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THERMAL BEHAVIOUR AND FIRING CHARACTERISTICS OF $Zr/KClO_4$ PRIMER MIXTURE CONTAINING DIFFERENT PARTICLE SIZES OF ZIRCONIUM

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ABSTRACT

The effect of the particle size of zirconium on the thermal behaviour and firing characteristics of $Zr/KClO_4$ primer mixtures was studied by thermoanalytical techniques. A pilot-scale process was developed for preparing pressure cartridges whose primer mixtures had different particle sizes of zirconium. The firing characteristics were evaluated by Bruceton's method and its related calculation. It was found that the $Zr/KClO_4$ primer mixture with average particle size of 3 or 5 μm is a suitable primer mixture for 1 A 1 W^{-1}, 5 min, No-Fire pressure cartridges.

INTRODUCTION

$Zr/KClO_4$ is a primer mixture capable of withstanding prolonged high temperatures, with no measurable change in the thermal cycle, [1]. This mixture is also typical of those being used by commercial producers to obtain 1 A 1 W^{-1}, 5 min, No-Fire electroexplosive devices [2]. In this study, the effect of the particle size of zirconium in $Zr/KClO_4$ primer mixtures on the thermal behaviour was investigated using thermogravimetry (TG) and differential thermal analysis (DTA). The mixtures with different particle sizes of zirconium, were then pressed into the charge holder of the pressure cartridges in order to produce the samples for the Bruceton test. The firing characteristics of the pressure cartridges were determined by following a statistical calculation [3].

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EXPERIMENTAL DETAILS

The zirconium metal powder used in these studies, supplied by Degussa, Germany, has an average particle size of 1.7 + 0.2, 3 + 0.5 and 5 + 0.5 μm with a purity of 96.5 $\pm$ 0.5%, 98.5 $\pm$ 0.5% and 99 $\pm$ 0.5% of zirconium plus hafnium respectively. Potassium perchlorate was obtained from Ferak Berlin Corporation, Germany, with a purity of 99.5%; it was first ground using a mortar and pestle and the fraction passing through 325 mesh (N.B.S.) was taken. A Mettler TG 50 thermobalance with a TA 3000 system, and a Rigaku-Denki model 8121 DTA were used in an atmosphere of air with a heating rate of 10 °C min^{-1}. The sample size was restricted to less than 5 mg and the DTA reference material was finely powdered α-Al_2O_3.

RESULTS AND DISCUSSION

The firing current–function time curve for the pressure cartridges are shown in Fig. 1. In this investigation, the test cartridge was assembled in a suitable closed test chamber. A direct current was applied to one hot wire circuit and the pressure–time curve was recorded. The function time of the pressure cartridge is identical to the time from the application of the firing current to 10% of peak pressure. Figure 1 shows that when a direct current of 5 A is applied to one hot wire, the function time does not exceed 5 ms.

Figure 2 shows the DTA plots for zirconium metal powder, Zr/$KClO_4$ primer mixtures with different particle sizes of zirconium and for $KClO_4$. The DTA curves for different particle sizes of zirconium in the Zr/$KClO_4$ primer mixtures exhibit an endothermic peak near 305 °C, followed by a

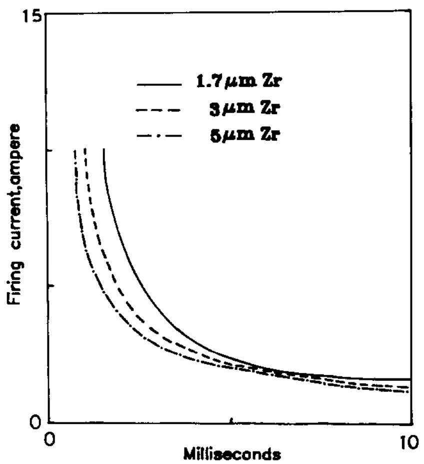

Fig. 1. Time from application of current to 10% peak pressure. Function of time vs. current for pressure cartridge with different particle sizes of zirconium.

