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Thermal Compatibility Between Magnetite Nanoparticles and Explosives in Common Use

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Abstract: The magnetite particles (Fe_3O_4) were successfully prepared by an oxidation-precipitation method. XRD technique was used to characterize the size of the sample. It indicates that the average size of particles in diameter is about 50 nm with a narrow size distribution. To explore the new application of magnetite nanoparticles, thermal compatibility between magnetite nanoparticles and explosives in common use including potassium perchlorate (PP), 2,2′, 4,4′,6,6′-hexanitrostilbene(HNS), hexadydro-1,3,5-trinitro-1,3,5-triazine (HMX) and 3,5-dinitro-2, 6-dipicrylaminopyridine (PYX) was determined by DSC technique. The results show that Fe_3O_4 powders with 50 nm in diameter have fair compatibility with PP or PYX,but poor compatibility with HNS and bad compatibility with HMX.

Key words: physical chemistry; magnetite; nanoparticle; explosive; compatibility

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1 Introduction

Magnetite nanoparticle (Fe_3O_4) is an important material, which has been widely used in pigment, activator, magnetic fluids, and magnetic record materials etc[1,2]; therefore, the studies on it always attract a lot of attention[3-8]. By using an oxidation-precipitation method, magnetite particles were successfully synthesized in our work. Since current studies on applications of magnetite nanoparticles are mainly focused on use for pigment, activator, magnetic fluids, and magnetic record materials etc, especially for drug delivery[1,2]. A little report can be seen on application of magnetite nanoparticles in energetic materials that is of important significance in military affairs and daily use.

Energetic materials such as PP, HNS, HMX and PYX are the main explosives of warheads and the energetic component system of composite propellants. They have occupied a key position in the field of explosives and propellant[9]. The thermal compatibility of those explosives and other materials is very concerned, because it touches the safety of those explosives in use and stock. The determination of thermal compatibility is clearly complicated, and there are many factors that influence the results of thermo analytical determinations. The objective of this work is to prepare magnetite nanoparticles and study their application in energetic materials. We determined the compatibility between magnetite nanoparticles and typical explosives including PP, HNS, HMX and PYX by differential scanning calorimeter (DSC). DSC is usually employed to determine thermal compatibility, which gives information about thermal stability, melting, decomposition, etc[10]. DSC technique has the advantage of using a small amount of sample, quickly, and frequently yield sufficient information for the accurate determination of kinetic parameters for the reaction[9]. In fact, any reaction or transformation involving absorption or release of heat can be detected with this technique.

2 Experimental

2.1 Materials

Iron sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), ammonia ($NH_3 \cdot H_2O$) and sodium nitrate ($NaNO_3$) used in this work were analytical reagent grade commercially available. Water was deionized with a resistance larger than 18 Ω. Glassware was cleaned with concentrated HCl, rinsed thoroughly with deionized water, and dried before use.

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PP, HNS, HMX and PYX were the raw materials used in this work and were used without further purification.

2.2 Preparation of magnetite nanoparticles

After the predetermined solution of iron sulfate heptahydrate was precipitated to form $Fe(OH)_2$ by the suitable concentration ammonia solution, the magnetite (Fe_3O_4) began to come into being when $Fe(OH)_2$ sol was pro rata oxidized to $Fe(OH)_3$ and the ratio of $Fe(OH)_2$ and $Fe(OH)_3$ was exactly 1 : 2. The method will be stated particularly in another paper.

2.3 Characterization of magnetite sample prepared

The structure of the magnetite sample prepared was characterized by X-ray powder diffraction, which was carried out on a Rigaku D/max-2500 (Japan) diffractometer using the Ka line of Cu as a radiation source. X-ray diffraction pattern was also used in the calculation of particle size.

2.4 Compatibility between magnetite nanoparticles and energetic materials

A differential scanning calorimeter (CDR-1, made in Shanghai) was used to determine the compatibility between magnetite nanoparticles and above explosives. The instrument was calibrated with standard samples of indium, zinc according to the manufacturer procedure, and α-Al_2O_3 was used as standard reference substance. The sample weight of the explosives varied from 1 mg to 5 mg. Binary mixture system ratios of magnetite nanoparticles and explosives were 1 : 1, and were mixed homogeneously in an agate mortar. To get the exact results, heating rates of 2, 5, 10 and 20 ℃ · min^{-1} were run in DSC under static atmosphere, and unsealed aluminum crucibles were utilized for experiments.

