

nected to a computer. A three-electrode-cell assembly was used, where the working electrode was an ITO-coated glass slide (7 mm × 50 mm × 0.6 mm, resistivity $R_s \leq 10 \Omega/\text{square}$, Delta Technologies Inc.). The counter electrode was a platinum wire, and a Ag wire was used as a pseudo-reference electrode. The pseudo-reference was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc⁺) in the electrolyte. Polymer films for spectroelectrochemistry were prepared by potentiostatic deposition on ITO-coated glass slides.

Monomer Synthesis: To a degassed solution of 20 mg (0.025 mmol) of diketobisfulleroid (**2**) [11] in 4 mL of *o*-dichlorobenzene was added 8.3 mg (0.03 mmol) of 3',4'-diamino-2,2':5',2''-terthiophene (**1**) in 1 mL of acetic acid [12]. The mixture was heated to 70 °C for 1 h. After cooling, 25 mL of methanol was added to precipitate the crude adduct. A black solid collected after centrifugation was washed several times with ether and hexane. The residual dark-brown powder was washed successively with methanol, toluene, ether, and *n*-pentane. Removal of solvent gave 24 mg (0.023 mmol, 92 %) of pure product **3** as a dark-gray solid. ¹H NMR (500 MHz, CDCl₃/CS₂ = 1:5, ppm) δ 7.15 (dd, 2H), 7.41 (dd, 2H), 7.79 (dd, $J = 3.7$ Hz, 2H). Due to the limited solubility of bisfulleroid **3** ¹³C NMR data could not be obtained. High-resolution mass spectrometry (HRMS) (m/z): [M + H]⁺ calcd. for C₇₆H₉N₂S₃ 1 044.9979; found, 1 044.9920.

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Synthesis and Reactivity of a Super-Reactive Metastable Intermolecular Composite Formulation of Al/KMnO₄**

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Mixtures of oxidizer and fuel with particle sizes in the nanometer range have been widely used for energetic-material applications and are termed metastable intermolecular composites (MICs). The prevailing wisdom in the potential use of nanoscale energetic materials is a presumed reduction in mass-transport limitations and the trend to increase the energy-release rate as the reaction becomes kinetically controlled.^[1] Out of a large number of possible thermite combinations that are thermodynamically feasible,^[2] only a few combinations have been investigated.^[3–5] While thermodynamic calculations of adiabatic flame temperatures and reaction enthalpies are tools to help in the choice of a desirable MIC formulation, they do not, in general, provide in a straightforward manner any insights into reaction kinetics.

The most widely used MIC formulations in the nanometer regime are nano-Al (fuel) with MoO₃, CuO, and Fe₂O₃ oxidizers. Much of the current research in the field is focused on better characterization of the phenomenological burning properties with respect to temperature and pressure.^[6] The two most common techniques employed to measure reactivity of MICs are open-burn tests for propagation-velocity measurements and pressure-cell tests for measurement of pressurization rates during confined combustion. Other studies have shown an excellent correlation between the two techniques, whereby materials with high pressurization rates also show high propagation velocities.^[7]

KMnO₄ is widely used for its strong oxidizing nature. With a +7 oxidation state, manganese can be reduced to an oxidation state of +4 in MnO₂ or 0 in Mn, and should provide a high oxidation potential for a thermite-type reaction. Pyrotechnic systems of micrometer-size Sb/KMnO₄ systems have been studied in the past,^[8,9] however, reactivity of nano-KMnO₄ with a more reactive fuel, Al, has not been studied. High adiabatic flame temperatures, high enthalpy of reaction of fuel

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with oxidizer, and high volatility of oxidizers at relatively low temperatures are the most desirable properties in a good oxidizer. Table 1 shows the adiabatic flame temperatures and enthalpies of reaction for different Al/thermite combinations. We notice that KMnO_4 has thermodynamic properties com-

