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SAND2009-0705

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Printed February 2009

Investigations of the Small-Scale Thermal Behavior of Sol-Gel Thermites

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Abstract

Sol-gel thermites, formulated from nanoporous oxides and dispersed fuel particles, may provide materials useful for small-scale, intense thermal sources, but understanding the factors affecting performance is critical prior to use. Work was conducted on understanding the synthesis conditions, thermal treatments, and additives that lead to different performance characteristics in iron oxide sol-gel thermites. Additionally, the safety properties of sol-gel thermites were investigated, especially those related to air sensitivity. Sol-gel thermites were synthesized using a variety of different techniques and there appear to be many viable routes to relatively equivalent thermites. These thermites were subjected to several different thermal treatments under argon in a differential scanning calorimeter, and it was shown that a 65 °C hold for up to 200 minutes was effective for the removal of residual solvent, thus preventing boiling during the final thermal activation step. Vacuum-drying prior to this heating was shown to be even more effective at removing residual solvent. The addition of aluminum and molybdenum trioxide (MoO_3) reduced the total heat release per unit mass upon exposure to air, probably due to a decrease in the amount of reduced iron oxide species in the thermite. For the thermal activation step of heat treatment, three different temperatures were investigated. Thermal activation at 200 °C resulted in increased ignition sensitivity over thermal activation at 232 °C, and thermal activation at 300 °C resulted in non-ignitable material. Non-sol-gel iron oxide did not exhibit any of the air-sensitivity observed in sol-gel iron oxide. In the DSC experiments, no bulk ignition of sol-gel thermites was observed upon exposure to air after thermal activation in argon; however ignition did occur when the material was heated in air after thermal treatment. In larger-scale experiments, up to a few hundred milligrams, no ignition was observed upon exposure to air after thermal activation in vacuum; however ignition by resistively-heated tungsten wire was possible. Thin films of thermite were fabricated using a dispersed mixture of aluminum and iron oxide particles, but ignition and propagation of these films was difficult. The only ignition and propagation observed was in a preheated sample.

Acknowledgements

The authors wish to thank Alexander E. Gash of LLNL for his assistance and extremely useful discussions regarding this project, as well as reporting the experiments that inspired this work. The authors also wish to thank Shubhra Gangopadhyay of the University of Missouri, Columbia for helpful discussions. The authors also wish to thank J. Patrick Ball and Jill C. Miller for conducting some of the experiments and Robert T. Patton for conducting the thermal analysis. Finally, the authors wish to acknowledge the funding support of Sandia National Laboratories' Laboratory Directed Research and Development Program.

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Nomenclature

ΔH	enthalpy, (of combustion)
DSC.....	differential scanning calorimetry, differential scanning calorimeter
EM	Energetic Material
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	iron nitrate nonahydrate
Fe_2O_3	iron oxide, iron(III) oxide
Fluorel® FC-2175.....	poly(vinylidene fluoride/hexafluoropropylene)
IPA.....	isopropyl alcohol
LLNL	Lawrence Livermore National Laboratory
MoO_3	molybdenum trioxide
T_{ad}	temperature, adiabatic (of combustion)
VitonA®.....	poly(vinylidene fluoride/hexafluoropropylene)

Introduction

In February of 2006, Alexander E. Gash of Lawrence Livermore National Laboratory (LLNL) reported on a series of incidents that had occurred with sol-gel iron oxide-based thermites at LLNL and other laboratories.[1] In his presentation, three specific incidents were described in which thermal treatment of sol-gel thermites resulted in auto-ignition of the materials. At LLNL, two incidents were reported involving 15 and 25 g of material, respectively. In the 15 g incident (September 24, 2001), a mixture of 53% sol-gel $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, 29% ultra-fine aluminum (lot# IH103000-1), 9% Viton® A, and 9% poly(propylene oxide) impurity auto-ignited after a 30-60 second glow (presumably due to heat release from oxidation) when removed warm from an oven where it had been heat-treated in a nitrogen atmosphere for five days at 105 °C. In the 25 g incident (February, 2004), a mixture of sol-gel iron (III) oxide, H-2 (Valimet, 2- μm) aluminum, and Viton® A auto-ignited while drying in an oven under house vacuum at 85 °C. The third incident occurred at Texas Tech University where thin films of sol-gel iron oxide with ultra-fine aluminum auto-ignited after being removed at room temperature from an oven after 250 °C treatment in an inert atmosphere. This was confirmed later via email.[2] In his presentation, Dr. Gash concluded that: 1) heat treatment of iron(III) oxide in inert atmosphere results in an air-sensitive material, 2) this phenomenon is not observed for nano- Fe_2O_3 in the absence of organic impurities, 3) self-heating of the material is likely due to partially-reduced iron oxide species that re-oxidize upon exposure to air, and 4) the high surface area and low thermal conductivity of the material exacerbates the issue. Based on this work, a project was started at Sandia to investigate further the safety and thermal properties of sol-gel iron-oxide thermites for potential use as thermal sources.

