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Thermoanalytical Studies on Pyrotechnic Reactions

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Thermogravimetry and DSC studies on a number of propagative pyrotechnic delay compositions have been made to study the reaction mechanism. The binary fuel/oxidant pyrotechnic systems were selected to provide the following fuel/oxidant phases at the temperature of the reaction: a) Molten fuel/solid oxidant, b) Solid fuel/molten oxidant, c) Solid fuel/solid oxidant and d) Solid fuel/decomposed oxidant. An attempt has been made to correlate the type of DSC trace with the reaction mechanism. Results showed that the temperature at which the oxidant undergoes physical or chemical changes has a significant role to play at the start of the main reaction. If either fuel or oxidant is in molten form at the reaction temperature, it results to a single exothermic peak. With truly solid-solid reactions, DSC traces have a double peak appearance.

INTRODUCTION

Thermoanalytical methods play an important role in the study of pyrotechnic reactions, since they thermally simulate the conditions in the propagation wave by following the reaction at high temperature. In applying dynamic thermal analysis methods, valuable information about the mechanism of reactions could be obtained from a single experiment. Such information is a prerequisite in the formulation and design of pyrotechnic devices. In order to improve the stability and repeatability of the linear burning time of pyrotechnic delay compositions, knowledge of the combustion mechanism of the mixture is required [1]. Due to high sensitivity, a Differential Scanning Calorimeter (DSC) can provide detailed information on the mechanism of combustion reactions [2,3]. DSC traces relating to any combustion reaction are generally represented by (an) exothermic peak(s). Such exothermic traces could be a consequence of one of many possible reaction mechanisms. Therefore, further tests and analysis will be needed in order to find out the reaction mechanism that such DSC traces represent. This work is an attempt to classify the types of DSC traces of pyrotechnic reactions, in terms of the mechanism of the reaction that takes place, thus, being able to readily interpret the DSC traces, in terms of the reaction mechanism and to obtain the necessary information from a single DSC test. Furthermore, in this report, DSC analyses of a number of propagative pyrotechnic systems have been made; the resulting DSC traces of such compositions were interpreted and correlation between the reaction mechanism and DSC traces were discussed.

The binary fuel/oxidant pyrotechnic systems were selected so that, at the temperature of the reaction, they would have the following different fuel/oxidant phases: a) Molten fuel/solid oxidant, b) Solid fuel/molten oxidant, c) Solid fuel/solid oxidant and d) Solid fuel/decomposed oxidant. The DSC traces of such systems were compared and discussions on the mechanism of reactions represented by DSC peaks took place. Thermogravimetry analysis was used as an aid to such studies.

EXPERIMENTAL TECHNIQUES

DSC measurements were performed in the temperature range of ambient to 725°C, using a Perkin Elmer DSC-2. Samples of 3-10 mg were heated in aluminum sample pans at a heating rate of 2.5-20°C/min with ordinate sensitivity from 0.1 to 20 mcal/s (0.4-83 mJ/s) full-scale deflection. Experiments were carried out in air and argon atmospheres. TG and DTG analyses were performed using Perkin Elmer TGS-2 equipment. Samples of any weight up to 1000 mg can be used with

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Table 1. Specification of materials.

Material	Particle Size μm	Surface Area m^2/gr	Purity %
Si	3.9	2.5	>98
PbO	18.5	0.19	>98
Pb_3O_4	5	0.42	>98
$KMnO_4$	-	0.46	99.5
Sb	4.6	0.509	98.5
$K_2Cr_2O_7$	-	-	>98
B	-	7.96	96
Mo	5.6	0.23	>97
BaO_2	20	-	>90
Se	15	-	97

the TGS-2 and it also possesses facilities to suppress, electronically, up to 1000 mg of the weight, so that a fraction of sample weight can be displayed on the Y-axis of the pen recorder.

