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Fabrication of Iron Oxide Thin Films from Sol-Gel Process and Thermite Reaction of Iron Oxide Induced from a Single Laser Shot

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FABRICATION OF IRON OXIDE THIN FILMS FROM SOL-GEL
PROCESS AND THERMITE REACTION OF IRON OXIDE INDUCED
FROM A SINGLE LASER SHOT

By

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To Seyeon, Justin and My parents
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Chi Dong Park

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<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>TOF-MS</td>
<td>time-of-flight mass spectrometry</td>
</tr>
<tr>
<td>XRD</td>
<td>Powder X-ray Diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>MIC</td>
<td>metastable interstitial composite</td>
</tr>
<tr>
<td>YAG</td>
<td>yttrium aluminum garnet (common garnet crystal used in lasers)</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>SQUID</td>
<td>superconducting quantum interference device</td>
</tr>
<tr>
<td>RCP</td>
<td>random close pack</td>
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</table>
ABSTRACT

This dissertation is comprised with two main research projects: fabrication of thin films through an epoxide-catalyzed sol-gel process, and the dynamics of the photothermal initiation of Al/Fe$_2$O$_3$ metastable interstitial composite (MIC) materials.

The first is a discussion on the fabrication of thin films that was achieved with an epoxide-catalyzed sol-gel process and thermal processing. The Fe$^{3+}$ oxide/hydroxide thin films on a quartz substrate, formed through the sol-gel process, were extremely uniform and homogenous with a film thickness of ~0.1µm. The Fe$^{3+}$ gel thin films that were formed could be converted to α-Fe$_2$O$_3$ film, Fe or γ-Fe$_2$O$_3$ films by calcination, which were characterized with UV-visible, XRD, AFM, and SEM. Also, Fe$^{3+}$ gel thin film on a Si wafer was transformed into a multilayer structure, containing Fe$_2$O$_3$ and a Fe layer, at lower temperatures then are required to initiate the combustion of bulk thermite. The reduced iron particles interfacially produced on silicon were confirmed by XPS and SEM. Finally, the photothermal initiation of Al (50 nm, 100 nm, and 3–4.5 µm) /Fe$_2$O$_3$ MIC materials with single 8 ns pulse of the 1064 nm of a Nd:YAG laser was studied with time-resolved spectroscopy in order to understand the dynamics occurring at early stages of the combustion. As well, the effects of stoichiometry (the Al/Fe ratio) and compressed sample density on combustion dynamics were explained with the initiation time and the deflagration duration as the size of Al particle was changed from 50 nm to 120 nm. The initiation energy required to combust Al/Fe$_2$O$_3$ MIC was obtained by changing the power of the laser.
INTRODUCTION

The research discussed in this dissertation is combined with three distinct projects. The first is the fabrication of iron and iron oxide thin films from an epoxide-catalyzed sol-gel method and characterization of thin films with various instruments. The second is the conversion of iron oxide films on a silicon wafer to an iron film from by way of a thermite reaction between the silicon and iron oxide. Finally, the thermite reactions between iron oxide (Fe$_2$O$_3$) and aluminum (Al), induced by a single laser shot have been investigated with a time resolved spectroscopy method.

The Fabrication of Iron Oxide Thin Films with Sol-gel Processing Involving Epoxide

A synthesis method for metal oxide materials using sol–gel chemistry is of considerable interest due to its convenience for processing at low temperature, low cost, and no requirement for special instruments, as well as their properties having high surface area and high porosity. These features make metal oxides prepared with sol-gel useful in various applications, such as insulators, ceramic precursors, and catalyst supports. Furthermore, the flexibility of sol-gel chemistry provides a means of controlling the shape, morphology, and textual properties of the final material.

Generally, sol–gel chemistry has employed the use of metal alkoxide precursors that readily undergo catalyzed hydrolysis and condensation to form a sol of metal oxide particles with nanoscale dimensions (1–100 nm). However there are some disadvantages. Some metal alkoxides are expensive, sensitive to moisture, heat, and light, all of which make the long-term storage of sol-gel materials difficult. In addition, some metal alkoxides are not commercially available or are difficult to obtain. These problems result in the exploitation of the other method for preparing sol-gel: the epoxide system.

This alternative sol-gel process makes use of epoxide as a catalyzing agent for condensation, rather than a metal alkoxide, and traditional approaches the transition metal salt form the aqueous precipitation with a base. Figure 1 shows the structures of epoxides that can
be used in this sol-gel system. Formation of sol-gel in this system is involved with irreversible ring opening of the epoxide by protonation.

**Figure 1.** Structures of a 1,2-epoxide (PO) and 1,3-epoxides (TMO and DMO)

The overall reaction can be suggested with several steps: the formation of acidic aqueous metal complex, the protonation of epoxide, and the condensation. In the formation of the acidic aqueous metal complex, water molecules on the aqueous metal complex $[\text{M(H}_2\text{O)}_y]^{x+}$ are relatively acidic due to charge transfer from water molecules to the center metal ion. In protonation of epoxide step, the acidic aqueous metal complex can donate protons to the added epoxide, which act as an irreversible proton scavenger caused by the ring opening of the epoxide upon reaction with the acidic metal oxide precursor, $[\text{M(H}_2\text{O)}_y]^{x+} \text{A}^{-}$ and the anion of the metal salt as shown in Scheme 1. Finally, aquo-hydroxy $([\text{M(OH(H}_2\text{O)}_{y-1}]^{(x-1)+})$ or oxo-hydroxy metal complex formed from the second step initiate the condensation reaction of olation and oxolation to form the metal oxide network $[(\text{H}_2\text{O)}_{y-1}]\text{M-O-M-(H}_2\text{O)}_{y-1}]$.

**Scheme 1.** Irreversible ring opening of propylene oxide
There is a change of pH after adding the epoxide, where the pH of solution is increased slowly and linearly due to the irreversible ring opening of epoxide to consume the protons from aqueous metal complex. As a result, the gel formation is favored. Furthermore, the anion used in the ring opening of the epoxide plays an important role in making the sol-gel due to the salt containing good nucleophilic anions such as Cl\(^-\), Br\(^-\), and CH\(_3\)CO\(_2\)\(^-\) which stabilized the ring opening of the epoxide, contrary to poor nucleophilic ions such as SO\(_4^{2-}\) and NO\(_3^-\). From this method, various transition metal and main group oxide gels were successfully synthesized by the Gash group and are summarized in Table 1.

**Table 1. Precursor and final compound of transition and metal group gel**

<table>
<thead>
<tr>
<th>Precursor Salt</th>
<th>Metal oxide</th>
</tr>
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<tbody>
<tr>
<td>Cr(NO(_3))(_3).9H(_2)O</td>
<td>Cr(_2)O(_3)</td>
</tr>
<tr>
<td>Fe(NO(_3))(_3).9H(_2)O</td>
<td>Fe(_2)O(_3)</td>
</tr>
<tr>
<td>Al(NO(_3))(_3).9H(_2)O</td>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td>In(NO(_3))(_3).5H(_2)O</td>
<td>In(_2)O(_3)</td>
</tr>
<tr>
<td>Ga(NO(_3))(_3).xH(_2)O</td>
<td>Ga(_2)O(_3)</td>
</tr>
<tr>
<td>SnCl(_4).5H(_2)O</td>
<td>SnO(_2)</td>
</tr>
<tr>
<td>HfCl(_4)</td>
<td>HfO(_2)</td>
</tr>
<tr>
<td>ZrCl(_4)</td>
<td>ZrO(_2)</td>
</tr>
<tr>
<td>NbCl(_5)</td>
<td>Nb(_2)O(_3)</td>
</tr>
<tr>
<td>TaCl(_5)</td>
<td>Ta(_2)O(_5)</td>
</tr>
<tr>
<td>WCl(_6)</td>
<td>WO(_3)</td>
</tr>
</tbody>
</table>

As shown above, this reaction is quite general and is successful in producing high-quality gels from a wide range of transition and main group metal ions, which provides considerable synthetic flexibility as to the composition and the final crystalline phase\(^1\).
To date, there have been no reports of the gels' applicability for thin film formation. This study shows that in the case of gels made from aquatic Fe\(^{3+}\) ions by this process, high-quality thin films on a fused quartz substrate can be readily produced. These films can, in turn, be thermally processed in a reductive or oxidative environment to produce metallic or oxidized films, which, in many cases, retain the film quality of the initial gel coating.

The structure of iron/iron oxide thin films made through thermal processing was determined by powder X-ray diffraction (XRD) and their surface morphology was characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The magnetic properties were measured with superconducting quantum interference device (SQUID).

**Metallic Iron Nanoparticles on a Silicon Substrate through Thermite Reactions**

Iron oxide/hydroxide films made from sol-gel chemistry with an epoxide can be converted by an appropriate choice of thermal processing pathway into good quality hematite (\(\alpha\)-Fe\(_2\)O\(_3\)) and maghemite (\(\gamma\)-Fe\(_2\)O\(_3\)) thin films. From this approach, there is an interesting aspect of sol-gel derived metal oxide materials made through epoxide catalysis that have been found to undergo thermite-type reactions upon the incorporation of a fuel during gelation. Thermal ignition of the metal/oxide gel composites initiates a self-propagating exothermic redox reaction to produce oxides and reduced metal products (eg. Fe).

Generally, the thermite reaction is characterized by large amount of heat release, involving reduction of less stable metal oxide or nonmetal oxide with metal to form a more stable metal oxide and related metal or nonmetal of the reactant oxide. The unique properties of the thermite reaction allow the various applications from energetic materials to ordnance. The typical thermite reaction is shown in equation 1\(^2\), in which Fe\(_2\)O\(_3\) is considered the oxidant and Al was as the fuel.

\[
\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe} \quad \Delta H = 3.97 \text{ kJ/g} \quad \text{(equation 1)}
\]
From this principle, nanoscale metallic Fe particles can be generated in the interface between the iron oxide/hydroxide film, where the iron oxide works as an oxidant and the silicon substrate as the fuel when iron gel thin films are calcined at low temperature.

The nanoscale Fe particles generated on the silicon substrate were confirmed with X-ray photoelectron spectroscopy (XPS). In the XPS study, the depth profile shows clearly that a metallic Fe layer has formed below the surface, close to the interface between the Fe$^{3+}$-gel film and the silicon surface. It is known that Ar$^+$ ion bombardment etching of metal oxides can lead to reduced-metallic species over the course of the etching. To confirm that the observed Fe is not the result of the etching process, the iron oxide films on a silica substrate were made by the same method, and then etched by an Ar$^+$ ion source under identical conditions of energy and time as the heated film on silicon. The Fe peak was not found in the depth profile for iron oxide on the quartz substrate, which verified that the Ar$^+$ etching process did not participate in the reduction of iron oxide on silicon. The morphology for thin films was also determined with AFM and SEM.

**Photo-thermal Initiation Processes of Metastable Interstitial Composite (MIC) Material: Al/Fe$_2$O$_3$**

Energetic materials based on metastable interstitial composites (MIC) have been the subjects of considerable research activity due to their reaction properties that produce highly exothermic inorganic redox-reactions, such as the so-called thermite reaction. The typical thermite reaction is shown in equation 1. This equation shows that the energy density for Fe$_2$O$_3$/Al MIC materials can be several times higher than conventional energetic organic compounds. For this reason, research is focused on the development of MIC materials. Despite the high energy density of MIC materials, the rate of energy release is significantly lower than conventional energetic materials, making them impractical for many applications. This is due to this system consisting of two phases, an oxidant and a fuel.

There can be two approaches that have been devised in overcoming the slow rate of energy release: the development of metastable interstitial composites (MIC) and the addition of conventional high-energy material, such as 2,4,6-trinitrotoluene (TNT); cyclo-1,3,5-
trimethylene-2,4,6-trinitramine (RDX) and pentaerythritol tetranitrate (PETN) into the inorganic system to form organic/inorganic hybrid composites\textsuperscript{3-5}. Between these two solutions for this problem, MIC materials can be easily achieved by employing the one or both of the components in the nanoscale dimension. The reduction of size of the fuel or oxidant to nanoscale dimensions allows a considerable increase in the contact area between the fuel and oxidant, thereby increasing the amount of material that can react at any instant of time\textsuperscript{6-8}. Also, the reduction in size is capable of contributing to a better intermixing and reduce the diffusion distance between the fuel and oxidant, allowing decreased initiation time and an increased reaction rate. Granier and Pantoya\textsuperscript{9,10} reported the size effect for fuel and oxidant in their detailed study of Al/Fe\textsubscript{2}O\textsubscript{3} and Al/MoO\textsubscript{3} MIC materials using laser-induced initiation coupled to high-speed imaging.

Mileham et. al. recently reported a study of the reaction of Al/Fe\textsubscript{2}O\textsubscript{3} metastable intermolecular composites (MIC) using laser induced desorption ionization time-of-flight mass spectrometry (LDI TOF-MS) which allowed the investigation of molecular species and reaction processes that occur during the very early stages of the photothermal initiation process. They showed that ion clusters resulting from reactions between the fuel and oxidant were observed in the plume. From this observation, single-pulse laser initiation of Al/Fe\textsubscript{2}O\textsubscript{3} was recorded with the time-resolved spectroscopic techniques to monitor the reaction dynamics, related to the initiation process. The study of plumes generated by a single laser shot from a ND/YAG laser (1064 nm) in the early stage show that the plumes from an Al nanoparticle mixture have a longer lifetime than a micron size Al mixture or a bulk Al stick due to the higher density of reactive species generated by the pulse. This is consistent with the observation from the TOF-MS, which show significantly more product formation in the plume of the MIC materials.