2.5 Kinetic studies of reactions

The activation energies of degradation reaction for the single component systems and binary mixture systems were determined by Ozawa's method[11]:

$$\lg \beta = -0.4567 \frac{E_a}{RT} + \lg \frac{AE_a}{R} - \lg F(\chi) - 2.315 \quad (1)$$

where β denotes the heating rate; E_a and T represents the activation energy of degradation reaction and the temperature of the exothermic peak, respectively; R is the ideal gas constant and $F(\chi)$ denotes the conversion dependent term.

This method provides an easy method of calculating the activation energy.

3 Results and discussion

3.1 Characterizations of magnetite nanoparticles

XRD pattern of the sample prepared by above method was shown in Fig. 1. The characteristic peaks at 2θ angles correspond very well to the standard card of magnetite (JCPDS: 19-0629), which proves that the sample can be identified as magnetite with the spinel structure.

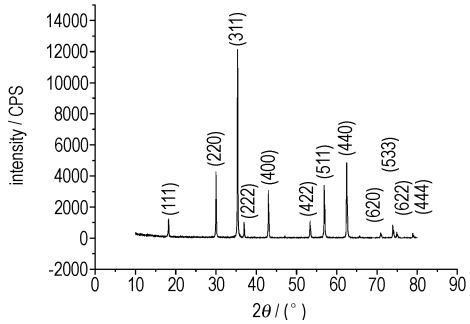

Fig. 1 The X-ray diffraction pattern of the magnetite sample

The mean diameter of magnetite particles calculated from the relevant XRD pattern (Fig. 1) by equation of $d = K\lambda/\beta\cos\theta$ increases from 32 nm to 80 nm. The mean particle diameter is about 50nm or less.

3.2 Compatibility

In this work the DSC technique was employed to determine the thermal compatibility between the above explosives and magnetite nanoparticles. The compatibility of Fe_3O_4 with PP, HNS, HMX and PYX, respectively, was investigated by comparison of the thermal behaviors between the explosives and magnetite nanoparticles. In order to detect any interaction between the ingredients, the temperature was run from 50 ℃ to 550 ℃.

3.2.1 Original data of the tests

Peak temperatures of exothermic peaks for single component systems and the binary mixture systems were listed in Table 1. The peak temperatures of PP and PP/Fe_3O_4 are the peak temperatures of melting peaks, which is due to that there are not degradation reaction of PP and PP/ Fe_3O_4 in the range of temperatures from 50 ℃ to 550 ℃, and the peak temperatures of PYX and PP/Fe_3O_4 are the peak temperatures of the first degradation, for there are three degradation reaction peaks of PP and PYX + Fe_3O_4 in the range of temperatures from 50 ℃ to 550 ℃, respectively. As can be seen

from Table 1, the peak temperatures of binary mixture system become lower than those of the relevant single component systems, which states that magnetite nanoparticles have acceleration on the degradation of the above four explosives.

Table 1　Peak temperatures for single component systems and the binary mixture systems

β_i/℃ · min^{-1}	2	5	10	20
PP	297.9	299.9	301.0	301.3
HNS	328.2	339.7	349.9	361.0
HMX	276.8	281.4	284.2	288.1
PYX	339.4	346.9	359.5	370.6
PP + Fe_3O_4	296.9	299.2	300.2	302.4
HNS + Fe_3O_4	322.4	331.7	342.5	355.3
HMX + Fe_3O_4	261.3	271.2	274.2	282.1
PYX + Fe_3O_4	327.7	346.1	356.6	368.0

3.2.2　Values of activation energy

Activation energies for the single component systems and the binary mixture systems obtained by Ozawa′s method, i.e. Equation (1) are listed in Table 2.

Thus the compatibility between the above four explosives and magnetite nanoparticles can be evaluated by employing the data in Tables 1 and 2.

Table 2　Activation energies for single component systems and binary mixture systems

sample	E/kJ · mol^{-1}	$-r$	standard deviation
PP	1601	0.9662	0.0135
HNS	211.5	0.9991	0.0023
HMX	503.9	0.9986	0.0274
PYX	219.9	0.9875	0.0823
PP + Fe_3O_4	1110	0.9925	0.0642
HNS + Fe_3O_4	203.9	0.9923	0.0646
HMX + Fe_3O_4	265.2	0.9888	0.0782
PYX + Fe_3O_4	174.1	0.9966	0.0433

Note: r, linear correlation coefficient.

