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RESEARCH OF THERMAL DECOMPOSITION KINETIC CHARACTERISTIC OF EMULSION EXPLOSIVE BASE CONTAINING Fe AND Mn ELEMENTS

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The kinetic characteristic of thermal decomposition of the Emulsion Explosive Base Containing Fe and Mn elements (EEBCFM) which was used to prepare nano-$MnFe_2O_4$ particles via detonation method was investigated by means of non-isothermal DSC and TG methods at various heating rates of 2.5, 5 and 7.5°C min^{-1} respectively under the atmosphere of dynamic air from room temperature to 400°C.

The results indicated that the EEBCFM was sensitive to temperature, especially to heating rate and could decompose at the temperature up to 60°C. The maximum speed of decomposition $(d\alpha/dT)_m$ at the heating rate of 5 and 7.5°C min^{-1} was more than 10 times of that at 2.5°C min^{-1} and nearly 10 times of that of the second-category coal mine permitted commercial emulsion explosive (SCPCEE). The plenty of metal ions could seriously reduce the thermal stability of emulsion explosive, and the decomposition reaction in the conversion degree range of 0.0~0.6 was most probably controlled by nucleation and growth mechanism and the mechanism function could be described with Avrami–Erofeev equation with $n=2$. When the fractional extent of reaction $\alpha>0.6$, the combustion of oil phase primarily controlled the decomposition reaction.

Keywords: *activation energy, emulsion explosive, Fe, kinetic, mechanism function, Mn, thermal decomposition*

Introduction

Nano-oxide powders preparation by detonation of emulsion explosive method (DEE) was a brand-new application for emulsion explosive besides the application in engineering blasting and few reports related to this research were found. By adding some target-elements such as Fe, Mn, Zn, Li in emulsion explosive, nano-Li_2ZnO_2 [1], $LiMn_2O_4$ [2] and $MnFe_2O_4$ functional powders were successfully synthesized by DEE method and the components of the detonation soot and morphology of particles could be effectively controlled via the adjustment of detonation parameters such as oxygen balance value or simple post-thermal treatment. This made DEE method have great and wide applying outlook and value at the aspect of preparing nano-oxide powders. Emulsion explosive for synthesis of nano-oxide powders, as a kind of special explosive, should possess not only high detonation performance but also fine physical and chemical stability, which was also considerably important in industrial production and application. However, in order to ensure the productivity of nano-oxide powders, metal ions concentration would be necessarily contained in as high as possible, but the high concentration of metal ions might seriously reduce the physical and chemical stability of the emulsion explosive. How to characterize and improve its stability thus became a subject in front of us. In case of energetic materials such as explosives, their chemical stability mainly means their thermal stability, and an effective and direct method to study it is the thermal analysis kinetics method. In the present paper, the thermal decomposition kinetic characteristic of the Emulsion Explosive Base Containing Fe and Mn elements (EEBCFM), which was used to prepare nano-$MnFe_2O_4$ powders by detonation method, was investigated by means of non-isothermal DSC and TG at various heating rates. And the results were compared with that of the second-category coal mine permitted commercial emulsion explosive (SCPCEE).

Experimental

Instrumental and testing methods

The samples were heated by DSC (METTLER TOLEDO DSC 822^e) and TG (METTLER TOLEDO TGA/SDTA 851^e) with uncovered alumina crucible at the heating rates of 2.5, 5 and 7.5°C min^{-1} respectively from room temperature (25~30°C) to 400°C under the

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atmosphere of dynamic air with flow rate of 50 mL min^{-1} for DSC and 120 mL min^{-1} for TG respectively. And the mass of the samples were 15.7 mg (2.5°C min^{-1}), 14.7 mg (5°C min^{-1}) and 24.3 mg (7.5°C min^{-1}) for DSC experiments and 55.4770 mg (2.5°C min^{-1}), 61.6230 mg (5°C min^{-1}) and 64.8060 mg (7.5°C min^{-1}) for TG experiments, respectively.

Thermal decomposition of the EEBCFM

Characteristic of thermal decomposition of the EEBCFM

The main ingredients of the EEBCFM were listed in Table 1 and the DSC and TG curves at various heating rates of 2.5, 5 and 7.5°C min^{-1} were shown in Figs 1, 2 and 3, respectively. while the Fig. 4 showed the DSC and TG curves of the SCPCEE at the heating rate of 5°C min^{-1} under the atmosphere of dynamic nitrogen [3].