Sol-gel thermites are composite energetic materials consisting of a nanometer-scale porous network of sol-gel-based metal oxide with dispersed aluminum (or other metal fuel) particles.[3] A general synthetic strategy has been developed that allows sol-gels to be synthesized from numerous elements.[4] For iron oxide sol-gels, this synthetic strategy consists of a simple mixing of iron salts in polar, protic solvents (methanol, ethanol) in the presence of propylene oxide as a gelation agent. A sol-gel then forms over the course of several minutes to hours, depending on reaction conditions. Immediately before the onset of gelation the aluminum particles are added and further mixed to yield a uniform distribution. By varying reaction conditions this strategy can be potentially used to tune ignition and combustion properties of the resulting thermite material.

Incorporation of aluminum into the sol-gel allows for a thermite to be formulated, which releases its energy via the reaction:



Interest in this material as a potential small-scale thermal source has necessitated investigation of thermal safety properties, especially in light of the incidents described above. This report summarizes investigations of sol-gel based Al/ Fe_2O_3 thermites at small scales as potential thermal sources with an emphasis on the heat release during thermal treatment of the sol-gel iron oxide.

Results and Discussion

Synthesis

The initial synthesis of sol-gel iron oxide was performed with a starting solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in ethanol (0.875 mL). It was determined in early syntheses that iron chloride was not a suitable starting material because gelation would not occur readily. Propylene oxide was added dropwise while this solution was sonicated in an ultrasonic bath. Gelation typically occurred within 7-10 minutes. The aluminum was suspended in isopropyl alcohol (0.5 mL, IPA) by sonicating in an ultrasonic bath for several minutes. This aluminum suspension was added before complete gelation of the sol-gel to ensure it was distributed uniformly in the sol-gel. In other experiments, aluminum powder was added to the iron solution prior to the addition of propylene oxide with no obvious effects on gelation.

The iron (as Fe^{3+} in ethanol) content was varied from 0.4-2 mmol, the ratio of propylene oxide to iron from 6-20, the molar aluminum to iron ratio from 0.5-1.5, and the aluminum particle size from 50 nm to 2- μm . Also, the addition of Fluorel® FC-2175 poly(vinylidene fluoride/hexafluoropropylene), MachI Inc., equivalent to VitonA®), and nanoscale MoO_3 (molybdenum trioxide, Climax Engineered Materials) was investigated. A summary of these experiments is shown in Table 1. Earlier experiments without the addition of aluminum are not shown.

Table 1. Summary of sol-gel synthesis variables for initial synthesis experiments.

Iron Content	Propylene Oxide : Iron	Al:Fe	Al size	Label	Comment	Mass Fe + Al
mM			nm			mg
0.8	11	1.0	50	1-29-08 #1	11x propylene oxide	140
0.8	11	1.0	50	1-30-08 #1	11x propylene oxide	137
0.8	6	1.0	50	1-30-08 #2	6x propylene oxide	135
0.8	20	1.0	50	1-30-08 #3	20x propylene oxide	141
0.4	11	1.0	50	2-5-08 #3	0.5 concentration	65
1.2	11	1.0	50	2-5-08 #4	1.5 concentration	206
2.0	11	1.0	50	2-6-08 #1	2.5 concentration	332
0.8	11	0.5	50	2-5-08 #1	2:1 Fe:Al	99
0.8	11	1.5	50	2-5-08 #2	2:3 Fe:Al	168
0.8	11	1.0	2000	2-6-08 #2	2 μm Al	120
0.8	11	1	80	4/9/2008	FC-2175 and new Al	N/A
1.8	14.8 M:PO	1 (Mo 2:1)	50	6/4/2008	10% FC-2175 10% MoO_3	N/A

The syntheses were carried out in small glass vials and the material was recovered after completion by allowing the material to air dry and shrink into a plug at the bottom of the vial. The material was then removed by breaking the plug up with a spatula into pieces that were small enough to fit through the mouth of the vial. A photograph of three vials with dried plugs of sol-gel thermite material is shown in Figure 1.

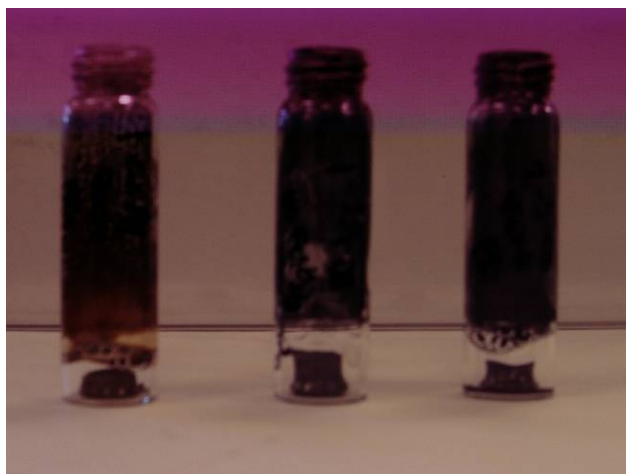


Figure 1. Three vials showing plugs of dried sol-gel thermite at the bottom of each vial.

After recovery of the dried, or partially-dried, material from the vials, the sol-gel material was subjected to further drying either in a differential scanning calorimeter (DSC) or vacuum firing chamber. Drying was carried out either before or during thermal analysis in order to remove trapped residual solvent from the nanoporous material. Details of thermal analyses are covered in the next sections.

