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Synthesis and Performance Characterization of a Nanocomposite Ternary Thermite: $Al/Fe_2O_3/SiO_2$**

By *Daniel Prentice, Michelle L. Pantoya,* and *Brady Clapsaddle*[*]

Making solid energetic materials requires the physical mixing of solid fuels and oxidizers or the incorporation of fuel and oxidizing moieties into a single molecule. The former are referred to as composite energetic materials (i.e., thermites, propellants, pyrotechnics) and the latter are deemed monomolecular energetic materials (i.e., explosives). Mass diffusion between the fuel and oxidizer is the rate controlling step for composite reactions while bond breaking and chemical kinetics control monomolecular reactions. Although composites have higher energy densities than monomolecular species, they release that energy over a longer period of time because diffusion controlled reactions are considerably slower than chemistry controlled reactions. Conversely, monomolecular species exhibit greater power due to more rapid kinetics than physically mixed energetics.

Reducing the diffusion distance between fuel and oxidizer species within an energetic composite would enhance the reaction rate.[1,2] Recent advances in nanotechnology have spurred the development of nano-scale fuel and oxidizer particles that can be combined into a composite and effectively reduce diffusion distances to nano-scale dimensions or less.[2,3] These

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nanocomposites have the potential to deliver the best of both worlds: high energy density of the physically mixed composite with the high power of the monomolecular species. Toward this end, researchers at Lawrence Livermore National Laboratory (LLNL) developed nano-particle synthesis techniques, based on sol-gel chemistry, for the production of thermite nanocomposites.[4] Thermite reactions are traditionally fuel and oxidizer powders that are mixed to make an energetic material based on the general oxidation reaction shown in Equation 1,

$$M^1 + M^2O_x \rightarrow M^1O_x + M^2 + \Delta H \qquad (1)$$

where M^1 is a fuel, such as aluminum metal, and M^2O_x is a metal oxide, such as Fe_2O_3.

Recently, Plantier *et al.* showed that the oxidizer synthesis technique is a strong function of the combustion behavior of the composite.[5] In that study, Fe_2O_3 was synthesized using sol-gel chemistry to create a high surface area, nano-particulate Fe_2O_3 aerogel powder and a lower surface area, nano-particulate Fe_2O_3 xerogel powder. The combustion velocities of these two oxidizers mixed with nano-scale Al particles were examined and compared to a commercially obtained nano-particulate Fe_2O_3 powder combined with the same nano-scale Al particles. The results showed that the combustion velocity ranged from 1 to 900 m/s, and the sol-gel derived, aerogel Fe_2O_3 outperformed all other oxide powders. The results also showed that a reaction can be tailored to a specific application by controlling the synthesis process.

More recently, Clapsaddle *et. al.* developed a generalized method for the synthesis of metal oxide-silicon oxide nanocomposites with the metal oxide as the major phase.[4c,4d] They applied this method to construct the first Fe_2O_3-SiO_2 mixed oxide nanocomposites with the iron (III) oxide as the major component. The resulting aerogel and xerogel nanocomposites showed a high degree of dispersion between the Fe_2O_3 and the SiO_2 on the nanoscale.[4c] These nanocomposite aerogel oxidizers have recently been shown to be of use in energetic

applications.[6,7] Such a composite requires that a more energetic metal oxide, such as Fe_2O_3, be the major phase in order to produce an exothermic reaction when the metal-oxide is combined with a fuel such as aluminum. The motivation for including a less energetic metal oxide, such as SiO_2, is to tailor the energy release properties to a specific application by changing the chemical and physical properties of the oxidizer.

The goal of this work is to examine the influence of SiO_2 on the energy release properties of the Al/Fe_2O_3 thermite reaction. This objective was accomplished by comparing the combustion velocities of two separate $Al\text{-}Fe_2O_3\text{-}SiO_2$ nanocomposites: one prepared from commercially obtained individual nano-scale particles; and, the other prepared by combining nano-scale Al with sol-gel synthesized $Fe_2O_3\text{-}SiO_2$ aerogel nanocomposites. In the case of the latter, aerogel powders were chosen due to their superior combustion velocities as demonstrated by Plantier *et. al.*[5]

Previous work showed that an Al/Fe_2O_3 composite burns at an optimum equivalence ratio (Φ) equal to 1.2 corresponding to a slightly fuel-rich mixture.[5] This composition is also consistent with the optimum combustion behavior of many other thermites and was selected as the composition for these experiments.[8] To calculate the correct proportions of each reactant component according to an equivalence ratio of 1.2, the stoichiometric reactions are needed. Equations 2 and 3 show the stoichiometric reactions between Al and Fe_2O_3 and Al and SiO_2 and the corresponding heats of reaction (ΔH_{rxn}) and adiabatic flame temperature (T_{af}).[9]