The time–resolved spectroscopic techniques also allows the determination of the kinetic parameters such as initiation time and deflagration time during the photothermal initiation of 50 nm, 100 nm and 120 nm Al/Fe\textsubscript{2}O\textsubscript{3} MIC materials. It was shown that the kinetics for Al/Fe\textsubscript{2}O\textsubscript{3} was also related to the effective amount of pure Al in Al particles, which consist of Al\textsubscript{2}O\textsubscript{3} (outer layer) and Al (inner). Comparing the initiation time and deflagration time of 50 nm Al/Fe\textsubscript{2}O\textsubscript{3} with 100 nm Al/Fe\textsubscript{2}O\textsubscript{3}, the 50nm sample has a slower initiation and a
longer deflagration than the 100 nm Al/Fe$_2$O$_3$ samples even though the 50 nm Al has a shorter diffusion distance to Fe$_2$O$_3$. This observation can be explained by the relationship between the effective Al amount in and Al$_2$O$_3$ amount in the Al.

Moreover, changing the ratio of Al/Fe$_2$O$_3$ significantly affects the time to initiation and deflagration time, as well as the minimum energy for initiation. The initiation and deflagration time were reduced in the Al/Fe$_2$O$_3$ sample with a 1.5:1 ratio Al/Fe$_2$O$_3$ sample due to the increase of effective Al amounts and the limitation of the oxidant upon reaction with the fuel. However, in a 2:1 ratio sample, the initiation time and deflagration time were slightly increased, compared with the 1.5:1 ratio sample. This increase in the fuel richest sample might be due to the increase in the of Al$_2$O$_3$ amount available to work as a heat sink in the thermite reaction. The minimum energy for initiation is decreased from low fuel ratio to high fuel ratio, due to the increase of the reactive species in early stages of the reaction.

In addition, the density of the sample also plays an important role in determining the threshold energy for initiation of the thermite reaction. The high-density sample has more energy to ignite than the low-density sample, which suggests that the Al nanoparticles in the sample prepared at a high compressed pressure might lose the particle properties, even more when converted to bulk.
GENERAL EXPERIMENTAL

Powder X-ray Diffraction (XRD)

X-ray diffraction is a non-destructive technique that is commonly used in determining the structure of a solid substance packed in a crystalline array. When a monochromatic X-ray beam with wavelength, \( \lambda \), is projected onto a crystalline material at an angle, \( \theta \), the interaction of the incident ray with the crystalline sample produce a constructive or deconstructive interference pattern, explained by Bragg’s law (\( n\lambda = 2dsin\theta \)). Bragg’s law is related to the wavelength of the electromagnetic radiation to the diffraction angle and the lattice spacing in the crystalline sample. Diffraction occurs only when constructive interference occurs which means that the repeat distance of the lattice spacing in the crystalline sample is about the same as the wavelength. These diffracted x-ray are then detected, processed and counted. All possible diffraction directions of the lattice should be obtained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral due to each mineral having a unique set of d-spacings.

XRD would be applied for identifying the crystalline phase and orientation as well as determining structural properties: lattice parameters, strain, grain size, epitaxy, phase composition, preferred orientation, order-disorder transformation and thermal expansion. Indeed, this method is also used in measuring the thickness of thin films and multi-layers. However, XRD cannot be used in ~2% of sample of mixed materials where diffraction peaks from a high angle may be overlaid and worse.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. Electron microscopes differ from optical microscope even though optical microscopes and electron microscopes basically have a similar theory and resolution limitation caused by using an illumination beam. In optical microscopes, the optical lens and visible light with wavelengths
from 400 to 700 nm are employed and the resolution is limited by the diffraction of light to about 1000 diameters magnification. So far, electron microscopes use electron lenses and electrons accelerated to 10,000 KeV with a wavelength of 0.012 nm where the resolution of the electron microscope is limited to magnifications of approximately 1,000,000 diameters, due to spherical and chromatic aberrations.

In SEM, an electron beam is generated from an electron gun fitted with a tungsten filament cathode in a vacuum. The electron beam is collimated by electromagnetic condenser lenses, focused by an objective lens, and scanned across the surface of the sample by electromagnetic deflection coils. The major imaging method in SEM is to collect secondary electrons that are ejected from the k-orbital of the specimen atoms on the sample surface. The secondary electrons are detected by a scintillator-photomultiplier system, in which flashes of light from electrons are generated from a scintillator and then amplified with a photomultiplier tube. The amplified signal is then displayed as a two-dimensional intensity distribution. By correlating the sample scan position with the resulting signal, the image displayed is similar to what would be seen through an optical microscope.

In preparing a sample for SEM, the sample must be electrically conductive, at least at the surface, and electrically grounded to preventing the accumulation of a static-electro charge at the surface, causing scanning faults and other image artifacts. Therefore, a nonconductive sample is usually coated with an ultrathin deposition of electrically conducting materials such as gold, gold/palladium alloy, platinum and so on.

**Atomic Force Microscopy (AFM)**

The atomic force microscope is a very high-resolution type of scanning probe microscope and one of the foremost tools for imaging, measuring and manipulating matter at the nanoscale dimension. The information is collected by interacting the surface with a micro-scale cantilever, shown in Figure 3 (a), which is typically made with silicon or silicon nitride with a tip on the order of nanometers.

When the tip is brought into proximity with a sample surface, a deflection of the cantilever according to Hooke's law occurs by mechanical contact force, Van der Waals
forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces, etc, which are normally measured by using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. The working process in AFM is summarized in Figure 2b.

![AFM cantilever image](image1.png)

![Diagram of Atomic Force Microscope](image2.png)

**Figure 2.** (a) AFM cantilever image, (b) Diagram of Atomic Force Microscope

The two primary image modes in AFM are static mode and dynamic mode. Static mode AFM is often called as contact mode and keeps the force between the tip and the surface constantly during scanning by maintaining a constant deflection. Dynamic mode is where the cantilever is externally oscillated at or close to its fundamental resonance or harmonic, where the phase and resonance frequency are modified by a tip-sample interaction force. The dynamic mode is also typically called tapping mode, in which the cantilever is oscillated by the piezoelectric element mounted in the AFM tip holder.

Compared with SEM, AFM does not require any special treatments and thereby there is no change or damage to the sample, where even liquid sample and even living sample may be used, and provides a three dimensional image of the surface profile. However, there are disadvantages in scanning for height and area because AFM can only image a maximum height on the order of micrometers and a maximum scanning area of around of 22500 µm², while SEM can image an area on the order of 1 mm² with a depth of field on the order of millimeter¹¹.
X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoemission Spectroscopy (XPS) typically is used in analyzing the surface chemistry of a material, and also known as Electron Spectroscopy for Chemical Analysis (ESCA). It is useful for XPS to detect all elements starting with Li, which results in the determination of the elemental composition, empirical formula, chemical state and electronic state of the elements within 1-10 nm of surface. Therefore, XPS is widely applied in analyzing inorganic compounds, metal alloys, semiconductors, polymers, elements, catalysts, glasses, ceramics, paints, and many others under an ultra high vacuum condition.

**Scheme 2.** XPS process, showing photoionization of an atom by the ejection of a 1s electron

The basic working principle of XPS is based on the photoelectric effect, which is electron emission from matter after the absorption of energy from electromagnetic radiation such as x-rays or visible light. The XPS process, photoionization of an atom, is shown in Scheme 2.

In XPS, an electron on a core level is ejected by an X-ray photon of energy \((h \nu)\), resulting in the measurement of the kinetic energy \((E_K)\) of the emitted electron by the spectrometer. However, the kinetic energy is not directly used in analyzing the surface because the kinetic energy is dependent on the photon energy of the x-ray employed. The work function must be used for acquiring the binding energy of the electron \((E_B)\) that
identifies the electron both in terms of its parent element and atomic energy level. The relationship involved in the XPS experiment is shown in equation 2, where $W$ is the spectrometer work function.

$$E_B = h\nu - E_K - W$$  \hspace{1cm} \text{(equation 2)}

The binding energy of the electron is calculated because all parameters on the right side of equation 2 are known and measurable. Practically, the binding energy is measured with the control electronics or data system associated with the spectrometer and presented as a graph of intensity (usually expressed as counts or counts/s) vs electron energy. Due to the binding energy for an element being analyzed by its intrinsic property and affected by the bonding environment with its neighbors, it is also easy to determine the chemical state of an atom or material of interested by comparing of the binding energy.

The depth profiling in XPS is achieved with two methods: non-destructive and destructive. The non-destructive method is often achieved by changing the angle of the sample, and take-off angle, resulting in the measurement of the relevant abundance of each element in the near surface (usually 1-10 nm). In destructive method, a sputtering process with an ion or atom beam is required to expose atoms in the underlying atomic layer, where a high-quality vacuum is essential for a good depth profile. There may be a problem in using the ion beam for the sputtering process, where the ion beam used can reduce the oxidation state of elements on surface\textsuperscript{12}.

**Nd:YAG laser**

The Nd:YAG laser is a type of solid-state laser that is equipped with a neodymium doped yttrium-aluminum-garnet (Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}) crystal as the lasing medium. The yttrium ion in the crystal is replaced with a small amount (~1%) of Nd\textsuperscript{3+} ions that can be excited from the ground state to the excited state by a flashlamp or laser diode. The excited neodymium ions are relaxed to the ground state by pumping process, where light is emitted dominantly at 1064
nm, with a slow decay time (~1 ms). These pumping and relaxation of neodymium ions result in the laser action.

 Particularly, the emission in the Nd:YAG laser can be simplified by a four-level pumping model, shown in Figure 3. First, the flashlamp excites the neodymium ions on the $E_0$ level (the ground state) to the $E_3$ level (the excited state) that represents the combination of all the levels above the upper laser level ($E_2$) in the real atomic system. Second, by nonradiative relaxation, the ions in the $E_3$ level transit to the upper laser level ($E_2$), which is usually a long-lived level. Third, laser action occur when the ions on the $E_2$ level are more populated than on $E_1$. The finally, the excited ions on the $E_1$ level return back to the $E_0$ level by relaxation. The laser may be operated both in a pulsed or continuous mode. The laser in pulsed mode is most often operated in the Q-switching mode that works as an optical switch. As a maximum population inversion in the neodymium is achieved, the Q-switching allow the light wave to run through the cavity, depopulating the excited laser medium. Consequently, the pulse is generated and is less than ten nanoseconds with an output power of 20 mW$^{13}$.

**Figure 3.** The four-level pumping Model
CHAPTER 1

FABRICATION OF IRON AND IRON OXIDE THIN FILMS FROM AN EPOXIDE-CATALYZED SOL-GEL PROCESS

Introduction

Iron oxide thin films are of technological interest for their potential magnetic, optical, and catalytic applications. Thin films of various iron oxide phases (i.e., α-and γ-Fe₂O₃ and Fe₃O₄) have most commonly been made using vacuum deposition techniques such as sputtering, chemical vapor, and arc-plasma spray deposition¹⁴-²⁰. Solution chemical (sol-gel) approaches have also been exploited successfully, albeit less frequently, to produce high-quality films. These approaches have generally involved the hydrolysis of organometallic precursors such as alkoxides or acetylacetonates using methods originally developed by Schroeder and Dislich or the use of soluble iron salts with organic gelling agents such as glycols or polymeric phases²¹-³².

Recently, Gash et al. have reported a new technique for the sol-gel synthesis of a wide range of metal oxides⁸,³³,³⁴. In their approach, gel formation occurs through the epoxide-catalyzed condensation of metals ions with an aquated inner coordination sphere. As shown by these authors, the reaction is quite general, producing high-quality gels from a wide range of transition and main group metal ions and affords considerable synthetic flexibility as to composition and the final crystalline phase¹.

To date, there have been no reports of the gels' applicability for thin film formation. In this study, we report that in the case of gels made from aquated Fe³⁺ ions by this process, high-quality thin films on a fused quartz substrate can be readily produced. These films can, in turn, be thermally processed in a reductive or oxidative environment to produce metallic or oxidized films, which, in many cases, retain the film quality of the initial gel coating.

Experimental Procedures

Thin Film Fabrication.
The films were formed from 0.64 M stock solutions of Fe$^{3+}$ dissolved in ethanol (2.59 g of Fe(NO$_3$)$_3$·9H$_2$O (Aldrich) in 10 mL of absolute ethanol). After dissolution, 1 mL of propylene oxide (Aldrich) was slowly added to 5 mL aliquots of the Fe$^{3+}$ solution. The solution was allowed to react over a period of 2 min during which time it turned from red to dark brown. At this point, using a disposable pipette, 5 drops of the Fe$^{3+}$ solution were dispensed on a quartz disk (2.5 cm) that had been placed on a spin-coater at ~3000 rpm. The coated substrates were allowed to age for several days at room temperature prior to analysis. Film thickness was estimated from profilometry traces acquired over a section scored to remove the film down to the substrate.

