Photothermal Initiation of Hybrid Organic/Inorganic Metastable Interstitial Composites: Synergistic Effects on the Dynamics of Energy Release

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The organic high-energy material pentaerythritol tetranitrate (PETN) was incorporated at low concentrations into Al (100 nm)/Fe_2O_3 metastable intersititial composites (MIC) to form a hybrid organic/inorganic high-energy material. Studies of the dynamics of energy release were carried out by initiating the reaction photothermally with a single 8 ns pulse of the 1064 nm fundamental of a Nd:YAG laser. The reaction dynamics were measured using time-resolved spectroscopy of the light emitted from the deflagrating material. Two parameters were measured: the time to initiation and the duration of the deflagration. The presence of small amounts of PETN (16 mg/g of MIC) results in a dramatic decrease in the initiation time. This is attributed to a contribution to the temperature of the reacting system from the combustion of the PETN that, at lower loadings, appears to follow an Arrhenius dependence. The presence of PETN was also found to reduce the energy density required for single-pulse photothermal initiation by an order of magnitude, suggesting that hybrid materials such as this may be engineered to optimize their use as an efficient photodetonation medium.

Introduction

A new approach to the development of high-output energetic materials is the exploitation of binary fuel/oxidant inorganic solid-state reactions typified by the well-known Fe_2O_3/Al thermite reaction.[1]

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe \quad \Delta H = 3.97\ \text{kJ/g}$$

The advantage to these inorganic materials is that the energy density can be several times higher than conventional organic high-energy compounds; however, due to the fact that they are a two phase system, the rate of energy release is usually significantly lower, making them impractical for many applications.

Two approaches have been devised to overcome this problem. One is the development of metastable interstitial composite (MIC) materials in which one of the components (typically the fuel) is of nanoscale dimensions. Improvements in the rate of energy release are generally attributed to better mixing of the components and more intimate fuel/oxidant contact.[2–5] Another approach, applied to conventional (i.e., micron scale) thermite-type compositions as well as to MIC materials, is to mix traditional organic high-energy materials, such as 2,4,6-trinitrotoluene (TNT), cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX), and pentaerythritol tetranitrate (PETN), into the inorganic system to form an organic/inorganic composite. In these systems, the energy release of the binary metal/oxide system is driven by the conventional explosive, thereby releasing energy much more rapidly and in a controlled fashion.[6–8] Studies to date have indicated that this approach affords great promise in exploiting the high energy density provided by binary inorganic energetic compositions.

Recently, we have studied various aspects of the interfacial chemistry between organic high-energy molecules such as TNT and PETN and the fuel and oxides typically used in fuel/oxide energetic compositions.[9,10] As a continuing part of that effort, we report here an investigation into the energy release dynamics of the Al/Fe_2O_3 MIC materials as a function of PETN incorporation. The study was carried out using short pulse (ns) photothermal initiation, with the dynamics of the process studied by time-resolved spectroscopic techniques.

TABLE 1

mg of PETN/ g of MIC composite	fraction of heat given off by PETN	energy of PETN/g of composite (kJ/g)
15.99	0.0343	0.1302
31.97	0.0615	0.2602
63.95	0.116	0.5206
95.92	0.164	0.7808
127.90	0.208	1.041

Experimental Section

Materials. The iron(III) oxide powder, <0.25 μm, was purchased from Aldrich, while the 100 nm aluminum was obtained from Argonide. All materials were used as received. Pentaerythritol tetranitrate (PETN) was prepared according to the literature and stored in acetone (Aldrich, HPLC grade) for safety purposes.[11]

Preparation of Samples. Pentaerythritol tetranitrate (PETN) was deposited onto the iron(III) oxide by a wet impregnation technique. A small amount, up to 1.053 mL, of PETN standard solution (~0.5 M) was added to 0.5 g of Fe_2O_3 in order obtain varying loadings of PETN in the final composite. (Table 1) The acetone of the stock solution of PETN was subsequently removed under a vacuum (10^{-3} Torr), leaving a dry powder. The thermite samples were prepared by mixing the Fe_2O_3/PETN samples with 100 nm aluminum particles in a 1:1 molar aluminum to iron ratio. The samples were thoroughly mixed

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by grinding the components together using a mortar and pestle in order to ensure a homogeneous mixture. Approximately 0.25 g of this mixture was compressed in a die at an applied pressure of 46 000 psi. The resulting pellets were 6.39 mm in diameter by 3.28 mm, giving an average density of 2.38 g/cm^3.