MATERIALS

Powdered metals and oxidants were supplied by Goodfellow Metals and BDH, with the purity above 96%. $KMnO_4$ crystals were powdered by rubbing lightly in an agate mortar before mixing with Sb powder. Compositions were prepared by dry-mixing the components. The average particle size and surface area of materials are presented in Table 1. The particle size of the powdered materials was measured using a Coulter Counter Model TA instrument and the surface area was measured utilizing a Strohlein area meter (Model OPI-Bd 119-E). This method is based on low temperature nitrogen adsorption, according to Brunauer, Emmet and Teller (BET Method).

RESULTS

Molten Fuel/Solid Oxidant Reactions

A selenium/barium peroxide mixture was studied in this category. Figure 1 shows a DSC trace corresponding to the 40/60 (gr/gr) mixture of Se/BaO_2, heated under a flowing argon atmosphere. Selenium was melted at 211°C, as indicated by a sharp endothermic peak on the DSC curve. The exothermic oxidation reaction of the molten selenium with barium peroxide is observed at around 350°C by the onset of a single exothermic peak.

The exothermic curve representing the oxidation of Se attained a maximum value at 420°C before returning to the zero line at 520°C. Changing the fuel/oxidant ratio did not alter the peak pattern, however, the size of the exothermic reaction peak is larger with the stochiometric mixture (37/63) and the size of the endothermic peak, corresponding to the melting, increases with an increase in the Se content of the test samples.

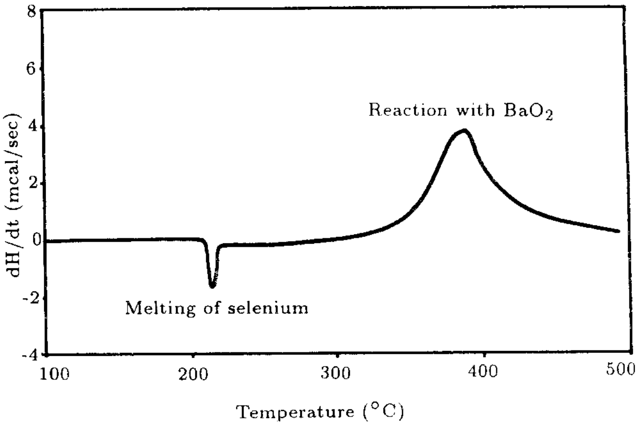

Figure 1. DSC trace of 40/60 mixture of Se/BaO_2 heated under argon atmosphere, heating rate 20°C/min.

Solid Fuel/Molten Oxidant

A DSC trace, relating to the reaction between boron and potassium dichromate under an argon atmosphere, is shown in Figure 2. A single exothermic peak at around 396°C is observed. The reaction of $K_2Cr_2O_7$ with molybdenum also resulted in the formation of a single exothermic peak at the same temperature range of around 396°C. This is the temperature at which $K_2Cr_2O_7$ melts, although both boron and molybdenum retain their solid form. The oxidation reaction, therefore, takes place at the solid-liquid phase. On DSC traces, the endothermic melting of the oxidant is superimposed by the exothermic oxidation reactions.

Since melting is a single-phase process, it was possible to separate the melting endotherm from the exothermic reaction peak with fast heating rates, as shown in Figure 3.

Berger et al. [4] studied the solid-solid oxidation of boron by $KClO_4$ in the presence of 1% nitrocellulose.

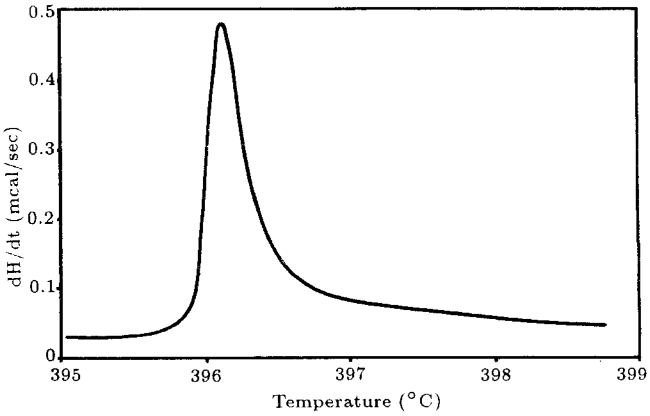

Figure 2. DSC trace of 30/70 mixture of $B/K_2Cr_2O_7$ under argon atmosphere, heating rate 2.5°C/min.