**Thermal Processing.**

Coated disks were placed in a tube furnace equipped with O$_2$ impermeable hoses under an N$_2$ flow and baked at 600 °C for a period of 6 h. Reduction to metallic iron was carried out in an analogous fashion under a flow of H$_2$ in N$_2$ (H$_2$/N$_2$ = 0.2 v/v) for 1 h. The Fe films were recovered by allowing them to cool to room temperature while still maintaining a reductive environment with the H$_2$/N$_2$ flow. Reoxidation to generate maghemite was performed by taking the just-reduced Fe films from 600 °C to room temperature at a rate of 5 °C/min under a flow of UHP grade N$_2$; the oxidant is believed to be trace O$_2$ (1 ppm in UHP N$_2$) in the N$_2$ stream, although some contribution from adventitious oxygen in the system cannot be ruled out.

**Characterization.**

X-ray diffraction was performed on a Siemens D-500 X-ray diffractometer with nickel filtered Cu Kα (λ= 1.540562). The XRD patterns of thin films were recorded in the range of 20-70° (scan speed = 2°/min). The X-ray tube operated at 40 kV/30 mA. Microscopy was carried out by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The AFMs were acquired in tapping mode at 290-360 kHz on a Digital Instruments Dimension 3000 equipped with silicon tips. The AFM images of thin films were processed using Nanoscope version 5.12 software. SEM data were collected on a JEOL JSM 840 operated at 10 and 20 kV. The samples were coated with Au/Pd by sputtering. UV-vis spectroscopy was
carried out on a Perkin-Elmer Lambda 900 spectrophotometer over a wavelength range of 200-900 nm. Spectra were acquired in transmission mode through the quartz deposited thin film. The magnetic properties of the films were measured on a Quantum Design XL-7 superconducting quantum interference device (SQUID).

Results and Discussion

Figure 4. Thin films spin-coated on a 2.54 cm quartz disk of epoxide-catalyzed Fe$^{3+}$ sol-gels (a) as-formed and (b) calcined at 600 °C.

Aged thin films formed from spin-coating propylene oxide-catalyzed Fe$^{3+}$ sol-gel solutions on a quartz substrate appear, qualitatively, continuous and extremely homogeneous (Figure 4a). The apparent smoothness is also observable on a microscopic scale in images obtained from atomic force microscopy (AFM) and scanning electron microscopy (SEM). The surface, as imaged by tapping mode AFM (Figure 5), is very flat with a measured root-mean-squared (rms) roughness of 2.30 nm and is typified by an array of small peaks ~1 nm in width. The SEM (not shown) showed the film to be essentially featureless and uniform with no obvious cracks or voids that are often seen in sol-gel derived thin films due to shrinkage during drying. The thickness of the as-prepared film, determined from profilometry, was found to be 119 nm. Taken together, these results suggest that the film forming characteristics of the epoxide-catalyzed Fe$^{3+}$ sol-gel are excellent, producing very high-quality thin films on both a macro- and microscopic scale. As reported by Gash et al., the product of the propylene oxide-catalyzed gelation of Fe(H$_2$O)$_6$$^{3+}$ is a largely amorphous iron oxide/hydroxide phase known as ferrihydrite that also contains organic products of the epoxide catalysis$^1$. 
Figure 5. AFM image of as-formed Fe$^{3+}$ oxide/hydroxide thin film (high areas on right are interpreted as surface debris).

Figure 6. UV-vis spectrum of Fe$^{3+}$ oxide/hydroxide thin films (a) as-synthesized, (b) after calcination at 600 °C under N$_2$ to form α-Fe$_2$O$_3$, and (c) calcination under N$_2$ followed by reduction under dilute H$_2$ to form Fe
Consistent with retention in the thin film of this essentially amorphous phase, no X-ray diffraction was observed.

The electronic spectrum, collected in transmission mode through the film (Figure 6a) is typical of related iron oxide hydroxide species (e.g., goethite and lepidocrocite) with relatively strong bands at $\lambda < 500 \text{ nm}$ associated with Fe(III) ligand field transitions$^{35}$.

While thin films of Fe$^{3+}$ oxide/hydroxide gels are not currently of direct technological interest, we have determined that under carefully controlled conditions, it is possible to convert these films into potentially useful metallic or oxidic phases while retaining much of the quality of the original Fe$^{3+}$ gel film.

![Scheme 3. Thermal process of Fe gel thin films](image-url)
As shown in Scheme 3, the amorphous Fe$^{3+}$ oxide/hydroxide thin film can either be oxidized to $\alpha$-$\text{Fe}_2\text{O}_3$ (Scheme 3, pathway a) or reduced to metallic Fe (Scheme 3, pathway b). Once formed, these films can be further converted through sequential oxidation and reduction processes to magnetic $\gamma$-$\text{Fe}_2\text{O}_3$.

**Figure 7.** Powder X-ray diffraction from Fe$^{3+}$ oxide/hydroxide gel thin films after (a) calcination at 600 °C under N$_2$ (Scheme 3, pathway a), (b) reduction under dilute H$_2$ (Scheme 3, pathway b), (c) calcination under N$_2$ followed by reduction under dilute H$_2$ (Scheme 3, pathway d), (d) reoxidation of Fe (Scheme 3, pathway c), and (e) reoxidation of Fe (Scheme 3, pathway e).
Oxidation to $\alpha$-Fe$_2$O$_3$ (Scheme 3, Pathway a).

Calcination of the FexOy gel films at 600 °C under either air or an inert atmosphere results in a color change from pale to dark orange (Figure 4b). The thickness of the film after calcination is ~49 nm, suggesting that the gel derived films shrink substantially upon thermal processing. The X-ray diffraction pattern of the calcined gel indicates that it has been converted to $\alpha$-Fe$_2$O$_3$ (Figure 7a). This conversion is further confirmed by the UV-vis spectrum (Figure 6b), which is identical to that reported for bulk hematite with an intense, well-resolved band at 430 nm associated with the ligand field $^6A_1 \rightarrow ^4E$, $^4A_1$ transitions and a resolved shoulder at 530 nm that has been assigned to the $2(^6A_1) \rightarrow 2(^4T_1(4G))$ pair excitation transition$^{36}$. Interestingly, the calcination product of the iron gel thin films under an inert atmosphere yields different products from those observed with bulk material where magnetite and hematite are produced under inert and oxidizing atmospheres, respectively. The origin of this difference in behavior is not known for certain; however, the as-synthesized iron oxide gel contains a significant amount of organic material (17% C for samples dried under N$_2$ at 75 °C for 24 h) that can act as reductants to convert the Fe$^{3+}$ to Fe$^{2+}$ to yield magnetite during calcination. In the thin film, these organic reductants may be lost rapidly during heating due to the high surface area and small volume, which causes Fe to remain in the $+3$ oxidation state.

Figure 8. AFM image of $\alpha$-Fe$_2$O$_3$ thin film formed from the calcination of thin films made from Fe$^{3+}$ oxide/hydroxide gels.
Figure 9. SEM images of $\alpha$-Fe$_2$O$_3$ thin films from calcination of Fe$^{+3}$ oxide/hydroxide thin films at (a) $\times$100, (b) $\times$25 000, (c) $\times$10 000 showing scored section, and (d) $\times$50 000 magnification.

The surface morphology of the calcined films, as analyzed by AFM (Figure 8), was found to be significantly rougher than the gel with an rms roughness of 4.63 nm. The surface exhibits a granular structure with a mean grain diameter of $\sim$100 nm. Scanning electron microscopy of the surface at ($\times$100; Figure 9a) shows the surface to be uniformly covered by the film with some cracks and pinholes observable in the image. At progressively higher magnifications, a brain-coral morphology becomes apparent with regions $\sim$200 nm in diameter separated by what appears to be troughs of $\sim$20 nm. A score mark across the film is imaged in Figure 9c, which shows that fragmentation occurs along the spaces between the globular regions, supporting the assertion that they are void spaces (troughs) in the film. Estimates of crystallite size obtained from applications of the Scherer equation to the XRD yields an average size of $\sim$28 nm, which suggests that the observed microstructure is composed of smaller Fe$_2$O$_3$ crystallites. Interestingly, the microscopic morphology we observe compares closely with those reported for films made from organic gelling agents, in
particular, that observed by Hida and Kozuka for hematite films made from solutions of ferric nitrate with polyvinylpyrrolidone (PVP) and for magnetite films fabricated by Chang et al. from Fe$^{2+}$ and Fe$^{3+}$ salts using ethylene glycol and citric acid as gelling agents$^{25,28}$. This similarity may arise from the relatively large amount of residual organic material, which remains in the iron gels coatings. If, as the gel dries, the organic phases separate into distinct regions, their removal with calcinations may leave the observed void space.

**Reduction to Metallic Fe.**

Direct reduction of the thin films Fe$^{3+}$ oxide/hydroxide gel (Scheme 3, pathway b) in a dilute, reducing atmosphere (H$_2$/N$_2$ = 0.2 v/v) at 600 °C results in the formation of a single crystalline phase as indicated by the XRD (Figure 7b), which proved to be metallic iron as indicated by the characteristic diffraction pattern with an intense [110] reflection and weaker [200] reflection observed at 2$\theta$ = 44.7 and 65°, respectively. Obviously, any amorphous phases present will not be detectable by XRD analysis.

**Figure 10.** SEM images at (a) $\times$10 000 and (b) $\times$50 000 Fe particles made from the reduction of Fe$^{3+}$ oxide/hydroxide thin films.

SEM imaging of the film surface at low magnification indicates that it is quite uniform; however, at higher magnifications (Figure 10), it becomes evident that the film is
composed of irregularly shaped iron particles distributed rather uniformly across the surface. The particles as formed cover a range of sizes with the small particles appearing to be on the order of ~100 nm and the larger particles being in the 400-500 nm range. The fact that the particles are so widely dispersed on the surface with interparticle distances on the order of several hundreds of nanometers in most cases is likely due to mass loss and shrinkage as the gel is heated and reduced.

Metallic iron films were also produced from reduction of the hematite films generated from oxidation of the Fe$^{3+}$ oxide/hydroxide gels (Scheme 3, pathway d). The reduction was carried out under the same conditions used to reduce the Fe$^{3+}$ oxide/hydroxide gel: 600 °C under a dilute hydrogen flow (H$_2$/N$_2$ = 0.2 v/v) for a period of 60 min. These conditions resulted in complete reduction to metallic Fe as indicated by the XRD (Figure 7c).

Figure 11. (A) AFM image and (B) SEM image at (a) ×10 000 and (b) ×25 000 magnification of the surface of metallic Fe formed from Scheme 3, pathway d.
Both the AFM and the SEM analyses (Figure 11) show the surface to be composed of submicrometer Fe particles dispersed relatively uniformly across the surface. Qualitatively, the surface is similar in appearance to films produced from direct reduction of the Fe$^{3+}$ oxide/hydroxide gel, but the iron particles are much more uniform in size and more evenly dispersed. Average grain size analysis of the AFM image gives a mean diameter of 223 nm. The broadness of the [110] reflection in the XRD, however, indicates that the materials are poorly crystalline, in comparison to metallic Fe produced through direct reduction of the Fe$^{3+}$ oxide/hydroxide gel (Scheme 3, pathway b), even though the observed particles are of a similar size. Scrutiny of the AFM and SEM image (Figure 11) shows no faceting, and the AFM indicates that the individual particles have a substructure, which is consistent with the irregular particles being composed of an agglomeration of small crystallites.

**Oxidation to $\gamma$-Fe$_2$O$_3$.**

Use of controlled processing conditions on the metallic iron films produced either from direct reduction of the Fe$^{3+}$ gel or from reduction of the hematite made from the gel could be converted to maghemite, the ferrimagnetic $\gamma$ phase of Fe$_2$O$_3$. This phase is of technological interest due to its extensive application in magnetic storage media. Commercially, maghemite is made from hematite, which is first reduced to magnetite and then reoxidized to maghemite$^{37}$. For the Fe$^{3+}$ oxide/hydroxide gel derived thin films, however, we were never successful in achieving a controlled reduction to magnetite. This contrasts with other sol-gel techniques in which magnetite could be produced directly$^{27,28,31}$.

Reoxidation of the metallic Fe films containing distinct Fe particles (Scheme 3, pathways b and d) was carried out by turning off the hydrogen flow after reduction and allowing the films to cool from 600 °C to room temperature at a rate of 5 °C/min under a stream of dry N$_2$ (UHP, 1 ppm O$_2$). The very low oxygen content and the long oxidation period produced maghemite from both of the particulate Fe films. Maghemite was characterized by XRD analysis of the films (Figure 7d,e), which showed that they are crystalline with a relatively intense [311] reflection at $2\theta = 35.6^\circ$ and a [440] reflection at $2\theta = 62.9^\circ$ characteristic of $\gamma$-Fe$_2$O$_3$. The XRD of the films made from Scheme 3, pathway e shows
a higher degree of crystallinity (Figure 7e) as evidenced by the more intense and better resolved diffraction that also allows observation of the [511] reflection at $2\theta = 57.3^\circ$.

![Image of AFM and SEM](image.png)

**Figure 12.** (A) AFM and (B) SEM at (a) $\times 10\,000$ and (b) $\times 50\,000$ magnification of maghemite made from reoxidation of Fe particles through Scheme 3, pathway c.

