Surface Passivation of Hydride Fuel Cell for Process Safety

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Abstract

The objective of this project is to determine if titanium (III) chloride ($TiCl_3$) will react with the outer layer of a pyrophoric hydride fuel to form an impermeable layer on the surface to prevent oxygen and water from reacting explosively with the hydride. Pyrophoric materials like the hydride in the fuel cell can take the form of a solid, liquid, or gas and will ignite immediately with oxygen or moisture in the air. Therefore these materials are very difficult to handle and transport safely. Additionally an unstable reaction, known as thermal runaway, can occur with excess heat buildup inside a battery cell. To prevent this exothermic reaction from occurring at a high rate the titanium trichloride theoretically should react with the aluminum to create an aluminum oxide or chloride to form a surface layer that will not react with air or water.

Due to the corrosive and harmful nature of the $TiCl_3$, necessary PPE and proper precautions must be taken during experimentation with this chemical. The first set of testing for determining if $TiCl_3$ will be a compatible and effective passivation agent is thermal sensitivity testing. If the $TiCl_3$ is stable at 100^{o}C where the thermal runaway occurs, surface area testing can occur. Using a scanning electron microscope (SEM), an elemental map can be created and surface images can be taken pre- and post-coating to see the differences and determine if the coating fully and completely covers the surface of the alumina pellets, aluminum granules, and aluminum hydride tablets. If all of this testing is successful the eventual goal would be to complete the same tests with the pyrophoric lithium aluminum hydride fuel itself.

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1. Introduction

Hydrogen fuel cells have the capacity to enhance a drone’s performance, for purposes of longer flight time and an overall improvement in the efficiency. This is traditionally achieved through the use of small gas cylinders that provide hydrogen gas to the system. There are drawbacks to this way of delivery as the cylinders add considerable weight to the system. Additionally, the hydrogen cylinders are not able to supply sufficient amounts of hydrogen that are consistent with the objective flight time parameters resulting in the need for more energy to fly. For purposes of combating this, Honeywell proposed an alternative fuel source that produced hydrogen from a hydride slowly reacting with small quantities of water supplied in the cell. This reaction offers high fuel density as the hydride reacts to form hydrogen gas. However, there is a safety concern in that this new fuel is a pyrophoric material and will react violently in the presence of water or air. Pyrophoric materials pose their own challenges in that they are not easily controllable once in contact with reactants that fuel thermal runaway. Additionally, when reacting with water or air, the exothermic reaction produces a considerable amount of heat, potentially damaging the fuel cell and other integral parts of the drone.

In order to prevent oxidants from entering the system, a passivation agent can be applied to the outside of the solid granular fuel source. Passivation can be understood as a coating that is applied to a surface in order to create an impermeable layer. The formation of the layer has the potential to be created using the chemical, $TiCl_3$, in the form of a liquid to physically coat the fuel pellets. Passivation of a hydride for hydrogen fuel cells is a novel concept that is lacking in the quantity of currently available literature. The extent of research on this is limited to the McMurry coupling reaction, a reaction commonly used to produce alkenes (Bongso). On account of this, the proposed experimentation and supporting background could be useful to those interested in this topic.

2. Background

a. Pyrophoric Materials

Though hydrogen is an efficient and promising energy carrier, this new method of generating hydrogen has great potential of overheating. The reaction is exothermic and releases significant amounts of heat while the reaction is proceeding. Additionally, this fuel is a pyrophoric material and has a higher reaction rate compared to non-pyrophoric materials. This category of materials will ignite upon contact with oxygen, with some igniting due to exposure to water. These materials have most commonly been used to catalyze or reduce particular reactions. Specifically, the lithium aluminum hydride (LAH) fuel being used for the drone is extremely sensitive to water. It is also noted that LAH has autoignited at its relatively low melting point of about 125°C, exemplifying that the temperature necessary for this reaction to proceed is fairly reachable (Merlic). In general, the decomposition of pyrophoric materials also has the potential of creating and releasing corrosive byproducts. Pyrophoric materials are hazardous to handle and transport as there is an increased likelihood of coming into contact with air or water.

b. Passivation

In an effort to counteract the hydride fuel's pyrophoric nature, a passivation layer can be coated around the surface of the hydride fuel to prevent the reaction from taking place. This will create an impenetrable layer that blocks oxidants or water from entering the fuel cell. This protective layer is created by reacting the surface layer of the fuel with $TiCl_3$. $TiCl_3$ is a catalyst that has been known to provide reversibility to the reaction of sodium aluminum hydride ($NaAlH_4$) (Mosher). $NaAlH_4$ is similar to the proposed fuel, $LiAlH_4$, but is even more reactive and unstable. Because of their closely related properties, LAH can also be expected to be compatible with $TiCl_3$.

In literature, there exists a relationship between LAH and $TiCl_3$ that reinforces the idea that these two chemicals bond strongly to one another. This is known as the McMurry coupling reaction, a reaction that is used to form alkenes (Bongso). The reaction uses low-valent titanium, such as $TiCl_3$, and any number of other reducing agents to proceed.

c. Lithium-Ion Batteries & Electric Vehicles

There are other methods when working with pyrophoric materials and preventing thermal runaway, taken from work done in the lithium-ion battery (LIB) field. LIBs work by the release of a thermal-runaway retardant (TRR) that slows the temperature increase caused by excess exothermic reactions occuring due to damage to the cell. Shi, Noelle, Wang et al. investigated the effectiveness of three different TRRs, benzylamine (BA), dibenzylamine (DBA), and trihexylamine (THA). The team found that THA was the most efficient as the wettability tests revealed that THA spreads out over a larger area to form a physical barrier that suppresses the heat generation through the exothermic reaction. Applying this concept to the hydride fuel cell means finding and testing an effective TRR for the hydride fuel. This TRR could coat the hydride or pipe where the fuel is contained, therefore creating a barrier that prevents the exothermic reaction from occurring at too high of a rate that generates too much heat causing potential fires and explosions in the fuel cell.