Instrumentation. A Spectra-Physics DCR-3G Nd:YAG laser using single pulses of both 1064 and 532 nm light was used in order to combust the thermite/PETN samples. At 1064 nm an 8 ns 900 mJ pulse was focused through a fused silica 75 mm focal length lens onto the pellet, while at 532 nm the laser pulse was 6 ns and 360 mJ. The focused beam diameter was calculated to be 11 μm, giving an energy density of 8.8×10^5 J/cm^2 at 1064 nm and 5.7 μm with an energy density of 1.4×10^6 J/cm^2 at 532 nm. The laser beam was focused through a hole in a protective steel plate, with the hole measuring 2.54 cm in diameter, which was covered by a fused silica window measuring 24 × 23 × 2 mm in order to catch any debris from the combustion of the pellet.

The kinetics of the combustion flash was recorded using three photodiode detectors (Thorlabs DET210, 0.8 mm^2 Si PIN, 1 ns risetime) and recorded by digital storage oscilloscopes (LeCroy LC 564A, 1 GHz bandwidth, 250 ps sampling rate for fast signals; LeCroy 9410, 150 MHz bandwidth, 10−50 μs sampling rate for slow signals). The photodiodes were placed 45° from the laser beam axis, looking down at the sample through a fused silica window, and filtered by either a heat-absorbing filter (Hoya HA30) to reduce the 1064 nm scattered light (fast signal) or a 520 nm band-pass filter (Thorlabs FB520−10, 10 nm fwhm) for both slow and fast signals. Spectra were collected through a 3 mm diameter liquid light guide (Oriel 77554, NA/0.47, >50% transmittance from 270 to 720 nm) placed above the sample at 45° from the laser beam axis coupled into a 300 mm spectrograph (Acton Research Corp. Spectra Pro 308i, 150 grates/mm grating blazed at 300 nm) using a biconvex fused silica lens (Spex, 1 in. diameter, $f = 28.6$ mm), and the light was dispersed onto a back-thinned CCD (1340 × 400 pixels, 20 μm square, Princeton Instruments LN/CCD-400EB-G1 operated at −90 °C). The timing for single shot operation was coordinated by triggering the CCD shutter, laser, and oscilloscope using a digital delay generator (EG&G PAR 9650) to trigger the CCD shutter to open for 30 ms and delaying the laser and oscilloscope triggers for 10 ms. The CCD exposure time, set in the software to 10 ms, was determined to be 30 ms by adjusting the laser trigger delay while observing the second harmonic 532 nm laser light.

Results and Discussion

The effect of PETN incorporation on the dynamics of Al/Fe_2O_3 MIC initiation and deflagration was investigated using time-resolved spectroscopic techniques.[12−14] In general, thermal initiation of the thermite reaction occurs when the reaction temperature reaches or exceeds the melting temperature of the fuel, in this case aluminum.[1] At this point there is a breakdown of the native oxide layer on the aluminum and the mass transport between the fuel and the oxide becomes large enough to propagate the reaction. For our studies, combustion of the samples was achieved photothermally using a single 8 ns pulse of the 1064 nm fundamental from a Spectra-Physics DCR-3G Nd:YAG laser, which allows the use of time-resolved spectroscopic techniques. As such, the dynamics was monitored over the total time regime of the process by light emitted from the reacting material, collected through a band-pass filter with $\lambda_{max} = 520$ nm.

The time-resolved data for the Fe_2O_3/A 100 nm Al MIC materials containing various amounts of PETN are shown in Figure 1. The emissive plume generated by the laser incidence event on the surface of the sample can be seen as a sharp spike, indicated by an arrow in the figure, while the irregular intensity that follows it in time is the plasma emission from the deflagration of the sample.[12,15] An important quantitative parameter of the reaction dynamics is the ignition time. For photothermally initiated binary fuel/oxidant materials, this is defined as the time at which the energy released by the reaction becomes greater than or equal to the energy put into the composite by the laser. For data collected photonically, the ignition time is generally taken as the time between the laser excitation and when emitted light can be detected.[5] In analyzing the data acquired from the time-resolved system employed here, we define the ignition time as the period between the sharp plume emission from the initial laser incidence and the point at which the intensity of the light emitted from the combusting sample is twice the intensity of the noise, as measured in the pretrigger region of the data. A plot of the initiation time against the amount of PETN in each sample at 1064 nm is shown in Figure 2. The ignition time at 1064 nm for the pure thermite sample was found to be 6.05 ± 0.28 ms; however, with the incorporation of PETN (16.0 mg/g of thermite), the ignition time drops precipitously to 3.35 ± 0.28 ms and continues to decrease until a minimum value of 1.60 ± 0.354 ms is observed with 64.0 mg of PETN/g of thermite. Above this amount of

