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Apparent activation energy for spontaneous combustion of sulfide concentrates in storage yard

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Abstract: In order to evaluate the spontaneous combustion hazard of sulfide concentrates in storage, three different kinds of sulfide concentrates (sulfur-rich sulfide concentrate, iron sulfide concentrate and copper sulfide concentrate) were obtained from a storage yard in Dongguashan Copper Mine, China. The reaction processes at different heating rates of 5, 10, 15, 20, and 25 °C/min in air flow from ambient temperature to 1 000 °C were studied by TG-DTG-DSC analysis. By the peak temperatures of DTG curves, the whole reaction process for each sample was divided into different stages, and the corresponding apparent activation energies were calculated by the Ozawa-Flynn-Wall method. It is found that the reaction process of each sample is considerably complex; the apparent activation energy values change from 36 to 160 kJ/mol in different temperature ranges; sulfur-rich sulfide and iron sulfide concentrates have lower apparent activation energy than copper sulfide concentrate below 150 °C; so they are more inclined to cause spontaneous combustion at ambient temperature.

Key words: apparent activation energy; sulfide concentrates; spontaneous combustion; thermogravimetry (TG) analysis; differential scanning calorimetry (DSC)

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1 Introduction

Sulfide concentrates produced in excess of demand have to be deposited in stockpiles. Spontaneous combustion is a common phenomenon when convenient conditions are available, especially where large quantities of sulfide concentrates are stored for extended periods. During the storage, a major source of SO_2 releases, then sulfide concentrates will lose both their economic values and cause environmental problems. In Dongguashan Copper Mine of China, spontaneous combustion of sulfide concentrates in the storage yard occurs frequently[1]. The maximum temperature of sulfide concentrate stockpile surfaces can reach 40 °C in summer, with strong sulfur gas odor. The metallic walls and ceilings have to be replaced frequently resulting from the acid erosion, leading to a large economic loss.

Based on the relevant literatures, reports on dealing with spontaneous combustion of sulfide concentrates were scarce. However, the oxidation of sulfide ores has been studied in detail[2−5] because of their importance in the acid generation in mine waters, mineral processing, and hydrometallurgical systems. Evaluation of the self-ignition hazard, considering the heat properties of sulfide concentrates, requires experimental methods. These experimental methods can be divided into self-heating and temperature-programmed experiments[6]. The self-heating methods[7−9] include adiabatic experiments, the standard wire mesh basket test and the appropriate Frank-Kamenetskii (F-K) analysis, as well as the crossing-point temperature (CPT) method. Differential scanning calorimetry (DSC), thermogravimetric analysis (TG), and differential thermal analysis (DTA) represent the temperature-programmed methods[10]. The main difference[6] is that in self-heating experiments, the temperature—time course is studied at a constant ambient temperature, whereas for the temperature-programmed

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experiments, a constant heating rate is applied to the sample. Although adiabatic experiments[11−12] can yield the most direct information on the low-temperature oxidation of sulfide concentrates, including such parameters as heats of adsorption and reaction, and activation energies, they are difficult to be performed.

In this study, chemical composition and mineral phase analysis of sulfide concentrates were carried out by precision instruments; the apparent activation energy values for the investigated processes were determined on the basis of TG-DTG-DSC results obtained at different heating rates by the methods of Ozawa-Flynn-Wall.

2 Experimental

2.1 Sample preparation and analysis

Three typical samples (sulfur-rich sulfide concentrate, iron sulfide concentrate, and copper sulfide concentrate) were collected from Dongguashan Copper Mine in China, of which the particle diameter was grinded to less than 0.2 mm.

The samples were analyzed by scanning electron microscopy (SEM), X-ray diffractometry (XRD), and Fourier transform infrared spectrum analysis (FTIR) in details. Table 1 indicates that the sulfur contents of three samples are high, iron sulfide concentrate has the highest iron content, and copper sulfide concentrate has the most copper content. Fig.1 shows that three sulfide concentrates are broken into rough particles or rods by grinding, and the caking of iron sulfide concentrate can be also observed.

