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The effect of different zirconium on thermal behaviors for Zr/$KClO_4$ priming composition

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Abstract

Zirconium powder is a powerful reducing agent and reactive with an oxidizer at elevated temperature to release enough heat to ignite pyrotechnic mixtures. The auto-ignition temperature, ignition temperature within 5 s of zirconium powder and the heat of explosion of the Zr/$KClO_4$ priming composition with different zirconium powders were investigated using thermal analysis techniques. The Zr/$KClO_4$ priming compositions, with different zirconium powders, were pressed into the change holder of a pressure cartridge. The firing characteristics of a pressure cartridge were evaluated by the Bruceton test and its statistical calculation. The data indicate that thermal behavior of Zr/$KClO_4$ priming composition were varied when using different zirconium powders. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zirconium powder; Zr/$KClO_4$; Thermal behavior; Auto-ignition temperature

1. Introduction

Zirconium is a highly active metal, like aluminum, seems quite passive because of its stable, cohesive, protective oxide film which is always present in air or water. Massive zirconium does not burn in air, but oxidizes rapidly above 600°C in air. Zirconium powder ignites quite easily. Zirconium powder ($\leq$44 μm or $-$325 mesh) prepared in an inert atmosphere by the hydride–dehydride process ignite spontaneously upon contact with air, however, if the Zr surface has been conditioned, i.e., pre-oxidized by slow addition of air to the inert atmosphere it will not ignite. Heated zirconium is readily oxidized by CO_2, SO_2, or water vapor, zirconium reacts more slowly with nitrogen than with oxygen. Heating in nitrogen for 3 min gives a 0.3 μm layer of zirconium nitrate at 700°C or a 0.2 μm layer at 900°C [1]. The nitrating rate is enhanced by the presence of oxygen in the nitrogen or on the metal surface.

The fuel/oxidizer mixture, Zr/$KClO_4$ is a typical mixture that is being used commercially for obtaining 1 A/1 W no-fire electro-explosive devices (EEDs). Zirconium in the sub-sieve size state is an easily ignited fuel in this fine size; it will ignite at a temperature of 180–200°C in air [2]. Larger size zirconium particles will generally require a higher temperature. Ellern [2] has reported that in a fuel/oxidizer mixture, an active fuel with an inactive oxidizer, the fuel determines essentially the ignition point. In this work, potassium perchlorate shows incipient decomposition at a higher temperature,

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and it is believed that when $Zr/KClO_4$ mixtures are fired under ambient conditions, the zirconium can initially react with the interstitial air in the voids of mix. In our early study [3], the thermal behavior and firing characteristic of $Zr/KClO_4$ primer mixtures with different particle sizes of zirconium were analyzed by DTA/TG and the Bruceton test. The primer mixture having an average zirconium particle size of 1.7 μm is not suggested as a suitable primer mixture for producing 1 A/1 W, 5 min, no-fire pressure cartridges. The thermal decomposition of $Zr/KClO_4$ primer mixtures containing different concentration of additives, such as graphite, Fe_2O_3 and Al_2O_3, has been studied by DSC/TG techniques [4]. The DSC/TG investigations make it clear that the additives Fe_2O_3 exhibited a remarkable acceleration effect on the decomposition of $Zr/KClO_4$ primer mixture.

In this work, the $Zr/KClO_4$ priming composition with different types of zirconium powders were first prepared by mixing zirconium powder with potassium perchlorate powder. Then the thermal properties of $Zr/KClO_4$ priming composition with different types of zirconium powder were also investigated using thermal analysis techniques. The firing characteristics of a pressure cartridge with $Zr/KClO_4$ priming composition with different types of zirconium powders were evaluated by the Bruceton test and its statistical calculation.

2. Experimental

Two types of zirconium powder were listed in Table 1, and the particle size distribution is shown in Fig. 1. Each of the zirconium powders were mixed with potassium perchlorate (−325 mesh) in a weight ratio of 50%. The mixtures were intimately mixed using a ball miller. Auto-ignition temperature and the ignition temperature within 5 s of zirconium powders are measured following MIL-STD-050-T514.1 and MIL-STD-650-T515.1. Differential scanning calorimetry was carried out using a TAI 2000 thermal analyzer (DSC, model 910). Approximately 5 mg of sample was heated up to 550°C at a rate of 10°C min^{-1} under a static air atmosphere and thermogravimetry (TAI TG, model 951) was also used in this study.

