

The DSC studies on the phase transition, decomposition and melting of potassium perchlorate with additives

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Abstract

It has been shown that the addition of metal oxide to potassium perchlorate gives rise to change in the thermochemical behavior of the potassium perchlorate. Some investigations on the particle sizes and materials were examined, and given data for choosing optimum weight percentage to achieve certain firing characteristics of hot-wire pyrotechnic devices. In this study, the additives (Al_2O_3 and Fe_2O_3) are found to have no effect on the crystal structure transformation, the fusion of KClO_4 and the fusion of KCl . But both of the metal oxide powders exhibited a remarkable acceleration effect on the decomposition of KClO_4 , especially Fe_2O_3 does. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

There are many changes of material that can be detected by differential scanning calorimetry (DSC), in a conventional DSC, operated at a normal heating rate of 10 K/min. With potassium perchlorate, e.g. the sample is heated, there is a small increase in volume and energy, until at T_g , known as the glass transition temperature, the material becomes more mobile. Further heating, in general, allows the material to melt and then decomposition. The equipment of thermal analysis has grown rapidly during the past few years, but it should be noted that, in many cases, the

use of thermal analysis techniques may not provide sufficient information about a given system, complementary or supplementary techniques may be required. The sensitivity of explosives/pyrotechnics would be changed by adding metal oxides/inorganic material powders. The catalytic effects of metal oxides on the decomposition of potassium perchlorate have been reported and the catalytic mechanisms were also proposed [1–8]. Pyrotechnic compositions containing zirconium metal powder have been reported for many applications. In the present work, the effects on the phase transition, melting and decomposition of KClO_4 with varied percentage of Al_2O_3 , Fe_2O_3 were investigated using Perkin-Elmer 7 series thermal analysis system (DTA in DSC mode). Data on the catalytic effects of potassium perchlorate would be a reference for preparing priming composition of electro-explosive devices.

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2. Experimental

99.5% pure KClO_4 (Ferak Berlin), 98.5% pure Al_2O_3 (Ishizu Pharam Ceutical), and 96% pure Fe_2O_3 (Hayashi Pure Chemical Industries) were sifted through a sieve of 325 mesh, respectively. KClO_4 and those containing Al_2O_3 and Fe_2O_3 are prepared by mixing KClO_4 with 1, 3, and 5 wt.% additives in an agate mortar and pestle. For studying the thermal properties of pyrotechnics, approximately 5 mg samples were measured by a Perkin-Elmer 7 series thermal analysis system (DTA in DSC mode) under a 50 ml/min air flow rate, and a 10 K/min heating rate. Powdered $\alpha\text{-Al}_2\text{O}_3$ was used as a reference material. Differential scanning calorimetry (DSC) measurements on the solid state reaction in the region 300–800°C were carried out using a Perkin-Elmer 7 series thermal analysis system (DTA in DSC mode). The measurement was reported three times on each composition in order to investigate the reproducibility of the thermal characteristics for KClO_4 with additives.

3. Results and discussion

The basis of every calorimetry is an energy measurement, since any reaction in a solid body is accompanied by a heat flow, these procedures can be applied to many different reactions. Modern instrumentation has made DSC a sensitive, simple and rapid laboratory technique. DSC analysis is often employed to characterize the physical properties of material, such as phase transition [9–13], melting and decomposition, etc. On the DSC curves, pure potassium perchlorate shows three endothermic peaks at 309, 608 and 770°C, and a sharp exothermic peak at 627°C. The first two endothermic peaks corresponded to the reversible crystallographic transformation, and the fusion of KClO_4 , respectively, the exothermic peak is related to the decomposition of potassium perchlorate. But the third endothermic peak indicated the fusion of KCl.

The DSC peak area, peak temperature and extrapolated onset temperature (EOT) measurements on the solid–solid state transition of KClO_4 and KClO_4 with

Table 1
Phase transition peak area, EOT and phase transition peak temperature of potassium perchlorate with additives

Sample	Average peak area (J/g)	Average EOT (°C)	Average peak temperature (°C)
KClO_4 (–325 mesh)	130	303	309
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 99/1$	130	303	309
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 97/3$	134	303	309
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 95/5$	124	303	309
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 99/1$	132	303	309
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 97/3$	123	303	309
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 95/5$	123	303	308

Table 2
Fusion temperature, the decomposition peak area, EOT and peak temperature of decomposition for KClO_4 with additives

Sample	Fusion temperature (°C)	Average peak area (J/g)	Average EOT (°C)	Average peak temperature (°C)
KClO_4	608	199	615	625
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 99/1$	596	228	603	615
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 97/3$	595	209	598	609
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 95/5$	594	242	597	606
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 99/1$	566	235	574	593
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 97/3$	552	250	559	584
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 95/5$	546	244	546	578

additives are recorded in Table 1. It is shown that the EOT, peak area and peak temperature of KClO_4 with additive were close to a value, respectively, and the EOT of KClO_4 (302.7–303.3°C) was in excellent agreement with the result of Berger et al. [14]. The additives (Fe_2O_3 and Al_2O_3) are found to have little effect on the heat of transformation (130 J/g for KClO_4 and 122–134 J/g for KClO_4 additives). In this study, the heat of transformation was 20–30 J/g higher than that reported in the literature (110 J/g [14], 103 J/g for KClO_4 [13]).