Table 1. Adiabatic flame temperatures and enthalpies of reaction (ΔH) of Al combustion with different oxidizers in stoichiometric proportions.

| Reaction | Adiabatic Flame Temp. [K] | H [kJ per mol of Al] |
|--------------------------------|---------------------------|----------------------|
| 2 Al + Fe_2O_3 | 3135 | -425 |
| 2 Al + 3 CuO | 2837 | -604 |
| 2 Al + MoO_3 | 3809 | -465 |
| 8 Al + 3 KMnO_4 | 3744 | -523 |

parable to those of the more widely used oxidizer. An advantage of using KMnO_4 is its high volatility. It decomposes at about 300°C , which is significantly lower than most other oxidizers under consideration. The low cost of KMnO_4 and the simplicity of the procedure with which it can be formed into nanoparticles are added advantages for its potential use as an oxidizer.

In this communication, we describe the formulation of a new MIC which employs KMnO_4 nanoparticles as the oxidizer, and we present a comparison of the pressurization rate with existing and more traditional nanoformulations. Reaction-rate measurements are performed in terms of pressurization rate under confined combustion of the MIC. We discuss the synthesis of KMnO_4 nanoparticles by an aerosol-phase spray-drying method, and pressurization-rate performance of a MIC in the form of a loose powder composed of Al/ KMnO_4 nanoparticles. As a comparison, we also measured the pressurization rates for Al/CuO nanoparticles. The CuO nanoparticles were synthesized by spray pyrolysis of a nitrate precursor, and the synthesis procedure has been briefly described in the Experimental section.

A fixed mass (25 mg) of MIC in the form of a loose powder was ignited in each shot, and the pressurization rate of the vessel due to the MIC ignition was measured. A typical pressure trace obtained is shown in Figure 1. The initial slope of the pressure curve is defined as the pressurization rate (dP/dt). Thermite mixtures of Al/CuO and Al/ KMnO_4 prepared in different stoichiometric proportions were tested in the pressure cell for pressurization rates.

Pressurization rates measured for Al/ KMnO_4 mixtures as a function of composition of the mixture are shown in Figure 2. Also shown in the figure are the maximum pressures attained in the vessel and the rise time, which is the time required to reach maximum pressure after ignition. The pressurization rate is calculated by taking the ratio of the maximum pressure to the rise time. The maximum pressurization rate was observed at ~ 35 wt.-% of Al in the reaction mixture, and was about $290 \text{ psi}\mu\text{s}^{-1}$ ($1 \text{ psi} = 6.895 \times 10^3 \text{ Pa}$). Similar trends of

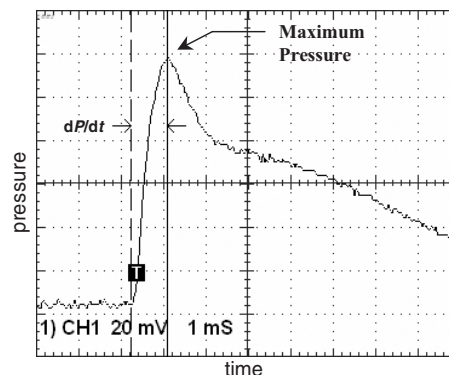


Figure 1. A typical pressure trace obtained as a function of time. Pressurization rate (dP/dt) is calculated as the initial slope of the curve. (The trigger point for capturing the response is indicated by T.)

