PYROPHORIC NANOPARTICLES AND NANOPOROUS FOILS FOR DEFENSE APPLICATIONS

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ABSTRACT

The formation of pyrophoric Fe-nanoparticles and foils from Fe(II)-oxalate and Fe-oxyhydroxide gel was investigated after thermal decomposition and reduction under H_2 atmosphere. The Fe(II)-oxalate was synthesized by a controlled nucleation process involving the addition of oxalic acid in an $FeCl_2 \cdot 2H_2O$ solution followed by separation and drying. The gel was synthesized using the Fe(II) salt, non-ionic surfactant, and propylene oxide. Oxalate powder was sandwiched between two mesoporous Y_2O_3 barrier layers on a metal foil, whereas the Fe-oxyhydroxide gel was coated directly on a foil to prepare the reactive substrates. In other experiments, the gel was infiltrated inside a porous alumina substrate. As-synthesized reactive materials were decomposed in a quartz tubular reactor at 450-520^oC, reduced with a gas mixtures containing 5-100 vol% of H_2 in N_2, and exposed to air at ambient conditions to determine their pyrophoric properties. The bulk powder and foils prepared from Fe-oxalate produced a pyrophoric reaction temperature of about 800^oC in less than 1 sec. The porous substrates containing reduced Fe from the gel produced a pyrophoric temperature above 900^oC. Tunable pyrophoric materials were obtained by mixing Fe-oxalate in different weight proportions in the Y_2O_3 gels, which showed a variation in pyrophoric reaction temperature from 80^o to 600^oC at the weight ratio of 30-80%.

Keywords: Fe-oxalate, nanorods, Fe-oxyhydroxide, α-Fe, reactive substrates, tunable pyrophoric materials

1. INTRODUCTION

Army defense systems are continuously being improved primarily to make soldiers in the combat zone less vulnerable to enemy and environmental threats. Gorilla war, roadside bombs, low-flying aircrafts, and unmanned aerial vehicles are some of these threats that soldiers are often subjected to in a war zone. Nanotechnology offers several great opportunities for improving defense systems and providing soldiers with unique capabilities to promptly react to various emergency situations in a battlefield environment. Because of its unique properties, nanomaterials find applications in early threat detection, blast protection, and temporary pain relief to injured soldiers etc. Pyrophoric nanomaterials are very versatile in this regard, as they can be utilized for making flares to distract the enemy or signal fellow soldiers in combat zone, infrared countermeasure decoy flares for low flying aircrafts, and activated heat wraps or air warmers. Many of these pyrophoric applications demand materials with tunable properties, which motivated us to undertake current research efforts using nanomaterials due to their unique properties.

Among several pyrophoric materials, iron (Fe) in the form of fine particles is extremely reactive and pyrophoric [1]. Fe is the most common transition metal abundantly available in the Earth's crust and it is the structural backbone of our industrial infrastructure. Nanoparticles of Fe are currently being investigated for electrical, dielectric, magnetic, optical, imaging, biomedical applications. Although the pyrophoric behavior of fine Fe particles was known for a long time, a very few studies report pyrophoric behavior of Fe-nanoparticles. Other specific applications of Fe-nanoparticles include catalysis [2], magnetic resonance imaging [3], magnetic data storage [4], coatings [5], synthesis of carbon nanotubes [6], synthesis of highly oriented and ordered nanostructures for field emission devices [7] etc.

The technology that is currently being employed to produce pyrophoric materials utilizes α-Fe coating onto a steel foil [8]. This coating is achieved by either dip coating or spraying homogenized slurry of Fe and Al powders in suitable solvent containing a binder. The coated foils are annealed to remove the solvent and binder components and heated further to about 1000^oC in reducing atmosphere to produce Fe/Al alloy. From this alloy, Al is selectively solubilized with hot NaOH solution, which produces high surface area foil containing reactive α-Fe [9-12]. The foil readily reacts with air and generates temperature of about 700-800^oC in less than 1 second [8] and burns for about 20-40 seconds. In general, decoy materials generate temperature of 820^oC in less than one second that sustains above 750^oC for twelve seconds after their exposure to air. The alloys can be

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further doped with boron, titanium, and tin to improve the pyrophoric action. Alternatively, the addition of oxides such as Al_2O_3 or SiO_2 can slow down the burn rate and make the pyrophoric response less intense. Although, the current process of manufacturing reactive foils containing Fe deserves many merits, the use of hot and concentrated NaOH solution making us to recognize the challenges involving the process safety and environmental hazards.