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe \quad \Delta H_{rxn} = 3955.6 \text{ J/g}; \; T_{af} = 3135 \text{ K} \qquad (2)$$

$$4Al + 3SiO_2 \rightarrow 2Al_2O_3 + 3Si \quad \Delta H_{rxn} = 2146.4 \text{ J/g}; \; T_{af} = 1889 \text{ K} \qquad (3)$$

Based on these reactions, the stoichiometric (*st*) fuel/oxidizer ratios are shown in Equations 4 and 5.

$$\left(\frac{Fuel}{Ox}\right)_{st,Fe_2O_3} = 0.338 \quad (4)$$

$$\left(\frac{Fuel}{Ox}\right)_{st,SiO_2} = 0.599 \quad (5)$$

To calculate the total stoichiometric fuel/oxidizer ratio for the combined reaction, a weighted average was determined from a specified mass percent oxidizer composition of Fe_2O_3 and SiO_2. Six combinations of oxidizers were prepared ranging from 100 % Fe_2O_3 and 0 % SiO_2 to 0 % Fe_2O_3 and 100 % SiO_2 in 20 % increments as shown in Fig. 1.

Equation 6 shows the calculation of the actual fuel/oxidizer ratio based on the stoichiometric ratios (Equations 4 and 5) and an $\Phi = 1.2$.

$$\left(\frac{Fuel}{Ox}\right)_{actual} = \Phi * \left(\frac{Fuel}{Ox}\right)_{st,total} \quad (6)$$

Equation 7 shows the calculation of the mass percent fuel for the each composition and Equation 8 shows the calculation of the mass percent oxidizer.

$$\left(\frac{Fuel}{Ox}\right)_{actual} = \frac{(\%\, mass\ Al) * (\%\, active\ Al\ content)}{(1 - \%\, mass\ Al)} \quad (7)$$

$$(1 - \%\, mass\ Al) = \%\, mass\ Ox \quad (8)$$

Equations 9 and 10 show the calculations of the mass percent of Fe_2O_3 and SiO_2.

$$(\%\, mass\ Fe_2O_3)_{composite} = (\%\, mass\ Ox) * (\%\, mass\ Fe_2O_3)_{oxidizer} \quad (9)$$

$$(\%\, mass\ SiO_2)_{composite} = (\%\, mass\ Ox) * (\%\, mass\ SiO_2)_{oxidizer} \quad (10)$$

The composite subscripts denote the total mass percent of the specific component and the oxidizer subscript denotes only the mass percent found in the oxidizer itself. For example, an oxidizer with 20% mass Fe_2O_3 and 80% mass SiO_2 would have 11.1 % mass Fe_2O_3 and 44.3 % mass SiO_2 in relation to the total mixed composite at Φ=1.2. Also, the previous example would

have 44.7 % mass Al. Furthermore the amount of Al fuel metal for each mixture varies by no more than 10% over the entire series.

Using the calculated ratios described above, two sets of energetic powders were produced, each containing binary Fe_2O_3/SiO_2 oxidizing phases. The first set was prepared by physically mixing commercial nm Al powder with an aerogel oxidizer composite in which the Fe_2O_3 and SiO_2 components were simultaneously generated in situ using sol-gel chemistry. The oxidizer composite is this mixture will be referred to as *Oxidizer A* and the fuel/oxidizer composite will be referred to as *Thermite A*. The second set consisted of commercially available nano-scale particles of Fe_2O_3 and SiO_2 that are combined with the same commercial nm Al powder through mechanical mixing using an ultrasonification process. This mixture contains discrete particles of Fe_2O_3 and SiO_2 as the oxidizer and will be referred to as *Oxidizer B*, and the fuel/oxidizer composite will be referred to as *Thermite B*. In this way, the effect of sol-gel synthesis on the oxidizer can be isolated with respect to the entire composite. A summary of oxidizing phase compositions for both the sol-gel (*Oxidizer A*) and mechanically prepared (*Oxidizer B*) composites is shown in Figure 1. The same weighted percentage method of calculating a total fuel/oxidizer ratio was applied to the aerogel oxidizers by using the oxidizer elemental analysis data shown in Table 1. With the exception of the use of Equations 9 and 10, which are unnecessary in the case of the aerogel oxidizers, the same mixing procedure was used for both sets of thermite composites (*Thermites A and B*).