From the DSC and TG curves shown in the Figs 1, 2 and 3, similar to the decomposition of the SCPCEE shown in Fig. 4, an intensive exothermic peak, as marked in the DSC curves as peak 5, could always be observed due to the oxidization and combustion of the oil phase when the temperature was higher than 200°C or the fractional extent of reaction (α) of the EEBCFM was larger than 0.6. The EEBCFM heated at various heating rates could decompose at very low temperature (<60°C, the temperature at which the TG curves offsetting the baseline) without the step of water-loss observed during the decomposition of the SCPCEE. Melting and decomposing of AN (Ammonium Nitrate, as marked as peak 3), followed by the decomposition of the ferrite nitrate (as marked as peak 2) and the manganese nitrate (as marked as peak 4) made the speed of decomposition reaction (dα/dT) of the EEBCFM dramatically enhanced, that was proved by the value of dα/dT of the EEBCFM reaching the maximum at the temperature adjacent to the decomposition of AN (about 170°C). The (dα/dT)$_m$ (the maximum speed of decomposition reaction) of the EEBCFM at 5°C min^{-1} was more than 10 times of that at 2.5°C min^{-1} and nearly 10 times of that of the SCPCEE, respectively. But the temperature corresponding to (dα/dT)$_m$ of EEBCFM (168°C) was nearly 100°C lower than that of the SCPCEE (259°C), as was indicated in Table 2.

Table 1 The chart of main ingredients of the EEBCFM

Components	Chemical name	Chemical formula	Formula mass/g mol^{-1}	Heat of formation $\Delta_f H_m^\ominus$/kJ mol^{-1}
Main oxidants (>70% contents)	Ferrite nitrate	$Fe(NO_3)_3 \cdot 9H_2O$	404.0	365.6
	Manganese nitrate	$Mn(NO_3)_2 \cdot 6H_2O$	287.0	670.7
Auxiliary oxidant	Ammonium nitrate	NH_4NO_3	80.0	635.6
Solvent	Water	H_2O	18.0	285.8
Combustibles	Paraffin wax	$C_{18}H_{38}$	254.5	567.4
	Vaseline	$C_{18}H_{38}$	254.5	567.4
	Machine oil	$C_{12}H_{26}$	170.4	350.9
Emulsifier	SP-80	$C_{24}H_{44}O_6$	428.0	956.5*
Waterproofing agent	Stearinic acid	$C_{18}H_{36}O_2$	284.0	947.0

Specification: All of the data are from Lange Handbook of Chemistry; the value of Heat of Formation is obtained under 1 atm and 298.15 K; *the data was calculated with the equation: $Q_P=Q_V+\Delta(nRT)$, and only the constant-volume heat can we obtain. Other doping agents such as solubilizer are omitted in the chart