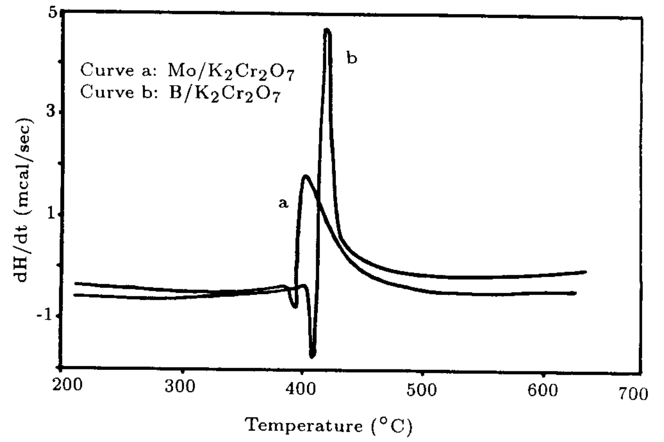

Figure 3. DSC traces of $Mo/K_2Cr_2O_7$ and $B/K_2Cr_2O_7$ compositions under argon atmosphere, heating rate 10°C/min and 20°C/min, respectively.

From thermal analysis results, it was concluded that oxidation takes place in two stages. A low energy surface oxidation reaction is followed by the main ignition reaction, leading to the formation of two exothermic peaks on the DSC traces. Work on several pyrotechnic systems revealed that the temperature of the solid-solid metal/oxidant reaction is influenced by the activity of the metal used [4,5], whereas, with solid-liquid metal/oxidant reactions, as observed in the present study, oxidation reaction takes place at the melting temperature of the oxidant, with either B or Mo. Further tests on various propagative metal/oxidant pyrotechnic systems are needed in order to generalize the mechanism observed.

Solid Fuel/Solid Oxidant

In Figure 4, DSC traces, corresponding to the solid/solid reactions of silicon with lead oxides, are presented, where both reactants are in solid form at the reaction temperature. This composition has previously been studied in detail [6,7]. Two exothermic peaks at a temperature range of 550 to 770°C represent the oxidation process, the first peak being smaller than the second peak for all mixtures used. With faster heating rates or a higher sample weight, ignition occurs at the temperature range of the second peak. The first peak is due to surface oxidation and the second peak due to bulk reaction. The relative size of the two peaks seems to depend on the particle size and the nature of the reactants, a layer of products being formed on the reactants interface preventing further oxidation at some stage. With an increase in temperature, the reactants diffuse through the product layer and bulk oxidation, with a higher rate of oxidation, takes place.

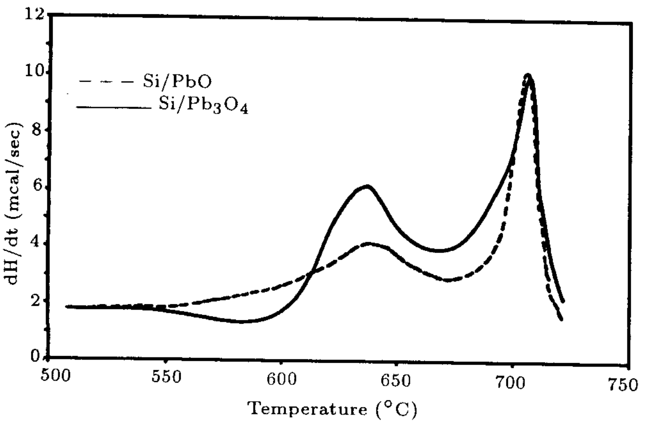

Figure 4. DSC traces 10/90 mixtures of Si/PbO and Si/Pb_3O_4 under argon atmosphere, heating rate 10°C/min.

In a detailed study on propagative PbO/Si and PbO/B compositions, Goodfield [8] showed that the DSC peak pattern obtained for the PbO/B system is somehow more complicated than that obtained for the PbO/Si system, giving DSC traces containing a maximum of four exothermic peaks. Goodfield confirmed, experimentally, that the two-peak DSC trace is typical for a solid-solid reaction between a metallic fuel and oxidant, in the absence of side reactions such as phase change or the further reaction of the products.

