Final Report 2003

Safe and Environmentally Acceptable Sol-Gel-Derived Pyrophoric Pyrotechnics

PP-1276

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Abstract

It was demonstrated that highly porous sol-gel derived iron (III) oxide materials could be reduced to sub-micron-sized metallic iron by heating the materials to intermediate temperatures in a hydrogen atmosphere. Through a large number of experiments complete reduction of the sol-gel based materials was realized with a variety of hydrogen-based atmospheres (25-100% H_2 in Ar, N_2, CO_2, or CO) at intermediate temperatures (350°C to 700°C). All of the resulting sol-gel-derived metallic iron powders were ignitable by thermal methods, however none were pyrophoric. For comparison several types of commercial micron sized iron oxides Fe_2O_3, and NANOCAT^{TM} were also reduced under identical conditions. All resulting materials were characterized by thermal gravimetric analysis (TGA), differential thermal analysis (DTA), powder X-ray diffraction (PXRD), as well as scanning and transmission electron microscopies (SEM and TEM). In addition, the reduction of the iron oxide materials was monitored by TGA. In general the sol-gel materials were more rapidly reduced to metallic iron and the resulting iron powders had smaller particle sizes and were more easily oxidized than the metallic powders derived from the micron sized materials. The lack of pyrophoricity of the smaller fine metallic powders was unexpected and may in part be due to impurities in the materials that create a passivation layer on the iron. Several recommendations for future study directions on this project are detailed.

Background

Pyrotechnics can be grouped into six families; decoy flares, illuminating flares, colored flares, smokes, igniters/starters and miscellaneous pyrotechnic items. Decoy flares include infrared (IR) and solid pyrophoric flares **[1-3]**. Aircraft pyrophoric decoy flares are solid pyrotechnic devices ejected as a precautionary measure or in response to a missile warning system. The most significant requirement of the device is that it develops a high-intensity, characteristic signature, rapidly. In order to meet this requirement, the energy radiated by the flare is typically provided by a pyrotechnic reaction. Pyrotechnic compositions have been shown to provide high energy densities and reasonable storage life at moderate cost **[4]**. The most common composition of a conventional pyrotechnic flare consists of pyrophoric iron. This composition provides the high energy density required for the decoy and also produces solid combustion products for good radiation efficiency. The net reaction is shown below:

$$2\ Fe(s) + 3/2\ O_2 \rightarrow Fe_2O_3(s) + \text{heat}$$

Decoy materials of this composition undergo the above reaction to reach temperatures of 820°C in less than one second and above 750°C for twelve seconds after their exposure to air. The thermal response can be increased or decreased with the addition of metals that

undergo very exothermic reactions when heated in air (e.g., B, Al, Zr, Ti) or inert metal oxides (e.g., SiO_2, Al_2O_3), respectively.

The current pyrophoric decoy flare is composed of pyrophoric iron coated onto steel foil **[5-10]**. The pyrophoric iron coating is prepared by mixing Fe and Al powders in a slurry containing a suitable solvent and binder. A very thin steel foil is then coated with the slurry by either dip coating or spraying. The resulting material is then rapidly heated to 500°C to drive off the solvent and binder to yield a coating of the metallic powders. The coated substrate is then heated to relatively high temperatures (~800-1000°C) in both H_2 and Ar atmospheres to from an iron/aluminum alloy. The resulting alloy can be leached with a hot (~100-200°F) caustic aqueous solution of 10-20 % sodium hydroxide (by mass) to leach the aluminum from the alloy and render the remaining iron porous and highly pyrophoric. Some patent processes claim that use of stannite (dissolved as $SnCl_2$ or Sn(*s*)) in the aqueous leaching solution increases the activity (i.e., makes the iron more pyrophoric) and the lifetime of the active decoy. There are several variations of the described manufacturing technique that allow the preparation of the pyrophoric iron as a powder or a coating on a metal foil. Pyrophoric foils are particularly attractive for their ability to be dispersed from the aircraft in a cloud-like pattern. The high surface area to mass ratio of the foils requires that they flutter after being ejected from the aircraft and take on the appearance of a moving hot cloud when several decoys are ejected in rapid succession. This signal is attractive to the IR-seeking missile.**[5-10]** Current pyrophoric decoy composition and performance can be modified through manipulation of the manufacturing process.

Having a small amount of a substance in intimate contact with the pyrophoric iron that undergoes an exothermic reaction when heated can increase the pyrophoric action of the decoy flare material. Metals, such as boron or titanium, can be added to the pyrophoric foils to achieve this desired result. Alternatively, the pyrophoric iron can be coated with aqueous solutions of commercially available alumina or silica sol that coat the porous base metal. The inert oxide coating blocks O_2 from getting to the iron too rapidly and hence slows down the burn rate and makes the pyrophoric response of the material less intense. The pyrophoric iron generated by the above processes can be stored in solvents such as acetone, ethanol, and methanol, under certain conditions, with little loss in their pyrophoric performance.**[5-10]** Although this process is well documented and provides functional and effective pyrotechnic flares it can and should be improved. The current process relies heavily upon the use of hot caustic leaching solutions to prepare the high surface area porous pyrophoric Fe metal. These solutions are corrosive and represent both a safety and environmental hazard.

Production of pyrophoric iron in a simple and safe manner would be advantageous from a safety and environmental point of view. Magnus reported that pyrophoric iron could be generated from reduction of iron compounds in a stream of H_2 at relatively low temperatures (360-420 °C) as early as 1825.**[11]** Since then many researchers have repeated this result using the iron (III) oxides as the iron-containing reagent.**[12-13]** New sol-gel methods, developed at Lawrence Livermore National

Laboratory (LLNL), can be employed to generate high surface area porous iron (III) oxide-based solids.**[14-19]** Chemical reduction of such porous solids at low temperatures will allow the preparation of high surface area porous iron with little sintering, with the only byproduct being water. It is very likely that such a material would be readily pyrophoric and would have utility in new decoy flares. The material, prepared by this synthetic route, would eliminate the use of hot caustic leaching solutions. In addition, it would not require the incorporation of any hazardous materials or processes that are not already used in the current production.

As a basic introduction, sol-gel chemistry utilizes the hydrolysis and condensation of molecular chemical precursors, in solution, to produce nanometer-sized primary particles, called "sols". Through further condensation the "sols" are linked to form a three-dimensional solid network, referred to as a "gel", with the solvent liquid present in its pores. Evaporation of the liquid phase results in a dense porous solid referred to as a "xerogel". Supercritical extraction of the pore liquid eliminates the surface tension of the retreating liquid phase and results in solids called, "aerogels". Sol-gel materials are distinctive in that they typically posses high surface areas, high porosities and small primary particle size. The properties unique to sol-gel materials lead to their enhanced reactivity**.** Therefore, sol-gel chemical routes are very attractive because they offer low temperature routes to synthesize homogeneous materials with variable compositions, morphologies, and densities.**[20]** A schematic representation of the sol-gel process and materials is shown in Figure 1.

