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DIFFERENTIAL THERMAL ANALYSIS AND TEMPERATURE PROFILE ANALYSIS OF PYROTECHNIC DELAY SYSTEMS: MIXTURES OF TUNGSTEN AND POTASSIUM DICHROMATE

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ABSTRACT

The self-propagating combustion reaction between tungsten and potassium dichromate has been studied by differential thermal analysis and temperature profile analysis. Two reaction stages have been distinguished in the combustion where the rate of temperature rise is $\geqslant 10^5$ K min^{-1}: in the first potassium dichromate is reduced by tungsten to form potassium chromate and in the second stage the potassium chromate reacts with more tungsten to form potassium tungstate and chromic oxide.

INTRODUCTION

Mixtures of tungsten and potassium dichromate burn smoothly over a wide range of compositions. For tungsten with a nominal particle diameter of one μm this range extends from 40 to 90%* tungsten. The combustion takes place with little change in weight and the mixtures are typical of so-called gasless pyrotechnic systems. A preliminary study[1] of the combustion process using differential thermal analysis (DTA) and temperature profile analysis has shown that the combustion is comprised of more than one reaction stage. In the present work attention has been focussed on the moderately slow burning composition containing 50% tungsten and 50% potassium dichromate. However, results are included for the wider range of compositions containing from 20 to 90% tungsten thus giving a more comprehensive account of the combustion process. An assessment of DTA and temperature profile analysis in their application to pyrotechnics has been made in a previous study[2] of mixtures of boron and potassium dichromate.

* Throughout this paper % = 100 × weight of the component/weight of the mixture.

EXPERIMENTAL

Materials

Tungsten powder (one μm grade) was obtained from Murex Ltd., and had an average particle diameter of 1.2 μm determined using the Fisher Sub-sieve Sizer. Potassium dichromate (B.D.H., AnalaR grade) was ball-milled to an average particle diameter of 4.6 μm (Fisher Sub-sieve Sizer).

Mixtures were prepared by sieving the components through a 200 mesh sieve and then brush-mixing the weighed components once through a 100 mesh sieve and twice through a 200 mesh sieve.

Differential thermal analysis

DTA studies were carried out using high temperature equipment (Stanton Redcroft, models DTA 673 and 674). This equipment uses platinum–platinum/13% rhodium thermocouples in single stem ceramic heads and furnaces wound with either nichrome or platinum/rhodium wire. The experiments were carried out in 0.6 cm diameter dimpled platinum/rhodium crucibles in a downward flow of high purity argon (100 cm^3 min^{-1}) to avoid aerial oxidation of the tungsten. Calcined aluminium oxide was used as the reference material.

Ignition experiments were carried out at a heating rate of 20 K min^{-1} using samples weighing 50–100 mg. Measurements under non-ignition conditions were made by reducing the heating rates to 3 K min^{-1} and using samples weighing less than 20 mg. The distinction between ignition and non-ignition experiments was discussed in ref. 2.

Quantitative measurements were made using a recorder (Leeds and Northrup, model W) fitted with an integrator (Disc. model 224). The differential thermocouple output was fed directly into the recorder, by-passing the DTA amplifier and thus reducing the response time of the recording system. The assignment of the base line of the peaks was discussed previously[2]. The DTA head was calibrated by recording the curves for fusions and crystalline transitions with well established enthalpy changes.

Temperature profile analysis

Temperature profiles were recorded with thermocouples made from 0.1 mm diameter, platinum and platinum/10% rhodium wires. The junctions of the thermocouples were embedded in the pyrotechnic mixture which was contained in steel tubes 3.8 cm long and of 0.64 cm internal diameter. Two increments of the pyrotechnic mixture each 0.6 cm long were pressed into the tube using a dead load press at 7 MPa (about 0.5 ton in^{-2}). The thermocouple was inserted through a hole 0.1 cm diameter, which was drilled along the radial axis of the tubes about 1.2 cm from one end. The position of the thermocouple was adjusted until the junction was at the centre of the tube (see Fig. 1). The next increment of the mixture was introduced, pressed by hand and then with the dead load press. The thermocouple was insulated from the steel tube by means of thin glass sleeves. The pyrotechnic mixture was