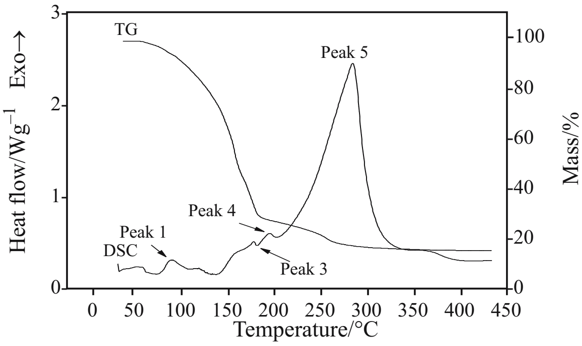

Fig. 1 DSC and TG curves at heating rate of 2.5°C min^{-1} of the EEBCFM

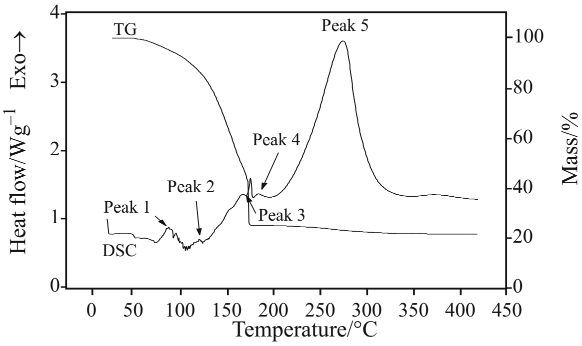

Fig. 2 DSC and TG curves at heating rate of 5°C min^{-1} of the EEBCFM

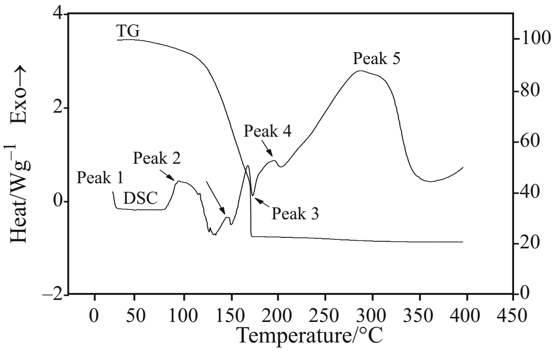

Fig. 3 DSC and TG curves at heating rate of 7.5°C min^{-1} of the EEBCFM

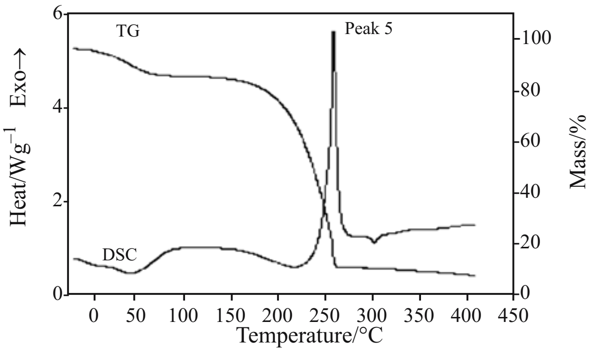

Fig. 4 DSC and TG curves at heating rate of 5°C min^{-1} of the SCPCEE [3]

Table 2 Thermal decomposition parameters of the EEBCFM and the SCPCEE

Samples	β/ °C min^{-1}	T_i/ °C	T_e/ °C	T_p/°C					(dα/dT)$_m$/ °C^{-1}	T_m/ °C	α_m
				Peak 1	Peak 2	Peak 3	Peak 4	Peak 5			
EEBCFM	2.5	46	49	79	/	165	177	261	0.01849	142	0.44
	5.0	51	50	87	118	165	178	264	0.21240	168	0.69
	7.5	53	75	97	148	175	197	289	0.23380	173	0.73
SCPCEE	5.0	10	10	/	/	/	/	261	0.02386	259	0.65

Specification: β is the heating rate (°C min^{-1}); T_i is the temperature of initial decomposition (°C, obtained from TG curves); T_e is the temperature of DSC curves offsetting baseline (°C); T_p is the temperature of characteristic peak (°C); $(d\alpha/dT)_m$ is the maximum speed of decomposition reaction (°C^{-1}), and T_m and α_m are the corresponding temperature and fractional extent of reaction to $(d\alpha/dT)_m$ respectively

Table 3 Raw data of T and α at various heating rates of the EEBCFM

β/°C min^{-1}	T/K					
	α=0.1	α=0.2	α=0.3	α=0.4	α=0.5	α=0.6
2.5	367.314	389.376	403.766	412.710	419.067	429.450
5.0	380.233	401.483	412.946	421.855	430.233	439.573
7.5	395.775	410.257	420.013	428.400	436.812	445.328

The decomposition peak of the ferrite nitrate (peak 2) was hardly observed at low heating rate (2.5°C min^{-1}) but could be distinctly distinguished at higher heating rate (5 and 7.5°C min^{-1}). It seemed to be comprehended that the ferrite nitrate decomposed so slowly at lower heating rate that it was not easily distinguished on DSC curves but quickly decomposed at higher heating rates.

The endothermic peaks lower or higher than 100°C in Figs 1, 2 and 3 was possibly caused by evaporation of water. However, what peak 1, the exothermic peak at around 80°C mean, was not completely explicit now and needed further study. All the thermal decomposition information obtained from above curves was listed in Table 2.

Kinetic mechanism of thermal decomposition of the EEBCFM

When α was larger than 0.6, as analysized above and shown in DSC curves, the decomposition reaction of the EEBCFM was primarily controlled by the combustion of oil phase. Here, the kinetic regularity of thermal decomposition of the EEBCFM was investigated only during the conversion degree range of 0.0~0.6.

Table 3 listed the raw data of temperature (T) and the fractional extent of reaction (α) at various heating rates.