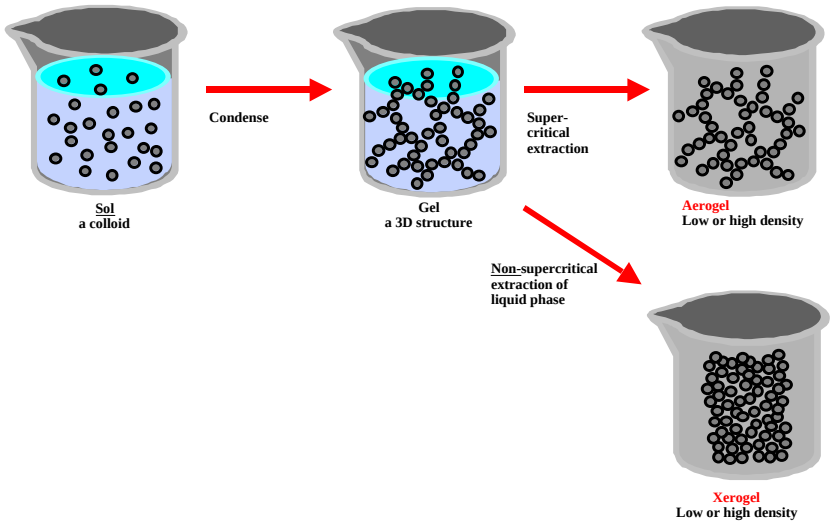


Figure 1. Here is a schematic representation of the sol-gel process and materials

Scientists at the Naval Research Laboratory have prepared and characterized thermally emitting aerogels.**[21]** Iron metal was deposited into the framework of silica, resorcinol-formaldehyde, and carbon aerogel materials using a metal organic chemical vapor deposition (MOCVD) system. One aerogel the iron doped-carbon material was a strong thermal emitter and burned at 600-700 °C. The results shown in this study are encouraging that sol-gel techniques can be used to prepare thermal emitters. However, the iron precursor used in the MOCVD process, iron pentacarbonyl, is highly pyrophoric and toxic.

Objective

The effort proposed will demonstrate that "sol-gel" chemical techniques can be used in water-, or another environmentally acceptable solvent, based processing can be used to prepare high surface area porous iron(III)oxides. These materials can then be reduced using molecular hydrogen, at elevated temperatures, to produce high surface area porous pyrophoric iron metal. This material will be used to provide a decoy with comparable performance characteristics to that currently used without the environmental and health concerns of using hot caustic leaching solutions, that are needed in the present production process of pyrophoric decoys.**[5-10]** Alternatively, "sol-gel" techniques can also be used to immobilize the pyrophoric iron generated by reduction of the sol-gel-derived iron(III)oxides, or from some alternative source, in an inert matrix which can be cast to parts with a variety of shapes and sizes. This second approach may allow the resulting pyrophoric pyrotechnic to be easily and desirably released, as well as having the versatility to control the composition of the matrix and tailor the material to provide a specific output response. Preliminary work has demonstrated that the sol-gel approach enables high control over chemical compositions and reaction rates, of energetic materials, and that the process is safe.**[14-19]**

Technical Approach

We propose to use "sol-gel" methodology to produce nanostructured energetic materials (i.e., pyrotechnics) while minimizing or eliminating the health and environmental hazards associated with their current fabrication. This sol-gel approach for preparing pyrotechnic formulations involves a fundamental change in the conventional manufacturing and fabrication processes of energetic materials. One particular application of this methodology can be used to eliminate the use of caustic leaching solutions associated with pyrophoric decoy flare manufacture, while maintaining or improving performance of the final products. Low temperature reduction of high surface area porous sol-gel-derived iron(III)oxide with molecular hydrogen will result in the formation of porous pyrophoric iron metal, suitable for use in pyrophoric decoy flares.

The effort will demonstrate that processing and preparation with environmentally acceptable media under neutral conditions can replace the current process used in pyrophoric flare manufacturing.

Sol-gel techniques can be used to produce a substrate for immobilization of the pyrophoric material in the flare and allow suitable dispersion when deployed. The extremely versatile nature of sol-gel chemistry may ultimately allow for the reformulation of materials that is not possible or practical with current systems, to allow decoy flares with special features to be readily and safely prepared. This effort is intended to advance the use of nanotechnology in defense applications and show that it is relevant to this, and potentially other energetic materials needs in the DoD and the DOE. Preliminary work has demonstrated that this approach enables high control over chemical compositions, particle size and distribution, and reaction rates and that the process is safe. Although sol-gel technology has the potential to impact a number of DoD and DOE needs, the focus will be on pyrophoric pyrotechnic needs in Navy decoys. The goal will be to produce a pyrophoric decoy whose processing and composition is acceptable by OSHA, EPA, the Clean Air Act, Clean Water Act, and Resource Recovery Act standards. This will be a joint effort between the Lawrence Livermore National Laboratory and the Naval Surface Warfare Center, Crane.

We propose to reduce sol-gel-derived high surface area porous iron(III)oxide aerogels and xerogels to pyrophoric iron using molecular hydrogen at elevated temperatures. Since first reported in 1825, many researchers have found that reduction powdered ferric oxide with hydrogen gas at temperatures between 360-600°C yields pyrophoric iron. Reduction at temperatures higher than 650°C resulted in non-pyrophoric iron. The general hypothesis used to rationalize these observations is that the temperature of reduction is low enough so as to reduce the iron species to metallic iron with minimal sintering of the final product.**[11]** At the lower temperatures the movement of atoms to orient then in a dense and more compact crystalline state is so slow that it does not occur to an appreciable extent. The result is the production of a very fine-grained porous Fe(*s*) powder that ignites upon contact with air.

As has been previously discussed, LLNL has developed a new procedure for the preparation of high surface area porous iron(III)oxide solids. Detailed studies on their synthesis and characterization and energetic materials formulation have been reported. **[14-19]** The iron(III)oxides produced using this method have surface areas and porosities significantly higher than those reported previously. The dry porous iron (III) oxides can be prepared using benign and environmentally acceptable solvents like water and ethanol, Fe(III) inorganic salts (chloride and nitrate), and propylene oxide. This material could be an ideal candidate for reduction to porous iron metal using hydrogen at temperatures between 360-600°C. Typical sol-gel particle and pore morphology is shown in Figure 2.

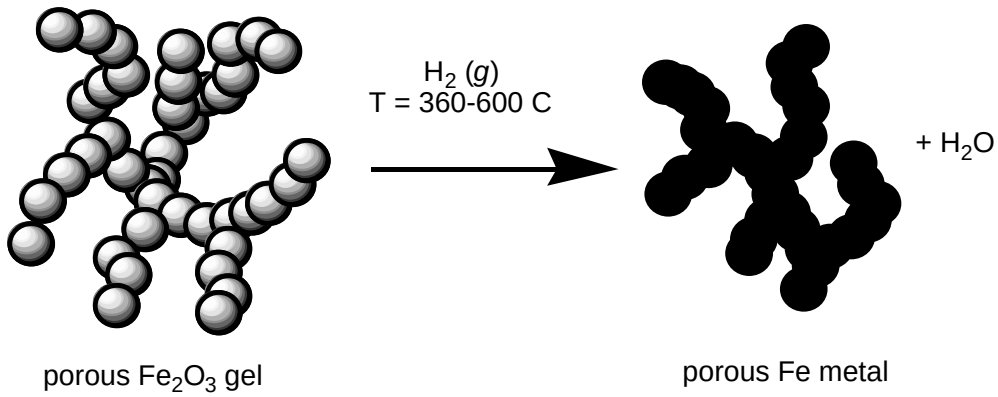


Figure 2. Schematic representation of the pseudomorphic reduction of porous iron(III)oxide to porous Fe^0 metal with hydrogen

In Figure 1 the porous iron (III)oxide is reduced to Fe(*s*) while retaining a significant amount of the porous skeletal framework of the precursor oxide material. This is feasible, provided that the reduction temperature is kept low enough to prevent sintering. Certainly there will be some sintering of the porous solid however, it is highly likely that material like that shown on the right side of the above scheme would be pyrophoric as it would have many of the characteristics (e.g., small particle size, high surface area) of finely divided iron that is pyrophoric. Inspection of Figure 3 demonstrates that the iron (III) oxide sol-gel materials produced at LLNL have a microstructure similar to that described and shown in Figure 2.