There have been efforts in preventing thermal runaway in large scale fuel cells, most often seen in the electric and hybrid vehicle industry. Plug-in vehicles have found some success with integrating a battery pack in direct contact with a metal hydride-based hydrogen storage system. This method works by ”efficiently [exploiting] the endothermic desorption process of hydrogen in metal hydrides” (Di Giorgio, Scarpati, Di Ilio et al.). The allowable weight and size parameters for cars, or even electric scooters and bikes, are much different than drones, as they need to have the ability to take flight. However, the strategy of preventing thermal runaway in the system by simultaneously enacting the endothermic reaction (shown below in Figure 1) has the potential to be scaled down to work on a drone.

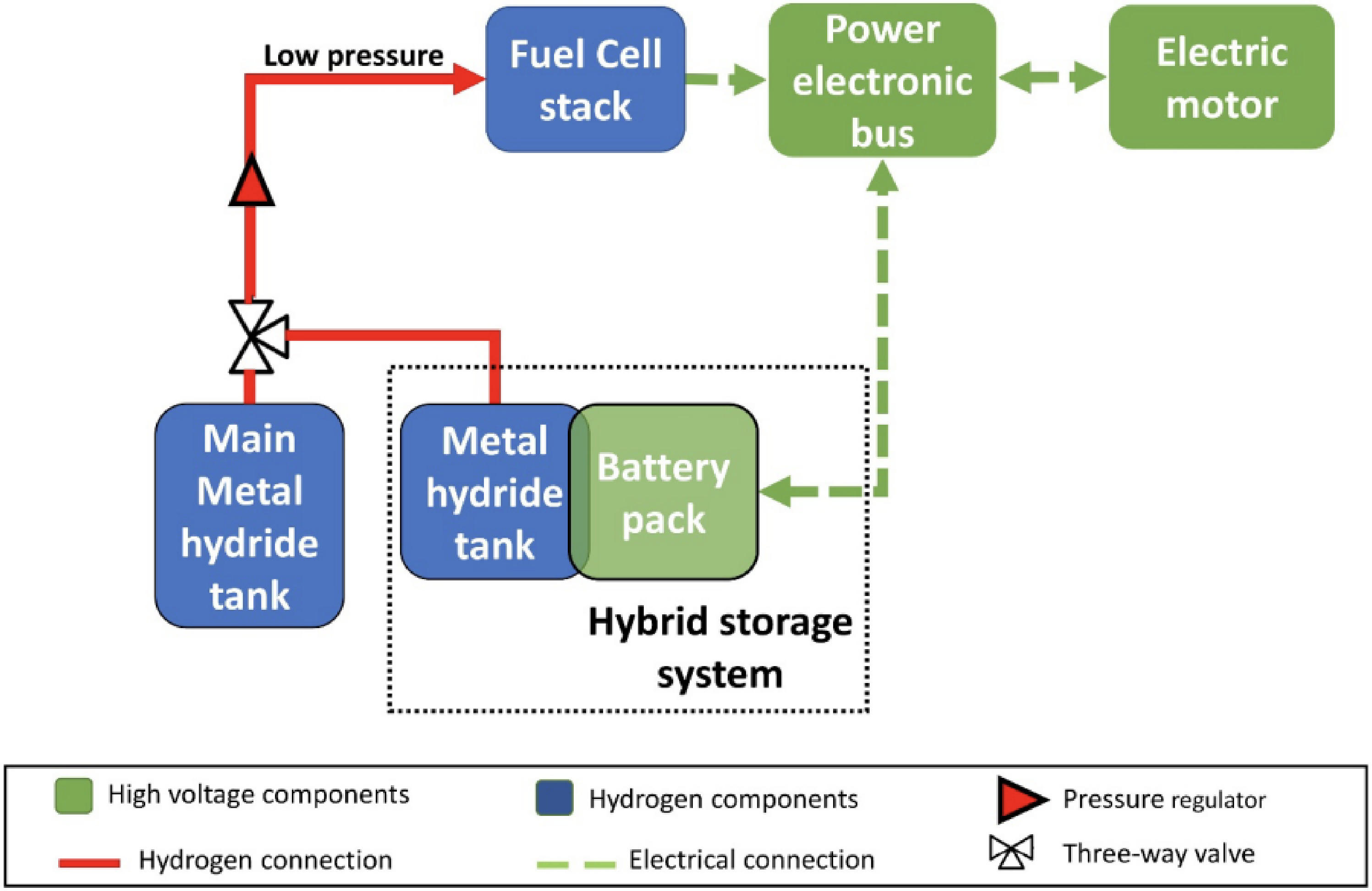

Figure 1: Power unit and hydrogen storage system architecture for the plug-in fuel cell electric scooter (from Di Giorgio, Scarpati, Di Ilio et al.).

3. Methods

a. Equipment

There are a lot of precautions that need to be taken to complete all of the experimentation with titanium (III) chloride because it is a hazardous chemical. In addition to $TiCl_3$ being corrosive to metals there is a possibility of chloride gas inhalation or dermal exposure due to splashing or spilling of the chemicals during testing (*Titanium (III) chloride*). In addition to working with $TiCl_3$ these experiments require the use of alumina pellets, aluminum granules, and aluminum hydride pellets (pictured below) which are all stable on their own but may react harmfully when met with the titanium trichloride.

Figure 2: From left to right the alumina pellets, the aluminum hydride tablets, and the aluminum granules.

