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Thermal Compatibility between Magnetite Nanoparticles and Explosives in Common Use (Ⅱ)

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Abstract: To explore the new application of magnetite nanoparticles, thermal compatibility between magnetite nanoparticles and explosives in common use including hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX), cadmium three-carbohydrazide permanganate (GTG), potassium 4, 6-dinitro-7-hydroxyl-7-hydrobenzofuroxanate (KDNBF) and pentaerythritol tetra nitrate (PETN) was determined by DSC technique. The results show that Fe_3O_4 powders with 45 nm in diameter have fair compatibility with KDNBF, but poor compatibility with RDX and PETN, and bad compatibility with GTG.

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

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1 Introduction

Magnetite nanoparticle (Fe_3O_4) is an important material[1-8], however a few reports can be seen on application of magnetite nanoparticles in energetic materials that is of important significance in military affairs and civil purposes. And, RDX is one of widely used nitramine explosives and energetic ingredients of propellants [9]. GTG is a new kind of primary explosive. It has been safely used in various detonators [10]. KDNBF has been used in primary explosives and initiating compositions since the early 1950′s and given more attention recently for its low pollution on environment [11]. PETN is one of the most important high-energy explosives used widely in military and civil affairs [12]. They have occupied key positions in the field of explosives and propellants. 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 thermal compatibility between magnetite nanoparticles and PP, HMX, HNS and PYX has been determined in our agone work [13]. The objective of this work is to prepare magnetite nanoparticles again and study in series their application in some more energetic materials. We determined the compatibility between magnetite nanoparticles and typical explosives including RDX, GTG, KDNBF and PETN by differential scanning calorimeter (DSC).

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.

RDX and PETN were the raw materials used in this work and were used without further purification. GTG and KDNBF were synthesized in our lab and were purified many times before use.

2.2 Methods

The methods of preparing and characterizing magnetite nanoparticles, conducting compatibility experiments, and calculating activation energies of decomposition reactions were the same as those in Ref. [13].

3 Results and discussion

3.1 Characterizations of magnetite nanoparticles

XRD patterns of the three samples prepared by above method in different concentrations were shown in Fig. 1. All the characteristic peaks at 2θ angles correspond very

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well to the standard card of magnetite (JCPDS: 19-0629), which proves that the samples can be identified as magnetite with the spinel structure.

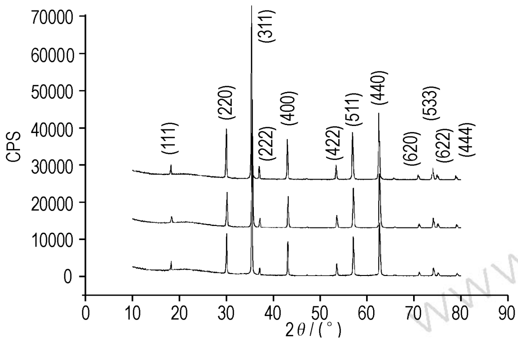

Fig. 1 The X-ray diffraction patterns of the magnetite sample

The mean diameter of magnetite particles calculated from the relevant XRD patterns (Fig. 1) by equation of $d = k\lambda/\beta\sin\theta$ increases from 30 to 78 nm. The mean particle diameter is about 45 nm 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 RDX, GTG, KDNBF and PETN, 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. All the peak temperatures of explosives and explosive/Fe_3O_4 are the peak temperatures of the first degradation. As can be seen from Table 1, the peak temperatures of binary mixture systems become lower than that of the relevant single component systems, which state that magnetite nanoparticles have acceleration on the degradation of the above four explosives.

3.2.2 Values of activation energy

Activation energies for the single component systems and the binary mixture systems were obtained from Ozawa's equation[14] using a calculation program of non-isothermal reaction kinetics of energetic materials programmed by LIU Zhi-xiong on the computer, and listed in Table 2.

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

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

β_i/ ℃ · min^{-1}	2	5	10	20
RDX	224.6	241.8	243.1	248.3
GTG	262.8	278.8	289	298.5
KDNBF	199.6	208.8	217.8	227.9
PETN	183.4	198.1	202.4	210.7
RDX + Fe_3O_4	216.0	228.2	235.6	245.5
GTG + Fe_3O_4	249.6	262.5	266.1	269
KDNBF + Fe_3O_4	200.1	207.6	217.9	219.3
PETN + Fe_3O_4	175.9	186.8	193.6	202.5

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

sample	E / kJ · mol^{-1}	r	standard deviation
RDX	182.2	0.9321	0.1895
GTG	155.3	0.9991	0.0041
KDNBF	151.6	0.9975	0.0037
PETN	147.5	0.9840	0.0093
RDX + Fe_3O_4	184.1	0.9990	0.0024
GTG + Fe_3O_4	245.0	0.9533	0.1580
KDNBF + Fe_3O_4	194.6	0.9721	0.1228
PETN + Fe_3O_4	147.8	0.9991	0.0022

Note: r, linear correlation coefficient.

3.2.3 Determination of compatibility between the explosives and magnetite nanoparticles

The compatibility between four explosives and magnetite nanoparticles was determined according to GJB772A - 97 method 502.1[15]. The standards of the method is as follows:

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

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

Poor incompatibility, i. e. grade 3, if $\Delta T_P > 2.0$ ℃, and $\Delta E/E_a \leq 20\%$;

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 formulas (1) and (2), respectively.

$$\Delta T_P = T_{P,S} - T_{P,m} \quad (1)$$

ΔT_P denotes the peak temperature difference between the single component system and binary mixture system; $T_{P,S}$ denotes the peak temperature of a single component system; $T_{P,m}$ denotes the peak temperature of a binary mixture system.

$$\frac{\Delta E}{E_a} = \left|\frac{E_a - E_b}{E_a}\right| \times 100\% \quad (2)$$

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

The percentage changes of activation energies calculated by Equation (2), i. e. $\Delta E/E_a$ and peak temperature differences calculated by Equation (1) 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 the explosives and magnetite nanoparticles

samples	ΔT_P/℃	$\Delta E/E_a$	grade
RDX + Fe_3O_4	13.6	1.04	3
GTG + Fe_3O_4	16.3	57.76	4
KDNBF + Fe_3O_4	1.2	28.36	2
PETN + Fe_3O_4	11.3	0.2	3

4　Conclusions

Tests show that magnetite nanoparticles (Fe_3O_4) of 45 nm or less in diameter prepared by the oxidation-precipitation method have fair compatibility with KDNBF, poor compatibility with RDX and PETN, and bad compatibility with GTG. At the same time, we can come to the conclusion that Fe_3O_4 has acceleration on the degradation of the above four explosives, especially on the degradation of RDX, GTG and PETN, 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(Ⅱ)

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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 45 nm,粒径分布狭窄。使用 DSC 技术研究了平均直径为 45 nm 的磁铁矿纳米粒子与常用的爆炸物黑索金(RDX),高氯酸三碳酰肼合镉(GTG),4,6-二硝基苯并氧化呋咱钾(KDNBF)和季戊四醇四硝酸酯(PETN)的热相容性。实验表明 45 nm 左右的磁铁矿纳米粒子与 KDNBF 热相容,与 RDX 及 PETN 不相容,与 GTG 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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