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SOME THERMAL STUDIES ON PYROTECHNIC COMPOSITIONS

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Abstract

Some applications of thermal analysis (TA) and temperature profile analysis (TPA) to the study of a variety of binary pyrotechnic systems are described. Factors that effect the combustion of such fuel/oxidant mixtures are discussed. Trends in burning behaviour and the experimental limitations of the techniques available are identified.

Keywords: burning rates, fuel/oxidant mixtures, pyrotechnics, temperature profile analysis

Introduction

In spite of the general association of 'pyrotechnics' with 'fireworks', there are far more important and less-frivolous applications in civilian and military systems [1]. A pyrotechnic mixture is a combination of an initially solid fuel (or fuels) with an initially solid source of the oxygen required for the self-sustaining combustion of the fuel (the oxidant or oxidants). Pyrotechnic compositions may be used to produce heat, light, gas or smoke and these products lead to numerous applications. Closely related to the field of pyrotechnic reactions is the self-propagating synthesis of high-temperature materials where the main interest lies in the properties of the solid product of combustion [2].

Typical fuels and oxidants are shown in Table 1. Combustion is the key chemical process in pyrotechnics and thermal analysis is one of the main experimental techniques for studying the complexity of this combustion. In pyrotechnics, combustion occurs by layer-to-layer propagation. Combustion of propellants is similar, but large volumes of gaseous combustion products are generated. Combustion of explosives leads to detonation and the establishment of a shock wave.

Laye and Charsley [3] have provided a comprehensive review (up to 1987) of the use of differential thermal analysis (DTA) and differential scanning calorimetry (DSC) in the study of pyrotechnics. More recently Charsley *et al.* [4] have provided an overview of how thermal analysis and calorimetry can be used to study reactivity, reaction mechanisms and ageing. Charsley *et al.* [5] have also evaluated the role of temperature modulated DSC in the study of pyrotechnic systems. A recent overview of the applications of thermal analysis in the study of pyrotechnic systems is in press [6].

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Table 1 Binary pyrotechnic systems (which have been studied at Rhodes University)

Fuels	Melting point/°C	Oxidants	Decomposition temperature/°C	Systems
Sb	631	$KMnO_4$	290 exo, 520 endo	$Sb/KMnO_4$
Fe	1535	BaO_2	500 endo	$Fe/KMnO_4$
Mo	2610	SrO_2	390 endo, 525 endo	Fe/BaO_2
Mn	1244	Fe_2O_3	melts 1565	Fe/SrO_2
Si	1410	SnO_2	melts 1630	Mn/BaO_2
C	–	Sb_2O_3	melts 656, sublimes	Mn/SrO_2
		KNO_3	melts 334, d400 endo	Mo/BaO_2
				Mo/SrO_2
				Si/SnO_2
				Si/Fe_2O_3
				Si/KNO_3
				Si/Sb_2O_3
				C/KNO_3

An extremely important use of pyrotechnic mixtures is as delay fuses in electric detonators (Fig. 1). One of the primary aims of studies in the field of pyrotechnics is to identify the factors which give rise to the wide range of observed burning rates when various fuels and oxidants are combined.

Pyrotechnic compositions are usually made by mixing the fuel and oxidant as finely-divided powders (sometimes additives are included to promote particular properties). During combustion, some constituents remain in the solid state, while others melt, vaporise, or decompose to yield some gaseous products. Mechanisms en-

