Characterization and Science of an Aluminum Fuel Treatment Process

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ABSTRACT

Presented is an inexpensive and highly effective method of activating bulk aluminum allowing it to react with water producing hydrogen gas and steam. The extreme energy density of the aluminum-water reaction, twice that of diesel fuel and forty-five times that of lithium-ion batteries, makes this new fuel a promising safe alternative to high-pressure hydrogen storage.

Aluminum is the most abundant metal in the earth's crust and has long been recognized as a potential fuel source. The challenge however is disrupting the protective oxide layer in a cost effective and safe manner. In this work, I show that by exposing aluminum to a heated liquid gallium-indium eutectic bath, the protective oxide coating is disrupted allowing the eutectic to penetrate the grain boundaries. The result is an activated aluminum fuel that is highly reactive with water. Unlike other methods, which involve explosive aluminum powders, this treatment process can successfully treat large pieces of aluminum that are safe to handle while using less than 4% gallium-indium eutectic.

The aluminum treatment process was characterized to maximize hydrogen yield and minimize gallium-indium content since these metals are expensive. Tests show that temperature of the liquid metal bath, immersion time, and treated metal composition affect hydrogen yield. A heated gallium-indium bath yielded activated aluminum that reacted to greater than 85% completion while using only 3-4 wt.% gallium-indium. The treatment process proved to be critically enhanced by cold working the aluminum allowing more favorable conditions for liquid metal to diffuse into the grain boundaries.

Activating bulk aluminum was previously thought to be impractical and current approaches to using aluminum as a fuel shifted towards the use of powdered aluminum even though it is extremely dangerous to process and handle. This work presented herein shows indium is the key activating metal in the heated treatment bath and samples that treated in baths with higher indium content exhibited higher reactivity yet contain less overall gallium-indium content.

This thesis provides the basic science and engineering know-how to guide the deterministic design of a large-scale aluminum treatment process for macro sized (e.g., 6 mm diameter spheres or wire), which was previously thought impractical.
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For nearly 60 years aluminum has been pursued as an energy source as it has one of highest energy densities of any non-nuclear material, with more than twice the volumetric energy density of gasoline or diesel fuel. However, the stable oxide layer that forms rapidly on the surface of aluminum in oxygen environments makes it difficult to extract energy from aluminum. Numerous inventions have been conceived that either burn aluminum in oxygen or somehow breakdown this oxide layer, however none of these technologies are cost-effective and safe enough to have achieved wide-spread adoption.

The purpose of this work is to characterize, analyze, and explain an aluminum treatment process which allows the aluminum to be reacted with water to generate large quantities of heat and hydrogen. Aluminum pieces are activated in a heated liquid gallium-indium eutectic bath and then allowed to sit in a hermetically sealed environment for several days. The gallium-indium eutectic breaks down the oxide layer and penetrates the grain boundaries of the aluminum. No gallium-indium eutectic need remain on the surface. When water contacts the spheres, it reacts with the exposed aluminum grains and producing inert aluminum hydroxide, which results in a continuing reaction that keeps exposing new grains until the sphere is completely consumed. This treated aluminum can be reacted in water at high efficiencies similar to activated aluminum powders, but with none of the safety concerns or logistical issues that
accompany aluminum powders. This treatment process produces an activated aluminum that is cost-effective, energy-dense, safe to handle, and has already been demonstrated in a working power system (summarized in Appendix A) [1][2].

1.1 Motivation

Lithium ion batteries are among the most common energy storage devices used in society today. They are used to power devices such as personal electronics, uninterruptible power supplies, and automobiles, however, a significant drawback of Li-ion technology is energy density [3][4]. Range anxiety and recharge time with electric automobiles are often deal breakers for some customers looking to buy a new car; for instance, the maximum range on a Tesla Model X is 250 miles and charges in 7 minutes. A comparable Ford Fusion can travel 500 miles and refuel in 3 minutes [5]. Another drawback to lithium ion is safety as they are potentially flammable and dangerous, which also limits their use in applications where safety is a primary concern [6][7]. Beyond the scale of automobiles, Li-Ion batteries are not cost-effective means of energy storage for applications at larger scales.

The internal combustion engine (ICE) is an even more widely used energy technology than lithium ion and was the primary means of powering automobiles and other machinery in the 20th century. Internal combustion engines offer relatively high efficiencies, sufficient energy density, and can be easily refueled. The waste products of burning fossil fuels in complete combustion are carbon dioxide and water, which are exhausted often in gaseous phases and are non-toxic. However, there are a number of drawbacks with ICE's, most notably the greenhouse gasses emitted by burning fossil fuels have been shown to be major contributors to global climate change [8]–[10].
ICE’s also do not scale down efficiently below 1-5 kW, generators in the single kilowatt scale have significantly lower efficiencies (10-20%) than generators with outputs above 10kW. For example a 2200W Ryobi mobile generator can run for 8.67 hours at a continuous power output of 450W or 5.6 hours at 900W [11]. This generator has a fuel tank size of 1 gallon and gasoline has a volumetric energy density of 33.41 kWh/gal, thus using their claimed run time and power, the efficiencies for the values are 11.7% and 15.1% respectively. For comparison, a CAT 4.4 (60 Hz) diesel generator set has a continuous power output of 100 kWe and consumes fuel at 7.9 gal/hour. Diesel has a volumetric energy density of 37.95 kWh/gal [12]. Thus, the total energy consumed per hour is 299.8 kWh (300 kWh was likely the original spec), and the total energy output over one hour is 100 kWh, thus the efficiency is approximately 33.3%, which is much higher than the smaller gas generator. These engines are noisy and because of incomplete combustion, produce noxious carbon monoxide, thus they cannot be run indoors.

Internal combustion engines and lithium ion batteries are both poorly suited for applications in the 500W-2kW power range. ICE’s are inefficient in single kilowatt applications they are noisey, and they cannot be run indoors as they produce toxic fumes. Lithium ion batteries can operate silently, however they are limited by their cost and their safety limits their use in some applications. One application where these technologies come up short is in emergency power generation for homes. Typically these generators are between 3-7kW and are often run by home owners. An aluminum-based backup power generator could be run indoors for low cost and almost silently as fuel cells need only fans for cooling.

1.2 Aluminum as an Energy Source

Aluminum is the most abundant metal in our Earth’s crust and one of the most commonly used materials in society today. Although frequently used in packaging and as a structural material,
aluminum is highly reactive: it reacts with water and has one of the highest energy densities of any non-nuclear material (at approximately 84 MJ/L, which is more than twice the energy density of gasoline (34 MJ/L) or diesel fuel (39 MJ/L). When reacted with water, aluminum generates large quantities of heat (15.5 KJ/g-Al) and hydrogen gas (0.11 g-H2/g-Al). The heat energy can be used for processes or work extracted using a heat engine, and the hydrogen can be used in a fuel cell to efficiently generate electricity. The byproduct of the aluminum-water reaction is aluminum hydroxide, which is non-toxic and can be easily made back into aluminum. Additionally, aluminum hydroxide carries potential value in its common use in products such as pharmaceuticals and flame retardants.

Figure 1 - Selected materials plotted by gravimetric energy density (MJ/kg) vs volumetric energy density (MJ/L). Note how Al has much greater volumetric energy density when compared to diesel and gasoline and has a similar gravimetric energy density (MJ/kg). (Figure credit: MIT Lincoln Laboratory)
These traits make aluminum an attractive fuel source for energy-dense power systems. However, a thin and naturally occurring oxide layer on the surface of aluminum typically protects it from reacting in most environments. This layer forms rapidly in the presence of oxygen, and is stable even at elevated temperatures [13][14]. Bypassing the aluminum oxide layer in a safe and efficient manner has remained a barrier to putting aluminum-water fuels into practice.

1.3 Hydrogen Storage and Goals

Aluminum can be reacted with water to generate hydrogen gas, the most efficient means of extracting energy from hydrogen gas is to use a hydrogen fuel cell. Some of the cheapest energy available is in the form of fossil fuels and in order for hydrogen fuel cells to be competitive, the price of hydrogen must compare to an equivalent amount of gasoline or diesel. The greatest challenges with using hydrogen are its generation, storage, and transportation. The United States Department of Energy (DOE) has set cost and storage goals for hydrogen to spur innovation in the field. Achieving cost equivalence with fossil fuels remains the biggest barrier to the adoption of hydrogen as a fuel. While fossil fuels are readily pumped out of the ground, hydrogen must be manufactured somehow. Ironically, the most ubiquitous method of producing hydrogen at present is from steam reforming of methane gas which produces large amounts of carbon dioxide as a byproduct. Other ways of producing hydrogen include electrolysis, solar thermochemical, photo-electrochemical, biological, and water separation methods. As hydrogen is not readily available in its diatomic state, and must be refined to such a state, it all comes down to how energy efficient the process is in procuring it.

In order to encourage more efficient energy-dense means of hydrogen storage, the U.S. Department of Energy Fuel Cell Technologies Office (FTCO) set hydrogen storage goals for the nation that by 2020 hydrogen storage technologies will meet the following [15]:
1. 1.8 kWh/kg system (5.5 wt.% hydrogen)
2. 1.3 kWh/L system (0.040 kg hydrogen/L)
3. $10/kWh ($333/kg stored hydrogen capacity).

Gasoline is approximately 12.8 kWh/kg with a volumetric energy density of 9.5 kWh/L. The cost of gas however is variable dependent on market prices - AAA national average for gas in the last year is $2.20 per gallon, so at approximately 34.0 kWh/gal gasoline costs $0.06 per kWh of energy. This shows just how cheap fossil fuels are with respect producing hydrogen.

With respect to comparable technologies, Tesla’s current lithium ion battery cells have an energy density of ~250Wh/kg with a cost of roughly $100-$150/kWh [16]. The cost however is not a fair comparison as the lithium ion batteries represent a fixed, upfront cost with low variable cost being the cost electricity purchased afterwards to recharge them. Figure 2 depicts the uphill battle facing hydrogen technologies as a comparison to petroleum fuel, which is already noticeably cheaper per kWh even though this plot was generated in 2004.
Figure 2 - Plot of hydrogen technologies in 2004 when compared to petroleum fuel [17]. Note that the proposed DOE goal here is outdated.

1.3.1 Hydrogen Storage Overview

The most common hydrogen storage methods are using compression or cryogenic containers which are either no practical as they are unwieldy, reduce energy density too much, or have lingering concerns about potential safety risks in the case of a major accident [18]. Cryogenics are not practical for long-term and energy-dense hydrogen storage as they require bulky storage and need to be vented over time. Thus, after several weeks or months a significant amount of hydrogen could be lost without generating any energy. Compressed hydrogen storage is an ongoing area in research that is highly focused on container materials – specifically related to their resilience in crash testing and ability to hold tremendous pressures (up to 10ksi).

Hydrogen storage tanks are already being employed in automobiles. In the case of the Toyota Mirai, reinforced carbon fiber tanks were designed to withstand significant crash tests – Toyota
released video footage of a head-on collision with one of their Mirai vehicles to demonstrate how the tanks would remain entirely intact in that case. They also shot a 50 caliber bullet at their tank at point blank range to demonstrate it would not burst, but rather leak gas out of the hole which they claim would disperse immediately and pose no significant threat (Figure 3).

![Crash Vehicle Test Vehicle](image)

**Figure 3** – *Stills from crash test video of the Toyota Mirai. Left is a collision camera of a head-on crash at 40 mph, and the right is the hydrogen tank just after being shot with a 50-caliber bullet at point blank range. Both specimens passed their respective testing criterion.*

Hydrides are promising means of generating hydrogen via a chemical reaction. They are compounds in which hydrogen atoms are bonded to a more electropositive element or group and are designed to have high gravimetric hydrogen densities [19]. There are two types of hydrides: metal and nonmetal hydrides. Metal hydrides are shown to have the most promise as a chemical means of storing hydrogen as they will readily react with water. Some of these metal hydrides come close to satisfying the requirements published by the DOE for hydrogen storage with respect to reaction thermodynamics [20]. The best hydrides have a low bonding energy between the electropositive element or group and the hydrogen atom, while containing as many bonded
hydrogen atoms as possible. This results in a compound that requires less energy to make, less energy to activate in a reaction which generates lower temperatures, and also yields more hydrogen per kg of reactant.

Metal hydrides with high gravimetric hydrogen densities include lithium borohydride, calcium hydride, Magnesium hydride, palladium hydride, and sodium borohydride. Issues with current hydrides include the cost associated with production, as well as the fact that some of them are toxic and can also produce toxic byproducts when reacted with water. However, since they have gravimetric densities that are within the desired range as defined by the DOE, these hydrides are considered strong candidates for feasible sources of hydrogen.

Of these listed metal hydrides and among most other chemical storage materials in general, lithium borohydride (LiBH₄) is among the most promising hydrogen carrier [21]. Figure 4 shows a plot of hydrogen storage potential of metal hydrides and hydrides against various hydrocarbons including methane and propane. Lithium borohydride has a hydrogen content of 19.6% by mass, making it superior to almost any other hydrogen storage material, and make it a
potential suitor for the DOE’s target hydrogen carrier goals. Thus, lithium borohydride will be explored in depth further for this paper along with hydrogen storage tanks.

Figure 4 – Hydrogen storage values of various hydrides – included are metal hydrides, hydrides, and hydrocarbons. It is important to note that this plot was generated in 2001, and thus no hydrogen storage tanks were viable to compete with these technologies. [44]

1.3.2 Materials Requirements for Hydrogen Storage Tanks and LiBH₄

High Pressure hydrogen storage tanks are the most common means of everyday hydrogen storage as they operate under simple concepts. The only critical components for this storage device is the tank material itself. As gas is being compressed to high temperatures, some of the primary functional requirements for tank storage are:

1. Withstand a given internal pressure (generally between 5-10 ksi)
2. Maintain strength even when the tank heats due to compression of the gas
3. Not react negatively with the stored hydrogen gas (steel and hydrogen cracking)
4. Minimize overall weight of the system

It is important to note that the materials used should have high strength to weight ratios so as to minimize the “hit” on energy density of the system as a whole. Also, the materials should maintain their strength at higher temperatures as pressurizing a gas results will heat the tank. Initially, aluminum was considered as a suitable material, however as pressure requirements increased and required filling times decreased, it was deemed not a suitable material for hydrogen storage for automobiles [18].

The tanks used in the Toyota Mirai are made from carbon fiber reinforced plastic (CFRP) and are known as composite overwrapped pressure vessels (COPV) which were chosen for their ease to manufacture and high thermal conductivity (reduces thermal gradients in the material) [22]. Storage tanks are generally spherical or cylindrical, but can also be toroidal and polymorphs [23]. There are 4 types of tanks, as classified by Barthlelemy et al: Type I thru Type IV shown in Figure 5. All but Type I, which is for low pressure applications that do not have the concern of energy density, are made up of composites of some sort. Type IV tanks are the ones used in the Toyota Mirai, and can withstand up to 15ksi (100MPa), but have a 10ksi (70MPa) working pressure. The plastic liners used in tanks II thru IV are generally polymers such as polyethylene or polyamide-based polymers. The composites in these tanks can either be carbon fiber, aramid, or glass fibers bonded together with an epoxy resin.
The challenge with using metals to store hydrogen, in particular steel, is the risk of hydrogen embrittlement, in which hydrogen makes its way into the lattice of steel and effectively preloads the atoms further causing it to “harden” and embrittle. This is a common phenomenon observed in welding high strength steel as hydrogen is highly soluble in liquid steel and must be baked out after welding, else risk catastrophic, and unpredictable failure of structures. Aluminum is generally less receptive to hydrogen embrittlement, but it is still possible for the aluminum to weaken with increased exposure [24]. As a result, tanks are not pressurized to their maximum so as to reduce the risk of failure if weakening in the outside metal liner were to occur.