Imaging of the films by SEM shows that they are characterized by an array of well-formed particles distributed on the surface. The maghemite generated in Scheme 3, pathway c, directly from the reduced Fe$^{3+}$ oxide/hydroxide gel, has relatively irregular particles that nonetheless show evidence of facets at the edges indicative of crystalline composition, although they are probably not single crystals (Figure 12). AFM imaging of the surface morphology also reflects the faceted edges and measures an average grain diameter of 575 nm. A qualitative assessment of the SEM (Figure 12B) shows some small particles of $\sim 100$ nm; however, most are considerably larger and appear to range from about 300 to 500 nm.
Consistent with the XRD, the maghemite produced from oxidation of the Fe particles generated from hematite reduction (Scheme 3, pathway e) shows a similar morphology in the SEM (Figure 13a-d) but with better formed and more regular crystallites that appear to be of a much narrower particle size distribution. Moreover, the SEM shows them to be more tightly packed with at least a qualitative semblance of order. The AFM shows closely arrayed crystallites with well-defined faces (Figure 13e). The crystallites are smaller than those generated through Scheme 3, pathway c with the particle sizes appearing to range from around 100 to 200 nm with some particles around 400 nm. The mean grain size determined from AFM grain size analysis is 271 nm.

**Magnetic Properties.**

The Fe films made from the reduction of hematite (Scheme 3, pathway d) and the maghemite made from these Fe films (Scheme 3, pathway e) appear to exhibit the best
microstructure in terms of the apparent crystallinity of the particles and the uniformity of their dispersal on the surface.

Figure 14. (A) Zero-field cooled Fe film (Scheme 3, pathway e) parallel (+) and perpendicular (O) to the magnetic field. (B) Magnetic hysteresis, recorded at 2 K, of Fe (Scheme 3) placed parallel and perpendicular to the magnetic field.

Figure 15. (A) Zero-field cooled $\gamma$-Fe$_2$O$_3$ thin film parallel (+) and perpendicular (O) to the magnetic field. (B) Magnetic hysteresis, recorded at 2 K, of $\gamma$-Fe$_2$O$_3$ placed parallel and perpendicular to the magnetic field.
These particles, however, are too large to be superparamagnetic, and no evidence of that behavior is observed. At the limit of a thin film, there is potentially a direction of long-range magnetic order in-plane and little or no ordering out-of-plane. As a result of this, the Fe samples (Figure 14) give a typical susceptibility typical of bulk iron in the in-plane direction, while in the out-of-plane direction, the susceptibility shows little dependence on temperature. No crystallographic orientation of the particles is expected to be present in these samples, and none is indicated by the data.

In the hysteresis plots, a similar coercivity is observed in both directions with a magnitude of 0.1 and 0.09 T. The main difference lies in the magnetization direction, where the in-plane direction is the direction of easy magnetization as compared to the out-of-plane film direction. The difference in the slopes implies a more ordered magnetization in the in-plane direction. Similar effects are observed in maghemite (Figure 15), although the effect is less significant.

**Conclusion**

The central conclusions of this study are that high-quality thin films can be made from a new epoxide-catalyzed sol-gel approach used to making Fe$^{3+}$ oxide/hydroxide gels. Calcination of the resulting Fe$^{3+}$ oxide/hydroxide gel films under either inert or oxidative conditions appears to produce only hematite. As such, this differs from some of the other sol-gel gel techniques where different oxide phases can formed directly through either the choice of gelation agent or the specific processing conditions. The oxide phase that does form is comparable morphologically to those formed with organic gelation agents and, in particular, is quite similar to the hematite formed from Fe$^{3+}$ oxide/hydroxide gels containing polyvinylpyrrolidone. Once formed, however, these films can be thermally processed to produce magnetic phases. Under reductive conditions, the Fe$^{3+}$ gel films and the hematite films both leave a more-or-less continuous distribution of sub-micrometer Fe particles on the surface. These discrete Fe particles, if reoxidized slowly at very low O$_2$ concentrations, yield films composed of very well-formed maghemite crystallites, the best of which are obtained from metallic iron generated from reduction of hematite. Given the broad array of the metal
ions that can be gelled using this approach, this may suggest a general route to producing metallic and oxidic thin films of a series of metals.
CHAPTER 2

IRON OXIDE THIN FILMS ON SILICON DERIVED THROUGH SOL-GEL METHOD: SURFACE PROPERTIES AND INTERFACIAL CHEMISTRY

Introduction

In a recent report we have shown that high-quality iron oxide thin films can be formed from the spin coating of iron oxide/hydroxide sol-gels on a silica substrate. In this approach, Fe(H₂O)₆³⁺ ions are condensed through the epoxide catalyzed deprotonation of water in the coordination sphere. This results in rapid reaction that is amenable to thin film formation just prior to gelation. Iron oxide/hydroxide films made in this fashion were converted by an appropriate choice of thermal processing pathway into good quality hematite and maghemite thin films. An interesting aspect of sol-gel derived metal oxide materials made through epoxide catalysis is that they undergo thermite-type reactions with the incorporation of a fuel (e.g. Al) during gelation. Thermal ignition of the metal/oxide gel composites initiates a self-propagating exothermic redox reaction to produce oxides and reduced metal products (e.g. Fe). We report here an investigation of whether the thin-film forming properties of the iron oxide/hydroxide gels can be combined with their oxidation-reduction processes to form multilayers if the film is deposited on a silicon substrate which can act as a fuel source. From a synthetic standpoint the ability to spontaneously form a multilayer structure from a simple one-step preparation afford some technological advantages.

Experiment

Sample Preparation

2.59g Fe(NO₃)₃·9H₂O was added to 10ml of absolute ethanol. After dissolving Fe(NO₃)₃·9H₂O, 1ml propylene oxide was added with stirring to 5 ml of the ethanolic Fe³⁺ solution. After 2 minutes the solution turned dark and 5 drops were used to spin coat an
untreated silicon wafer at 2800 rpm. The product of the propylene oxide catalyzed gelation of Fe(H₂O)_₆³⁺ is a largely amorphous iron oxide/hydroxide phase known as ferrihydrite which also contains organic products of the epoxide catalysis (henceforth referred to as Fe³⁺-gels).¹ As deposited on the silicon wafer using this procedure, the Fe³⁺-gel formed yellow films with a highly uniform appearance (Figure 16a). The film thickness, obtained from profilometry across a scored region of the film, is ~1 μm. Atomic force microscopy in tapping mode shows the film to be quite flat (Fig 17a) with a surface mean roughness of 0.364 nm. The imaged surface is characterized by small, spike-like features ~20 nm in diameter.

Conversion of the gels to an oxide film was accomplished either by the insertion into a tube furnace at a temperature of 300 °C in air or N₂. Heating resulted in an instantaneous transformation of the film from yellow to blue-gray (Figure 16b). The transformation occurs with qualitative retention of the film quality. After heating, the film is about 50% of its original thickness with a measured value of ~0.5 μm. Atomic force microscopy (Figure 17b), collected in tapping mode, indicates that the surface of the heated sample is rougher than the

Figure 16. Thin films of Fe³⁺-gels spin coated on a silicon wafer (a) as deposited and (b) after heating to 300 °C

Conversion of the gels to an oxide film was accomplished either by the insertion into a tube furnace at a temperature of 300 °C in air or N₂. Heating resulted in an instantaneous transformation of the film from yellow to blue-gray (Figure 16b). The transformation occurs with qualitative retention of the film quality. After heating, the film is about 50% of its original thickness with a measured value of ~0.5 μm. Atomic force microscopy (Figure 17b), collected in tapping mode, indicates that the surface of the heated sample is rougher than the
gel with an rms roughness of 2.06 nm. The surface shows sharp needle-like features that are narrower than the unheated sample.

Figure 17. AFM image of the surface of (a) as-synthesized and (b) heated (300 °C) Fe³⁺-gel films on silicon.

Result and discussion

The thermite reaction between Fe₂O₃ and Si produces metallic Fe and the iron(II) silicate, Fe₂SiO₄ (equation 2). As such, we would expect under the best of circumstances to
observe completely reduced and partially reduced iron if the reaction goes to completion upon heating.\textsuperscript{41}

\[ 4\text{Fe}_2\text{O}_3 + 3\text{Si} \rightarrow 3\text{Fe}_2\text{SiO}_4 + 2\text{Fe} \] (equation 2)

The identification and characterization of Fe containing phases in the both as-synthesized and thermally produced thin-films were carried out by using \textsuperscript{57}Fe conversion electron Mössbauer spectroscopy (CEMS) and \textsuperscript{57}Fe conversion x-ray Mössbauer spectroscopy (CXMS). The integral CEMS and CXMS spectra were recorded in a constant acceleration mode using a \textsuperscript{57}Co radioactive gamma-ray source and a proportional continuous gas flow counter for room temperature zero field measurements. A mixture of 90\% He (CEMS) or 90\% Ar (CXMS) and 10\% CH\textsubscript{4} was used as a counting gas. Mössbauer spectra were registered in 1024 channels. Escape (probing) depth of 7.3 keV K-shell conversion electron is approximately 300 nm, whereas 6.3 keV characteristic K\textsubscript{\alpha} conversion X-rays can contain information from 1-10 µm thick surface layer of the sample.

CEMS of the as-synthesized sample (Figure 18a) presents one doublet with hyperfine parameters (\( \delta_{\text{Fe}} = 0.37 \text{ mm/s}, \Delta E_{\text{Q}} = 0.71 \text{ mm/s} \)) typical for (super)paramagnetic iron(III) oxides or hydroxide. Relatively narrow spectral lines (\( I_{1/2} = 0.40 \text{ mm/s} \)) indicate a narrow distribution of particle size. No magnetically split component has been detected. CEMS inspecting whole thickness of the film exhibits practically the same parameters as CXMS. The comparable results from CXMS and CEMS reflect a high degree of homogeneity of the film through the measured thickness. CEMS of the heated sample (Figure 18b) was also evaluated by one doublet (\( \delta_{\text{Fe}} = 0.34 \text{ mm/s}, \Delta E_{\text{Q}} = 0.83 \text{ mm/s} \)), which can be ascribed to (super)paramagnetic \text{Fe}_2\text{O}_3, however the spectral lines are broader (\( I_{1/2} = 0.60 \text{ mm/s} \)). This can be related to the changes in particle size and morphology during the heat treatment in accordance with AFM observations. CXMS measured on the heated sample shows the spectrum with almost same parameters as in the case of CEMS. It is clear from the CEMS and CXMS spectra that the film is an iron oxide similar to what was observed on inert silicon substrate suggesting that a self-propagating redox reaction that consumes all of the iron film does not occur. This result, however, does not preclude reactivity at the interface, which would be of interest in forming multilayers.
Figure 18. CEMS of the (a) as-synthesized and (b) heat treated (300 °C) iron(III) oxide thin films.
The composition of the thermally produced thin-film was analyzed through depth profiling x-ray photoelectron spectroscopy (XPS) to specifically access the interfacial region between the oxide and the silicon. The XPS spectrum (Figure 19) was collected at a 45° takeoff angle from a sample of the heated film on silicon. Consistent with the CXMS and CEMS results, the surface of the film is an iron oxide layer as indicated by the position of the $2p_{3/2}$ and $2p_{1/2}$ binding energies at 710.3 and 723.8 eV respectively. The film was etched with an Ar$^+$ ion gun set at a voltage of 5 keV with an etch rate of ~12 Å/sec. As a function of etching time the XPS spectrum changes dramatically with $2p_{3/2}$ ionization narrowing significantly and shifting to 707.3 eV and $2p_{1/2}$ shifting to 720.3 eV (Figure 19).

Figure 19. XPS of thermally treated (300 °C) Fe$^{3+}$ gel thin films on silicon as a function of Ar$^+$ ion etching.
This spectrum is characteristic of metallic Fe and indicates that metallic Fe has formed below the surface, close to the interface between the Fe$^{3+}$-gel film and the silicon surface. To further verify this result a control sample of the Fe$^{3+}$-gel was deposited on a non-fuel fused quartz substrate, heated to form iron oxide and depth profiled under identical conditions. This sample showed that, during the course of the etching, only trace amounts of metallic Fe were ultimately observed. The formation of these small amount was consistent with the actions of the Ar$^+$ ion bombardment which are sometimes known to generate small amount of reduced metallic species during etching.

![Figure 20](image-url) **Figure 20.** Field emission SEM images of the (a) un-etched and (b) Ar$^+$ ion etched surface of thermally treated (300 °C) Fe$^{3+}$oxo/hydroxy thin films.

Of interest is the nature of the metallic iron that forms at the interface, some characteristics of which are observable in images obtained from scanning electron microscopy (SEM). The field emission SEM image of a heated film surface (Figure 20a) shows it to be relatively uniform with some cracking observable in the image. The morphology observed in the SEM compares qualitatively to the Fe$_2$O$_3$ films obtained from heating thin films of the Fe$^{3+}$oxo/hydroxy gels deposited on silica. The dimension of these features on silica were on the order of ~200 nm while the films formed on the silicon wafer were significantly smaller (<100 nm across). Imaging of the Ar$^+$ ion etched region of the sample is shown in Figure
20b. Clearly observable in this image are irregular particles whose length is on the order of 50-100 nm residing on what appears to be an amorphous background. Close imaging of the particles does not show any direct evidence of crystallinity such as crystal faces, suggestive of crystallite formation. Attempts to obtain x-ray diffraction data were not successful due to the low concentration of the iron and the dominance of the silicon diffraction. As such while the particles do not appear to be crystalline that cannot be ruled out completely.

