Thermochimica Acta, 173 (1990) 211–218
Elsevier Science Publishers B.V., Amsterdam

A STUDY OF ZIRCONIUM/POTASSIUM PERCHLORATE PRIMER MIXTURES

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(Received 25 April 1990)

ABSTRACT

The effect of varying the percentage of Zr in Zr/$KClO_4$ primer mixtures has been studied. The thermal properties of the mixtures were investigated by thermogravimetry (TG), differential thermal analysis (DTA); and adiabatic calorimetry. In TG analysis, the primer mixtures show abnormal behavior when the Zr content exceeds 70%. DTA of the two-component system shows one endotherm and two exotherms, the endothermic peak near 305°C being the characteristic crystalline transition of $KClO_4$ from a rhombic to a cubic lattice. The first exotherm is due to the reaction between Zr and $KClO_4$ and the second to decomposition of residual $KClO_4$. $KClO_4$ is found to be essential to start the reaction of Zr/$KClO_4$ primer mixtures and the autoignition temperature of such mixtures was determined using DTA data extrapolated to a near-zero heating rate. A pilot scale process was developed for preparing pressure cartridges for the Bruceton test and the threshold firing current and No-Fire characteristics were obtained by statistical calculation. The results show that mixtures of Zr content 40–60 wt.% are suitable fuel/oxidizer primer mixtures for 1 A/1 W, 5 min, no-fire, electro-explosive devices (EEDs).

INTRODUCTION

An electro-explosive device (EED) is a system for converting electrical energy into heat which then triggers an explosive reaction. The thermal properties of primer mixtures, which are placed next to the hot wire in such devices, are important for assessing EEDs.

Perchlorates are powerful oxidising agents and decompose at elevated temperatures to give oxygen as one of the major products. Extensive studies have been made on the thermal properties of potassium perchlorate [1,2] and its mixtures with metal oxides [3,4] because of their use in pyrotechnic and explosive compositions. Zr/$KClO_4$ mixtures are typical primers in commercial 1 A/1 W, 5 min, no-fire EEDs [5], and the thermal properties and

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decomposition kinetics of primer mixtures based on $KClO_4$ have been investigated by many researchers [6–8].

In this report, the thermal properties of $Zr/KClO_4$ primer mixtures of various Zr contents were evaluated by TG, DTA and adiabatic calorimetry, then suitable primer mixtures were pressed into the charge holder of pressure cartridges to produce samples for the Bruceton test. The no-fire characteristics of the various mixtures in these pressure cartridges were determined by statistical calculation. The autoignition temperature of various $Zr/KClO_4$ primer mixtures were determined from DTA data at several heating rates extrapolated to a near-zero heating rate [9].

EXPERIMENTAL DETAILS

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

A Parr adiabatic calorimeter was used to obtain the heat of explosion. The Mettler TG 50 thermobalance fitted with the TA 3000 system and a Rigaku–Denki model 8121 DTA were operated in air atmosphere at 10 °C min^{-1} heating rate. To determine the autoignition temperature, primer mixtures were tested at nominal heating rates of 20, 10, 5 and 2 °C min^{-1}. The sample size was restricted to less than 5 mg and the reference material for DTA was finely powdered α-Al_2O_3.

RESULTS AND DISCUSSION

Figure 1 shows the heat of explosion of $Zr/KClO_4$ primer mixtures of various Zr contents. The heat of explosion increases with the Zr content,

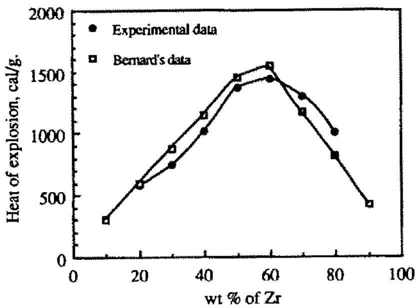

Fig. 1. Effect of Zr content on the heat of explosion of $Zr/KClO_4$ primer mixtures.