After the crystal structure transformation, the DSC curves showed an endothermic peak followed by a sharp exothermic peak. The fusion temperature, decomposition peak area, EOT and peak temperatures of decomposition for KClO_4 and KClO_4 with additives are listed in Table 2. The fusion temperatures (608°C for KClO_4 but 594–596°C for Al_2O_3 addition and 546–564°C for Fe_2O_3 addition), EOT (615°C for KClO_4 but 597–603°C for Al_2O_3 addition and 546–574°C for Fe_2O_3 addition) and peak temperatures of decomposition for KClO_4 with additives (625°C for KClO_4 but 606–615°C for Al_2O_3 addition and 578–593°C for Fe_2O_3 addition) were shifted to lower value, especially for Fe_2O_3 . Rudloff and Freeman [15] have been concluded that metal oxides that are p-type semiconductors are active catalysts for the decomposition of potassium perchlorate. Haralambous et al. [3] also shared this conclusion that p-type oxide are active catalysts for the decomposition of potassium perchlorate. The peak areas of decomposition for KClO_4 and KClO_4 with additives (199 J/g for KClO_4 but 209–242 J/g for Al_2O_3 addition and 235–250 J/g for Fe_2O_3 addition) increased, as known [16], Fe_2O_3 has a remarkable accelerating effect on the decomposition. Fig. 1 shows the DSC curves of KClO_4 with additives,

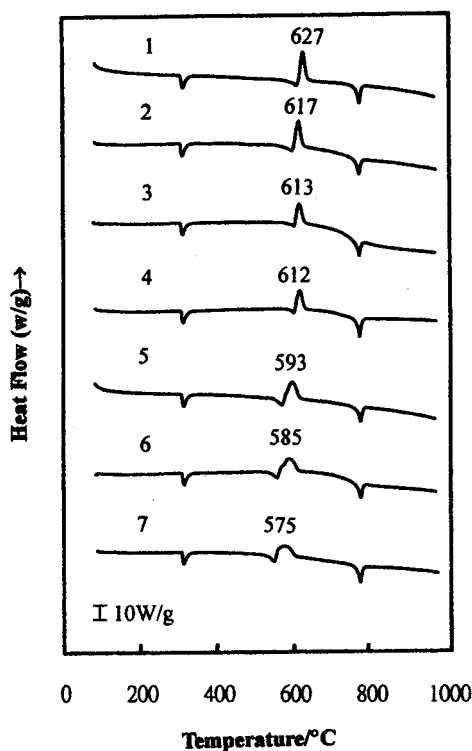


Fig. 1. DSC curves (DSC in DTA mode) of KClO_4 and KClO_4 containing metal oxide additives under a 30 ml/min air flowing rate with a 10°C/min heating rate: (1) KClO_4 ; (2) KClO_4 with 1 wt.% Al_2O_3 ; (3) KClO_4 with 3 wt.% Al_2O_3 ; (4) KClO_4 with 5 wt.% Al_2O_3 ; (5) KClO_4 with 1 wt.% Fe_2O_3 ; (6) KClO_4 with 3 wt.% Fe_2O_3 ; (7) KClO_4 with 5 wt.% Fe_2O_3 .

the Fe_2O_3 – KClO_4 mixtures give a broader exothermic peak and lower EOT than that of KClO_4 .

After the decomposition stage, another endothermic peak was observed, corresponding to fusion of

Table 3
Melting peak area, EOT, peak temperature of melting for KCl with residual

Sample	Average peak area (J/g)	Average EOT (°C)	Average peak temperature (°C)
KClO_4	187	762	770
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 99/1$	186	761	770
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 97/3$	172	760	770
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 95/5$	192	762	770
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 99/1$	193	761	770
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 97/3$	171	762	770
$\text{KClO}_4/\text{Al}_2\text{O}_3 = 95/5$	200	762	770

KCl. The EOT of melting, melting peak area and peak temperature of melting for KCl in the residual material are listed in Table 3. The peak temperature of melting of KClO_4 is close to 770°C , in agreement with the result of Berger et al. [14]. The additives (Al_2O_3 and Fe_2O_3) were found to have no effect on the melting of KCl. These results are good for choosing optimum firing characteristics of oxidizer.

4. Conclusions

The additives Fe_2O_3 and Al_2O_3 have an accelerating effect on the decomposition of KClO_4 . Especially, the Fe_2O_3 additive lowers the decomposition temperature of potassium perchlorate. Fe_2O_3 is a transition metal oxide that contains metal cations with partially filled d-orbitals have unfilled valence orbitals, they have some d-orbitals to accommodate the electron pairs from the perchlorate. Although the activity of Fe_2O_3 is lower than the transition metal oxide which contains d^0 configurations, the catalyst activities of Fe_2O_3 is high enough to behave as catalyst on the decomposition of potassium perchlorate.

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