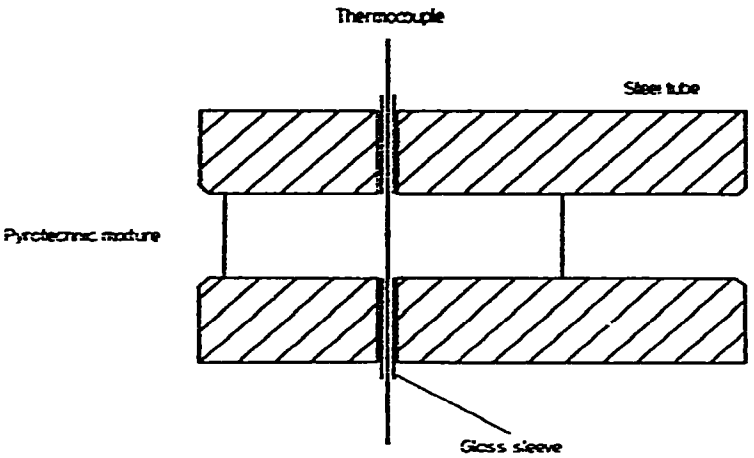

Fig. 1. Experimental arrangement for measuring temperature profiles.

ignited with a fuse and the thermocouple signal was captured by a transient recorder (Data Laboratories, model DL905). The theory of the analysis has already been summarised[2].

Ancillary measurements

Reaction exothermicities were measured using an adiabatic combustion calorimeter (Baird and Tatlock) which was calibrated with benzoic acid (B.D.H., thermochemical grade). The pyrotechnic mixtures were burnt compacted in silica crucibles in an atmosphere of argon. Temperatures were recorded using a quartz thermometer (Hewlett-Packard, model 2801A) with a resolution of 10^{-4}K.

RESULTS

Differential thermal analysis

DTA under ignition conditions showed that all the mixtures containing from 20 to 90% tungsten ignited in the range 650–660 K to give a single exotherm with a measured temperature rise of between 50 and 400 K. The temperature rise of the samples themselves was considerably greater. The curve for the mixture containing 50% tungsten and 50% potassium dichromate is shown in Fig. 2.

Under non-ignition conditions the DTA curve showed the presence of an exotherm below the melting temperature of potassium dichromate (671 K). For mixtures containing 50% or less tungsten the fusion endotherm could be observed superimposed on this exotherm. The main exotherm had a peak temperature of about 700 K. Curves for mixtures containing 20, 50 and 70% tungsten are shown in Fig. 3. For mixtures containing 30% or more tungsten there was evidence of a further exotherm at about 1000 K but, with the small sample size needed to avoid ignition, the exotherm was poorly defined. DTA experiments were therefore carried out on larger samples prepared by combining the products from heating small amounts through the

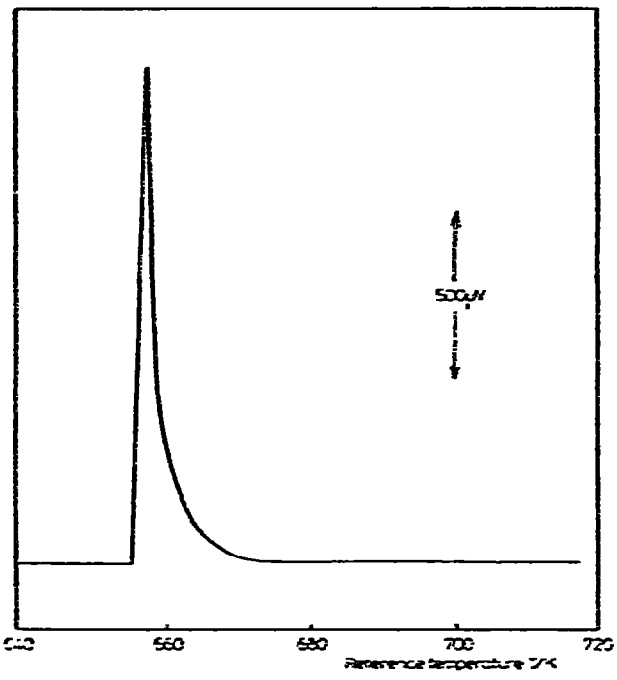

Fig. 2. DTA curve for a mixture containing 50% tungsten and 50% potassium dichromate recorded under ignition conditions. Sample weight 50 mg; heating rate 20 K min^{-1}; argon atmosphere, flow rate 100 cm^3 min^{-1}.