The elemental composition of the various regions was measured using energy dispersion spectroscopy (EDS) collected from a 5-10 nm spot, which was able to analyze a specific particle. The elemental composition of the un-etched surface of a heated sample is, as expected, dominated by silicon with large contributions from the gold/palladium coating applied for imaging. Iron and oxygen are observed in approximately a 1:3 mole ratio consistent with the Fe$_2$O$_3$ surface detected by CXMS, CEMS and XPS. The excess oxygen likely arises from the SiO$_2$ present on the silicon. Imaging of the etched region shows a sharp decrease in the amount of oxygen present relative to the amount of iron, consistent with reduced iron species, particularly the metallic iron detected by XPS. The composition measured in the region between the particles and of the individual particles themselves gave Fe:O mole ratios of 1.3:1 and 2.0:1 respectively. This suggests that the nanoparticles are indeed richer in iron that forms at the interface during thermal treatment. The oxygen present in the etched region at the interface has several probable origins, one is from the iron silicate product, Fe$_2$SiO$_4$, and SiO$_2$ that is either already present on the surface. These particles appear dispersed in a medium that is also contains reduced iron (possibly amorphous).

**Conclusion**

Clearly a key aspect of this interfacial reaction is that it is not a self-propagating high-temperature reaction such as has been used to produce granular Fe-Al$_2$O$_3$ films from Al and iron oxide bi and multilayers. In this system, reduced iron is produced only at the interface and at a temperature well below what is required to initiate the combustion of bulk thermite. In fact, attempts to initiate a self-propagating reaction using higher temperatures were not
successful. The size and distribution of the reduced iron particles at the interface and the low temperatures at which they form may be due to the thickness and irregularities of the native oxide layer on the silicon surface. The native oxide layer growth in air at R.T. is typically ≤20 Å, depending on the silicon surface and the specific condition of oxidation, moreover, the surface is rough with variation in thickness observed by techniques such as scanning force microscopy.47-49 The reduced-iron particles may well form in the thinner regions, which affords more intimate contact and lowers the activation barrier to electron and oxygen atom transfer processes.
CHAPTER 3

DYNAMICS OF Al/Fe$_2$O$_3$ MIC COMBUSTION FROM A SHORT SINGLE-PULSE PHOTOTHERMAL INITIATION AND TIME-RESOLVED SPECTROSCOPY

Introduction

Energetic materials based on metastable intermolecular composite (MIC) have been the subjects of considerable research activity. These materials are based on highly exothermic inorganic redox reactions, typified by the well-known thermite reaction$^{50}$.

$$\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe} \quad \Delta H = 3.97 \text{ kJ/g}$$

In MIC materials, one or both of the components has dimensions in the nanometer size range, which provides a significant enhancement in the rate of energy release which is attributed in part to more intimate mixing of the fuel and oxidizer$^{10,51-53}$. In studies of MIC materials, the use of laser-induced photothermal initiation has been exploited to allow instantaneous coupling of high-speed cameras for quantitative determination of properties such as the ignition time and the burn rate$^{9,54}$. Such studies have been essential in quantifying the effect of particle size and other factors on the combustion properties of these materials. Recently, studies in our laboratory have focused on trying to elucidate some of the molecular species and reaction processes that occur during the very early stages of the photothermal initiation process$^{55}$. In particular, we’ve recently reported a study of the reaction of Al/Fe$_2$O$_3$ metastable intermolecular composites (MIC) using laser induced desorption ionization time-of-flight mass spectrometry (TOF-MS). In that study, ion clusters resulting from reactions between the fuel and oxidant were observed in the plume. In this chapter we report the single-pulse laser initiation of Al/Fe$_2$O$_3$ MIC, which allows the use of time-resolved spectroscopic techniques to monitor the reaction dynamics, related to the initiation process. Such an approach was used recently by Dlott et. al. to study the reaction between aluminum and nitrocellulose by flash-heating with a 100 ps laser pulse in the near infrared$^{56,57}$. 
Experiment

Samples and preparation

Samples for initiation were composed of Fe$_2$O$_3$ and Al in a 1:1 Fe:Al stoichiometry. Three Al sizes were used; 3-4.5 µm (Aesar) and 50 nm and 100 nm particle sizes (Argonide). Fe$_2$O$_3$, ≤ 5 µm particle size and >99% purity was obtained from Aldrich and used as received. The combined powders were ground thoroughly in a mortar and pestle to ensure homogeneous dispersal of the components. This grinding and mixing process proved to be essential to achieve single-pulse photothermal initiation. After grinding, 3.0 g samples were compressed in a die at an applied pressure of 26,000 psi. The resulting cylindrical pellets were 1.27 cm diameter by ~ 0.9 cm. The average density of the samples was 2.63 g/cm$^3$.

Instruments

Combustion was achieved using single pulses of 1064 nm light from a Spectra-Physics DCR-3G Nd:YAG laser. The final configuration used an 8 ns 900 mJ pulse focused through a fused silica 75 mm focal length lens onto the compressed thermite pellet. The focused beam size is calculated to be 11 µm in diameter with an energy density of 8.8 x 10$^5$ J/cm$^2$. The laser beam is focused through a 2.54 cm diameter hole in a protective steel plate covered by a 25x37x1 mm fused silica window.

The kinetics of the combustion flash was recorded using three photodiode detectors (Thorlabs DET210, 0.8 mm$^2$ Si PIN, 1 ns rise time) and recorded by digital storage oscilloscopes (LeCroy LC564A, 1 GHz bandwidth, 250 ps sampling rate for fast signals; LeCroy 9410, 150 MHz bandwidth, 10-50 µs sampling rate for slow signals). The photodiodes were placed at 45 degrees from the laser beam axis looking down at the sample through the fused silica window and filtered by either a heat absorbing filter (Hoya HA30) to reduce the 1064 nm scattered light (fast signal) or a 520 nm band-pass filter (ThorLabs FB520-10, 10 nm FWHM) (both slow and fast signals). Spectra were collected through a 3 mm diameter liquid light guide (Oriel 77554, NA/0.47, >50% transmittance from 270 to 720 nm) placed above the sample at 45 degrees from the laser beam axis coupled into a 300 mm spectrograph (Acton Research Corporation Spectra Pro 308i, 150 gr/mm grating blazed at 300
nm) using a biconvex fused silica lens (Spex, 1" diameter, f = 28.6 mm), and the light dispersed onto a back-thinned CCD (1340x400 pixels, 20 μm square, Princeton Instruments LN/CCD-400EB-G1 operated at -90°C). Timing for single shot operation was coordinated by triggering both the CCD shutter, laser and slow oscilloscope using a digital delay generator (EG&G PAR 9650) to trigger the CCD shutter to open for 30 ms and delaying the laser and oscilloscope triggers by 10 ms. The CCD exposure time, set in software to 10 ms, was determined to be 30 ms by adjusting the laser trigger delay while observing the second harmonic 532 nm laser light.

**Result and discussion**

Thermal initiation of thermite-type reactions involving Al as fuel occur at temperatures around and above the melting point of the Al where breakdown of the native oxide layer and mass transport between the fuel and oxidant becomes efficient enough to propagate the reaction. In photothermal initiation, the laser excitation event and the subsequent ignition and propagation of the reaction are extremely high temperature processes, which generate both a liquid and a gas phase (plasma). Preliminary energy density tests indicate that the threshold of combustion for thermite made with 100 nm aluminum particles occurs between $3.8 \times 10^5$ J/cm$^2$ and $4.2 \times 10^5$ J/cm$^2$. Estimates of the temperature attained by each component during the excitation, using calculations outlined previously, indicate that at the energy density threshold required for single pulse initiation both components have liquid and vapor phase components. As such, the initiation process involves chemical reactions between species occurring within and between these phases and with the solid material all of which contribute to the initiation and net combustion process. At the threshold the MIC materials could be reproducibly combusted in a single 8 ns pulse. In contrast, thermite made with micron-scale Al could be initiated in a single pulse infrequently (<10 % of the time), even at very high energy densities. This is consistent with the larger amount of reactive species generated per pulse in the MIC materials, as was observed in TOF-MS studies.

The dynamics of the entire photoinitiation-deflagration process, as monitored by the emitted light collected through a bandpass filter at $\lambda_{\text{max}}=520$ nm, is seen in Figure 21.
The time-to-ignition of MIC materials is defined as the time at which the energy released by the reaction becomes greater than or equal to the energy put into the composite by the laser. For data collected photonically, the initiation time is generally taken as the time between the laser excitation and when emitted light can be detected. In analyzing the data, we define time-to-ignition as the period between the laser spike and the point at which the intensity of the light emitted from the sample is twice the intensity of the noise in the system. The time-to-initiation for the micron scale Al is 26.6 ms while that of the 50 and 100 nm MIC materials are 11.8±0.8 and 4.9±0.1 ms, respectively. The values reported for the nanoscale fuels represent the average of 8-12 independent measurements with the errors being the standard deviation of those measurements. Due to the difficulty of achieving single-pulse initiation of the micron scale fuel, data collected over the total time regime and, hence, the value reported for the time-to-ignition is from a single experiment.
As expected, we observe a significant decrease in the time-to-ignition for MIC materials when compared to the micron scale thermite. If we compare these results to those reported by Granier and Pantoya for the Al//MoO$_3$ it is clear that our values for the ignition time are systematically smaller by a factor of ~2-4 depending on the particle size.$^{9,10}$ Given that the driving force for the Al//MoO$_3$ is greater than that of Al//Fe$_2$O$_3$ some consideration of the origin of this difference is appropriate. One possible origin of the difference may lie in the larger dynamic range of the photodiodes employed in our experiments, which allow earlier observation of light emitted from the onset of ignition. Another factor that may be at contributing to the discrepancy may be the thermal stresses that accompany pulsed laser heating.$^{59-61}$ The generation and propagation of thermoelastic waves induced by laser heating is well understood and, in general, for materials receiving the same temperature change the induced stress increases as the pulse duration decreases.$^{61}$ As such, the shorter pulse duration and high heating rates used in our experiments (~2x10$^{10}$ K/s for the Al phase) may cause heightened mechanical stresses that rupture the oxide layer or compressively assist in the initiation process thereby causing more rapid initiation times to be observed. Clearly, as more studies involving pulsed laser initiation are performed, as deeper understanding of the mechanical factors accompanying photothermal pulses will be required.

Notwithstanding the above discussion, the relative changes in the initiation time as a function of particle size are quite consistent with those observed by Granier and Pantoya including the observation that the 100 nm Al consistently shows a faster time-to-ignition than does the 50 nm. Their studies by have shown that the burn rate of MIC materials increase as the particle size of the Al gets smaller, however, the rate is optimum at ~100 nm and begins to drop again as the particle size decreases. This is attributed to the higher oxide-to-aluminum ratio as the particle size decrease.$^9$ The high heat capacity of the excess Al$_2$O$_3$ present in smaller particles inhibits heat flow in the system thereby decreasing the measured burn rate. An analogous argument based on the metal-to-oxide ratio can be made about the time-to-ignition. In short single-pulse laser initiation, the time-to-ignition will be related to the amount and type of reactive species generated during the pulse. The 100 nm Al will provide a larger amount of reactive aluminum during the pulse than the 50 nm, which will generate a more substantial degree of reaction initially leading to a faster time-to-ignition. Notably, this
is consistent with the TOF-MS experiments, which show more pure Al ions (i.e. $[\text{Al}]^+$ and $[\text{Al}_2]^+$) for the 100 nm particles generated per pulse than for the 50 nm. Finally, the oscillations seen in the broad emission from the combustion of the sample are likely due to the deflagration of the sample, which modulates the light. Interestingly, the intensity of the light emitted over time from the three samples is significantly less for the micron sample. Since the integrated intensity should be approximately proportional to the energy, this implies that the sample containing micron Al is delivering much less total energy suggestive of incomplete burning.

Figure 22. Time-resolved emission decay of the laser induced break down for Al, Fe$_2$O$_3$ and Al/Fe$_2$O$_3$ composites made with 3-4.5 $\mu$m, 100 and 50 nm aluminum particles.
The decay dynamics of the laser-induced breakdown emission (i.e., laser plume) for the independent aluminum and Fe$_2$O$_3$ components and the MIC materials are shown in Figure 22. The kinetics of the decays are complex and could not be fit reliably to a mono- or bi-exponential decay function. A comparison of the decay profiles of the plume emission for the independent Al and Fe$_2$O$_3$ components and the micron scale thermite materials is shown in Figure 22. The emission decay of the component materials and the thermite composite made with micron scale Al are virtually identical and, moreover, decay much more rapidly then does the 50 and 100 nm MIC materials. We interpret the longer lifetime of the MIC materials as arising from more exothermic reactions taking place in the plume due to the higher density of reactive species generated by the pulse when the Al is nanoscale. This is consistent with the observations from TOF-MS, which show significantly more product formation in the plume of the MIC materials.

