Design of a Recycling Method for Treated Aluminum Fuel

by

Wesley Cox

Submitted to the
Department of Mechanical Engineering
in Partial Fulfillment of the Requirements for the Degree of
Bachelor of Science in Mechanical Engineering

at the
Massachusetts Institute of Technology

June 2017

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Signature of Author:  

Department of Mechanical Engineering  
May 12, 2017

Certified by:  

Douglas Hart  
Professor of Mechanical Engineering  
Thesis Supervisor

Accepted by:  

Rohit Karnik  
Professor of Mechanical Engineering  
Undergraduate Officer
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Abstract

An experimental study was performed to characterize the waste byproduct of a high energy density aluminum fuel in order to identify an effective recycling method. A sample of fuel waste was generated and viewed under a scanning electron microscope. The sample was then subjected to an energy-dispersive X-ray spectroscopy analysis which focused on points of interest identified by the scanning electron microscope.

The results of the imaging and analysis showed that gallium and indium, which are used in the fuel manufacturing process, are randomly scattered around the reacted aluminum waste. These metals were found in their elemental form, meaning they do not react alongside the aluminum fuel. As such these metals can be recovered by suspending them in water and using mass differences to isolate them from the remainder of the waste.

Thesis Supervisor: Douglas Hart
Title: Professor of Mechanical Engineering
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Introduction

As technology has evolved over the years, there has been an increased need for reliable and portable power sources. Lithium ion batteries are commonly used to power devices ranging from portable electronics to electric vehicles. Despite the abundance of lithium ion batteries, they suffer from some serious drawbacks. Even at the highest levels of efficiency, lithium batteries have a peak energy density in the range of 2-3 MJ/L [1]. Additionally, they are expensive, with commercial batteries being priced as high as $167/MJ [2]. The most troubling aspect of lithium ion batteries is the fire hazard they impose on the user. Multiple consumer electronics have been reported to catch fire due to battery defects in just the past few years.

The limitations of lithium batteries have led to the exploration of alternative methods of energy storage. One such alternative is hydrogen gas, which can reach energy densities of 142 MJ/kg. Hydrogen, when combined with oxygen in a fuel cell, can generate electricity to replace batteries in applications like electric vehicles. However, hydrogen suffers from its own limitations. Predominately, hydrogen is explosive in high concentration, which makes storage hazardous. Pressurizing and storing the gas also reduces the overall energy density of a hydrogen powered system, since the gas is very light compared to the storage vessel.

One solution to this is to store the hydrogen chemically instead of physically. There are a variety of ways to chemically produce hydrogen, but one method that stands out is the use of aluminum metal. Aluminum has one of the highest energy densities of any non-nuclear material, roughly 40x that of lithium ion batteries [3]. Aluminum can be activated using gallium and indium, rendering it highly reactive with water. When activated, aluminum reacts according to the following exothermic reaction:

\[ 2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \]

Recently, a method for treating aluminum with a heated eutectic was discovered at MIT [4]. This method was able to achieve high reaction completion with only trace amounts of gallium and indium.

Treated aluminum has a lot of potential as a hydrogen fuel source, but at this time there is no method to recycle the aluminum hydroxide byproduct of the reaction. Normally the aluminum hydroxide could simply be reduced back into aluminum using the Hall-Heroult process. However, this method is insufficient because the gallium and indium used to activate the aluminum are still present in the byproduct. These metals make up more than 50% of the fuel cost, thus recovering them is essential for making an economic fuel [4].

The purpose of this study is to examine the aluminum fuel reaction in order to determine the exact chemical makeup of the waste. This study also aims to examine what happens to the gallium and indium during and after the reaction to determine whether or not they are easily recoverable.
Background

Aluminum is naturally reactive with both water and air, but it forms an aluminum oxide layer that inhibits these types of reactions. Despite being only a few nanometers thick, the surface coating is inert and prevents any reaction of the material underneath. By disrupting the aluminum oxide layer, the aluminum under the surface can react. In the case of the aluminum fuel studied at MIT, low temperature liquid metal is used to disrupt the oxide layer [4]. More specifically, a gallium indium eutectic is the liquid metal used to activate the aluminum.

This liquid has proven effective since gallium naturally wets to the surface of aluminum and diffuses across the grain boundaries. Once the gallium has passed through the oxide layer, it forms a two-phase mixture with aluminum, since aluminum is soluble in gallium at low concentrations. The high concentration of gallium in the mixture causes grain boundary separation of the aluminum which results in the liquid metal embrittlement of the bulk aluminum. The addition of the indium allows for the gallium interaction with aluminum to occur at lower temperatures. When indium and gallium are alloyed together, the resulting compound will remain a liquid at room temperature.