With regards to the polymer liners used in hydrogen COPVs – issues arise with the fact that fuel cells require high-purity hydrogen in order to function properly. The polymer liners inside the tank are there to prevent permeation of hydrogen to the other materials, it provides no structural integrity to the tank. However, some polymers can retain water, which can be harmful to fuel cells as a whole. Polymer selection is limited to materials that have low permeability so as to limit the diffusion of hydrogen gas through their structures to the carbon fiber and metal casings. As hydrogen storage tanks in cars will never truly be “free” of hydrogen, these polymers must perform indefinitely until the end of life of the tank, else risk a compromised tank from the
hydrogen gas exposure. Further research however is still needed to reduce the permeability through these polymers [25]. Finally, the polymers must also be able to withstand temperature differentials between -40°C and 130°C.

The most critical piece of the tank is the carbon fiber wrap of the COPV, which is included in types II, III, and IV tanks as it must hold the high stresses associated with pressurization. Not only does it have to hold the static load of pressure from gas, but also the fatigue cycles that accompany pressurization and depressurization. Thus tank must have high fatigue strength as well. In addition to fatigue strength, the material must also not undergo a major failure if a crack or other localized defect were to occur such as a puncture hole (hence the 50 caliber bullet test done by Toyota).

The challenge with composite materials is that it is much more challenge to determine damage simply by visual inspection – individual plies can shear their bonding layer, thus weakening the material but would otherwise look fully intact to the naked eye. Thus regulated inspection of the COPV is mandatory in which detailed inspection is done of the tank inside and out as well as hydraulic proof testing or acoustic sensing.

As discussed before, a promising alternative hydrogen storage technology is lithium borohydride, which is capable of reacting with water to generate hydrogen (Eq. 1). This is a hydrolysis reaction in which the 4 hydrogen atoms bound to the boron atom are liberated in favor of boron binding to oxygen. Water is also a common reducing agent of LiBH₄ as it is highly abundant and non-toxic [26][27]. This hydride utilizes two highly energy dense materials – both lithium and boron alone have higher specific energy densities than gasoline, at 11.97 kWh/kg and 58.9 kWh/kg respectively.

\[
\text{LiBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{LiBO}_2 + 4\text{H}_2
\]  

(1)
As a standalone material, lithium borohydride contains 19.6% hydrogen by weight, however once the weight of water is included this efficiency drops to 13.9 wt. %. This still makes it a highly competitive hydrogen carrier, and unlike other hydrides which can require endothermic reactions, LiBH₄ has a favorable reaction with water, however some studies show that this reaction can be slow and hard to control despite its high hydrogen yield [19].

Lithium borohydride in comparison is not currently a widely adopted technology as it is very expensive and is currently used as a reducing agent for various esters, carboxylic acids, amides, and epoxides. It is also a highly reactive chemical that is powderized when handled, giving it incredibly high surface area to complement its already high reactivity with water, thus keeping it dry and away from water is imperative for safety. Also, any material lost due to reduction with water is money lost. Though not a clear metric of economies of scale, LiBH₄, 95% purity material can be purchased on Sigma Aldrich at $285.50 for 25g of material. This is ridiculously expensive for a material that is seen as a “plausible” hydrogen carrier for automobiles. Using just these cost numbers, the total cost of energy from lithium borohydride is $157 per kWh of energy, compared to gasoline which is $0.06 per kWh. Thus hydrocarbons are four orders of magnitude cheaper, all but making this promising hydride highly impractical simply from a cost standpoint, not to mention the capital equipment needed to manufacture it.

Aluminum has been compared to other hydrides, as seen in Table 1.1, in order to highlight the differences in total hydrogen yield per unit mass and volume. In terms of cost per amount of hydrogen, aluminum is several orders of magnitude better as a solution as it is a readily available material. It has a low gravimetric density, relative to other hydrides, but if an aluminum fuel can be made in a cost-effective manner, it would be competitive with hydrogen simply from a cost standpoint due to the abundance and economic advantage of using
Aluminum. In fact, a DOE annual report in 2014 even confirmed that hydrides, though effective at satisfying most DOE requirements for hydrogen storage, are simply too impractical for use on a large scale [28].

<table>
<thead>
<tr>
<th></th>
<th>Aluminum</th>
<th>Sodium Borohydride (NaBH4)</th>
<th>Calcium Hydride (CaH2)</th>
<th>Lithium Borohydride (LiBH4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Produced at STP</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(Liters)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moles of Reactant</td>
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<td>0.011</td>
<td>0.022</td>
<td>0.011</td>
</tr>
<tr>
<td>Mass of Water Consumed</td>
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<td>0.40</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Density (g/cc)</td>
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<td>1.07</td>
<td>1.7</td>
<td>0.66</td>
</tr>
<tr>
<td>Liters of Material</td>
<td>0.297</td>
<td>0.395</td>
<td>0.553</td>
<td>0.368</td>
</tr>
<tr>
<td>Required (mL or cc)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cost of material</td>
<td>2</td>
<td>600</td>
<td>500</td>
<td>1500</td>
</tr>
<tr>
<td>($/kg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cost (dollars/Liters</td>
<td>0.002</td>
<td>0.253</td>
<td>0.470</td>
<td>0.365</td>
</tr>
<tr>
<td>of H2)</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 1 - Comparing Aluminum to Hydrides for hydrogen production

density and cost. It is clear here that aluminum does not have as high gravimetric hydrogen density as hydrides, it is orders of magnitude cheaper, making it much more practical as a hydrogen source.

Given their high gravimetric densities, hydrides have uses in applications that require only small amounts of material, such as where mass is a limiting factor, or heat production must be minimized. Thus from a simple cost standpoint aluminum will be a more effective hydrogen source alone than hydrides if these factors are not major concerns.
1.4 Applications for Activated Aluminum

1.4.1 Soldier Power

An activated aluminum fuel has a wide range of potential applications where competing technologies like primary lithium ion batteries and internal combustion engines fall short. Providing power to dismounted soldiers is a major challenge for the military as lithium ion batteries are not energy-dense enough, potentially flammable, and expensive (approximately $300/lb.). These batteries must also be destroyed or carried out of the field once they can no longer power soldiers' gear since they still have enough charge for enemies to trigger IED's and other explosive devices.

Currently, fire-teams of soldiers must carry 20-25lbs of lithium ion batteries for a standard 3-5-day mission to power gear such as night vision goggles and GPS equipment. The battery weight is in addition to the essential equipment that soldiers need to survive and carry out other mission critical tasks, totaling approximately 60-100 pounds per pack [29]. Increasing the energy density of soldiers' power systems reduces their pack weight, increases mission flexibility, and reduces the strain and fatigue on a soldier over the duration of the mission. The power output needed to run their gear is on the order of 30W, which is too low for a generator to run efficiently at – also the noise and toxic fumes associated with burning fossil fuels make them impractical to use.
Figure 6 - Standard issue battery packs used by the United States Army. Shown left are batteries such as the BA-2590 and the BA-5590 which were designed to fit into battery boxes and not meant to be worn by soldiers. Right is the conformable battery pack which is designed for soldier use [30].

Currently, lithium-ion batteries are the best power source for these dismounted soldiers, however they are not ideal for this application. An aluminum power-system that generates hydrogen for a fuel cell by reacting with water can provide power for dismounted soldiers with less weight than a battery. 11.3 kg (25 lbs) of batteries are needed for a single mission and with an energy density of 150 Wh/kg, this is approximately 1700Wh of energy [31]. Aluminum has a specific energy density of approximately 8600 Wh/kg – 4300 Wh/kg of energy is dedicated to hydrogen potential energy, while the rest is heat exhaust. If a fuel cell efficiency of 40% is assumed, and a reaction completion of 90% (efficiency shown in this thesis) is obtained, the fuel has a useful energy density of 1550 Wh/kg, meaning that 1.1kg of aluminum fuel can supply the entire mission with energy. Since the aluminum can be reacted with any water source, such as urine, it can be discounted from the overall system weight as soldiers involuntarily carry this weight with them wherever they go. A conservative estimate of the system weight including the
fuel cell, fittings, and containment would be 1kg, while the fuel weight required to supply 1700 Wh is 1.1kg. A total system weight conservatively would be 2.1 kg, compared to the current battery system weight of 11.3 kg, thus reducing the soldier power weight by approximately 80%. This improvement would drastically aid with soldier fatigue and lower the safety concerns that surround lithium batteries strapped to soldiers’ bodies.

1.4.2 Powering Forward Operations Bases

Convoys and supply lines are serious risks for soldiers as fuel is often trucked in power forward operating bases along with other essential supplies – 1 out of every 24 convoys results in a casualty and nearly 38% of all US casualties from the Iraq and Afghanistan wars were from IED’s [32]–[34]. Since fossil fuels are so volatile and their containment can only be so well protected, tanker trucks are prime targets for insurgents since they can produce such a large blast with little effort [35]. Exploded or spilled fuel also means the base expecting that fuel could face potential power-outages if more fuel is not delivered quickly enough. One of the challenges with stockpiling fossil fuels like diesel is that they foul after approximately 1-2 years, thus fuel stores either must be replenished regularly or be discarded due to spoiling [36].
Activated aluminum can serve as a viable alternative to fossil fuels as it offers greater energy density and is not volatile or explosive, which eliminates a potential target for insurgents and increases the likelihood that fuel can be delivered to a base. Spilled activated aluminum can cleaned up easily and used as intended and it can be stored indefinitely if kept hermetically sealed. Fuel cells scale from single watts to several kilowatts efficiently, run quietly as they have only fans to dissipate the heat generated, and can be run indoors, which makes them easier to protect and store [37]. The byproduct of fuel cells is recombined water, which is pure and clean, thus dirty water or waste can be supplied to the activated aluminum to generate hydrogen, and clean water is exhausted by the fuel cell for use on the base. Since the aluminum also gives off waste heat, excess waste water can be delivered to the reaction chamber and evaporated, desalinating and cleaning the water. An aluminum generator on a forward operations base has
purpose as both a power generation system and as a water purification unit, which further reduces the number of trucks needed to carry supplies in.

1.5 Fundamental Thesis Contributions

There are numerous aluminum activation methods that have been presented in the prior art and in the literature. This aluminum treatment process was invented by the author and is unique in that it is the first process to successfully treat bulk aluminum while using less than 5 wt.% activation metal. Previously, only casting of aluminum with liquid metals like gallium and indium from a high temperature furnace to crucibles yields bulk aluminum fuel, however with this process, pieces 30x30x90mm have been successful treated and activated. Chapters 3-5 pertain to the specific science used to investigate this treatment process and explain how it works and why it is fundamentally new and different.

The first contribution of this thesis is in the treatment process itself and identifying the critical parameters that allow the heated gallium-indium bath to activate the aluminum. It was discovered that the temperature of the bath is critical for achieving activation of the aluminum – samples that were treated in a bath at room temperature did not achieve noticeable hydrogen yields, however when bath temperature was raised above 90°C while holding all other parameters constant, hydrogen yield of the aluminum when reacted with water neared 90%. Exposure time to the bath was also investigated – aluminum spheres that were exposed for 90-120 minutes obtained the highest reaction rates while having acceptable amounts of surface corrosion as a result of being in the bath. Samples held longer in the bath exhibited slightly lower yields and more surface corrosion. Finally, activation metals were also identified as critical – treating the aluminum with just a heated gallium bath for instance resulted in the spheres nearly dissolving into the bath. Further, when the spheres were exposed to water, they underwent a brief
surface reaction and then ceased to react further. Indium is the key element in activation, tin was also investigated when added to the melt which was also capable of activating aluminum, but an indium-gallium eutectic resulted in activated aluminum with the highest hydrogen yields when reacted with water.

Another fundamental contribution of this work is an analysis of how the state of stress inside the aluminum affects activation. High strength steel has been shown to corrode faster than mild steels, especially when under stress [38]–[43]. In this application, the assumption is aluminum has a rapidly forming oxide layer –there is also no applied stress to influence corrosion. Further, the alloy of aluminum demonstrated in this work is pure aluminum, which has limited hardening properties, unlike alloyed aluminum. After extensive experimentation, it was shown that cold-working aluminum and thus inducing residual stresses in the grain structure and then treating the aluminum in the hot liquid metal bath results in higher reaction rates and hydrogen yields. Cold-forging and rolling aluminum pieces and then treating them in the heated eutectic bath were both shown to have dramatic effects on reactivity. Smaller grains in the aluminum as a result of the cold working and heat treatment resulted in more reaction sites as the aluminum disintegrates in water, resulting in higher surface area which allows the temperature to rise faster, thus increasing reactivity and yield.

A final contribution is with respect to the aluminum-water interaction. It was shown that indium affects the treatment process and increases hydrogen yield of the activated aluminum. The initial hypothesis was that indium was forming a galvanic cell with the aluminum in water by acting as a more noble metal. Gallium does not have a great enough potential to react favorably with aluminum thereby splitting water. Instead, results show that the reaction is simply a hydrolysis reaction in which aluminum reduces water; it results in the formation of aluminum
hydroxide and hydrogen gas. Further investigation and experimentation will be needed to fully
determine the role indium plays in enabling the reaction to proceed

1.6 Thesis Organization

1.6.1 Chapter 1: Introduction

The introduction aims to give the reader context and motivation for this project. Aluminum is a highly energy-dense power source with a wide range of applications. It can also potentially enable new applications where those fuels or systems simply aren't sufficient. Aluminum has a unique utility in that it has a high energy density, but can be used to generate hydrogen gas on demand using only water, and it has non-toxic byproducts. This chapter explores some of the basic thermodynamics and chemistry behind the aluminum-water reaction and discusses potential applications of an aluminum power-system and compares it to the current state of the art technologies.

1.6.2 Chapter 2: Aluminum as a Fuel Source

Chapter 2 gives a brief overview of the history of aluminum manufacturing in order to provide context and to show how energy intensive the electrolytic process is. The chemistry of aluminum and water reactions is then discussed. Different energy densities can be obtained if this reaction is pressurized – higher pressures result in more favorable reaction products such as aluminum oxide, which require less water to produce. Next, previous work on aluminum fuels is discussed; the oxide layer on aluminum can be removed using many methods, such as heat, acidic or basic solutions, and as shown in this thesis, by exposing the aluminum to liquid metal solutions of gallium and indium. Finally, aluminum phenomenon called liquid metal embrittlement and diffusion is discussed, particularly when aluminum is exposed to gallium.
1.6.3 Chapter 3: Aluminum Treatment Process

Chapter 3 outlines the science of the aluminum treatment process discussed in this thesis and quantifies its performance in terms of reaction completion and gallium-indium content. This portion also outlines investigation into the different parameters of treatment and how they affect the overall hydrogen yield of the fuel; 6mm 99.9% aluminum spheres were used. Temperature of the gallium-indium bath, the fuel exposure time, the types of liquid metals (i.e. relative concentrations) used in the hot bath, all were found to have variable degrees of effecting hydrogen yield. Aluminum that is exposed to the heated eutectic bath for between 90 and 120 minutes at 120°C produced the most hydrogen gas – any more time in the heated bath resulted in similar hydrogen yields, but significantly more corrosion and less exposure time in the bath resulted in lower hydrogen yields. Hydrogen yield data from the treated aluminum spheres shows that the treatment process is capable of producing aluminum that can react with up to 90% efficiency in water while containing only 3-4 wt.% gallium-indium to activate it. This completion percentage and gallium-indium content is similar to aluminum powders, but this is activated bulk aluminum which is nearly incapable of exploding or being inhaled.