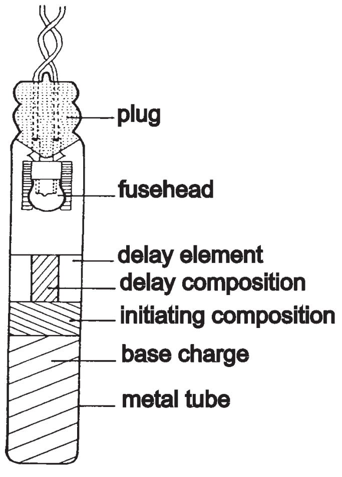

Fig. 1 Electric delay detonator

countered may thus cover the wide field of solid–solid, solid–liquid, solid–gas, and possibly even liquid–gas and liquid–liquid reactions. When studying pyrotechnic systems it is important to distinguish between ignition conditions, where the sample undergoes a combustion reaction, and non-ignition reactions which may be resolved into several stages. The conditions required to prevent ignition depend on the reactivity of the pyrotechnic system and the design of the equipment. Generally small sample masses and slow heating rates need to be used. High-purity, inert atmospheres are necessary to exclude interference from aerial oxidation, so that, eventually, the influence of air on the pyrotechnic reaction can be evaluated. The general approach is to examine the behaviour of the fuels (oxidation in air) and of the oxidants (decomposition) separately, before examining the behaviour of mixtures (interactions and ignition). Reactants and combustion residues have also been examined using scanning electron microscopy, infrared spectroscopy and X-ray diffraction. Some of the factors influencing intersolid pyrotechnic reactions are listed in Table 2.

Table 2 Factors influencing intersolid pyrotechnic reactions

Separate fuels and oxidants
Preparation, impurities, grinding
Surface oxidation and/or adsorption (e.g. H_2O)
Some decomposition
Mixtures
Primary interactions
Adsorption on storage
Pressing
Further interaction
Ignition
Heating, expansion, desorption
Solid transitions, sintering, melting, sublimation
Oxidation by evolved gas or trapped air
Decomposition with evolution of volatile products
Catalysis by products
Fluxing by solid-solution formation
Movement of temperature and pressure fronts
Solid-solid reaction, problems of contact
Product layers (protective/non-protective), diffusion
Recrystallization

Oxidation of the fuels

The oxidation reactions of the fuels, by air or oxygen, can be studied using TG or DSC. Some of the information available is summarized in Table 3. Surprisingly, it is difficult to locate relevant kinetic information in the literature. Factors which are often referred to as influencing the oxidation of metals include the relative molar volumes of the oxide (per mole of metal atoms) and the parent metal (the Pilling and Bedworth ratio [7]) and the M–O bond energy (calculated [8] as $B=(-\Delta H^{\circ}_{\mathrm{f,oxide}}/2n)+(Q_D/4)$, where n is the number of O atoms in the oxide, and Q_D is the dissociation energy of the O_2 molecule = 490 kJ mol^{-1}). Values of both of these quantities are given in Table 3. Neither set of values seems to show sufficient variation to account for the different reactivities and neither quantity includes allowance for the particle-size or surface area of the fuel.

Table 3 Oxidation of the fuels in air or oxygen

Melting point/°C	Onset of oxidation/ °C	E_a/ kJ mol^{-1}	Oxides possible	$\Delta H^{\circ}_{\mathrm{f,oxide}}$/ kJ (mol fuel)$^{-1}$	P & B ratio [7]	M–O bond energy/ kJ mol^{-1}
Sb 631	300		Sb_2O_3	–348	1.45	238
			Sb_2O_4	–448	1.45	234
			Sb_2O_5	–490	2.34	220
Fe 1535	200	60–210	FeO	–267	1.78	256
			Fe_3O_4	–372	2.10	262
			Fe_2O_3	–411	2.15	259
Mo 2610	440	300–330	MoO_2	–589	2.11	270
			MoO_3	–746	3.26	247
Mn 1244	360	33–44	MnO	–385	1.70	315
			Mn_3O_4	–428	2.06	283
			Mn_2O_3	–441	2.30	269
Si 1410	700	60–130	SiO_2	–911	1.88	350

Onset of oxidation of all of the fuels listed occurs at temperatures well below their melting points, T_m, and also well below the empirical Tamman temperatures (=0.52 T_m in K) regarded as marking the approximate onset of considerable mobility of constituents of the crystal lattice [9].

Decomposition of the oxidants

The thermal events observed on heating the oxidants separately in an inert atmosphere are summarized in Table 1. Most decompose endothermically either on or after melting, $KMnO_4$ is an exception in that it decomposes exothermically in the solid state.