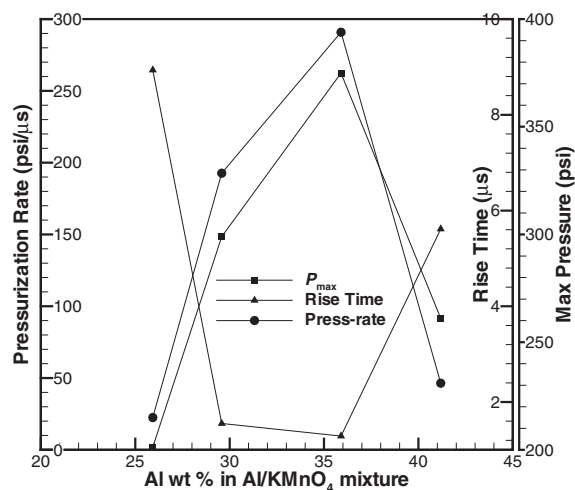


Figure 2. Pressurization-rate, maximum-pressure, and rise-time measurements at different stoichiometries for the Al/ KMnO_4 MIC ($1 \text{ psi} = 6.895 \times 10^3 \text{ Pa}$).

pressurization rate with respect to composition were observed for CuO and MoO_3 .^[7] Typical values of pressurization rates measured in this study (Al/CuO and Al/ KMnO_4) and from the literature for different thermite nanocomposites are presented in Table 2. Although the source of Al nanoparticles may not be the same in each of these measurements performed by different groups, we get an idea as to which MIC formulation can be most reactive. We notice that Al/ KMnO_4 exhibits pressurization rates almost two orders of magnitude higher than that observed for Al/CuO or Al/ MoO_3 particles, and several orders of magnitude higher than that observed for Al/ Fe_2O_3 .

Although thermodynamically the thermite combinations seem to be similar in characteristics (Table 1), Al/ KMnO_4 exhibits a much faster pressurization rate. Figure 3 shows the mole fraction of free atomic O at the adiabatic flame temperature as a function of equivalence ratio for the various MICs

Table 2. Comparison of pressurization rates of MICs composed of 40 nm Al and different oxidizer particles. Measurements for CuO and KMnO_4 were performed in this study, while other data have been taken from the literature.

| Oxidizer | Synthesis/source | Oxidizer particle size [nm] | Al at $(dP/dt)_{\max}$ [wt.-%] | $(dP/dt)_{\max}$ [$\text{psi } \mu\text{s}^{-1}$] ^[a] |
|----------------------------------------|------------------|-----------------------------|--------------------------------|--------------------------------------------------------------------|
| Fe_2O_3 | NanoCat Technol. | 80 | - | ~0.017 |
| Fe_2O_3 ^[4] | Aero-sol-gel | 200 | - | ~0.000096 |
| CuO | Spray-pyrolysis | 250 | 30 | 4.45 |
| MoO_3 ^[7] | - | 40 | 45 | 8 |
| KMnO_4 | Spray-drying | 250 | 35 | 290 |

[a] 1 psi = 6.895×10^3 Pa.

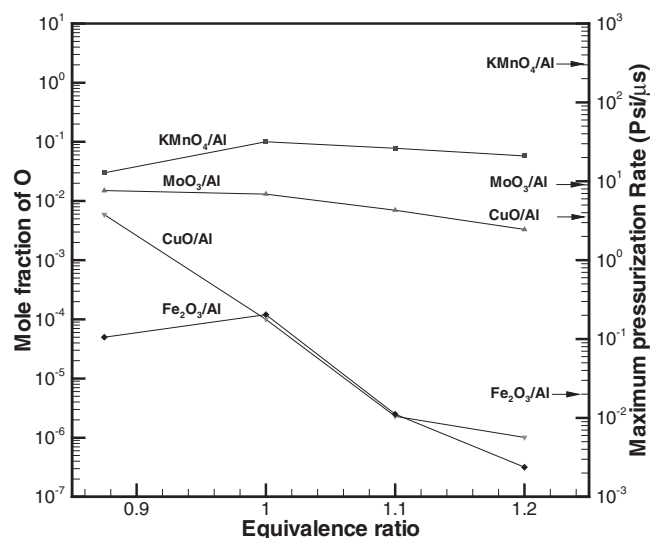


Figure 3. Calculated mole fractions of nascent O as a function of equivalence ratio for Al with different oxidizers at the adiabatic flame temperature. The maximum pressurization rates obtained for different MICs are indicated by arrows on the right-hand ordinate.