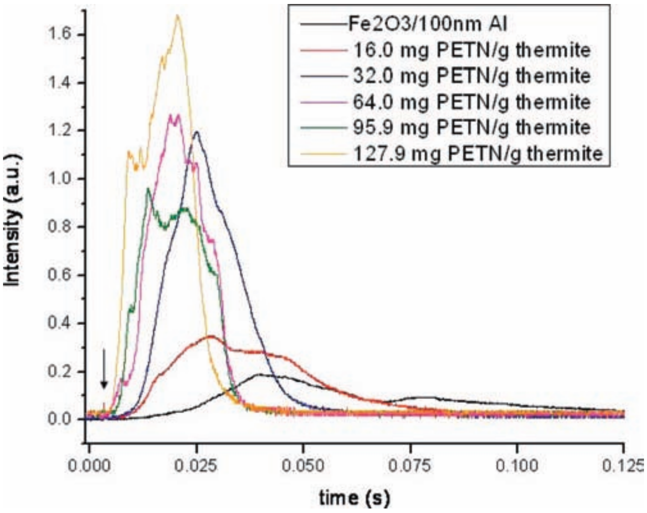

Figure 1. Photothermal initiation of Fe_2O_3/100 nm Al samples with increasing amounts of PETN at 1064 nm (arrow indicates the position of the laser plume emission).

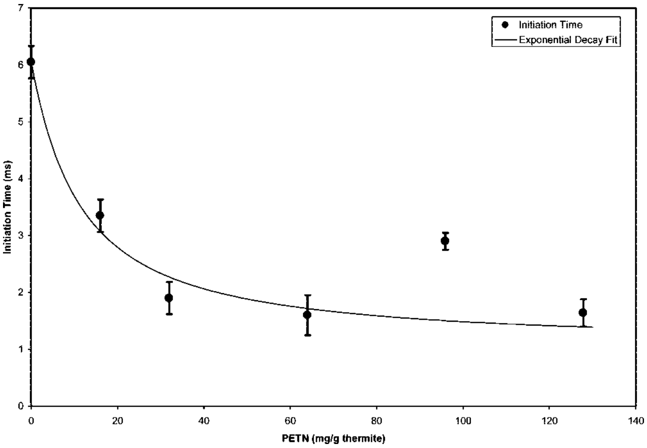

Figure 2. Initiation time (ms) as a function of PETN coverage in milligrams at 1064 nm.

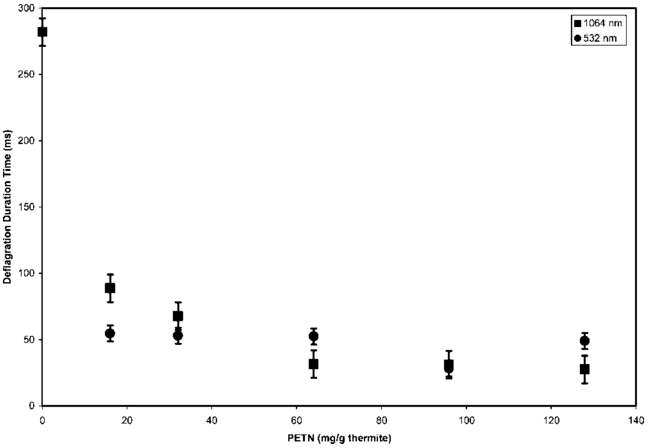

Figure 3. Deflagration duration time (ns) as a function of the amount of PETN for 1064 nm and 532 nm excitation.

PETN there is no further decrease and, in fact, a small but reproducible increase is observed. For safety reasons, it was not possible to obtain data for higher concentrations of PETN.

The intense, irregular peak that follows ignition (Figure 1) is the time-evolution of the plasma emission from the deflagration of the sample. The apparent oscillations in the emission intensity are attributed to modulation of the light by the deflagration process, with the duration of this emission being directly related to the total time it takes for the sample to deflagrate. From the data, the deflagration duration is measured from the previously determined ignition time to the time when the emission intensity has returned to a value of twice the noise level. A plot of the deflagration duration as a function of PETN loading is shown in Figure 3. As can be seen in Figures 1 and 3, the incorporation of a small amount of PETN into the MIC material has a pronounced effect on the deflagration duration. The deflagration of a control sample of Al/Fe_2O_3 MIC materials with no organic phase present shows a weak broad emission with a long (282 ms) duration. The addition of a small amount of PETN (16.0 mg/g of thermite) results in a significant decrease in the deflagration duration to 88 ms. The deflagration duration continues to decrease as more PETN is added, albeit more gradually, until it plateaus at 31.5 ms for 64.0 mg of PETN/g of thermite. Scrutiny of the spectral data in Figure 1 shows that, in general, the decrease in deflagration duration is accompanied by an increase in the emission intensity, which suggests that, as expected, more energy is being released in a short time period.