Mixtures

The number of possible fuel/oxidant combinations is huge, even if only binary combinations are considered. When allowance is made for more than one fuel and/or more than one oxidant, the possibilities are almost limitless. The pyrotechnic compositions used in real applications are further complicated by inclusion of additives to improve their flow properties, stability on storage, etc. A very limited selection of binary systems is given in Table 1.

The best known pyrotechnic mixture is black powder (gunpowder). TG and DTA studies of both the ternary mixture and the binary mixtures of its components [10, 11] show that charcoal and KNO_3 undergo a strongly exothermic reaction between 380 and 550°C. During conventional thermal analysis experiments no significant reaction is observed between sulfur and KNO_3 because sulfur vaporizes below the melting temperature of KNO_3. However, if escape of sulfur is retarded, then some reaction occurs, which is regarded as a pre-ignition reaction leading to the higher temperature reaction between charcoal and molten KNO_3, and this is responsible for propagating the combustion.

Temperature-time profiles

Although conventional thermal analysis techniques, such as TG and DSC, can provide significant information on the thermal behaviour of pyrotechnic mixtures, the small samples used and slow heating rates usually give results related to interactions under non-ignition conditions. Considerably more information, under more realistic conditions, can be obtained by measurement of temperature-time profiles through the combustion wave. The method was developed by Hill and co-workers [12, 13] and the theory has been fully developed by Boddington and Laye's research group at the University of Leeds [14, 15]. Although temperature profile analysis (TPA) is not strictly a thermal analysis technique, an argument could be made out for regarding it as a variation in which the temperature is determined by the properties of the sample. The information obtainable certainly complements DTA and DSC in providing information from measurements made directly on the combustion process. Figure 2 shows the apparatus in which a thermocouple is stretched across a stainless-steel channel into which the pyrotechnic mixture is pressed. Glass sleeves are used to insulate the thermocouple. Provision is also made for simultaneous measurement of the burning rate. The technique is limited by the maximum temperature to which the equipment can be exposed (<1700°C for Pt/10% Rh, Pt thermocouples) and by the response times of the sensors involved. Information on reaction kinetics can be derived from analysis of the profiles, provided that information on the thermal diffusivity of the composition is known or can be measured [16].

A selection of temperature–time profiles, for the various systems listed in Table 1, is given in Fig. 3. The behaviour of the Si/Fe_2O_3 system is exceptional [17], but the other systems give profiles over a surprisingly narrow time scale.