The method of producing high surface area porous reactive Fe by sol-gel technique has been invented by Lawrence Livermore National Laboratory (LLNL). The major advantage of this method is that it does not involve addition of the hot NaOH solution. The porous reactive substrates produced by this method, however, are disadvantageous because they are not readily pyrophoric. Interestingly, the investigators reported that they are thermally ignitable [8] and their pyrophoric action improves by the addition of W or Sn. In the studies reported by these investigators [8], the sol-gel derived porous Fe(III) oxide material was prepared by using the precursors such as $Fe(NO_3)_3.9H_2O$, $FeCl_3.6H_2O$, and anhydrous $FeCl_3$. These gels were reduced in the reducing atmosphere of 25-100% H_2 in Ar/N_2, or CO_2/CO at the temperatures of 350^o-700^oC. After reduction, the reactive Fe produced as porous foils was thermally ignitable. As the invention [8] indicates some success in producing pyrophoric nanoparticles or foils by the sol-gel approach, it is worth continuing the efforts to understand the fundamental aspects of the pyrophoric reactions and further development of pyrophoric foils. Alternatively, thermal decomposition of Fe-pentacarbonyl, plasma processing of Fe precursors, and thermal reduction of Fe-oxides or oxalate in H_2 environment can also produce pyrophoric fine Fe.

Our research group [13,14] has recently reported synthesis of pyrophoric Fe nanoparticles from oxalate and oxide precursor powders. After thermal decomposition and reduction of these precursors, the fine Fe nanopowder was found to be pyrophoric upon exposure to the ambient air. The pyrophoric reaction temperature of 800^oC was achieved for the Fe-oxalate precursor synthesized in our laboratory [13,14]. For the specific defense applications especially for the flares, the reactive Fe needs to be immobilized on a thin substrate. In this regard, we adopted two synthesis routes; in route-I, Fe-oxalate particles were sandwiched between the two mesoporous barrier layers on a metal foil. The selection of Y_2O_3 is based on the rationale that this barrier material does not interfere with the IR radiations. Tunable pyrophoric materials were also prepared by combining the Y_2O_3 gel with Fe-oxalate at various mass loadings. In route-II, the sol-gel method was adopted where non-ionic surfactants were combined with Fe(II) sol solution and the gelation was accomplished with a proton scavenger. The gels were also coated on a metal foil to immobilize the reactive Fe-nanoparticles. Additionally, the as-prepared Fe(II) gels were infiltrated inside the thin porous alumina substrate. All the substrates were thermally decomposed, reduced in H_2 atmosphere, and finally, exposed to ambient air to determine their pyrophoric response.

2. EXPERIMENTAL

2.1 Materials

Ferrous chloride ($FeCl_2{\cdot}2H_2O$) and oxalic acid (HOOCCOOH) were purchased from Alfa-Aesar and Sigma-Aldrich, respectively and used for the synthesis of the Fe-oxalate powder. Yttrium chloride ($YCl_3{\cdot}7H_2O$), ethanol, Brij-76 surfactant and propylene oxide used were procured from Sigma-Aldrich whereas the P123 surfactant was purchased from BASF. Stainless steel foil and porous alumina substrate were obtained from the McMaster Carr.