Solid Fuel/Decomposed Oxidant

Brown et al. utilized thermomagnetometry, as well as TG and DTA, to study the iron-containing pyrotechnic systems. The pyrotechnic systems were examined with iron powder as fuel and potassium permanganate, barium peroxide or strontium peroxide as oxidant. In all three Fe/oxidant systems, the oxidation of Fe took place either after decomposition of the oxidant or coincided with the oxidation process.

A number of pyrotechnic systems fall into this category, since, in most compositions, the initiation depends on the decomposition of the oxidant and the release of oxygen or active non-gaseous products. Thermogravimetry analysis of such mixtures in loose powdered form, under a static or flowing inert atmosphere, showed that gaseous oxygen, resulting from the decomposition process, leaves the sample without any significant reaction with the metal [9]. However, in the DSC analysis, reaction between the solid decomposition products and the fuel is observed. In Figure 4, the DSC trace, corresponding to the reaction between Si and PbO, resulting from the decomposition of Pb_3O_4, is presented. Thermogravimetry studies have shown [7] that oxygen resulting from the decomposition of Pb_3O_4, leaves the sample, therefore, the DSC trace corresponds to the solid-solid reaction between decomposition product PbO and Si, analogous to the category-C reactions.

However, comparison of DSC traces from the reactions of Pb_3O_4/Si and PbO/Si mixtures, revealed that the first peak was larger with the Pb_3O_4/Si system. This is probably due to the enhanced reactivity of freshly formed PbO from Pb_3O_4 decomposition. The oxidation reaction of the Sb/$KMnO_4$ mixture also begins after decomposition of the oxidant (Figure 5). The TG/DTG traces reveal the occurred weight loss due to the release of oxygen, therefore, no Sb/O_2 reactions occur under a flowing inert atmosphere (Figure 6), similar to the Pb_3O_4/Si system [10].

In a detailed investigation of the thermogravimetry study on iron containing pyrotechnics, Brown [9] showed that a major weight loss occurs when the oxidants decompose at a lower temperature, before onset of the oxidation of Fe. DSC traces of Sb/$KMnO_4$ are relatively complicated (Figure 5), due to the variable valences of Sb and the formation of intermediate oxides of Mn [11,12]. However, DSC traces of the oxidation of powdered antimony in a static air atmosphere, showed two exothermic peaks. Corresponding TG/DTG results showed a two-stage weight gain, due to the surface and bulk oxidation of Sb (Figures 7 and 8).

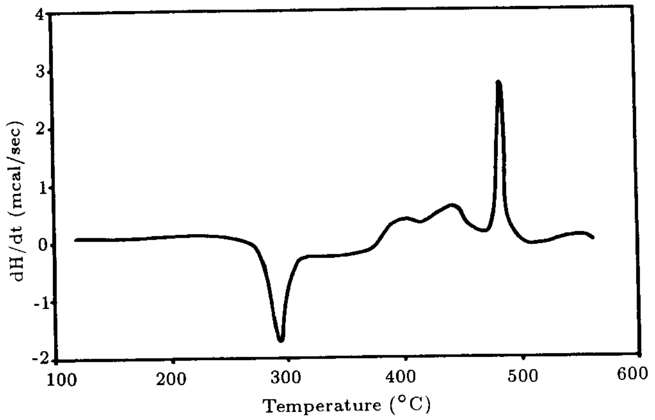

Figure 5. DSC trace of 50/50 mixture of Sb/$KMnO_4$ under argon atmosphere, heating rate 20°C/min.

