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Thermal properties and firing characteristics of the $Zr/KClO_4$/Viton A priming compositions

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Abstract

Zirconium powder is a powerful reducing agent that reacts with oxidizer at elevated temperature, releasing enough heat to ignite pyrotechnic mixtures. In this work, the thermal properties of $Zr/KClO_4$/Viton A priming compositions made by different preparation methods were first investigated using thermal analysis techniques. Then these priming compositions were pressed into the charge holders of pressure cartridges. The firing characteristics of the pressure cartridge were evaluated by using the Bruceton method. The data indicate that the thermal behavior and firing characteristic of $Zr/KClO_4$/Viton A priming compositions were changed because of the different methods of preparation.

Keywords: Viton A; Bruceton method; Thermal properties; Energetics; Priming compositions

1. Introduction

Energetic materials composed of metal powders and oxidizing agents can be used as the first-fire composition for igniters, for fuel components, such as gas generators, and fireworks. Typical pyrotechnics are made with the metals zirconium (Zr), magnesium (Mg) or aluminum (Al), etc. and inorganic salts for powder oxidizers, such as potassium perchlorate ($KClO_4$), potassium nitrate (KNO_3) or ammonium perchlorate (NH_4ClO_4). Many of the pyrotechnics contain binders, such as Viton, nitrocellulose or include some lubricant, such as graphite powder to reduce friction sensitivity in automatic loading operations. Imbedding the pyrotechnics in a polymer can also change the sensitivities of the pyrotechnic. Only a small change in the formulation of a pyrotechnic can influence its properties drastically.

The fuel/oxidizer mixture $Zr/KClO_4$ is typical of mixtures being used by commercial producers to obtain 1 A/1 W no-fire electro-explosive devices (EEDs). In our previously studies, decomposition of $Zr/KClO_4$ first-fire compositions containing different concentration of additives, such as CuO [1], graphite, Fe_2O_3 and Al_2O_3 [2] have been investigated by DSC/TG techniques. The firing characteristics of these first-fire compositions have also been examined by the Bruceton method and adiabatic calorimetry [3,4]. The metal oxide additives exhibited a remarkable acceleration effect on the decomposition of the $Zr/KClO_4$ first-fire composition. The present work is an attempt to examine the thermal decomposition and firing characteristics in $Zr/KClO_4$/Viton A first-fire compositions.

2. Experimental

The Zr metal powder used (Ventron) had average particle size of 1–3 μm and purity 94% (as Zr + Hf).

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Potassium perchlorite (Ferak, Berlin) had purity 99.5%. It was first ground with a mortar and pestle and then the fraction passing through a 325 mesh (N.B.S.) sieve was taken (average particle size 44 μm). Three kinds of Zr/$KClO_4$/Viton A first-fire composition were prepared as follows. For priming composition A, 49 wt.% of $KClO_4$ powder was mixed with 2 wt.% of Viton A solution. After mixing, the mixture was dried and sieved through a 325 mesh sieve. Then 49 wt.% of zirconium powder was introduced to make a first-fire composition.

For priming composition B, 49 wt.% of zirconium was first mixed with 2 wt.% of Viton A solution. After mixing, the powder type mixture was dried and sieved through a 325 mesh sieve. Then 49 wt.% of $KClO_4$ powder was introduced to make a first-fire composition.

For priming composition C, 49 wt.% of zirconium powder was first well mixed with 49 wt.% of $KClO_4$ powder. Then 2 wt.% of Viton A solution was introduced, the mixture of Zr/$KClO_4$/Viton A was dried and sieved through a 325 mesh sieve.

For studying the thermal decomposition of first-fire compositions, samples masses for less 5 mg were strictly limited. The DSC/TG curves of Zr/$KClO_4$/Viton A first-fire compositions were obtained using a TA 2000 system with 951 TG and 910 DSC, under a static air atmosphere with 5, 10, 15 and 20 °C min^{-1} heating rate.