2.2 Synthesis of Fe(II)-oxalate

In the synthesis approach, an oxalic acid solution in de-ionized water was gradually added to the $FeCl_2{\cdot}2H_2O$ solution. The solution mixture was heated to 60-70^oC under magnetic stirring and maintained for 2 hrs prior to centrifugation. Details on the synthesis procedure can be found elsewhere [13,14]. Fe-oxalate nanorods were synthesized using polyethylene glycol (PEG-600) surfactant. In this, oxalic acid, $FeCl_2{\cdot}2H_2O$ and PEG-600 were homogeneously mixed together for about 30 min. The contents were diluted with de-ionized water and ethanol, sonicated for 4 h and finally centrifuged to recover the precipitate. More detailed description was reported elsewhere [14].

2.3 Synthesis of Fe(II) sol-gel

The method used for the synthesis of Fe(II) gel started with the mixing of ethanol, $FeCl_2{\cdot}xH_2O$, and Brij-76 or Pluronic P123 surfactant. Next, the mixture sonicated until both the $FeCl_2{\cdot}xH_2O$ and surfactant were completely dissolved in the ethanol. Propylene oxide was added to the solution mixture and it was sonicated for few minutes and left undisturbed for gelation to occur. The gel time was found to be dependent on the amount of propylene oxide addition with respect to the concentration ratio of the precursor to surfactant.

2.4 Synthesis of Y-oxyhydroxide gel embedded with Fe-oxalate particles

To synthesize the Y-oxyhydroxide gel, Solution-A containing $YCl_3{\cdot}7H_2O$ in ethanol and Solution-B of Brij-76 (20-30 wt%) in ethanol were prepared by ultrasonic mixing. Solution-B was added drop wise to Solution-A and after mixing these two solutions, propylene oxide was added, which resulted in a transparent gel in 5 minutes. The synthesis procedure is similar to the one reported by the other investigators [15]. To the gels, Fe-oxalate powder was added and they were sonicated for few minutes. The oxalate loading was varied between 30-80 wt% based on the weight of the YCl_3 initially taken.

2.5 Preparation of the reactive substrates

2.5.1 Reactive substrate containing Fe-oxalate

This method involves dip or spin coating of a metal foil with a Y-sol solution followed by coating a layer of the oxalate and finally, dip-coating this foil again in Y-sol solution. To synthesize the gel, Y-sol solution was prepared by introducing $YCl_3 \cdot 7H_2O$ and Brij-76 (20-30 wt%) in ethanol followed by ultrasonic mixing and the addition of propylene oxide as mentioned earlier in the Experimental section 2.4. Prior to gelation, a stainless steel foil was dip coated with Y-sol solution and annealed at 100°C for 5 minutes. Next, Fe(II)-oxalate slurry in acetone containing 20 wt% polycarbonate binder was prepared and spin coated on the metal foil already coated with Y-sol solution. After drying the oxalate film for a few minutes, the foil was again dip coated in the Y-sol solution and dried at 90°C.

2.5.2 Reactive substrate with Fe(II) gel

Fe(II) sol-solution was prepared as per the method outlined in the Experimental Section 2.3. Just before the gelation, i.e. at the 80% of the total gel time, the viscous sol-solution was spun on a stainless steel foil. The thickness of the gel film was monitored by controlling the spin speed. In the other method, Fe(II) sol-solution was infiltrated inside the porous alumina substrate. Once the substrate was saturated with the sol solution, propylene oxide was added to accomplish the gel formation.

2.6 Calcination, thermal decomposition, reduction and oxidation

Calcination of the reactive substrates either coated on a stainless steel foil or infiltrated with the Fe(II) gel inside porous alumina was performed inside a muffle furnace at 400°C for 4 hrs. The heating rate of 0.5°C per minute was used to avoid possibility of defect formation due to the thermal stresses.