For this study characterizing the energetic performance involved measuring the combustion velocity. There are several different experimental configurations that can be employed to measure and quantify combustion velocity. Some include examining flame propagation in loose powders either confined within a tube[5, 10] or open to the environment.[5] For

this analysis, flame propagation was examined for loose powders in a channel open to an air environment. Figure 2 is a photograph of the transparent acrylic block burning apparatus. In this configuration, the powder is confined on three sides by the channel but open to an ambient air environment on the top. Although the amount of material and the volume of the channel are controlled, density gradients may still exist along the sample length. Care was taken to ensure homogeneity in the quality of the sample.

Figure 3 shows the combustion velocity as a function of weight percent SiO_2 content and as a function of the oxidizer synthesis technique. Each data symbol represents an average measurement from 3 or 4 experiments. The standard deviations in measurements are ± 0.001 m/s and thus the error bars associated with each data symbol are too small to appear in Fig. 3.

For both composites, as the weight percent SiO_2 content increases, the velocity is reduced. This trend is not surprising because the thermal properties of SiO_2 are more insulative than the highly conductive thermal properties of Fe_2O_3.[11] For example, the thermal conductivity for Fe_2O_3 is 20.0 W/m K and for SiO_2 is 1.38 W/m K.[11] The presence of SiO_2 hinders flame propagation by behaving as a thermal heat sink and resisting the transport of heat through the mixture, thereby reducing the velocity. Although SiO_2 contributes to the chemical energy generated (as shown in Equation 4), adding SiO_2 reduces the overall speed of the reaction by inhibiting thermal transport and reducing the combustion temperature.

A similar decrease in velocity with increasing content of an additive, such as Al_2O_3, has been well established for intermetallic combustion.[12] For self-propagating high temperature synthesis (SHS) of metallic alloys, Al_2O_3 can be added to a reactant matrix and act as a diluent. This additive offers advantages in the macroscopic behavior of the product alloy. [12] For example, small quantities of Al_2O_3 (i.e., less than 2 wt %) have been incorporated into a reactant

matrix to enhance the overall strength of the SHS product alloy. [12c,d] Only small concentrations will be effective such that flame propagation behavior will not be significantly impacted. [12c,d] In this present study, the SiO_2 additive is not acting as a diluent but does posses enough thermal resistance to impede flame propagation. In this way, the SiO_2 additive allows control of the rate of flame propagation through the mixture ratio of SiO_2 to other reactants. This is a distinctly different advantage than that described for SHS, but equally important for tailoring energy release rates.

An interesting aspect of Figure 3 is the relationship between the aerogel oxidizer composite (*Oxidizer A*) and the mechanically mixed oxidizer particles (*Oxidizer B*). When a negligible amount (or no) SiO_2 is within the mixture, *Oxidizer A* produces more than a factor of 4 increase in the velocity over *Oxidizer B* (i.e., 40.5 compared with 8.8 m/s, respectively). This difference is attributed to chemical rather than physical variations between the two oxidizers. For example, Tables 1 and 2 show that the surface area for both oxidizers at 100 % Fe_2O_3 is roughly the same (44.1 versus 47.8 m^2/g). Therefore, the key difference in these two mixtures is that *Oxidizer A* is prepared as an aerogel while *Oxidizer B* is discrete particles. The relationship between velocity and synthesis technique shown here is consistent with previous velocity results for the Al/Fe_2O_3 composite synthesized as an aerogel compared with discrete particles. [5] Specifically, Plantier et al. [5] showed that Al combined with the Fe_2O_3 aerogel (prepared in the same manner as this study) resulted in a 10 % increase in velocity when compared to the Al combined with a commercial nm Fe_2O_3 (also the same nm Fe_2O_3 used in this study). This was explained by differences in the chemical properties between the aerogel and commercial Fe_2O_3. Specifically, the aerogel was shown to be α-Fe_2O_3, the most thermodynamically stable form of Fe_2O_3. The commercial particles were shown to exist as amorphous hydrated ferric oxide which

is a poorly crystalline hydrated ferrihydrite phase that possess bonded water (-OH) within its structure. This chemical impurity was shown to inhibit flame propagation. Therefore, in Fig. 3 when 0 % SiO_2 is contained within the mixture, *Thermite B* exhibits a reduced velocity over *Thermite A* because the chemical phase associated with *Oxidizer B* contains an –OH impurity that impedes flame propagation.