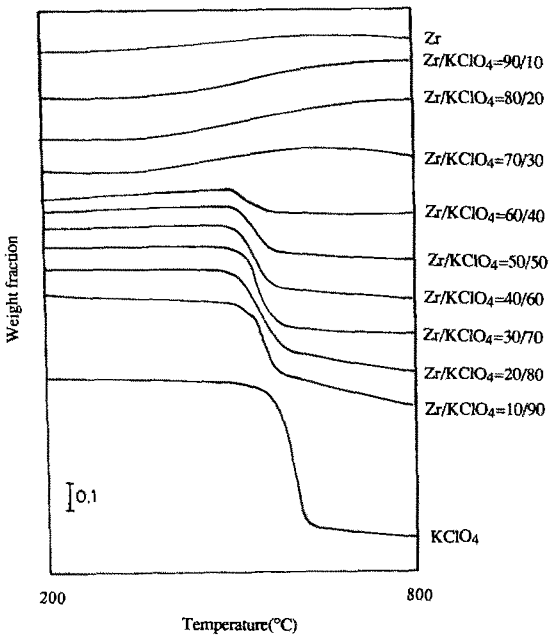

Fig. 2. TG curves of Zr, $KClO_4$ and the $Zr/KClO_4$ primer mixtures in an air atmosphere at a heating rate of $10\,°C\ min^{-1}$.

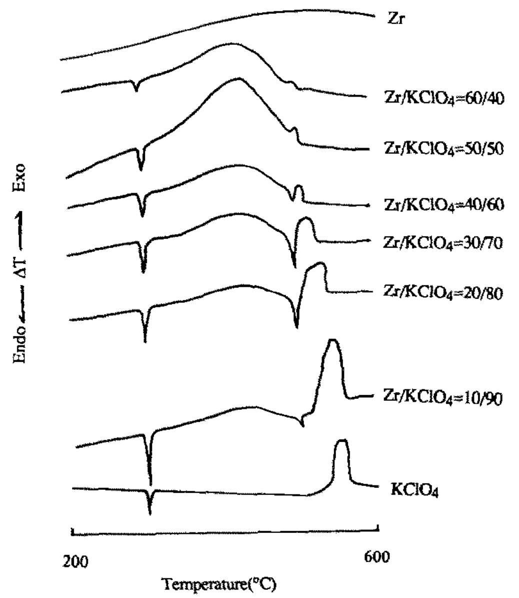

Fig. 3. DTA curves of Zr, $KClO_4$ and the $Zr/KClO_4$ primer mixtures in an air atmosphere at a heating rate of $10\,°C\ min^{-1}$.

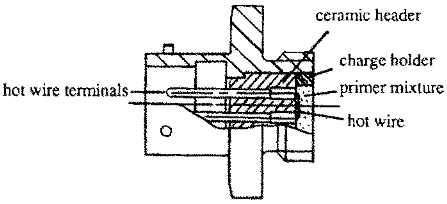

Fig. 4. Cross section of pressure cartridge.

reaching a maximum at 50–60% Zr, a result similar to that reported earlier [8].

The TG and DTA plots of Zr metal powder, Zr/$KClO_4$ primer mixtures and $KClO_4$ are shown in Figs. 2 and 3. The TG curves shows that the weight of Zr/$KClO_4$ primer mixtures with Zr content above 70 wt.% increases, quite unlike the behaviour of standard primer mixtures. Such mixtures will not be useful as primers in EEDs.

The DTA curves exhibit an endotherm near 305 °C, followed by a broad exotherm and a second exotherm 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 exotherm indicates the reaction between Zr and $KClO_4$ and the second exotherm shows the decomposition of residual unreacted $KClO_4$. The second exotherm increases as the Zr content decreases, producing primer mixtures of poorer performance.

The configuration of pressure cartridges made by the pilot scale process is shown in Fig. 4 and the physical properties of the hot wire and primer

TABLE 1

Properties of pressure cartridge materials

Hot wire material (Deguss Pt/Ir 80/20 alloy)	
Resistance (Ω)	1.0 ± 0.1
Resistance/length (Ω cm^{-1})	4.38
Wire length (cm)	0.28
Wire diameter (cm)	0.003
Length : diameter ratio	93.3
Distance between posts (cm)	0.28
A_w (surface area) (cm^2)	0.002638
A_{cs} (cross-sectional area) (cm^2)	0.00000765
A_w/A_{cs}	373.4
Density (g cm^{-3})	21.4
Temp. coefficient of resistance (α_b) (°C^{-1})	0.0008
Primer mixture material (Zr/$KClO_4$ blend)	
Particle size (μm)	$\leqslant 44$
Density (g cm^{-3})	2.8