3. Results and discussion

Viton is a copolymer of vinylidene fluoride and hexafluoropropylene, used as synthetic rubbers, which can withstand a temperature of 200 °C in contact with most oils, chemical solvents and fuel, and has good mechanical properties. Viton A contains about 65% fluorine, has a density of 1.85 g cm^{-3}, a relatively low molecular weight and dissolves in acetone, making a Viton A solution which is easily blended with pyrotechnics.

Fig. 1 shows the photograph of three priming compositions with various enlargements that spreading in amyl acetate solution. The dark clusters are Zr powders, the transparent crystals are potassium perchlorate and gray, half-shadowy amoeba-like are Viton. Only for the priming composition B, the metal powder and oxidizing agent were wrapped in the polymer. This phenomenon may be an effective factor on the direct current sensitivity and thermal behavior of priming composition. The melting points (T_m), the peak temperature (T_p) of exothermic peaks, and the decomposition kinetic parameters that obtained by non-isothermal technique for Viton A and three priming compositions are listed in Table 1.

DTA curves of Viton A are shown in Fig. 2. In the Viton A curves, a broad but big exothermic peak with the maximum is observed at 459–508 °C, and also following a small exothermic peak from 508 to 585 °C. The distribution of small exothermic peak of Viton A in DTA curves with different heating rate were shift higher temperature, this indicate that the residual of Viton A is hard to removal by heat when use as a binder. The DSC curves of Viton A, Zr/$KClO_4$ and three priming compositions under static air atmosphere with a 10 °C min^{-1} heating rate are shown in Fig. 3. In the three priming composition curves, one sharp endothermic peak is observed around

Table 1
T_m, T_p and decomposition kinetic parameters for Viton A and the three priming compositions

Priming composition number	T_m (°C)	T_p (°C)	E (kJ mol^{-1})	$-\gamma_b$	A (s^{-1})	Temperature range (°C)
A	304.7	431.3	119	0.9793	8.43×10^{10}	414–463
B	303.1	389.1	80	0.9835	1.22×10^{11}	389–458
C	306.3	393.8	117	0.9757	1.21×10^{11}	393–441
Viton A	–	467.2	267	0.9852	1.91×10^{21}	461–485

T_m and T_p obtained from DSC curves under static air atmosphere with a 10 °C min^{-1} heating rate; $-\gamma_b$, correction coefficient of linear regression.