To ensure the safety of those conducting these tests the use of a fume hood, or more ideally a glovebox, is required to prevent any potential chloride gas inhalation or release into the air. Using a glovebox removes the risk of exposing the materials to air while experimenting and would be especially important when working with the pyrophoric aluminum hydride fuel. Additionally, proper PPE including chemically resistant thick rubber gloves, chemical aprons, lab coats, and goggles must be worn during experimentation.

b. Procedure

Testing the feasibility of titanium (III) chloride as a passivation agent for the aluminum hydride fuel cell first requires determining the compatibility of $TiCl_3$ at high temperatures as this is where thermal runaway occurs in the fuel cell. Thermal resistance and sensitivity testing should be run with the $TiCl_3$ solution. For thermal sensitivity and resistance testing 10mL of the solution is measured out and placed in a 100mL beaker before being placed onto a hot plate. A glass thermometer placed in the beaker will provide a visualization of the solution temperature. As the solution is being heated to $100^{o}C$ the process would be videotaped with a phone camera and notes should be taken of any physical or visual changes that occur as the solution is heated and reaches $100^{o}C$. When the desired temperature is reached, if no changes occur, the recording can be stopped, the hot plate turned off and once it is cooled down the beaker should be removed from the hot plate. If this testing is successfully completed and the $TiCl_3$ is proven to be stable at the necessary temperature, surface area testing via scanning electron microscope (SEM) can begin.

In addition to being stable at high temperatures to be an effective passivation agent, the $TiCl_3$ must react with the surface of the fuel to create a barrier layer that will not react explosively with air and moisture. In order to successfully create this boundary layer, it is very important that the titanium trichloride solution fully and completely coats the surface of the fuel. For surface area testing a scanning electron microscope should be used to not only determine if a reaction occurs on the surface of the pellet but if there are any gaps in the surface coating. To start this experiment a sample of a dry alumina pellet is imaged on the SEM to have a baseline for later comparison with the wetted pellets. Before coating the pellets with the solution, the reaction should be tested at small quantities that have correspondingly low energy levels to ensure no major reaction will occur between the alumina and the titanium trichloride. To do this a glass rod is used to drip a small amount of $TiCl_3$ onto the pellet and if it is clear there will be no harmful or explosive reaction, the pellet can be dropped into a small beaker containing $TiCl_3$. Then the pellet needs to be removed, rinsed with DI water, and dried overnight before being transported to the SEM. With the SEM's X-ray diffraction (XRD) or energy-dispersive X-ray (EDX) functions, an elemental map can be created that shows if there are any chloride or oxide deposits from the surface reaction. Additionally the magnified SEM images of the wetted pellet surface can be obtained for comparison with the dry pellet. The surface area testing should then be repeated with the lesser $TiCl_3$ compatible aluminum granules and aluminum hydride tablets.

4. Results

Due to extended supply chain delays, we were unable to obtain the $TiCl_3$ solution, and the proposed experiment was unable to be completed. We attempted to generate the $TiCl_3$ solution by dissolving the titanium (III) chloride - aluminum (III) chloride or $(TiCl_3)_3AlCl_3$ powder, which was available, in hydrochloric acid. A small amount of the powder was added into a beaker full of 37% hydrochloric acid. However, the $(TiCl_3)_3AlCl_3$ powder is air sensitive to the point that it immediately fumes and reacts when the container is opened, releasing what is assumed to be chloride gas. Once added to the HCl, the fuming increased and the powder itself did not dissolve to create the necessary solution. Although the intended experimentation was unable to be completed, the SEM images of the three fuel alternatives were taken to use as a baseline case for future work on this project (as seen in Figures 3-5 and in the Appendices). Each SEM image was taken at multiple different magnitudes ranging from 50x to 2500x, allowing for comparison to the surface images of the $TiCl_3$ coated materials.

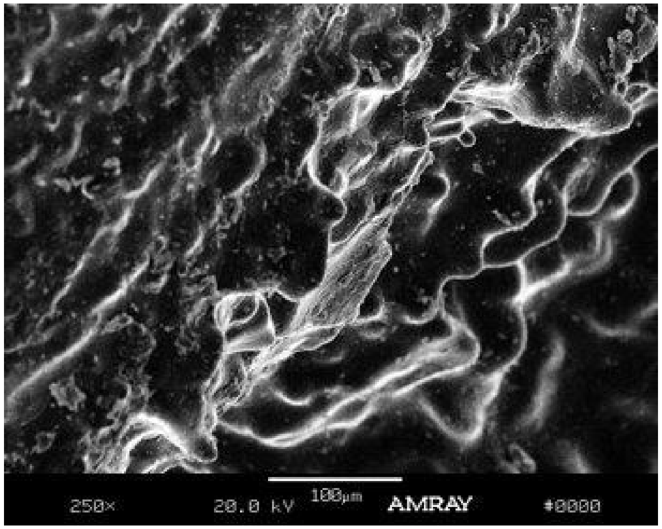

Figure 3: SEM image of alumina pellet at 250x magnification.

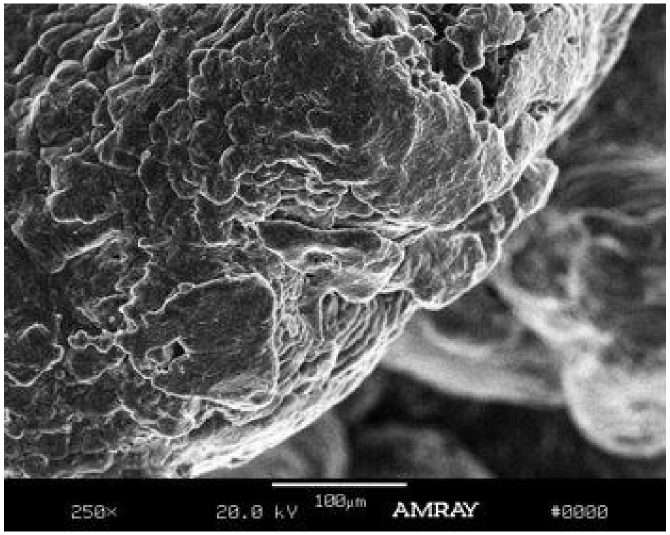

Figure 4: SEM image of aluminum granules at 250x magnification.

