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用加速量热仪研究 PBX-HKF 的热稳定性

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摘要: 采用加速量热仪(ARC)研究了一种由HMX、苦味酸钾、增塑剂、粘结剂组成的新型PBX-HKF炸药的热稳定性,得到了塑性炸药样品在绝热条件下热分解温度和压力随时间的变化曲线以及自热速率、分解气体产物压力随温度的变化曲线,分析了在绝热条件下热分解反应动力学,计算了表观活化能 E_a 为337.32 kJ·mol^{-1},指前因子 A 为9.32E34 s^{-1}。结果表明所测试的PBX-HKF具有良好的热稳定性。

关键词: 物理化学; 加速量热仪; 塑性炸药; 热分解; 活化能
中图分类号: TJ55; TQ564 **文献标识码:** A

1 引 言

塑性粘结炸药一般由主体炸药、粘结剂、增塑剂组成。由于威力大,爆速高,可加工成任何形状粘附到任何干燥表面,而且处理特性良好、撞击感度低,塑性粘结炸药得到了广泛应用。鉴于其用途的广泛性和复杂性,要求塑性粘结炸药具有良好的安全性能,以保证在生产、运输和使用过程中的安全可靠性。

苦味酸钾一般用于延期药、点火药,作为塑性粘结炸药组分很少。目前,塑性粘结炸药的热分解及稳定性研究普遍采用差热分析(DTA)或差示扫描量热分析(DSC)。由于DTA和DSC方法所需要的样品量小、测试时间短;均采用程序升温的方式加热样品,所测得的物质热分解温度会因升温速率的不同而发生变化。因而这两种方法的物质热分解过程进行分析所得的动力学参数等都与实际生产应用、勤务处理相差较大。加速量热仪(ARC)是一种基于绝热原理设计的热分析仪器。可使用较大的样品量,热惰性较小,同时提供温度和压力数据。ARC已成为国际上评价物质热稳定性的常用测试方法之一,并逐步成为标准测试发展方向。

2 实 验

2.1 样 品

所测试的新型塑性粘结炸药PBX-HKF样品由炸药(奥克托今、苦味酸钾)、增塑剂、粘结剂组成。

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2.2 仪器及测试条件

所用仪器为美国哥伦比亚科学工业公司产品。ARC原理及结构的详细描述参见文献[1,2]。

将0.2653 g样品装到质量为6.5637 g的样品室中,测试起始温度设置为180 ℃,斜率敏感度0.02 ℃·min^{-1}。当样品反应系统(包括样品和样品室)温度达到180 ℃后,量热仪开始加热-等待-搜寻的循环操作过程,当样品室热电偶检测到反应系统的温升速率超过了斜率敏感度(0.02 ℃·min^{-1})时,反应系统将依靠反应放热加热自身,加速量热仪的数据采集系统自动记录整个绝热分解过程的温度和压力随时间的变化。所测样品量及测试条件如表1所示。

表1 样品质量及测试条件

Table 1 Mass of samples and measuring conditions

sample	HKF
sample mass/g	0.2653
sample chamber mass/g	6.5637
initial temperature/℃	180
rate of temperature rise/℃·min^{-1}	0.020

3 结果与讨论

在绝热条件下,PBX-HKF样品的加速量热仪测试数据及热分解特性参数的测试数据分别见表2、表3。

PBX-HKF样品在180 ℃时没有发生放热分解,经过数个加热-等待-搜寻的周期循环,由于热惰性存在,在182.52~202.91 ℃的温度范围内升温速率有一定幅度的波动,从202.91 ℃开始,反应系统放热,温升速率(大于系统设定的斜率敏感度0.020 ℃·min^{-1})持续增加,在系统温度达到226.06 ℃时,反应系统的

温度和压力都出现了陡升,在 0.02 min 内温度由 226.06 ℃上升到 264.74 ℃(对应的温升速率分别为 103.5 ℃·min^{-1}和 934 ℃·min^{-1}),压力由 146 MPa 增大到 576.7 MPa,反应系统在 264.74 ℃出现最大温升速率(934 ℃·min^{-1})。在 280.41~299.02 ℃ 和 301.95~346.06 ℃ 范围时,系统均出现放热,但放热速率不高。在 PBX-HKF 发生热分解过程中,系统测得最高温度值为 346.08 ℃,最大压力值为576.7 MPa。

