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PREDICTION OF SHOCK RESPONSE OF PYROTECHNIC MIXTURES FROM THERMAL ANALYSIS

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Abstract

The thermal behavior of metal, oxide, and oxidizer mixtures, some with fluorine compound additions, has been studied in order to examine the influence of thermal properties on the initiation conditions for chemical reaction of pyrotechnic powders under dynamic loading conditions. The autoignition energies of the mixtures obtained from thermal analyses were compared with shock initiation energies, determined from planar shock measurements. Although some mixtures showed an approximate equivalency between the energies obtained from the two different experiments, the experimental results indicated that any comparison should be made with great care.

Keywords: autoignition, pyrotechnic mixtures, shock initiation

Introduction

Studies of pyrotechnic mixtures by Hardt [1, 2] and Schwarz [3, 4] have provided evidence of a possible equivalence between autoignition enthalpy (i.e., enthalpy required to raise the temperature of the mixture to the autoignition temperature) and the energy required for shock initiation. In addition to providing insight into the shock initiation mechanism, the conclusion was made that it should be possible to determine the initiation behavior of pyrotechnic mixtures under shock loading conditions from thermochemical and constitutive properties and without the need for extensive shock initiation experiments.

Our recent unpublished studies of several pyrotechnic mixtures have provided additional data to examine the latter conclusion. The data include both shock initiation threshold and unreacted Hugoniot measurements obtained by

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planar shock experiments, along with heat capacities and autoignition temperatures obtained by thermal measurements.

Thermal and shock reactivity data were compared using the methodology proposed by Hardt [2]. The approach used measured values of autoignition temperature and heat capacity to obtain ignition enthalpy values, and shock Hugoniot relationships and measured threshold pressures for chemical reaction to obtain shock initiation energy values. Ignition enthalpy, H_i, (i.e., energy per unit mass of heated material) is defined as:

$$H_i = C_p(T_i - T_o) \quad (1)$$

where C_p is the heat capacity of the mixture, T_i is the autoignition temperature, and T_o is the starting temperature (~27°C).

Shock initiation energy, E_i, (i.e., energy per unit mass of shocked material) is defined as:

$$E_i = 0.5u_p^2 \quad (2)$$

where u_p is the particle velocity at the initiation threshold pressure, P. The relationship between u_p and shock pressure, P, is defined as:

$$P=\rho_o U_s u_p \quad (3)$$

where p_o is the initial density of the mixture and U_s is the shock velocity. Equation (3) is the Rankine-Hugoniot relation for the conservation of momentum [5].

Experimental

Materials

Table 1 summarizes three pyrotechnic powder mixtures examined in this study. The two Teflon-containing mixtures were mixed by hand using a mortar and pestle while the other was mixed using a twin shell blender. The mixed powder was used for thermal measurements. Disk-shaped samples for planar shock testing were formed using a double-action press operating at 20 Kpsi. The $KClO_4$/Mg-Al alloy/Ca Resinate mixture was pressed to 84% of theoretical maximum density (TMD), the Ti/Teflon mixture to 85% TMD, and the Fe_2O_3/Al/Teflon (Thermite/Teflon) mixture to 78% TMD.

Table 1 Pyrotechnic powder mixtures

Material	Particle size (μm)
(49% $KClO_4$+49% Mg/Al+2% Ca Resinate)	$KClO_4$:≈100, Mg/Al:≈80
(80% Ti+20% Teflon)	Ti:35, Teflon:35
(90% (Fe_2O_3–4 Al)+10% Teflon)	Fe_2O_3:35, Al:15, Teflon:35