3.2.3　Determination of compatibility between the explosives and magnetite nanoparticles

The compatibility between the four explosives and magnetite nanoparticles was determined according as GJB772A-97 method 502.1[12]. The standards of the method is as follows:

Good compatibility, i.e. grade 1, if $\Delta T_p \leqslant 2.0$ ℃, and $\Delta E/E_a \leqslant 20\%$;

Fair compatibility, i.e. grade 2, if $\Delta T_p \leqslant 2.0$ ℃, and $\Delta E/E_a > 20\%$;

Poor compatibility, i.e. grade 3, if $\Delta T_p > 2.0$ ℃, and $\Delta E/E_a \leqslant 20\%$;

Bad compatibility, i.e. grade 4, if $\Delta T_p > 2.0$ ℃, and $\Delta E/E_a > 20\%$ or $\Delta T_p > 5.0$℃;

ΔT_p and $\Delta E/E_a$ were calculated by following formulas (2) and (3), respectively.

$$\Delta T_p = T_{p,s} - T_{p,m} \tag{2}$$

ΔT_p denotes the peak temperature difference between the single component system and binary mixture system; $T_{p,s}$ denotes the peak temperature of single component system; $T_{p,m}$ denotes the peak temperature of binary mixture system.

$$\frac{\Delta E}{E_a} = \left|\frac{E_a - E_b}{E_a}\right| \times 100\% \tag{3}$$

$\Delta E/E_a$ denotes the parcentage change of activation energy between the single component system and binary mixture system; E_a denotes the activation energy of single component system; E_b denotes the activation energy of binary mixture system.

The percentage change of activation energies calculated by Equation (3), $\Delta E/E_a$ and peak temperature difference calculated by Equation (2) according to the peak temperatures with a heating rate of 5 ℃ · min^{-1}, i.e. ΔT_p are listed in Table 3.

Table 3　The compatibility between explosives and magnetite nanoparticles

samples	ΔT_p/℃	$\Delta E/E_a$/%	grade
PP + Fe_3O_4	0.7	30.67	2
HNS + Fe_3O_4	8.0	3.59	3
HMX + Fe_3O_4	10.2	47.37	4
PYX + Fe_3O_4	0.8	20.83	2

4　Conclusion

Tests show that magnetite nanoparticles (Fe_3O_4) of about 50 nm or less in diameter prepared by the oxidation-precipitation method, have fair compatibility with PP or PYX, poor compatibility with HNS and bad compatibility with HMX. At the same time, we can come to the conclusion that Fe_3O_4 has accaleration on the degradation of the above four explosives, which would establish basal data for further application.

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磁铁矿(Fe_3O_4)纳米粒子与常用爆炸物的热相容性研究

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摘要:利用氧化-沉淀法成功制备出了磁铁矿纳米粒子,经过 XRD 技术表征,磁铁矿纳米粒子的平均直径约为 50 nm,粒径分布狭窄。使用 DSC 技术研究了平均直径为 50 nm 的磁铁矿纳米粒子与常用的爆炸物高氯酸钾(PP),六硝基芪(HNS),奥克托今(HMX)和二苦氨基二硝基吡啶(PYX)的热相容性,得到有意义的结论。实验表明,50 nm 左右的磁铁矿纳米粒子与 PP 及 PYX 热相容,与 HNS 不相容,与 HMX 严重不相容。

关键词:物理化学;磁铁矿;纳米粒子;爆炸物;相容性

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Selectivity of Sub-micron Explosive Sensitivity to Shock Wave

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Abstract: The shock sensitivity of sub-micron explosive was studied by small-scale gap test and slapper initiation test; and the shock wave was low pressure-long pulse in the small-scale gap test,and high pressure-burst pulse in the slapper initiation test. The explosive is safe when motivated by a generic environmental force,i. e. low pressure-long pulse and it is sensitive when motivated by special environmental force,i. e. high pressure-burst pulse. Moreover, the shock sensitivity decreases with the reduction of explosive particle size when ignition is a dominant process in the course of shock wave initiation; but oppositely,the shock sensitivity increases when detonation buildup is dominant.

Key words: explosion mechanics; sub-micron explosive; shock sensitivity; high pressure-burst pulse; low pressure-long pulse; ignition; growth