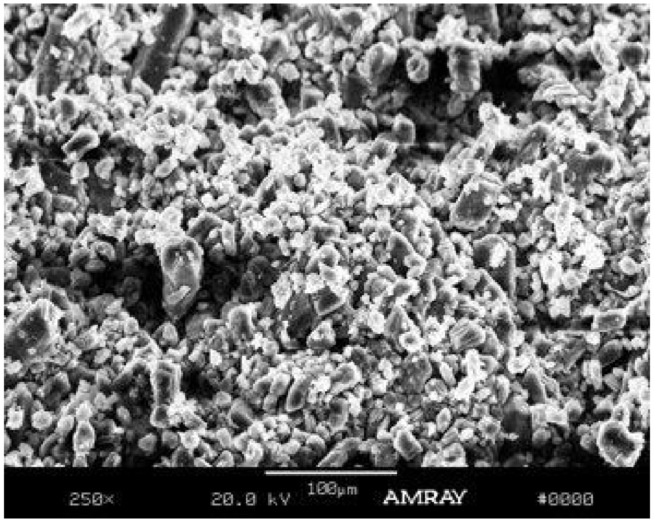

Figure 5: SEM image of aluminum hydride pellets at 250x magnification.

5. Conclusion and Recommendations

Due to extended supply chain delays, the passivation agent was not received therefore the experiment was unable to be completed within the time constraint. We believe the concept of passivating the hydride with $TiCl_3$ remains valid and should be investigated once the $TiCl_3$ becomes available. Before starting any wet chemical experiments we recommend conducting surface area calculations of each of the materials. These calculations are an accurate way to predict how much $TiCl_3$ solution is needed to coat the surface of each material or if it would coat it at all. Safety precautions are the number one concern throughout the entire experiment so we recommend that all experimentation be done in a glovebox to minimize any hazards like inhalation, explosions, or spillage. Using a fume hood remains a good option, but using a glovebox would greatly improve the safety of the entire experiment. Lastly, if there are positive results for creating the expected impermeable layer on the alumina, aluminum, and aluminum hydride pellets we recommend obtaining the lithium aluminum hydride being used by Honeywell. The pyrophoric properties of this material are difficult to replicate and there are no alternatives that will react similarly. If it is not possible or viable to obtain the LAH, then there is potential for collaborative efforts working alongside the chemists and engineers at Honeywell to carry out this testing in the company's pre-existing labs. Testing on the lithium aluminum hydride would be the last step in proving the viability of this method of process safety for pyrophoric materials.

6. References

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7. Appendices

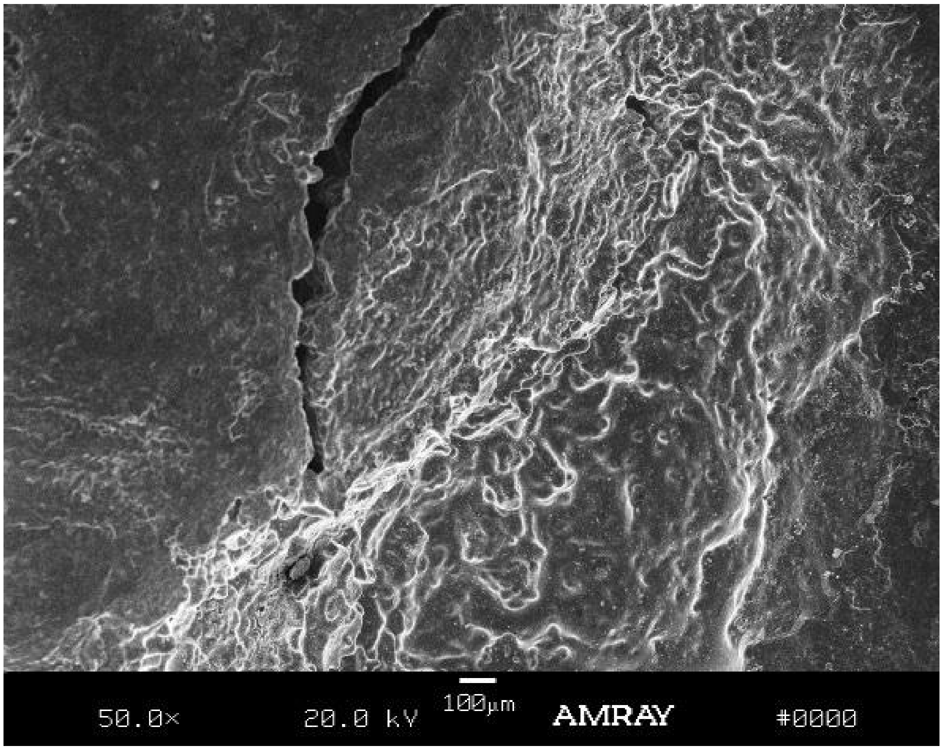

Figure 6: SEM image of alumina pellet at 50x magnification.