Planar shock experiment

Planar impact techniques, in-situ polyvinylidene difluoride (PVDF) shock-pressure gauges [6], and VISAR measurements of free surface (particle) velocities were used to obtain unreacted shock Hugoniot and chemical reaction data for the pyrotechnic powder mixtures. Samples were shocked by impacting a thin gun-launched, sabot-mounted flyer plate having well characterized shock properties [7] against a buffer (i.e., driver) plate of the same material upon which the sample was mounted (Fig. 1). A 76 mm evacuated powder gun was used as the launcher, and polymethyl methacrylate (PMMA) as flyer/buffer materials. The sabot had a cutout at the flyer plate interface so that all but the outer edge of the flyer plate rear surface was free. As the flyer plate impacted the buffer plate (i.e., sample holder) a compressive shock was generated in both materials and in the test sample. The subsequent reflection of the shock from the flyer rear free surface produced a rarefaction wave that propagated back to the test sample, providing the desired release behavior.

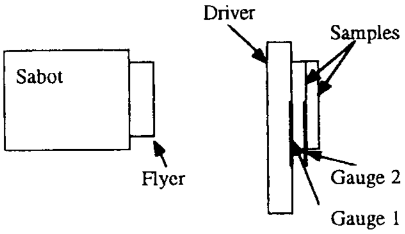


Fig. 1 Schematic of planar shock experiment

Each test sample consisted of a sandwich of two 3 to 5 mm thick discs of the pyrotechnic mixture along with two stress gauge packages, one mounted on the front (impact) surface of the first (upstream) disc and the second at the interface with the second disc. Each gauge package contained a 0.025 mm thick PVDF stress transducer (K-Tech Model B-25-09) with a 3 mm square active area. The gauges were covered with 0.038 mm thick sheets of Teflon foil to provide mechanical armoring. Each gauge package was bonded to the discs using urethane-based adhesive (Hardman D-50) to fill voids and prevent gas pockets in the sample near the transducer.

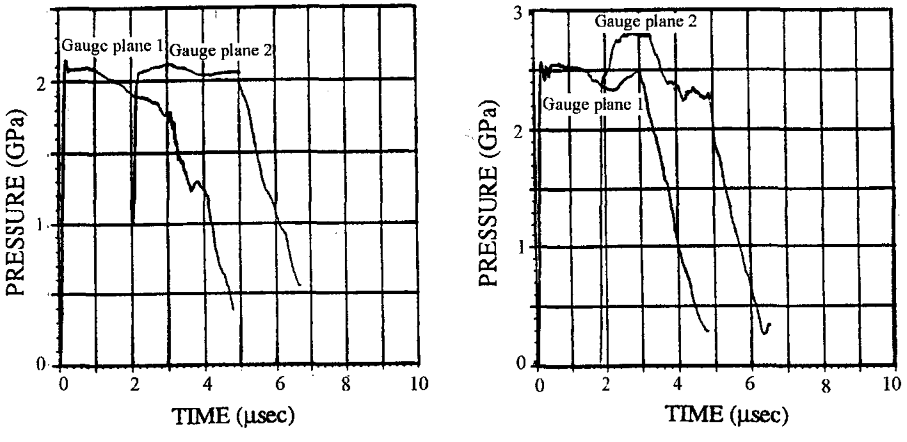
Thermal measurement

Thermal analyses of the pyrotechnic mixtures were performed using a TA 2000 system. Differential scanning calorimetry (DSC, TA 2910), at a heating rate of 10°C min^{-1} and atmospheric pressure, was used to obtain autoignition temperatures, T_i, and heat capacities, C_p, of the pyrotechnic mixtures. The autoignition temperature was determined as the temperature where significant exothermic reaction was observed from the curves. The heat capacity measurement was made by heating a small sample at a fixed rate (10°C $\min^{-1}$) from 40 to 200°C, where the sample was held in thermal equilibration before and after dynamic heating. Test samples were all contained in crimped aluminum pans which provided partial encapsulation of the materials. The simultaneous thermogravimetric and differential thermal analyzer (SDT, TA 2950), at a heating rate of 10°C $\min^{-1}$ and atmospheric pressure, was also employed to compare the decomposition and reaction behavior of unconfined pyrotechnic mixtures with the partially confined materials examined with DSC. Use of the SDT analyzer also permitted measurements over a wider range of temperatures (room temperature to 1000°C) than DSC (limited to 600°C for aluminum pans).