Small-scale thermal analysis

Thermal analysis was conducted using a DSC (Model 2910 MSDC V4.4E, TA Instruments, Wilmington, DE) to evaluate the behavior of the sol-gel thermite on exposure to different thermal treatments. The purpose of such thermal treatment was to evaluate low-temperature residual solvent removal (propylene oxide, IPA, and ethanol), as well as high-temperature residual carbonaceous impurity removal. The goal of the low-temperature solvent removal treatment was to reduce the amount of time required for air-drying prior to use of the material. This may expedite formulation by eliminating the solvent extraction step that has been used by some researchers.[6] The purposes of the high-temperature treatment was to promote iron oxide formation and to remove impurities that could be detrimental to the final combustion properties of the material. It is believed that this high-temperature thermal treatment reduces some of the iron oxides, resulting in high-surface area iron that can rapidly oxidize upon exposure to air.

Caution: Several auto-ignitions have been observed at other laboratories during this thermal treatment (in large samples), or after exposure to atmosphere following this thermal treatment (in smaller samples).[1]

Numerous experiments were conducted on the different sol-gel thermite formulations using between 25 and 125 mg of material. These masses were total material masses and certainly included residual solvent and other impurities from the synthesis and formulation steps. The amount of residual solvent in the material may have been different from sample to sample based on variables in the deliberate pre-treatment, such as the length and temperature of drying beforehand. Heating within the DSC was conducted in argon and using an open DSC pan. A typical thermal cycle involved heating to 65 °C and holding for up to 200 minutes. Holding the material at this temperature allowed trapped solvent removal without boiling, thus preventing the material from being spread around the calorimeter. After this step, the material was taken to a higher temperature (typically 200 °C) to dry additional solvent and complete activation of the thermite. After this activation step, the material was cooled to room temperature. When the material was at room temperature the gas was switched from argon to air. This

gas switch was intended to simulate an accident scenario in which material was moved from an inert environment (e.g., an oven) to ambient atmosphere. The relative energy release of a material (in J/g) was determined by integrating the heat flow under the exotherm that typically happened on this gas switch and dividing by the quantity of material. In some of the experiments, the material was then taken to ignition by heating in air. This served to verify that the material was energetic after the thermal treatment. Explosive waste was disposed of by placing used DSC pans in a vial with minimal water, thus mitigating any concerns with potential electrostatic discharge initiation. An example of a thermal cycle is shown in Figure 2.

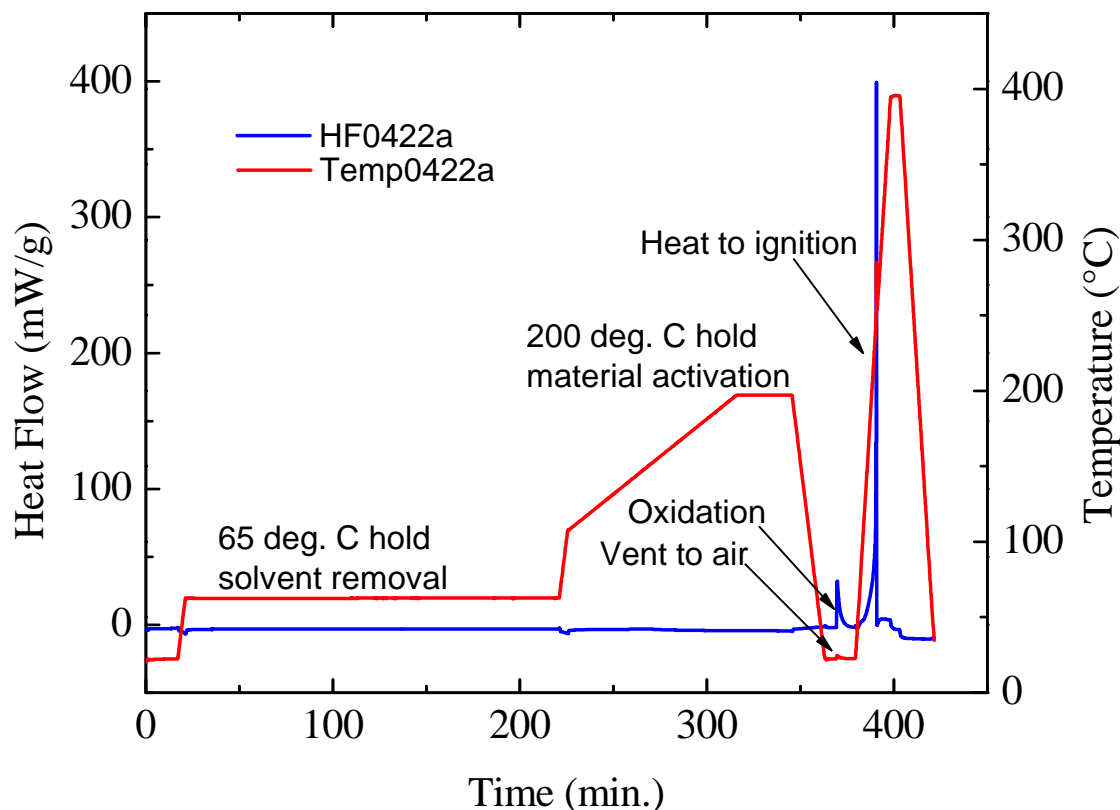


Figure 2. Typical heating cycle and heat flow in a sol-gel thermite sample.