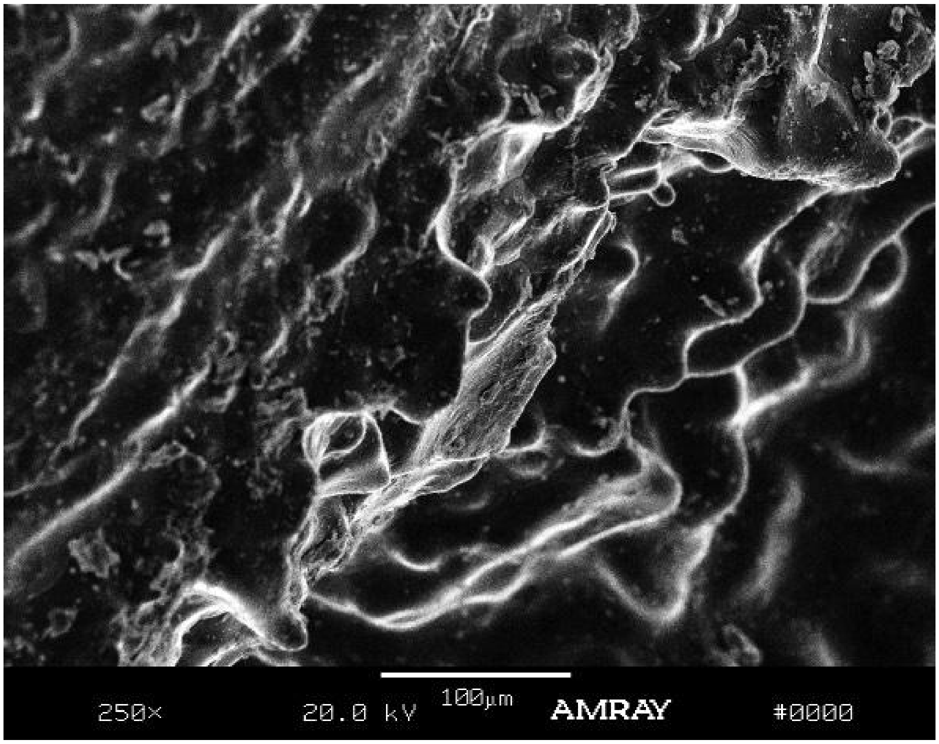

Figure 7: SEM image of alumina pellet at 250x magnification.

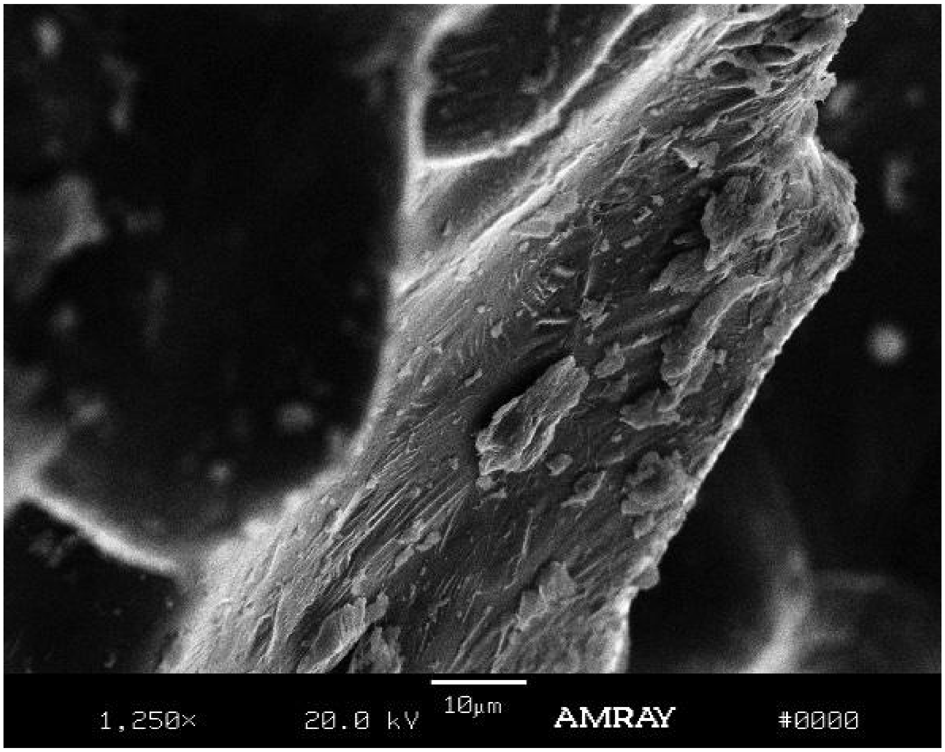

Figure 8: SEM image of alumina pellet at 1250x magnification.

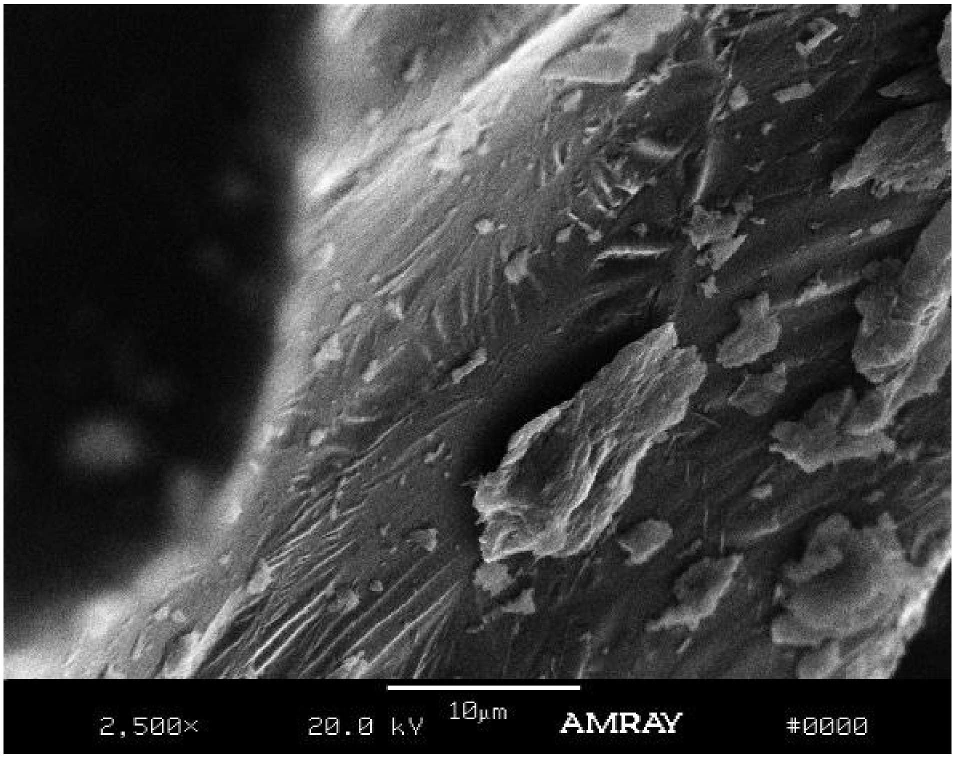

Figure 9: SEM image of alumina pellet at 2500x magnification.