first exotherm. Measurements were made in the temperature range ambient to 1800 K at a heating rate of 10 K min^{-1}. Figure 4 shows the DTA curve for the sample prepared from the mixture containing 50% tungsten and 50% potassium dichromate. Three peaks were observed: a broad exotherm at 980 K, a smaller exotherm at 1090 K and an endotherm at 1190 K. The other samples also showed the broad exotherm but not the smaller exotherm at 1090 K. The endotherm was shown by samples prepared from mixtures containing 30 and 40% tungsten, but not by those from mixtures containing more than 50% tungsten (see Fig. 5). The mixture containing 20% tungsten and 80% potassium dichromate did not show evidence of the high temperature exothermic reactions and the product from the first exotherm contained unreacted potassium dichromate. There was a tendency for the sample to spread over the DTA block, this tendency being consistent with the behaviour of potassium dichromate at high temperatures.

Temperature profile analysis

A temperature profile for the 50% tungsten/50% potassium dichromate mixture is shown in Fig. 6. It was recorded over a time of one s and shows a rapid temperature rise to the maximum value of 1900 K and a temperature decay which is approximately exponential. Figure 7 shows the form of the power function derived from the temperature profile. The two peaks are exotherms with maxima at about 1000 and 1300 K and, although they overlap, the second appears to be the larger. The

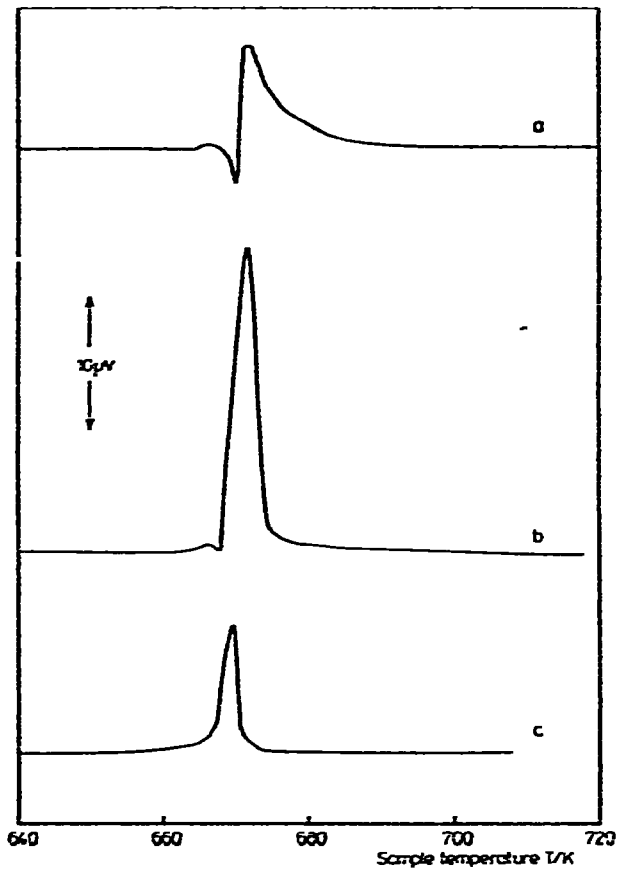

Fig. 3. DTA curves for mixtures containing (a) 20%, (b) 50%, and (c) 70% tungsten, recorded under non-ignition conditions. Sample weights 10–20 mg; heating rate 3 K min^{-1}; argon atmosphere, flow rate 100 cm^3 min^{-1}.

power functions derived from different temperature profiles show considerable variation. In part, this is caused by the uneven nature of the flame front and variations in the microscopic environment of the thermocouple junction. A further complication arises in the numerical processing since there is no single unequivocal procedure for treating the raw experimental data. The assignment of the ignition temperature is uncertain and values range from 600 to 800 K. The maximum burning temperature is more secure with values from 1870 to 1900 K. Most of the power functions have the two main exotherms as a common feature. An endotherm immediately preceding ignition is shown by some of the power functions and most probably corresponds to the fusion of potassium dichromate. An endotherm at 1300–1400 K superimposed on the second exotherm is sometimes observed, but the shape of both these endotherms is sensitive to the smoothing procedures adopted in the numerical processing.