The initial low-temperature heating step was established based on maintaining a temperature lower than the boiling point of ethanol (78 °C) in the samples. After initial experiments with 65 °C holds of 0, 15, and 200 minutes, a 65 °C hold for 200 minutes was selected to give sufficient time for ethanol to migrate through the nanoporous sample and evaporate. In early experiments without this solvent removal step, the material was spread around the DSC chamber by the expansion of the vaporizing solvent. A comparison of experiments with the 15-minute hold and the 200-minute hold is shown in Figure 3. This figure shows the pronounced endotherm associated with solvent boiling as the material is heated through the boiling point of ethanol. The less-pronounced endotherm after the 200-minute hold shows greater solvent removal. All further experiments were conducted with the initial solvent removal step.

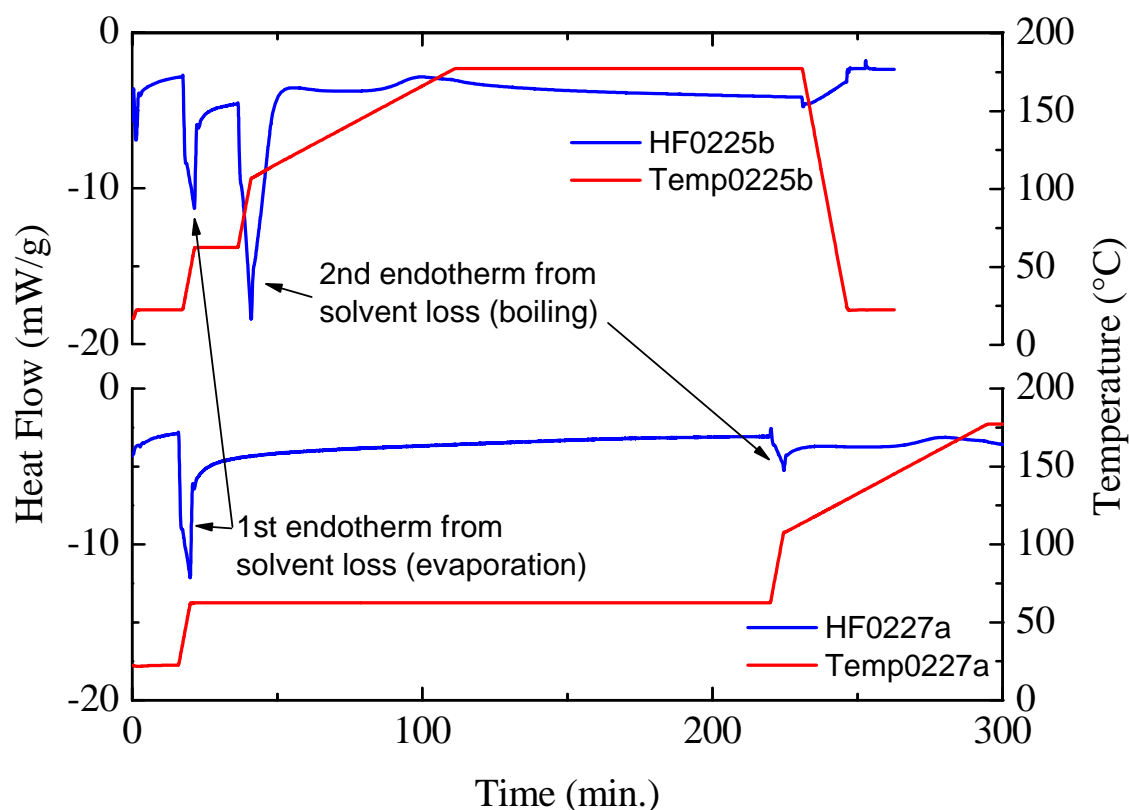


Figure 3. A comparison of 65 °C holds for 15 minutes (top) and 200 minutes (bottom). The endotherm associated with boiling solvent is much less pronounced after the longer hold time, indicating greater solvent removal.

In a few of the experiments, the material was vacuum-dried prior to thermal analysis in order to further enhance solvent removal. The vacuum drying was conducted at room temperature and at a pressure less than 10 mtorr. This did increase heat release from the material, as shown in Figure 4, however, the relative contributions of the act of vacuum drying versus simply analyzing material that had more actual energetic material per unit mass (i.e., due to solvent removal) is unknown. In the experiment shown in Figure 4, the vacuum-dried material had an exotherm of 151.8 J/g and the air-dried material had an exotherm of 22.5 J/g upon switching from argon to air. Vacuum drying should be used prior to (or in concert with) thermal treatment of sol-gel thermites to expedite activation. Additionally, it should be assumed that vacuum-dried material poses a greater hazard than material wet with solvent.

