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THE THERMAL PROPERTIES AND FIRING CHARACTERISTICS OF $Zr/KClO_4$
Priming compositions containing graphite, Fe_2O_3 and Al_2O_3 additives

Jinn-Shing Lee[1,2,3], *Chung-King Hsu*[1], *Li-Kuo Lin*[3,4] *and Chin-Wang Huang*[2]

[1]Department of Material and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan
[2]Department of Chemistry, Chung-Yuan Christian University, Chung-Li, Taiwan
[3]P.O.Box. 90008-15-9, Chung-Shan Institute of Science and Technology, Lung-Tan, Taiwan
[4]Department of Chemical Engineering, National Central University, Chung-Li, Taiwan, R.O.C.

Abstract

Thermal decomposition of $Zr/KClO_4$ priming compositions containing different concentration of additives, such as graphite, Fe_2O_3 and Al_2O_3 have been studied by DSC/TG techniques. The firing characteristics of these primer mixtures have also been examined by Bruceton test and by adiabatic calorimeter. The results of these experiments suggest that strong interaction has been occurred between $KClO_4$ and Fe_2O_3 in the solid state.

Keywords: Fe_2O_3 and Al_2O_3 additives, firing characteristics, thermal properties, $Zr/KClO_4$ priming compositions containing graphite

Introduction

Zirconium/potassium perchlorate is the preferred first fire composition widely used in contact with a bridgewire in low voltage ('hot wire') EEDs (Electro-Explosive-Devices) (squibs, primers, ignition elements, initiators, detonators, etc.). $Zr/KClO_4$ in its many formulations and used with the proper bridgewire, can meet the 1 amp/1 watt/5 minute no-fire safety requirement imposed by U.S. military design specifications (e.g., MIL-I-23659). As well as being widely used in EEDs, $Zr/KClO_4$ is used in optical initiation for laser initiated systems. Some formulations of $Zr/KClO_4$ priming composition have no binder (many of the other $Zr/KClO_4$ formulations contain binders, such as viton, nitrocellulose), but include 1% graphite. The graphite was originally added to reduce electrostatic sensitivity of the formulation (which it did not but was retained as a lubricant to reduce friction sensitivity in automatic loading operation.

The effect of various additives [1, 2], especially metal oxide, in course of thermal decomposition has been extensively studied during recent years. The present work is an attempt to get more information on the decomposition, firing characteristics in $Zr/KClO_4$/additive systems.

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Experimental

99.5% pure $KClO_4$ (Ferak Berlin), 99.9% pure graphite powder (<1 μm Alfa Johnson Matthey Co. Ltd.), 96% pure Fe_2O_3 (Hayashi Pure Chemical Industries Ltd.) and 98.5% pure Al_2O_3 (Ishizu Pharma Ceutical Co. Ltd.) are shifted through a sieve of 325 meshes, respectively. The mixtures of $KClO_4$ with 1, 3, 5 wt% additives were prepared by mixing $KClO_4$ and additives in an agate mortar with pestle. For studying the thermal properties, approximately 5 mg samples were measured using DuPont TA 2000 with 951 TG and 910 DSC under static air atmosphere with a 10°C min^{-1} heating rate. A Parr adiabatic calorimeter was used to obtain the heat of explosion.

Results and discussions

Potassium perchlorate is important for its applications as an oxidizer in pyrotechnic formulations, since the Zr/$KClO_4$ priming composition is a primer mixture capable of withstanding prolonged high temperature, with no measurable change in the thermal cycle. Although the thermal properties and decomposition kinetics of the

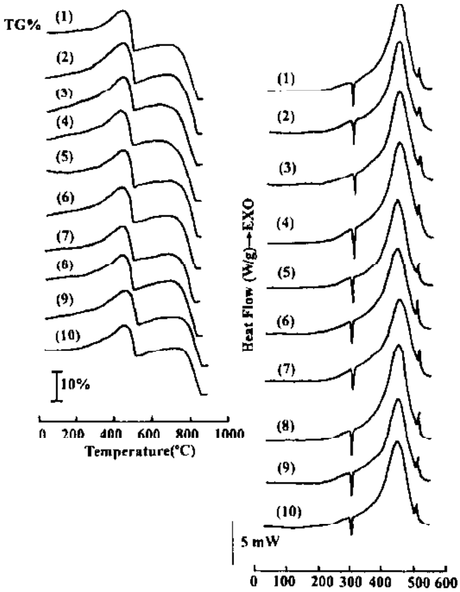

Fig. 1 TG and DSC curves of Zr/$KClO_4$ priming composition containing graphite, Fe_2O_3 and Al_2O_3 additives under static air atmosphere with a 10°C min^{-1} heating rate.
(1) Zr/$KClO_4$=50/50; (2) Zr/$KClO_4$/*G*=50/49/1; (3) Zr/$KClO_4$/*G*=50/47/3; (4) Zr/$KClO_4$/*G*=50/45/5; (5) Zr/$KClO_4$/*F*=50/49/1; (6) Zr/$KClO_4$/*F*=50/47/3; (7) Zr/$KClO_4$/*F*=50/45/5; (8) Zr/$KClO_4$/*A*=50/49/1; (9) Zr/$KClO_4$/*A*=50/47/3; (10) Zr/$KClO_4$/*A*=50/45/5;

primer mixture basis of $KClO_4$ have been investigated by many researchers [3–8], in some case how to decrease the trigger level but maintain the 1-amper/1-watt, 5 min no-fire level is still the major goal in this work.