Thermal decomposition and reduction experiments were performed in an isothermal quartz tubular flow reactor supported inside a split furnace. The reactor was connected to the volumetric flow meters for measuring the flow rates of H_2 and N_2 gases and achieving their desired volumetric mixtures. The oxalate bulk powder, stainless steel foil coated with Y_2O_3 barrier layers sandwiching the oxalate powder, the foil coated with Fe-gel, and porous alumina substrate infiltrated with the gel were individually placed inside reactor and heated to 450°-600°C under N_2 flow. Bulk powder or reactive substrates were reduced under varying H_2 concentration of 5-100 vol% in N_2 for 5-30 minutes. The samples were then allowed to cool down under H_2 or N_2 flow, removed from the tube furnace, and exposed to air at ambient conditions. Transient temperature profile of pyrophoric reaction was recorded using a Fluke IR pyrometer mounted above the sample.

2.7 Characterization

As-synthesized and calcined powder and coated substrates of the FeC_2O_4 and Fe-oxyhydroxide gels were analyzed using Fourier Transform Infrared (FTIR) (Bio-Rad Division FTS-40A) spectrometer and their microstructural characterization was performed using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

3. RESULTS AND DISCUSSION

The scanning and transmission electron microscopic images of as-synthesized and nanoscale oxalates are shown in Figure 1a and 1b, respectively. The microstructure reveals plate and rod-like particle morphology for the oxalate synthesized without the use of surfactant and nanorod morphology for the oxalate synthesized in presence of PEG. The as-synthesized and nanoscale oxalate powders were thermally decomposed at various temperatures between 450-600°C, reduced in H_2 environment and exposed to ambient air allowing α-Fe to undergo oxidation. Figure 2 shows that when 5 vol% H_2 was used at the decomposition temperature of 500°C, the maximum pyrophoric reaction temperature produced was 750°C. However, using 25 and 35 vol% H_2 at 500°C, the maximum pyrophoric temperature achieved was lower than the one observed for the oxalate reduced using 5 vol% H_2.

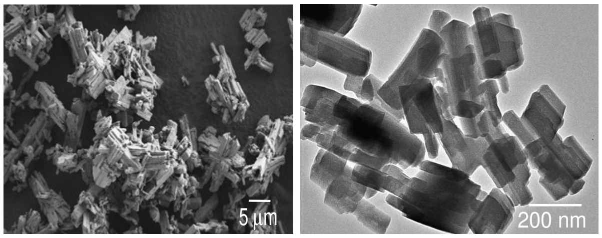


Fig. 1: a) SEM image of as-synthesized Fe-oxalate, and b) TEM image of oxalate nanorods.

The conceptual construction of a pyrophoric foil and fabrication of actual foil specimen are shown in Figure 3a and 3b, respectively. The schematic shows that the Y_2O_3 film is coated on a metal foil and on this film, an oxalate film is deposited. Finally, Y_2O_3 film is coated on top of the oxalate film.

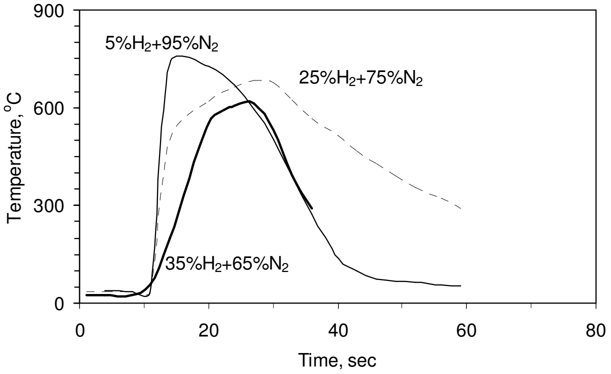
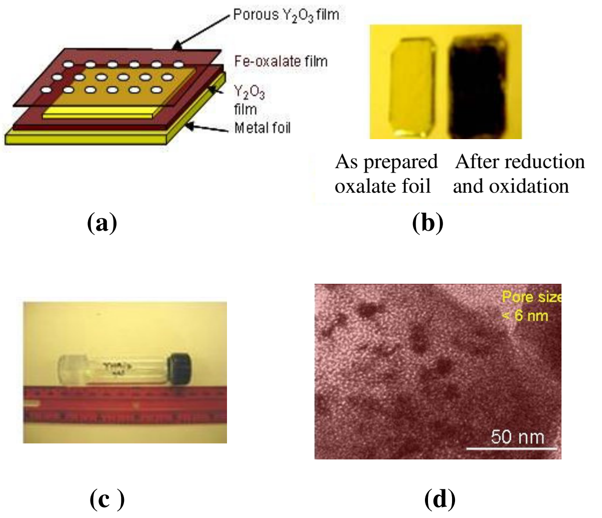