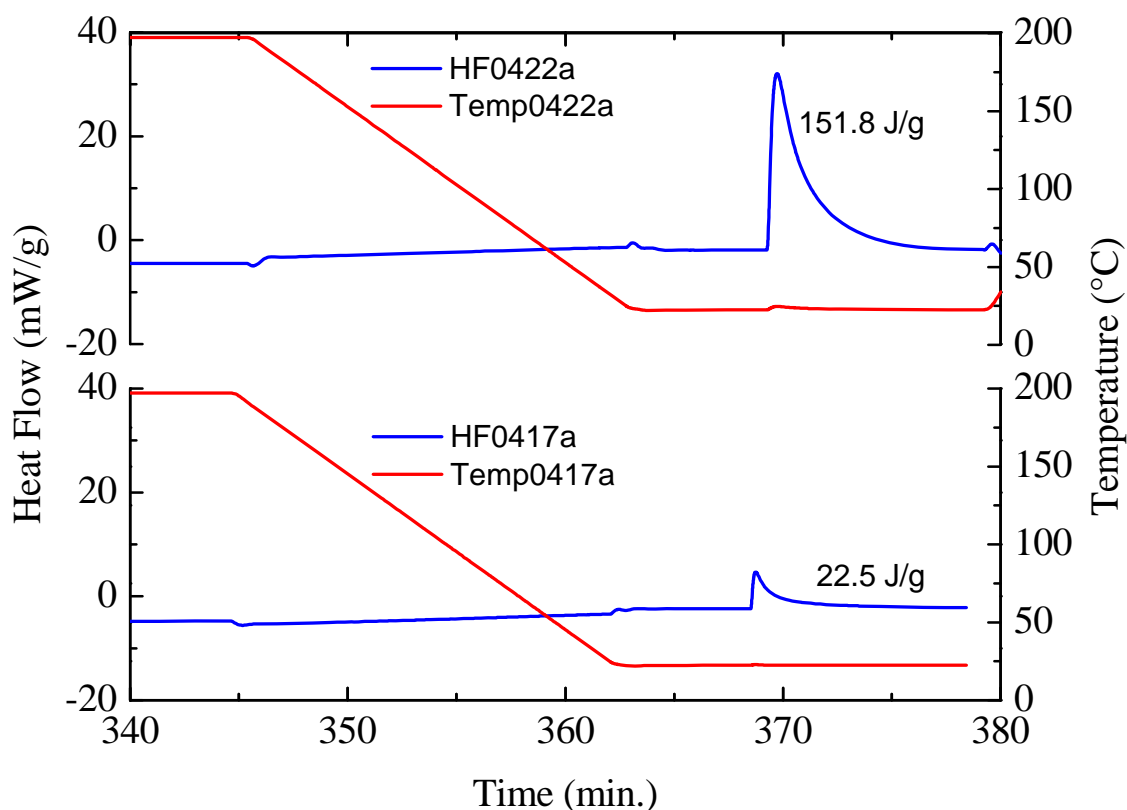


Figure 4. Graph showing the comparison between air-dried (bottom) and vacuum-dried (top, after air drying) sol-gel thermite materials upon exposure to air (exotherm at ~368 min).

The effect of additives (Fluorel® FC-2175, and MoO_3 , molybdenum trioxide) was also investigated. A large amount of research has been conducted on nanocomposite thermites composed of nanoaluminum and MoO_3 , [7] and it was of interest to see if there was an effect on ignition sensitivity upon addition of MoO_3 to a sol-gel. The addition of FC-2175 was investigated due to evidence that it had contributed to previous auto-ignition incidents. [1] In our experiments with these additives, the material was heated to ignition in the DSC after the gas switch from argon to air. This allowed for verification that the material was energetic. In all of the experiments with these additives, the exotherm upon switching from argon to air was less pronounced than in those experiments without these additives. This effect is likely due to reduction of the total amount of sol-gel iron oxide that was available to react upon exposure to air, and possibly to the additives acting as a heat-sink. It can't be assumed that at a certain scale, additives would increase the sensitivity, but at our small scales (~25 mg) this was not observed. Three different activation temperatures (200, 250, and 300 °C) were tried with this material but no apparent effect on the heat release upon the gas switch was seen. There was, however, an effect on the temperature of ignition during the final heating step as shown in Figure 5. The materials with additives displayed a decreased ignition temperature (material was more sensitive) at the lower activation temperature of 200 °C. At the highest activation temperature (300 °C), the material did not appear to ignite during the final heating ramp.