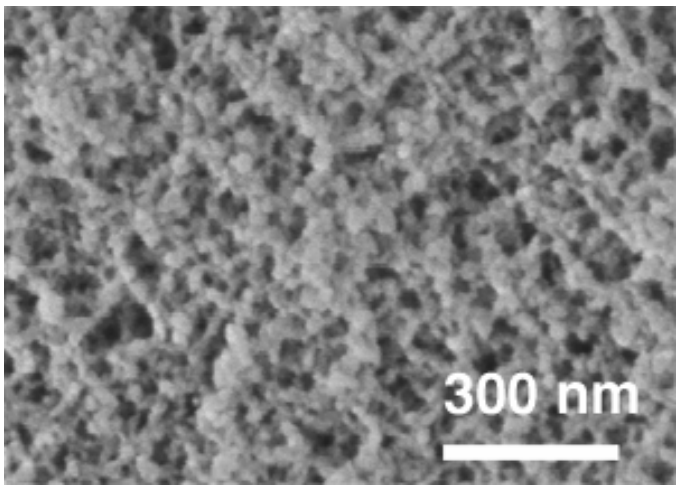


Figure 3. Scanning electron micrograph of sol-gel derived iron (III) oxide aerogel material. Note the highly porous network along with the very small particle size.

In the proposed synthesis, the pyrophoric iron would be produced using water or ethanol, Fe(III) salts, propylene oxide, and hydrogen. This method is not without hazards. The flammable nature of hydrogen requires that necessary safety steps be taken. However, hydrogen is both used as a reagent and generated as a byproduct of the caustic leach process in the current manufacturing method.**[5-10]** There is reason to believe that such a sol-gel approach to the preparation of pyrophoric iron from high surface area porous iron(III)oxides, based on previous work performed at LLNL.

Pyrophoric tin oxide-based aerogels have been produced at LLNL.**[22]** The catalyzed hydrolysis and condensation of tin alkoxides in alcoholic media followed by rapid high-temperature supercritical extraction yields products that combust on exposure to air. Our preliminary investigations have indicated that the high temperature extraction step results in the reduction of some of the oxide to high surface area porous pyrophoric tin metal. This work indicates that porous pyrophoric metals can be prepared utilizing aspects of the sol-gel method. Although not in the scope of this study, the pyrophoric tin oxide could be coated onto a variety of different substrates for a myriad of energetic needs related to decoy flares. The application of sol-gel methods to decoy countermeasure devices may extend beyond the preparation of pyrophoric iron.

It is probable that sol-gel methodology could be utilized to provide and effective medium for the dispersion of the pyrophoric iron in decoy flares, that rivals the performance of current materials. Small particle sized native metals can be incorporated into a sol-gel metal oxide network composite decoy materials could involve the generation of the pyrophoric iron in the gel matrix *insitu*. This has been performed previously on Fe_2O_3-doped SiO_2 and Al_2O_3 gels. Reports have shown that reduction of the dried mixed Fe_2O_3-doped metal oxide matrix with molecular hydrogen at elevated temperatures gave nanoparticles of Fe(*s*) in the oxide matrix.**[23-24]** The particles are generally have very small diameters (2-20 nm), high surface areas, and may be pyrophoric. The spatial isolation of Fe_2O_3 particles from one another precludes them from diffusing together and sintering to larger particles. At LLNL numerous metal oxide/iron (III)oxide gels have been readily prepared using the epoxide addition method from solutions of mixed Al(III) or Si(IV) and Fe(III) molecular precursors with high levels of iron.**[25-26]** The matrix oxide will act as a burn rate modifier in these types of materials as well as a substrate for processing into decoy parts.

The rheological properties of the sol allow gels of it to be cast and processed into a variety of complex and precise sizes and shapes. It is certain that the composite sols could be cast and processed to give parts (e.g., thin discs or wafers) that have a large surface area to mass ratio. Parts with this property would very likely respond to ejection from a moving aircraft by fluttering in the air as the current pyrophoric decoy foils do. In addition, the large surface area to volume ratio of these composites should ensure rapid diffusion of air into the part and complete ignition of the pyrophoric iron. The production of thin aerogel or xerogel SiO_2 discs containing pyrophoric iron may be an appropriate way to achieve a desirable dispersion of the decoy material once deployed. The pore size of the matrix material is dependent upon its processing conditions and can be readily

varied with some degree of precision. This might allow the preparation of decoy flares with varied burn rates. For example, for faster burn rates one would employ processing conditions that yielded larger pores and conversely smaller pore sizes may result in slower burn times.

Experimental Methods

Iron (III) oxide aerogel and xerogel materials used in this study were made from the salts $FeCl_3 \bullet 6H_2O$ and $Fe(NO_3)_3 \bullet 9H_2O$ using sol-gel techniques described elsewhere.**[14-19]** As a control, samples of Fe_2O_3(Aldrich) and NANOCAT™ (a commercial source of 3 nm particle size amorphous iron (III) oxide) were also reduced.

A thermogravimetric analyzer (TGA) was set up to accommodate and monitor the reduction of iron (III) oxide aerogels. TGA measurements were performed using a Cahn model 141 TGA balance. Measurements were preformed on two iron oxide nanocomposites. The oxides can be reduced in pure H_2 or mixtures of Ar/H_2 and N_2/H_2. For the same heating rates, the rate of reduction was found to vary with the concentration of H_2 in the gas mixture, thus the reduction does not appear to be diffusion limited. The samples decrease to about 52 wt% for maximum temperatures above 350°C. This weight loss corresponds to 3 moles of oxygen to 1 mole of iron in the starting composite, assuming only the presence of iron and oxygen. The reduced material displays a small amount of weight gain on cooling, probably due to the surface re-oxidation from reaction with water in the gases. Background measurements confirm that this increase is not due to buoyancy changes in the system.

The powder X-Ray diffraction patterns were obtained using a Siemens DIFF500 diffractometer. The iron oxide aerogel materials are amorphous. For samples reduced to 52-wt%, the patterns show the presence of metallic iron. For samples not fully reduced, the patterns show the presence of Fe_3O_4. Fourier transform-infrared (FTIR) spectra were collected on pressed pellets containing KBr (IR-grade) and a small amount of solid sample. The spectra were collected with a Polaris™ FTIR spectrometer.