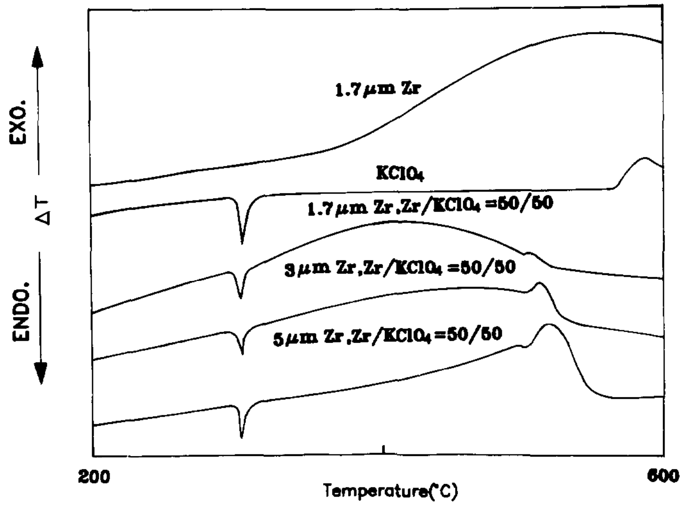

Fig. 2. DTA curves of zirconium, $KClO_4$ and primer mixtures of $Zr/KClO_4$ with different particle sizes of zirconium, in air atmosphere with a 10 °C min^{-1} heating rate.

broad exothermic peak, and a second exothermic peak at higher temperatures. The endothermic peak indicates the characteristic crystalline transition of $KClO_4$ from a rhombic to a cubic lattice at about 305 °C [4–8] and the broad exothermic peak indicates the reaction between zirconium and $KClO_4$. The second exothermic peak shows the decomposition of the remaining unreacted $KClO_4$. The broad exothermic peak becomes smoother and the second exothermic peak increases with increasing average particle size of zirconium. The temperature of the exothermic peaks also increased

TABLE 1

Pressure cartridge data

Hot-wire material	Degussa Pt/Ir 80/20 alloy
Resistance	$1.0 \pm 0.1\ \Omega$
Resistance/length	$4.38\ \Omega\ cm^{-1}$
Wire length (L)	0.28 cm
Wire diameter (D)	0.003 cm
L/D	93.3
Distance between posts	0.28 cm
A_w (suface area)	$0.002683\ cm^2$
A_{cs} (cross-sectional area)	$0.00000765\ cm^2$
A_w/A_{cs}	373.4
Density	$21.4\ g\ cm^{-3}$
Resistivity αb	$0.0008\ °C^{-1}$
Primer mixture material	$Zr/KClO_4$ blend
Particle size	$\leqslant 44\ \mu m$
Density	$2.8\ g\ cm^{-3}$

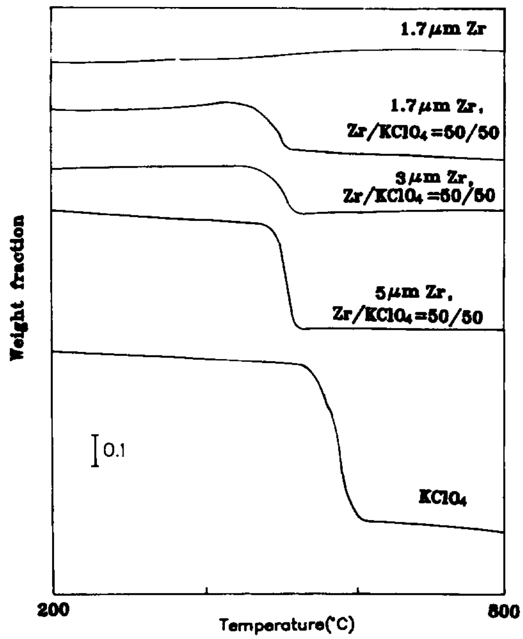

Fig. 3. TG curves of zirconium, $KClO_4$ and primer mixtures of $Zr/KClO_4$ with different particle sizes of zirconium, in an atmosphere of air with $10\,^{\circ}C\ min^{-1}$ heating rate.

with increasing average particle size of zirconium. This means that the $Zr/KClO_4$ primer mixtures with the larger average particle sizes of zirconium will explode at higher temperatures.