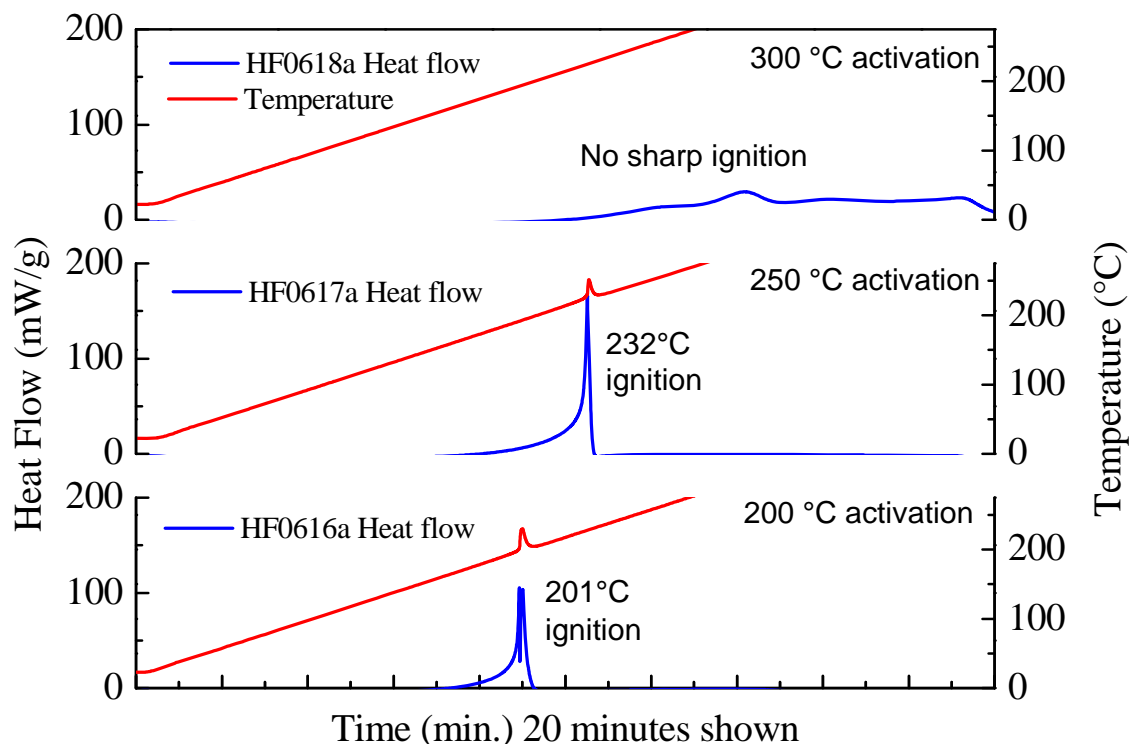


Figure 5. Ignition (in air) behavior of sol-gel thermite as a result of different final activation (in argon) temperatures. This thermite was formulated with the additives MoO_3 and Florel® FC-2175. Lower activation temperatures resulted in lower ignition temperatures during the final heating phase. Activation at 300 °C resulted in material that did not ignite.

Control experiments were conducted using standard fine-particle iron oxide to determine if a similar activation effect could be seen with high-surface area iron oxide by heating in an inert atmosphere with added hydrocarbon impurities. A formulation was made with 80% NANOCAT® Superfine Iron Oxide (MachI Inc.), 10% SPAN® 80 (Uniqema, ICI Americas Inc., used as a dispersed carbon source), and 10% Fluorel® FC-2175. The material was formulated by ultrasonication in mixed esters and evaporating off the solvent. Thermal analysis was conducted on the material with activation temperatures of 200, 250, and 300 °C. There was no evidence of any exothermic behavior upon switching from argon to air. This material was taken to ignition (despite not having any aluminum) and a similar trend in ignition behavior was seen as that with sol-gel thermites as shown in Figure 5. For the three different activation temperatures of 200, 250, and 300 °C, the ignition temperatures were 230, 244, and 281 °C, respectively. This exothermic behavior is presumed to be oxidation of reduced iron species; however it is not understood why these species exhibited no exothermic behavior on the initial gas switch from argon to air.

Large-scale thermal analysis

While the DSC experiments were conducted with ~25 mg of material, larger-scale experiments were conducted with several hundred milligrams in order to evaluate scaling effects. These experiments were conducted in a firing chamber due to the increased amounts of material. A vacuum pump attached to the chamber allowed for the system to be pumped down to a pressure lower than 10 mtorr. This facilitated residual solvent removal as well as limited the available oxygen that could react during the activation heating process. In these experiments, a portion of the sol-gel thermite was placed on a small heater surface in the firing chamber. The sample was enclosed using a small glass tube (open at the top and the bottom) to provide light confinement of the reaction. A tungsten wire was used as a secondary ignition source. This experimental arrangement is shown in Figure 6.

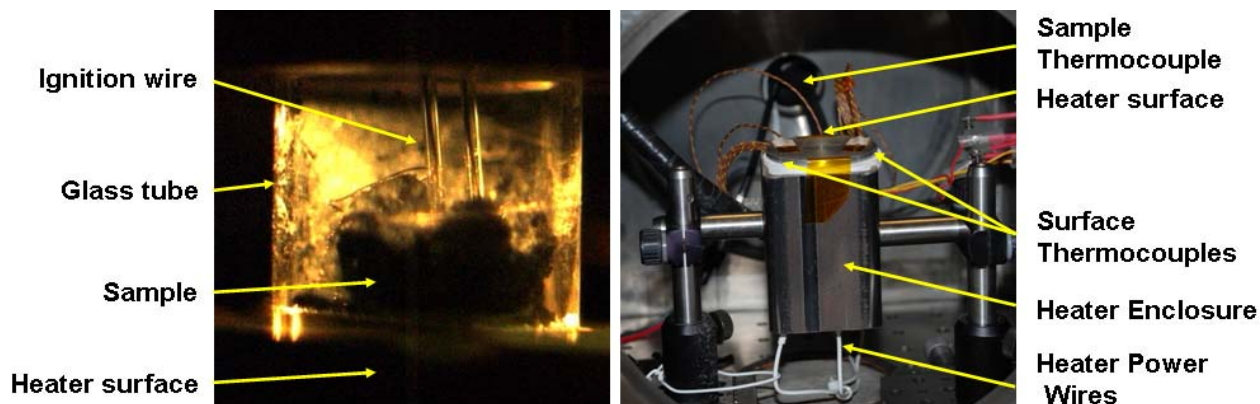


Figure 6. Experimental arrangement for larger-scale sol-gel thermite experiments. The left photo shows the glass tube surrounding a ~100 mg sol-gel sample on the heater with a tungsten secondary ignition wire on top of the sample. The right photo shows the heater and thermocouple wires in the vacuum firing chamber.