The raw data listed in Table 3 were substituted into the Ozawa equation [4] (in the conversion degree of 0.3~0.6),

$$\lg\beta_i = \lg\frac{AE}{G(\alpha_{ij})R} - 2.315 - 0.4567\frac{E}{RT_i}$$

Table 4 Kinetic parameters of the EEBCFM and the SCPCEE calculated with the Ozawa method

Samples	Parameters	α=0.3	α=0.4	α=0.5	α=0.6
EEBCFM	E/kJ mol^{-1}	91.17	98.34	89.47	104.32
	r	0.9980	0.9990	0.9999	0.9999
	Q	0.02183	0.01512	0.003054	0.005149
SCPCEE [3]	E/kJ mol^{-1}	119.12	121.99	124.39	127.90
	r	0.9983	0.9990	0.9993	0.9991
	Q	0.027	0.021	0.018	0.018

and the Šatava–Šesták equation [5],

$$\lg G(\alpha_{ij})=\lg\frac{AE}{\beta_i R}-2.315-0.4567\frac{E}{RT_{ij}}$$

and the Universal Integral equation [6] for the dynamics calculation respectively.

$$G(\alpha_{ij})=\frac{A}{\beta_i}(T_{ij}-T_{0i})e^{-\frac{E}{RT_{ij}}}$$

where, i=1, 2, 3; j=1, 2, …, 6; $G(\alpha_{ij})$ is the mechanism function; A is the preexponential factor, s^{-1}; E is the apparent activation energy, kJ mol^{-1}; R is the universal gas constant, R=8.314 J mol^{-1} K^{-1} and T_{0i} is the initial temperature at which TG curves offsetting the baseline, K; r and Q are the correlation coefficient and the residual variance respectively.

The results obtained from the Ozawa method were listed in Table 4 and the results obtained from Šatava–Šesták method and the Universal Integral method were listed in Table 5 respectively.

Calculation results with the Ozawa method indicated that the value of apparent activation energy (E) of the EEBCFM had no large-range fluctuation (89.47~104.32 kJ mol^{-1}) within the conversion degree range of 0.3~0.6 and the average value of apparent activation energy was 95.83 kJ mol^{-1} which was much smaller than that of the SCPCEE, 123.35 kJ mol^{-1} (both calculated from the data in Table 4). This indicated that the EEBCFM was more thermal unstable than the SCPCEE to a certain extent. Logical choice method indicated that, as shown in Table 5, parameters of three probable mechanism functions obtained from the Šatava–Šesták method were consonant with

Table 5 Kinetic parameters calculated with the Šatava–Šesták method and the Universal Integral Method of the EEBCFM

Method	β/°C min^{-1}	$G(\alpha)$	E/kJ mol^{-1}	r	Q	lg$A$
Šatava–Šesták method	2.5	①	82.81	0.9978	0.04873	7.3434
		②	93.23	0.9954	0.07895	8.8494
		③	87.89	0.9967	0.06254	9.0309
	5	①	92.37	0.9990	0.03243	7.9674
		②	104.13	0.9979	0.0533	9.6130
		③	98.10	0.9986	0.04062	9.7227
	7.5	①	115.06	0.9972	0.0542	10.3956
		②	130.12	0.9993	0.03025	12.4381
		③	122.39	0.9985	0.04278	12.3436
Universal integral method	2.5	①	69.55	0.9952	0.1315	3.8578
		②	191.79	0.8848	1.9352	22.1988
		③	121.09	0.9948	0.2371	11.1400
	5	①	80.19	0.9981	0.08564	5.2330
		②	215.01	0.8759	2.0360	24.7661
		③	86.21	0.9973	0.1090	7.0149
	7.5	①	105.01	0.9969	0.1148	8.2411
		②	259.25	0.8277	2.4225	29.8440
		③	112.72	0.9984	0.08874	10.2159

①: $G(\alpha)=[1-(1-\alpha)^{\frac{1}{3}}]^2$, Jander equation, three-dimension diffusion, 3D, n=2, spherical symmetry;
②: $G(\alpha)=[(1-\alpha)^{-\frac{1}{3}}-1]^2$, Z–L–T equation, three-dimension diffusion, 3D;
③: $G(\alpha)=[-\ln(1-\alpha)]^2$, Avrami–Erofeev equation, nucleation and growth, n=2