1.6.4 Chapter 4: Cold-Working Aluminum and its Effect on Reactivity in Water

Chapter 4 investigates how the parameters of the aluminum pieces affect treatment and consequently hydrogen yield when reacted with water. Liquid metal diffusion and liquid metal embrittlement are still not fully understood phenomena. It is known that stressing aluminum grains increases diffusion rates of liquid metal (typically gallium) down the grain boundaries. Microscopy of the 6mm spheres show that they were extensively cold-worked and had not undergone any stress-relief – it was hypothesized that this resulted in more favorable conditions for liquid metal diffusion throughout the aluminum bulk. To test this, samples were annealed and
plastically deformed using different processes and then treated in the heated gallium-indium bath. It was found that an increase in plastic strain and thus work hardening of the material due to cold-working results in an increase in hydrogen yield.

1.6.5 Chapter 5: Activated Aluminum Reaction in Water

It is accepted in the literature that gallium naturally disrupts the oxide layer on aluminum, allowing it to react. This can be observed by wiping liquid gallium on the surface of an aluminum plate. Adding water to this area will cause hydrogen to bubble and aluminum hydroxide to form. Data collected in this research shows that heated baths with different indium contents yield activated aluminum that reacts more efficiently depending on how much indium was in the bath. The bath with the highest indium content produced fuel with the highest hydrogen yields. Aluminum that is treated in a heated gallium-only bath and then exposed to water will have a brief surface reaction of hydrogen and then cease to react further. Thus, indium is necessary for activation. It was hypothesized that indium acts as a cathode for micro-galvanic cells in the aluminum bulk in which aluminum is the consumed anode. Indium is a more noble metal than gallium, thus it might act as a potential cathode which would explain why this treatment process is unique. However preliminary tests show that indium does not corrode aluminum when a macro-scale galvanic cell is created with aluminum in the presence of an electrolyte. Further work will be needed to conclude how and why this activated aluminum reacts with water and if it is different than prior aluminum fuels demonstrated in the literature.

1.6.6 Chapter 6: Conclusions and Future Work

Chapter 6 summarizes and concludes the results of chapters 3-5 and presents suggestions for further research into the aluminum treatment process and aluminum-water reaction. Different
The proposed areas of research are directed towards further understanding the fundamental science so that more efficient and cost-effective aluminum fuels can be created.
1.7 Chapter 1 References


2013.


Aluminum is a highly versatile structural material as it has a higher strength to weight ratio than iron and its protective oxide coating prevents it from corroding in most environments. The same can be said about aluminum as an energy source: it is highly energy dense, stable in oxygen environments if it is not a powder, and it can react with almost any type of water source. To understand aluminum as a material, this chapter first provides some context by exploring the history of aluminum, how it is manufactured, and why it was such a difficult material to refine. The primary challenge with both refining and extracting energy from aluminum is controlling or disrupting the highly stable and rapidly forming oxide layer that forms on aluminum. Exposing the aluminum to corrosive liquids or liquid metals are the most effective means of breaking down the oxide layer, however there are safety concerns with handling corrosive liquids. When aluminum is contacted by certain liquid metals, they will naturally break down the oxide layer and diffuse into the grain structure of aluminum causing a phenomenon known as liquid metal embrittlement. Understanding the fundamental physics behind the treatment process of the activated aluminum presented in this thesis and chemically what happens when it is exposed to water is critical to understanding and interpreting the data presented in future chapters of this work.
2.1 History of Aluminum as a Material

Aluminum is a relatively new material in the history of human civilization when compared to iron or bronze. Before the invention of the Hall-Héroult Process in 1886, aluminum was considered a precious metal, and at one point it was more than twice the value of gold or platinum. Napoleon had his own personal cuirass of armor made from aluminum and believed it to be an untapped resource that could be used to great effect in war. The top of the Washington monument is capped with an aluminum pyramid, because aluminum was considered a precious metal when construction of the monument was completed in 1884. As Aluminum in its purest form is a highly reactive metal; reducing aluminum oxide to form pure aluminum is difficult due to the three-free outer-shell electrons. Lavoisier, a notable French scientist, was the first to predict aluminum's existence in 1782 describing it as, “the oxide of a metal whose affinity for oxygen is so strong that it cannot be overcome by carbon or any other known reducing agent”[1].

As Aluminum in its purest form is a highly reactive metal: reduction to a purely reduced form is very difficult to accomplish due to the three free outer-shell electrons. Lavoisier, a notable French scientist, was the first to predict aluminum’s existence in 1782 describing it as, “the oxide of a metal whose affinity for oxygen is so strong that it cannot be overcome by carbon or any other known reducing agent” [1]. It wasn’t until 1825 however when Danish Scientist H.C. Oersted produced the first sample of pure Aluminum. It was found to be a light, malleable, and strong metal with excellent corrosion resistance. Following Oersted’s discovery, new processes were developed to produce Aluminum in larger quantities. Most these were costly processes and which yielded only small amounts of pure aluminum, contributing to its consideration as a special metal. It was not until the invention of the electrolytic process that the price of aluminum dropped [2].
The electrolytic process was the next logical step forward in aluminum manufacturing and is founded on years of empirical knowledge generated by metallurgists and scientists over roughly a century. It was the simultaneous invention of American inventor Charles Martin Hall and Frenchman Paul L. T. Héroult, who worked independently of one another, arriving at their conclusions almost simultaneously. Thus they are both credited with the invention. The electrolytic process of aluminum involves dissolving aluminum oxide in cryolite, which is a fluoride salt of aluminum, and then electrolyzing it. This causes pure and molten aluminum to deposit on the cathode while other impurities develop on the anode [2].

Sir Humphry Davy and Henry Sainte-Claire Deville were early pioneers of aluminum manufacturing, they had both tried electrolytic processing of aluminum before Hall and Héroult, but abandoned the idea. Hall was the one who eventually found that cryolite was a suitable salt that would readily and easily dissolve aluminum. Despite prior work, Hall and Héroult isolated the process that lead to the rise of a massive industry that would result in the production of alloys that are stronger than steel by weight. The space age, aluminum beverage cans, and the aerospace industry were all enabled by the Hall-Héroult process of aluminum electrolysis.

2.2 Aluminum Refinement: The Bayer Process

Primary aluminum manufacturing begins with bauxite ore, Brazil and Australia for example are large producers of bauxite. Bauxite is the oxidized form of aluminum and depending where it is found, can contain between 30-50 percent alumina with the rest being iron oxides, clay minerals, and other impurities in small amounts [3]. In order to extract the alumina in a pure form, the bauxite must undergo the Bayer Process. The first step in this process involves washing the bauxite and crushing it to increase the surface area for the digestion process. The digestion process involves dissolving the crushed bauxite ore into a heated sodium hydroxide (NaOH)
solution in pressurized containers. This process forms a super-saturated sodium aluminate ($\text{Al(OH)}_4^-$) solution and a bauxite residue, which consists of insoluble iron and silicon oxides. These impurities settle inside the tanks and are then separated from the aluminum-rich solution (pregnant liquor). These impurities are called red mud, which is a highly caustic sludge that poses significant disposal challenges. The sodium aluminate is then filtered and cooled, causing it to form small crystals of aluminum hydroxide ($\text{Al(OH)}_3$). When aluminum hydroxide is heated above 300 °C, it decomposes to give off water vapor, yielding pure aluminum oxide [3]. This aluminum oxide is then shipped to aluminum refineries to be reduced into Aluminum. The Bayer Process is extensive and highly energy intensive, consuming approximately 12,000 MJ for every metric ton of aluminum produced. This is the equivalent amount of energy to produce a single metric ton of recycled aluminum [4][5].

**Figure 8** – The Bayer Process involves separating the aluminum oxide from the aluminum ore (bauxite) using a super saturated solution and then cooling it to precipitate out aluminum hydroxide crystals which are then decomposed into pure aluminum oxide.

The Bayer Process is far less energy intensive than the electrolytic process to smelt aluminum, however the primary challenge it presents is the large quantities of red mud produced...
during manufacturing. Since the late 19th century to 2008, the world has generated over 2.7 billion metric tons of red mud – current annual production is estimated to be 120 million metric tons [6]. The best bauxite ore will generate about 2 tons of red mud for every ton of alumina that is produced and every ton of alumina produced yields about 0.5 tons of aluminum [7]. It is highly caustic and toxic, which presents a significant challenge for safe disposal also leading to further energy needed to potentially process it safely.

2.3 Modern Aluminum Manufacturing

The smelting of aluminum via the Hall-Héroult process has changed very little conceptually since its invention in 1886. The fundamental chemistry is to reduce aluminum oxide using carbon to produce pure aluminum and carbon dioxide (Eq. 1). A typical aluminum smelter consists of a carbon-lined cell or pot containing a molten salt bath called cryolite (Figure 9). Alumina is dissolved into the cryolite bath and sacrificial carbon anodes are inserted into the bath. Current is then run through the bath to run the electrolytic process – oxygen from the alumina in the cryolite bath bonds with the anodes producing carbon dioxide and pure molten aluminum, which is denser than the cryolite bath, is poured out the bottom of the tank into crucibles [8]. The molten aluminum is then sent to alloying furnaces and then cast into ingots, T-bars, or cylindrical extrusion billets.

\[
2Al_2O_3(cryolite) + 3C(anode) \rightarrow 4Al_{\text{liquid}} + 3CO_2(g)
\]  
(Eq. 1)
This is the most energy intensive process in all of aluminum manufacturing as it involves the actual reduction of aluminum oxide [8].

Though the fundamentals of the Hall-Héroult process have not changed, it is the most energy intensive part of primary aluminum manufacturing, making up 90-95 percent of energy for the entire process. Even if run completely from renewables, primary aluminum production still utilizes carbon for electrodes and produces carbon dioxide as a byproduct. Current efforts to improve the process are to reduce the energy consumed during smelting such as reducing heat lost to the environment and lowering the overall resistivity of the setup – this in turn results in less CO₂ emitted by the process due to running at higher efficiencies [9][10].

As a result of the high energy intensity and other costs associated with the Hall-Héroult process, research has been done on alternative methods of aluminum production. Dutta et al summarizes the advantages and disadvantages of several processes which have proven to
produce aluminum have over the Hall-Héroult process in Table 2 [11]. The challenge associated with these processes is they either have trouble scaling up to necessary outputs or technical barriers prevent any significant production to occur. Thus there is significant research being done to find a more energy efficient and carbon-neutral process than the Hall-Héroult process. Despite these other attempts, there is a fundamental minimum required amount of energy to reduce aluminum oxide which guarantees primary aluminum production will consume a significant amount of energy.

<table>
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<tr>
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<th>Disadvantages</th>
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<tbody>
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<td>Aggressive stress corrosion with handling gaseous AlCl₃</td>
</tr>
<tr>
<td>Alcoa Process</td>
<td>Higher conductivity of Electrolyte, Lower energy consumption, and higher efficiency</td>
<td>Problem related to chlorine handling, corrosion, environment issues</td>
</tr>
<tr>
<td>Carbon Reduction Process</td>
<td>R&amp;D Phase – cheaper, less energy, and lower emissions with less capital cost</td>
<td>Higher temperatures which lead to higher electricity consumption</td>
</tr>
<tr>
<td>Reynolds Process</td>
<td>Low capital cost</td>
<td>Furnace construction and material stability at operational conditions</td>
</tr>
<tr>
<td>Toth Process</td>
<td>Can utilize ores with low Al₂O₃ content to make aluminum</td>
<td>Low aluminum yield, higher cost</td>
</tr>
</tbody>
</table>

*Table 2 – List of other viable processes to produce aluminum.*

*Some of these processes are still being tested and explored for further validity. One of the key challenges with aluminum id reducing the energy needed to reduce it (from Dutta et al) [11].*

With regards to the energy consumption and carbon emissions of worldwide aluminum production, in 2009 547 megatons of CO₂e were emitted by the aluminum industry compared to
the 31.7 gigatons of CO$_2$ the world emitted in 2009. Using these numbers, aluminum makes up roughly 1.7 percent of global carbon emissions, and makes up roughly 4 percent of all energy consumption in the world it. Despite this, half of the energy used to create aluminum is from hydroelectric generation and though there was an increase in aluminum demand by 90% from 1990 to 2009, CO$_2$ emissions from aluminum have dropped by as much as 75 percent [12][13]. However, this can be improved even further with more efficient manufacturing of aluminum and through better recycling of aluminum waste, which is far more energy efficient than primary aluminum production. The recycling of aluminum waste however carries its own difficult challenges such as how aluminum is used with certain products, implementing more closed-loop recycling systems, and separation of lumped scrap.