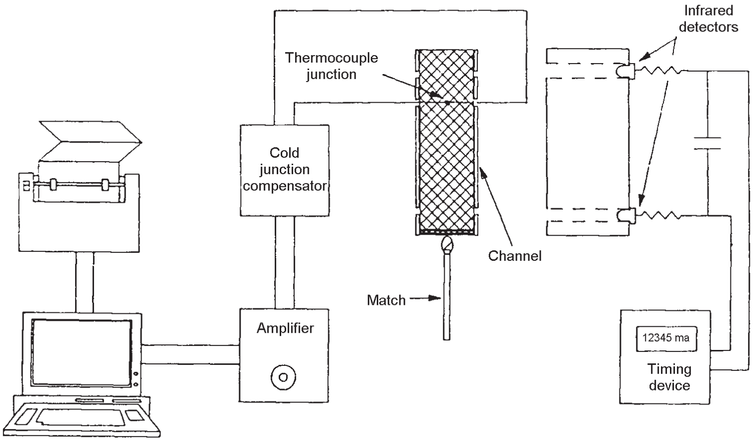

Fig. 2 Apparatus for temperature profile measurement

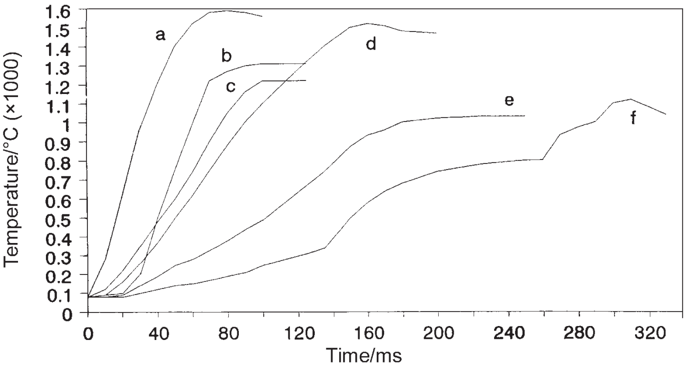

Fig. 3 A selection of temperature – time profiles, for some of the systems listed in Table 1. a – 20% Mn/BaO_2; b – 40% Si/SnO_2; c – 50% Mn/SrO_2; d – 50% Mo/BaO_2; e – 40% Mo/SrO_2; f – 40% Si/Fe_2O_3

All of the systems studied (except for Mo/SrO_2) sustained combustion over a wide range of fuel-oxidant compositions. The lower limits of the burning rate ranges (Fig. 4) showed more consistency than the upper limits and it is probable that failure of burning occurs below ~2 mm s^{-1} on account of heat losses from the stainless-steel channel of fixed dimensions. The upper limits varied from system to system from 2.3 mm s^{-1} for 40% Mo/SrO_2 to ~115 mm s^{-1} (with considerable irreproducibility) for 40% $Fe/KMnO_4$. Excluding this latter system, the maximum burning rates of the majority of the systems lie between 9 and 12 mm s^{-1}. The heat outputs, ΔH_{exp}/(kJ (g mixture)$^{-1}$) were also similar (1–2 kJ g^{-1}) except where KNO_3 was oxidant (Si or C as fuels). Systems for study were selected only if T_{max} measured during combustion lay below the ~1750°C limit of the thermocouple material, so the upper limits of the T_{max} values recorded reflect this restriction.

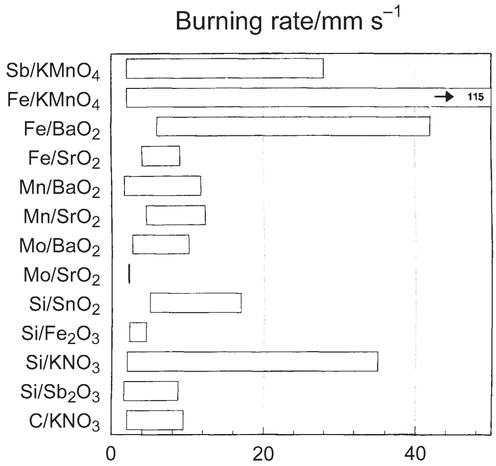

Fig. 4 Linear burning rates (mm s^{-1}) for the systems listed in Table 1

Burning rates and particle-size

Variation of the chemical constituents of a binary mixture generally has the greatest effect on burning rate, followed often by variation of the composition in a given combination. The particle-size of the fuel is another extremely important factor which is often less accessible to study because of its large effects. Where possible, different samples of fuel powders have been characterized and compared in reaction with the same sample of oxidant. A plot of burning rate against the ratio of the mean radius of the fuel particles (r_f) to the mean radius of the oxidant particles (r_o) is shown in Fig. 5. The trend is only very broadly towards higher burning rates at lower r_f/r_o ratios. For the Sb/$KMnO_4$ system, with fixed particle-size of oxidant, the burning rate decreases almost linearly as r(Sb) increases in the range 2 to 14 μm, as shown in Fig. 6.

Burning rates and additives

The effect of inert additives such as Al_2O_3 or SiO_2 on the systems studied has generally been the expected decrease in the burning rate, probably through physical blocking of reactant contact, combined with heat capacity effects. The presence in, or addition of small amounts of water to the systems has a similar effect. Increasing the proportion of additive (or water) eventually causes failure of burning.