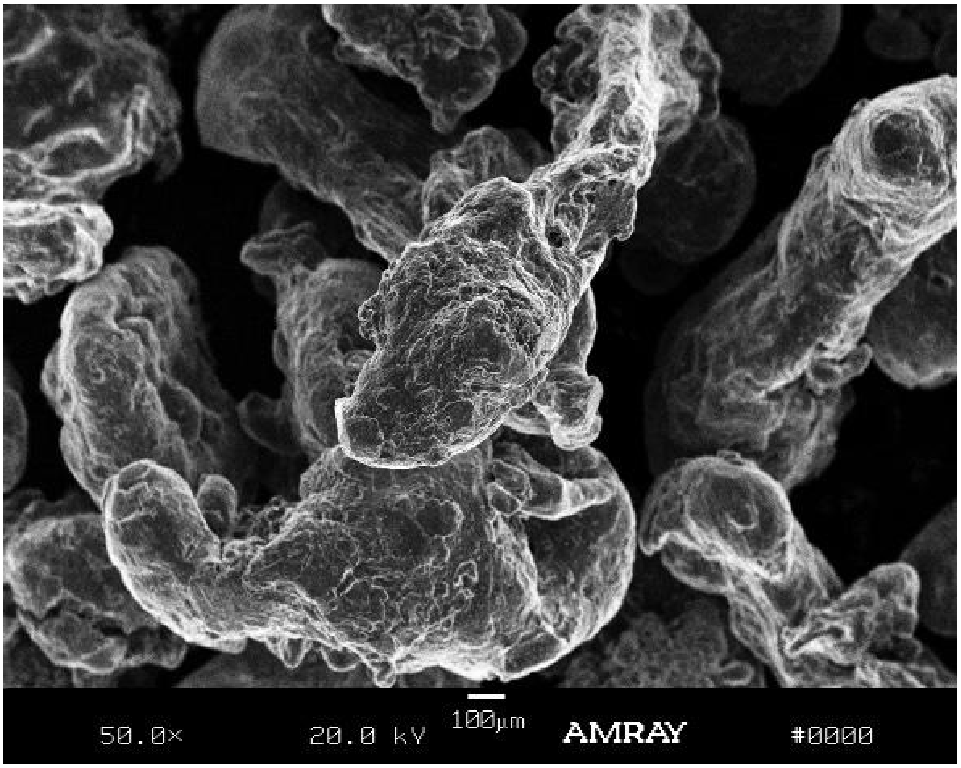

Figure 10: SEM image of aluminum granules at 50x magnification.

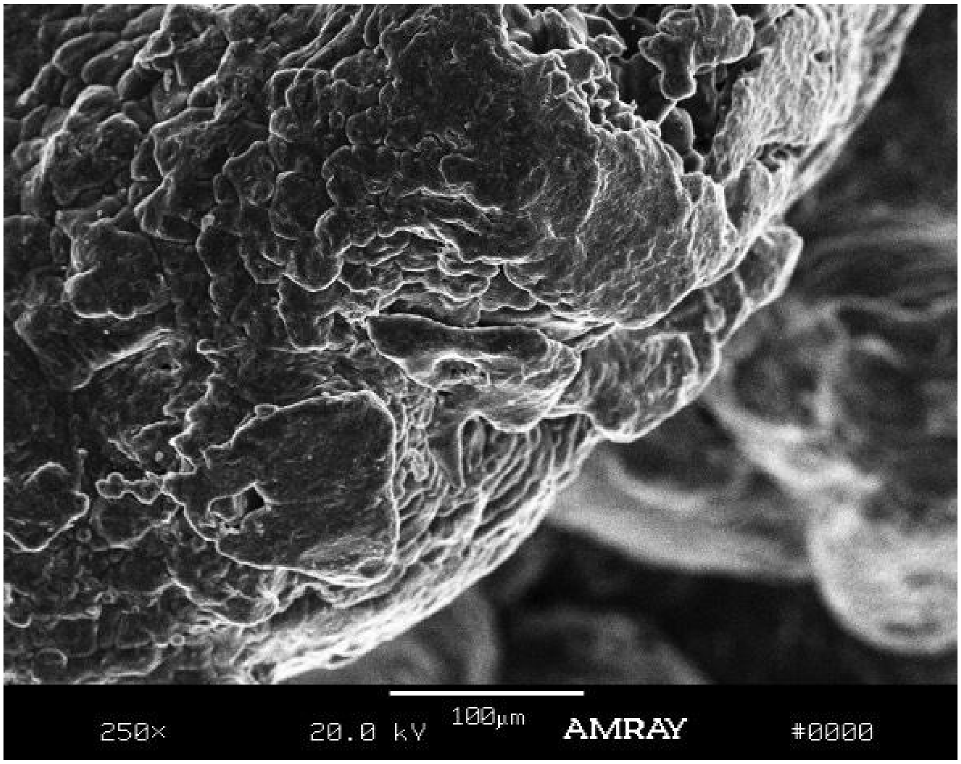

Figure 11: SEM image of aluminum granules at 250x magnification.