Figure 23. Time averaged emission spectra of deflagrating Al/Fe$_2$O$_3$ made with 3-4.5 µm, 100 and 50 nm aluminum particles.
The emission from single shot combustion of Fe$_2$O$_3$/Al pellets made with 50nm, 100nm and 3-4.5 µm Al are shown in Figure 23. The spectra all show a large broad asymmetric emission band centered in the visible around 600 nm, which is the time average of the plasma emission from the total deflagration of sample. All spectra show a sharp peak almost at the center of the emission, which is from Na, which is an impurity in the Fe$_2$O$_3$ that was used (Na = 163.51 ± 1.6 ppm as determined by ICP-MS). It should also be noted that the spectra all show some truncation above 700 nm because of absorption from the liquid light guide used to collect light from the sample. Notwithstanding this, the centroid of emission falls at longer wavelength for the micron size Al particles than it does for the MIC material. This may be due to a difference in the average energy of the plasma emission (i.e., higher excited states generated or a different distribution of emitting species) and/or from a larger contribution from blackbody radiation in the visible as the fuel size decreases suggestive of a higher thermal temperature. Regardless of the origin, it suggests that with smaller fuel particles there is a higher energy output during the combustion. Notably, the 100 nm is somewhat more blue shifted than the 50 nm, consistent with the larger particle reacting more vigorously due to the higher amount of free Al that it provides. Previous time-resolved emission spectra of deflagrating Al/MoO$_3$ reported by Moore et al. showed that in the early stages of the reaction the emitted light was essentially thermal in nature while at later times it deviates from that due to other emission processes.$^{62}$

Our time-averaged results are consistent with this since the intense plasma emission of the combustion process, occurring after initiation and at later times, dominates the spectra in the visible. While the resolution is poor, all of the spectra show some structure from atomic emission lines superimposed on the broad emission envelope. The weak resolved bands below 600 nm can be assigned to atomic Fe species.

**Conclusion**

In conclusion, the dynamics of the photothermal initiation of Al/Fe$_2$O$_3$ MIC materials obtained from time-resolved spectroscopy can be well explained in terms of the species
generated during the pulse as a function of the Al particle size. In particular, the well-established advantage of MIC material over micron scale materials is observable in their much shorter times-to-ignition. More interestingly, the effect of the higher Al₂O₃ to Al metal ratio for the 50 nm MIC on the time-to-ignition is measurable in these experiments. This approach, we believe, is particularly useful in studying the rapid events occurring between the photothermal event and ignition and, as such, is complementary to state-of-the-art fast-imaging studies that are employed to study these energetic materials.
CHAPTER 4

EFFECTS OF STOICHIOMETRY AND SAMPLE DENSITY ON COMBUSTION DYNAMICS OF Al/Fe$_2$O$_3$ METASTABLE INTERSTITIAL COMPOSITES

Introduction

Reactions of binary fuel-oxidant compositions are often characterized by a large exothermic driving force such as typified by the well known thermite reaction\textsuperscript{50}.

\[
\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe} \quad \Delta H = 3.97 \text{ kJ/g}
\]

Reactions of this type have been used as synthetic pathways for the production of a number of binary inorganic materials and the large heat and energy release has been exploited in metallurgy and in the development of high-output energetic materials.\textsuperscript{51,63-65} With regard to the latter application, the energy density of binary fuel-oxidant systems can be several times higher than conventional high-energy organic compounds such as 2,4,6-trinitrotoluene (TNT).\textsuperscript{66} However, the rate of energy release in binary fuel-oxidant systems is significantly lower due to the fact that energy release is not a unimolecular but a bimolecular process. To increase the rate of reaction, thereby making these materials more useful for high-energy applications, they have been formulated as metastable interstitial composites (MIC) where one or both of the components are present in the nanoscale dimensions.\textsuperscript{51,63} For this class of materials, large improvements are observed in the rate of energy release, which are qualitatively attributable to a more intimate fuel/oxidant contact.

The dynamics of these highly exothermic reactions are difficult to study due to the large amount of heat generated and the auto-acceleration that results from it. Earlier studies of these materials were typically carried out using temperature profiles of the reaction of bulk materials and non-isothermal kinetics on small amounts of material, carried out in the thermal analysis instrumentation.\textsuperscript{67-69} Contemporary dynamic studies, particularly of MIC materials, have been carried out using high speed cameras and to record the onset of initiation, usually carried out photo-thermally with the 10.8 $\mu$m fundamental of a CO$_2$ laser, and the subsequent burning of a length of bulk materials. Indeed, much of what we know about the initiation
time and burn rate of these materials and the dependence of these properties on factors such as particle size, comes from these studies.\textsuperscript{9,10,52,53,70} More recent studies have employed a somewhat different approach to the study of the dynamics of the initiation and deflagration of metastable interstitial composites (MIC). These studies utilize a single, short-pulse (8 ns) photothermal initiation of the MIC materials using the 1.064 $\mu$m fundamental of a Nd:YAG laser with the dynamics measured using time-resolved spectroscopy of the light emitted during initiation and deflagration. These studies provide information about the dynamics that are, for some aspects of the process, directly comparable to those carried out by high-speed photography while for others provide complementary information. In previous studies, we have used this technique to investigate the effects of a high-energy organic phase (PETN) on the initiation and deflagration of Al/Fe$_2$O$_3$ MIC materials and, in related work, we have used time-of-flight mass spectrometry to investigate the composition of the reactive species occurring in the plume of the same MIC compositions during the laser initiation event. In this report, we will describe the results of an extensive structure-property study of the initiation and deflagration dynamics of macroscopic samples of Al/Fe$_2$O$_3$ MIC materials as a function of Al particle size, the density of the bulk sample and the effects of performing the reaction in a vacuum. Important aspects of the observed trends are explained in terms of the maximum packing fraction of the MIC materials as a function of composition and particle size obtained through a series of Monte Carlo simulations.

**Experimental**

**Samples and preparation**

Iron (III) oxide powder, <0.25 $\mu$m, was purchased from Aldrich, aluminum powder in 100 nm and 50 nm sizes was obtained from Argonide and 120 nm from Novacentix. All materials were used as received.

The MIC composite samples were prepared by mixing Fe$_2$O$_3$ with 50 nm, 100 nm and 120 nm aluminum particles in a 1:1, 1:1.5, 1:2 molar iron-to-aluminum ratio. The samples were thoroughly mixed by grinding the components together using a mortar and pestle to help ensure a homogenous mixture. Approximately 0.7 g of this mixture was
compressed in a die at an applied pressure of 60,000 psi, 40,000 psi, and 20,000 psi. The resulting pellets were 6.40 mm in diameter by 9.22-11.23 mm high giving a density of 1.94-2.36 g/cm³.

**Instruments**

Laser initiation was carried out with a Spectra-Physics DCR-3G Nd:YAG laser using single, 8 ns pulses of the 1064 nm light fundamental. The laser was focused through a fused silica 75 mm focal length lens onto the pellet. The focused beam diameter was calculated to be 11 µm giving an energy density of 8.8 x 10⁵ J/cm² at 1064 nm. The laser beam was focused through a hole in a protective steel plate, with the hole measuring 2.54 cm in diameter, which was covered by a fused silica window measuring 24x23x2 mm in order to catch any debris from the combustion of the pellet.

For experiments carried out under vacuum condition, the laser beam passed through one more fused silica window with 3.5 cm diameter and 1 cm thickness on the stainless bomb to keep the vacuum (~5x10⁻³ torr).

The kinetics of the combustion flash was recorded using three photodiode detectors (Thorlabs DET210, 0.8 mm² Si PIN, 1 ns rise time) and recorded by digital storage oscilloscopes (LeCroy LC 564A, 1 GHz bandwidth, 250 ps sampling rate for fast signals; LeCroy 9410, 150 MHz bandwidth, 10-50 ms sampling rate for slow signals). The photodiodes were placed 45 degrees from the laser beam axis, looking down at the sample through a fused silica window and filtered by either a heat absorbing filter (Hoya HA30) to reduce the 1064 nm scattered light (fast signal) or a 520 nm band-pass filter (Thorlabs FB520-10, 10 nm FWHM) for both slow and fast signals. Spectra were collected through a 3 mm diameter liquid light guide (Oriel 77554, NA/0.47, >50% transmittance from 270 to 720 nm) placed above the sample at 45 degrees from the laser beam axis coupled into a 300 mm spectrograph (Acton Research Corporation Spectra Pro 308i, 150 gr/mm grating blazed at 300 nm) using a biconvex fused silica lens (Spex, 1 in. diameter, f = 28.6 mm) and the light was dispersed onto a back-thinned CCD (1340x400 pixels, 20 mm square, Princeton Instruments LN/CCD-400EB-G1 operated at -90 °C). The timing for single shot operation was coordinated by triggering the CCD shutter, laser and oscilloscope using a digital delay
generator (EG&G PAR 9650) to trigger the CCD shutter to open for 30 ms and delaying the laser and oscilloscope triggers for 10 ms. The CCD exposure time, set in the software to 10 ms, was determined to be 30 ms by adjusting the laser trigger delay while observing the second harmonic 532 nm laser light.

**Results and Discussion**

The effects of Al particle size and the Al:Fe stoichiometry on the time-resolved spectra are shown in Figure 24. The emissive plume generated by the laser pulse incidence event on the surface of the sample can be seen as a sharp spike, indicated by an arrow in the figures, while the irregular intensity that follows it in time is the plasma emission from the deflagration of the sample. The initiation time, which we define in our data as the time period after the laser pulse at which the intensity of the light emitted from the emissive plume of the sample is twice the intensity of the noise in the system, decreases by a factor of 2 (Table 2) for the stoichiometric (1:1 Al:Fe) composition as the Al particle size decreases from 120 nm to 100 nm but rises again as the particle size drops to 50 nm. The relative changes in the initiation time as a function of particle size are consistent with those observed by Granier and Pantoya for the Al/MoO\(_3\) binary system including the observation that the 100 nm Al consistently shows a faster time-to-ignition than does the 50 nm. This trend is attributed to the higher oxide-to-aluminum ratio as the particle size decreases. The high heat capacity of the excess Al\(_2O_3\) present in the smallest particles inhibits heat flow in the system thereby increasing the measured initiation time. In short, for single-pulse laser initiation, the initiation time will be related to the amount and type of reactive species generated during the pulse. The 100 nm Al will provide a larger amount of reactive aluminum during the pulse than the 50 nm, which will generate a more substantial degree of reaction initially leading to a faster time-to-ignition. Notably, this is consistent with our prior TOF-MS experiments, which show more pure Al ions (i.e. [Al]\(^+\) and [Al\(_2\)]\(^+\)) for the 100 nm particles generated per pulse than for the 50 nm. Similarly, the deflagration duration in our system is measured from the initiation time to the time when the emission intensity returns to twice the noise level.
Figure 24. Time-resolved emission of single-pulse initiated Al/Fe₂O₃ MIC materials made with 1:1, 1:1.5 and 1:2 Fe:Al ratio with (a) 50nm Al, (b) 100 nm Al and (c) 120 nm Al.
This value, which is indirectly related to the burn rate, represents the time for the entire sample to deflagrate. For variations in the deflagration duration as the Al particles decrease in size, for stoichiometric (1:1 Al:Fe) samples, a trend similar to that of the initiation time is observed with a decrease from 332.4 ms to 259.6 ms observed in going from 120 to 100 nm then a subsequent rise to 319.5 ms as the particle size drops to 50 nm. While the effect is less dramatic for the deflagration time than for the ignition time, the origin is likely the same in that the amount of available Al in the 50 nm particles is small (relative to the oxide layer) thereby inhibiting propagation of the reaction.

Within each particle size, changes in the Al:Fe ratio from stoichiometric (1:1) to progressively more fuel rich (1.5:1 and 2:1) alters the dynamics of the initiation time and deflagration duration (Table 2).

**Table 2.** The time-to-ignition, deflagration and the minimum energy for stoichiometry ratio of Al(50 nm to 120nm):Fe

<table>
<thead>
<tr>
<th>Al diameter</th>
<th>Al:Fe</th>
<th>Initiation Time (msec)</th>
<th>Deflagration Duration (msec)</th>
<th>Threshold Energy (J/cm²)</th>
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</thead>
<tbody>
<tr>
<td>50 nm</td>
<td>1:1</td>
<td>8.0±0.1</td>
<td>319.5</td>
<td>0.220</td>
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<td></td>
<td>1.5:1</td>
<td>1.4±0.1</td>
<td>212.6</td>
<td>0.010</td>
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<td></td>
<td>2:1</td>
<td>1.7±0.1</td>
<td>237.1</td>
<td>0.0125</td>
</tr>
<tr>
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<td>1:1</td>
<td>4.2±0.1</td>
<td>259.7</td>
<td>0.300</td>
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<td>1.0±0.1</td>
<td>112.5</td>
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<td>1.2±0.1</td>
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<tr>
<td></td>
<td>2:1</td>
<td>1.1±0.1</td>
<td>231.0</td>
<td>0.010</td>
</tr>
</tbody>
</table>
The time-to-ignition for each sample is shown in Table 2, where going from stoichiometric (1:1) to 1.5:1 Al:Fe, within each Al particle size, shows a large decrease in the initiation time. Going above that ratio to the very fuel rich 2:1, however, results in, at best, a slight increase in the initiation time for each Al particle size.