Reaction exothermicities

Table 1 shows the exothermicity of the ignition reaction for the mixture containing 50% tungsten and 50% potassium dichromate measured by temperature profile

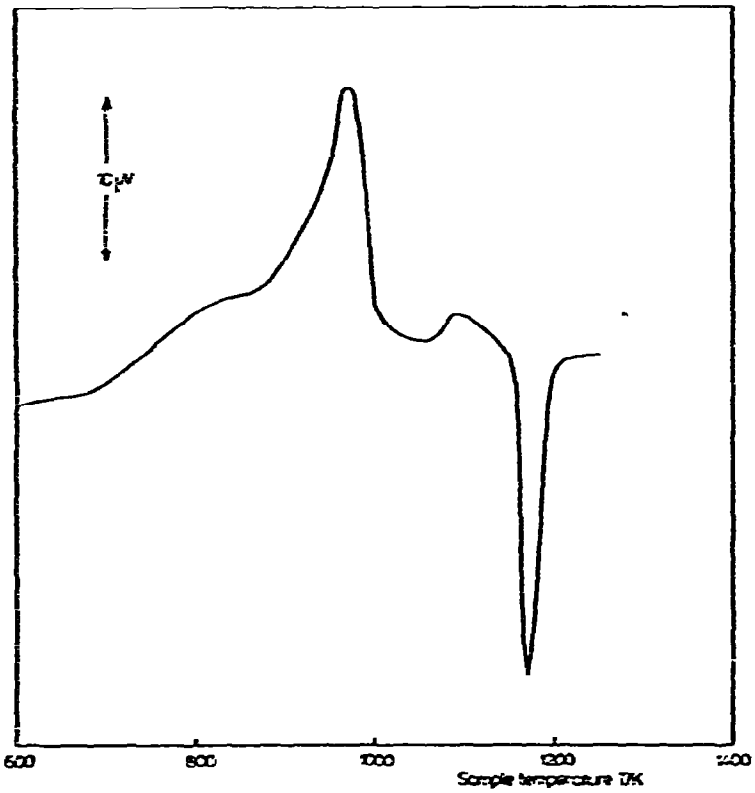

Fig. 4. DTA curve, recorded under non-ignition conditions, for the combined sample prepared by heating a mixture containing 50% tungsten through the first exotherm. Sample weight 120 mg; heating rate 10 K min^{-1}; argon atmosphere, flow rate 100 cm^3 min^{-1}.

TABLE 1

EXOTHERMICITY[a] OF THE IGNITION REACTION FOR A MIXTURE CONTAINING 50% TUNGSTEN AND 50% POTASSIUM DICHROMATE

Temperature profile analysis	*DTA*	*Combustion calorimetry*
1.26 ± 0.25	1.06 ± 0.07	1.14 ± 0.02

[a] In kJ g^{-1}, where the units refer to one gram of mixture.

analysis, DTA and combustion calorimetry. The result from temperature profile analysis is derived by integrating the power function. The mean value 0.64 J K^{-1} g^{-1} for the specific heat capacity was estimated on the basis of differential scanning calorimetry (Perkin Elmer, model DSC 1B) in the temperature range ambient to 773 K. The relevance of this value is not entirely certain because of the large temperature range and complex chemistry of the combustion process. An uncertainty of ±25% has been assigned to the specific heat capacity and this is reflected in the large error associated with the exothermicity. For the DTA and combustion calorimetry results