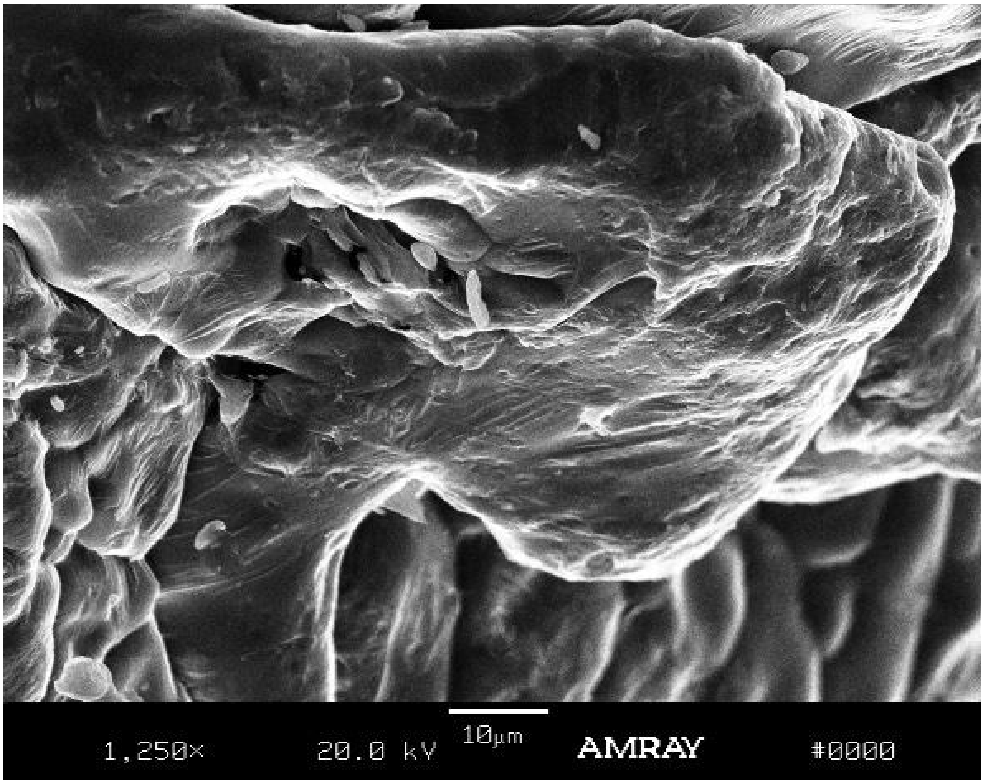

Figure 12: SEM image of aluminum granules at 1250x magnification.

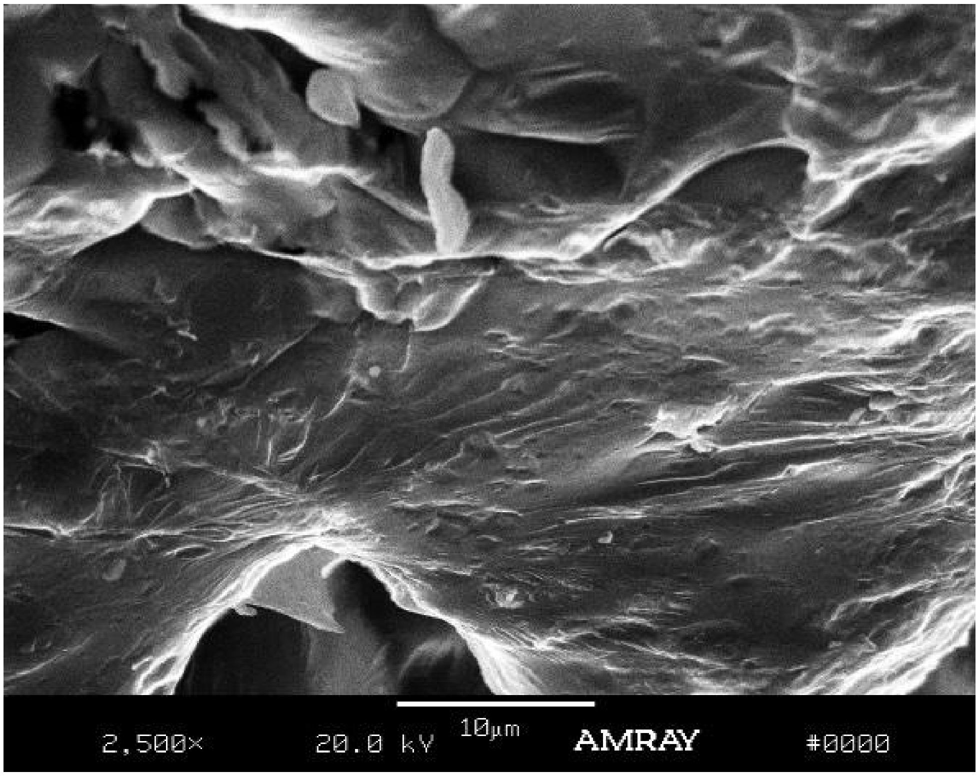

Figure 13: SEM image of aluminum granules at 2500x magnification.

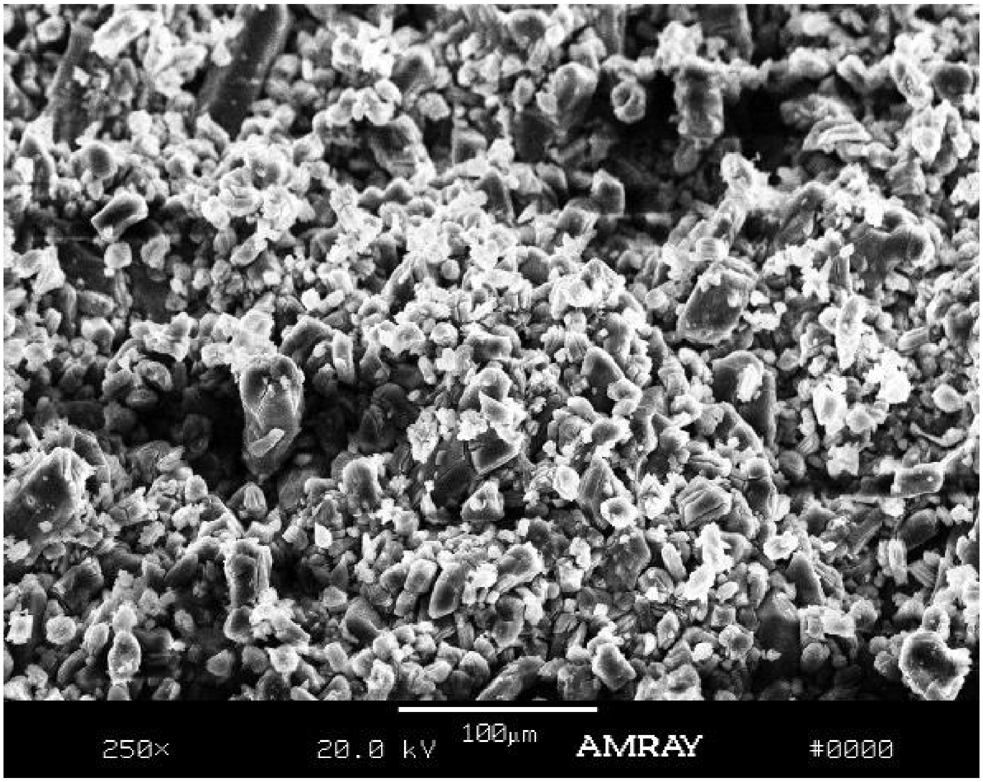

Figure 14: SEM image of aluminum hydride tablets at 250x magnification.