In the laser initiation event there is rapid heating of the sample in the volume defined by the area of the focused laser beam and the thermal diffusion length of the reaction. The minimum energy required to initiate the deflagration of the MIC materials reproducibly in a single pulse is of interest in determining the adaptability of these materials to use as photonic-based fuse or detonator materials. For the range of particle sizes for a fixed fuel-oxidant ratio, the minimum threshold energy densities required for reproducible single pulse initiation are compiled in Table 2. As can be seen, there is little particle size effect in the initiation threshold among the sizes studied. It is important to note, however, that when micron scale Al (3-4.5 µm) is used, the ability to initiate the materials in a single pulse becomes highly irreproducible regardless of the energy density. This suggests that the reproducibility of single pulse initiation may depend on the particle size down to a certain point but then is relatively constant. Conversely, the fuel/oxidant ratio dramatically affects the initiation threshold. In going from stoichiometric to fuel rich the threshold energy drops by over an order of magnitude. This is because the component of the MIC composition that is primarily melted and vaporized during the laser incidence event is the Al fuel. In fact, at the energy densities used for initiation of the stoichiometric materials the entire Al content in the volume heated by the laser is melted. With higher Al content much less laser power is required to generate the same amount of reactive Al thereby making initiation more facile at lower energy densities. Along with the composition of the MIC material, there is reason to expect the density of the compressed bulk sample and the presence of reactive oxygen in the free space of the sample may also have an effect on the threshold energy required for single pulse initiation.

To explore this, samples were made with various applied pressures with the final density of the cylindrical monoliths determined from their weight and measured volume. Samples made in this way range in density from about 1.9-2.4 g/cm³ or between 44.9 and 56.7 % of the theoretical maximum density (TMD) of Al/Fe₂O₃ thermite. The threshold energy
density required for initiation, both under air and in vacuum, are listed in Table 3. As can be seen, the thresholds for initiation decrease dramatically, by over an order of magnitude, as the density decreases. This effect likely arises from the higher available surface area in the low-density material, which provides more reactive sites for the mobile aluminum to react with. In addition, the amount of air in the pores, which will be larger at lower density, can react exothermally with the aluminum to generate heat that will contribute to the initiation of the overall reaction. This concept was tested directly by initiating the reaction in a vacuum (Table 3). As can be seen from the data, the absence of air results in a modest but measureable increase in the photoinitiation energy threshold suggesting that external oxygen does contribute to the initiation process but appears not to be as significant as the surface area effects.

Table 3. Energy density (J/cm²) required in order to initiating combustion in thermite having stoichiometric ratio Fe/Al (1:1) with 50 nm, 100 nm and 120 nm Al particle size compressed at different pressures

<table>
<thead>
<tr>
<th>Al diameter</th>
<th>Density (g/cm³)</th>
<th>% TMD</th>
<th>Threshold energy (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>air</td>
</tr>
<tr>
<td>50 nm</td>
<td>2.4</td>
<td>56.5</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>54.1</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>49.4</td>
<td>0.01</td>
</tr>
<tr>
<td>100 nm</td>
<td>2.4</td>
<td>56.5</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>54.1</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>49.4</td>
<td>0.01</td>
</tr>
<tr>
<td>120 nm</td>
<td>2.1</td>
<td>56.5</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>54.1</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>49.4</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Pantoya and Granier have studied the effect of sample density on the dynamics of energy release, specifically the burn velocity, for the Al:MoO$_3$ system.$^{10}$ In those studies it was found that for the MIC materials, the burn rate decreased as the density of the sample increased until it reached a value close to zero at 50-60 % TMD. Paradoxically, materials made with micron scale Al showed the reverse trend with the burn rate essentially constant until a density of ~50 % TMD at which point the burn rate began to increase. These opposing trends were addressed in more detail in a recent paper where it was suggested that the decrease in burn rate for the MIC materials was due to compression-induced damage to the oxide shell at high densities with the concomitant reduction in free volume around the particles suppressing the melt-dispersion mechanism and therefore retarding the burn velocity. For micron scale thermites the flame propagation proceeds by a conventional diffusion mechanism that increases with increased density.$^{71}$ For the Al:Fe$_2$O$_3$ MIC system the two primary parameters measured in our experiments, the initiation time and the deflagration duration, were measured as a function of sample density (Table 4).

**Table 4.** The initiation time and deflagration duration for density as function of sample density

<table>
<thead>
<tr>
<th>Density (g/cm$^3$)</th>
<th>% TMD</th>
<th>Initiation Time (msec)</th>
<th>Deflagration Duration (msec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.30</td>
<td>30.6</td>
<td>10.8</td>
<td>376</td>
</tr>
<tr>
<td>1.35</td>
<td>31.8</td>
<td>7.5</td>
<td>379</td>
</tr>
<tr>
<td>1.65</td>
<td>38.9</td>
<td>4.9</td>
<td>353</td>
</tr>
<tr>
<td>1.86</td>
<td>43.9</td>
<td>4.2</td>
<td>365</td>
</tr>
<tr>
<td>2.00</td>
<td>47.1</td>
<td>3.8</td>
<td>360</td>
</tr>
<tr>
<td>2.16</td>
<td>50.9</td>
<td>1.1</td>
<td>362</td>
</tr>
<tr>
<td>2.31</td>
<td>54.4</td>
<td>0.9</td>
<td>279</td>
</tr>
<tr>
<td>2.36</td>
<td>55.7</td>
<td>3.7</td>
<td>260</td>
</tr>
<tr>
<td>2.50</td>
<td>59.0</td>
<td>14.7</td>
<td>356</td>
</tr>
</tbody>
</table>
Figure 25. (a) Initiation time and (b) deflagration duration as a function of sample density.

A plot of the initiation time and deflagration duration as a function of the % TMD of the samples is shown in Figure 25. The initiation time (Figure 25a) shows a clear decrease with a minimum occurring around 55 % TMD, after which it rapidly increases again as the density goes to 60 % TMD. The trend observed for the deflagration duration is less well
defined due to scatter in the data, however there appears to be a modest decrease in the time as a function of density with an abrupt, albeit reproducible, drop in the deflagration duration around 50-60 %. Since the deflagration duration is indirectly related to the burn rate a comparison of this data with the burn velocity reported by Pantoya is justified. Qualitatively the trends are similar in the low density region, in particular, in the density range from 30-45 % TMD the values are slowly changing with the lowest values occurring around 50 % TMD.\textsuperscript{71} In the deflagration data the decrease that occurs close to this point is more abrupt and we also observe an increase in the duration at the highest density that was not reported for the Al:MoO\textsubscript{3} system.

In MIC thermite materials the density of the samples is usually referenced to the theoretical maximum density (TMD) of the binary fuel/oxidant system, which is the density that would be realized if all free volume between the particles could be removed. In particular, for MIC materials prepared for experiments such as ours, the samples are poured as powders into a die and then compressed, the measured density in grams per volume of the sample after compression is then expressed as a percent of the TMD. While this provides a useful basis for comparison, what is overlooked in this protocol are differences in the maximum packing density of binary fuel-oxidant systems of different particle sizes and composition.

\begin{equation}
\eta = \eta_{\text{Fe}_2\text{O}_3} + \eta_{\text{Al}} = \frac{V_{\text{Fe}_2\text{O}_3} + V_{\text{Al}}}{V} \tag{1}
\end{equation}

\begin{equation}
d = \eta_{\text{Fe}_2\text{O}_3} d_{\text{Fe}_2\text{O}_3} + \eta_{\text{Al}} d_{\text{Al}} \tag{2}
\end{equation}

Specifically, the maximum density obtainable by a binary set of particles is given by their maximum packing fraction (\(\eta\)), which is the volume of the two components divided by the volume they occupy (V) (Eq. 1). Equation 2 relates the typically cited density in mass/volume units to the packing fraction. The maximum packing fraction will in turn depend on the relative size of the fuel and oxidant particles and on their relative number. The maximum packing fraction for each size ratio will therefore represent a different percent of TMD and, as a result, the amount of compression necessary to arrive at a specific percent TMD for each composition will also be different. In general, for a specific composition the
maximum packing fraction will increase, as the size difference between the two types of particles gets larger. For a sample that is initially loose packed, compression will primarily reduce interparticle volume and increase overall density until the maximum packing fraction is attained. Compression to densities above that fraction will necessarily involve stress-induced deformation of the particles, which will affect the dynamics of energy release. In compressing a sample to a specific % TMD the amount of deformation experienced by the sample will depend on the difference between the density of its maximum packing fraction and the TMD. Samples whose maximum packing fraction is much less than the TMD will require more compression to achieve a particular percent % TMD and, hence, undergo more deformation. Since the maximum packing fraction depends acutely on the particle size this effect is likely to be important in comparing micro and nano-scale thermite composites.

To quantify the maximum packing fractions for different size ratios and compositions of conventional and MIC thermite materials we have conducted a series of Monte Carlo simulations. While details of the computational methodology are given in the experimental section, briefly, following a published protocol, we assume a hard sphere model with the packing statistics determined from letting the particles fall under the acceleration of gravity. When the particle falls, the lowest point is recorded and the procedure repeated until the absolute lowest point is determined. In general a large number of trials are required to obtain tight packing. What emerges from these calculations is information about the packing densities for the different size ratios and compositions and quantitative information about the number of contact points between the particles, which provides a very clear picture of the origin of the advantages of MIC materials in energy release.

A snapshot taken from the simulation of the conventional and MIC thermites at stoichiometric compositions are shown in Figure 26, which facilitates visualization of the vast differences between conventional and MIC materials. In particular, Figure 26a shows the maximum packing fraction of a conventional thermite with both the fuel and oxidant having the same particle size (3 µm) whereas Figure 26b,c show MIC materials (3 µm Fe₂O₃, 100 nm Al) both at a stoichiometric composition. Clearly evident is the “sea” of Al particles in contact with the Fe₂O₃ (Figure 26b) and in Figure 26c the close packed array the large Fe₂O₃ spheres assume with the interstices containing the Al.
Initially calculations were carried out on conventional thermite materials where the aluminum and iron oxide particle were assumed to be the same size (3 µm) and the composition is stoichiometric (i.e. 1:1 Al:Fe). From the simulation we obtain the maximum packing fraction, \( \eta \), which is defined as the sum of the volumes of the Al and Fe\(_2\)O\(_3\) spheres divided by the volume they occupy (Eq. 1). For simple monodispersed hard spheres the maximum packing corresponds to the random close pack (RCP) limit, which typically has a value of \( \eta_{rcp} \approx 0.60 \). For the conventional thermite, even though it is a binary system, since the size of both components is the same, it will behave as monodispersed with a maximum packing fraction that will correspond to a RCP limit. The packing fraction obtained from the

**Figure 26.** (a) Maximum packing of binary fuel-oxidant system of the same particle size (3 µm), (b) maximum packing for MIC materials with 3 µm oxidant (red) and 100 nm fuel (gray), showing the fuel surrounding the oxidant and (c) emphasizing the close packed array of oxidant particles.
simulation is $0.5534 \pm 0.003$, which, while close to the RCP values for a simple hard spheres, is slightly lower and falls into what is referred to as random loose packing.\textsuperscript{74} The mass density is obtained Equation 2 and the free volume will be given by $1 - \eta$ with TMD reached at $\eta = 1$. For the conventional thermite the maximum packing fraction has a mass density of 2.45 g/cm$^3$, which is equal to 56.2 % of TMD.

For binary systems of hard spheres that are not monodispersed, the maximum packing fraction will depend strongly on both the size ratio and the composition. In the limit of an infinite size ratio the theoretical packing fraction as a function of composition can be computed using Equations 3. For metastable interstitial composites, the RCP packing fraction ($\eta_{\text{RCP}}$) to be used in Eq. 3 is $0.5534 \pm 0.003$, determined as before from the simulation of the monodispersed conventional thermite. Using this value, the theoretical packing fraction as a function of composition is shown in Figure 27 with the maximum packing fraction ($\eta_{\text{max}}$) associated with a specific composition ($w_{\text{max}}$), which is the volume fraction of the oxide ($\text{Fe}_2\text{O}_3$) component, computed from Equations 3 and 4, respectively.

![Figure 27](image-url)
The plot shown in Figure 27 can be divided into two compositional regions. At \( w_{\text{max}} \) itself, the larger spheres make up an RCP array with the smaller particles completely filling the interstitial spaces. In the region above the maximum, \( w > w_{\text{max}} \), the number of large spheres outnumbers the small spheres thereby forming an RCP array with the small particles distributed in, but not filling, the interstices. In the region below the maximum, \( w < w_{\text{max}} \), small particles start to dominate, overfilling the interstitial region, effectively suspending the \( \text{Fe}_2\text{O}_3 \) particles in a sea of Al which reduces the packing fraction until, at the limit of zero \( \text{Fe}_2\text{O}_3 \), they attain a monodispersed RCP close packing.