XRD measurement was performed on a Riguku D/Max 3041 system to analyze the mineragraphy composition of samples. XRD patterns were recorded with Cu K_α (λ = 0.154 2 nm) radiation and the X-ray tube was operated at 40 kV and 20 mA with time constant of 0.5 s. Step scans were taken over a range of 2θ from 10° to 90° at a speed of 2 (°)/min. The results display that sulfur-rich sulfide concentrate is mainly composed of pyrite (FeS_2), pyrrhotite ($Fe_{1-x}S$), gypsum ($CaSO_4 \cdot 2H_2O$), isocubanite ($CuFe_2S_3$), and quartz (SiO_2); iron sulfide concentrate mostly contains magnetite (Fe_3O_4),

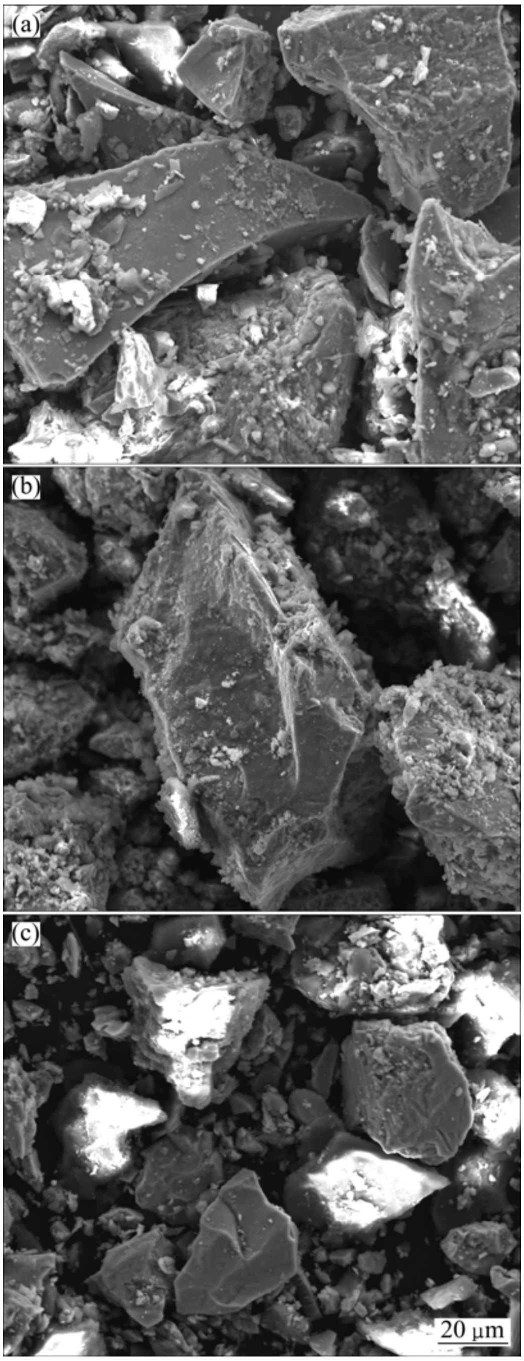

Fig.1 SEM images for three samples: (a) Sulfur-rich sulfide concentrate; (b) Iron sulfide concentrate; (c) Copper sulfide concentrate

Table 1 Chemical composition of three sulfide concentrates (mass fraction, %)

Sample type	Fe	S	O	Si	Mg	Ca	Cu	Al	K
Sulfur-rich sulfide concentrate	34.82	23.50	26.16	6.80	4.26	3.28	−	0.82	0.36
Iron sulfide concentrate	51.38	13.11	28.07	2.82	2.80	1.48	−	0.35	−
Copper sulfide concentrate	21.34	16.03	23.16	11.17	9.24	1.43	17.43	0.21	−

pyrrhotite ($Fe_{1-x}S$), pyrite (FeS_2), $Ca[B(OH)_4]_2\cdot 2H_2O$ (hexahydroborite), and $(CaSO_4)\cdot 2H_2O$ (gypsum); copper sulfide concentrate contains mainly chalcopyrite ($CuFeS_2$) and zinc sulfide (ZnS).

Each sample was smeared onto a potassium bromide disc and the corresponding absorbance peaks were obtained by the diffuse-reflection mode of FTIR (type NEXUS 670). The wave length scanning range is from 4 000 to 400 cm^{-1}, and number of scans is 32. The results show that FTIR spectra of three samples are extremely similar, with the structure of bisulfide, sulfate, silicon compound, and water structure.