The system was pumped down and the sample was held at lower than 10 mtorr for a minimum of 4 hours and a maximum of several days. This process expedited removal of any residual solvent. At this point the heater was turned on and a heating profile, based on the DSC experiments mentioned earlier, was performed. This heating profile involved heating the sample to 65 °C, holding for one hour, then heating to 200 °C (240 °C in one experiment), holding for one half hour, and finally cooling to room temperature. At this point a valve on the vacuum chamber was opened to allow ambient air in. In no instance did the sol-gel thermite ignite and propagate a reaction; however the thermocouple inserted in the material always detected a temperature increase of a few degrees. At this point the tungsten ignition wire was used to ignite the sample and determine if it was reactive. In every instance the ignition of the material occurred and propagated throughout the sample, as shown in Figure 7. A total of seven different materials from different syntheses were testing using this method. It can be concluded that small samples of sol-gel thermite (a few hundred milligrams) do not present a significant auto-ignition hazard from this thermal treatment, but unintentional reaction may occur in larger samples based on others' work.[1]

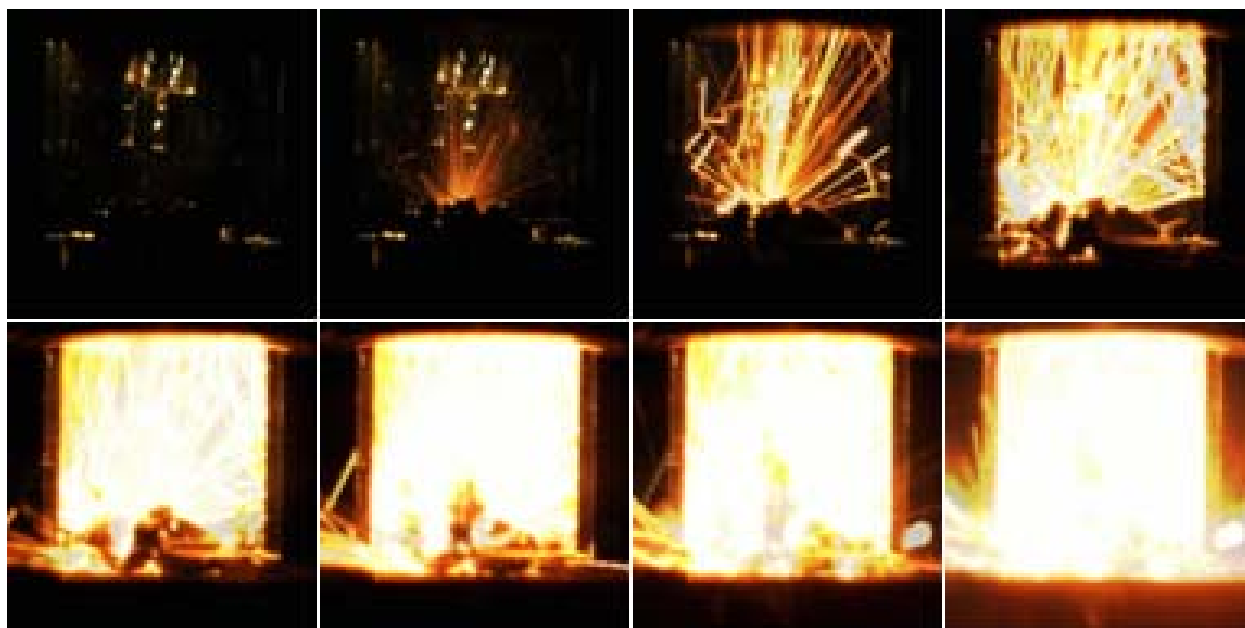


Figure 7. Series of eight frames from 1000-fps video of ignition of roughly 100 mg of sol-gel thermite. This material was ignited by a resistively-heated tungsten wire.

Coating experiments

Because the sol-gel process inherently involves the use of a fluid, experiments were conducted to determine if this material could be coated on a surface and could leave a coherent film after solvent evaporation. During the gelation process, and after addition of the propylene oxide, agitation of the mixture was critical to ensure proper gelation and mixing with the fuel particles. The viscosity of the material rapidly changed during this gelation process and sufficient mixing was not always apparent until the material had gelled. Different types of morphologies in the dried material were observed as a result of different synthesis conditions, ranging from solid plugs to plugs with a network of cracks through them. Due to these variables, as well as concerns with working with nanomaterials that arose at Sandia during this project, coating experiments with sol-gel thermites were not attempted. As a proof-of-concept, thermite with larger particle sizes of dispersed fuel and oxidizer was used.