Because of the reaction violence of the materials used in this study, all thermal experiments are required to be done with safety precautions and expertise of scientist working on similar materials.

Results and discussion

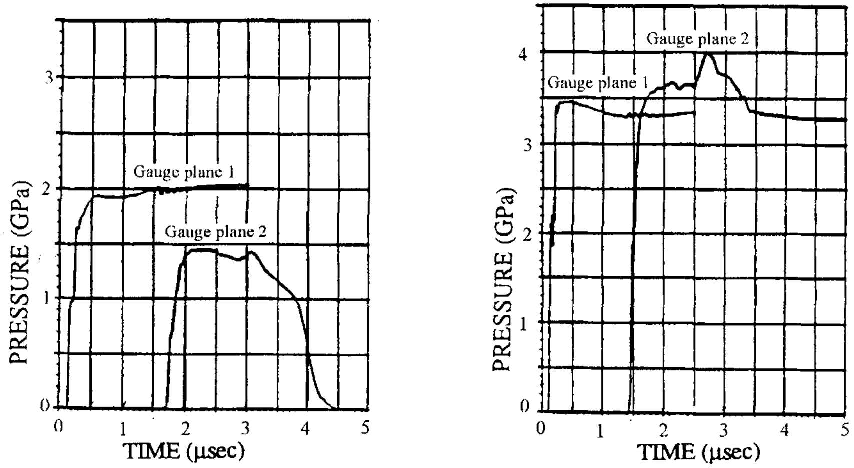
Shock pressures, P, at the onset of chemical reaction, were estimated from a comparison of input and downstream pressure histories (Figs 2–4). The onset of chemical reaction was marked by a significant increase in downstream pressure levels above input levels. The estimated threshold pressure was 2.1–2.6 GPa for the $KClO_4$/Mg-Al alloy/Calcium Resinate powder mixture, 1.9–3.5 GPa for the Ti/Teflon mixture, and <1.7 GPa for the Fe_2O_3/Al/Teflon mixture.



Input pressure 2.6 GPa

Input pressure 2.1 GPa

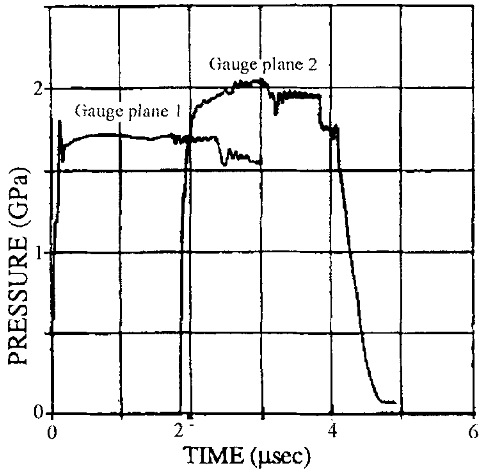
Fig. 2 Pressure histories for $KClO_4$/Mg-Al alloy/Calcium Resinate powder mixture showing absence (left) and presence (right) of chemical reaction at second gauge plane



Input pressure 3.5 GPa

Input pressure 1.9 GPa

Fig. 3 Pressure histories for Ti/Teflon powder mixture showing absence (left) and presence (right) of chemical reaction at second gauge plane



Input pressure 1.7 GPa

Fig. 4 Pressure history for Fe_2O_3/Al/Teflon powder mixture showing presence of chemical reaction at second gauge plane

From these values and unreacted shock Hugoniots, plotted in P-u_p space (Fig. 5), values of u_p at the onset of reaction were then estimated. Using this procedure, u_p values of 0.56–0.63 mm μs^{-1}, 0.28–0.40 mm μs^{-1}, and <0.33 mm μs^{-1} were obtained for the $KClO_4$/Mg-Al alloy/Ca Resinate, Ti/Teflon, and Fe_2O_3/Al/Teflon mixture, respectively.