The opposite trend, however, is observed for *Thermites A and B* when SiO_2 is included in the oxidizer mixture. With 20 % SiO_2, *Thermite A* exhibits a 99.4 % reduction in combustion velocity, versus only a 76.3 % reduction in combustion velocity for *Thermite B*. As more SiO_2 is included, further reductions in velocity are observed but the difference in velocity between *Thermites A and B* remained constant. This consistent reduction in velocity with increased SiO2 content, may result from physical differences that affect the homogeneity of the mixture. Table 1 shows that for Oxidizer A the surface area dramatically increases from 44 to 384 m2/g with the addition of SiO2. Table 2 shows a marginal increase in surface area for Oxidizer B with added SiO2. The increased surface area will enable more contact between the fuel and oxidizer particles improving the homogeneity of the mixture. Even incremental improvements in mixture homogeneity will reduce diffusion distances between fuel and oxidizer particles such that the combustion velocity will increase.

Figure 4 shows still frame images of flame propagation for 0 and 40 wt % SiO_2 content for both sets of composites. For composites containing no SiO_2 (Figure 4a and 4b), the reaction appears to consume all particles, which rise into the air and convectively cool as smoke. More importantly, all of the particles appear to react at the same time. Figure 4b demonstrates the faster progression of the flame front for *Thermite A*.

A different looking reaction for the composites containing 40% SiO_2, however, can be seen in Figure 4c and 4d. In Figure 4c, many discrete particles can be seen radiating in these frames. The reaction between Al and Fe_2O_3 may be so exothermic that SiO_2 particles are forced into the air while still radiating and reacting. These radiating particles appear to burn much slower and are apparent even after the plume has disappeared. The physical mixing of discrete particles may facilitate the ejection of the slower reacting SiO_2 from the Al and Fe_2O_3 reaction zone. This behavior, however, is not apparent in Figure 4d for the 40% SiO_2 *Oxidizer A*. In this case, flame propagation is considerably slower than that shown in Figure 4c, but discrete particles ejected from the flame zone are not apparent. This may result from the sol-gel synthesis of the oxidizer intertwining the Fe_2O_3 and SiO_2 matrices such that they exist as an interpenetrating network in single particles instead of separate particles.[13] In this way, discrete SiO_2 particles cannot be easily ejected from the more exothermic Al + Fe_2O_3 reaction because SiO_2 does not exist as discrete particles. Overall the propagating reaction is more sluggish because the less exothermic Al + SiO_2 reaction is forced to occur simultaneous with the Al + Fe_2O_3 reaction, thus reducing the overall velocity. As more SiO_2 is added to the oxidizer matrix, a consistent reduction in velocity is observed. This finding suggests that there may be a larger amount of unreacted material in *Thermite B*; although Thermite A propagates slower, more reactants are consumed and the combustion process is more complete.

This study examined the combustion velocity of two ternary composites both consisting of Al/Fe_2O_3/SiO_2 but mixed using two different preparation methods. The first was chemically combined oxidizers using sol-gel processing combined with nano-Al particles (*Thermite A*). The second physically mixed discrete nano-scale particles together in solution using sonic waves (*Thermite B*). The inclusion of SiO_2 was used as a means to control the combustion velocity.

Results show that SiO_2 acts as a heat sink and retards flame propagation reducing the combustion velocity. An interesting finding from this study is determined from examining the flame propagation behavior as a function of preparation method. The aerogel composites are "intertwined" such that a more complete reaction between the Al fuel and both oxidizers is forced to occur. For the physically mixed discrete particles, the less exothermic SiO_2 particles are ejected from the more exothermic Al + Fe_2O_3 reaction zone prior to their complete reaction. This behavior suggests that the sol-gel processing of a composite allows for increased homogeneity between reactants and products which promotes more complete combustion. Finally, the combustion velocity can be controlled by the amount of SiO_2 added to the composite, and the manner by which the SiO_2 is mixed into the oxidizing phase.

Experimental

Aerogel Synthesis

Aerogel oxidizers were prepared via a previously described sol-gel technique followed by supercritical processing in a Polaron™ supercritical point dryer.[10c] All aerogels were subsequently heated at 10 ºC/min to 410 ºC and held for 4 hours. Following calcination, the oven was switched off and the aerogel oxidizers were allowed to cool to room temperature overnight.