under consideration, estimated using the National Aeronautics and Space Administration (NASA) chemical equilibrium program CEA (Chemical Equilibrium with Applications). The concentrations of O seen at equilibrium are very different for the various MICs, and can range over five orders of magnitude. KMnO_4 is calculated to have the highest concentration of O, and is the only one that does not show a significant decrease in O concentration with increasing equivalence ratio. This is particularly significant, because it has been shown by a number of workers that the most reactive conditions are on the fuel-rich side, and therefore the observation of high O concentrations even under fuel-rich conditions are particularly striking.^[7–10] If we now compare the concentrations of O to the measured pressurization rates, the correlation is quite self-evident. The MICs with high O concentrations, KMnO_4 being the highest, also have the highest pressurization rates. It is likely then that it is this nascent oxygen that rapidly reacts with the fuel to release energy. Moreover, KMnO_4 is known

to thermally decompose at about 300 °C, which is significantly lower than that for other oxides. This rapid decomposition may be another contributing factor to the higher pressurization rates observed for the Al/ KMnO_4 MIC.

In summary, we present a new MIC formulation of Al/ KMnO_4 which shows ultra-fast reactivity compared to the more widely known formulations. We observed a strong correlation between pressurization rates for several MIC combinations and the fraction of reactive oxygen present in the combustion product.

Experimental

The KMnO_4 nanoparticles were synthesized by a spray-drying method. A schematic for the synthesis procedure is shown in Figure 4. Using a 5 wt.-% aqueous solution of KMnO_4 , droplets of the precursor solution of about 1 μm geometric mean diameter (measured by a high-sensitivity laser aerosol spectrometer) were generated using a

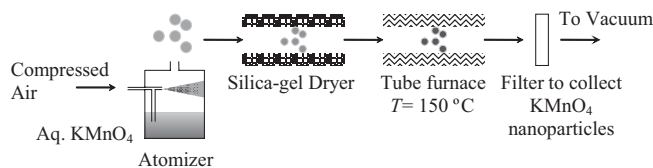


Figure 4. Aerosol synthesis of KMnO_4 nanoparticles by spray-drying method.

collision-type atomizer. The moisture from the aerosol was absorbed in a silica-gel diffusion dryer, following which the aerosol was passed through a tube furnace maintained at 150 °C to vaporize the remaining moisture. The residence time of the aerosol in the furnace is about 1 s for a nominal flow rate of 3 L min^{-1} . Nanoparticles of KMnO_4 of ~250 nm mean diameter were collected on a 0.6 μm filter manufactured by Millipore (filter code DTTP). For the synthesis of CuO nanoparticles, the same experimental setup was used to aerosolize a 5 wt.-% aqueous $\text{Cu}(\text{NO}_3)_2$ precursor solution. The aerosol was heated to a temperature of 500 °C to thermally decompose the nitrate to form CuO. Scanning electron microscopy (SEM) images of CuO and KMnO_4 particles synthesized (Fig. 5) show the particles to be spherical and unagglomerated.

Figure 6 shows the experimental apparatus (adapted from Dr. Steve Son, Los Alamos National Laboratories [7]) for the pressurization-rate measurements for nanocomposite thermite mixtures. It consists of a constant volume (~13 mL) reaction vessel, the real-time pressure of which is measured with a high-frequency pressure sensor (PCB Piezotronics Model J113A/061A01) with a maximum range of 3000 psi. The reaction mixture is ignited with a Nichrome wire, which is heated using a direct current of about 2 A at 3 V. Ignition of the metastable intermolecular composite (MIC) pressurizes the vessel. The pressure sensor is capacitive and records pressure in terms of charge which is of the order of picocoulombs (corresponding to a few hundred psi). The signal is amplified by an in-line charge amplifier (PCB Piezotronics Model 422E12; gain ~10) and then fed to a signal-conditioner (PCB Piezotronics Model 482A21; unity gain) which transforms the signal to voltage output. The voltage output is then recorded by a digital Tektronix oscilloscope (TDS 2014; bandwidth: 100 MHz).