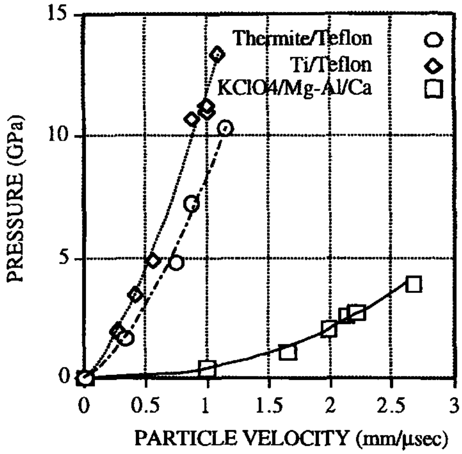


Fig. 5 P-u_p plots for pyrotechnic powder mixtures

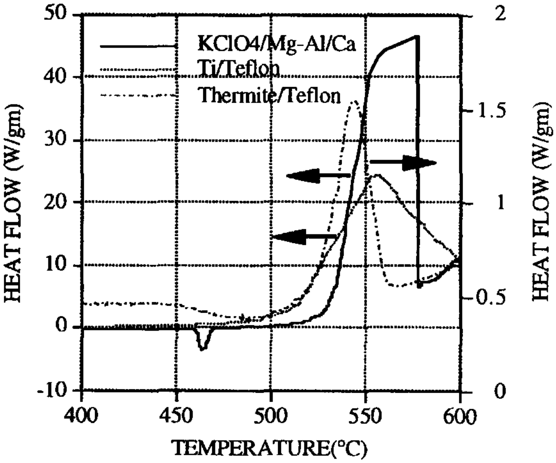


Fig. 6 DSC curves of pyrotechnic mixtures

Figure 6 shows the DSC curves and Fig. 7 shows the plot of heat capacity, C_p, as a function of temperature for the three pyrotechnic powders. From the curves, autoignition temperatures for the $KClO_4$/Mg-Al alloy/Ca Resinate, Ti/Teflon, and Fe_2O_3/Al/Teflon powder mixtures were estimated (from the intercepts of tangent lines at the onset of reaction) at 534, 511 and 506°C, respectively.

Assuming that the heat capacity values used in Hardt's analysis [2] represent ambient temperature measurements, the data in Fig. 7 were extrapolated to 27°C, using linear regression techniques, to obtain the corresponding heat capacity values for comparison. Using this approach, heat capacity values of 0.459, 0.256

Table 2 Comparison of autoignition and shock initiation energies

Material	TMD/ %	C_p/ J (g°C)$^{-1}$	T_i/ °C	H_i/ J g^{-1}	P/ GPa	u_p/ mm μs^{-1}	E_i/ J g^{-1}
(49% KClO4+49% Mg/Al+2% Ca Resinate)	84	0.459	534	233	2.1–2.6	0.56–0.63	157–198
(80% Ti+20% Teflon)	85	0.256	511	124	1.9–3.5	0.28–0.40	38–80
(90% (Fe_2O_3–4 Al)+10% Teflon)	78	0.679	506	325	<1.7	0.33	54
3 Fe_3O_4–8 Al*	38	0.67	936	626	12	1.13	634
3 Fe_3O_4–8 Al*	52	0.67	936	626	15	1.17	684
(33% $TiH_{0.65}$+67% $KClO_4$)*	75	0.69	500	329	2.9	0.72	259
2 B–Ti*	71	0.67	1000	653	>14	1.35	912
3 Pt–Hf*	46	0.21	235	43.7	2	0.29	43.5