those of the Ozawa method. That is to say, the thermal decomposition reaction of the EEBCFM in the conversion degree range of 0.0~0.6 would be probably controlled by three-dimension diffusion mechanism or nucleation and growth mechanism. And Jander equation (①) Z–L–T equation (②) or Avrami–Erofeev equation (③) might possibly describe the reaction mechanism. However, for a special decomposition reaction, if it was controlled by one deterministic mechanism, the kinetic parameters calculated from one reasonable method should approximately equal to another reasonable method [7, 8]. The Universal Integral equation was then employed in order to determine the mechanism function of the decomposition of the EEBCFM, and the results were also listed in Table 5, which indicated that, however, the Z–L–T equation could not reasonably characterize the reaction mechanism of decomposition of the EEBCFM while the results of the other two were well conformed to that of the Šatava–Šesták method. All data synthetically considered, one could infer that the decomposition reaction of the EEBCFM in the conversion degree range of 0.0~0.6 was most probably controlled by nucleation and growth, and the mechanism function was Avrami–Erofeev equation with n=2. The kinetic equation could be expressed as follows (the Šatava–Šesták method, at the heating rate of 5°C min^{-1}):

$$\frac{d\alpha}{dT}=3.168\cdot10^{10}\,e^{-\frac{1.180\cdot10^{4}}{T}}(1-\alpha)[-\ln(1-\alpha)]^{-1}$$

The less probably mechanism was three-dimension spherical symmetry diffusion, 3D, and the mechanism function was Jander equation with n=2. The kinetic equation could be expressed as follows (the Šatava–Šesták method, at the heating rate of 5°C min^{-1}):

$$\frac{d\alpha}{dT}=1.670\cdot10^{9}\,e^{-\frac{1.111\cdot10^{4}}{T}}(1-\alpha)^{\frac{2}{3}}[1-(1-\alpha)^{\frac{1}{3}}]^{-1}$$

Results and discussion

The EEBCFM was a homogeneous dispersed system of multi-components which was bound to very sophisticated for its thermal decomposition. For example, what caused the exothermic peak appearing at around 80°C, the similar heat-releasing phenomena occurred too in our past experiments of preparing the EEBCFM, was not completely understood at present time. The reference [9] indicated that at about 80°C, when Fe^{3+} was dissolved in the oxidizing solution such as ClO^{-}, the following transitions would occur:

$$Fe^{3+}\leftrightarrow Fe^{4+}\leftrightarrow Fe^{6+}$$

However, whether these transitions would occur or not in the emulsion needed further study and verification. We presumed that the oxidation of the '–OH' of SP-80 or the oil by Fe^{3+} maybe another reason resulting in the heat-releasing. And that whether the nucleation and growth mechanism or three-dimension diffusion mechanism was more conformed to real decomposition reaction on earth was also required confirming by other means. The ferrite nitrate, with its strong oxidizing property, was very sensitive to temperature, especially to heating rate; this made the EEBCFM very unstable and unsafe. Its thermal decomposition, or together with the coactions with other ions, could rapidly enhance the speed of decomposition reaction of the explosive, which could even result in the explosion-type chain reactions if it was heated under bad heat-dissipation surroundings. A lesson had already taught us that explosion accidents would happen in the experiments when the base containing ferrite nitrates was prepared in a closed vessel. Fortunately, the EEBCFM was not sensitive to detonator without sensitizing agent, but as far as the safety was concerned, the factors such as temperature, pressure and surroundings should all be carefully considered in the experiments of preparing these explosives.

In addition, the kinetic data obtained from this research were also valuable for commercial explosive production because of that metal ions such as Fe^{3+} might possibly be mixed in during the production of commercial explosives, which might be one of the important reasons causing catastrophic explosion accidents.

Conclusions

Research indicated that the EEBCFM was very sensitive to temperature, especially to the heating rate and could decompose at about 50°C. The decomposition speed of the EEBCFM reached the maximum value at the temperature nearly 100°C lower than that of the SCPCEE, and the $(d\alpha/dT)_m$ at the heating rate of 5°C min^{-1} of the EEBCFM was more than 10 times of that at 2.5°C min^{-1} and about 10 times of that of the SCPCEE at 5°C min^{-1}, respectively.

The facts that the average value of apparent activation energy of the EEBCFM, 95.83 kJ mol^{-1}, was much smaller than that of the SCPCEE, 123.35 kJ mol^{-1} and that the maximum decomposition reaction speed of the EEBCFM was nearly 10 times of that of the SCPCEE and the corresponding temperature was nearly 100°C lower than that of the SCPCEE indicated that plenty of metal ions could seriously reduce the thermal stability of emulsion explosive.

The decomposition reaction in the conversion degree range of 0.0~0.6 was most probably controlled by nucleation and growth mechanism, and less probably controlled by three-dimension diffusion. When the fractional extent of reaction α>0.6 (or the temperature was higher than 200°C), the combustion of oil phase primarily controlled the decomposition reaction.

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