Sample Preparation

The energetic composites were prepared by physically mixing commercially obtained fuel and oxidizer particles or by physically mixing fuel and the aerogel oxidizers. The fuel particles were 80 nm average diameter aluminum (Nanotechnologies Inc.) passivated with an alumina (Al_2O_3) shell that is roughly 4 nm thick and encapsulates the core Al particle. Based on

thermal analysis, the manufacturer determined that this powder has an active Al content of 81 %. Active Al is defined as the portion of powder not in the form of Al_2O_3. The commercial oxidizer powders were submicron SiO_2 (Alfa Aesar) and 3 nm diameter Fe_2O_3 (Sigma-Aldrich). The purity of both of the oxidizer chemicals was reported to be greater than 99 % and assumed to be 100 % pure for our stoichiometric calculations.

Mixing was accomplished by suspending the relevant amounts of Al, Fe_2O_3, and SiO_2 (set 1) or Al and aerogel Fe_2O_3/SiO_2 (set 2) in 60 mL of hexane. The mixtures were sonicated using a Misonix Sonicator 3000 sonic wand and the hexane was allowed to evaporate on a hot plate at a temperature of ~80˚C. Once the powders were dry, a homogeneous mixture was ready for further experimentation.

Combustion Velocity Measurements

Combustion velocities were measured using a Phantom IV high-speed camera (*Vision Research*) that records images up to 32,000 frames per second (fps). The camera records visible emission at 128 x 32 pixels and uses a Nikon AF Nikkor 28 mm 1:2.8 D lens. The camera interfaces with a computer which transfers the recorded file from the camera and has a data analysis program from *Vision Research* that measures velocity. For each test, 150 mg of thermite powder mixture was used. Ignition was achieved using a spark ignition system for loose powders in a 0.3175 cm square channel 10 cm in length cut into a transparent acrylic block, as shown in Figure 2. All combustion velocities were measured in an open air environment.

Physical Characterization

Surface area measurements and pore size distributions of the aerogel oxidizers were determined by nitrogen adsorption/desorption using a Micromeretics ASAP2000 gas adsorption analyzer. Surface areas were calculated from a 5 point data analysis between 0.05 and 0.2

relative pressure at 77 K using BET (Brauner, Emmett, and Teller) theory. Pore volumes were determined from $N_2(g)$ desorption isotherms using BJH (Barrett-Joyner-Halenda) theory. Chemical analysis was performed on the aerogel-oxidizer samples by Galbraith Laboratories Inc. (Knoxville, TN). The levels of carbon and hydrogen were measured simultaneously based on the concentration liberated during combustion using an IR or thermal conductivity detector. Concentration levels of CO_2 and H_2O were also determined using an IR detector. Levels of iron and silicon were measured by dissolving the solid in a mineral acid and using an Inductively Coupled Plasma - Optical Emission Spectrophotometer (ICP-OES). The surface areas and purity of the aerogel-oxidizers are reported in Table 1.

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Figure Captions

Figure 1. Schematic diagram illustrating bimodal oxidizer mixture ratios for A. sol-gel synthesized oxidizer composites (*Oxidizer A*); and, B. commercial powders physically mixed (*Oxidizer B*).

Figure 2. Photograph of open channel apparatus used for measuring combustion velocity.

Figure 3. Combustion velocity as a function of SiO_2 content on a logarithmic velocity scale. *Thermite A* corresponds to the Al combined with sol-gel synthesized aerogel Fe_2O_3/SiO_2 composite and *Thermite B* corresponds to the Al combined with discrete nm particles of Fe_2O_3 and SiO_2.

Figure 4. Still frame images from high speed photographic data for A. 0 % wt SiO_2 Thermite B; B. 0 % wt SiO_2 Thermite A; C. 40 % wt SiO_2 Thermite B; and, D. 40 % wt SiO_2 Thermite A.

Table 1. Chemical[a.] and physical analysis of sol-gel prepared Fe_2O_3/SiO_2 (*Oxidizer A*).