Surface area and pore volume and size analyses were performed by BET(Brunauer-Emmet-Teller) methods using an ASAP 2000 Surface Area Analyzer (Micromeritics Instrument Corporation). Samples of approximately 0.1-0.2 g were heated to 200˚C under vacuum (10^{-5} Torr) for at least 24 hours to remove all adsorbed species. Nitrogen adsorption data was taken at five relative pressures from 0.05 to 0.20 at 77K, to calculate the surface area by BET theory.

Scanning electron microscopy (SEM) was carried out using a Hitachi S-4500 cold field emission SEM. Typical accelerating voltages used for aerogel samples ranged from 1.8-6 kV and depended on sample conductivity. No sample preparation (i.e., coating with conductive layer of Au) was performed on the samples. The SEM micrographs showed the products of the TGA reduction to consist of large (>100 micron) porous chunks. These pieces were found to consist of clusters of smaller particles of about 200 nm. The transmission electron microscopy (TEM) was performed

on a Philips CM300FEG operating at 300 kev using zero-loss energy filtering with a Gatan energy Imaging Filter (GIF) to remove inelastic scattering. The images where taken under BF (bright field) conditions and slightly defocused to increase contrast. The images were also recorded on a 2K × 2K CCD camera attached to the GIF.

Results

Consideration of the composition and phase of the initial iron (III) oxide material is extremely important. The presence of trace impurities can affect the properties of materials dramatically. To complex the situation there are thirteen known phases of iron oxides, each of which having distinct properties and chemical characteristics. We have determined that the sol-gel derived iron (III) oxide materials made by the LLNL method consist mainly of the compound Ferrihydrite, $Fe_5HO_8 \bullet 4H_2O$ (Formula Weight = 480 g/mol). This is a highly hydrated poorly crystalline iron (III) oxide phase that was determined by XRD. Elemental analyses on the sol-gel derived materials indicated significant levels of carbon (2-6 wt. %) and hydrogen (1-3 wt %) and chloride (1-5 %; note chloride only present in the samples made from $FeCl_3 \bullet 6H_2O$). The presence of chloride can be especially problematic for pyrophoric iron production. According to Crowley the presence of HCl in the reduction gas leads to a product with reduced pyrophoricity. Although not completely understood, this observation may be due to the formation of small amounts of ferrous chloride that stabilizes the powders to pyrophoric tendencies. It is important to take this into account when attempting to draw conclusions from this study.

The central hypothesis of this work was to demonstrate that sol-gel iron (III) oxide materials would be reduced by molecular hydrogen to metallic iron while maintaining the small particle size and porosity that are characteristics of the reactant sol-gel material. To demonstrate this a number synthetic experiments were performed. The objective being to optimize the synthetic and processing conditions that would result in Fe production, while at the same time minimizing the concentration of hydrogen needed as well as keeping the reduction temperature low. This objective serves two purposes: 1) safety and 2) materials performance.

By using the minimum amount of H_2 (mixed with an inert gas like Ar or N_2) to affect the reduction, any hazards associated with the use of pure hydrogen would be diminished. The use of the lowest possible reduction temperature would minimize all of the processes involved in sintering (surface, vapor, and volume diffusion). This may lead to the production of elemental Fe that retains the high surface area porous structure of the reactant iron (III) oxide sol-gel material. It is highly probably that such a material would be pyrophoric. As can be seen in Table 1 numerous synthetic experiments were run to determine optimal conditions for the reduction of iron (III) oxide aerogel to porous Fe metal. Parameters that were varied included the composition of the reduction gas, the heating rate, and temperature.

For the sake of brevity, and in accordance with our objective, the synthesis results will be summarized. Samples of iron (III) oxide aerogel can be reduced to metallic Fe in the following reducing atmospheres at given temperature ranges: 25-100% H_2 in Ar or N_2 at temperatures between 350 °C and 700 °C, 75% H_2/25% CO_2 at 700 °C, and 75% H_2/25% CO at 650°C. Table 1 also contains the final weight percent as well as the weight percent at maximum temperature during the reduction process. These values were monitored by TGA and will be discussed shortly.

From the entries in Table 1 it is apparent that hydrogen levels below ~20% are not sufficient to bring about complete reduction of the sol-gel iron (III) oxide material. Even at temperatures up to 600 °C the reaction does not go to completion at lower hydrogen concentration levels (2.5 % H_2). That temperature is significantly higher than those reported in patents from several decades ago. **[12-13]** Certainly lower reduction temperatures would be more desirable (e.g. 200-400 °C)

It appears that there is a temperature threshold for complete reduction. For example at 300 °C and 100% H_2 the reduction is incomplete. However, at 350 °C the reaction goes to completion. From the entries in Table 1 it is not clear that heating rate affects the reaction to a discernable degree.

Table 1. This is a summary of experimental conditions for experiments run to reduce iron (III) oxide aerogel with H_2.

Temp C	Atmosphere	Final Wt. %	Wt. % at max T	Heating Rate (C/min.)	Products	Comments
600	2.5%H_2/N_2	68.4		5	Fe	Reduction not complete
600	2.5%H_2/N_2	55		5		
600	2.5%H_2/N_2	68.5		5	Fe3O4	Reduction not complete
600	2.5%H_2/N_2	71.4		5	Fe3O4	Reduction not complete
600	2.5%H_2/N_2	50.6		5		
300	2.5%H_2/N_2	75.9		5	Fe + Fe3O4	Reduction not complete
400	2.5%H_2/N_2	72.3		5	Fe	Reduction not complete
500	2.5%H_2/N_2	59.5		5		
600	5.0%H_2/N_2	51.9		5		
550	5.0%H_2/N_2	52.1		5		
350	18% H_2/Ar	54.1		5	Fe	
375	25% H_2/Ar	55.2	55.2	5	Fe	
375	50% H_2/Ar	55.9	55.9	5	Fe	
375	50% H_2/Ar	56.5	55.9	5		
400	50% H_2/Ar	56.7	56.4	5		
400	75% H_2/Ar	54.8	54.4	5		
400	100% H_2	57.2	56.6	5		
500	100% H_2	53.9	55.4	5		
600	100% H_2	53.9	53.7	5		
600	100% H_2	53.7	53.6	5	Fe	
500	100% H_2	54	54.2	5		
500	25% H_2/Ar	52	50.9	5		
400	25% H_2/Ar	51.8	52	10		
400	25% H_2/Ar	55.6	52	20		
400	100%H2	56.6	52.7	1		
400	100%H2	56.9	54.8	0.5	Fe	
350	100% H_2	58.3	53.5	0.5	Fe	
350	100% H_2	55.6	55.2	1	Fe	
350	50% H_2/Ar	56	55.4	0.5		
350	25% H_2/Ar	56	55.4	0.5		
400	100% H_2	56.2	54.3	0.5		
400	50% H_2/N_2	60	52.3	2		
400	50% H_2/N_2	53.1	48.9	20		
400	50% H_2/N_2	62.1	58.6	25		
700	75% H_2/CO_2	56.9	55.6	10		
400	100% H_2	57.3	54.6	2.5		

700	100% H_2	52.6	51	2.5	Fe	
300	100% H_2	79.7	79.1	2.5		Reduction not complete

Thermogravimetric analysis (TGA) proved to be a very valuable technique for monitoring the progress of the reduction reaction. This technique permits monitoring of the extent of reaction with time and thus, determines when the reaction is completed. When iron oxide is reduced to metallic iron and water (see Figure 1), at elevated temperatures, there is a net loss in the solid mass of the system. By monitoring the mass of the sample under reducing conditions the onset and end of the chemical reactions that produce the transformation can be determined. Once the mass loss levels off one can reasonably conclude that the reaction has gone to completion under those conditions. In addition, by examining any weight gain of the sample as it cools, the fidelity of the experimental system to atmospheric impurities (e.g., O_2 or water) can be evaluated. If the system is pristine there should be no weight change. If there is a source of contamination (e.g. leak) the sample will oxidize, and likely passivate, and as such a weight gain would be observed.