Fig. 2: Transient temperature profiles obtained after oxidizing the α-Fe produced by reducing the oxalate at various processing conditions.

The schematic also shows that the Y_2O_3 film is porous, which is desired for the heat transfer processes to occur. In Figure 3b, actual fabricated foil and the foil after pyrophoric reaction are presented. The foil was prepared as per the procedure outlined the Experimental Section, which involved sandwiching an oxalate film between the two Y_2O_3 films. As prepared Y_2O_3 gel and the microstructure of Y_2O_3 film are shown in Figure 3c and 3d, respectively. The film structure shows presence of the mesopores in the size range of 4-8 nm. The mesoporous film is desired to allow oxygen transport across the barrier and for the containment of the oxalate particles.



(a) **(b)**

(c) **(d)**

Fig. 3: a) Schematic of a pyrophoric foil, b) actual foil fabricated by sandwiching FeC_2O_4 between porous Y_2O_3 films and foil after reduction and oxidation, c) photo showing a transparent Y_2O_3 gel prepared using Brij-76 surfactant and d) TEM image of a Y_2O_3 film.

The sandwich type of oxalate foil was thermally decomposed at 500°C and reduced using 5 vol% H_2 in N_2. After reduction, the foil containing α-Fe in between the Y_2O_3 layers was exposed to ambient conditions. The transient temperature profile was recorded using an IR pyrometer and it is shown in Figure 4, which indicates the peak temperature of 840°C. The sandwich film shows satisfactory pyrophoric behavior, however, the total number of processing steps involved in making these reactive substrates and the higher processing time made us to investigate further into the alternative approaches. Additionally, in this type of the reactive substrate, the temperature could not be sustained for longer duration (e.g. >20 sec) due the less amount of α-Fe available for the pyrophoric reaction.

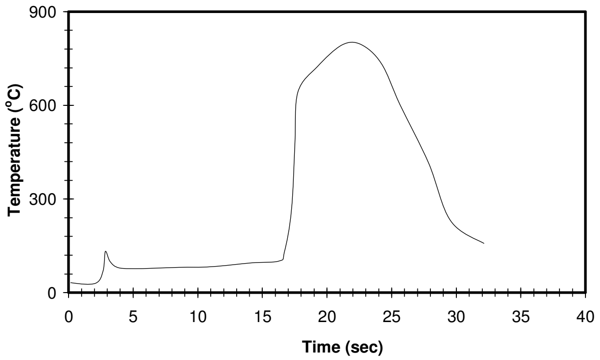


Fig. 4: Pyrophoric response of the reactive foil prepared by sandwiching FeC_2O_4 in mesoporous Y_2O_3 mesoporous layers.

Limitations associated with the sandwich type of approach are longer processing times, less reactive Fe, and delayed response of the pyrophoric reaction. Alternatively, Fe-oxyhydroxide gels can be used to produce the reactive substrates. There are several studies reported on synthesizing Fe-gels using various precursors [8,16], however, information on fabricating pyrophoric substrates is extremely meager. In this investigation, Fe(II) gels were prepared in the presence and absence of a non-ionic surfactant as outlined in the Experimental Section. FTIR spectra of various gels are shown in Figure 5. In the as-synthesized gels (not shown here), -CH vibrations were observed at around 2930 cm^{-1} suggesting the presence of organic impurities. In the calcined gel samples, residual organic impurities were found to be negligible. The broad absorption peak around 500–700 cm^{-1} can be associated with the Fe-O linkages.