Kinetics

Apparent activation energies obtained from kinetic analyses of many temperature profiles (Table 4) are in the low range (10–30 kJ mol^{-1}) generally found [18] and attributed to control of combustion by diffusion or heat transfer processes. Very different values are obtained from thermal analysis experiments (also listed in Table 4) and the relationship between these sets of values has been discussed [10]. Kinetic param-

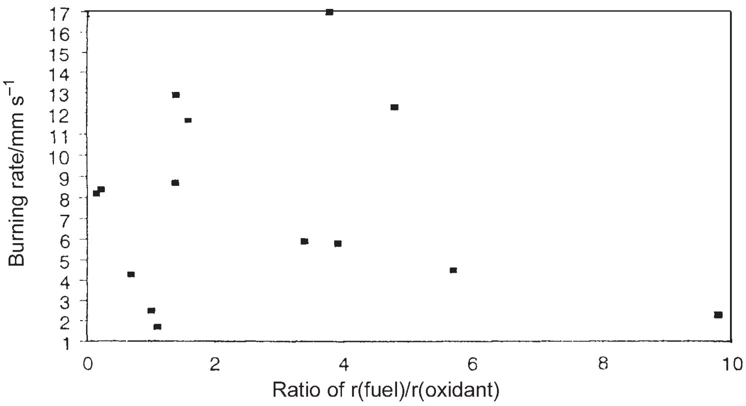

Fig. 5 Plot of burning rate *vs.* radius ratio (fuel/oxidant)

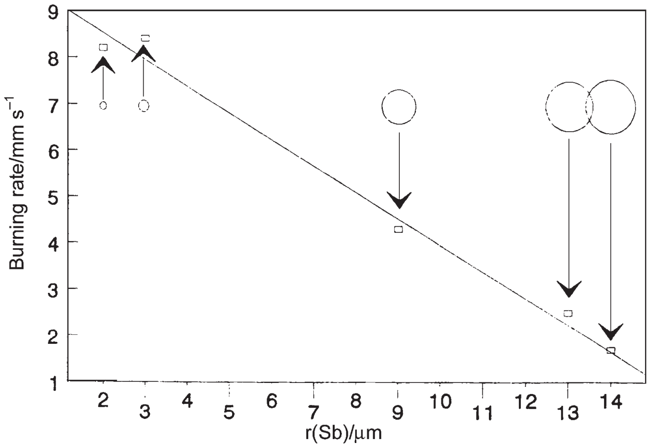

Fig. 6 Plot of burning rate *vs.* radius of the fuel particles in the Sb/KMnO4 system

eters obtained using Arrhenius kinetics predict too great a reaction rate for pyrotechnic compositions at low temperatures. A more complex relationship was suggested [10], including a diffusion coefficient. Arrhenius behaviour at low temperatures, which predicts a rapid rise in temperature, is combined with diffusion controlled behaviour at high temperature, where the rate becomes less dependent on temperature.

Considering the results for the Si/oxidant systems, and interpreting the activation energy, in the simplest terms, as the temperature coefficient of the reaction rate, the Si/KNO_3 system with a definitely molten oxidant has a greater dependence on T than the Si/Sb_2O_3 system, where the oxidant sublimes and melts. Both of these systems have E_a values greater than that for the Si/$O_2(g)$ reaction. The Si/$O_2(g)$ reaction is known to be hindered by the formation of a protective layer of SiO_2 product. In the other systems, there is the possibility of disruption or dissociation of such a layer by the molten oxidant or by formation of eutectic melts.

For the 40% Si/Sb_2O_3 composition [19] and the 40% Mn/SrO_2 composition [20] it was possible to compare the kinetic parameters obtained from thermal analysis with those obtained from temperature profile analysis (Table 4).

Table 4 Comparison of kinetic parameters from thermal analysis (TA) and temperature profile analysis (TPA)

	E_a/kJ mol^{-1}	A/s^{-1}
40% Si/Sb_2O_3		
TA	339±8	(1.12±0.04)·10^{20}
TPA	13.3±4.7	81±16
40% Mn/SrO_2		
TA	434±9	(2.0±0.3)·10^{42}
TPA	13.9±1.5	1379±100

The rate coefficients derived from classical Arrhenius kinetic data from temperature profiles (k_{TP}) and thermal analysis (k_{TA}) for a 40% Si/Sb_2O_3 mixture and the rate coefficient from the modified equation (k_{comb}), are compared in Fig. 7.