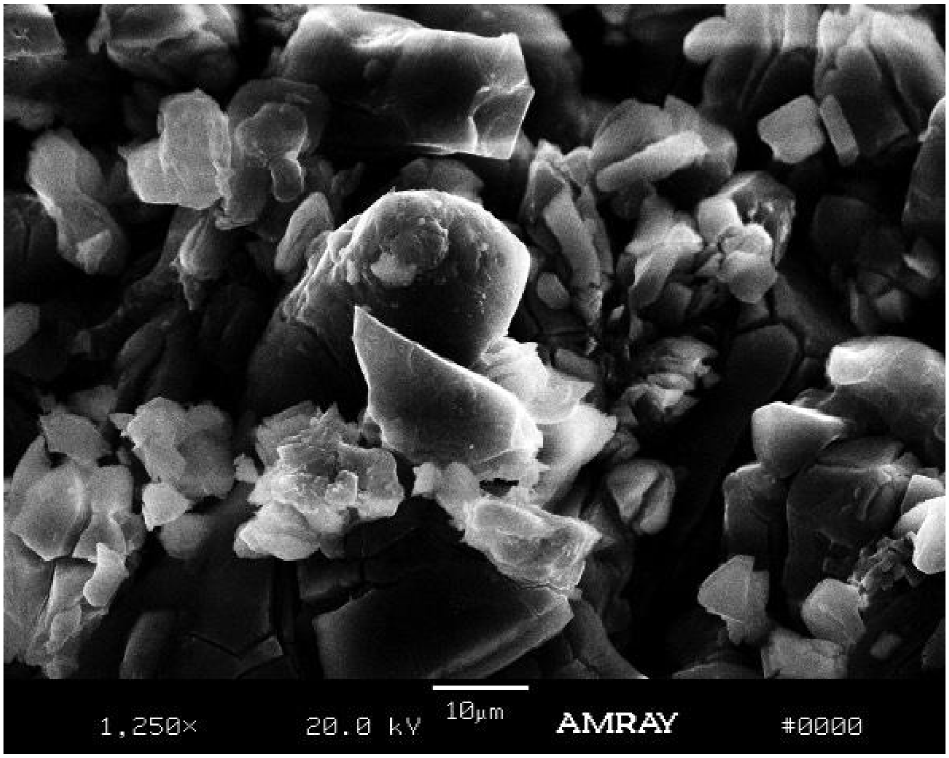

Figure 15: SEM image of aluminum hydride tablets at 1250x magnification.

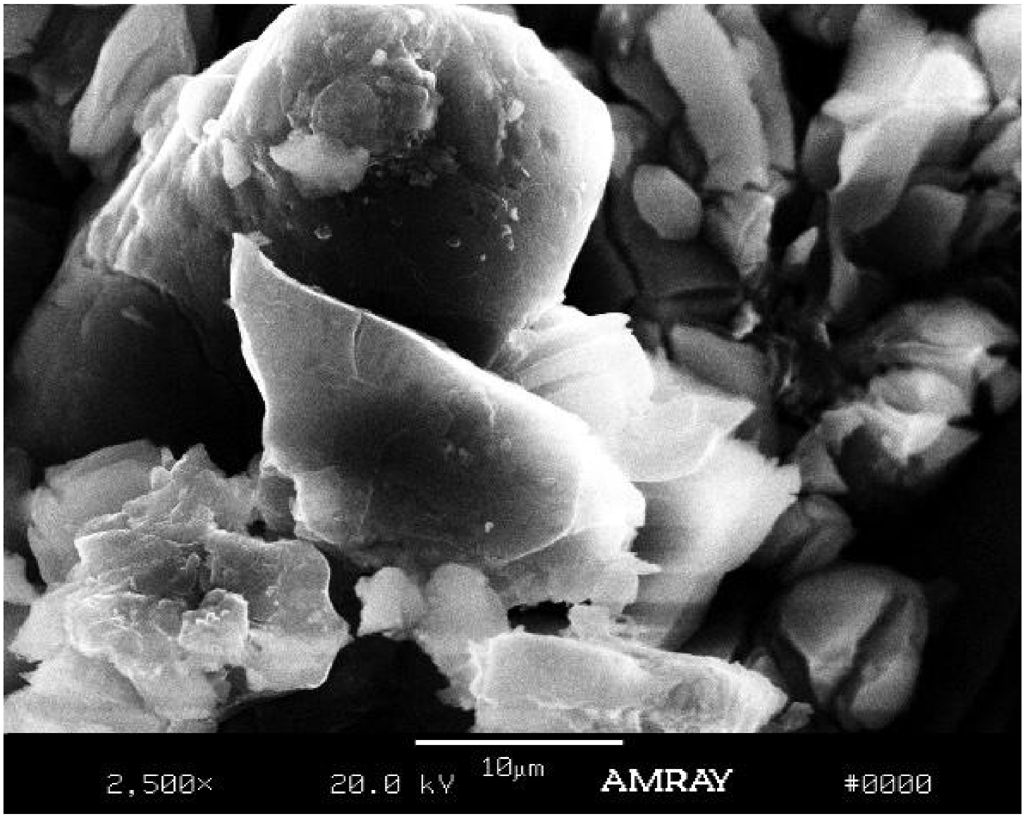

Figure 16: SEM image of aluminum hydride tablets at 2500x magnification.