Figure 4 shows a typical TGA trace for the reduction of an iron (III) oxide aerogel in a 100% hydrogen atmosphere at 700 °C. From this TGA trace it can be seen that the mass loss levels out after about four hours under these conditions. Therefore, it can be inferred that the reduction is complete at this time. Inspection of the region of the weight loss/gain curve in the cooling region (from 10-16 hours) indicates a weight gain of ~1.5 %. It is difficult to assign any significant meaning to this weight gain, as it is very slight.

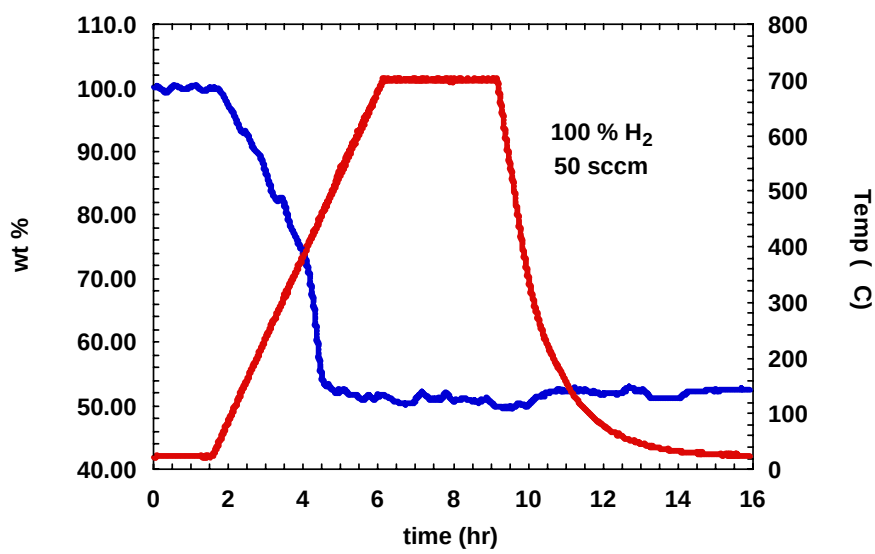


Figure 4. Here is a typical TGA trace for the reduction of iron (III) oxide aerogel.

It was observed that the sol-gel derived iron (III) oxide materials had mass losses of between 44-48% weight percent upon completion of the reduction. Again completion was inferred from a lack of weight gain after prolonged reaction time. If one considers the iron (III) oxide aerogel material to be Ferrihydrite, the reduction of this iron oxide phase to metallic iron would result in a 42% mass loss.

$$Fe_5HO_84H_2O \text{ (F.W. = 480 g/mol)} \rightarrow 5\ Fe \text{ (F.W. = 55.9 g/mol)} + H_2O$$

As previously stated, elemental analyses indicate a background level of organic contaminant (C and H) of 4-9 wt. %. Taking this into account, as well as the reduction mass loss and the dehydration the expected weight loss of the iron (III) aerogel should be range from 46 to 51 weight percent. It is therefore reasonable to infer that the mass losses seen in these experiments and tabulated in Table 1 are consistent with the reduction and dehydration of Ferrihydrite. The presence of water and hydrocarbon based impurities in the base iron (III) oxide aerogel material was also confirmed using Fourier-Transform infrared (FT-IR) spectroscopy.

Figure 5 is and overlay of the FTIR spectra of the iron (III) oxide aerogel and its vacuum dried (200˚C) product. The spectrum of the "as-is" aerogel (Fig. 5a) contains several prominent absorptions. The intense and broad absorption in the 3200-3600 cm^{-1} region likely corresponds to ν(O–H) stretching vibrations of adsorbed water (sample was synthesized, stored, and FTIR spectrum was taken under room conditions) and O–H moieties present in the solid. In addition, the absorption at ~1630 cm^{-1} is likely due to the bending mode of water $\delta(H_2O)$.[18] The presence of O–H groups in the IR of iron (III) oxides synthesized by solution methods is very common.

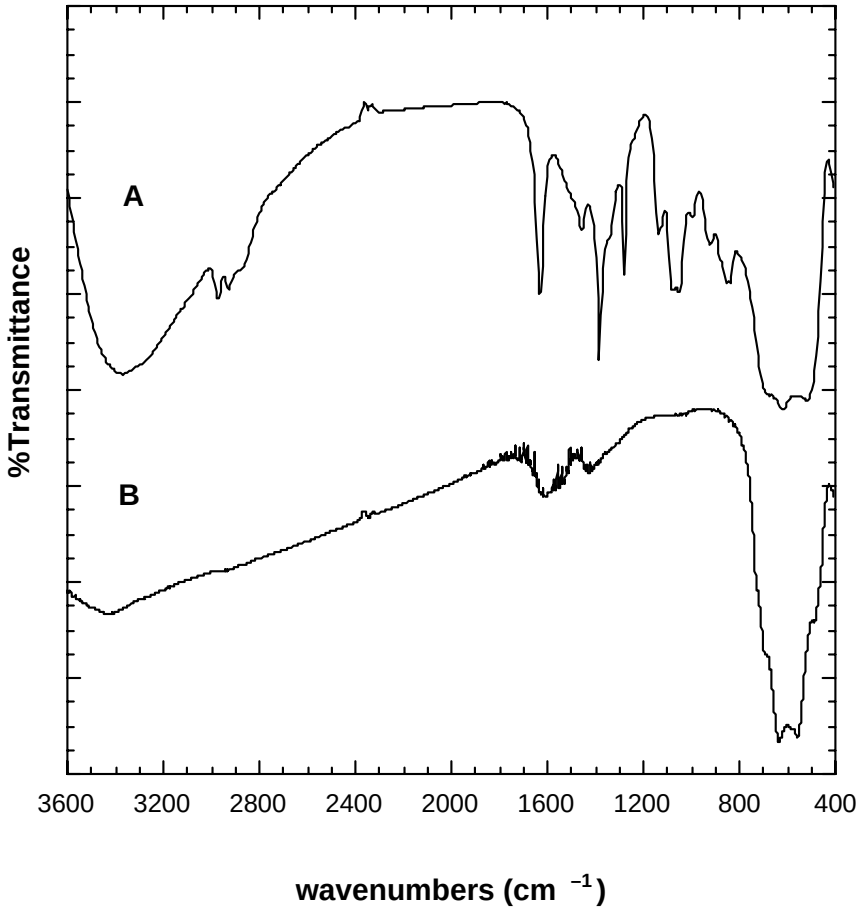


Figure 5. Infrared spectra of A) iron (III) oxide aerogel material and B) iron (III) aerogel heat-treated at 200 °C under vacuum.