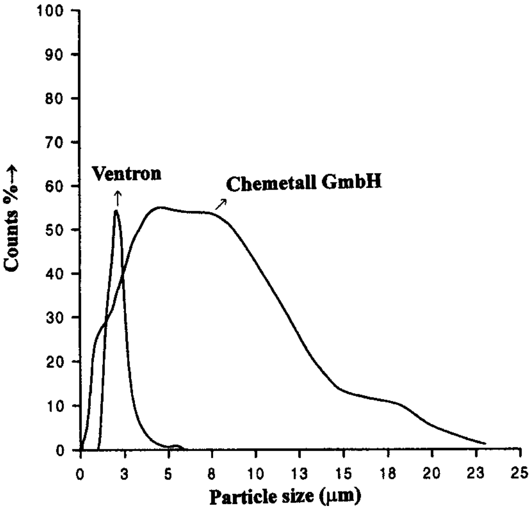

Fig. 1. Particle size distribution of two types of zirconium powders.

3. Results and discussion

The measurements of time-to-ignition have proved to a popular route to determine chemical activation energy on explosives, propellants and pyrotechnics. In the analysis of explosive, it is often assumed for the purposes of modeling and estimating safety that deflagration or detonation is described by a first-order

Table 1
Physical properties of two different types of zirconium powders

Manufacturing	Purity (%)	Apparent density (g cm^{-3})	Ignition point (°C)	Oxidation value % (mass increase after combustion)
Ventron (Alfa stack No. 00624)	≥94	Approx. 1.05	–	33.3 ± 1.6
Chemetall GmbH (zirconium metal powder CA)	97.4 ± 0.8	Approx. 1.1	180 ± 20°C	31.5 ± 1.0

Arrhenius equation. Experimentally, it is found that many energetic materials appear to obey such a law, except for a region at long ignition delays [5].

$$\lambda n(t_{\mathrm{ign}}) = \frac{E_{\mathrm{a}}}{RT} + \mathrm{const.} \qquad (1)$$

where E_a is the activation energy in the above equation using the adiabatic approximation. That is, the energetic material or at least some small critical region of it rapidly comes to the temperature of ignition. The moment there is a delay in the ignition, the sample is generating heat which eventually leads to thermal runaway and ignition. The auto-ignition temperature, 5 s ignition temperatures of zirconium powders and activation energies of decomposition for zirconium powders, calculated from Eq. (1) are listed in Table 2.

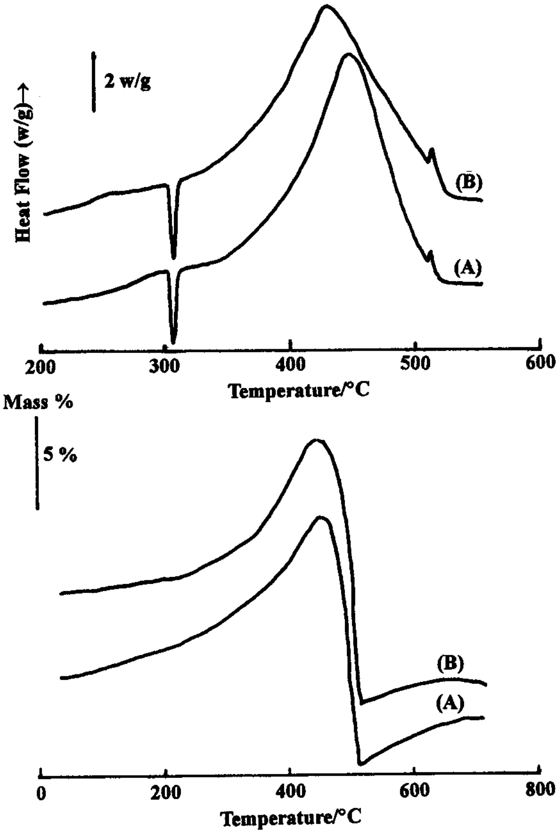

Fig. 2. DSC/TG curves of $Zr/KClO_4$ priming composition with different types of zirconium: (A) Ventron; (B) Chemetall GmbH.