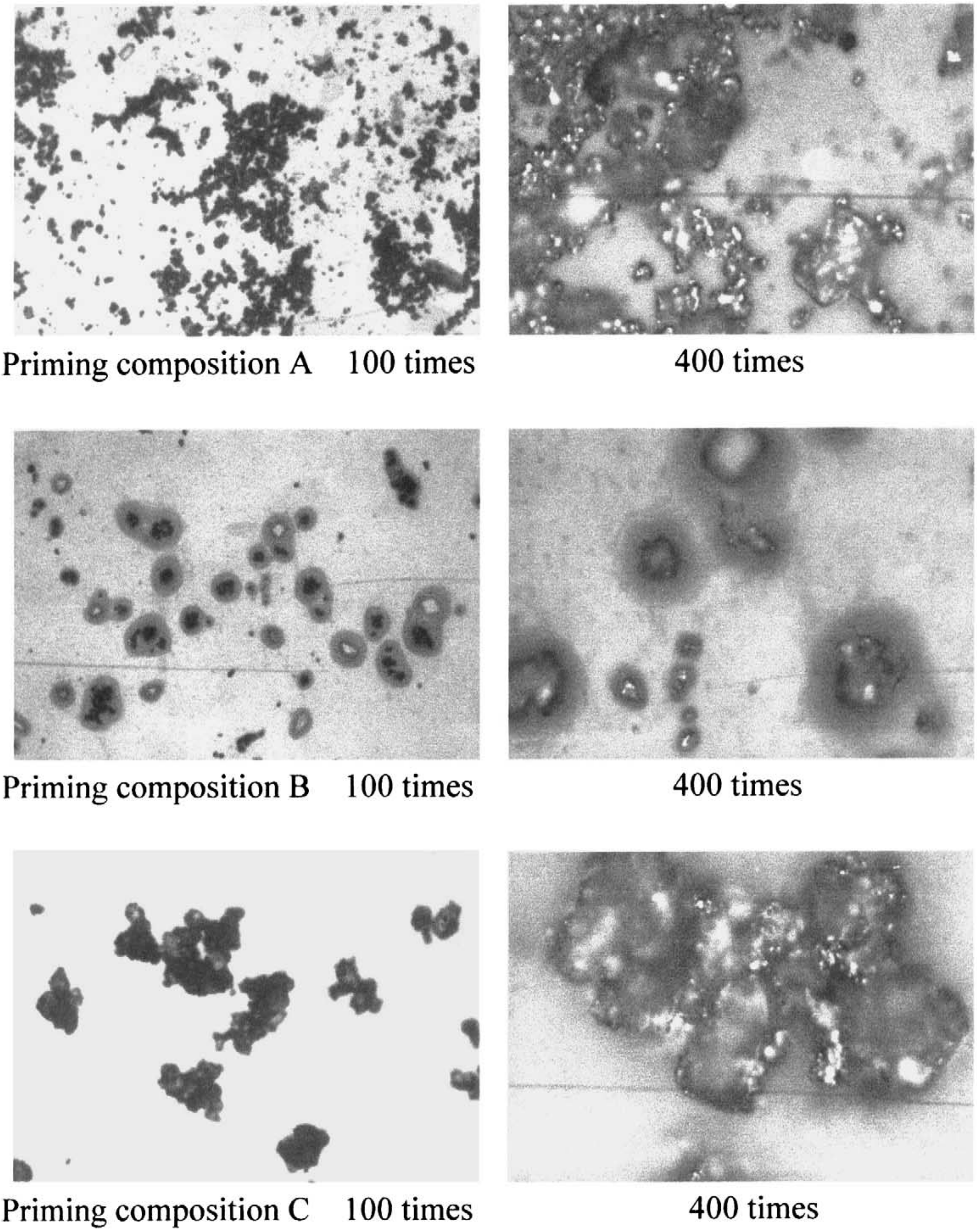

Fig. 1. Morphology of priming compositions.

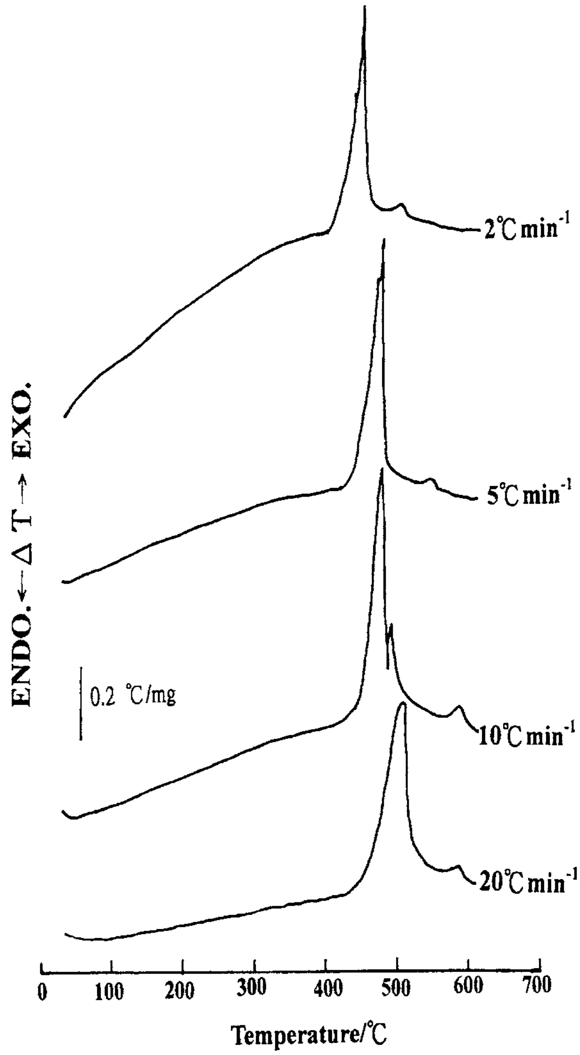

Fig. 2. DTA curves of Viton A, at static air atmosphere with 2–20 °C min^{-1} heating rate.