根据绝热加速热量仪的温升速率方程:

$$m_T = \frac{dT}{dt} = \Delta T_{ad} k [\frac{T_f - T}{T_f - T_0}]^n$$

可知:$k = \dfrac{m_T}{\Delta T_{ad}[\dfrac{T_f - T}{\Delta T_{ad}}]^n}$

由 Arrhenius 方程可得:$\ln k = \ln A - \dfrac{E_a}{R}(\dfrac{1}{T})$

表 2 用 ARC 测试 PBX-HKF 炸药热分解数据

Table 2 The thermal decomposition data of PBX-HKF determined by ARC

time / min	temperature / ℃	pressure / MPa	self heating rate / ℃·min^{-1}
1257.89	202.91	67.1	0.047
1307.51	206.45	78.7	0.104
1358.95	217.55	120.3	0.583
1364.99	222.05	137.6	1.05
1366.37	223.99	146.0	1.573
1366.39	226.06	576.7	103.5
1366.41	264.74	545.9	934.0
1366.43	270.33	540.0	279.5
1366.45	273.54	537.8	160.5
1366.47	275.63	536.3	104.5
1366.49	276.92	535.1	64.5
1366.51	277.59	533.9	33.5
1433.75	280.37	481.3	0.054
1433.83	280.41	481.2	0.056
1458.67	281.79	469.1	0.059
1693.65	293.99	388.0	0.042
1735.91	296.12	377.0	0.059
1798.77	299.03	362.1	0.048
1799.05	299.02	362.1	0.044
1847.74	301.3	351.5	0.05
1860.74	301.92	348.8	0.054
1860.81	301.95	348.8	0.049
1861.81	301.99	348.6	0.05
2174.99	321.69	295.8	0.075
2312.57	331.78	274.2	0.075
2362.05	335.33	266.8	0.062
2444.31	341.23	254.9	0.064
2506.59	345.52	246.0	0.084
2517.30	346.06	244.4	0.749

表 3 PBX-HKF 炸药热分解特性参数测试结果

Table 3 The thermal decomposition characteristic data of PBX-HKF determined by ARC

M/g	0.2653	$T_{0,s}$/℃	202.91
$m_{0,s}$/℃·min^{-1}	2.652	$T_{f,s}$/℃	346.08
$\Delta T_{ad,s}$/℃	166.08	$m_{m,s}$/℃·min^{-1}	934
$\theta_{m_{0,s}}$/min	1366	$p_{m,s}$/MPa	576.7

note: M—sample mass;
$T_{0,s}$—initial self-heating temperature;
$m_{0,s}$—self-heating rate at $T_{0,s}$;
$T_{f,s}$—maximum temperature rise for reaction system;
$\Delta T_{ad,s}$—adiabatic temperature rise for reaction system;
$m_{m,s}$—maximum self heating rate for reaction system;
$\theta_{m_{0,s}}$—maximum self heating rate time for reaction system;
$p_{m,s}$—maximum pressure.

最大温升速率时间和温度曲线近似呈一直线关系,即 $\ln k \sim 1/T$ 为直线,由直线的斜率和截距可求活化能 E_a 和指前因子 A。求得 PBX-HKF 炸药分解的活化能 E_a 和指前因子 A 分别为 337.32 kJ·mol^{-1}和 9.32E34 s^{-1}。

4 结 论

(1)该炸药在经过一段缓慢的升温过程过渡阶段之后,发生迅速的分解反应,释放出反应热并生成大量的气体产物,反应系统温度和压力骤然大幅度增加。

(2)炸药在绝热条件下具有良好的热稳定性。其初始分解温度为 202.91 ℃,最高分解温度为 346.08 ℃,绝热分解时的活化能较高,为 337.32 kJ·mol^{-1}。该炸药具有良好的热稳定性,在生产过程和使用过程中是安全的。

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Recent Development on Crystal Transition Technology of Hexanitrohexaazaisowurtzitane

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Abstract: The development of crystal transition technology for HNIW in the last five years is reviewed, including the modified procedures in the laboratories and the industrial process for HNIW's crystal transitions. The solvents, non-solvents, modifiers and the detailed technological conditions for HNIW's crystal transition are all described. The effects of various technological parameters on crystal quality are discussed.

Key words: physical chemistry; hexanitrohexaazaisowurtzitane; crystal transition; explosive

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Study on Thermal Stability of PBX-HKF by Accelerating Rate Calorimeter

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Abstract: The thermal stability of a new plastic bonded explosive PBX-HKF composed of main explosives (HMX and potassium picrate), plasticizer and binder, has been studied by an accelerating rate calorimeter. The curves of thermal decomposition temperature and pressure versus time, self-heating rate and pressure versus temperature were obtained. According to adiabatic theory, the activation energy E_a = 337.32 kJ · mol^{-1} and pre-exponential factor 9.32E34 s^{-1} are obtained. The decomposition history and safety of PBX-HKF were analysed. It is indicated that the new plastic bonded explosive possesses very good.

Key words: physical chemistry; accelerating rate calorimeter (ARC); plastic bonded explosive; thermal decomposition; activation energy