The changes observed in both the ignition time and the duration of deflagration as a function of PETN addition appear to follow the same basic trend: increasing amounts of PETN result in a decrease in the time to ignition and the deflagration duration, the effect of which ultimately plateaus at about 64.0 mg of PETN/g of thermite. In general, these effects can be thought of as originating from the contribution of the heat of combustion of the organic phase to that of the fuel/oxidant inorganic matrix, which acts to accelerate the binary reaction. PETN is a high-energy molecule with a heat of combustion of 2572 kJ/mol.[16] The amount of energy provided by the PETN and its contribution to the total energy output of the composite material at various levels of incorporation are given in Table 1. At the highest loading studied, the PETN accounts for about 20% of the total energy liberated by the composite during combustion.

The effect of the PETN on the initiation time is likely due to its combustion during or immediately after the laser excitation event. Specifically, the laser excitation rapidly heats a volume of the composite defined by the diameter of the beam and the thermal diffusion length of the material.[13,14] During the course of the 8 ns pulse, both the aluminum and the iron oxide are heated, with the relative temperature attained by each phase being dependent primarily on its optical absorbance at 1064 nm and its thermal diffusivity. The PETN is not absorbing at this wavelength, so its combustion occurs from heat flow from the other components. This will happen relatively efficiently, since the combustion temperature of the PETN is 205 °C, while the temperature reached by the inorganic components will be at or above their melting point. The PETN will contribute heat back into the inorganic components when combusted, thereby raising the temperature further and accelerating the initiation processes. Since even at the lowest incorporation level the combustion of PETN provides sufficient heat to melt all of the Al in the composite, its contribution to the initiation process will be substantial; this is directly reflected in the data.

The decrease in the initiation time as a function of PETN concentration (Figure 2), particularly in the region before the plateau in the time is reached, is not linear but instead appears to be approximately exponential. This suggests possible Arrhenius behavior in the rate (lifetime) of the initiation. Earlier studies in the rates of binary fuel/oxidant systems have suggested that the behavior of the rate is Arrhenius in the early stages before autoacceleration of the reaction occurs, due to the extreme exothermicity.[17,18] This suggests that Arrhenius-type behavior may also be valid during the initiation process prior to deflagration. The rate (lifetime) of initiation in the composite will depend on the temperature of the material, which is set to an initial value by the laser pulse and is, subsequently, augmented by the combustion of the PETN. The contribution of the PETN to the final temperature will be approximately proportional to the product of the mass of PETN and the heat of combustion: $T \propto \Delta Hm$. An Arrhenius expression incorporating this relationship is shown in eq 1, where the initial temperature, T_0, is attained from the laser pulse, while the contribution from the PETN is a function of the mass, m, with the constant, C, representing the heat of combustion of the PETN and the thermal conductivity and heat capacity of the inorganic components that are being heated by it.

$$\frac{1}{t_{\mathrm{init}}} = A \exp\left(-\frac{E_{\mathrm{a}}}{R(T_0 + Cm)}\right) \tag{1}$$

This form of the Arrhenius equation fits well to the initiation time data, particularly at low PETN loadings, which is consistent with our basic model of how the PETN affects the dynamics. The deviation from Arrhenius behavior as the initiation time plateaus at PETN loadings >64 mg/g thermite is somewhat unclear, but it may simply be that the maximum rate has been reached and that additional heat placed into the melting and vaporization of the inorganic components will have only a minimal effect.

As discussed, the deflagration duration (Figure 3) of the reaction decreases rapidly with the addition of PETN and, like the initiation time, it reaches a relatively constant value at ≥64 mg/g. The lifetime of the deflagration is not described by the Arrhenius temperature dependence; however, this is expected due to the high exothermicity and concomitant autoacceleration of the reaction. The leveling off of the deflagration time may represent a limiting value determined by the PETN combustion time, initiated in this fashion, as it begins to dominate the energetics of the composites.