The absorptions present at 2800-3000 cm^{-1} are due to ν(C–H) vibrations. These, as well as the absorptions present from 1400-800 cm^{-1} are probably due to ethanol (solvent used), residual propylene oxide, or side products of the ring opening of the propylene oxide. The propylene oxide is used in the synthesis of the aerogel materials as a gelation agent. The absorptions between 700 cm^{-1} and 500 cm^{-1} are those from the Fe–O linkages that make up the framework of the aerogel. All of the phases of iron oxides and oxyhydroxides have characteristic IR vibrations in this region. The assignment of the spectrum shown in Fig. 5a to one particular phase of iron oxide is not straightforward. Notwithstanding, with the FTIR evidence shown here we tentatively conclude that the non-heat-treated aerogel material is probably an iron oxyhydroxide phase.**[27]**

The spectrum shown in Fig. 5b is that of the aerogel material that has been heated to 200˚C under a dynamic vacuum. This heat treatment results in a mass loss of ~30% of

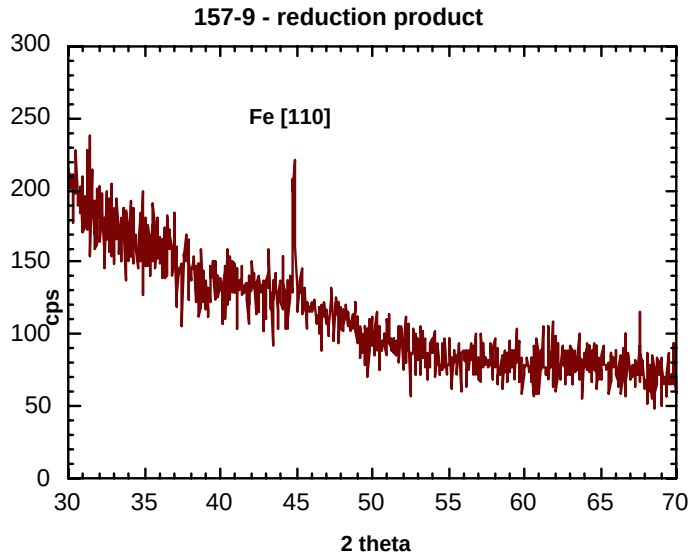
the material. There are three notable differences between this spectrum and that of the iron (III) oxide aerogel. First, the absorption in the 3200-3600 cm^{-1} region of the spectrum is much less intense in the heat-treated sample. This is possibly due to the removal of a large percentage of the O–H moieties present in the original aerogel through condensation of two neighboring OH groups to give a single oxygen bridge. Second, there is no trace of the absorptions assigned to C–H bonds present in the heat-treated sample. These organic constituents have also been removed in the heating process. And finally, the two intense absorptions at 510 and 615 cm^{-1} in the original aerogel have shifted and split into three peaks at 565, 585, and 630 cm^{-1} respectively. The location of the IR bands present in the heat-treated sample match very well to those reported for maghemite, the γ-phase of Fe_2O_3. It is worthwhile to note that maghemite is magnetic and that the heat-treated material in Fig. 3b is also magnetic.

Characterization of materials

The primary analytical tools used to evaluate the relative success of each experiment to reduce the aerogel materials to metallic iron were TGA and powder X-ray diffraction. By monitoring the mass loss or gain under reducing or oxidizing conditions and knowing the composition of the starting material one could determine if the reaction went to completion. This has already been discussed. Analyzing the reaction products by PXRD and comparing the results to known standards allowed additional confirmation.

Representative XRD patterns for reaction products are shown in Figure 6. The top XRD pattern indicates prominent lines for the compound Fe_3O_4, magnetite, a well-known magnetic form of iron oxide in which the iron atoms in the lattice have either a +2 or +3 oxidation state. This compound is often observed as an intermediate in the reduction of iron (III) oxides to elemental iron and is representative of incomplete reduction. The bottom XRD pattern in Figure 6 has diffraction peaks from metallic iron and is a fine example of what is observed when reduction is complete.

A)



B)

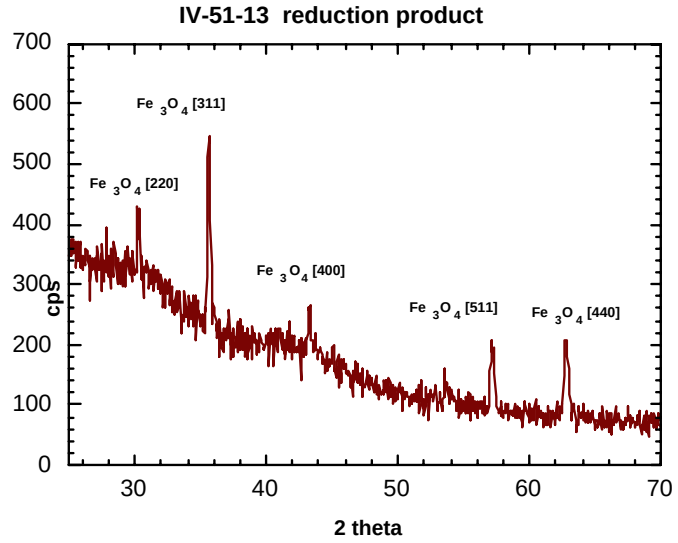


Figure 6. Powder X-ray diffraction results for two samples reduced with H_2. The pattern in A) indicates the presence of the final reduction product Fe metal. The pattern in B) indicates that an intermediate reduced phase Fe_3O_4, magnetite, has been formed.

Using TGA-monitored reduction several iron oxide based powders were examined. Powders from commercial sources, different phases of iron oxides, as well as sol-gel derived aerogels and xerogels were evaluated. According to the results a sol-gel based composition, iron (III) oxide aerogel (made with $Fe(NO_3)9H_2O$ precursor) reduced to metallic iron the most rapidly under constant conditions (50%H_2/50 Ar @ 450 °C). This is possibly related to the extremely high surface area of the aerogel material.

Simultaneous differential thermal analysis (combination of TGA and DTA) was shown to be an effective method to monitor the oxidation of native iron powders produced via this approach. It appears that iron produced from the reduction of aerogel iron (III) oxide material oxidizes at ~340 °C. This temperature is at least 75 °C less than is seen for the oxidation of iron particles made from commercial Fe_2O_3 (Aldrich) ($T_{oxidation}$~ 415 °C). This is potentially is very interesting result. It is known that ultra-fine grained Al powders prepared by vapor phase condensation oxidize at much lower temperatures than micron sized powders. The UFG grained Al has shown exceptional enhancement in energy release rates in mixtures with oxidizers and is currently being examined for a myriad of applications in energetic compositions.

Microscopy of Fe metallic Products

To more fully characterize the final Fe metallic powders both scanning and transmission electron microscopies (SEM and TEM) were utilized. These methods will allow good characterization of the particle size, morphology, and distribution of the metallic Fe products from reduction of sol-gel iron (III) oxide materials. Figure 7 contains a TEM image of the Fe metal powder product from the reduction of an iron (III) oxide aerogel material. This TEM image is a typical image obtained from this analysis and provides a fine representation of the overall sample analyzed. The sample appears to consist of nominally spherical particles with a diameter or approximately 200-500 nm. These diameters are submicron but are significantly larger than the primary particle size of the aerogel starting material (~5-20 nm). This is indicates that significant sintering has taken place upon transformation. The particles are so thick that suitable surface imaging with the TEM is difficult. For a good look at the surface of these types of materials we utilized SEM.