The Fe-oxyhydroxide gel was coated on a stainless steel foil and also attempted to infiltrate inside the porous alumina substrate. As-prepared gel film on a metal foil was decomposed at 500°C in N_2 atmosphere and reduced with 5 vol% H_2 for 10 min. After exposing to ambient air, the temperature of the pyrophoric reaction could rise only to 60°C, whereas for the gels prepared using the surfactant, the temperature increased to 150°C. It is believed that the use of surfactant has induced porosity and thereby led to higher

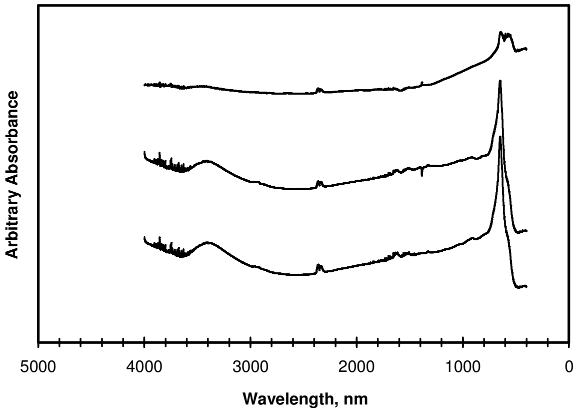
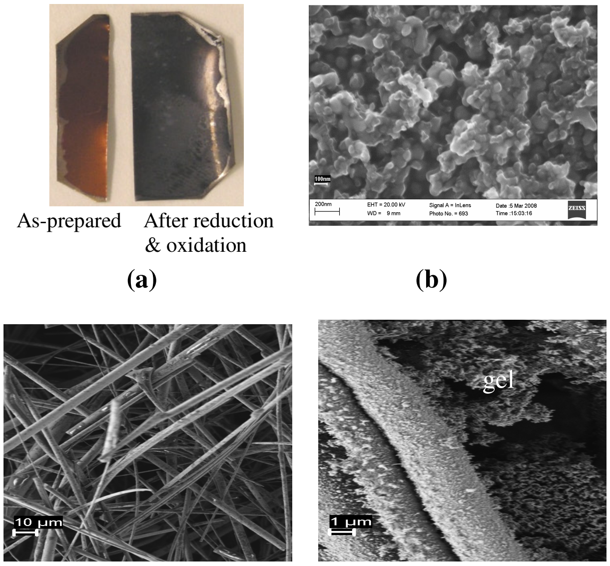


Fig. 5: FTIR spectra of Fe(II) gels prepared using non-ionic surfactants and calcined at 400°C for 4-5 hrs.

pyrophoric reaction temperature. A photo of as-prepared film and film after reduction and oxidation is shown in Figure 6a and the SEM image is depicted in Figure 6b.



(a) **(b)**

(c) **(d)**

Fig. 6: a) Photograph of reactive substrate before and after pyrophoric reaction prepared by spin coating Fe-gel, and SEM images of b) stainless steel substrate coated with Fe(II) gel after calcination, c) as-received porous alumina substrate, and d) alumina substrate containing Fe after pyrophoric reaction.

From the SEM image presented in Figure 6b, we can notice that the substrate is highly porous creating high surface area for the reaction of Fe with air. The adhesion of the Fe-oxyhydroxide film on stainless steel foil was excellent and did not show any flaking or dusting even after pyrophoric reaction for several days. One of the problems with the stainless steel foils is that the amount of Fe that was coated on the surface of the substrate was very low and it was not sufficient to get the desired pyrophoric reaction temperature.

