to 192 °C on the DSC curve obtained by scanning mixture of diaspore sample and caustic solution. Following the same procedure described in section 3.1, the calculated results run by Matlab program are shown in Table 3. It is indicated that eight functions show the non-existence results because the iteration is more than 500 times. And the values of apparent activation energy of three functions are negative and the preexponential constant values of 13 functions are beyond the value range of 10^6 to 10^{13}. Among the left six functions, Nos.28−30 show the correlation coefficient over 0.99, and the low residual variance. However, GU et al[7−8] revealed the apparent activation energy of diaspore ore digesting in sodium aluminate solution was around 44 kJ/mol and 85 kJ/mol for two reaction phases, respectively. Therefore, the last function (30) is the most suitable differential mechanism function to describe the process of diaspore dissolving in caustic solution. The kinetic parameter, apparent activation energy, with respect to the No.30 function, $f(\alpha)=2(1-\alpha)^{3/2}$, is 73.858 kJ/mol, and the preexponential constant A is 5.752×10^7 s^{-1}.

Table 3 Kinetic parameters obtained by iterative method of 30 differential mechanism functions using data of DSC curve of diaspore sample dissolving in caustic solution

No.	Apparent activation energy, E/(J·mol^{-1})	Preexponential Constant, A/s^{-1}	Correlation Coefficient, r	Variance, Q	Iterative times
1	$4.197\,6\times10^4$	$2.918\,5\times10^3$	0.812 1	1.090 5	25
2	$6.813\,6\times10^4$	$4.133\,1\times10^6$	0.925 2	0.937 2	19
3	$7.952\,1\times10^4$	$2.894\,1\times10^7$	0.948 9	0.839 2	18
4	$1.019\,4\times10^5$	$2.612\,8\times10^{10}$	0.973 5	0.687 5	15
5	0	0	0	0	501
6	0	0	0	0	501
7	$2.023\,5\times10^4$	$5.453\,2\times10^{-1}$	0.624 7	0.767 3	40
8	$1.731\,1\times10^5$	$6.615\,9\times10^{19}$	0.995 1	0.352 7	12
9	$4.278\,6\times10^4$	$9.374\,6\times10^3$	0.989 3	0.047 6	25
10	$1.701\,9\times10^4$	$4.375\,0\times10^0$	0.765 0	0.246 1	45
11	$5.813\,2\times10^3$	$1.444\,6\times10^{-1}$	0.296 9	0.419 3	85
12	0	0	0	0	501
13	$3.476\,9\times10^5$	$6.903\,1\times10^{42}$	0.976 9	6.940 6	9
14	0	0	0	0	501
15	$1.363\,5\times10^5$	$8.224\,3\times10^{15}$	0.988 8	0.508 7	13
16	$2.402\,3\times10^5$	$1.407\,4\times10^{29}$	0.980 7	2.744 5	11
17	$1.554\,4\times10^4$	$1.236\,2\times10^0$	0.986 3	0.008 1	47
18	$-2.675\,9\times10^5$	$-1.308\,8\times10^{-37}$	0.996 9	0.537 2	19
19	$-2.088\,6\times10^5$	$-1.170\,7\times10^{-29}$	0.977 7	2.409 7	57
20	$-3.369\,9\times10^5$	$-5.985\,1\times10^{-47}$	0.999 6	0.111 9	13
21	$2.410\,3\times10^4$	$1.096\,4\times10^1$	0.988 3	0.016 5	36
22	2.8590×10^4	$3.193\,8\times10^1$	0.988 7	0.022 5	32
23	0	0	0	0	501
24	$1.520\,25\times10^4$	$1.491\,6\times10^0$	0.681 9	0.318 9	48
25	0	0	0	0	501
26	0	0	0	0	501
27	0	0	0	0	501
28	$1.074\,5\times10^5$	$3.089\,1\times10^{12}$	0.991 4	0.242 3	15
29	$1.074\,5\times10^5$	$3.089\,1\times10^{12}$	0.991 4	0.242 3	15
30	$7.385\,8\times10^4$	$5.751\,8\times10^7$	0.990 4	0.128 0	18

4 Conclusions

1) A single non-isothermal DSC curve is the simple method to investigate the kinetics of AlOOH dissolving in sodium hydroxide solution, by carrying out high-pressure DSC technology. Though boehmite and diaspore have the same chemical formula, AlOOH, their differential mechanism functions, which are logically selected from 30 types of functions by carrying out iterative method and linear least square method, are different.

2) The most probable differential mechanism function of boehmite dissolving in caustic solution is $f(\alpha)=1-\alpha$, which shows the first-order reaction with apparent activation energy of 79.178 kJ/mol and the preexponential constant of 1.031×10^8 s^{-1}.

3) The mechenism function, $f(\alpha)=2(1-\alpha)^{3/2}$, can probably describe the dissolution of diaspore sample in alkali solution. The calculated results of kinetic parameters are apparent activation energy of 73.858 kJ/mol, preexponential constant of 5.752×10^7 s^{-1} and reaction order of 1.5.

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利用高压 DSC 研究一水铝石在碱液中的溶出动力学

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摘 要：研究一水铝石(包括一水软铝石和一水硬铝石)在氢氧化钠溶液中溶出过程的机理函数并确定相应的动力学参数。将一水铝石矿和氢氧化钠溶液在高压 DSC 设备中以 10 °C/min 的速度加热，用微分方程法分析得到 DSC 曲线，同时借助 Matlab 程序利用迭代法和线性最小二乘法计算微分方程，从 30 种机理函数的微分形式中分别逻辑地选择了两种一水铝石矿和苛性碱溶液的反应过程的最可能的机理函数。计算结果表明：一水软铝石溶解于苛性碱溶液的最可能的机理函数为 $f(\alpha)=1-\alpha$，表观活化能为 79.178 kJ/mol，指前因子为 1.031×10^8 mol/s，反应级数为 1；一水硬铝石在苛性碱溶液中溶解的最可能的机理函数为 $f(\alpha)=2(1-\alpha)^{3/2}$，表观活化能为 73.858 kJ/mol，指前因子为 5.752×10^7 mol/s，反应级数为 1.5。

关键词：微分机理函数；一水软铝石；一水硬铝石；表观活化能；指前因子

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