The pressure cell test was used to compare the pressurization rates of MICs of Al/CuO and Al/ KMnO_4 as a function of weight ratio of fuel and oxidizer. For preparing the MICs, oxidizer and fuel (40 nm

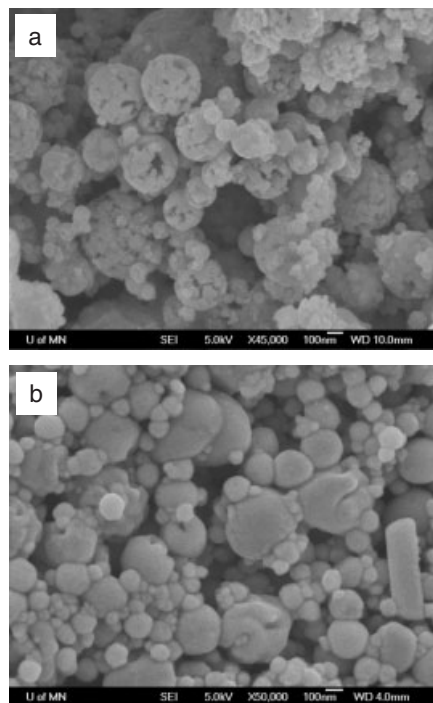


Figure 5. SEM images of oxidizer nanoparticles synthesized by the aerosol method. a) CuO and b) KMnO_4 nanoparticles.

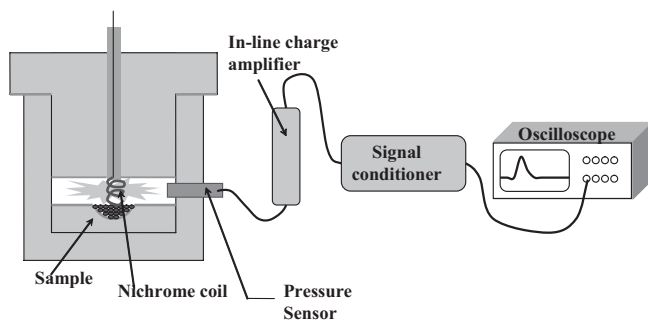


Figure 6. Schematic for measurement of pressurization rates for MIC ignition.

Al; 70 wt.-% Al content; from Technanogy) components were physically mixed and dispersed in hexane. The dispersion was then ultrasonicated for 20 min, and thereafter the mixture was heated at about 100 °C to vaporize the dispersant.

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Thickness-Driven Orthorhombic to Triclinic Phase Transformation in Pentacene Thin Films**

By Lawrence F. Drummy and David C. Martin*

The field of plastic electronics has generated significant recent interest due to the excellent electrical properties measured from several organic materials. Understanding the relationship between thin-film processing parameters and the resulting crystal structure will be critical in integrating organic materials into useful devices. The processing/structure/properties relationship in ordered organic materials for electronic applications has recently been reviewed, with focus on aromatic molecules.^[1,2] The aromatic hydrocarbon pentacene is currently under investigation for use as the active layer in flexible electronic devices such as thin-film field-effect transistors.^[3–5] Pentacene thin films have shown tendencies for polymorphism, and a unique “thin film” phase of pentacene has been characterized by many researchers.^[3–10] In a thin-film field-effect transistor, charge-carrier transport through the active layer will take place in the region of the film nearest to the dielectric layer. It is likely that this region will consist solely of the thin-film phase polymorph. Due primarily to the small crystal sizes in these films, however, the detailed structure of this phase has remained elusive. Using electron diffraction (ED), low voltage electron microscopy (LVEM), low-dose high resolution electron microscopy (HREM) and molecular simulations we have determined that thin films of

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