Porous substrates have many advantages to the system such as increased surface area, possibility of more Fe infiltration, better handling capability etc. This idea was tested using alumina porous substrates. The gel was infiltrated into the porous alumina substrate and later calcined at 400°C for few hours. The pyrophoric reaction temperature profile obtained for the infiltrated inside the porous substrate is shown in Figure 7, which indicates a temperature of the pyrophoric reaction above 900°C. It also shows the pyrophoric responses of the Fe-oxyhydroxide film prepared on a stainless steel foil and Fe-oxalate sandwich type film. We can notice that in the case of the Fe-gel film deposited on a stainless steel foil, the pyrophoric temperature barely increased to 600°C whereas for the oxalate type of film the temperature reached to 840°C. Interesting observations can be made from the results presented in this figure. The gel film deposited on a metal substrate via spin coating, shows a temperature response with three temperature peaks, which is difficult to explain unless further investigation into the mechanistic aspects of the reaction is conducted. Fe-oxalate sandwich type of film shows a pyrophoric temperature greater than 820°C, however, its pyrophoric response is delayed compared to the gel film on a metal foil. This may be due to the fact that the mesoporous structure of the Y_2O_3 has induced resistance for the oxygen diffusion and subsequent oxidation.

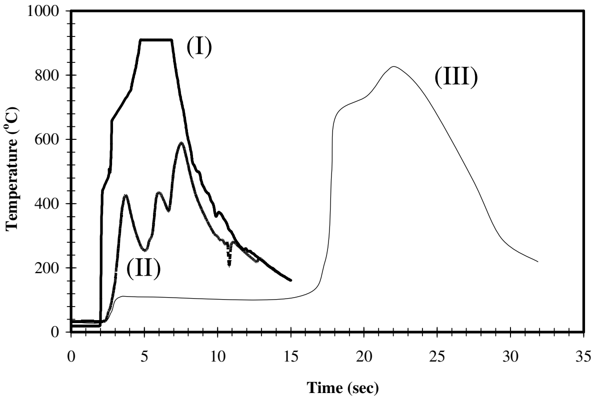


Fig. 7: Comparison of the pyrophoric temperature profiles of Fe-oxyhydroxide film coated on stainless steel foil (I), gel infiltrated inside porous alumina substrate (II), and Fe-oxalate sandwiched between two mesoporous Y_2O_3 barrier layers (III) coated on a stainless steel foil.

The Fe-oxyhydroxide gels were also prepared in the presence and absence of Brij76 and P123 surfactants. These gels were infiltrated in a porous alumina substrate and calcined at 400°C. Next, the substrates were thermally decomposed and reduced at 500°C for 20 min. The pyrophoric temperature profiles obtained for the porous substrates are shown in Figure 8. Each substrate reached a pyrophoric temperature greater than 900°C indicating that the addition of surfactant to the gel has little effect on the maximum pyrophoric temperature. In several experiments performed for the porous substrate infiltrated with Fe-oxyhydroxide gel, a pyrophoric reaction temperature of >900°C was achieved.

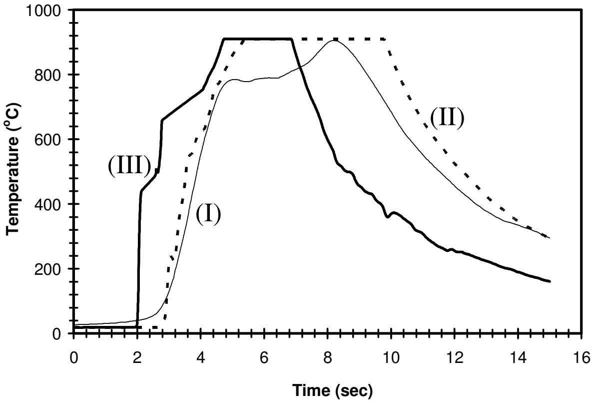


Fig. 8: Comparison of the pyrophoric temperature profiles of Fe-oxyhydroxide film prepared in presence and absence of a surfactant (I: Brij-76, II: P123, and III: no surfactant) and infiltrated inside porous alumina substrate.

To tune the pyrophoric response of the Fe-containing materials, Y_2O_3 gels were mixed with the Fe-oxalate by sonication at 30-80 wt% levels. The gels prepared by this synthesis route were heated to 500°C in N_2 atmosphere and reduced in presence of 5 Vol% H_2. The transient temperature profiles obtained after exposing the reduced gels containing various oxalate loadings are shown in Figure 9.