Studies of the ignition time and deflagration duration were carried out with visible excitation at 532 nm. Since this

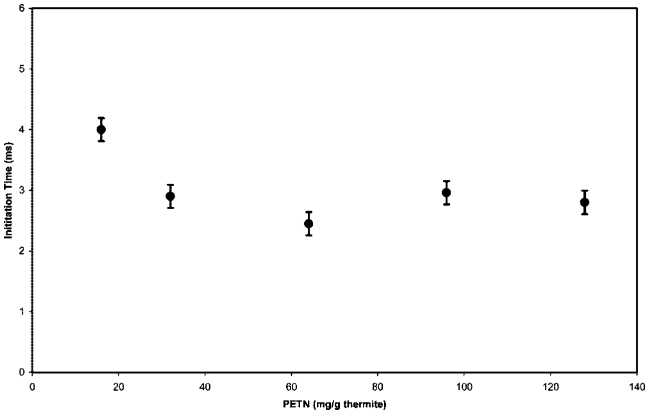

Figure 4. Initiation time of Al/Fe_2O_3 MIC materials with various concentrations of PETN initiatied with a single pulse of 532 nm radiation.

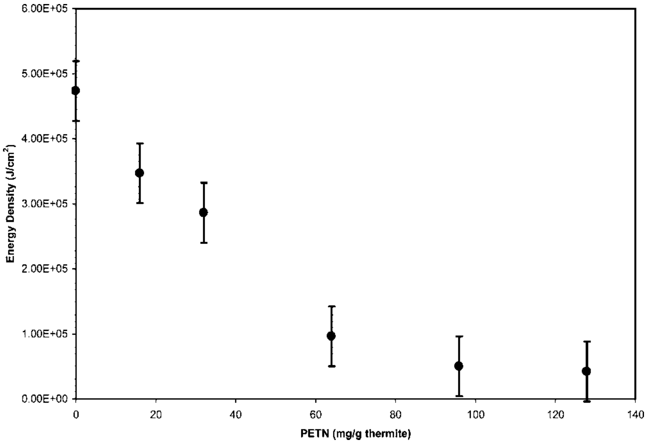

Figure 5. Energy density (J/cm^2) required in order to initiate thermite/PETN mixtures at 1064 nm.

wavelength is achieved through frequency doubling of the 1064 nm fundamental, the highest energy density that could be realized was 1.4×10^6 J/cm^2. At this energy density it was not possible to initiate the combustion of the pure Al/Fe_2O_3 MIC materials; however, the presence of a small amount of PETN (16.0 mg/g thermite) resulted in reproducible single-pulse initiation. This effect is explainable in terms of the prior discussion. While the energy provided at 532 nm is insufficient to initiate the pure thermite, it does provide sufficient heat to combust the PETN, which then provides enough heat to drive the overall combustion. Notably, PETN does not absorb at 532 nm, so there is no optical contribution to the effect. Consistent with this interpretation, the initiation time for 532 nm excitation (Figure 4) is always longer than what is observed for 1064 nm excitation, which is expected from less total heat going into the system and the fact that initiation is achieved secondarily through the PETN. The deflagration duration is essentially the same as that observed with 1064 nm initiation (Figure 3), which is consistent with the idea that the duration of deflagration is dictated by the energy release of the composite system and is independent of the initiation conditions.

The results at 532 nm excitation suggest that one of the propitious effects of PETN incorporation is to lower the threshold energy required for single-pulse initiation. This could have an impact on strategies for developing efficient photodetonation systems.[19,20] To quantify this effect, the initiaton threshold energy was determined for the range of PETN loadings using 1064 nm initiation. The threshold energy density required to initiate pure Al/Fe_2O_3 MIC samples at 1064 nm is quite high at 4.7×10^5 J/cm^2. The addition of PETN results in a relatively linear decrease in threshold energy required for initiation at 1064 nm up to 64.0 mg of PETN/g of thermite with the energy reaching a minimum value of 5.03×10^4 J/cm at 95.9 mg of PETN/g of thermite (Figure 5), which represents almost an order of magnitude decrease in the necessary energy density.

Conclusion. In conclusion, the addition of high-energy materials, in this case PETN, to metastable interstitial composites (MIC) such as thermite-type Al/Fe_2O_3 compositions changes the energy release dynamics compared to that of traditional MIC compositions. This is observed as a decrease in the initiation time and the duration of deflagration of the sample. This effect is attributed to the contribution to the overall heating of the sample due to the combustion of the PETN. Since the PETN does not absorb light, the process occurs through the indirect heating of the PETN from the inorganic phases to the point where combustion occurs. The initiation time and deflagration duration decease with increasing PETN loadings but reach a minimum at about 64.0 mg of PETN/g of thermite. Compositions containing PETN were found to require a much lower threshold energy for photothermal initiation. These results indicate that the incorporation of an organic phase, even at low concentrations, can have a profound affect on the reaction dynamics of MIC materials. This, we believe, affords the possibility of tailoring the organic phase to better optimize the desired properties of the materials.

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