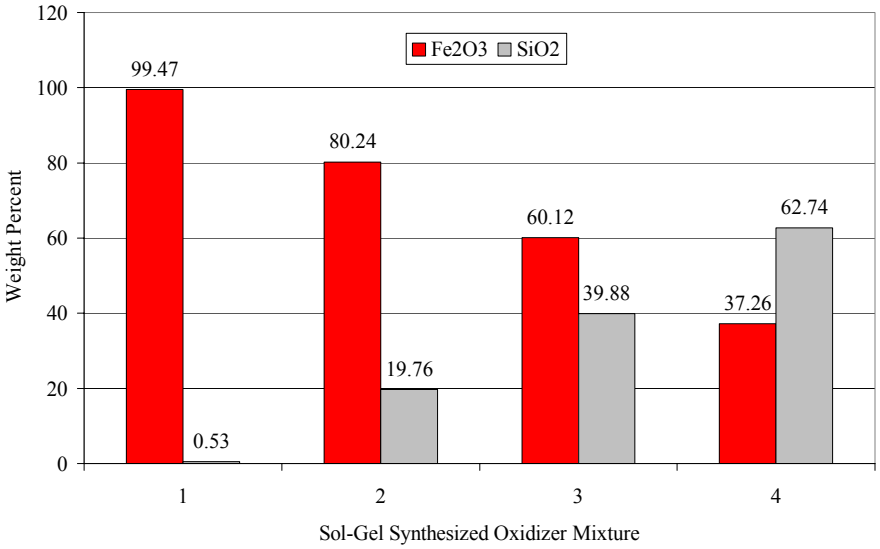
oxidizer	**%Fe**	**%Si**	**%C**	**%H**	**%Fe_2O_3[a.]**	**%SiO_2**	**surf. area (m^2/g)**	**pore volume (cm^3/g)**
100/0	64.1	0.23	< 0.5	< 0.5	99.5	0.5	44.1	0.32
80/20	53.5	8.81	< 0.5	0.9	80.2	19.8	384	3.74
60/40	38.2	16.9	< 0.5	1.1	60.1	39.9	350	1.54
40/60	23.9	26.8	< 0.5	1.24	37.3	62.7	342	1.21

a. All chemical compositions are reported as weight percents. The small amounts of carbon and hydrogen present were not taken into consideration for calculation of % Fe_2O_3 and % SiO_2.

Table 2. Surface area and pore volumes for discrete particles Fe_2O_3 and SiO_2 mechanically mixed (*Oxidizer B*).

oxidizer composition[a.]	**surface area (m^2/g)**	**pore volume (cm^3/g)**
100% Fe_2O_3	47.8	0.23
80% Fe_2O_3/20% SiO_2	54.9	0.31
60% Fe_2O_3/40% SiO_2	66.9	0.32
40% Fe_2O_3/60% SiO_2	76.5	0.32
20% Fe_2O_3/80% SiO_2	–	–
100% SiO_2	93.4	0.28

[a.] Mixtures are reported as weight percents.



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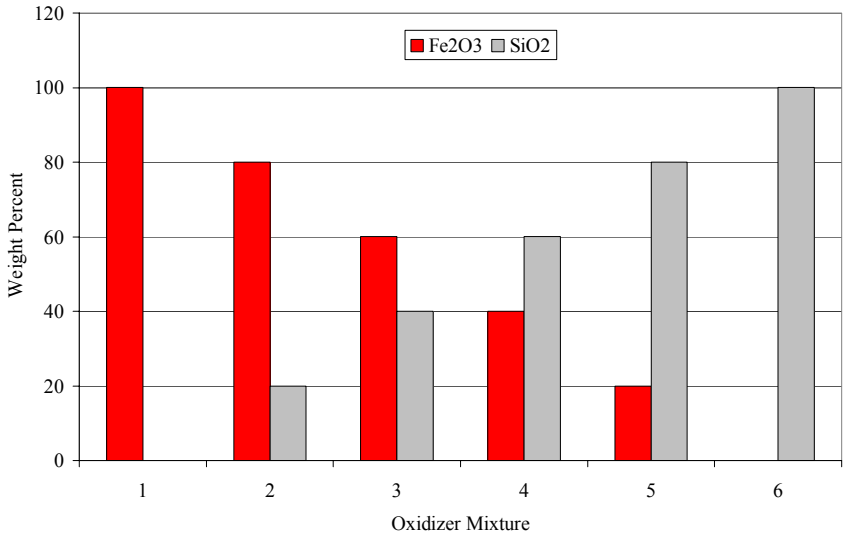
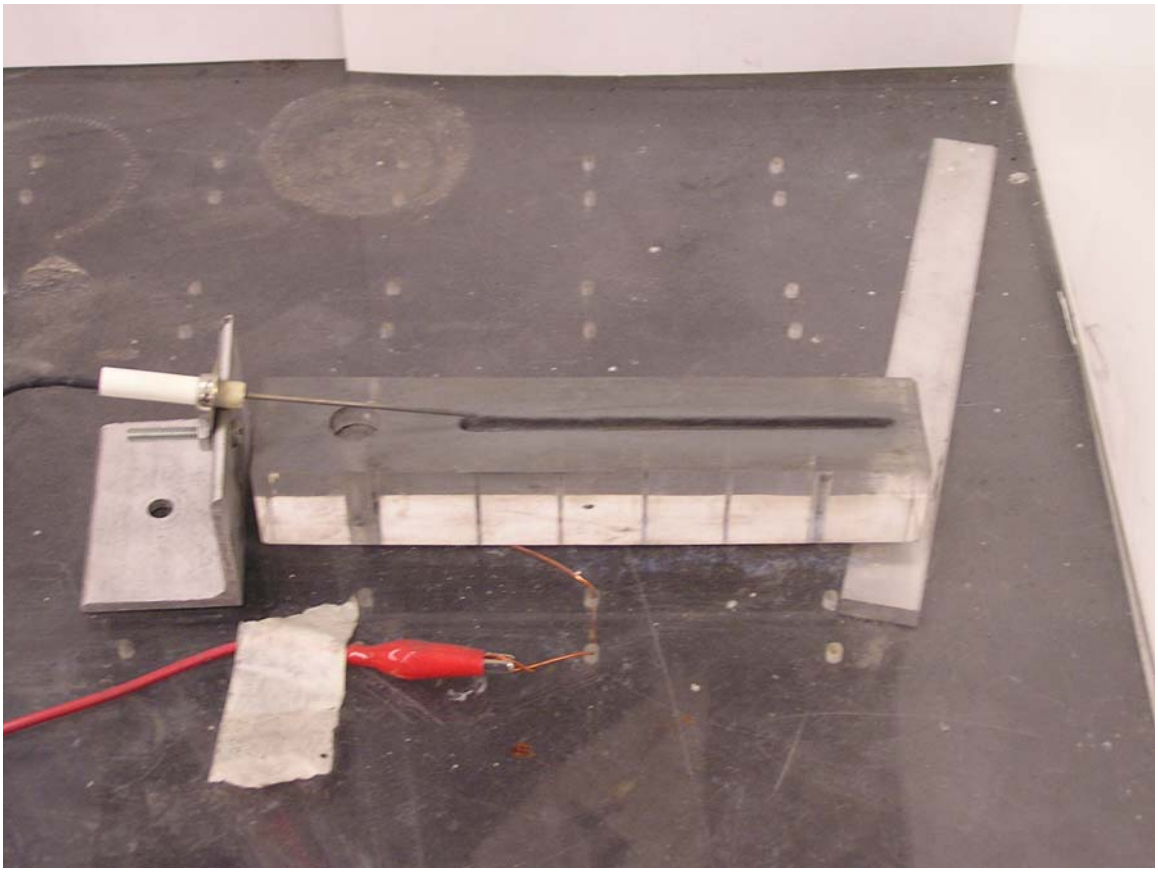