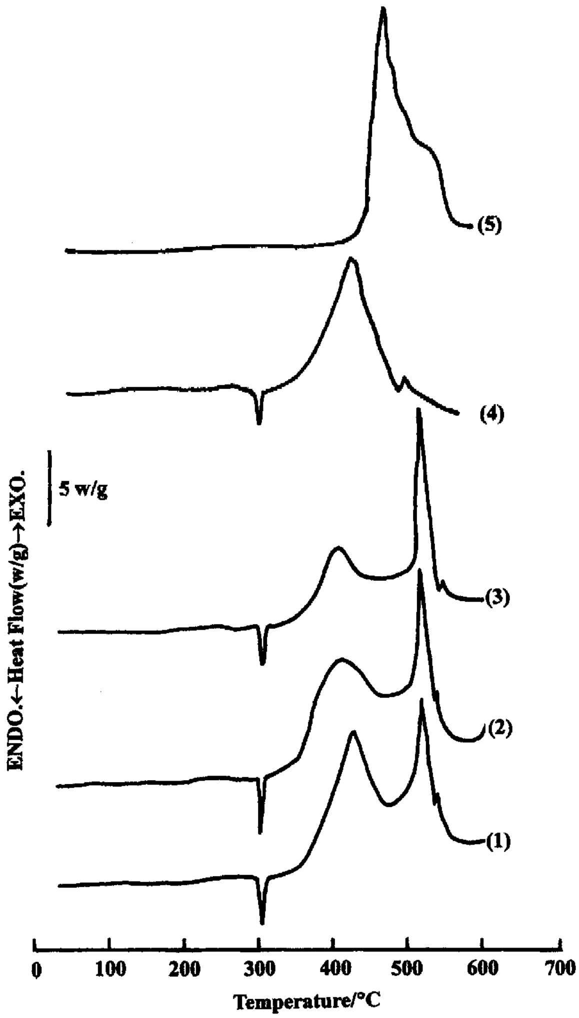

Fig. 3. DSC curves of priming composition at a 10 °C min^{-1} heating rate under static air atmosphere: (1) priming composition A; (2) priming composition B; (1) priming composition C; (4) Zr/ $KClO_4$ = 50/50 by weight.

303–306 °C, corresponding to the crystal structure transformation of potassium perchlorate. Then decomposition occurs and a broad exothermic is observed at 431.3, 389.1 and 393.8 °C, respectively, which represents the reaction between zirconium powder and potassium perchlorate. The DSC curves of Zr/$KClO_4$ mixture also gave one sharp endothermic peak around 303 °C, but immediately a big, broad exothermic peak which indicate the reaction between Zr and $KClO_4$. And the sharp exothermic peak of three priming compositions are corresponding to the decomposition of unreacted $KClO_4$.

The TG curves of three priming composition under static air atmosphere with a 10 °C min^{-1} heating rate can be seen in Fig. 4. All of the TG curves show slightly mass gain owing to the reaction of Zr and O_2 under a slow heating rate, and then decomposition immediately. Because of the random initial mass loss