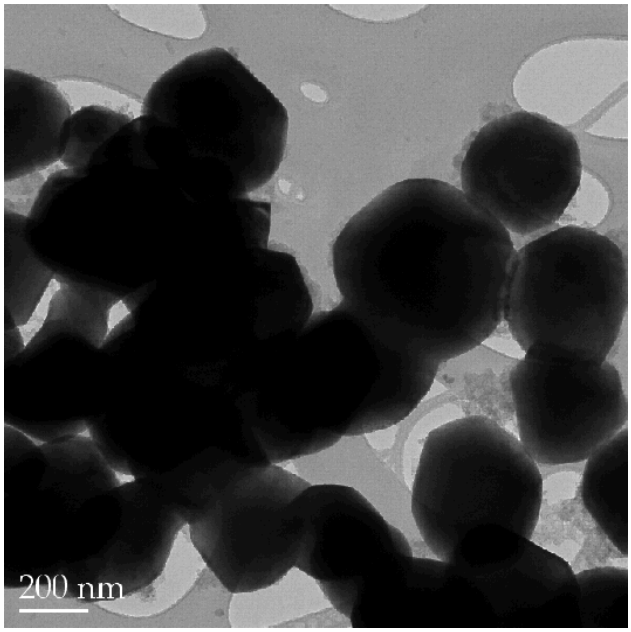
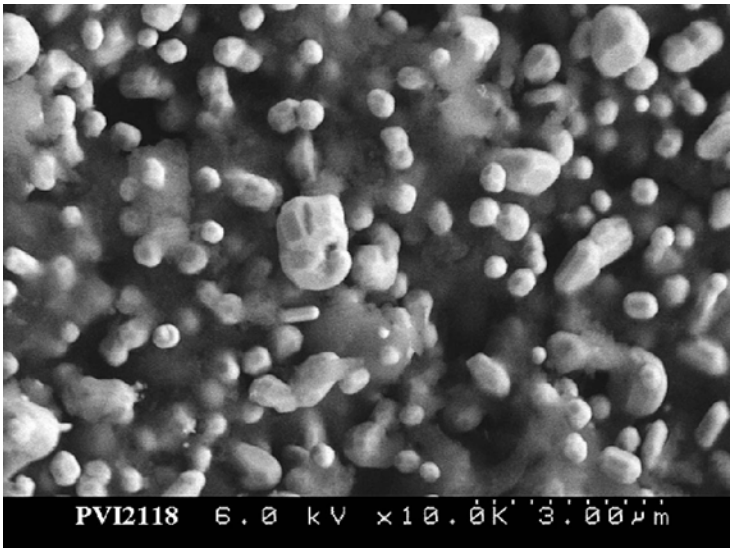


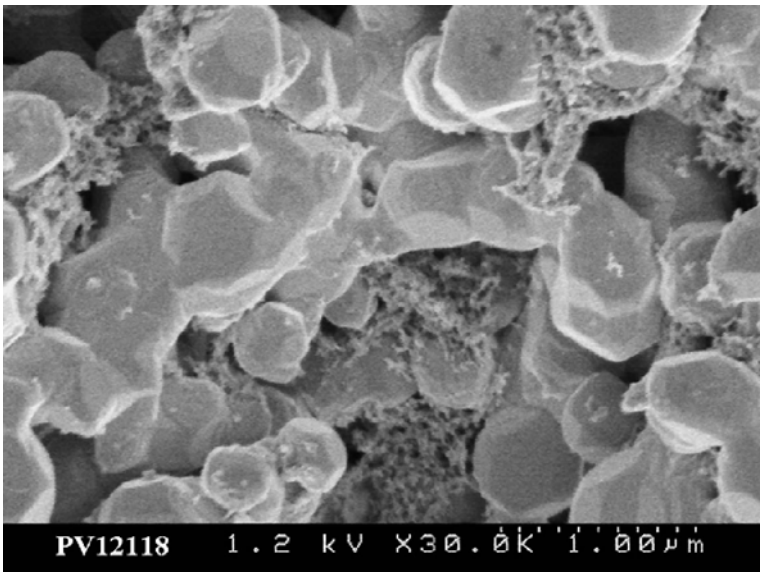
Figure 7. TEM image of native Fe metal particles produced by the reduction of iron (III) oxide aerogel material.

SEM has proven to be a more useful method of surface characterization of these materials. Figure 8 shows several SEM images of Fe metallic materials. From these images one can get an estimation of the nature of the surfaces.

A)



B)



C)

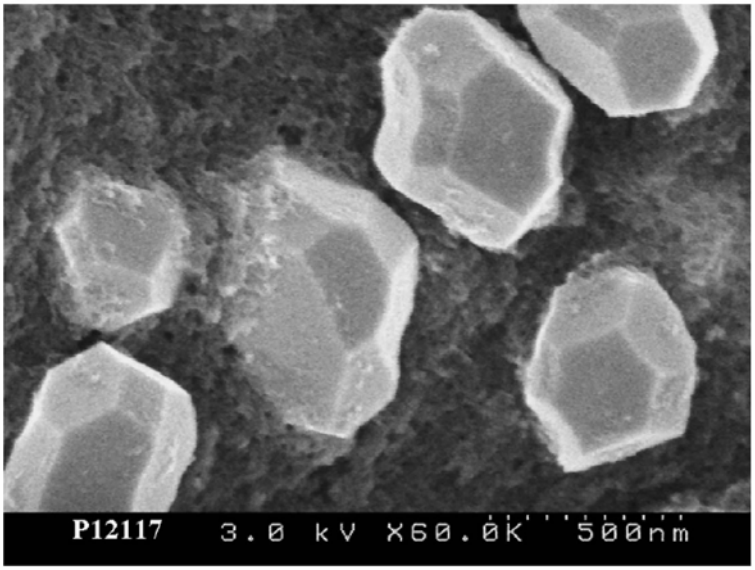


Figure 8. SEM images of Fe particles from the reduction of iron (III) oxide aerogel with hydrogen.

It appears that the reduced metallic iron powder is made up of submicron-sized particles. From Figure 8B it seems that the metallic iron has retained some of the porosity of its precursor material.

Phenomenological observations of burn behavior

The objective of this work was to produce pyrophoric Fe for decoy flares in a safe and non-toxic manner using sol-gel methods and materials. Therefore, the phenomenological behavior of the metallic powders on exposure to the atmosphere is of critical importance. After reduction in the TGA, samples were cooled and kept in an inert environment (Ar or N_2). Once cool, the sample was removed from the TGA apparatus and rapidly exposed to room atmosphere. Careful attention was paid to the sample at this time to observe for pyrophoric behavior. To date, none of the reduced iron (III) oxide sol-gel materials showed pyrophoric behavior upon exposure to room atmosphere.