The TG plots for 1.7 μm zirconium metal powder, $KClO_4$ and three different particle sizes of zirconium in the $Zr/KClO_4$ primer mixture are given in Fig. 3. The TG curves show that the initial weight-loss temperature increases when a larger average particle size of zirconium is used in the $Zr/KClO_4$ primer mixture. The TG experiment gave the same result as the DTA.

The configuration of the pressure cartridge in the pilot-scale process is shown in Fig. 4, and the physical properties of the hot wire and primer mixture are listed in Table 1.

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

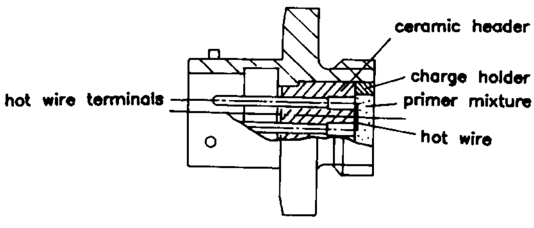

Fig. 4. Cross-section of pressure cartridge.

TABLE 2

Bruceton test record of pressure cartridge with 1.7 ± 0.2 μm Zr, 50 wt.% Zr in primer mixture (for No-Fire test) [a]

Lever	Current (A)	1	2	3	4	5	6	7	8	9	0	-	2	3	4	5	6	7	8	9	0	-	2	3	4	5	6	7	8	9	0	-	2	3	4
4	1.316																																		
3	1.257		X						X												X						0		X		X				X
2	1.200	0		X		X		0		X				X				X		0		X				0				0		X		0	
1	1.146				0		0				X		0		X		0		0				X		0								0		
0	1.094											0				0								0											

I	i^2	N	iN	i^2N	M	iM	i^2M
4	16	1	4	16	0	0	0
3	9	6	18	54	1	3	9
2	4	7	14	28	6	12	24
1	1	3	3	3	7	7	7
0	0	0	0	0	3	0	0

	X	0
N	17	17
A	39	22
B	101	40
M	0.6782	0.6782
m	0.0751	0.0751
s	0.0236	0.0236

$d = 0.02$
$m = 0.0751$
$s = 0.0236$
$s/d = 1.1809$
$G = 0.9864$
$H = 1.4550$
$\delta_m = 0.0057$
$\delta_s = 0.0083$
$t = 2.1199$

$R = 99.99\%$ $C = 95\%$

$I_{NF} = 0.8326$ (A)

[a] X, fired; 0, did not fire.

TABLE 3

Bruceton test record of pressure cartridge with 3 + 0.5 μm Zr, 50 wt.% Zr in primer mixture (for No-Fire test) [a]

Lever	Current (A)	1	2	3	4	5	6	7	8	9	0	-	2	3	4	5	6	7	8	9	0	-	2	3	4	5	6	7	8	9	0	-	2	3	4
3	1.361							X								X						X		X		X								X	
2	1.330				X		0		X		X				0		X		X		0		0		0		X		X				0		0
1	1.300	X		0		0				0		X		0				0		0								0		X		0			
0	1.270		0										0																			0			

I	i^2	N	iN	i^2N	M	iM	i^2M
3	9	6	18	54	0	0	0
2	4	7	14	28	7	14	28
1	1	3	3	3	8	8	8
0	0	0	0	0	3	0	0

	X	0
N	16	18
A	35	22
B	85	36
M	0.5273	0.5062
m	0.1208	0.1212
s	0.0093	0.0089

$d = 0.01$
$m = 0.1210$
$s = 0.0091$
$s/d = 0.9105$
$G = 1.0180$
$H = 1.3522$
$\delta_m = 0.0022$
$\delta_s = 0.0030$
$t = 2.1199$

$R = 99.99\%$ $C = 95\%$

$I_{NF} = 1.1823$ (Å)

[a] For notation, see footnote to Table 1.

