Note

Ignition and reaction of boron fueled pyrotechnic
delay compositions

Part 1. Boron–potassium dichromate and boron–silicon–potassium dichromate systems

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From a study of the burning of $W–BaCrO_4–KClO_4$ gasless pyrotechnic delay compositions Zimmer-Galler[1] concluded that tungsten delay compositions had no liquid reaction zone and the burning rate was primarily controlled by the thermal conductivity of the system. Hössjer[2], investigating the ignitability and reaction mechanisms of three series of systems $Sn–CuO–PbCrO_4$, $Sn–CuO$ and $BaCrO_4–Ni–Zr–Bonosol$, considered transport processes involving gas, liquid and solid phases. Mechanisms were rationalized in terms of gas phase transport ($Sn–CuO$) and solid phase diffusion ($BaCrO_4–Zr–Ni–Bonosol$). Similarly Sulacsik[3] proposed partial release of O_2 from MnO_2 followed by gaseous diffusion as initial steps in the mechanism of combustion for the delay system $MnO_2–FeSi90$.

In contrast, this note shows that for the $B–K_2Cr_2O_7$ system the ignition process is dependent on transport in the liquid phase. The combustion zone then propagates as a molten front. This explanation can be extended to describe the combustion process in the two-fuel $B–Si–K_2Cr_2O_7$ system.

EXPERIMENTAL

Investigations in the temperature range from ambient to 770 K (instrument limit) were carried out using a Perkin-Elmer differential scanning calorimeter (DSC-1B). Samples of 10 mg were heated in open aluminium pans at heating rates of 8 and 16 K min^{-1} with ordinate sensitivity from 8 to 64 mcal sec^{-1} full scale deflection. Studies were performed in an atmosphere of flowing dried oxygen (flow-rate 40 cm^3 min^{-1}).

Compositions were prepared by dry-mixing the component materials. Average particle sizes of ingredients were: boron, 1 μm; silicon, 4 μm; potassium dichromate, 5 μm; sodium dichromate, 5 μm.

Each ingredient was examined separately under conditions described above. Formulations of $B-K_2Cr_2O_7$, $Si-K_2Cr_2O_7$ and $B-Si-K_2Cr_2O_7$ were similarly investigated. The systems were further studied by replacing potassium dichromate with sodium dichromate and with a 50:50 mixture of both dichromates. Materials and formulations investigated together with thermal analysis data, are detailed in Table 1.

TABLE 1

FORMULATION INVESTIGATED AND DSC RESULTS

Components	Composition	Transition temperature (K)		
		Fusion	Ignition	Combustion
Boron	100	Small endotherm at 380 K, then inert		
Silicon	100	—	—	—
$K_2Cr_2O_7$	100	663	—	—
$Na_2Cr_2O_7$	100	592	—	—
$K_2Cr_2O_7-Na_2Cr_2O_7$	50:50	570	—	—
		excess $K_2Cr_2O_7$ 633		
$B-K_2Cr_2O_7$	4:96	660–665	660	660–670
$B-K_2Cr_2O_7$	10:90	660–665	660	660–670
$B-Na_2Cr_2O_7$	4:96	590–600	590	590–620
$B-Na_2Cr_2O_7$	10:90	masked by combustion	590	590–610
$B-K_2Cr_2O_7-Na_2Cr_2O_7$	4:48:48	570	570	570–650, 650–666
$B-K_2Cr_2O_7-Na_2Cr_2O_7$	10:45:45	570	570	570–650, 650–666
$Si-K_2Cr_2O_7$	5:95	660	—	—
$Si-K_2Cr_2O_7$	20:80	660	—	—
$B-Si-K_2Cr_2O_7$	4:5:91	masked by combustion	659	659–673
$B-Si-K_2Cr_2O_7$	10:20:70	masked by combustion	659	659–700
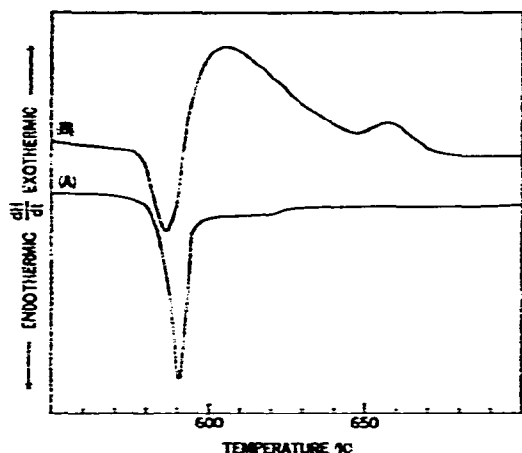
Fig. 1. DSC curves of (A) $Na_2Cr_2O_7-K_2Cr_2O_7$, 50:50. (B) $B-Na_2Cr_2O_7-K_2Cr_2O_7$, 4:48:48. 10 mg samples heated at 16 K min^{-1} in flowing dried oxygen.

RESULTS

Apart from a small endotherm in the region of 380 K for amorphous boron, the boron and silicon fuels are inert up to 770 K. The oxidants potassium dichromate and sodium dichromate melt at 663 and 592 K, respectively, but undergo no other thermal processes. The 50:50 mixture of sodium and potassium dichromate shows melting at the solidus, 570 K, dissolution of further potassium dichromate in the melt followed by melting of the excess potassium dichromate to the liquidus at 633 K (Fig. 1A).