2.4 Aluminum Reaction with Water

Aluminum is a highly reactive material as it has 3 valence electrons it can donate. When aluminum reacts with water at standard temperature and pressure, these electrons are used to reduce hydrogen, the byproducts of this reaction are heat, hydrogen gas, and aluminum hydroxide (Eq. 2). The total potential energy stored in aluminum is approximately 31.0 MJ/kg; stoichiometry shows that 1 kg of aluminum produces 0.112 kg of diatomic hydrogen using (Eq. 2) and assuming 100% reaction completion, which has an energy density of 141.86 MJ/kg. Thus 15.89 MJ of energy are stored in the hydrogen gas released by the reaction, leaving 15.1 MJ of heat energy released by the reaction.

$$2Al + 6H_2O \rightarrow 3H_2 + Al_2(OH)_3 + Q$$

(Eq. 2)

Aluminum has other favorable reactions with water as well if the temperatures and pressures are changed. As the temperature and pressure are raised during the aluminum-water reaction, the next favorable byproduct is aluminum hydroxide-oxide, followed by aluminum
oxide shown in (Eq. 3) and (Eq. 4) respectively. To intuitively understand this, aluminum hydroxides are also known as hydrated alumina, thus they are lower energy compounds. As mentioned before, aluminum oxide is procured in the Bayer process in which water is evaporated out of the bauxite ore. The following hydrolysis reactions of aluminum and water show that aluminum can be reacted with less water as the temperature and pressure at which the reaction takes place are raised. This is because increasing energy of the system reduces the energy required to cleave both hydrogen ions from the water molecules.

\[
\begin{align*}
2Al + 4H_2O &\rightarrow 3H_2 + Al(OOH) + Q \\
2Al + 3H_2O &\rightarrow 3H_2 + Al_2O_3 + Q
\end{align*}
\]  
(Eq. 3)  
(Eq. 4)

Recent developments of the aluminum-water reaction were made by Kelsey Seto in her thesis in which she reacted activated aluminum in sealed chamber. She observed that reacting the fuel shown in this thesis at different temperatures and pressures produced different byproducts [14]. She found that \( Al(OOH) \) became a favorable byproduct at \( 142.38 \, ^\circ C \) and \( 387kPa \) and \( Al_2O_3 \) became favorable at \( 174.21 \, ^\circ C \) and \( 889 \, kPa \). These results show that aluminum can be reacted at high efficiencies in high energy-density systems at relatively low temperatures and pressures. These results are contrary to data provided by the Department of Energy report published by the U.S. government in 2008 that showed AIOOH can be produced to 100% conversion at \( 296 \, ^\circ C \). In this thesis, aluminum is reacted at room temperature and pressure and all stoichiometry is based on (Eq. 2, the favorable reaction at these conditions

\[2.5 \quad \textbf{The Aluminum Oxide Layer}\]

Aluminum is protected by a naturally occurring oxide layer which forms almost instantly and is stable even at high temperatures [15][16]. Materials like steel and iron rust because the iron oxide that forms on the surface chips off due to the volume of the oxide. This effect can be
explained by the Pilling-Bedworth ratio, denoted $R_{PB}$, which is the ratio of the volume of oxide to the volume of pure metal it is replacing shown in (Eq. 5) where $M$ is the molar mass, $\rho$ is the density of the material, and $n$ is the number of moles. In aluminum’s case, the aluminum oxide takes up approximately the same volume as the aluminum atoms it replaces, thus the oxide will not self-destruct and flake off as it continues to form. This also explains why the oxide layer is so thin, on the order of nanometers thick, oxygen cannot easily penetrate and diffuse through the aluminum oxide layer to reach further aluminum and thus the aluminum cannot react further. The layer is in fact thin enough that visible light is not absorbed and is transparent; all aluminum is viewed through an aluminum-oxide “window”.

$$ R_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide} \cdot \rho_{metal}}{n \cdot M_{metal} \cdot \rho_{oxide}} $$  

(Eq. 5)

Figure 10 – (Left) Illustration of the aluminum oxide layer on top of raw aluminum and (right) is an SEM image of an anodized aluminum surface showing individual aluminum oxide crystals on an aluminum surface[17][18]. This oxide layer forms a dense, stable coating that protects the raw aluminum underneath from further oxidation.
2.6 Disrupting the Oxide Layer

The oxide layer on aluminum can be disrupted in many ways, however not all these methods are necessarily cost effective, safe, or practical. These methods of disrupting the aluminum oxide layer are:

1. Burn the aluminum at high temperatures (>660°C)
2. Immerse the aluminum in corrosive liquids which either react with or dissolve the oxide
3. Continuously physically scrape it off to expose raw aluminum underneath
4. Use salt additives to ball-mill aluminum powders to favorably reactive size
5. Alloy the aluminum with metals that naturally disrupt the oxide layer

Burning aluminum at high temperatures is a well-known means of releasing the energy in aluminum, however for high energy-density power systems this is impractical and unsafe, and for grid-scale power consuming aluminum is an inefficient use of energy [19].

Alkaline and acidic solutions can be used to dissolve or corrode the protective oxide coating from aluminum [19–21]. Aluminum hydroxide, aluminum hydroxide-oxide, and aluminum oxide are amphoteric materials and have different reactions with acids and bases, aluminum hydroxide for example is highly soluble in strong acids and bases (Figure 11), but aluminum oxide reacts with HCL to form aluminum chlorate which is a potent neurotoxin. A common reaction demonstrated in the literature is to combine aluminum with sodium hydroxide, which undergoes the following series of reactions (Eq. 6); this reaction produces sodium aluminate and hydrogen gas [22]. This reaction was first utilized in an invention in 1907 in a patent filed by Hans Foersterling and Herbert Philipp [23]. Foersterling and Philipp invented a system that reacts aluminum with a strong acid to produce a steady flow of hydrogen gas. The
hydrogen gas produced from this reaction at the time was cheaper than using an electrolytic process.

\[ 2\text{Al} + 2\text{NaOH} + 6\text{H}_2\text{O} \rightarrow 2\text{NaAl(OH)}_4 + 3\text{H}_2 \quad \text{(Eq. 6)} \]

\[ \text{NaAl(OH)}_4 \rightarrow \text{NaOH} + \text{Al(OH)}_3 \quad \text{(Eq. 7)} \]

\[ 2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2 \quad \text{(Eq. 8)} \]

Figure 11 - Solubility of Al(OH)₃ as a function of pH.

When aluminum reacts with a strong acidic or basic solution, the liquid will remain clear as the hydroxide goes into solution [22].

Since Foersterling and Philipp's invention, there have been advancements to react aluminum with different caustic solutions or by using different additives to either improve reaction rates or safety while maintaining high hydrogen yields. Initially, some results deemed hydrogen production from aluminum surfaces was too slow for fuel cells, however with ball-milling to powderized the aluminum and increase surface area, hydrogen production rates became more than adequate [24]. Porciúncula et al. reacted aluminum with different
concentrated solutions of NaOH and KOH, both strong bases in solution and determined that the reaction completion of the aluminum is highly dependent on the concentration of the basic solution and temperature of the reaction [25]. Samples of aluminum used were on the order of 30-40 mg, which is not a powder, however the mass is an order of magnitude less than the activated bulk aluminum demonstrated in this thesis (300mg).

Recent attempts have been made to react aluminum with slightly less caustic solutions. Macanás et al. reacted aluminum powders by reacting them with safe-to-handle pH solutions, in the range of 11-12, using various additives to show that aluminum can be reacted efficiently in solutions less hazardous than the NaOH solutions others have used [21]. Aluminum typically passivates in solutions where pH is between 5-9, however Czech et al. found that ball-milling aluminum powders with inorganic salts such as KCL and NaCl allowed the aluminum powder to react in near neutral solutions [26]. Thus the current state of the art with caustic solutions is to use a powderized aluminum, potentially with an additive like an inorganic salt to accelerate the oxidation of the aluminum to generate hydrogen gas. Though these de-passivation methods are efficient, they still require the use of corrosive solutions which create safety and logistical complexities associated with their containment and transport, significantly increasing overhead cost [19–21,25–27].

Aluminum is capable of reacting with water continuously in neutral conditions as well. This makes for potentially safer reactions as there are legitimate concerns with handling and transporting caustic solutions. The simplest means of removing the oxide layer is to scrape it off via a tool or machine. One method involved grinding the aluminum underwater, however once the grinding stopped, the hydrogen production stopped too. Any method which involves an
energy-intensive process to react aluminum reduces energy density of any system it may be used in [28].

The most practical method of bypassing the oxide layer is to use elements such as gallium, indium, zinc, tin, and alloy them with aluminum. These metals have relatively low melting points (less than 300°C) and will naturally embrittle aluminum grains when melted. Aluminum is most commonly activated with gallium, which has a strong affinity for aluminum grain boundaries and will activate aluminum surfaces on contact. Aluminum that is activated with these metals can readily react in different solution types including neutral solutions. The one drawback of using metals like gallium and indium is that they cost on the order of $200-$300/kg, thus limiting their use is essential to making cost-efficient aluminum. Aluminum that has been activated with zinc, gallium, indium, tin or some combination has not been adopted as a viable technology because alloys either do not have high enough reaction completion, contain too much alloying metal, or use powderized aluminum [27,29–31]. These particular methods will be discussed in further detail in chapter 3 as background. The activation of aluminum described and characterized in this thesis can potentially solve all of these issues with activated aluminum alloys.

2.7 Interaction of Aluminum with Liquid Metals

Aluminum that is activated with liquid metals like gallium, indium, or tin can be practical and economical as hydrogen sources as these activation metals are relatively safe to handle with minimal personal protective equipment (PPE), and can be cost effective if used in small amounts and recycled [20]. A side effect of activating aluminum with metals like gallium and indium is a phenomenon called liquid metal embrittlement. This is when a liquid metal penetrates the grain boundaries of aluminum and weaken the lattice structure by cleaving metallic bonds. Research on liquid metal embrittlement is extensive and coincidentally, aluminum and gallium are a
commonly studied phenomenon since gallium has a strong affinity for aluminum grain boundaries [32-35].

The interaction between aluminum and liquid gallium is one of the most discussed examples of grain boundary diffusion and liquid metal embrittlement primarily because gallium has such a strong affinity for aluminum grain boundaries [32–36]. Although the mechanism of liquid metal embrittlement (LME) and the possible role of grain boundary diffusion in the process is not fully understood, certain rate-controlling parameters have been identified: temperature, duration of liquid metal exposure, surface conditions, microstructure, and internal stresses, particularly those induced by cold working, which all can be tuned to provide favorable conditions for LME and liquid metal diffusion [32–37].

A successful treatment can be identified with embrittlement of aluminum by wetting and penetration of grain boundaries by a certain liquid metal. The presence of a liquid metal in the grains can affect the fracture toughness of the solid metal depending on the type of solid-liquid metal interaction, how deep the liquid metal has penetrated the microstructure of the solid, and the relationship between the liquid metal and the tip of a developing crack [35]. When considering different solid-liquid metal couples, the respective fracture toughness of each pairing can vary greatly, even from the base fracture toughness of the pre-treated solid [38]. As stated by Hugo and Hoagland in their paper on aluminum embrittlement by gallium: “in order for this to occur, the surface of the solid metal must be wetted by a certain liquid metal” [39]. Thus, a sample of aluminum whose grains have been wetted with pure gallium may exhibit significantly different mechanical properties than one whose grains have been wetted with a liquid metal pair of gallium, tin, or indium.
Gallium is miscible in aluminum and wets both the aluminum metal and the aluminum oxide. However, aluminum is nearly immiscible in a gallium-indium eutectic [40]. LME has been proposed to be a chemisorptive process that modifies the cohesive strength of the attacked metal (an adsorption reduction of cohesion) and thereby leads to brittle failure at stresses that otherwise would result in a ductile response [41]. Although LME of aluminum is most commonly observed in polycrystalline aluminum, it can also occur in single crystal specimens, in which the loss of cohesion is observed along low-index crystallographic planes [41–43].

With ductile metals like aluminum, failure generally occurs via slow discontinuous crack growths. This process is greatly accelerated when a liquid metal, like gallium, enters the microstructure. In order for liquid metal embrittlement to occur in a ductile material, the liquid metal must be adsorbed by a crack tip on the surface of the metal and penetrate deep enough into the microstructure to cause intergranular fracture [42] [43]. Ab initio simulations have shown the embrittling metal to contribute thermodynamically to a lack of grain boundary cohesion by lowering vacancy energies and surface energies of free boundary surfaces relative to bonded surfaces [44]. As a result, it is generally more feasible to induce liquid metal embrittlement of a metal piece that has been heavily cold worked as cold working leads to grain refinement (an increase in the number of grain boundaries on the surface) as well as an increase of residual stress in the metal piece. The aluminum spheres used in this thesis, which have been extensively cold worked via extrusion, forging, and polishing, provide highly favorable conditions for gallium and indium induced LME.

Liquid metal embrittlement of aluminum via gallium is a well-known phenomenon, however it is not fully understood how gallium travels along the grain boundaries [35]. There is evidence that shows it is dependent on multiple factors. A study in 1976 done at Laboratoire de
Metalurgie in Paris investigated the absorption of gallium into aluminum grain boundaries by changing the grain boundary size of aluminum via cold rolling [36]. They found that the amount of gallium absorbed as well as the ductility of the aluminum was dependent on how large the aluminum grain boundaries were (which were affected by cold rolling), the time in which the aluminum was exposed to the gallium, as well as the temperature of the gallium.

Rabkin et al. proposed a model for the kinetics of how liquid gallium travels along aluminum grain boundaries. They claim that the entrance of liquid gallium atoms into an aluminum grain via a crack in the surface caused changes in the crystal lattice, resulting in elastic strain of the lattice [45]. This change in strain puts the bulk out of equilibrium slightly and results in a net force on the liquid metal, pulling it further into the structure [46]. Hoagland et all observed this process occurring at several $\mu/s$, showing that this is a very fast process, and grain boundary diffusion rates are orders of magnitude higher than bulk diffusion rates, thus polycrystalline aluminum is the preferred microstructure for liquid metal embrittlement [34] [43].

2.8 Conclusion

The greatest challenge with using aluminum as an energy source is bypassing the aluminum oxide layer in such a way that the aluminum underneath can be reacted to completion in a safe and cost effective manner. The aluminum manufacturing process is highly energy intensive which attributes to aluminum’s cost to manufacture and makes it more difficult to compete against fossil fuels or other structural materials. Thus aluminum is not a grid-scale power source, however since it has such a high energy-density, it has potential utility in applications ranging from single-watt power systems for personal electronics to back-up power stations for hospitals and homes.
Currently, there are many different methods of disrupting the aluminum oxide layer, however to the author’s knowledge, there is no activated aluminum fuel on the market that can be readily used to power a fuel cell efficiently. This is because the methods proposed are either too expensive, logistically impractical, use unsafe chemicals, or the form of aluminum used is too unstable and unsafe to handle. The alloying of aluminum with metals such as gallium and indium is the most practical of these methods as they can be potentially used in small amounts, they are relatively safe to handle, and can react the aluminum to near completion.
2.9 Chapter 2 References


[38] Burke, J J, Norman L, Weiss V. Surfaces and Interfaces II, Physical and Mechanical Properties. 1968.


The aluminum treatment process presented in this chapter produces an activated aluminum which can be reacted in water to produce high hydrogen yields using only small amounts of gallium and indium. What sets this treatment process apart from other methods is it can activate large pieces of aluminum that can be reacted to near completion when immersed in water. Though gallium and indium can be used to activate aluminum, they are very expensive, thus limiting their use is essential to being cost effective. Currently, there is no real practical way of introducing gallium and indium into bulk aluminum which limits their use and maximizes reactivity. This chapter outlines different methods used to activate aluminum using these methods then presents the activation method that is discussed and explored in this thesis. This activation process is characterized and the activated aluminum is evaluated for hydrogen yield and gallium indium content in order to validate its potential as a viable aluminum fuel.

3.1 Background on Aluminum Activated with Liquid Metals

Aluminum can be activated when exposed to liquid metals such as gallium, indium, and tin as they will naturally break down the oxide layer that forms on aluminum surfaces. As discussed further in chapter 2, this activation is generally accompanied by a phenomenon known as liquid
metal embrittlement in which these metals, particularly gallium, will travel along aluminum grain boundaries and weaken the grain structure. This effectively turns aluminum from a ductile material into a brittle one. Activating aluminum using these metals allows it to react in neutral solutions, thus reducing the logistical dangers involved with transporting and handling caustic solutions which would remove the protective aluminum oxide layer also. These metals are also not fully consumed during the reaction, thus they can be reclaimed from the waste either by mechanical or chemical separation.

There are numerous means of activating aluminum with gallium, indium, tin, and other metals. Most notably is work done by Prof. John Woodall from U.C. Davis who proposed a cast aluminum alloy in which aluminum, gallium, indium, and tin or some combination of these metals are all introduced into a heated crucible in a known quantity and then allowed to cool into a homogenous alloy. Ziebarth and et al. investigated binary alloys of aluminum and gallium at different concentrations of aluminum as well as quarternary alloys containing aluminum, gallium, indium, and tin [1]. It was found that alloys formed with just gallium and aluminum were capable of reacting as the temperature of water it was reacted in was raised to approximately 30°C. The samples with the highest reaction rates were those made with gallium, indium in tin, which contained 50 wt. % aluminum, 34 wt. % gallium, 11 wt. % indium, and 5 wt. % tin, producing on average 83.8% of the expected hydrogen.