TABLE 2

Bruceton test record of a pressure cartridge containing a primer mixture of 40 wt.% Zr content

Firing current (A)	Shot number [a]																																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
1.885	x																						x		x		x				x		x	
1.842		x																		x		o		o		o		x		o		o		o
1.8			x		x		x				x		x		x				o		o								o					
1.759				o		o		x		o		o		o		x		o																
1.719									o								o																	

I	i	F (n)	NF (n)	A in	B i^2n			
						$R = 99.99\%$	$C = 95\%$	
						$D = 0.01$		
0.2752	4	6				$n = 17$	$Zr = 3.72$	$I_m - ZrS = 0.1885$
0.2652	3	3	6	18	54	$A = 30$	$t = 1.745$	$I_{nf} = 1.38$ A
0.2552	2	6	3	6	12	$I_o = 0.2352$		
0.2452	1	2	6	6	6	$B = 72$		
0.2352			2			$I_m = 0.2578$		
	sum	17	17	30	72	$M = 1.1211$		
						$S = 0.01863$		

[a] x denotes fired; o denotes did not fire.

TABLE 3

Bruceton test record of a pressure cartridge containing a primer mixture of 50 wt.% Zr content

Firing current (A)	Shot number [a] 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
1.928	x																												x		x		x	
1.885		x						x		x														x		x		o		o		o		o
1.842			x		x		o		o		x								x		x		o		o		o							
1.8				o		o						x		x		x		o		o		o												
1.759													o		o		o																	

I	i	F (n)	NF (n)	A in	B i^2n			
						$R = 99.99\%$	$C = 95\%$	
						$D = 0.01$		
0.2852	4	4				$n = 17$	$Zr = 372$	$I_m - ZrS = 0.2001$
0.2752	3	5	4	12	36	$A = 27$	$t = 1.745$	$I_{nf} = 1.56$ A
0.2652	2	5	5	10	20	$I_c = 0.2452$		
0.2552	1	3	5	5	5	$B = 61$		
0.2452			3			$I_m = 0.2661$		
	sum	17	17	27	61	$M = 1.0657$		
						$S = 0.01773$		

[a] x denotes fired, o denotes did not fire.

TABLE 4

The threshold firing current and maximum no-fire current within 5 min for pressure cartridges of various Zr contents

Composition of primer mixture	Threshold firing current (A)	Maximum no-fire current within 5 min (A)
$Zr/KClO_4 = 40/60$	1.759	1.38
$Zr/KClO_4 = 50/50$	1.800	1.56

TABLE 5

Autoignition temperature of $Zr/KClO_4$ primer mixtures

Primer mixture	Autoignition temperature (°C)
$Zr/KClO_4 = 60/40$	363
$Zr/KClO_4 = 50/50$	365
$Zr/KClO_4 = 40/60$	361
$Zr/KClO_4 = 30/70$	361
$Zr/KClO_4 = 20/80$	359
$Zr/KClO_4 = 10/90$	353

mixtures are listed in Table 1. Results of the Bruceton test (Tables 2 and 3) and statistical calculation, allowed the threshold firing current and no-fire characteristics to be calculated (Table 4). The data indicate that these pressure cartridges possess 1 A/1 W, 5 min, no-fire character.

The autoignition temperature of the $Zr/KClO_4$ primer mixtures with Zr content lower than 70 wt.% were obtained using the DTA method described and results are reported in Table 5. Since the autoignition temperatures reported here are based on a minimal heating rate, it is theoretically possible for ignition to occur at lower temperature. However, in general, the maximum hot wire temperature of a normal 1 A/1 W, 5 min, no-fire EED will not exceed 185 °C [10], far below the autoignition temperature. Therefore, the primer mixtures of 40–60% Zr content are suitable for 1 A/1 W, 5 min, no-fire EEDs.

CONCLUSIONS

Thermal analysis of $Zr/KClO_4$ primer mixtures shows that those of 40–60 wt.% Zr content are suitable for producing 1 A/1 W, 5 min, no-fire pressure cartridges.

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