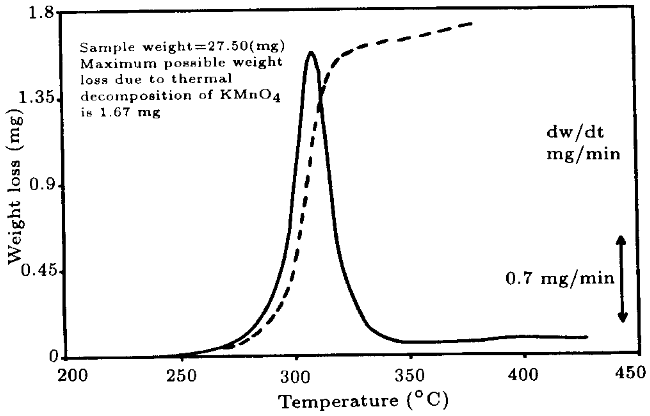

Figure 6. TG/DTG trace of 40/60 mixture of Sb/$KMnO_4$ under argon atmosphere, heating rate 20°C/min.

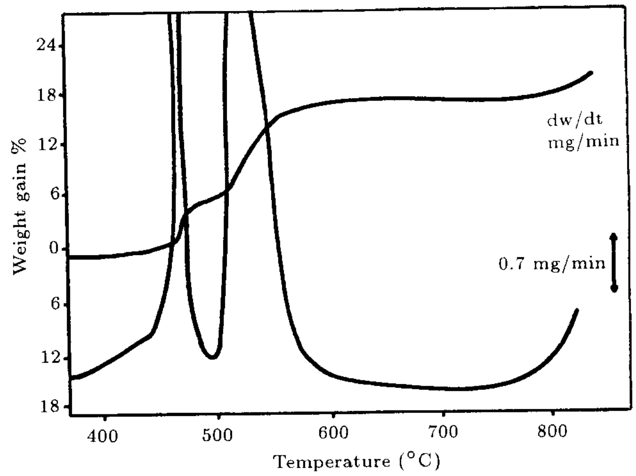

Figure 7. TG/DTG traces of oxidation of antimony in static air atmosphere at heating rate 20°C/min.

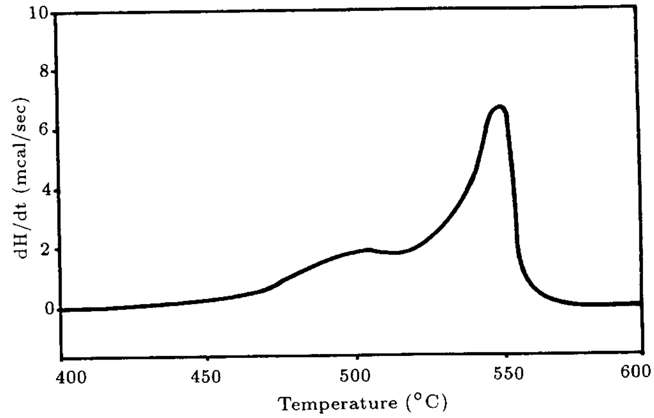

Figure 8. DSC trace of oxidation of antimony in static air atmosphere at heating rate 20°C/min.

DTG results of the oxidation of powdered Fe in a static air atmosphere is presented in Figure 9. Curve 1 corresponds to the oxidation of Fe powder up to 730°C, which is the end of the first peak. When the sample was cooled and reheated, as shown by curve 2, no further reaction took place. Curve 3 shows the weight gain after sample 2 was regrounded mechanically and reheated. Similar results were obtained on the DSC studies of Si/PbO compositions [7]. The first peak was reversible and, on regrounding the sample, a reaction at the temperature range of the first peak was detected. The extent of the surface reaction increased with an increase in metal content.

DISCUSSIONS

A review of the DSC results of various metal/oxidant pyrotechnic systems showed that, with an increase in temperature, the melting of the oxidant initiates the oxidation reaction. With $K_2Cr_2O_7$/metal mixtures, reactions begin at the melting point of the oxidant.