B.

Figure 1. Schematic diagram illustrating bimodal oxidizer mixture ratios for A. sol-gel synthesized oxidizer composites (*Oxidizer A*); and, B. commercial powders physically mixed (*Oxidizer B*).



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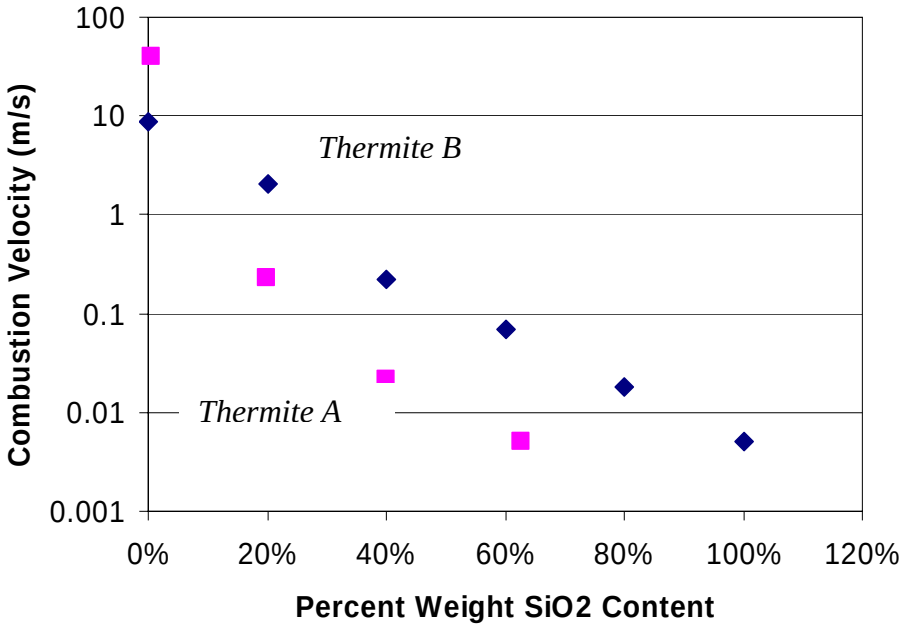

Figure 3. Combustion velocity as a function of SiO_2 content on a logarithmic velocity scale. *Thermite A* corresponds to the Al combined with sol-gel synthesized aerogel Fe_2O_3/SiO_2 composite and *Thermite B* corresponds to the Al combined with discrete nm particles of Fe_2O_3 and SiO_2.