* Ref. 2

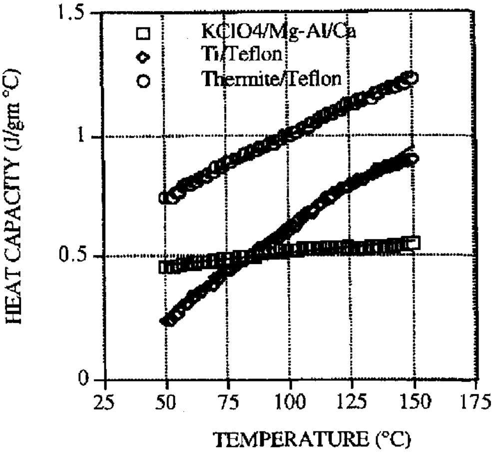


Fig. 7 Heat capacity *vs.* temperature of pyrotechnic powder mixtures

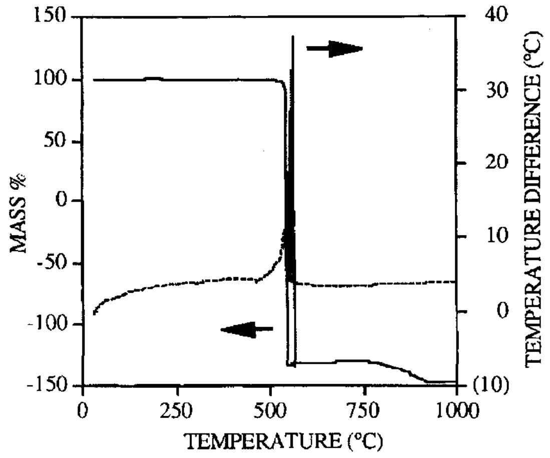


Fig. 8 Simultaneous TG-DTA curves of $KClO_4$/Mg-Al alloy/Ca Resinate powder

and 0.679 $J(g°C)^{-1}$ were estimated for the $KClO_4$/Mg-Al alloy/Ca Resinate, Ti/Teflon, and Fe_2O_3/Al/Teflon powder mixtures, respectively.

Autoignition energies, H_i, and shock initiation energies, E_i, were then calculated from Eqs (1) and (2). Table 2 summarizes the calculated values of H_i and E_i for the three materials along with those for other pyrotechnic materials compared in Hardt's earlier studies [2].

While a comparison of autoignition and shock initiation energies for the five pyrotechnic materials studied by Hardt [2] shows reasonable agreement (Table 2), only two of the three materials examined in the present study ($KClO_4$/Mg-Al