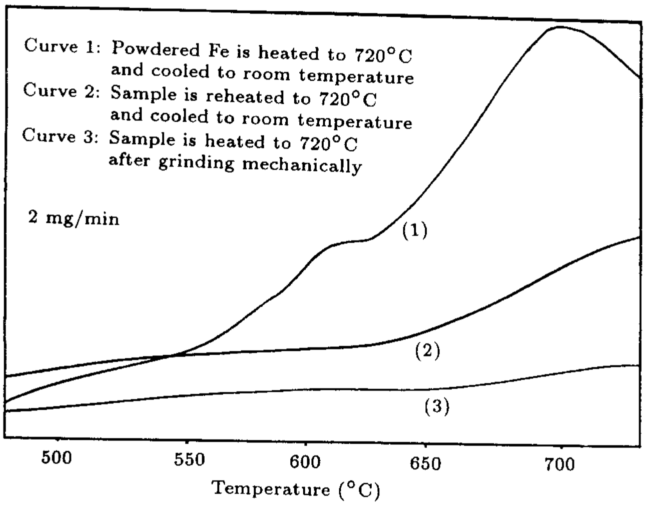

Figure 9. DTG traces of oxidation of powdered Fe under static air atmosphere, heating rate 10°C/min.

On the contrary, the melting of fuel does not initiate an oxidation reaction, as observed in the BaO_2/Se DSC trace. Selenium melts at 211°C, but its reaction begins long after at 350°C. Therefore, the temperature at which physical or chemical changes occur in the oxidant plays a more significant role in the start-up of the main reaction. When either the fuel or oxidant is in molten form, the reaction on the DSC trace appears as a single exothermic peak. Howlett and May [13] showed that the reaction and ignition of B/$K_2Cr_2O_7$, B/$Na_2Cr_2O_7$ and B-Si/$K_2Cr_2O_7$ compositions occur at the fusion temperature of the oxidants and the reaction is represented by a single exothermic peak. Studies on the black powder KNO_3-C-S mixture [14,15], showed that the melting of sulphur at 115°C does not lead to its reaction with KNO_3, however, it reacts at the fusion point of oxidant KNO_3 and the reaction of molten KNO_3 with C forms a single exothermic peak. Similar results were shown with $NaNO_3$ as an oxidizer, except that the reaction of sulphur with an oxidizer does not take place immediately after the melting of $NaNO_3$. In compositions where both fuel and oxidant are in solid form at the reaction temperature, the DSC trace of such reactions is a double exothermic peak. The first peak is related to surface oxidation of the fuel and the second peak due to bulk oxidation. Spice and Stavely [16,17], in a detailed investigation of the propagation reactions of gasless delay compositions, proved that truly solid/solid propagation reactions proceed through a pre-ignition stage, which raises the temperature so that the self-sustained propagation can be operative. The progress was followed by the reaction of Fe/BaO_2 and Fe/$K_2Cr_2O_7$ compositions due to the magnetic effect of Fe in the mixtures.

On the DSC examinations, the pre-ignition stage is probably presented by the first exothermic peak and the main combustion reaction by the second peak. In thermoanalytical studies of pyrotechnic compositions, involving decomposed oxidants at the temperature of reaction, the released oxygen usually leaves the mixture unreacted [18]. Therefore, the DSC trace is related to the reaction of the fuel with a non-gaseous product. However, when such a mixture is ignited in a confined form, the gas/solid and solid/solid oxidation of the fuel takes place. Also, with some pyrotechnic delay systems, the reaction of the released gaseous oxygen with the fuel is essential for the mixture to be propagative [16].

CONCLUSIONS

Thermal analysis results from a limited number of propagative pyrotechnic compositions showed that:

1. The temperature at which the oxidant undergoes physical or chemical change has a significant effect on the start of the main reaction;
2. If either fuel or oxidant is in molten form at the reaction temperature, it results in a single exothermic peak;
3. With truly solid-solid reactions, DSC traces always demonstrate a double peak appearance, the first peak being smaller than the second. This confirms Spice and Stavely's findings that such reactions take place through a pre-ignition reaction;
4. With decomposed oxidant, a major difference exists between the reaction in a DSC furnace and the reaction in a compressed confined form, as used in pyrotechnic devices. In the former, oxygen leaves the environment without reacting with the fuel;
5. Solid-gas oxidation of fuel particles in the atmospheric air takes place via a surface reaction and the extent of surface oxidation varies with particle size. Grinding the reacted fuel particles results in a fresh surface and, hence, an exothermic DSC trace upon re-heating.

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