Figure 1 shows the TG and DSC thermograms of Zr/$KClO_4$ priming composition containing graphite, Fe_2O_3 and Al_2O_3 additives. The DSC curves exhibit an endothermic peak near 305°C, followed by a broad exothermic peak and a second exothermic peak at higher temperature, the endothermic peak is the characteristic crystalline transition of $KClO_4$ from rhombic to cubic lattice at about 305°C. The broad exothermic peak indicates the reaction in Zr–$KClO_4$-additives systems and the second exothermic peak shows the decomposition of residual unreacted $KClO_4$. The broad exothermic peak of Zr/$KClO_4$ priming composition containing graphite, Fe_2O_3 and Al_2O_3 additives shift to lower temperature, especially for Fe_2O_3, it was proposed that in order to be an active catalyst, a metal oxide must be a P-type semiconductor which can change to an n-type semiconductor at the decomposition temperature [9,10].

The TG curves under static air atmosphere with a 10°C min^{-1} heating rate are also shown in Fig. 1, the initial mass loss temperature (that is the temperature of first detectable mass loss percentage just below 100%) of the Zr/$KClO_4$ priming composition containing graphite, Fe_2O_3 and Al_2O_3 additives were also shifted to lower temperature, and the mass loss percentage of solid-solid state reactions below 600°C are closed 10%. In our composition, the amount of oxidization of KClO4 is higher than KClO4 of the theoretical solid-solid reaction ($2Zr+KClO_4 \rightarrow 2ZrO_2+KCl$), the value of mass loss percentage may be produced by the oxygen release from $KClO_4$, but this value also indicated that the solid state reaction has gone to approximately 90% completion.

Table 1 Firing characteristics of Zr/$KClO_4$ priming composition containing graphite, Fe_2O_3 and Al_2O_3 additives

Composition	50% probability of firing/Amps[a)]	Heat of explosion/cal g^{-1}	
		in O_2[b)]	in N_2[c)]
$KClO_4$/Zr=50/50	1.82	1359.4	1350.2
$KClO_4$/Zr/*G*=50/45/1	1.59	1461.2	1275.7
$KClO_4$/Zr/*G*=50/47/3	1.40	1468.6	1293.1
$KClO_4$/Zr/*G*=50/45/5	1.69	1226.8	1257.4
$KClO_4$/Zr/*F*=50/49/1	1.43	1199.0	1189.5
$KClO_4$/Zr/*F*=50/47/3	1.45	1197.3	1210.9
$KClO_4$/Zr/*F*=50/45/5	1.59	1278.6	1185.5
$KClO_4$/Zr/*A*=50/49/1	1.35	1237.0	1190.6
$KClO_4$/Zr/*A*=50/47/3	1.42	1213.2	1172.1
$KClO_4$/Zr/*A*=50/45/5	1.62	1140.8	1147.8

[a)]evaluation by the Bruceton test and statistical calculation
[b)]evaluation in O_2 atmosphere (25 atm) by Parr adiabatic calorimeter
[c)]evaluation in N_2 atmosphere (25 atm) by Parr adiabatic calorimeter
G= graphite powder, *F*= Fe_2O_3, *A*= Al_2O_3

Using the Bruceton method and associated statistical calculation, in the 'up-and-down' approach of the Bruceton test only one sample is tested at a time. Before measurements can be taken, it is necessary to determine the approximate amperage at which 50% of the components will burn. Then starting at a level where about 50% responses are expected, the test level is moved up one level after each non-response and down one level after each response. The firing characteristics of EEDs, which have different composition of primer were calculated. Table 1 shows the 50% probability of firing level of EEDs which has the primer mixture containing additives tend to lower fining level, this results are agree with DSC and TG results. The heat of explosion of Zr/$KClO_4$ priming composition containing graphite, Fe_2O_3 and Al_2O_3 additives are also listed in Table 1. The heat of explosion of Zr/$KClO_4$ priming compositions did not change significantly under different atmospheres (O_2 and N_2) when the additives of Fe_2O_3 and Al_2O_3 are added into the Zr/$KClO_4$ priming composition. But with increase the additives content in the Zr/$KClO_4$ priming compositions, the heat of explosion of Zr/$KClO_4$ priming compositions gradually decrease. However, in case of graphite in O_2 atmosphere, the heat of explosion for Zr/$KClO_4$ is 1350–1360 cal g^{-1}, which is close to the theoretical value (1400 cal g^{-1}) and this is another interesting point for EEDs designer.

Conclusions

Studies on the thermal decomposition of mixtures of Zr/$KClO_4$ with different additives suggest that the additives, such as graphite, Fe_2O_3 and Al_2O_3 play a major role in the decomposition processes. However, DSC/TG investigations make it clear that the additive Fe_2O_3 exhibited a remarkable acceleration effect on the decomposition of Zr/$KClO_4$ priming composition. The firing characteristics, such as 50% probability of firing and heat of explosion, also play an important role on EEDs designing.

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