The method for manufacturing the fuel being studied starts by treating 6mm aluminum spheres with a heated indium and gallium bath. The aluminum is left in the heated bath for two hours to cure, and then it is removed. The curing time allows the eutectic to penetrate the grain boundaries of the aluminum, resulting in liquid metal embrittlement of the bulk. After curing, the treated spheres are centrifuged to collect as much of the excess eutectic as possible. Once the spheres are centrifuged, they are sealed in glass jars for 24 hours. After that, the fuel is active and will react readily with water.

When the activated fuel is submerged in water, it begins to break apart, rapidly heating the water and releasing hydrogen. In this time the aluminum continuously expands as it reacts with the water, forming foam that floats to the top of the water. As the reaction continues, the waste byproduct forms a grey colored suspension with the water. The waste settles over time, becoming a solid powder that can be recovered by evaporating the water. The powder is visually homogenous, giving no indication of the location or form of the gallium and indium post-reaction.

Methods

To identify the chemical makeup of the fuel waste, a sample of the waste was observed under a scanning electron microscope (SEM). A sample of aluminum fuel was reacted with water and the water was evaporated out. The dried fuel waste was crushed with a metal rod into a fine powder. The powder was viewed under a JEOL 6610LV scanning electron microscope and images of the sample were taken. Figure 1 shows a backscatter image of the fuel waste viewed at 700x magnification.
Figure 1. A backscatter image of aluminum fuel waste at 700x magnification. The bright spots represent silver colored material distributed throughout the grey powder.

After imaging the sample, an energy-dispersive X-ray spectroscopy (EDS) analysis was run to determine the elemental makeup of the sample. One scan looked at a wide view of the sample, to determine total composition and the general ratio of elements. Another scan highlighted points of interest within the SEM images. This was done to determine if visual differences in the fuel waste were structural differences or elemental differences.

**Results**

The results from the EDS can be seen in Figures 2 and 3. Figure 2 shows aluminum as red and oxygen as green. This image shows the primary product, aluminum hydroxide, taking up the vast majority of the fuel waste. Figure 3 shows gallium as violet and indium as yellow. This image shows that the bright spots viewed in the SEM images were gallium and indium. Comparing this with Figure 3 shows that the gallium and indium were in locations where oxygen was absent. This suggests that neither metal oxidized during the fuel reaction. Another observation is that the gallium and indium were spread throughout the aluminum hydroxide. In some sections had both metals while other sections had one or the other. This indicates that the indium and gallium became separated from each other during the reaction.
Figure 2. An EDS analysis image of the fuel waste divided by element. A.) The presence of aluminum shown by a red colored map B.) The presence of oxygen shown by a green colored map C.) The presence of gallium shown by a violet colored map D.) The presence of indium shown by a yellow colored map

Four areas of concentrated gallium and indium were studied further with EDS in order to determine the ratio of the metals. The areas consist of a rectangular section and three points shown in Figure 4. The first section, seen in Figure 5 shows the EDS results of a section of fuel waste with a mix of aluminum, gallium, and indium. Figure 6 shows the EDS results of a point that is predominately gallium, with traces of other metals. Figures 7 and 8 show the EDS results of points that are predominately indium, but the ratio of the metals varies. This shows that the separation of indium and gallium is random. There is no ratio maintained during separation and the separation does not go far enough to fully isolate the two metals from each other. As a result, the two metals must be recovered together and separated afterwards.
Figure 3. A backscatter SEM scan of fuel waste with four highlighted areas. The areas consist of one rectangular section the center and three points in the bottom left, bottom right, and left. These areas were the subjected to a focused EDS analysis.

Figure 4. An EDS analysis of the first area of interest. This graph shows a rectangular section of the fuel waste with a mix of aluminum hydroxide, gallium, and indium.
Figure 5. An EDS analysis of the second area of interest. This graph shows a point of the fuel waste with predominately gallium and trace amounts of indium and aluminum hydroxide.

Figure 6. An EDS analysis of the third area of interest. This graph shows a point of the fuel waste with predominately indium and trace amounts of gallium and aluminum hydroxide.
Figure 7. An EDS analysis of the fourth area of interest. This graph shows a point of the fuel waste with predominately indium and trace amounts of gallium and aluminum hydroxide. Since neither metal is chemically bonded to the aluminum, they can be separated using the difference in relative gravities. When the fuel waste is put into suspension with water, the gallium and indium will sink to the bottom, since they are heavier than the aluminum hydroxide. Once isolated, the aluminum hydroxide can be poured off the top and the gallium and indium can be collected. Future includes the determination of the exact percentage of these metals that can be recovered using this method.

Conclusion

Using a scanning electron microscope, a sample of aluminum fuel waste was imaged and analyzed. The analysis showed that the indium and gallium do not react during the fuel reaction. Instead the metals are non-uniformly distributed throughout the aluminum hydroxide waste in unreacted form. This makes for easy recovery, since neither metal is chemically bonded to the aluminum and neither needs to be processed to return it to elemental form.
References