However, the fine metallic powders, produced via the described synthesis and processing conditions, could be burned with the application of a thermal source (flame, and soldering iron were used). Once ignited, the powders burned smoothly with a blue flame and left behind a red residue, a telltale sign of hematite Fe_2O_3. Initially there was some concern that the sample size of the powders may not be sufficient to facilitate self-heating to combustion. That is, the surface area to volume ratio of a small amount (~ 100-200 mg) of metallic powder may be high enough that localized heating did not occur to an appreciable extent. As any heat generated by oxidation of the submicron Fe particles was rapidly dissipated to the surroundings. To try and mitigate this potential scale effect larger samples of sol-gel iron (III) oxide aerogel were reduced in a tube furnace (up to 2500 mg at a time). Unfortunately these samples were not pyrophoric either. The fact that the materials burned indicates that complete oxidation did not take place in the TGA apparatus while the material was cooling. Control experiments were performed to determine if the apparatus was compromised and resulted in slow oxidation

As a set of control experiments, the same TGA and tube furnace set up were used to reduce some commercial sources of iron oxide. Hematite (Fe_2O_3-50 microns) from Aldrich, and NANOCAT™ (a commercial source of 3 nm diameter iron oxide particles from MACH I, Inc., King of Prussia, PA) were reduced under the same conditions as the iron oxide aerogel materials. These experiments were effective in reducing the oxide to the base Fe metal. The products from these experiments had similar burn behavior to the sol-gel derived iron powders. They were not pyrophoric but did burn promptly when thermally ignited.

Conclusions and Recommendations

The reduction of iron oxide ores to iron, being a major step in the commercial production of steel, is the subject of an extremely large number of patents. Many of these patents refer to processing conditions that leave the final Fe metal in a variety of forms (e.g., consolidated brick, powders, pellets). These conditions are particularly important to determine, as they dictate the final form of the product metal. However, to our

knowledge there are no reports of the conditions needed to effect the reduction of sol-gel-derived iron oxides to metallic iron. Sol-gel materials are unique in that they typically posses high surface areas, high porosities and small primary particle size. The properties unique to sol-gel materials lead to their enhanced reactivity. In our estimation, the iron powder products from the reduction of sol-gel iron oxides may be highly reactive and will be very useful in applications involving energetic materials.

One important result of this study was the identification of optimum reduction conditions for the production of sub-micron Fe powders from sol-gel derived-iron (III) oxide precursors. Previous publications indicate that finely divided iron powders can be pyrophoric.**[12-13]** Taking the characterization done here into account, there is little doubt that the particle sizes of the powders made by this approach are as, or more finely divided than pyrophoric powders. The starting materials in those reports were micron-sized iron oxides. It is very likely that significant agglomeration and consolidation occurred upon reduction. While in our case, the reactant oxide particles are much smaller and more highly porous. In our estimation, the non-pyrophoric behavior of these materials cannot be justified by having too large a particle size.

One rationale for the non-pyrophoric behavior of these materials could be iron particles with a stable passivation surface. Iron metal readily reacts with oxygen or water to passivate its surface and generate heat. With high surface area powders, the heat generated can be significant enough to ignite the entire iron particle. These are the processes that lead to the pyrophoric nature of finely divided iron. However with a suitable oxide coating the iron particles can be very stable. It is possible that the powders reduced in our experimental procedure get slightly passivated soon after reduction. The oxidation can come from the interaction of the newly formed Fe surface with water or O_2 impurities in the reduction gases or with the water produced as a byproduct of the reduction. Additionally, the sol-gel material is the compound Ferrihydrite ($Fe_5HO_8 \bullet 4H_2O$), which contains highly levels of water in it.

Percival and co-workers report in a patent issued in 1959 on the importance of low water content in the system used to reduce finely divided Fe_2O_3 to pyrophoric iron.**[13]** It is possible that the system studied here, may suffer from too much water present, which leads to gentle passivation and non-pyrophoric materials.

The results presented here suggest that the reduction of porous, high surface area iron (III) oxide sol-gel materials gives submicron metallic iron powders. The production of iron powders via this approach is beneficial from a safety and environmental standpoint as it eliminates the need for caustic leaching solutions used in the current production of pyrophoric decoy flares. Although the powders produced here are not pyrophoric they are indeed energetic and burn promptly and in a self-sustained manner when ignited with a thermal source. It is our belief that the powders produced here can be made pyrophoric through the one or more additional processing steps.

First, it is our recommendation that sol-gel derived starting materials be heated to and held at elevated temperatures for some time before starting reduction. Temperatures used will be high enough to drive off organic impurities as well as any bound or unbound

water without causing the sintering of the porous iron (III) oxide network. Heat treatment to temperatures below 300 °C lead to contaminant removal and phase changes in the iron (III) oxide sol-gel material without a significant reduction in porosity or increase in primary particle size (See Figure 9).

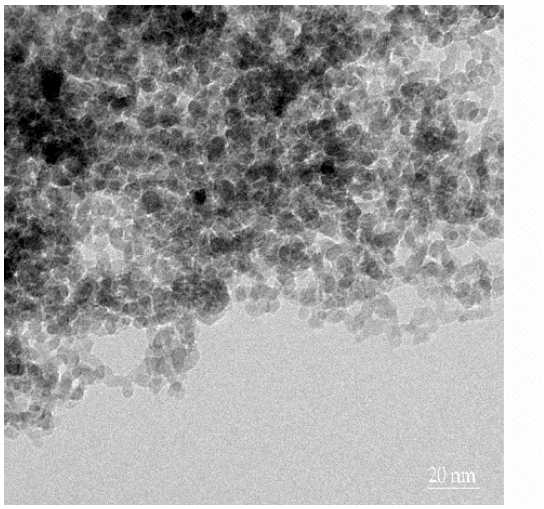


Figure 9. TEM image of iron (III) oxide aerogel that has been heated to 300 °C under vacuum. Note that the small particle size and the nanostructure of the material have been retained. The material has undergone a phase transition to Maghemite, γ-Fe_2O_3

Second, it will be useful to use two separate reduction steps. That is initial reduction followed by cooling and then a second reduction step. This type of methodology is used in current production of pyrophoric foils and may serve to reduce any last small amounts of surface oxide on the metallic powders.**[5-10]**

Third, all sol-gel materials used should be derived from chloride-free precursors. This is to minimize the chance for residual chloride ions in the solid forming iron chloride species that are believed to inhibit the pyrophoric nature of the solid.**[12]** In the future residual chloride in the starting material may be used to tune the degree of pyrophoricity however for this initial work it should be avoided.

Fourth, it appears as though impurities may play a larger than expected role in the behavior of these materials and therefore all future attempts to make this material must emphasize rigorous elemental analyses on all reactants and products.

Finally, to increase the pyrophoricity of these materials it should be possible to incorporate small amounts of more reactive metals into the final product powders as an igniter, using sol-gel techniques. Two specific materials, tungsten and or tin oxide, are of particular interest. Both tungsten and tin oxide precursors can be incorporated into the iron oxide sol and gelation will create a mixed oxide.**[25-26]** Upon reduction, after drying, the tin or tungsten oxide particles will be reduced to their native metal along with

the iron powder. When exposed to air the reactive tungsten or tin metal will ignite which will help ignite the less reactive Fe powders. This approach does not make the process any less acceptable from an environmental and safety standpoint. It has been already been demonstrated that pyrophoric tin oxide materials can be made with sol-gel techniques.**[22]**

Acknowledgements

The Strategic Environmental Research and Development Program funded this work; project number PP-1276. University of California Lawrence Livermore National Laboratory performed this work under the auspices of the U.S. Department of Energy under contract No. W-7405-Eng8.

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