Experiments were conducted to evaluate the ability to coat thermite on surfaces by drop-casting. The thermochemical code Cheetah[8] was used to optimize the formulation of the three ingredients, iron oxide (Fe_2O_3), aluminum, and FC-2175. The FC-2175 was fixed at a relatively high concentration (16 and 20 weight %) to ensure proper binding of the iron oxide and aluminum particles to allow coherent film formation. The two calculated formulations that were investigated for coating were Al/ Fe_2O_3 /FC-2175 25/59/16 and 25/55/20 (weight percent). A small amount (1.5%) of the dispersant Solsperse 32500 was added to assist with mixing and dispersion of the particles. A mixture of ethyl acetate and ethyl lactate (30:70) was used as a mixing fluid. Batches of 100 mg were made by simultaneously ultrasonically dispersing the aluminum (Silberline Flake DF-1667) and Fe_2O_3 (Cerac I-1077, 0.44- μm) in the mixed esters with pre-dissolved FC-2175. The 16% binder formulation was mixed at 200 mg solids/mL and did not have a high enough viscosity to coat films that were very thick, but the drop-coated films were very uniform. The 20% binder formulation was mixed at 300 mg solids/mL and resulted in films that were thicker (up to several hundred microns), but had rough surface topography. This higher concentration material was used to coat pieces of bare silicon that had an alumina housing glued on top to

prevent the material from flowing off the sides of the silicon. A tungsten wire was attached to the surface of the bare silicon to ignite the material and material was drop-cast such that it covered the wire. Photographs of drop-cast glass with the two formulations and the drop-cast bare silicon are shown in Figure 8.

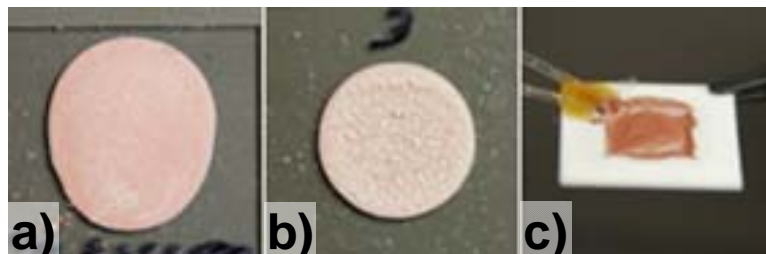


Figure 8. a) Drop-cast thermite on glass using 200 mg/mL solids with 16% FC-2175, and b) 300 mg/mL solids with 20% FC-2175. c) Drop-cast thermite on bare silicon with an alumina housing using 300 mg/mL with 20% FC-2175.

Several attempts were made to ignite the drop-cast samples with embedded tungsten wires. A power supply was used to resistively heat the wire to a high temperature within a few seconds. These were unsuccessful with the wire always opening at some point outside the thermite prior to ignition. After several failed ignition experiments, an experiment was conducted with a tungsten wire placed on top of the thermite, rather than being imbedded inside the thermite during the coating process. Thus, when power was applied to the wire it preheated the thermite sample and finally ignited it at one point where the wire was touching the thermite. An ignition front ran through the thermite and it reacted completely as shown in Figure 9. It is reasonable to expect that ignition and propagation in thin thermite films would be enhanced by the use of smaller fuel and oxidizer particles or through the use of a more reactive oxidizer, such as MoO_3 or Bi_2O_3 .

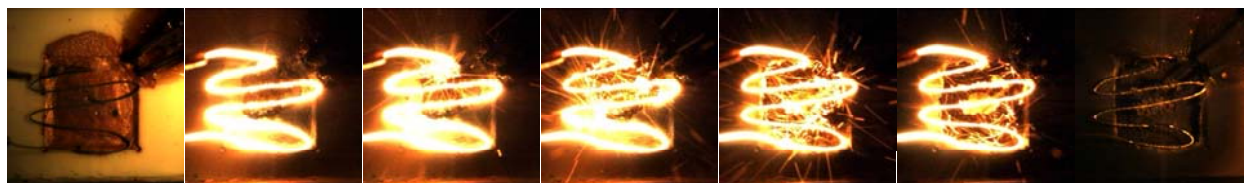


Figure 9. Images of combustion in drop-cast thermite at 10 fps. A resistively-heated tungsten wire was used to preheat and ignite the thermite. The first and last images show the thermite before and after the test.

Conclusions

Sol-gel thermites, formulated from nanoporous oxides and dispersed fuel particles, may provide materials useful for small-scale, intense thermal sources, but understanding the factors affecting performance is critical prior to use. We synthesized sol-gel thermites using a variety of different techniques and discovered that there are many viable routes to relatively equivalent thermites. These thermites were subjected to a variety of thermal treatments under argon in a DSC and it was shown that a hold for up to 200 minutes at 65 °C was effective for removal of residual solvent, thus preventing boiling during the final thermal activation step. Vacuum-drying prior to this heating was shown to be even more effective. The addition of aluminum and molybdenum oxide reduced the total heat release per unit mass upon exposure to air, probably due to decreasing the amount of reduced iron oxide species in the thermite.

Of the different thermal activation temperatures for sol-gel thermite containing the polymer FC-2175, 200 °C resulted in increased ignition sensitivity over 232 °C, and 300 °C resulted in non-ignitable material. Non-sol-gel iron oxide did not exhibit any of the air-sensitivity observed in sol-gel iron oxide. In the DSC experiments, no bulk ignition of sol-gel thermites was observed upon exposure to air after thermal activation in argon. However ignition did occur when the material was heated in air after thermal treatment. In larger-scale experiments, up to a few hundred milligrams, no ignition was observed upon exposure to air after thermal activation in vacuum; however, ignition by resistively-heated tungsten wire was possible. Thin films of thermite were coated on glass and silicon substrates using dispersed particles of aluminum and iron oxide, but ignition and propagation of these films was difficult. The only ignition and propagation observed was in a preheated sample. Further work could be conducted on optimized formulations for coating using different materials, larger masses of material, and smaller particle sizes.

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