The proposed mechanism of reaction by Ziebarth and Woodall is the diffusion of raw aluminum phase surrounded by a liquid gallium, indium, and tin liquid phase that contains small quantities of aluminum. Though the aluminum is near soluble in this phase, Ziebarth et al. propose that the aluminum reaches the water by diffusing through this liquid metal layer to react with the water layer on the surface. They argue that the metal being liquid is responsible for this
mobility of aluminum and the reaction of aluminum at the surface results in a concentration
gradient which allows more aluminum to be dissolved reacted at a water interface (Figure 12).
Figure 12 – Proposed model by Ziebarth and Woodall et al. of a cast aluminum alloy containing gallium, indium, and tin. The liquid metal layer allows aluminum to diffuse from aluminum rich
regions to water via concentration gradients, thus producing 

*aluminum hydroxide and hydrogen gas* [1][2].

Another method of activating aluminum with these metals is to ball mill aluminum powders with these activating metals [3–8]. This form of activated aluminum contains small amounts of activating metals, approximately 2-5% and is capable of obtaining high hydrogen yields when it is exposed to water. Ilyukhina et al. manufactured an activated powder produced by high-energy ball milling with 2-3% wt. Ga-In-Sn that obtained a near 100% hydrogen yield when reacted at 60°C [4]. Though encouraging, powders pose challenges related to both their explosivity and their tendency to oxidize in air due to their high surface areas; in addition, handling very fine powders is difficult in large quantities and poses a health risk if inhaled.

In-situ methods can be used as well to react the aluminum metal. Using liquid gallium, the aluminum can be dissolved in small amounts at high temperatures and then reacted at a water surface. This method was demonstrated by Erich Brandeau who investigated using aluminum as a potential energy source for underwater autonomous vehicles [9]. This method is capable of producing high hydrogen yields, but requires a significant amount of liquid gallium as aluminum is approximately 2-3% soluble in gallium at about 30°C (Figure 13). This makes for an impractical system as the dissolution of aluminum into gallium is slow, even at elevated temperatures thus becoming a rate-limiting step to producing hydrogen gas.
Figure 13 – A binary phase diagram of aluminum and gallium.

Aluminum is approximately 2-3% soluble in gallium at 30°C [10].

The next section of this thesis shows a new method activating aluminum with gallium and indium in which bulk pieces of aluminum containing only 3-4 wt. % Ga-In produce hydrogen at high efficiencies close to 90%. This is an advantageous method as it does not have the safety or logistical concerns associated with handling and transporting aluminum powders, yet has similar hydrogen yields and approximately the same amount of activating metal. This process is characterized using 6mm diameter aluminum spheres which are the same shape of the original pieces of aluminum that were used when this process was discovered.
3.2 Activating the Aluminum

6mm diameter aluminum spheres were surface treated by placing them in a 120°C gallium (80% wt.)-indium (20% wt.) eutectic bath for periods of 30, 60, 90, and 120 minutes (Figure 14 (a)). Excess eutectic was then centrifuged from the surface of the spheres (Figure 14 (b)) and the spheres were transferred to a hermetically sealed container and aged for one week to facilitate the diffusion of the eutectic into the grain boundaries (Figure 14 (c)). To evaluate hydrogen yield, the treated spheres were reacted with 18.2 MΩ deionized water in 5mL flasks (Figure 14 (d)) until hydrogen was no longer noticeably produced (Figure 14 (e)). Hydrogen was directed from the flask to an inverted column of water and the volume was recorded visually via a graduated scale.
Figure 14 – 6 mm aluminum spheres are surface treated by wetting them in a gallium-indium bath which allows the liquid metal to begin diffusing (a). Removal of excess liquid metal via centrifuge so that it can be reclaimed and reused (b), and curing the spheres in a hermetically sealed container before it is ready to react with water (c). Spheres are reacted in 5 mL of 18.2 MΩ deionized water (d) until hydrogen is no longer produced (e).
3.3 Corrosive Effects Due to Surface Treatment

After surface treatment, treated spheres typically showed signs of surface corrosion with only partial areas of some samples resembled the shape of a sphere (Figure 15 (a)). Some spheres exhibited noticeable pits in the surface (Figure 15 (b)). While corroded spheres react with water in the same general manner as un-corroded spheres, only measurements from intact spheres (Figure 15 (c)) were used in the determination hydrogen yield to avoid comparing samples with differing aluminum content, surface areas, and volumes. The frequency of spheres deemed acceptable for accurate testing dropped with treatment time as indicated in Table 3.
Figure 15 – Severely corroded (a), corroded (b), and intact (c) treated aluminum spheres from a 120-minute treatment in the liquid gallium-indium bath at 120 °C. Sphere (a) has a mass of 0.297g, sphere (b) is 0.307g, and sphere (c) has a mass of 0.310g.

The mass of the aluminum spheres and eutectic are recorded before and after treatment to estimate how much gallium-indium eutectic diffused into the spheres. Table 3 shows masses of the eutectic and treated spheres both before and after treatment as well as an upper value eutectic composition inside of the spheres. The overall estimate of gallium and indium in the samples is an upper bound percentage as not all of the remaining eutectic could be practically recovered – some is lost while cleaning tools or the remaining wetted spheres after centrifuging.

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>% of Intact Spheres post Treatment</th>
<th>Ga-In Not Recovered (g)</th>
<th>Aluminum Mass Before Treatment (g)</th>
<th>Aluminum Mass Post Treatment (g)</th>
<th>Max wt. % Ga-In in Aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 Minutes</td>
<td>85 %</td>
<td>0.97</td>
<td>20.08</td>
<td>20.33</td>
<td>4.55 %</td>
</tr>
<tr>
<td>60 Minutes</td>
<td>66 %</td>
<td>0.89</td>
<td>20.09</td>
<td>20.59</td>
<td>4.14 %</td>
</tr>
<tr>
<td>90 Minutes</td>
<td>43 %</td>
<td>1.13</td>
<td>20.10</td>
<td>20.39</td>
<td>5.25 %</td>
</tr>
<tr>
<td>120 Minutes</td>
<td>58 %</td>
<td>1.12</td>
<td>20.08</td>
<td>20.72</td>
<td>5.12 %</td>
</tr>
</tbody>
</table>

Table 3 – Frequency of intact spheres are shown as well as the mass of gallium-indium lost and aluminum before and after treatment.

The frequency of intact spheres decreases with treatment time. The maximum weight percent of gallium-indium in the spheres is greater in samples treated for 90 and 120 minutes than 30 and 60 minutes.
3.4 Reaction Efficiency

Reacting the treated spheres in water and measuring hydrogen output provided an accurate representation of how much of the aluminum reacted in water. Intact treated spheres were weighed and then each reacted with 5mL of deionized water at room temperature in a sealed reaction chamber. Prior research on aluminum fuels was typically done with samples being reacted at specific temperatures in an excess of water [1,5,11]. Although the stoichiometry indicates that each sample only needs 0.6 mL of water to react (assuming the amount of aluminum in each treated sphere is 0.3g), there is substantial heat produced by the reaction which is released rapidly enough to evaporate much of the water, resulting in an incomplete reaction. Thus depending on the reaction vessel, there is a specific amount of water needed that is greater than the implied stoichiometric quantity in order to produce the maximum amount of hydrogen from a single treated sphere. The aluminum hydroxide that is a reaction byproduct is hydrophilic and retains some of the water as the reaction progresses. In an unconstrained space, 5mL of water was determined empirically to produce the largest quantity of hydrogen from a 6mm (0.3 grams) treated sphere. Excess water was found to cool the reaction and resulted in lower hydrogen yield. During a typical test, the sample was allowed five minutes to fully react; no sample produced any measurable hydrogen beyond this time. In a constrained space, only about 1.2 mL/6 mm sphere was needed to complete the reaction.

As shown in Figure 16, an increase in surface treatment time produces a greater hydrogen yield and correspondingly greater percent reaction completion of a sphere of the same size until it reaches an asymptote at a treatment time of 90 minutes. The sphere mass is also shown to increase with time in the bath with 90 and 120 minutes having nearly equal sphere masses.
Figure 16 – Reaction completion of samples soaked in the In-Ga bath at 120 °C plotted against the time spent in the treated bath.

Only intact treated spheres were used.

Hydrogen production efficiency was calculated by comparing the measured hydrogen to the expected hydrogen assuming a complete reaction. For a 0.300g of aluminum (the mass of an untreated sphere) it is expected that 0.404 L of hydrogen will be produced at room temperature and pressure. This is a conservative estimate as the expected hydrogen volume would be greater if not for some aluminum lost due to minor surface spalling in the treatment process. As samples were selected visually, there is also some variation in overall mass of the treated spheres. The average mass of the samples as well as their average hydrogen yields and error have been calculated, demonstrating a correlation between treatment times and overall treated sphere
efficiency. As indicated previously, the overall hydrogen yield appears to reach an asymptote after 90 minutes of treatment at 120 °C.

\[
\% \text{Yield} = \frac{V_{\text{H}_2} \text{measured}}{V_{\text{H}_2} \text{expected}} \quad (\text{Eq. 2})
\]

3.5 Treated Sphere Composition

Spectroscopic analysis was performed on intact treated aluminum spheres to determine the gallium-indium content in each sample. Figure 17 shows that spheres treated for 60 minutes have a similar gallium-indium content to those treated for 90- and 120-minute samples, but the overall hydrogen yield is about 6% less comparatively. Treatment times greater than 60 minutes did not result in greater internal gallium-indium content, but the increased time did result in increased hydrogen yield from samples. The treated spheres demonstrated that aluminum can be reacted to approximately 90 percent completion with less than 4 percent gallium. Such a high reaction completion has only previously been achieved using aluminum powders [4–6,12–14].
Figure 17 – Gallium-indium content in aluminum spheres treated for different times. Data were collected using Inductively Coupled Plasma Mass Spectroscopy (ICPMS).

The hydrogen yield from various treatment times and their respective gallium-indium compositions show that these parameters are coupled in this treatment process. For these samples, a minimum of a 60-minute treatment results in hydrogen yields of over 80% when reacted in 5mL of DI water at room temperature. Samples treated for 90 minutes show nearly one percent more gallium-indium content than samples treated for 120 minutes yet provide a similar hydrogen yield; thus, it appears that additional gallium-indium is not necessary for successful activation. The presence of this excess metal is likely to be found on the surface of the spheres due to the liquid metal’s tendency to wet the aluminum sphere’s surface. Further testing is needed however to determine the root cause of this excess metal.
3.6 Gallium-Indium Interaction with Aluminum

Scanning Electron Microscopy (SEM) was performed on untreated (Figure 18 (a)) and treated spheres (Figure 18 (b)-(f)) to ascertain production-related features and observe how the gallium-indium eutectic modified the microstructure. Spheres treated for 30, 60, 90, and 120 minutes at 120°C were examined. Immediately after treatment, the aluminum spheres exhibited ductility when subjected to compressive force, however when allowed to age for several days, the spheres became embrittled. Treated spheres were identified and cleaved using fine nosed pliers as a test for embrittlement. The microstructure of untreated spheres (Figure 18 (c)-(f)) revealed a heavily worked structure which confirms these spheres were extruded, cut, forged, and polished.
Figure 18 – SEM images of an untreated sphere surface (a), a treated sphere surface (b) for 120 minutes, and fractured surfaces (c)-(f) of the aluminum spheres which had been treated for various time intervals. Grain boundaries are etched here by the gallium-indium liquid metal.
The aluminum sphere grain size was observed to be approximately 1-10 μm. The fineness of the grains is noteworthy as typical bulk aluminum processed via casting, forging etc. has grains on the order of 10 to 100 μm [15]. This order of magnitude reduction in the grain size of the spheres relative to more common bulk aluminum is expected to play a significant role in the gallium-indium treatment and subsequent water reaction process.

Spheres treated for 30 minutes did not fracture as cleanly as samples treated for longer durations. The SEM images in Figure 18 show the extent of gallium and indium penetration and confirm a preferred penetration path along grain boundaries of the aluminum spheres (Figure 18 (d)-(f)). The presence of voids and general decohesion is also apparent in the longer-treated samples. While there is evidence of eutectic in the grains of the 30-minute treated sample, (Figure 18 (c)), the embrittlement is incomplete. The incomplete diffusion of eutectic in grain boundaries of samples treated for 30 minutes is consistent with the observation that such samples did not fracture in a purely brittle manner but rather showed a degree of ductility. The extent of liquid metal diffusion appears to be similar for samples treated for 60, 90, and 120 minutes; however samples treated for 90 and 120 minutes experienced greater hydrogen yields. Thus, more progressed decohesion appears to increase activation of the spheres.

3.7 Treatment with Different Temperatures and Metals

Temperatures other than 120 °C were also examined. Spheres treated at 90 °C for 120 minutes produced less than 47% yield and samples treated at 70 °C for 120 minutes produced less than 17% yield. 88% of spheres treated at 70 °C experienced a brief surface reaction before ceasing to react entirely when placed in water. Samples that were treated at room temperature for 120 minutes were nearly inert in water. When the temperature was increased to 150 °C for 120 minutes, the
corrosion on the spheres after treatment was too severe for it to be considered a viable treatment temperature. As much as entire halves of spheres were missing at this treatment temperature.

Different liquid treatment metals were also examined. Treatment with pure gallium for 120 minutes at 120 °C produced severely corroded spheres, which generated no significant hydrogen. Samples treated with a gallium, indium, and tin eutectic for 120 minutes at 120 °C, averaged 70.0 ± 4.6% hydrogen yield with an average mass of 0.305 ± 0.002g. Thus, the addition of tin to the eutectic does not appear to increase hydrogen yield of treated spheres. Further tests are needed, however, to determine if tin might be able to be substituted for Indium and/or Gallium as it is less expensive than gallium or indium and could potentially reduce the cost of the treatment process. The current tests show, however, that indium, even in the small amounts that were used, is a key component for producing activated aluminum spheres that produce high hydrogen yields.

3.8 Discussion and Conclusion

The data show that aluminum spheres can be activated via a surface treatment with a gallium-indium eutectic bath. Though not fully characterized for all conditions, treatment temperature and duration play an important role. It is likely that other parameters not explored in the current study have a strong effect as well. It is known that the internal stresses and grain structure of aluminum are dependent on forming processes and the alloy content of the aluminum [16–20]. The aluminum spheres used in this study were 99.90% aluminum (before treatment) and were extruded, forged, and polished. These spheres have a fine grain structure and residual stresses as a result of the cold-forming manufacturing processes they underwent. These processes create favorable conditions for the gallium-indium to penetrate the grain boundaries during treatment and activate the internal aluminum. The fine grain structure and internal stresses are believed also to contribute to the high reactivity of the spheres in water.
At present, activated aluminum powders can obtain reaction completions of over 90% with less than 10% other metal content (gallium, indium, and/or tin). It has also been observed that producing activated aluminum alloys with even less metal content (e.g. 5%), have reaction completions around 50% [1]. For pelletized or bulk aluminum fuels, 50% aluminum and 50% other metals are able to obtain high reaction completions. A common explanation for the reaction described here suggests that aluminum diffuses through the liquid metal and reacts with water at the interface [1,2,21]. However, when spheres are treated with just gallium in the same manner presented in this paper, it was observed they do not react in water to completion even in water at elevated temperatures. Thus, it is likely there is another mechanism that drives the activated aluminum’s reactivity.