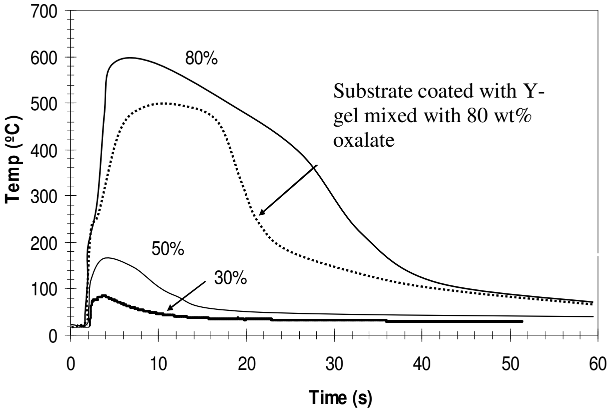


Fig. 9: Transient temperature profiles obtained after oxidizing the α-Fe produced from reducing the Y_2O_3 gels mixed with the oxalates.

It is observed that the pyrophoric reaction temperature increases as the loading of the oxalate increases from 30 to 80% (w/w). At the level of 30 wt% oxalate mixed with Y_2O_3 gel, the pyrophoric temperature could reach to 80°C whereas with 80 wt% oxalate, the pyrophoric temperature increased to 600°C. Another important observation is that the temperature sustained for longer time at the higher levels of the oxalate, which is obvious because the higher reactive Fe content produced from higher loadings of the oxalate. Thus, tunable pyrophoric materials can be easily obtained by combining Fe-oxalate or Fe-oxyhydroxide to the Y_2O_3 gel.

The porous substrates allow for the diffusive transport of atmospheric oxygen into the material where it reacts with active Fe and heat is produced. The rate at which the reaction of atmospheric oxygen occurs with the Fe depends on foil characteristics such as porosity, pore size, specific surface area, thickness of the film etc. All these characteristics of the substrate contribute to the heat capacity, heat transfer coefficient, and transport profile. In addition, ambient conditions such as temperature, oxygen concentration, air velocity and other laboratory environments (e.g. moisture) may influence the pyrophoric reactions of Fe. Our investigation explicitly provides evidences of pyrophoric reaction temperatures as high as 900°C generated after exposing the active Fe sample to the ambient air. However, we did notice inconsistencies in the pyrophoric temperatures obtained for various reactive foils. We are currently investigating the effect of several parameters on the pyrophoric behavior of reactive foils containing α-Fe for eliminating inconsistencies in the pyrophoric reaction temperature.

Presently, we are also developing a mathematical model for pyrophoric reactions that incorporates diffusive mass and heat transports, chemical reactions, and materials characteristics.

CONCLUSIONS

The α-Fe produced after thermal decomposition and reduction of the Fe-oxalates at 500°C using 5 vol% H_2 was found to be reactive in air with a pyrophoric reaction temperature as high as 800°C was achieved. The Fe-oxyhydroxide gels synthesized with and without the use of non-ionic surfactant were found to be pyrophoric as well, as they could easily react with air at ambient conditions. When the Fe-gels were coated onto a stainless steel foil and thermally reduced, a pyrophoric reaction temperature of approximately 600°C was generated. For the Fe-gel infiltrated inside the porous alumina substrate, temperatures in excess of 900°C were realized. This is the maximum temperature reported in the literature for the reactive substrates prepared with Fe-gels. The pyrophoric response of this type of reactive substrate was found to be superior as compared with Fe-oxalate based sandwich film in which case the temperature rise was delayed probably due to diffusion limitations associated with the heat transport across the mesoporous barrier layers.

Tunable pyrophoric response was obtained after thermal reduction and oxidation of α-Fe produced from the Y_2O_3 gels mixed with various loadings of the oxalate.

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