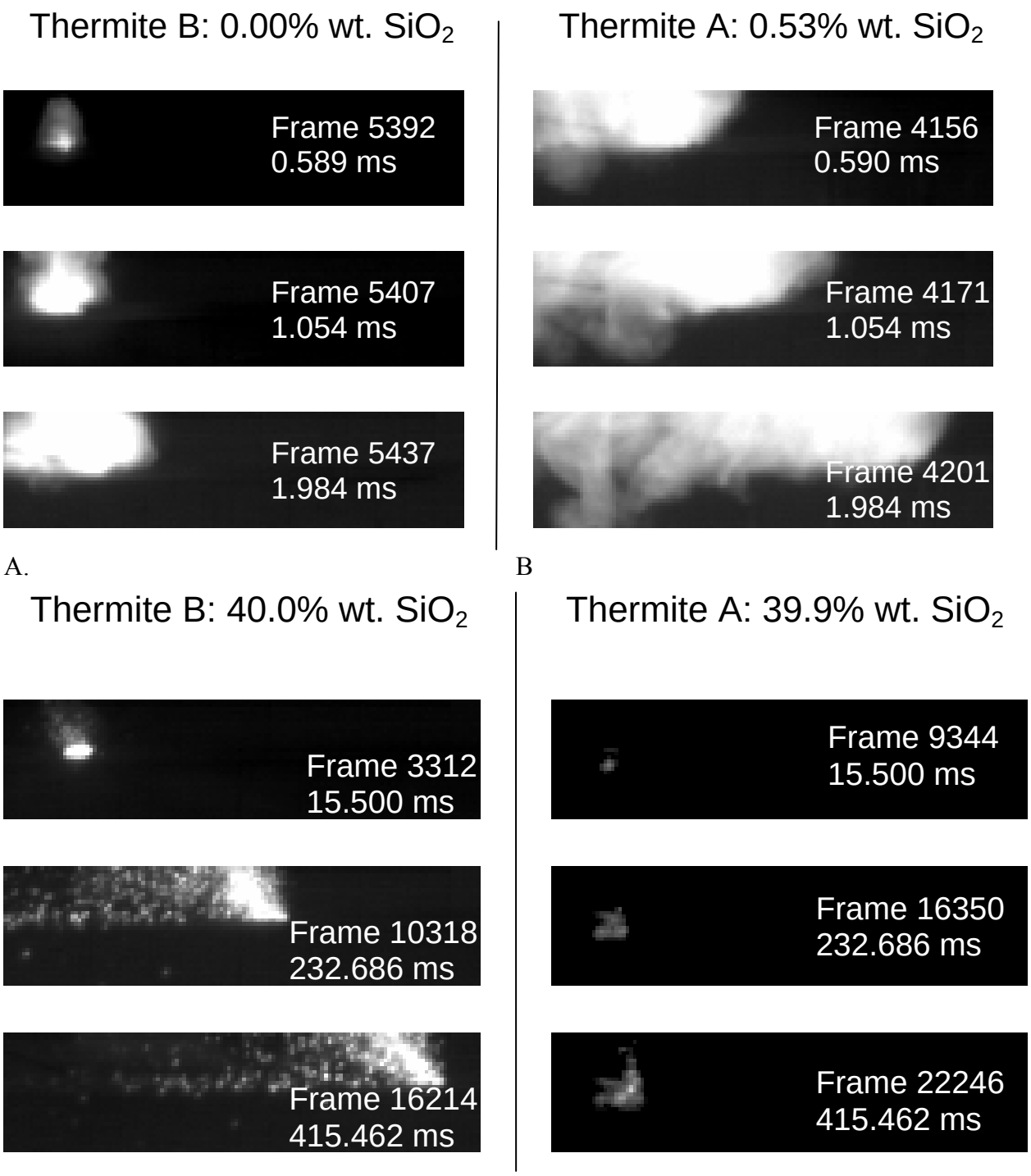

Figure 4. Still frame images from high speed photographic data for A. 0 % wt SiO_2 Thermite B; B. 0 % wt SiO_2 Thermite A; C. 40 % wt SiO_2 Thermite B; and, D. 40 % wt SiO_2 Thermite A.