As the treated spheres react, internal stresses contribute to rapid structural disintegration of the spheres. Intergranular fracture of the fine-grained aluminum spheres results in higher surface areas in contact with the water much like occurs with powders resulting in high reaction rates and leading to a more complete, cascading reaction. The drawback of powders is their high surface area makes them susceptible to rapid oxidation and fine grains make them unsafe to handle either due to inhalation or explosion hazards. The pelletized or bulk aluminum fuel discussed here has the advantage of a lower surface area to volume ratio which minimizes oxidation during handling. The treated aluminum spheres in this study present a much safer source of energy as they are safer to handle yet react rapidly when placed in contact with water. To the authors’ knowledge, only Ziebarth and Woodall et al have produced a bulk activated aluminum alloy which has similar reaction completions, however the alloy is comprised of 50% activation metal which adds significantly to its weight and cost.
A new treatment process has been created and validated by treating 6 mm aluminum spheres in a heated gallium-indium eutectic bath. The treated spheres react in water to nearly 90% reaction completion and require significantly less gallium and indium (3.5-4.5%) than prior attempts at activating bulk aluminum. It has been shown that temperature, duration of treatment, and grain structure all affect the reaction completion and hydrogen yields. Spheres treated with a gallium-indium eutectic at 120 °C for 120 minutes showed reaction completions of greater than 85%. Prior to this treatment process, only activated aluminum powders using similar amounts of activation metal could obtain high hydrogen yields when reacted with water reaction. The treated aluminum spheres presented in this paper represent a significant advancement as they can be safely handled and stored for use in high energy density power generation systems.
3.9 Chapter 3 References


CHAPTER 4

COLD-WORKING ALUMINUM AND ITS EFFECT ON Reactivity IN WATER

The activation of aluminum via the treatment process described in chapter 3 is shown to be dependent on time spent in the liquid metal bath, temperature of the liquid metal bath, and type of liquid metal used. These factors directly affect the embrittlement of the aluminum (liquid metal embrittlement) which is needed for the efficient generation of hydrogen from aluminum. Furthermore, it is shown in this thesis that cold worked aluminum immersed in a bath of liquid gallium and indium allows the liquid metal to penetrate the grain boundaries of the aluminum even more efficiently, thereby resulting in liquid metal embrittlement and activation of the bulk aluminum while using a minimal amount of gallium and indium. This hypothesis was reactivity of the treated 6mm aluminum spheres was due to how they were manufactured Microscopy of the sectioned spheres showed forming lines from the spheres which indicated they were extruded, cut into smaller pieces, cold forged into a rough ball shape, and then polished to spherical shapes. This results in a highly-worked grain structure, which involves cold-working at nearly every step.

This chapter shows the importance of residual stresses on reactivity by comparing treated, stress-relieved aluminum spheres with cold-worked aluminum that has been plastically
strained to different amounts. Both cold forging of the aluminum spheres and cold-rolling of 
1100 aluminum plate are investigated. Cold-working the aluminum results in hardening of the 
material via residual stresses in the grains, providing favorable conditions for liquid metal 
embrittlement and thus activation of the aluminum. Hydrogen yield from the aluminum-water 
reaction is measured to quantify energy efficiency and the effect residual stresses have as a result 
of cold-working on activation of the aluminum. Results show that an increase in plastic strain of 
the bulk aluminum results in an increase in hydrogen yield.

4.1 Deformation Processing of Materials

4.2 Corrosion of Stressed Metals in Water

Cold-working metals can result in residual stresses, which is equivalent to work-hardening 
of the metal. The material does not have the energy for particular grains to re-align to lower 
energy states, thus they remain stressed (preloaded against each other like springs) and the free 
energy of the system is higher than an annealed sample [1]. Annealing a hardened metal causes it 
to lose strength and relax: temperature and time allow the crystal lattice to expand, which in turn 
creates more space for grains to realign and settle into lower-energy states. The residual stress is 
essentially a preload on the crystal lattice and between grains, which is why a hardened material 
will yield at a higher stress than an annealed sample of same size and composition.

There is some evidence of a correlation between the hardness of a metal and how quickly it 
corrodes in the environment. Unlike aluminum, which has a natural protective coating, steel 
needs some form of protection from corrosion since iron oxide readily flakes off the surface of 
steel, exposing un-corroded surfaces. Corrosion can result in a critical loss of structural material, 
allowing stress concentrations to form which lead to more rapid failure of the structure [2]. The
corrosion of steel often occurs where protective coatings are thin such as in crevices or hard to reach areas [3][4].

The most prevalent research in this area is for structural steel where corrosion is detrimental, for example in offshore structures and rebar for reinforced concrete, as opposed to the case for treating aluminum for hydrogen where corrosion is desired. Ambrazhey et al. investigated corrosion behavior of cold-rolled steel rebar approximately 10mm in diameter by exposing it to an alkaline solution (Ca(OH)₂) and recording current density and electrode potential of the steel as a function of time. They found that residual macrostresses from cold-rolling the bar results in an increase in corrosion of the metal in concrete. They recommend that in order to help quell this increased corrosion, the steel needs to be artificially aged or mechanically cycled in order to help stabilize the metal’s structure [5].

Another paper by Ranji et al. analyzed corrosion behavior of different carbon content, low strength, and high strength steels in the presence of chloride solutions. Samples were immersed in a chloride solution and then subjected to a constant tensile stress. Samples were massed over time and the authors found that for the first 144 hours of testing, there material lost to corrosion was near identical across all samples of steel, however after this time period, the corrosion of high strength steels accelerated greatly in comparison to lower strength samples [6].

There is also data that contrary to the notion that high-strength steels experience faster corrosion rates. Aminul Islam compared the corrosion rates of high strength (500MPa yield) and low strength (300 MPa yield) steel rebar for reinforced concrete and found no difference in corrosion rates in seawater or in freshwater between the two types of steel. Instead, the author found that different alloying elements added to the steel such as copper, nickel, and chromium
instead gave the steels increased corrosion resistance and that steel with refined grains also helps with preventing corrosion.

In the case of corroding aluminum in water for the sake of power generation, there is little research that has been done to the author’s knowledge to determine a correlation between working the aluminum prior to reacting it. Czhech et al hypothesized that the increase of reactivity of aluminum powder over bulk aluminum is a result of high-energy ball milling which results in plastic deformation of the aluminum. This in turn affects the residual stresses inside the aluminum and redistributes constituents in the aluminum bulk. However, upon comparing ball-milled aluminum powder with powder that had been annealed and stress-relaxed, the authors found no difference in hydrogen evolution when it reacted with water. It was thus still inconclusive whether plastically deforming aluminum will increase its reactivity in water.

It is well known that aluminum is susceptible to liquid metal embrittlement via grain boundary diffusion of liquid metals. Applying stresses to aluminum grain boundaries has been shown to increase the extent and speed of grain boundary diffusion of liquid metals [7–11]. Cold-working the metal introduces more dislocations and other defects into the microstructure as well as the surface and an increase in residual stress throughout the aluminum. This increase in free-energy of the aluminum bulk makes it more susceptible to liquid metal diffusion. In this chapter, it is shown that plastically deforming the aluminum and introducing redundant work prior to treatment in a heated gallium-indium eutectic bath results in increased reactivity after treatment.
4.3 Experimental Setup

4.3.1 Cold-Forging Aluminum Spheres

Aluminum spheres 6mm in diameter and weighing 0.3g were annealed at 412°C (775°F) for 3 hours, 315°C (600°F) for 2 hours, and at 200°C (400°F) for two hours. Different annealing treatments were done to determine a correlation between grain size and hydrogen yield in water. Samples from the 315°C annealing treatment were then compressed via an arbor press to predetermined heights of 0.82±0.02mm, 1.83±0.02mm, 2.76±0.02mm, and 3.39±0.02mm using pre-fabricated height gauges to ensure the spheres were consistently deformed (Figure 19). This process is the equivalent of barrel cold forging the spheres. The annealed spheres (412°C and 315°C) and the deformed spheres were then treated in heated Ga-In eutectic baths for two hours then allowed to cure for 7 days. The spheres were then reacted in 5mL of deionized water and the hydrogen volume was recorded after no noticeable hydrogen was being generated by the reaction. SEM imaging was then done on fractured sphere sections
Figure 19 - Annealed spheres at different steps of preparation for plastic deformation. Top shows the setup of the deformation process. Middle shows the sphere deformed to a known height sandwiched between two parallels. Bottom shows spheres compressed to the different heights. At least 20 samples of each height were made for treatment in the heated Ga-In eutectic bath.

4.3.2 Cold-Rolling Aluminum Plate

Cold rolled pieces were also tested as well since cold forging involves more redundant work than rolling. 1100 series aluminum pieces were cut from 6.31mm (0.250”) annealed sheet stock using an abrasive waterjet cutter. Samples were annealed at 400°C for 2 hours and all but a single sample were put through a rolling mill at 0.318mm (0.0125”) increments until desired thicknesses were reached. An unrolled-sample remained at 6.31±0.01mm while the other samples were rolled to 5.74±0.01mm, 5.11±0.01mm, 4.54±0.01mm, 3.86±0.01mm, and
2.45±0.01mm (Figure 20). Once rolled, some of the pieces had significant curvature due to the rolling, thus they were cut into slivers 6mm wide approximately. These slivered samples were then treated in the heated gallium-indium eutectic bath at 120°C for two hours.

![Image](image.png)

**Figure 20** – 1100 series aluminum samples cold-rolled to different thicknesses prior to treatment. Samples started at 6.31mm in thickness and were incrementally rolled to approximately 0.635 increments.

4.3.3 Comparing Compressive and Tensile Residual Stress

The processes demonstrated so far have only involved compressing the aluminum metal, resulting in negative strains inside the bulk of the aluminum microstructure. In papers where liquid metal embrittlement is studied, stress is normally applied in tension. To determine qualitatively any difference in reactivity of aluminum that has been stressed in tension or in compression, an annealed 1100 series aluminum beam was deformed in three-point bending
prior to treatment (Figure 21). Since the beam is in equilibrium after bending, it was assumed that the magnitude of compressive and tensile residual stresses are of the same magnitude.

![Figure 21 - An annealed 1100 series aluminum beam being deformed under an arbor press via three point bending. The sample was plastically deformed to ensure tensile and compressive residual stresses would be present in the beam prior to treatment.](image)

4.4 Results

4.4.1 Cold-Forging Aluminum Spheres

The results show that annealing the spheres has a significant effect on hydrogen yield when the spheres were reacted in water (Figure 22). Compressing and plastically deforming the annealed spheres via a press, results in an increase in hydrogen production. Hydrogen yield was calculated by comparing the measured $H_2$ volume to the expected $H_2$ volume for 0.3g of aluminum.

Aluminum spheres that were annealed at 315°C for 2 hours then deformed to 2.76mm and then treated, yielded the most hydrogen, generating $77.2 \pm 3.7\%$ of the predicted hydrogen amount. In comparison, spheres annealed at 315°C for 2 hours yet left un-deformed yielded $33.9 \pm 2.4\%$ of
the expected hydrogen. Results are compared to the benchmark unchanged spheres treated for 120 minutes at 120°C produced in the analysis from chapter 3.

![Graph showing hydrogen yield vs sphere deformation](image)

**Figure 22** - Aluminum spheres annealed and then compacted via an arbor press to different known heights were treated in the heated Ga-In bath and then reacted. Hydrogen yield as a function of sphere deformation is shown.

Scanning electron microscopy was then conducted on the spheres to analyze grain structure to determine or find any changes in grain structure (Figure 23). The spheres became embrittled as a result of the heated Ga-In treatment, thus they were cleaved in order to view the microstructure. There is significant grain growth as a result of both annealing treatments – however there is no apparent grain size change between spheres that were plastically deformed.
It was also observed that spheres annealed at 315°C for 2 hours still had some of the extrusion lines from their original manufacturing.

Figure 23 - Images from scanning electron microscopy (SEM) compare the annealed spheres that were compressed and then treated in a heated Ga-In bath to a non-annealed sphere. Grain
growth and recrystallization are shown in the spheres that were annealed, while pancaked grains are apparent in the un-annealed spheres.

Different annealing treatments were performed as well to determine the effect of grain size on reactivity. Spheres were annealed at 415°C for two hours, 315°C for three hours, and 200°C for two hours and then treated in the heated eutectic bath. They were then reacted in the same manner as compressed spheres with 5mL of deionized water and the hydrogen gas was collected in an inverted cylinder (Figure 24).

**Figure 24** - Three different annealing treatments were performed on the 6mm aluminum spheres to determine the effect of grain size on reactivity. This plot shows that as the annealing treatment is less severe, there is an increase in hydrogen yield.
SEM imaging of the different annealed spheres shows that there is no recrystallization that occurred from the 200°C (Figure 25). Recrystallization occurs however with the spheres that were annealed at 315°C for 2 hours and 4

Figure 25 - SEM imaging of spheres that were annealed at different temperatures and times and then treated in the heated gallium-indium eutectic bath at 120°C for two hours. Imaging shows there is no apparent recrystallization for samples annealed at 200°C for 2 hours, yet there is an increase in grain size for the other annealing treatments. This indicates that there is an increase in reactivity associated with smaller grains.
4.4.2 Cold-Rolling Aluminum Plate

The 1100 series aluminum plates which were annealed, then rolled to varying thicknesses, and then treated in the heated Ga-In eutectic. When the samples were treated, a significant amount of gallium remained on the surface. Since they could not be placed in a centrifuge, all samples were manually wiped off using a towel to remove excess liquid metal still wetted to the surface. Since samples could not be broken off in approximately 0.3g pieces, amounts of water were adjusted accordingly. Sample masses reacted with DI water ranged from 0.169g to 0.501g. Compressive strain was calculated for the samples using (Eq. 9). Hydrogen yields were recorded and used to compare different thickness samples by the induced strain.

\[ \varepsilon_{\text{total}} = \frac{\Delta t}{t} \]  
(Eq. 9)

![Graph showing hydrogen yields of cold-rolled aluminum samples.](image)

**Figure 26** - Hydrogen yields of cold-rolled aluminum samples. The pieces were annealed prior to rolling. Hydrogen yields increase as the equivalent strain in the pieces increase.
Samples that were not reacted were imaged using SEM imaging. The treated aluminum pieces were embrittled because of liquid metal embrittlement from the Ga-In eutectic and were cleaved using pairs of needle-nose plyers. Imaging was done on all variations of the treated aluminum samples (Figure 27).
Figure 27 - SEM images of the cold-rolled aluminum pieces after treatment. Samples were fractured and then images were taken of cross sections. As the compressive strain increases, the grains become more pancaked and elongated.

To determine if the samples were work-hardened because of the cold-rolling, untreated pieces were subjected to a Brinell hardness test. Hardness data was collected using an Instron machine outfitted with a 12.7mm diameter ball used to indent the surface of the aluminum with 1000N (Figure 28).