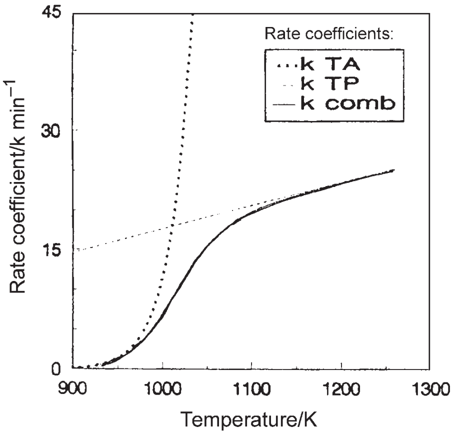

Fig. 7 Comparison of the rate coefficients for 40% Si/Sb_2O_3. a – k_{TA} from thermal analysis; b – k_{TP} from temperature profiles; c – $k_{combined}$

General trends

A summary of the various trends related to the burning of Si/oxidant compositions is given in Table 5. T_{max} and maximum v_{exp} followed the same trends. The trend for ΔH_{exp} was different, but matched that of c, while trends for v_{exp} (at 40% Si) and D (thermal diffusivity) matched.

Table 5 Summary of the burning behaviour of Si/oxidant systems

Property	Order of decrease
Burning rate, v_{exp} (40% Si)	SnO_2>Sb_2O_3>Fe_2O_3>KNO_3
Maximum v_{exp}	KNO_3>SnO_2>Sb_2O_3>Fe_2O_3
Maximum temperature, T_{max}	KNO_3>SnO_2>Sb_2O_3>Fe_2O_3
Heat output, ΔH_{exp} (kJ (g mixture)$^{-1}$)	KNO_3>Fe_2O_3>SnO_2>Sb_2O_3
Specific heat capacity, c (J K^{-1} g^{-1}) (298 K or 1600 K)	KNO_3>Fe_2O_3>Sb_2O_3>SnO_2
Thermal conductivity, λ (W m^{-1} K^{-1}) (298 K)	SnO_2>KNO_3>Sb_2O_3>Fe_2O_3
Thermal diffusivity, D (m^2 s^{-1}) (298 K)	SnO_2>Sb_2O_3>Fe_2O_3>KNO_3
Activation energy, E_a (kJ mol^{-1})	Fe_2O_3>Sb_2O_3>SnO_2

The values of the thermal diffusivities calculated from the measured rise times and burning rates ($D=v_2/t_r$) [21] were much greater than those determined from room-temperature experiments. Since the thermal diffusivity depends on both λ and c, and c increases substantially with temperature, λ for the system would be expected to increase with increasing temperature. Of the little information available, λ for bulk SiO_2 does increase with T, but λ for bulk SnO_2 decreases. In powdered mixtures, the effect of temperature will be more complicated and phase transitions and/or decompositions will introduce further uncertainties.

For the Mn/BaO_2 system, the lowest values of activation energy were recorded for the 15 and 65% Mn compositions at the extremes of the range which supported combustion and which have reasonably slow burning rates and low maximum temperatures. Compositions with high burning rates burn at higher temperatures and have higher activation energies.

Of the binary metal/peroxide systems, the Mn/SrO_2 system burnt with the fastest rate (~12 mm s^{-1} for the 70 and 75% Mn compositions). The composition which burnt with the slowest rate, but still with reliable combustion, was the 65% Mn/BaO_2 composition (~1.7 mm s^{-1}). Based on the mass percent of fuel, or on a common mole ratio, the four binary metal/peroxide systems show the trends given in Table 6. The closest correlation is between E_a and ΔH_{exp}.