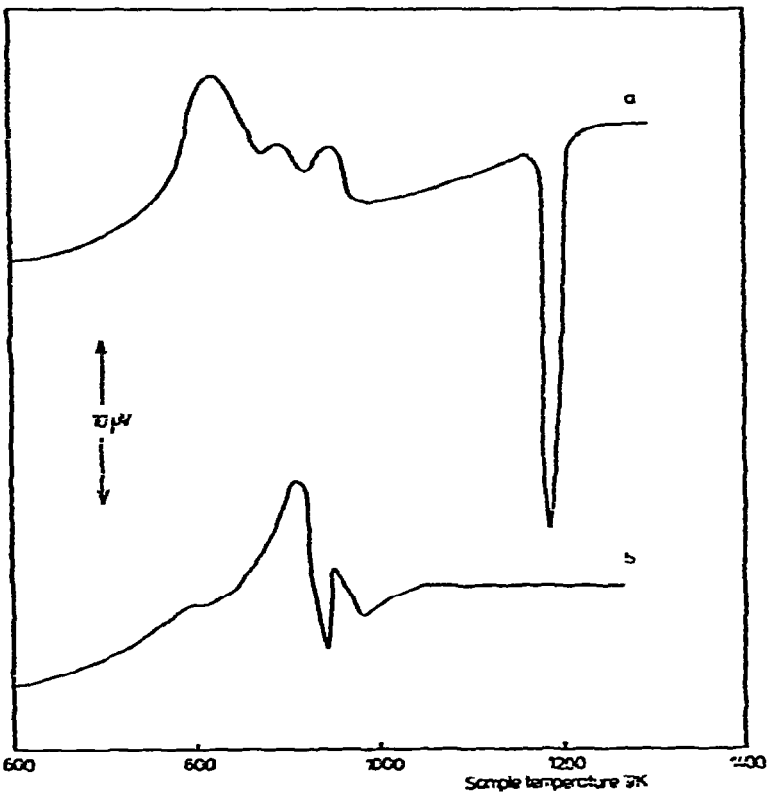

Fig. 5. DTA curves, recorded under non-ignition conditions, for the combined samples prepared by heating mixtures containing (a) 30%, and (b) 70% tungsten, through the first exotherm. Sample weights 100 mg; heating rate 10 K min^{-1}; argon atmosphere, flow rate 100 cm^3 min^{-1}.

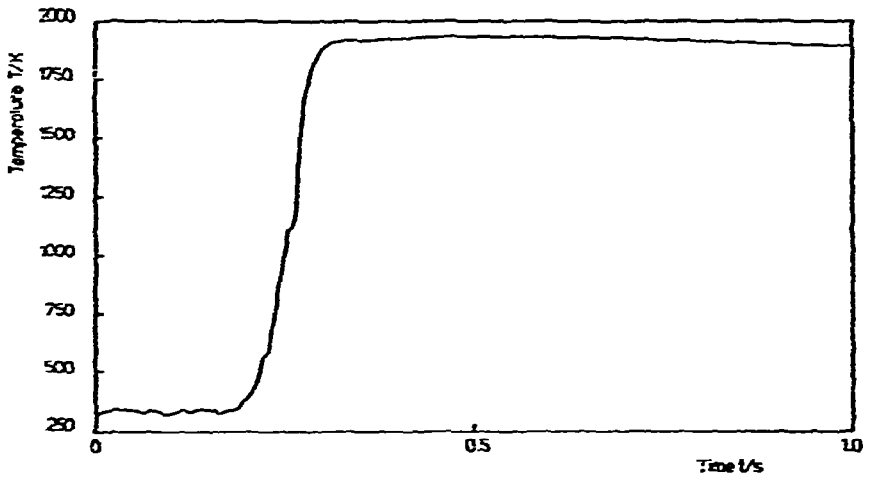

Fig. 6. The temperature profile for a mixture containing 50% tungsten and 50% potassium dichromate.