![Setup used to conduct the Brinell hardness testing.](image)

Figure 28 - Setup used to conduct the Brinell hardness testing.

Samples were placed into the machine and indented with the shown ball at 1000N. The indentation was then measured using software to determine the area of deformation.

The indentations were then viewed under a microscope and their respective diameters were measured to determine the hardness of the samples (Figure 29).
Figure 29 - Brinell hardness indentations made using a round sphere. The purpose of this test is to determine to what extent of work hardening done on the aluminum pieces. Diameters of the indentations were measured using the software in the microscope.

The hydrogen yields were then plotted as a function of hardness in order to compare how hardening had affected the reactivity of the activated aluminum (Figure 30).
Figure 30 - Hydrogen yields of treated cold-rolled 1100 series aluminum plotted as a function of the hardness due to work-hardening of the aluminum. Hardness was calculated using a Brinell hardness test using 1000N load across all samples.

It was also observed that the reactivity of the spheres increased as a function of compressive strain due to cold working. Treated samples with strains of 0.000, -0.281, and -0.612 strains were observed via video microscopy (Figure 31). Water was swabbed onto the surface just after video was started. The sample compressed to -0.612 strains reacted in approximately 7.5 seconds, the sample compressed to -0.281 strains reacted in 16.5 seconds, and the uncompressed sample finished reacting in 35.0 seconds.
Figure 31 - Video stills of treated cold-rolled 1100 series aluminum both before reacting with a swab of water (top) and after reacting. Samples that were strained more resulted in higher hydrogen yields and faster reaction rates.

4.4.3 Comparing Compressive and Tensile Residual Stress

The test sample that was plastically deformed via three-point bending was analyzed using video microscopy to determine qualitatively any difference in reactivity between the compressive and tensile stressed sides of the beam. Both sides of the beam were swabbed with...
water using a wicked cotton tip. An unstressed portion of the beam that was also treated was swabbed with water. No noticeable difference in reactivity was observed between the area of the beam that was most stressed in tension versus the area that was most stressed in compression; however, low stressed regions had much lower reactivity. SEM imaging was also done on the different sites of the beam to determine the extent of grain boundary etching and if any grain refinement occurred (*Figure 32*). Etching of the aluminum grains on the surface was observed more on the surfaces that were most stressed compared to the annealed surface.

*Figure 32* – *SEM imaging of the surface of the bent aluminum beam which was treated in the heated Ga-In eutectic bath.*

*Compressive* (b) and *tensile* (a) images were taken in the middle of...
the beam where the stress is maximum and show more etching of grains compared to the annealed and unstressed (c) section of the beam.

4.5 Discussion

4.5.1 Cold-Forging Aluminum Spheres

Results show that cold-forging the spheres prior to treatment in the heated Ga-In bath results in an increase in reactivity in water after treatment. Hydrogen yields increased the more plastically deformed spheres, meaning the more redundant work put into the spheres increases the free energy of the grains, providing more suitable conditions for grain boundary diffusion of the liquid gallium-indium eutectic. SEM imaging showed that there was little to no difference in the grain structure, which means that the increase in reactivity must have come from plastically deforming the spheres. Compressing the spheres results in a shorter path for the liquid eutectic to travel thus making it easier for it to more effectively penetrate the bulk of the aluminum. Fully intact and unchanged aluminum spheres however present a greater distance for the eutectic to travel, yet produce more hydrogen, thus the thickness of the samples due to cold-working can be discarded as a reason for better activation.

Annealing spheres results in a decrease in reactivity, which is contrary to what was hypothesized by Czech et al when they annealed their aluminum powders after ball-milling them. Microscopy showed different degrees of recrystallization of the grains depending on the temperature and duration of annealing. Coupled with the hydrogen yields, it is shown that grain size of the aluminum also likely affects the hydrogen yield once it is treated. There is also a clear increase in mass the spheres experience as the annealing becomes less severe. It is likely that
surface cracks and greater plastic strain on the surface of the spheres provided more diffusion sites for the liquid metal to penetrate. It was observed that annealed spheres did fracture in an entirely brittle fashion, and spheres that were annealed more intensely were harder to separate into halves. This suggests that the liquid eutectic was not able to deeply penetrate the grain structure due to the grains having much lower free energy. This is in agreement with what has been shown in the literature – faster liquid metal diffusion rates are observed in aluminum that is stressed [12,11,13,10,14].

4.5.2 Cold-Rolling Aluminum Plate

The hydrogen yields of the activated cold-rolled aluminum plate further supports the hypothesis that cold-working the aluminum prior to treatment allows for better diffusion which in turn results in a higher reactivity. Plastically deforming the aluminum to approximately -0.281 strains resulted in a hydrogen yield of 97.2 ± 3.5%. After this amount of strain, hydrogen yields reach an asymptote as this is near full completion, however the reaction rate of the aluminum samples increased in the samples that were more plastically deformed. Plastically deforming the aluminum can result in a high hydrogen yield fuel and if higher reaction rates are desired, the aluminum can be stressed more. Thus, the aluminum treatment process described in this thesis can now be utilized to make activated aluminum that can react at a given rate and to a known completion by plastically deforming the aluminum prior to treating in a heated Ga-In bath.

4.5.3 Comparing Compressive and Tensile Residual Stress

There was no apparent difference in reactivity between the compressive and tensile stressed sides of the plastically deformed beam, however these sides both reacted more rapidly than the annealed side at either end of the beam, which has undergone minimal plastic
deformation. Further research is needed to quantify the extent of compressive and tensile residual stresses and how they compare in reactivity.

4.6 Conclusions

The goal of this chapter was to show the affect cold-working aluminum prior to treatment has on the reactivity of the activated metal. Two different deformation processes were examined: cold-forging of the aluminum spheres used to characterize the treatment process in chapter 3 and cold-rolling of 1100 series aluminum plate. Samples were annealed to relax the grain structure to provide a starting point of reactivity and it was observed that annealing reduces the reactivity of the activated aluminum. Samples that had undergone more plastic deformation experienced greater hydrogen yields. In the case of activated cold-rolled aluminum samples, hydrogen yields reached an asymptote at -0.281 strain, however reactivity increased in samples that were plastically deformed even further. Using this new finding, it is now potentially possible take a piece of aluminum and plastically deform it a known amount in order to obtain a desired hydrogen yield and hydrogen generation rate.
4.7 Chapter 4 References


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Activated Aluminum Reaction in Water

Aluminum will readily react with water in a hydrolysis reaction at room temperature and pressure to produce hydrogen gas, aluminum hydroxide, and heat energy. This is confirmed by the presence of only aluminum hydroxide (Al(OH)$_3$) as a byproduct, as the production of aluminum hydroxide-oxide (Al(OOH)) and aluminum oxide (Al$_2$O$_3$) are thermodynamically less favorable due to insufficient temperature and pressure [1]. Chapter 3 showed that treatment time, temperature of the bath, and different metals all affect the reaction yields of the activated bulk aluminum. In particular it was shown that the gallium indium eutectic bath produced activated aluminum with the highest hydrogen yields. Chapter 4 showed that both plastically deforming the aluminum prior to treatment and the presence of finer grains result in higher reaction yields and that further deforming the aluminum will also increase reaction rates.

The activated aluminum shown in this thesis produces similar hydrogen yields to reactive aluminum powders, which are the current state of the art, but with none of the logistical or safety concerns. To the author’s knowledge, no other bulk aluminum fuel can obtain high reaction completions while using only a fraction of activation compound. This chapter aims to understand
how and why this activated aluminum reacts with water in order to reach such high reaction yields.

5.1 Aluminum Liquid Metal Diffusion Theory

It is well known that aluminum will react with aluminum on contact, however it is still not fully understood how aluminum alloys containing gallium, indium, and tin are capable to sustain a reaction without the protective oxide layer forming. These metals can disrupt the naturally occurring oxide layer on aluminum and penetrate the metal’s grain boundaries. How these metals actually allow the aluminum to react with water is still not fully understood, however there have been some hypotheses proposed in the literature.

Ziebarth and Woodall et al. propose a liquid phase transport model for their cast aluminum alloy containing gallium, indium, and tin. They theorize that the liquid phase of these metals prevents a protective oxide film from forming on their surface – in contrast, solid phases of gallium and indium form an oxide coating similar to that of aluminum as they are in the same group on the periodic table. The liquid phase that exists in the grain boundaries of their alloy contains a small amount of aluminum, which when brought to an interface with water, is allowed to react via a hydrolysis reaction. Thus the aluminum is reducing water into H⁺ and OH⁻; the aluminum bonds to the hydroxide ions while the hydrogen ions bond to each other to create hydrogen gas. As the interface of liquid metal with water is depleted of aluminum, it creates a concentration gradient which results in more aluminum diffusing through this liquid metal layer. As their alloy is consumed, they hypothesize that the reaction front moves inward towards fresh aluminum grains until the aluminum is either entirely reacted or no active aluminum surfaces remain. Inefficiencies in their reaction they claim are a result of ejected aluminum grains from
the reacting piece that do not have this liquid metal diffusion layer and thus passivate with dissolved oxygen in water before all the aluminum is consumed [2][3].

A dissertation by Go Choi, a student of Prof. Woodall’s continued the investigation of this liquid phase theory by testing several cast aluminum alloys that would either be solid phase or liquid phase [4]. Choi found that all aluminum alloys containing 80 wt. % aluminum and 20 wt. % gallium showed some reactivity when reacted in water at 60°C and that if unreacted and left alone over time, would precipitate out gallium rich zones as he describes like a chocolate chip cookie. Choi reports that these zones were still liquid and claims they are responsible for the partial reactivity of the alloy in water. He also found that by adding tin and indium to the alloy greatly increased reactivity due to the prevalence of a clear liquid phase existing in the grain boundaries. The freezing point of the gallium tin metal is 10°C unlike the 16°C eutectic temperature of a gallium-indium eutectic. Choi found that when solid alloy samples were immersed in an ice-water bath, they exhibited little to no reactivity, indicating that the liquid metals had solidified, thus halting the reaction of aluminum.

This model was also supported in a paper by Ilyukhina et al. in which they mechanochemically ball-milled an aluminum powder with a gallium-indium alloy (70:30 wt. % respective ratio) which is above the liquid eutectic point by 10 wt. % indium. They discovered that after low energy ball-milling, the surface of their alloy powder is covered with a thin liquid layer of gallium and indium containing only 0.3 wt% of aluminum. Their analysis showed that powders that had undergone high energy ball-milling were much more reactive and had surfaces that were gallium depleted, leaving a non-liquid and indium-rich surface. Both forms of ball-milling produced an activated aluminum that reacted to near completion, however the high-energy ball-milling had hydrogen generation rates two orders of magnitude higher than low
energy ball-milling. Ilyukhina et al found that on the surface of the high-energy method surfaces contained a significant amount of aluminum metal. They attribute the high-reactivity due to a significant defects found in the aluminum surface which result in more activation sites. The gallium penetrates the aluminum bulk and even into the single aluminum grains themselves, while the indium remains in the grain boundaries and on the surface. It is not fully understood as to why a non-liquid layer was present on the high-energy milled surfaces and if or how that contributed to the added reactivity.

5.2 Galvanic Corrosion Theory

It was originally hypothesized in the authors master’s thesis that the treated aluminum spheres are made up many micro-galvanic cells due to the fact that the electric potential between indium and aluminum is slightly greater than gallium and aluminum which is just above the potential needed to split water into hydrogen and oxygen. This is potentially an inaccurate claim because the potential needed to split water into H₂ and O₂ is indeed 1.23 volts, however since reacting aluminum is forming aluminum hydroxide, the aluminum is only splitting a single hydrogen atom from water since the hydroxide group must bond to aluminum to form aluminum hydroxide. This is also supported by the fact that it is less favorable for aluminum reacting with water to form aluminum oxide and aluminum hydroxide-oxide at room temperature and pressure. The potential needed to reduce water into OH⁻ and H⁺ is only 0.81V, which is within the potential difference between gallium.
5.3 Experimental Setup

5.3.1 Importance of Indium

It was shown in Chapter 3 that indium is critical to activating the aluminum. Since indium is more expensive than gallium, it is desirable to limit its use in the activation process. Thus 5 different liquid metal mixtures containing different quantities were constructed for this experiment: 4 wt. %, 8 wt. %, 12 wt. %, 16 wt. %, and 20 wt. %. The last being the original amount required to form a eutectic of gallium and indium at room temperature and pressure. Aluminum spheres were treated in the different liquid metal baths at 120°C for two hours. Samples were then centrifuged of any residual gallium-indium and stored for seven days before reacting.

5.3.2 Cyclic Voltammetry

To test the theory of a potential galvanic cell being formed, cyclic voltammetry was performed using an aluminum anode to determine if indium serves as a more favorable metal for hydrogen evolution in a potential galvanic cell. The aluminum anode was paired with different working electrodes: gallium, indium, and platinum were each tested individually. Samples were tested in a potassium carbonate electrolyte.
Electrode Figure 33 - Potentiostat setup - an aluminum anode was tested against gallium, indium, and platinum separately in a potassium carbonate electrolyte solution. A reference electrode was used for measurement against the working electrodes.

5.3.3 Liquid Metal Transport Theory

Ziebarth and Woodall et al. showed evidence of their liquid metal alloy theory by immersing their aluminum alloy in ice water at 0°C. At this point, the Ga-Sn-In mixture used would be a single solid phase – thus aluminum transport would be impossible through a solid metal. Activated aluminum spheres were put into an ice-water bath. Samples at room temperature and at 2°C were exposed to the ice water to test if freezing any liquid metal in the activated sphere prior to exposing it to cold water would have any effect.
5.4 Results

5.4.1 Importance of Indium

After the aluminum spheres were treated in their respective indium content baths and then cured for 7 days, they were reacted with 5mL of deionized water and their produced hydrogen was collected in an inverted cylinder with a column of water Figure 34.

Figure 34 - Hydrogen yields of aluminum spheres treated in different liquid metals that vary in indium content (remaining is gallium). It was shown in chapter 3 that aluminum treated with a heated gallium bath produced no noticeable hydrogen, but aluminum treated with a Ga-In eutectic produced the most hydrogen.
Since masses changed and different hydrogen yields were observed, material content was found using inductively coupled plasma mass spectroscopy (ICPMS). Elemental indium, gallium, aluminum, and other trace elements were identified.

![Graph showing Ga-In content of sphere samples treated in different liquid metal baths containing different quantities of indium. Data was taken using mass spectroscopy (ICPMS).](image)

**Figure 35 - Gallium indium wt. % content of sphere samples treated in different liquid metal baths containing different quantities of indium. Data was taken using mass spectroscopy (ICPMS).**

### 5.4.2 Cyclic Voltammetry

Cyclic Voltammetry was performed for indium, gallium, and platinum working electrodes paired with an aluminum anode to determine hydrogen evolution voltages for the working electrodes (*Figure 36*). Platinum provided a baseline as a well-known ideal cathode.
Measurements were taken using an Ag/AgCl reference electrode. Voltage was swept from 0 through -1.4V to find peaks that indicate changes in current for all the working electrodes.

Figure 36 - Voltamgrams of indium, gallium, and platinum working electrodes paired with an aluminum anode. Voltage was swept for each sample from 0 to 1.4 volts to determine at what voltage hydrogen evolution would occur.