Figure 2 illustrates curves obtained for the boron–oxidant mixtures. Silicon–oxidant mixtures did not react within the temperature range investigated. Curves for the three-component system boron–silicon–potassium dichromate are shown in Fig. 3.
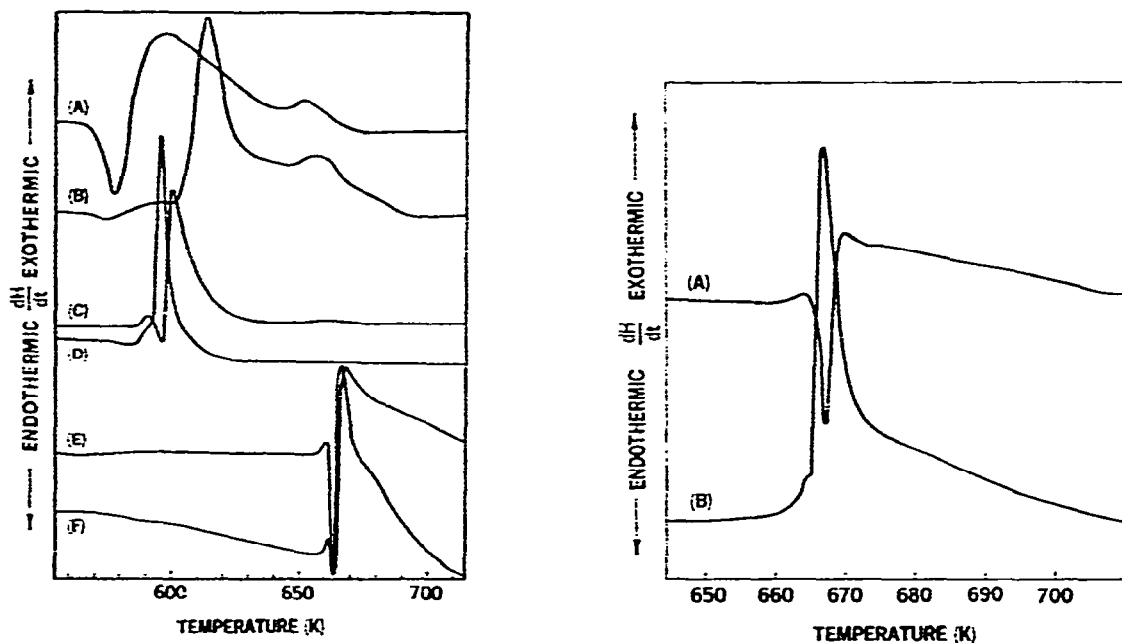

Fig. 2. DSC curves of (A) $B-K_2Cr_2O_7-Na_2Cr_2O_7$, 4:48:48. (B) $B-K_2Cr_2O_7-Na_2Cr_2O_7$, 10:45:40. (C) $B-Na_2Cr_2O_7$, 4:96. (D) $B-Na_2Cr_2O_7$, 10:90. (E) $B-K_2Cr_2O_7$, 4:96. (F) $B-K_2Cr_2O_7$, 10:90. 10 mg samples heated at 16 K min^{-1} in flowing dried oxygen.

Fig. 3. DSC curves of (A) $B-Si-K_2Cr_2O_7$, 4:5:91. (B) $B-Si-K_2Cr_2O_7$, 10:20:70. 10 mg samples heated at 16 K min^{-1} in flowing dried oxygen.

DISCUSSIONS

It can be seen that for the boron–oxidant systems (Fig. 2) all formulations show ignition and combustion in the region of oxidant fusion. With either sodium or potassium dichromate as oxidant, the combustion process is recorded as a single

exotherm immediately following the onset of dichromate fusion. Upon heating the 50:50 mixed oxidant composition (Fig. 1B, 2A and B) the DSC curves show melting at the solidus (570 K) accompanied by ignition and combustion of fuel. As the sample is further heated excess potassium dichromate melts, providing a supply of molten oxidant for the burning fuel, until the liquid phase is exhausted. A much broader exotherm than that for single oxidant systems results. When the remaining solid potassium dichromate melts at 660 K, a further exotherm occurs as the residual fuel burns.

In all cases, evidence of the melting endotherm is visible although in the more fuel-rich formulations it does not appear to be as large. With increased boron content exothermic reaction between fuel and molten oxidant occurs more rapidly, thus more nearly balancing out the endothermic fusion peak.

The coincidence of oxidant fusion and sample ignition temperature, and the dependence on the continued presence of liquid phase oxidant for propagation of the combustion process show that in the boron–dichromate system the rate-determining step involves a solid–liquid phase reaction between boron and the molten oxidant.

In the boron–silicon–dichromate system (Fig. 3), again ignition occurs immediately after fusion of the oxidant. Since binary silicon–dichromate mixtures do not ignite in this region, it is proposed that the ignition process and initial reaction in the two-fuel system is the same as for boron–dichromate formulations. The boron burns in a matrix of molten oxidant, then at a later stage the silicon reacts as a back-up reaction, burning with a lower rate of energy release than boron. This results in a slower burning, less energetic composition and extends the effective delay time of the formulation.

CONCLUSION

In contrast to previously reported pyrotechnic delay systems[1-3] and the boron–lead oxide system[4], boron–potassium dichromate and boron–silicon-potassium dichromate systems are dependent on liquid phase transport for ignition. The reaction zone then propagates as a molten front. This mechanism may account for the apparently anomalous effect of pressure on burning rate[5].

REFERENCES

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