For the MIC materials made with 100 nm Al, the composition at the maximum packing density, \( w_{\text{max}} \), corresponds to a mole ratio of 0.35:1 Al:Fe that is sub-stoichiometric in Al for the chemical reaction. For stoichiometric (Al:Fe 1:1) and fuel rich (Al:Fe 1.5:1) MIC materials the \( \text{Fe}_2\text{O}_3 \) fraction occurs at \( w_{\text{Fe}_2\text{O}_3} = 0.608 \) and 0.540, respectively, which will be expected to have a lower packing fraction due to the excess of small particles which more than fill the interstitial spaces. In short, due to the stoichiometric constraints, MIC materials will usually have values for their packing fraction well below the maximum. Simulations to determine the maximum packing fraction of the actual MIC materials which have a size ratio of \( R=30 \) were carried for both stoichiometric and fuel rich composition. The values obtained are listed in Table 5 and plotted on the graph in Figure 27.

\[
\eta = \frac{\eta_{\text{RCP}}}{1 - w_{\text{Fe}_2\text{O}_3} (1 - \eta_{\text{RCP}})} \quad \text{for} \quad w_{\text{Fe}_2\text{O}_3} < \frac{1}{2 - \eta_{\text{RCP}}} \tag{3}
\]

\[
\eta = \frac{\eta_{\text{RCP}}}{w_{\text{Fe}_2\text{O}_3}} \quad \text{for} \quad w_{\text{Fe}_2\text{O}_3} > \frac{1}{2 - \eta_{\text{RCP}}} \tag{4}
\]

\[
\eta_{\text{max}} = \frac{V_{\text{Fe}_2\text{O}_3} + V_{\text{Al}}}{V} = \eta_{\text{RCP}} (2 - \eta_{\text{RCP}}) = 0.801 \tag{5}
\]

\[
w_{\text{Fe}_2\text{O}_3}^{\text{max}} = \frac{V_{\text{Fe}_2\text{O}_3}}{V_{\text{Fe}_2\text{O}_3} + V_{\text{Al}}} = \frac{1}{(2 - \eta_{\text{RCP}})} = 0.701
\]
As would be expected they fall below the theoretical limit of infinite size ratio but follow the same trend. Both of the compositions lie below \( w_{\text{max}} \) in the region where the small particles exceed the available interstitial voids thereby disrupting the RCP structure of the larger particles leading to a lower packing fraction. The stoichiometric MIC materials with 100 nm Al have a maximum packing fraction of 0.605, higher than the conventional thermite and corresponding to 2.55 g/mol or 58.8 % of TMD. When the composition of the MIC materials are shifted to a fuel-rich composition (1.5:1 Al:Fe) the packing fraction drops to 0.596±0.01 as would be expected for the larger amount of small spheres, this packing fraction corresponds to a weight density of 2.44 g/ml. Since the TMD for the fuel rich composition (4.07 g/cm\(^3\)) is lower than that of the stoichiometric composition the maximum packing fraction actually corresponds to 60.0% of TMD even though it has a lower maximum packing fraction. In either case, if compression occurs that results in densities greater than those corresponding to the maximum packing fraction it will necessarily involve mechanical stresses being applied to the components, which, on a microscopic level can result in deformation and defect formation in the surface oxide that can affect reactivity. It is evident from density data in Table 4 that most of the densities achieved from relatively large applied pressures result in packing fractions well below even the random loose packing limit, with the application of pressure resulting primarily in the movement of particles toward the maximum

<table>
<thead>
<tr>
<th>Al</th>
<th>( w_{\text{Fe2O3}} )</th>
<th>( R ) (( d_{\text{Fe2O3}}/d_{\text{Al}} ))</th>
<th>( \eta )</th>
<th>( \eta_{\text{Fe2O3}} )</th>
<th>( \eta_{\text{Al}} )</th>
<th>( d(\text{g/cm}^3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 ( \mu \text{m} ) (1:1 Al:Fe)</td>
<td>0.540</td>
<td>1</td>
<td>0.5534±0.003</td>
<td>0.355</td>
<td>0.218</td>
<td>2.45</td>
</tr>
<tr>
<td>100 nm (1:1 Al:Fe)</td>
<td>0.608</td>
<td>30</td>
<td>0.605±0.01</td>
<td>0.363</td>
<td>0.242</td>
<td>2.55</td>
</tr>
<tr>
<td>100 nm (1:1.5 Al:Fe)</td>
<td>0.540</td>
<td>30</td>
<td>0.596±0.01</td>
<td>0.323</td>
<td>0.277</td>
<td>2.44</td>
</tr>
</tbody>
</table>
packing fraction. Obviously, in the real system the particles will not simply slide frictionlessly into more efficient packing but will also experience stress related fractures and deformations.

Notwithstanding this, it is reasonable to assume that a significant component of the compression process will be a rearrangement of the particles into more efficient packing. This will result in an increase in the interparticle contacts that would be expected to enhance mass transfer as the reaction becomes initiated. This would explain the decrease in initiation time as a function of compression at the lower density region of Figure 25. In the very high density range, at values of the % TMD that fall well above the maximum packing fraction, the Al particles distort and ultimately fuse to form larger particles - in essence the MIC materials begin to resemble micron scale conventional thermites, which is reflected in their energy release kinetics. This assertion is supported by microscopy analysis of compacted Al:MoO$_3$ MIC materials performed by Pantoya.$^{71}$

Based on this analysis we would expect dramatic changes in the dynamics when a thermite material has been compressed beyond its maximum packing fraction. From our simulation of the stoichiometric compositions of the MIC materials the density at maximum packing fraction is 2.5 or 58.36 % TMD. As can be seen in Figure 25, this agrees extremely well with the minimum reached for both the initiation time and deflagration duration in the MIC materials with a rapid increase in both quantities occurring at densities above this limit. Notably, this point in the density is also in good agreement with the minimum in the burn rate observed by Pantoya for the Al:MoO$_3$ MIC material.$^{10}$ Finally, the maximum packing fraction of the conventional thermites corresponds to a density of around 2.45 or 57.7 % TMD, which is also in good agreement with the upturn in burn rate that was observed for the micro scale thermite materials. In both size regimes it is when the materials are compressed above their maximum density that changes in the mechanism occur. The mechanistic changes that occur at this point will differ between micro and nanoscale thermite as has been analyzed in detail.$^{71}$

In addition to the packing fraction realized for specific compositions and particle size ratios, another factor that will impact reactivity is the number of fuel-oxidant contacts. The simulations provide a quantitative measure of these interparticle interactions (Table 6). As would be expected, the number of fuel-oxidant contacts increases dramatically, by in excess of two orders of magnitude in the MIC materials, when compared to conventional thermite.
Moreover, as the composition becomes more fuel-rich, the number of fuel-oxidant contacts increases further. In studies of the effect of the fuel/oxidant ratio on the initiation time and burn rate for the Al/MoO$_3$ system it was found that the maximum of each was realized at a slightly fuel rich composition.

**Table 6.** Average number of contacts per Fe$_2$O$_3$ particle

<table>
<thead>
<tr>
<th></th>
<th>Al-Fe</th>
<th>Fe-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 μm Al (1:1 Al:Fe)</td>
<td>2.32</td>
<td>3.56</td>
</tr>
<tr>
<td>100 nm Al (1:1 Al:Fe)</td>
<td>1.51x10$^3$</td>
<td>1.83</td>
</tr>
<tr>
<td>100 nm Al (1.5:1 Al:Fe)</td>
<td>1.56x10$^3$</td>
<td>1.55</td>
</tr>
</tbody>
</table>

We observe a similar effect for the Al/Fe$_2$O$_3$ system where composition of 1.5:1 Al:Fe has shorter initiation times and deflagration durations. At composition ratios >2:1, the time to ignition begins to increase again. The origin of this effect may be attributed in part to the specific packing parameters. The effect of increasing the amount of fuel will be to increase the number of fuel-oxidant contacts. As can be seen in Table 3, our simulations predict an increase in Al-Fe$_2$O$_3$ contacts in going from stoichiometric to 1.5:1 (Al:Fe) excess fuel. Clearly the increase in contacts is slowly varying and will only approach the maximum number of contacts, which we estimate to be ~1.708x10$^3$, at very large amounts of Al. When this happens, the thermal and energetic effects of the excess Al will overshadow any advantage gained by the increase in contacts. In studies by Granier and Pantoya, the trend in reactivity at modestly fuel rich compositions has been attributed to a contribution to the overall heat evolution by the reaction of the excess fuel with available oxygen.$^9$ This is not inconsistent with our analysis since the excess Al will also decrease the packing fraction leaving more free volume for oxygen.
Conclusions

There are systematic changes in the energy release dynamics of Al/Fe$_2$O$_3$ MIC materials as a function of both the density of the samples and their composition (fuel/oxidant ratio). As the density of the samples increase the initiation time and deflagration duration decrease until a density of ~55-60 % TMD is attained, after which these processes again increase. Similarly as the fuel/oxidant ratio goes from stoichiometric to fuel rich the initiation time and deflagration duration dramatically decreased in the fuel rich sample (1.5:1 Al:Fe) but this trend reverses as the sample become even more fuel rich (i.e., 2:1 Al:Fe). It was found theoretically, through a series of Monte Carlo simulations, that these trends could be explained in part by the particular packing properties of the disparately sized binary spheres that make up the MIC materials. In particular when these trends are considered in terms of the maximum packing fraction of a particular composition and sphere size ratio, it can be seen that in the range of 55-80 % TMD the close packing of the material has been exceeded and compression forces are going into stressing, deforming and fusing the particles. Similarly the effect of fuel rich compositions on energy release dynamic is attributable, at least in part, on the increased number of fuel oxidant contacts that come with higher fuel content.
SUMMARY

This study has shown that the high-quality thin films can be made from a new epoxide-catalyzed sol-gel method used to make Fe$^{3+}$ oxide/hydroxide gels. The resulting Fe$^{3+}$ oxide/hydroxide gel films can be converted to hematite, maghemite, or iron through calcination. Under either inert or oxidative conditions, the Fe$^{3+}$ oxide/hydroxide gels films appear to produce only hematite, the morphology of film that is quite similar to those formed with organic gelation agents. Thermal processing under a reducing condition can convert either the Fe$^{3+}$ gel films or the hematite films to a continuous distribution of submicrometer Fe particles on the surface. When discrete iron particles on the surface were reoxidized slowly with a very low O$_2$ concentration, the formed film was composed with of a very well-formed maghemite crystallites. This approach may suggest a general route for producing metallic and oxidic thin films of a series of metals. Moreover, it was found that multilayer structures containing a surface oxide phase of Fe$_2$O$_3$ were produced through the thermite reaction when Fe$^{3+}$ oxide/hydroxide gels thin films were fabricated on a silicon substrate and thermally processed at a low temperature. There were metallic iron particles between the Fe$_2$O$_3$ layer and the silicon surface, that was produced by reduction at the silicon surface, only at the interface and at a temperature well below what is required to initiate the combustion of bulk thermite. The size and distribution of the reduced iron particles at the interface and the low temperatures at which they form may be due to the thickness and irregularities of the native oxide layer on the silicon surface. This result represents a new method for making multilayer structures.

Also, the dynamics of the photothermal initiation of Al/Fe$_2$O$_3$ MIC materials with an 8 ns single pulse of a Nd:YAG laser were studied by time-resolved spectroscopy of the light emitted from the igniting and deflagrating material plasma of the reacting material. In the initial stage, the dynamics from the initial laser excitation to combustion could be explained by the amount and type of reactive species generated during the pulse as a function of the Al particle size. The time-to-ignition of the ~3-4.5 µm size Al/Fe$_2$O$_3$ MIC material was much shorter than the 100 nm and 50 nm Al MIC samples. These results were attributed to the higher oxide-to-aluminum ratio observed as the particle size decreases due to the high heat
capacity of the excess $\text{Al}_2\text{O}_3$ present in small particles inhibiting the heat flow in the system. Also, the effect of stoichiometry and compressed sample density were studied with measuring two fundamental parameters: the time to initiation time and deflagration duration. In the effect of stoichiometry, the initiation time and deflagration duration for Al (50nm, 100nm, and 120 nm)/ $\text{Fe}_2\text{O}_3$ MIC samples were dramatically decreased as Al/Fe ratio goes from stoichiometry to the fuel rich sample (1.5:1 Al:Fe) but the trend of these reverses in the most fuel rich (2:1 Al:Fe) sample. These trends could be attributed to the increased number of fuel oxidant contacts that come with higher fuel content. In effect of density of the compressed sample, as the density of the samples is increased the initiation time and deflagration duration decrease until a density of $\sim 55$-60 % TMD is attained, after which these processes again increase. These trends could be explained theoretically, through a series of Monte Carlo simulations, as the particular packing properties of the disparately sized binary spheres that make up the MIC materials. In particular when these trends are considered in terms of the maximum packing fraction of a particular composition and sphere size ratio, it can be seen that in the range of 55-80 % TMD the close packing of the material has been exceeded and compression forces are going into stressing, deforming and fusing the particles.
REFERENCES


BIOGRAPHICAL SKETCH

The author was born in Changyoung, KyungNam, South Korea. He completed his Bachelor of Science degree in Chemistry in February 1999 at SungKyunKwan University in Seoul, South Korea. He started graduate work in inorganic chemistry at SungKyunKwan University, where he received a Master’s of Science in inorganic chemistry at February 2001. He enrolled doctoral program in Department of Chemistry and Biochemistry in fall of 2002 and received Ph. D. in inorganic chemistry in fall of 2009.