Multiple runs were done to ensure drift in the working electrode potential was not a major factor. Only gallium appeared to have drifted some, a derivative was taken of the data with respect to voltage to see if peaks would be more discernable (Figure 37).
Figure 37 - A derivative of figure 3 was taken to determine changes in slope of the plots to more clearly determine at what voltage hydrogen evolution began occurring.

5.4.3 Liquid Metal Transport Theory

Aluminum spheres that were treated in the heated gallium-indium bath were immersed in ice water at 0°C. Spheres at both 2°C and room temperature were tested. Upon immersion in the liquid water, both samples of aluminum spheres showed immediate hydrogen evolution.
Figure 38 - Treated aluminum spheres immersed in ice baths to see if hydrogen evolution would occur at temperatures below the freezing point of the gallium-indium eutectic. Aluminum samples were put into the bath at 20°C (left) and at 2°C (right). Bubble trains from the spheres indicate that hydrogen evolves from spheres in ice water.

Treated aluminum spheres were allowed react in the ice bath for 10 minutes, after which all the aluminum was visibly consumed. The spheres reacted in an excess of ice water similarly to how they react in room temperature water. Spallation of the surface occurred after a minute of reacting and the aluminum spheres fragmented. Hydrogen nucleation on the surface of these ejected pieces carried them to the surface of the water, allowing them to react further (Figure 39 left). After 10 minutes of reacting, a hydroxide had developed on the surface (Figure 39 right). In room temperature water, this froth normally gets warm as a result of the hydroxide foaming and insulating still-reacting aluminum particulates, however in the case of the ice-water reaction, the froth remained cold, at approximately 2.5°C.
Figure 39 - Reaction progression of the aluminum spheres in ice-water. Ejected aluminum granules were the surface by nucleating hydrogen bubbles (left) This formed a hydroxide froth on top of the ice-water (right) which has been observed in reactions held in an excess of water at room temp. This froth however stayed cool and did not facilitate high-temperatures.

5.4.4 SEM Elemental Analysis of Activated Spheres

Activated aluminum spheres were observed under the SEM Energy Dispersion X-Ray Spectroscopy (EDS) tool to determine how the gallium-indium eutectic had concentrated throughout the aluminum bulk. The imaging on the surface of the sphere was done after it was wiped of any developed hydroxide from the environment, leaving the raw etched surface exposed (Figure 40). Tests were done on the grain boundaries (1), a single aluminum grain (2), and an area of the surface to get an average elemental content. The grain boundary and grain contained mostly elemental aluminum with proportions of gallium and indium similar to that of
the eutectic. The area EDS analysis (3) showed near identical results (*Figure 41*) to the point sections tested at (1) and (2).

![Figure 40 - 500x SEM image of the surface of a treated aluminum sphere. Aluminum grains are etched by the gallium-indium eutectic. Three regions were tested: a grain boundary (1), a grain of aluminum (2), and a large area (3).](image-url)
Figure 41 - EDS counts for the area region (3) shown in the above figure. The spikes indicate approximate elemental quantities detected in the region. The ratio of gallium to indium is approximately the wt. % ratio of the eutectic used to treat the spheres.

EDS analysis was also performed on a sectioned aluminum sphere to compare gallium-indium content. An area analysis like (3) in Figure 40 was performed as no definite aluminum grain or grain boundary could be identified as on the surface of the sphere. The EDS counts showed that higher indium contents exist inside analyzed area.
Figure 42 – SEM image of a sectioned treated aluminum sphere - only an area EDS analysis was done as no grain etching was visible to target.

Figure 43 – EDS element counts of the area highlighted on the SEM image. Higher indium peaks are seen here than on the surface of the treated aluminum sphere.
5.5 Discussion

5.5.1 Importance of Indium

It is clear from Figure 34 that the indium content of the melt affects the activation of the aluminum. The addition of indium results in activated aluminum with higher hydrogen yields, whereas a melt with 4 wt. % or less indium used to treat aluminum will produce inert aluminum. The gallium-indium content of the spheres shown in Figure 35 is higher in samples treated with more gallium-rich heated baths. This might be a result of the higher solubility of aluminum in these melts and due to gallium’s strong affinity to wet aluminum surfaces. Indium appears to affect how well gallium wets the surface of aluminum as aluminum treated with a heated bath of 20 wt. % indium has the lowest mass, yet the highest hydrogen yield. Thus indium has a double positive affect on treatment: ironically it is the more expensive of the two metals used in treatment yet it is responsible for reducing the amount of liquid metal used and it also increases the reactivity of the activated aluminum. This affect has been noticed in the prior art, particularly in Ziebarth and Woodall et al in which they created a solid alloy of pure aluminum and gallium that was completely inert in water [2].

5.5.2 Cyclic Voltammetry

Data for cyclic voltammetry show that there is little difference between gallium and indium and their ability to generate hydrogen gas when paired with aluminum in a galvanic cell. Indium arguably begins producing hydrogen gas bubbles at a slightly higher voltage than gallium. This data however is inconclusive as there is evidence to suggest in the literature that indium affects the electrochemistry of aluminum in water. Aluminum is a popular anode material, notably used in sacrificial anodes for marine environments, and it has been shown that
the addition of indium and zinc increases current exchange density of the surface [5–7]. This is a well-known phenomenon that is employed already in commercially available anodes, however it is still unknown as to why the addition of indium in particular is has such a substantial effect [8][9]. Mechanisms have been proposed as to why indium is such a potent additive. The most popular mechanism is that indium ions deposited in the local electrolyte solution from the aluminum surface redeposit themselves on the surface of the aluminum, disrupting the oxide layer. This method is contrary to indium simply disrupting the oxide layer through grain boundary diffusion. In the case of activated aluminum spheres, indium is present in the grain boundaries as shown in Figure 43; aluminum cannot be activated using the method in this thesis if the activating metal is only on the surface. It is not clear what role indium has in activating the aluminum, however its presence in the heated treatment bath and in the aluminum bulk may have a similar effect to how indium improves performance of aluminum sacrificial anodes.

5.5.3 Liquid Metal Transport Theory

By immersing the aluminum spheres in ice water as well as cooling the spheres before reacting them in ice-water, it is likely that a liquid phase diffusion reaction is not responsible for the aluminum reacting at high efficiencies in water. The addition of indium does lower the melting point of the metal alloy in the aluminum grain boundaries to below room temperature, however adding indium also reduces the solubility of aluminum into this liquid metal [10]. Aluminum is approximately 2-3 percent soluble in liquid gallium at 30°C and from a ternary phase diagram of aluminum, gallium, and indium at 180°C it is approximately 3 percent in a high gallium content alloy. Aluminum was also treated in a gallium bath and then reacted with heated water, so as to ensure the gallium would be liquid in the aluminum grain boundaries. Though the spheres were embrittled, they did not react in the heated water. Further experimentation is
needed to confirm if the metal alloy inside the aluminum grains is truly solidified when immersed in water. Perhaps there is exposed aluminum on the surface and localized heat from the hydrolysis reaction melts the alloy locally, thus promoting transport of fresh aluminum to the water interface.

5.5.4 SEM Elemental Analysis of Activated Spheres

SEM analysis of the spheres both on the surface and internally show that the indium and gallium have penetrated the bulk of the aluminum in unexpected ways. From Figure 42 there appears to be a larger concentration of indium than gallium, contrary to the surface (Figure 41) where there is a significantly larger ratio of gallium. More sample areas are needed to confirm this observation, however this observation is also contrary of what Ilyukhina et al. found in high-energy ball-milling powders where they recorded increased indium content on the surface. From a pure geometry standpoint, it would make more sense to find a higher concentration of gallium in the aluminum bulk since indium (2.2 angstroms) has a larger atomic radius than gallium (2.1 angstroms), thus it would be easier for gallium to diffuse down aluminum grains.

5.6 Conclusion

Indium is clearly a key metal in activating aluminum in the treatment process shown in this thesis, however it is not entirely clear why it can activate aluminum. Neither gallium or indium alone can activate the aluminum bulk, there must be both gallium and indium present in the heated bath. It is also apparent that as more indium is added, the mass of the spheres decreases. Cyclic voltammetry done using an aluminum anode and pairing it with gallium, indium, and platinum as working electrodes show that indium is barely a favorable electrode over gallium which would imply that it does not form a galvanic couple with aluminum when exposed to
water, yet it is shown in the literature for that indium added to a sacrificial aluminum anode
significantly improves its performance. It is likely that the addition of indium to the heated bath
to activate aluminum is somehow related to the addition of indium to sacrificial anodes, however
it is not understood what the mechanism is. By adding indium to the heated liquid metal bath, the
activated aluminum actually retains less liquid metal yet as more indium is introduced the
reactivity increases. Thus it might not be how much activation metal is present but rather getting
the ideal ratios of these activating metals together with aluminum.
5.7 Chapter 5 References


CONCLUSIONS AND FUTURE WORK

This thesis shows that a minor amount of a gallium-indium eutectic can be used to activate bulk pieces of aluminum to react efficiently in water. The state of the art in aluminum activation has been towards developing finer and more efficient aluminum powders, which are inherently explosive and have inhalation hazards associated with their handling and use. Attempts have been made at producing bulk aluminum fuels, however these methods either require too much gallium-indium to be cost-efficient or simply do not have high reaction completions to be practical. It has been shown that the key to activating bulk aluminum is to maintain a high temperature of the eutectic bath and expose the aluminum for sufficient time. The reactivity of this activated aluminum can be increased by cold-working prior to treatment.

This allows engineers or designers to create a wide range of power systems that have rapid response times to power changes or produce very steady power outputs without sacrificing efficiency. The reaction efficiency and liquid metal content in this fuel are similar to that of powders, however it may be possible to obtain better performance with even less activating material. Also, if this activated aluminum is to be commercially viable, it must be manufactured as cheaply and efficiently as possible. Understanding the aluminum-water interaction and reaction as well as how the liquid metal activates the aluminum will provide guidance on how to achieve these goals.
6.1 Improving the Manufacturing Process

The manufacturing process consists of a heated bath that aluminum pieces are placed into for a specified amount of time. These aluminum pieces are not stacked on top of one another to facilitate contact on all sides with the water; the current process is surface area limited, which drastically increases capital equipment cost and limits production quantities of fuel. Volume-based methods have been attempted, but not extensively researched or characterized. Aluminum spheres have been mixed with a small quantity of gallium-indium eutectic and heated to 120°C for 2 hours in order to activate them. This is capable of activating aluminum that reacts identically to the original process, however spheres treated using this method increase in mass by approximately 10% likely as a result of excess gallium and indium that remains wetted to the surface and could not be removed.

The benefit of having a surface area driven manufacturing process is that spheres are only half-immersed in the liquid bath. If exposed surface area to the liquid bath is limited, pitting areas where gallium-indium have high surface tension that resists the centrifuge removal process are also limited. Thus, a column of aluminum immersed in a heated eutectic bath could potentially be activated, while limiting surface area. Liquid metal embrittlement is not be limited by gravitational forces, however the time in which the column must sit in the heated bath would need to be more than 120 minutes depending on how large it is.

6.2 Aluminum-Water Reaction

This thesis does not characterize the method by which aluminum reacts with water nor does it provide a mechanism that explains why the reaction proceeds. It does provide guidance that builds on the prior art, but it also contradicts some of the theories put forth in the literature. For instance, the theory that aluminum passes through a liquid metal layer to reach a water
interface to react is refuted by the fact that the aluminum fuel reacts in ice-water, which is well below the freezing point of the eutectic used to treat activate the aluminum. The spheres were also pre-cooled in order to freeze the eutectic below 15°C. Localized heating might have heated the eutectic and melted it, however it is also possible another reaction mechanism is occurring or perhaps this mechanism is happening simultaneously and there is no single reaction in charge of oxidizing aluminum.

The importance of indium has been recognized in the prior art for nearly three decades as a means to improve current exchange density of sacrificial aluminum anodes, yet there is not a definitive explanation or model that shows why the indium is critical to the increase in reaction rate. A similar trend is shown in this thesis with regards to activating aluminum reacting in water: indium or gallium alone cannot activate the aluminum, the indium and gallium must both be present together in the heated bath. Cyclic voltammetry performed on gallium and indium show they have similar hydrogen evolution potentials when paired with an aluminum anode meaning they have similar galvanic qualities, however the addition of indium to sacrificial anodes increases exchange current density and thus their performance. It may be that this is a coincidence and indium has advantageous anode properties and also is effective at disrupting the oxide of aluminum so that it can react in water. Further experimentation is needed to determine the effects of different metals.
6.3 Finding the Ideal Processing Method

So far, only two different cold-working processes have been attempted to activate aluminum prior to treatment, however there are other means of modifying residual stresses such as heat treating and quenching. Aluminum with smaller grains is shown to produce more hydrogen, however a specific stress state inside the aluminum as well as an ideal grain size might exist. The consistency of such a grain structure and stress state may also affect how efficiently and rapid the activated aluminum will react in water. These refinement processes must also be quick and with high yields to be viable in mass-manufacturing. A small sacrifice in performance of the activated aluminum may be necessary if it eliminates critical bottlenecks and significantly reduces costs. The next steps should characterize the most common cold-forming processes at a known temperature and quantify how they affect hydrogen yields once the aluminum is activated. The grain shapes and sizes produced by cold-working might also allow for a model based on equivalent induced plastic strain and the amount of redundant work performed on the aluminum piece.

6.4 Scaling and Modeling

The aluminum treatment process and the reaction of the aluminum in water can be modeled to improve reaction characteristics and limit gallium-indium content. When limited water is exposed to activated aluminum, it wets the surface and travels via capillary action around the surface and into the bulk of the aluminum. As grains are broken and dissolved, ejected, and reacted, the water penetrates deeper into the aluminum, followed by an abrupt and significant temperature increase. The aluminum hydroxide expands rapidly due to a rapid release of steam and hydrogen gas and then the reaction stops due to a lack of water. This is only one method of reacting the aluminum to extract the hydrogen. The envisioned reaction vessel would
simply be a sealed tank filled with activated aluminum and a water-input around the aluminum. Fuel shape, size, water input methods, and hydroxide handling all are ignored in this design, however these can be changed and optimized to improve areas such as reaction response time, reducing water needed to react the aluminum, and maximize hydrogen yield of the fuel.

6.5 Conclusion

The aluminum treatment process developed in this thesis is not optimized for hydrogen production or for minimizing the use of the gallium and indium, however the process produces a safe-to-handle aluminum fuel that yields large amounts of hydrogen while utilizing sufficiently low amounts of gallium-indium eutectic. The significant contributions made in this work have been characterizing important parameters in the treatment process while explaining how to potentially increase hydrogen yield and reactivity through pre-processing the aluminum via cold-working prior to treatment. Insights to the water reaction as well as relevant activation metals provide insights to why this bulk-treatment process is so effective and the fuel is so highly reactive.

There are several potential research projects or areas this work suggests such as improving and further reducing the use of activating metals, optimizing reaction characteristics and improving reaction methods, as well as determining the ideal liquid metal content and how the reaction works on a microscopic scale. This thesis serves as a platform from which to improve on or understand better the storage of hydrogen fueled machines. Further research to improve the understanding and fundamental science of this treatment will improve the activated aluminum process where it is commercially competitive with many alternative fuels and hopefully bring a new generation of clean and energy-dense power systems.

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