TABLE 4

Bruceton test record of pressure cartridge with 5 ± 0.5 μm Zr, 50 wt.% Zr in primer mixture (for No-Fire test) [a]

Lever	Current (A)	1	2	3	4	5	6	7	8	9	0	-	2	3	4	5	6	7	8	9	0	-	2	3	4	5	6	7	8	9	0	-	2	3	4
4	1.623																									X									
3	1.586																		X				X		0		X								
2	1.550	X		X				X				X		X				0		X		0		0				X		X		X			
1	1.515		0		X		0		X		0		0		X		0				0								0		0		X		X
0	1.480					0				0						0																		0	

I	i^2	N	iN	i^2N	M	iM	i^2M
4	16	1	4	16	0	0	0
3	9	3	9	27	1	3	9
2	4	9	18	36	3	6	12
1	1	5	5	5	8	8	8
0	0	0	0	0	4	0	0

	X	0
N	18	16
A	36	17
B	84	29
M	0.6667	0.6836
m	0.1853	0.1860
s	0.0116	0.0119

$d = 0.01$
$m = 0.1856$
$s = 0.0118$
$s/d = 1.1751$
$G = 0.9870$
$H = 1.4528$
$\delta_m = 0.0028$
$\delta_s = 0.0041$
$t = 2.1199$

$R = 99.99\%$ $C = 95\%$

$I_{NF} = 1.3230$ (A)

[a] For notation, see footnote to Table 1.

TABLE 5

Bruceton test record of pressure cartridge with 1.7 ± 0.2 μm Zr, 50 wt.% Zr in primer mixture (for All-Fire test) [a]

Lever	Current (A)	1	2	3	4	5	6	7	8	9	0	-	2	3	4	5	6	7	8	9	0	-	2	3	4	5	6	7	8	9	0	-	2	3	4
4	1.315										X		X										X						X		X				X
3	1.285									0		0		X		X		X				0		X				0		0		X		0	
2	1.256		X				X		0						0		0		X		0				X		0						0		
1	1.227	0		X		0		0												0						0									
0	1.199				0																														

I	i^2	N	iN	i^2N	M	iM	i^2M
4	16	6	24	96	0	0	0
3	9	5	15	45	6	18	54
2	4	4	8	16	6	12	24
1	1	1	1	1	5	5	5
0	0	0	0	0	1	0	0

	X	0
N	16	18
A	48	35
B	158	83
M	0.8750	0.8302
m	0.1038	0.1033
s	0.0151	0.0143

$d = 0.01$
$m = 0.1036$
$s = 0.0147$
$s/d = 1.4706$
$G = 0.9655$
$H = 1.5618$
$\delta_m = 0.0034$
$\sigma_s = 0.0056$
$t = 2.1199$

$R = 99.99\%$ $C = 95\%$

$I_F = 1.5353$(A)

[a] For notation, see footnote to Table 1.

TABLE 6

Bruceton test record of pressure cartridge with 3 ± 0.5 μm Zr, 50 wt.% Zr in primer mixture (for All-Fire test) [a]

Lever	Current (A)	1	2	3	4	5	6	7	8	9	0	-	2	3	4	5	6	7	8	9	0	-	2	3	4	5	6	7	8	9	0	-	2	3	4
4	1.570				X								X		X														X						
3	1.534	X		0		X						0		0		X										X		0		X					
2	1.499		0				X				0						X				X		X		0		0				X				X
1	1.465							X		0								X		0		0		0								X		0	
0	1.432								0										0														0		