Table 6 Summary of trends within the four binary metal/peroxide systems

	Decreasing order
v_{exp}	Mn/SrO_2>Mn/BaO_2>Mo/BaO_2>Mo/SrO_2
T_{max}	Mo/BaO_2>Mo/SrO_2>Mn/BaO_2>Mn/SrO_2
E_a	Mn/BaO_2>Mn/SrO_2≈Mo/BaO_2>Mo/SrO_2
ΔH_{exp}	Mn/BaO_2>Mo/BaO_2>Mn/SrO_2≈Mo/SrO_2

Conclusions

Several features arise on surveying the systems listed in Table 1. Most of the oxidants, except Fe_2O_3, Sb_2O_3 and SnO_2 decompose with some release of $O_2(g)$ at temperatures (Table 1) often well below the recorded values of T_{max}. Sb_2O_3 melts and vaporizes, KNO_3 melts and decomposes. The melting points of the fuels (Table 1) are high (excluding Sb and the complex thermal behaviour of charcoal that puts it in a separate class of fuels). Substitution of SrO_2 for the apparently chemically similar oxidant, BaO_2, does not affect the burning rate of Mn/peroxide compositions as much as it affects the Mo/peroxide compositions. Thus variation of the constituents of the binary mixtures listed can result in burning rates of from 2–115 mm s^{-1}. This range is also the maximum variation observed with change of composition (20–70% fuel) of the fixed binary combination (Fe/$KMnO_4$). The Sb/$KMnO_4$ and Si/KNO_3 systems also show above average ranges of burning rates with varying composition.

Variation of the particle-size of the fuel in the Sb/$KMnO_4$ system from a radius of 14 to 2.0 μm changed the burning rate (Fig. 6) from 2 to 8 mm s^{-1} compared to the range of 2 to 28 mm s^{-1} with change in composition (Fig. 4). Decreasing the particle-radius of Mo from 17.2 to 6.9 μm produced faster burning Mo/peroxide mixtures than were possible by varying the composition of the mixtures with the larger Mo particles.

Combustion studies of pyrotechnic systems are severely hampered by limitations of the techniques available. Both thermal analysis and temperature profile measurement using thermocouples are limited to temperatures below 1700°C by the materials of construction. Materials available for use at higher temperatures usually require inert atmospheres and are thus incompatible with the presence of oxidants. Materials should also not alloy with the fuels which are often metals, usually with relatively low melting points. Thermal analysis is also limited by the response of the sensor system [8, 21]. Pyrometry has been considered [7, 10, 22], but has the limitations of response, spatial resolution of the area of surface measured and emissivity changes of the surface during reaction. The surface temperatures will also be different to those within the material.

The constraints above mean that the systems studied lie in a relatively limited region of the multi-dimensional matrix of variables and broader trends may be inaccessible until new techniques and/or sensors suitable for rapid measurement of high temperatures become available.

Symbols used

B=Pilling and Bedworth ratio [7, 8]
n=number of O atoms in a metal oxide
Q_D=the dissociation energy of the O_2 molecule=490 kJ mol^{-1}
T_m=melting point
Tamman temperature=0.52 T_m in K
ΔH_{exp}/(kJ (g mixture)$^{-1}$)=heat output per g of mixture

T_{max}=maximum temperature measured during combustion
r_f=the mean radius of the fuel particles
r_o=the mean radius of the oxidant particles
E_a/kJ mol^{-1}=apparent Arrhenius activation energy
A/s^{-1}=corresponding Arrhenius pre-exponential factor
k_{TA}=rate coefficient from thermal analysis
k_{TP}=rate coefficient from temperature profiles
$k_{combined}$=combined rate coefficient $(k_{combined})^{-1}=(k_{TA})^{-1}+(k_{TP})^{-1}$
v_{exp}=burning rate
c/(J K^{-1} g^{-1})=specific heat capacity
λ/(W m^{-1} K^{-1})=thermal conductivity
D/(m^2 s^{-1})=thermal diffusivity
t_r=measured rise time

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