2.2 Test method

Thermogravimetric (TG) and differential scanning calorimetry (DSC) are the most commonly used techniques to follow the course of solid state reactions; the relative sensitivities of the two techniques depend upon the change in mass for the process (processes) (TG) or the enthalpy of the process (processes) (DSC)[13]. Simultaneous TG/DSC instrument Netzsch Model STA449C/3/MFC/G was performed, and synthetic air (20.5% O_2 (quality 4.5 g) in N_2 (quality 5.0 g)) was used as the purge gas with an air flow rate of 20 mL/min. The samples with mass of about 20 mg were measured at the heating rates of 5, 10, 15, 20, and 25 °C/min respectively, from ambient temperature to1 000 °C.

2.3 Results and discussion

The curves of simultaneous TG-DTG-DSC analysis for the oxidation reaction of the investigated sulfide concentrates in air at different heating rates are exemplarily shown in Fig.2 and Fig.3, which indicate the complexity of each reaction process. At diverse heating rates, the gained curves are different. In general, increasing the heating rate results in higher temperature values for the oxidation and decomposition reaction.

Table 2 shows the maximum peak temperatures detected on the DTG curves from ambient to 800 °C, which depends on the heating rate.

The obvious mass loss (gain), and endothermic (exothermic) peaks can be found from Fig.2 and Fig.3, which show the formation of sulfate, the oxidation of the sulfide, and the decomposition of sulfates. For the oxidation of sulfide minerals under air condition, the direct formation of oxide can be expressed in general as follows[14]:

$$2MS_{(s)} + 3O_{2(g)} \longrightarrow 2MO_{(s)} + 2SO_{2(g)} \qquad (1)$$

The formation of SO_2 is highly exothermic, and

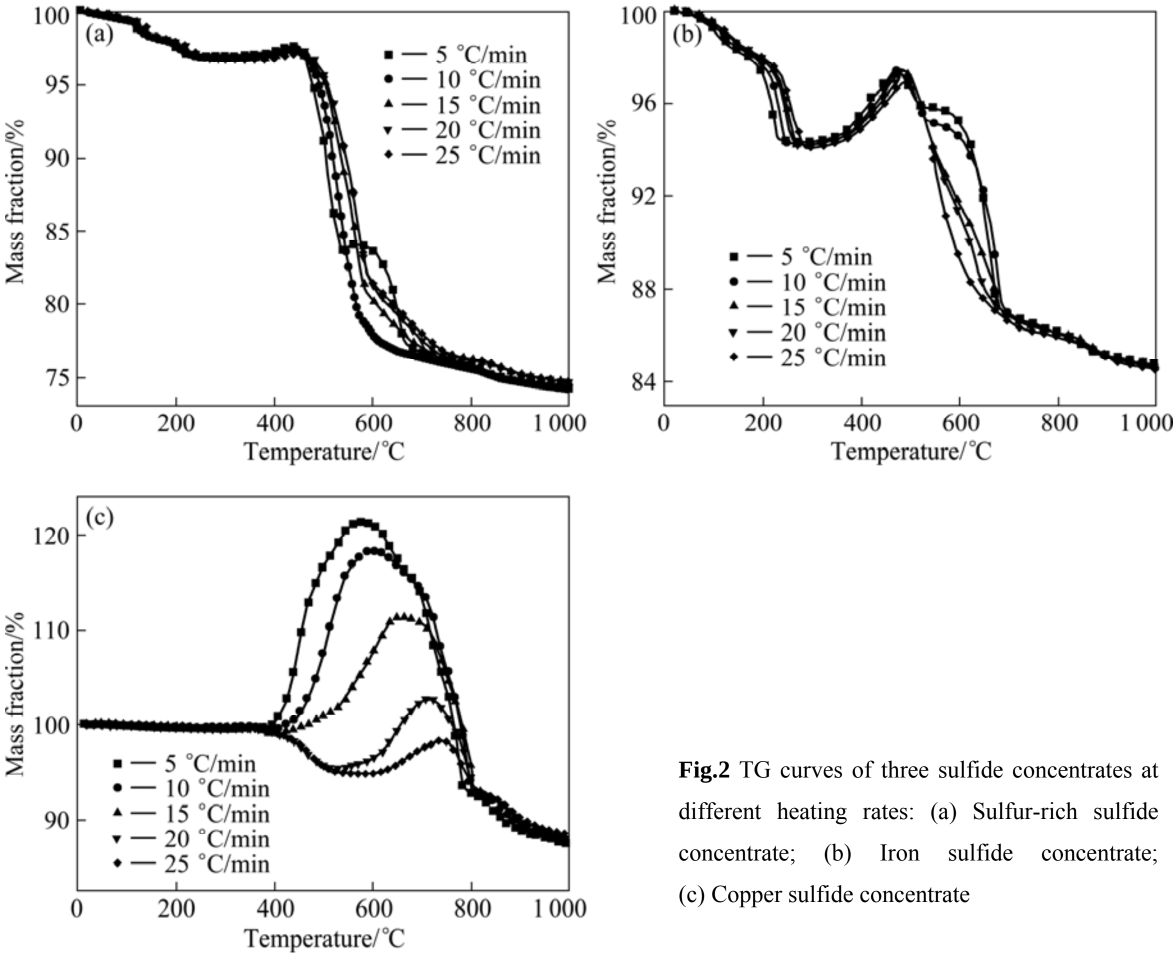

Fig.2 TG curves of three sulfide concentrates at different heating rates: (a) Sulfur-rich sulfide concentrate; (b) Iron sulfide concentrate; (c) Copper sulfide concentrate