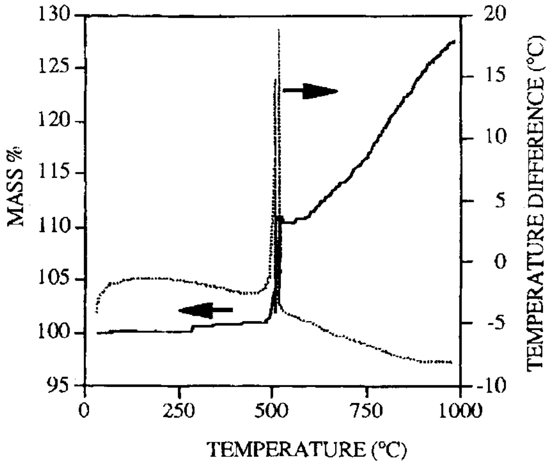


Fig. 9 Simultaneous TG-DTA curves of Ti/Teflon powder

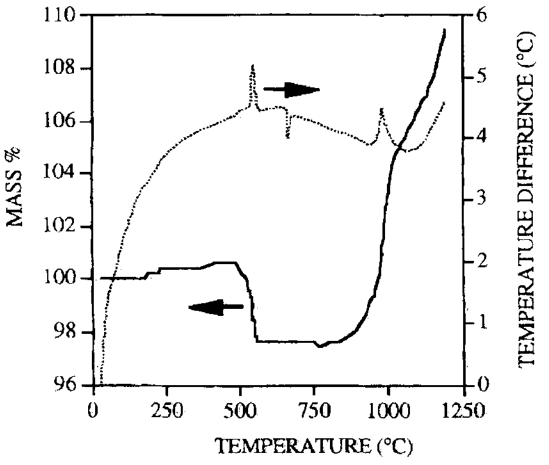


Fig. 10 Simultaneous TG-DTA curves of Fe_2O_3/Al/Teflon powder

alloy/Ca Resinate and Ti/Teflon mixtures) show similar agreement. A comparison of DSC curves with curves of unconfined samples using SDT measurements (Figs 8–10) shows a strong, single exothermic reaction associated with significant mass change, indicative of vigorous reaction, for both $KClO_4$/Mg-Al alloy/Ca Resinate and Ti/Teflon mixtures. On the other hand, the SDT curve of the Fe_2O_3/Al/Teflon mixture shows two exothermic reactions at 540 and 960°C due to decomposition of Teflon and oxidation processes, respectively, and an endothermic peak at 663°C due to the melting of aluminum. This indicates that the

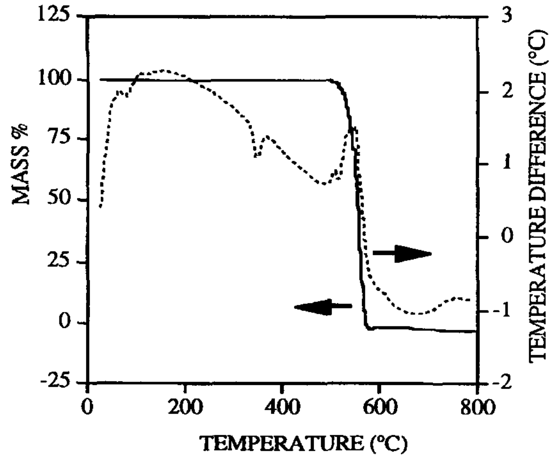


Fig. 11 Simultaneous TG-DTA curves of Teflon powder (35 μm)

exothermic peak observed at ≈550°C from DSC curve of Thermite/Teflon (Fig. 7) is most likely due to the decomposition of Teflon (Fig. 11) rather than a reaction between the different constituents. If so, this could mean that the disagreement between autoignition and shock initiation energies for the Fe_2O_3/Al/Teflon mixture is, in fact, even larger.

The reason for this large disparity for the Fe_2O_3/Al/Teflon mixture is not obvious; however, it may simply reflect the reduced level of confinement for the thermal measurements. Another possibility would be an erroneous heat capacity value. Although the calculation of autoignition energies were made using C_p values at room temperature, it is evident from an inspection of Fig. 7 that C_p is temperature dependent. A third possibility would be an incorrect value for the reaction threshold pressure, P. It is clear that the threshold pressures used in this comparison represent minimum values. Without additional information on the nature of the event(s) observed in the pressure records (e.g., as provided by real time spectroscopy or postmortem analyses), it is not obvious that the overpressures observed at the second gauge plane represent complete reaction between the constituents or merely decomposition of the oxidizing material, or perhaps limited reaction.

An equivalency between autoignition and shock initiation energy infers that the bulk temperature of the powder mixture is approximately the same for both test conditions [1, 2]. This might be a reasonable assumption for highly porous powders in which mass mixing is considered to be a major factor in enhancing reactivity under shock loading conditions [8]. If reaction occurs only in localized areas of the sample, however, it is unlikely that the bulk temperature of the sample would reach the autoignition temperature.

Conclusion

A comparison of thermal and shock initiation energies for three pyrotechnic powder mixtures tends to support earlier observations concerning the equivalency of the two energies; however, the study also revealed that any attempt to use the autoignition energy as a substitute for the shock initiation energy should be approached carefully because of the temperature dependence of heat capacity, possible dependence of autoignition temperature on sample confinement conditions (i.e., pressure influences), and uncertainties regarding the source of the overpressures observed in the planar shock experiments.

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