I	i^2	N	iN	i^2N	M	iM	i^2M
4	16	4	16	64	0	0	0
3	9	5	15	45	4	12	36
2	4	6	12	24	4	8	16
1	1	3	3	3	5	5	5
0	0	0	0	0	3	0	0

	X	0
N	18	16
A	46	25
B	136	57
M	1.0247	1.1211
m	0.1764	0.1765
s	0.0176	0.0192

$d = 0.01$
$m = 0.1764$
$s = 0.0184$
$s/d = 1.8373$
$G = 0.9485$
$H = 1.6924$
$\delta_m = 0.0042$
$\delta_s = 0.0075$
$t = 2.1199$

$R = 99.99\%$ $C = 95\%$

$I_F = 1.9204$ (A)

[a] For notation, see footnote to Table 1.

TABLE 7

Bruceton test record of pressure cartridge with 5 ± 0.5 μm Zr, 50 wt.% Zr in primer mixture (for All-Fire test) [a]

Lever	Current (A)	1	2	3	4	5	6	7	8	9	0	-	2	3	4	5	6	7	8	9	0	-	2	3	4	5	6	7	8	9	0	-	2	3	4
4	1.780				X																X		X												X
3	1.739	X		0		X		X						X						0		0		X				X						0	
2	1.699		0				0		X				0		X		X		0						X		0		X		X		0		
1	1.661									X		0				0		0								0				0		0			
0	1.623										0																								

I	i^2	N	iN	i^2N	M	iM	i^2M
4	16	4	16	64	0	0	0
3	9	6	18	54	4	12	36
2	4	6	12	24	6	12	24
1	1	1	1	1	6	6	6
0	0	0	0	0	1	0	0

	X	0
N	17	17
A	47	30
B	143	66
M	0.7682	0.7682
m	0.2329	0.2329
s	0.0133	0.0133

$d = 0.01$
$m = 0.2329$
$s = 0.0133$
$s/d = 1.3312$
$G = 0.9745$
$H = 1.5108$
$\delta_m = 0.0031$
$\delta_s = 0.0049$
$t = 2.1199$

$R = 99.99\%$ $C = 95\%$

$I_F = 2.2064$ (A)

[a] For notation, see footnote to Table 1.

is tested at a time. Before the Bruceton test proper can be commenced, it is necessary to determine the approximate amperage at which 50% of the parts will fire. 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.

In this report, pressure cartridges with different particle sizes of zirconium were divided into two groups; for each group, at least 30 pressure cartridges should be fired in the Bruceton test to produce reliable data. For No-Fire testing, the d.c. current is applied to the pressure cartridge for at least 5 min; if the pressure cartridge does not fire, this is recorded as "0" in the table. The second shot will then be at the next higher level. A 34-units Bruceton No-Fire test was conducted. The data and analysed results are tabulated in Tables 2–4. For All-Fire testing, the d.c. current is applied to the pressure cartridge for 30 ms; if the pressure cartridge response is within 30 ms, this is recorded as "X" in the table. The second shot will then be at the next lower level. A 34-units Bruceton All-Fire test was also conducted in this case. The Bruceton All-Fire data and relative results are shown in Tables 5–7.

The data from the Bruceton tests show that the pressure cartridge has a 1 A 1 W^{-1}, 5 min, No-Fire character, except when the average particle size of zirconium is 1.7 ± 0.2 μm. The maximum No-Fire current and the minimum All-Fire current of the pressure cartridge were increased by increasing the average particle size of zirconium.

CONCLUSION

The thermal behaviour and firing characteristics of $Zr/KClO_4$ primer mixtures with different particle sizes of zirconium, were analysed by DTA, TG and the Bruceton test. The primer mixture having an average zirconium particle size of 3 or 5 μm is suggested as a suitable primer mixture for producing 1 A 1 W^{-1}, 5 min, No-Fire pressure cartridges.

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