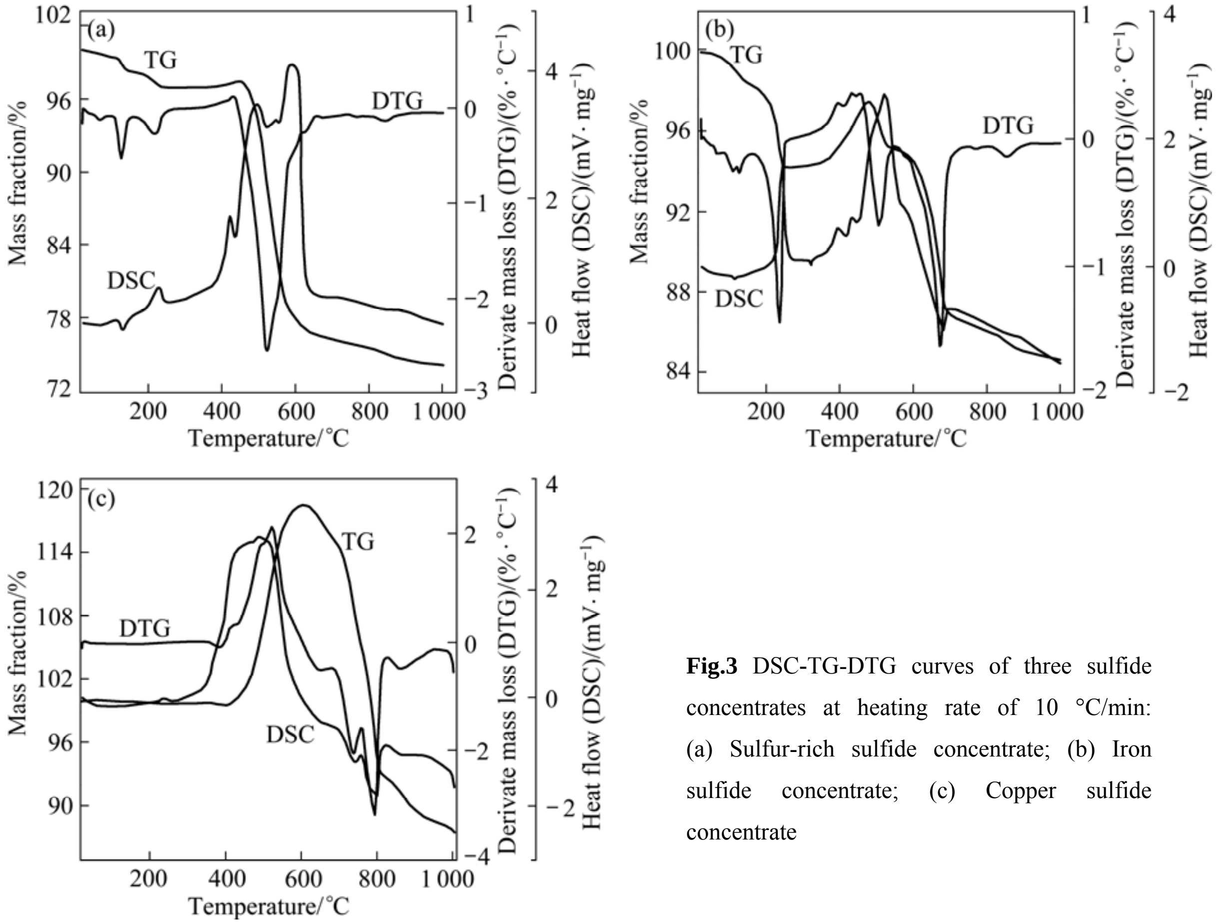

Fig.3 DSC-TG-DTG curves of three sulfide concentrates at heating rate of 10 °C/min: (a) Sulfur-rich sulfide concentrate; (b) Iron sulfide concentrate; (c) Copper sulfide concentrate

Table 2 DTG results for peak temperatures T_m in different reaction stages at various heating rates

Sulfide concentrate type	Reaction stage	Peak temperature/°C				
		5 °C/min	10 °C/min	15 °C/min	20 °C/min	25 °C/min
Sulfur-rich sulfide concentrate	1	118.216	127.695	138.285	142.005	143.302
	2	197.466	219.745	232.535	239.755	242.052
	3	513.466	523.125	563.535	567.755	569.302
Iron sulfide concentrate	1	118.851	128.037	137.637	140.636	146.439
	2	225.351	238.037	242.637	250.386	256.689
	3	413.601	458.537	457.887	462.136	465.689
	4	502.851	507.787	524.137	520.636	548.439
Copper sulfide concentrate	1	104.281	113.495	118.799	123.980	127.532
	2	190.504	198.495	209.299	225.230	227.199
	3	447.031	521.495	607.799	653.48	673.29
	4	725.281	737.745	744.299	790.04	797.23

corresponding reactions are readily detected as an exothermic peak in the DSC curve (Fig.3). The conversion of sulfide to oxide produces a mass loss coincident with the exothermic event. Formation of sulfate can take place by direct oxidation of the sulfide and sulfation of the oxide with sulfur trioxide. The formation of sulfate is also an exothermic process, but the reaction is relatively slow and takes place over a wide range of temperature, so there are the broad exothermic peaks in Figs.3(a) and (c).

For sulfur-rich sulfide concentrates, pyrite and pyrrhotite are two main sulfide minerals. The moisture of the samples is lost in a temperature range of 100−150 °C, indicated by a mild loss of mass on the TG curve. At about 520 °C dissociation of pyrite begins, indicated by a loss of mass on the TG curve. A sharp DTG peak shows a fast process. Because this stage takes place in an oxidative atmosphere, sulfur released during dissociation of pyrite is oxidized to SO_2. Oxidation of FeS to Fe_2O_3 is also taking place. A summary of these reactions are as follows[14−15]:

$$FeS_2=FeS+S_0 \tag{2}$$

$$S_2+2O_2=2SO_2 \tag{3}$$

$$4FeS+7O_2=2Fe_2O_3+4SO_2 \tag{4}$$

For iron sulfide concentrate, magnetite, pyrrhotite, and pyrite are three primary minerals. As is shown in Fig.3(b), the oxidation reaction of magnetite mineral particles is also highly exothermic, indicated by a mass gain on the TG curve. The corresponding reaction equation is written as follows[16]:

$$4Fe_3O_4+O_2=6Fe_2O_3 \tag{5}$$

For copper sulfide concentrates, it can form a protective layer on the surface during oxidation at low heating rates, and access to unreacted surface is greatly hindered and oxidation slows greatly[17]. Under high heating rates, the first exothermic effect on the DSC curve occurs with a loss of mass on the TG curve at about 470 °C. This indicates that during the dissociation, chalcopyrite releases elemental sulphur which is oxidized to SO_2. At above 500 °C the oxidation of Cu_2S starts, formed by dissociation of chalcopyrite, giving copper sulphates, which corresponds to further increase in mass on the TG curve. A summary of these reaction processes are as follows[18]:

$$2CuFeS_2+O_2=Cu_2S+2FeS+SO_2 \tag{6}$$

$$Cu_2S+SO_2+3O_2=2CuSO_4 \tag{7}$$

$$2Cu_2S+5O_2=2(CuO\cdot CuSO_4) \tag{8}$$

$$CuFeS_2+2O_2=CuS+FeSO_4 \tag{9}$$

$$CuS+2O_2=CuSO_4 \tag{10}$$

$$12FeSO_4+3O_2=4Fe_2(SO_4)_3+2Fe_2O_3 \tag{11}$$

3 Theoretical analysis

The methods used for analyzing the data obtained from temperature programmed experiments can be classified as differential and integral methods, and the two methods are classified further based on data acquired for one or more heating rates[13]. It is figured out that methods based on the experiments carried out under different heating rates give more reliable results than those based on data from a single heating rate, and that the integral methods are subjected to fewer experimental errors[19].

In this study, the way for determining the apparent activation energy has been performed by Ozawa-Flynn-Wall (OFW) method[13, 19−20], which is attributed to the integral methods. Ozawa has quantified the dependence between the maximum peak temperature and the heating rate in the following equation:

$$\lg\beta=-0.4567\frac{E}{RT_{\mathrm{m}}}+\lg\frac{AE}{RG(\alpha)}-2.315 \tag{12}$$

where β is the heating rate; T_{m} is the maximum peak temperature; E is the activation energy; R is the gas constant; A is the pre-exponential; and a is the conversion degree.

By plotting $\lg\beta$ versus $1/T_{\mathrm{m}}$, one can obtain E from the slope of the resulting straight line, regardless of the reaction order of the system. The validity of this equation is based on the assumption that the conversion at the peak maximum is constant for different heating rates[20].

4 Apparent activation energy of sulfide concentrates

In order to determine the kinetic parameters for the oxidation processes of sulfide concentrates in air, experimental results were treated according to Eq.(12). Fig.4 shows the dependencies of $\lg\beta$ versus $1/T_{\mathrm{m}}$, where T_{m} is the maximum temperature on the DTG curve. The linear regression to the experimental values is excellent. The apparent activation energy in different reaction stages can be obtained from the slope of the regression line. All the results are listed in Table 3. It can be found that the apparent activation energy values vary in different temperature ranges, with 36−160 kJ/mol; sulfur-rich sulfide and iron sulfide concentrates have lower apparent activation energy than copper sulfide concentrate below 150 °C.

Table 3 Apparent activation energy of sulfide concentrates for different reaction processes from ambient temperature to 800 °C

Sample type	$E/(\mathrm{kJ\cdot mol^{-1}})$			
	Reaction stage 1	Reaction stage 2	Reaction stage 3	Reaction stage 4
Sulfur-rich sulfide concentrate	75.761	65.885	116.542	−
Iron sulfide concentrate	75.165	109.529	106.189	160.900
Copper sulfide concentrate	82.888	69.949	35.988	149.339