The auto-ignition temperature and the activation energy of decomposition for Ventron zirconium powder are higher than that of Chemetall GmbH zirconium powder. However, the ignition temperature within 5 s is contrary, this may be due to the particle size distribution of zirconium. The TG and DSC plots of $Zr/KClO_4$ priming composition with different types of zirconium powders were shown in Fig. 2. In DSC analysis, both $Zr/KClO_4$ priming compositions exhibit an endothermic peak near 304°C, followed by a broad exothermic peak. The broad exothermic peak is probably the reaction between zirconium and potassium perchlorate. The exothermic peak for the $Zr/KClO_4$ priming composition with Ventron zirconium powder is higher than that of Chemetall GmbH zirconium powder. The shape of exothermic peak for the $Zr/KClO_4$ priming composition with Ventron zirconium powder is also sharper than that of Chemetall GmbH zirconium powder. $Zr/KClO_4$ priming composition with Ventron zirconium powder seems to be a hard ignition than that of Chemetall GmbH zirconium powder. The $Zr/KClO_4$ priming composition was pressed into the charge holder of pressure cartridges to produce samples for the Bruceton test. The up-and-down procedure, sometimes 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 the Bruceton test can commence, it is necessary to determine the approximate amperage at

Table 2
The auto-ignition temperature, 5 s ignition temperatures and activation energy of decomposition for zirconium powders

Manufacture	Auto-ignition temperature (°C)	5 s ignition temperature (°C)	Activation energy of decomposition (kJ mol^{-1})
Ventron	312	306	77.9 (0.991/8%)[a]
Chemetall GmbH	298	3214	70.1 (0.993/6.7%)[a]

[a] A/B, where A is the correlation coefficient and B the relative error.

Table 3
Bruceton test for pressure cartridge with Zr(Ventron)/$KClO_4$ priming composition

Ampere	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1.7600								×												
1.6800	×				×		○		×		×				×		×			
1.600		×		○		○				○		×		○		○		×		○
1.5270			○										○						○	

Table 4
Bruceton test for pressure cartridge with Zr(Chemetall GmbH))/$KClO_4$ priming composition

Ampere	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1.6400						×		×		×										
1.5700	×		×		○		○		○		×		×		×		×			
1.5000		○		○								○		×		○		×		○
1.4320			○												○				○	

Table 5
The heat of explosion, and firing characteristics of Zr/$KClO_4$ priming composition with different types of zirconium powders

Zirconium powder types	Heat of explosion (cal/g)	Maximum no-fire current (A)[a]	Threshold firing current (A)[b]	Minimum all-fire current (A)[a]
Ventron	1173 ± 18	1.34	1.62	1.96
Chemetall GmbH	1215 ± 30	1.19	1.54	2.00

[a] 99.9% probability, 95% confidence.
[b] 50% probability, 95% confidence.

which 50% of the parts will fire. Starting at a level about 50% response are expected, the test level is moved up one level after each non-response and down one level after each response. The Bruceton test data are shown in Tables 3 and 4. The firing characteristics of pressure cartridges calculated from the Bruceton test, the activation energy evaluated by a dynamic DSC method and the heat of explosion of Zr/$KClO_4$ priming composition, with different types of zirconium powders are shown in Table 5.

The data from the Bruceton test show that the pressure cartridges have 1 A/1 W, 5 min no-fire character for Zr/$KClO_4$ priming compositions with both types of zirconium powders. The pressure cartridge with Ventron zirconium powder process a narrowed firing characteristic, and the heat of explosion of Zr/$KClO_4$ priming composition with Chemetall GmbH zirconium powder is higher than that of Ventron. The values of activation energy are in good agreement with the firing characteristic analysis and the ignition temperature within 5 s analysis.

4. Conclusion

The thermal behaviors and firing characteristics of Zr/$KClO_4$ priming composition with different types of zirconium powders were analyzed by DSC, TG, adiabatic calorimeter and the Bruceton test. This priming composition is suggested as a suitable priming composition for producing 1 A/1 W 5 min no-fire pressure cartridges. However, the priming composition with Ventron zirconium powder is more suitable in first fire composition for producing EEDs.

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