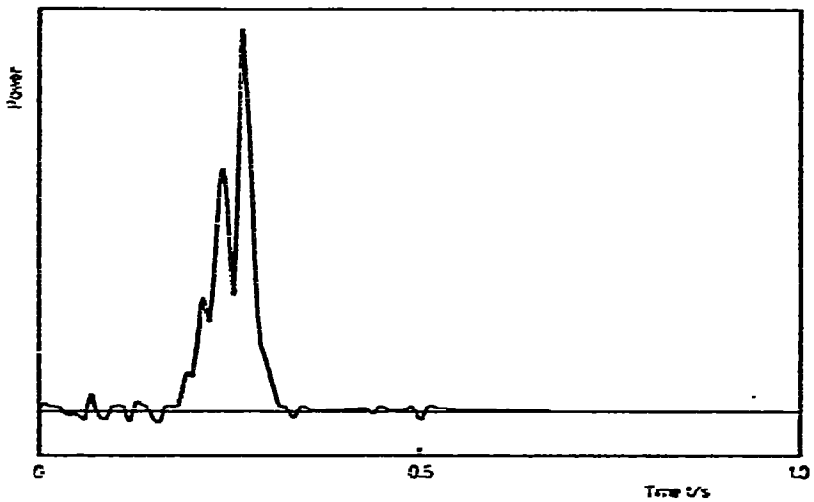

Fig. 7. The power function derived from the temperature profile for a mixture containing 50% tungsten and 50% potassium dichromate.

TABLE 2

EXOTHERMICITY OF THE IGNITION REACTION FOR MIXTURES CONTAINING FROM 30 TO 90% TUNGSTEN

% *Tungsten*	*Exothermicity (kJ g^{-1})*[a]	
	DTA	*Combustion calorimetry*
30	0.57 ± 0.03	
35	0.97 ± 0.05	
40	1.20 ± 0.06	1.34 ± 0.02
45	1.15 ± 0.06	
50	1.06 ± 0.07	1.14 ± 0.02
60	0.89 ± 0.07	0.88 ± 0.02
70	0.68 ± 0.06	0.68 ± 0.02
80		0.43 ± 0.03
90	0.25 ± 0.01	0.21 ± 0.03

[a] The units refer to one gram of mixture.

the errors include the uncertainty in the calibration experiments. The results obtained from the three techniques are seen to be in agreement. Table 2 gives the results obtained by DTA and combustion calorimetry for a wider range of mixtures. For the mixture containing 30% tungsten the combustion was incomplete, and when the residue was heated to 1300 K the DTA curve indicated further exothermic reaction.

DISCUSSION

DTA and temperature profile analysis show that the mixture containing 50% tungsten and 50% potassium dichromate ignites at about the melting temperature of potassium dichromate. Under non-ignition conditions, DTA revealed the presence of

a small pre-ignition exotherm followed by the fusion endotherm of potassium dichromate and the main exotherm. Direct observation, using hot stage microscopy in conjunction with high speed cine photography[3], showed that, at a heating rate of 100 K min^{-1}, the composition ignited from a point source in the partially molten mixture. The ignition of the bulk sample will depend not only on the composition but also on the experimental conditions including the sample mass and packing and the heating rate. Appreciable reaction occurs below the melting temperature of the potassium dichromate when samples are heated at 640–650 K for several hours. Under DTA conditions mixtures containing 20 to 90% tungsten may be ignited whereas at ambient temperature mixtures containing less than 40% tungsten do not self-propagate combustion.

X-ray and chemical analysis of the products from both DTA under ignition conditions and temperature profile analysis on the 50% tungsten mixture showed the presence of potassium tungstate, chromic oxide and unreacted tungsten. The presence of potassium tungstate was confirmed by the fusion endotherm at 1193 K when the products from the DTA ignition experiments were heated to 1300 K. The following equation may represent a major component of the combustion process:

$$W + K_2Cr_2O_7 = K_2WO_4 + Cr_2O_3 \quad (1)$$

in which the stoichiometric proportion of tungsten is 38.5% and the calculated exothermicity is 1.45 kJ g^{-1}. This value gives 1.17 kJ g^{-1} for the 50% tungsten