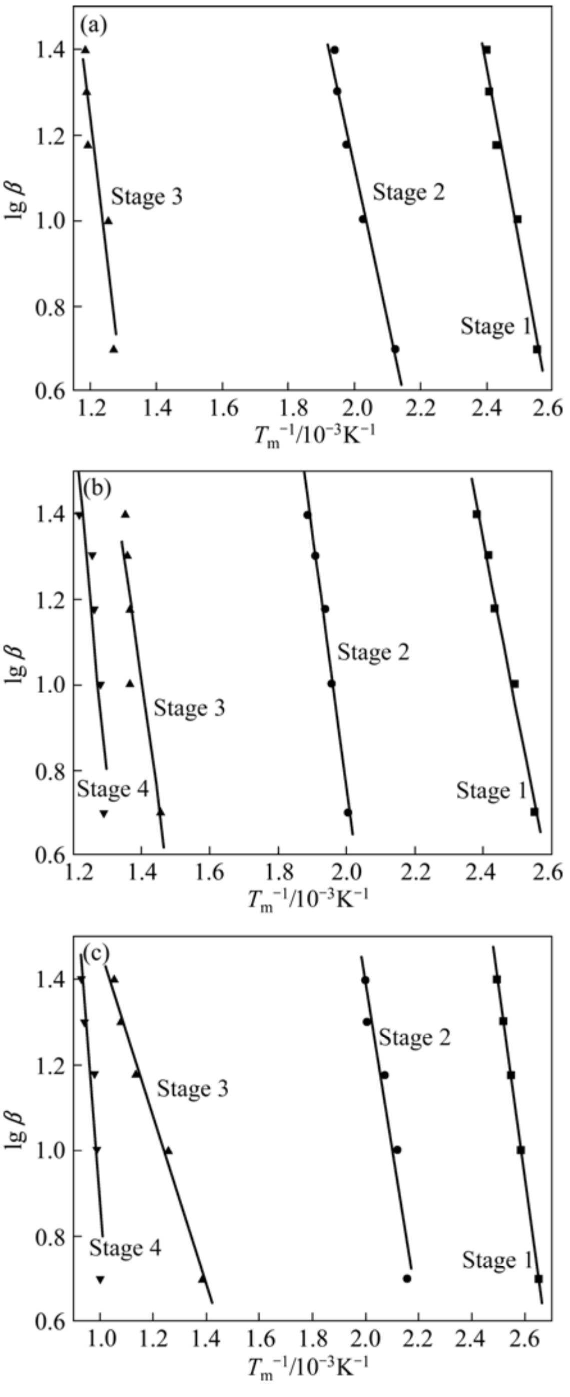

Fig.4 Arrhenius plots for DTG experiments: (a) Sulfur-rich sulfide concentrate; (b) Iron sulfide concentrate; (c) Copper sulfide concentrate

5 Conclusions

1) Three types of representative sulfide concentrates, including sulfur-rich sulfide concentrates, iron sulfide concentrates, and copper sulfide concentrate in a storage from a typical metal mine, were obtained. The chemical compositions and mineral phases of each sample are approved to be complex by XRD, SEM, and FTIR measurements.

2) According to the TG-DTG-DSC curves, the heating rate has a significant effect on the chemical reactions of each sample, influencing not only the amount of residues but also the DTG and DSC peak temperatures. By the Ozawa-Flynn-Wall method, the apparent activation energy values of each kind of sulfide concentrates were calculated. The results show that apparent activation energy of each sample varies in different thermal degradation temperature ranges, with 35−160 kJ/mol from ambient temperature to 800 °C.

3) Below 150 °C, sulfur-rich sulfide and iron sulfide concentrates have lower apparent activation energy value than copper sulfide concentrate, so they are more susceptible to oxidize than copper sulfide concentrate at ambient temperature, and may cause spontaneous combustion.

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矿仓硫精矿自燃的表观活化能

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摘 要：为了判定储存在矿仓内的硫精矿是否存在自燃危险性，从冬瓜山铜矿矿仓采集了不同类型的 3 种矿样(高硫精矿、硫铁精矿、硫铜精矿）。利用同步 TG-DTG-DSC 分析技术对 3 种矿样在升温速率分别为 5、10、15、20 和 25 °C/min 的条件下，在空气气氛中的化学反应过程进行深入研究。利用 DTG 曲线上的峰值温度，将每种矿样的反应过程划分为不同阶段，基于 Ozawa-Flynn-Wall 方法求得相应区间的表观活化能。结果表明：每种矿样的反应过程相当复杂，求得的表观活化能随着反应温度区间的不同而发生改变，从室温到 800 °C，3 种矿样在各个反应阶段的活化能为 36~160 kJ/mol；高硫精矿与硫铁精矿在 150 °C 以下的表观活化能较铜精矿的低，因此在室温条件下高硫精矿与硫铁精矿更容易引发自燃。

关键词：表观活化能；硫精矿；自燃；热重分析；差示扫描量热法

(Edited by YANG Hua)