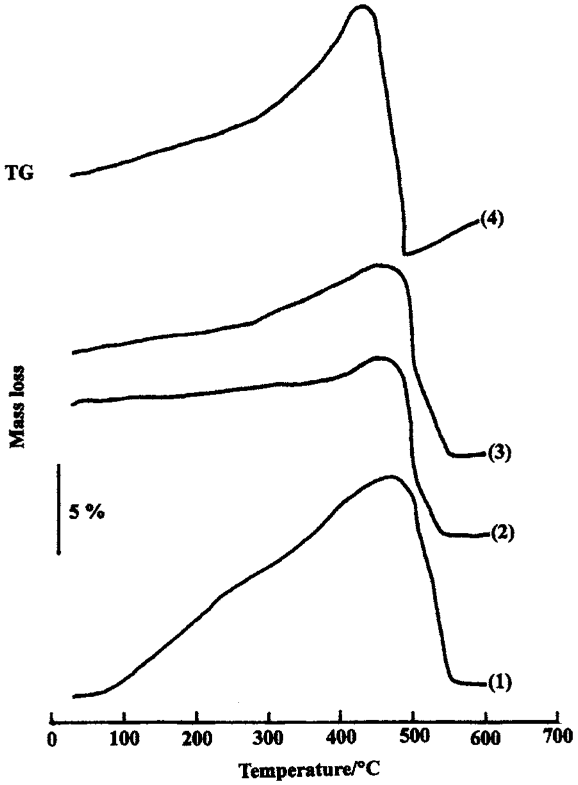

Fig. 4. TG curves of priming composition at a 10 °C min^{-1} heating rate under static air atmosphere: (1) priming composition A; (2) priming composition B; (3) priming composition C; (4) Zr/ $KClO_4$ = 50/50 by weight.

temperature (that is the temperature of first detectable mass loss percentage just below 100%), the kinetic parameters of decomposition cannot be obtained from the dynamic TG technique.

The three priming compositions were pressed into the charge holder of the EEDs in order to evaluate the dc sensitivity by the Bruceton method [3]. The up-and-down procedure, sometime called the Bruceton method, is one of a class of procedures. In the up-and-down procedure only one object is tested at a time. Before a measurement can be taken, it is necessary to determine the approximate amperage at which 50% of the components will fire, then start at 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 three groups of EEDs were determined by following the Bruceton test results (Table 2) and associated statistical calculation. Table 3 shows the firing characteristics of the EEDs prepared using primary compositions A–C. The data in Table 3 indicate that the EEDs prepared using primary compositions A–C still possess 1 A/1 W, 5 min, no-fire character, but not for the EED which contains the priming composition B, and the dc sensitivity of $Zr/KClO_4$ priming compositions tend to decrease with introduction of Viton A. This result is supported by the exothermic peak behavior of DSC curves. Priming composition B gave lower decomposition

Table 2
Bruceton test records of three groups of EEDs

Firing current (A)	Shot number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Priming composition A															
1.69	×												×		
1.58		×		×				×		×		○		×	
1.47			○		×		○		○		○				○
1.37						○									
Priming composition B															
1.26								×							
1.18	×		×				○		×		×				×
1.10		○		×		○				○		×		○	
1.03					○								○		
Priming composition C															
1.48	×				×						×				×
1.38		×		○		×		×		○		×		○	
1.29			○				○		○				○		

'×' denotes fired.'○' denotes did not fired.

Table 3
The firing characteristics of EEDs

Firing characteristics (under a 95% confidence level and 99.9% reliability)	Priming composition			$Zr/KClO_4 = 50/50$ [4]
	A	B	C	
Maximum no-fire dc current (A)	1.14	0.80	1.09	1.63
50% Firing current (A)	1.53	1.13	1.38	1.82
Minimum all-fire dc current (A)	2.05	1.60	1.74	2.30

temperature in DSC curves, and also gave lower activation energy.

4. Conclusions

Although the $Zr/KClO_4$ or $Zr/KClO_4$/binder priming compositions have been widely investigated by many researchers [5–12], this work examines the effects on thermal behavior and firing characteristics of priming compositions with Viton binder additive were examined specifically. Quantitative studies using DSC and the Bruceton method to assess the influence of Viton A on the reaction between zirconium and potassium perchlorate are also investigated. Experimental results indicated that the polymer binder (Viton A) exhibited a remarkable acceleration effect on the decomposition of $Zr/KClO_4$ priming composition and priming composition A and priming composition C still possess 1 A/1 W, 5 min, no-fire characteristic when used as a first-fire mixture of initiators.

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