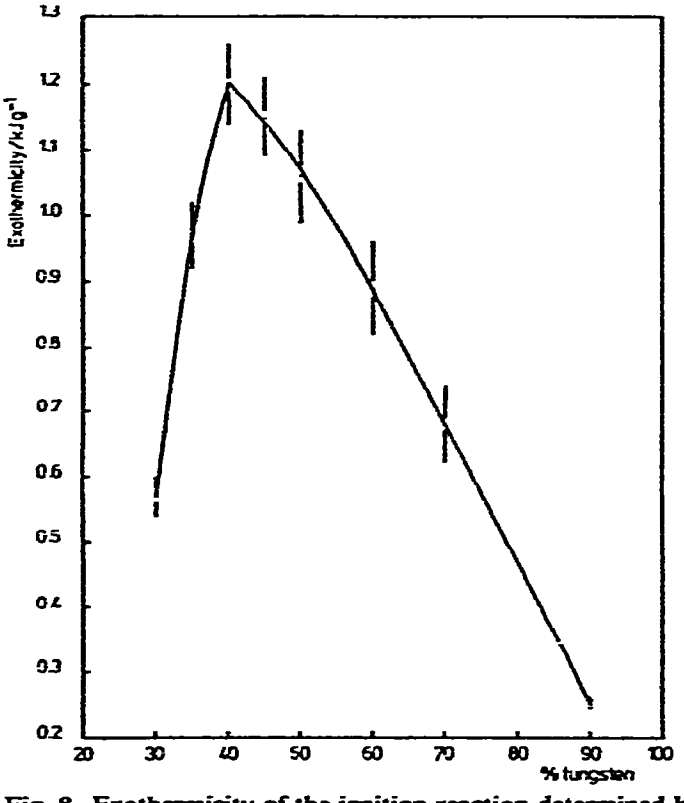

Fig. 8. Exothermicity of the ignition reaction determined by quantitative DTA.

mixture which may be compared with 1.13 kJ g^{-1} which is the weighted mean of the experimental results. The results from quantitative DTA for the composition range 30–90% tungsten are plotted in Fig. 8. The maximum of the curve is at about 40% tungsten which provides further confirmation of the proposed reaction stoichiometry.

There is general similarity between the results of the DTA experiments under non-ignition conditions and the power function derived from the temperature profiles. Both show two main exothermic reactions and, although there are differences in the temperatures, these are not unexpected in view of the considerably greater heating rates in the temperature profile experiments ($\geqslant 10^5$ K min^{-1}). The fusion endotherm of potassium tungstate which is shown by DTA may also be evident in some of the power functions but occurs within the exothermic region. Whilst DTA permits reaction intermediates to be isolated, it should be borne in mind that in these experiments, carried out under non-ignition conditions, the sample does not actually burn.

The products from the first reaction stage are not well defined and only potassium chromate has been established clearly. One possible representation of the reaction might be

$$W + 2K_2Cr_2O_7 = WO_3 + 2\,K_2CrO_4 + Cr_2O_3 \qquad (2)$$

which leads to the reaction

$$W + WO_3 + 2\,K_2CrO_4 = 2\,K_2WO_4 + Cr_2O_3 \qquad (3)$$

as the second stage. Subsidiary DTA experiments have shown that mixtures of tungsten, tungstic oxide and potassium chromate give an exotherm with a peak temperature at 900–1000 K which is similar in appearance to the second reaction exotherm. There is also evidence of further reactions at higher temperatures but the relevance of these reactions to the combustion process is uncertain, bearing in mind the much longer time scale of the DTA experiments. The exothermicity of the first stage, derived from quantitative DTA, is about 0.44 kJ g^{-1} for the 50% tungsten mixture which compares with 0.57 kJ g^{-1} based on the proposed stoichiometry. The third exotherm which is observed in the DTA curve is small when compared with the two main exotherms. It is not resolved in temperature profile analysis and appears to be associated with crystallisation of the products from the second reaction stage. Mixtures containing 30 and 40% tungsten do not show this peak but otherwise their behaviour is similar to the mixture containing 50% tungsten. Mixtures containing 60% or more tungsten shows some differences: an endotherm is observed superimposed on the second exotherm and the fusion endotherm of potassium tungstate is no longer evident.

The pyrotechnic reaction between 50% tungsten and 50% potassium dichromate shows some similarity to that of the slow-burning mixtures of boron and potassium dichromate: both involve two main exothermic stages in the temperature range 700–1600 K. With the boron system, the second stage can be established independently of the first and will self-propagate combustion. In contrast, a mixture of tungsten, tungstic oxide and potassium chromate with the stoichiometry represented by eqn. (3)

does not readily self-propagate combustion at ambient temperature. Furthermore, the burning velocity of the 50% tungsten mixture is reduced when this ternary mixture is added. This lack of reactivity of the second stage is reflected in the broad, ill-defined DTA peak, in marked contrast with the well-defined second peak in the boron system.

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