Reaction of Titanium Subhydride with Multiple Passivating Gasses

Erik C. Strobert Jr

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REACTION OF TITANIUM SUBHYDRIDE WITH MULTIPLE PASSIVATING GASSES

by

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THESIS

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B.S. Chemical Engineering, University of New Mexico, 2017

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ABSTRACT

Sandia National Laboratories has used substoichiometric titanium hydride as a pyrotechnic fuel for decades. Production of titanium subhydride requires partial dehydriding of titanium hydride powder and subsequent chemical passivation to render the resultant bare titanium surface nonreactive and the powder non-pyrophoric. Novel passivation techniques, using a gas other than air, have been suggested in the past but have never been investigated. This work examines the reaction kinetics of titanium subhydride with three passivating agents, nitrogen, oxygen, and propane. These passivation experiments took place under isothermal conditions (420 °C) with varied dehydriding and passivation time periods. It was found that the kinetic model for these reactions demonstrated a combination of logarithmic and parabolic mass gain terms. Post reaction material characterization showed that the each passivation method resulted in a titanium oxide surface layer. This work concludes that these passivation techniques result in minimal differences in surface characteristics.
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Chapter 1

Titanium Subhydride as a Pyrotechnic
1-1 Introduction

Developing energetic materials, such as explosives and pyrotechnics, requires a constant effort to improve both the safety and performance of the materials. When Sandia National Laboratories established an effort to produce the pyrotechnic titanium subhydride/potassium perchlorate, there was a renewed interest in manipulating the material characteristics of titanium subhydride. Manipulation of titanium subhydride had not been conducted at Sandia National Laboratories since the 1980’s. This work seeks to investigate novel techniques for the passivation of titanium subhydride. The goal of novel passivation techniques would ultimately be to achieve a level of surface engineering which improves the pyrotechnic safety and/or performance of titanium subhydride/potassium perchlorate. This work investigates the reaction kinetics involved with novel passivation techniques of titanium subhydride as well as post reaction characterization the passivated material.

1-2 History of Pyrotechnic Titanium Subhydride

A pyrotechnic is a mixture of a solid fuel and an oxidizer which is capable of self-sustaining combustion in the absence of air. Pyrotechnics differ from explosives in their respective combustion characteristics. Explosives combust via detonation where a thermal front propagates through a material above the speed of sound, creating a shock wave. Pyrotechnics combust via deflagration where a thermal front expands rapidly but remains subsonic. Pyrotechnics do not easily create a shockwave.1,2

The pyrotechnic of interest in this study, titanium subhydride/potassium perchlorate (THKP), was implemented in Sandia National Laboratories’ energetic device designs following a series of policy decisions beginning in the 1970’s. The first of these decisions
was to transition away from the use of primary explosives to reduce the risk of accidental
detonation via electrostatic discharge (ESD) from a human body. This decision led to the
increased use of the pyrotechnic mixture titanium/potassium perchlorate (TKP).³

In 1974, researchers discovered that replacing titanium with titanium hydride rendered the
pyrotechnic mixture insensitive to electrostatic discharge. Unfortunately, titanium
hydride/potassium perchlorate exhibited multiple detriments including ignition failures and
long-term material compatibility concerns. These detriments led to an experimental program
which would investigate the performance effects of removing hydrogen from the titanium
lattice. This program produced titanium subhydrides with hydrogen compositions ranging
from 0.45 (TiH₀.₄₅) to 1.70 (TiH₁.₇₀). Pyrotechnic mixtures using these subhydrides
demonstrated greater reliability than titanium hydride/potassium perchlorate while
maintaining some electrostatic discharge insensitivity.³

![Figure 1: Electrostatic Discharge required for initiation versus Hydrogen Content of TiHₓ. ³](image)

Following the findings of this work, Sandia National Laboratories began using TiH₀.₆₅ in
its formulation of THKP. That pyrotechnic was soon replaced by THKP containing TiH₁.₆₅ in
the early 1980’s, after a requirement for improved ESD sensitivity was implement. The TiH$_{1.65}$ formulation of THKP is used in Sandia devices to this day.$^3$

1-3 Pyrotechnic Electrostatic Discharge Sensitivity

Accidental initiation of energetic material poses the greatest operational risk to those who work with it. The main cause of accidental initiation is ESD, which predominantly originates from human activity near an energetic material. Prior to the previously mentioned systematic effort, ESD risk was primarily mitigated through engineering and operational precaution. The scientific understanding of the phenomenon of ESD initiation has allowed for inherent safety improvements ever since.$^4$

Characterization of ESD initiation followed Sandia’s 1970’s effort to reduce the risk posed by primary explosives. Notable works examined the mechanism of these initiations as well as material characteristics which affect sensitivity.$^{4,5}$

Prior to 1980, It was a common belief that ESD initiation of TKP and THKP was due to a pyrotechnic reaction, where electrostatic discharge provided the necessary energy required to oxidize the fuel (titanium in TKP, titanium subhydride in THKP) via the oxidizer (potassium perchlorate). An investigation of this mechanism was conducted to determine if the molar concentration of atmospheric oxygen would affect the energy requirement for ESD initiation. The results showed that decreasing the molar oxygen concentration increased the energy requirement for ESD initiation. This relationship proved that ESD causes a metal/air reaction, where the fuel is initially oxidized by oxygen in the atmosphere. The investigation also showed that a higher surface area decreased the energy required for ESD initiation.$^4$ These characteristics suggest that ESD sensitivity is a property of the surface of the fuel particles.
Figure 2: The relationship between nominal electrostatic energy required for the initiation of TiH$_{0.15}$ (triangle), TiH$_{0.65}$ (circle), and TiH$_{1.3}$ (square) in atmospheres of varying oxygen concentration in nitrogen. Dashed line indicates mixture with KClO$_4$.  

1-4 Production of Titanium Subhydride

The processes which yielded the titanium subhydride used in Sandia’s devices was developed by Monsanto Research Corp. and patented in 1982. The patent for this process provides no prior art for a method to reproducibly prepare titanium subhydride for a specific and/or uniform hydrogen concentration.

The original intention of the process was to produce a titanium subhydride having an approximate hydrogen concentration of TiH$_{0.63}$ to TiH$_{0.67}$. The titanium subhydride was to be in the form of a free flowing, dust-free powder, with particles having a size of about 2 µm. The process was also designed to avoid sintering of the particles.

The process described in the patent takes place in a closed cylinder containing a tray-supporting assembly to hold static trays. Each tray is to be filled with titanium hydride (TiH$_2$) powder with a depth of 0.5 to 1.0 cm, uniform throughout each tray. The cylinder is also
fitted with an apparatus which allows dynamic vacuum control. The cylinder is heated to a
temperature in the range of 425° to 450°C and held at a vacuum pressure between 515 µm
Hg and 640 µm Hg. As hydrogen is evacuated from the powder, it is captured, and its
volume recorded. This method prevents the system from ever reaching equilibrium. The
measured volume of evacuated hydrogen is used to calculate the stoichiometry of the powder
within the reactor.  

The process is claimed to take about 20 hours to reach a stoichiometric ratio of TiH$_{0.675}$. Once the desired stoichiometry is achieved, the powder can be treated with a suitable amount of passivating gas to render it non-pyrophoric. This passivation can be conducted at temperature or after the powder has been sufficiently cooled. This is claimed to be achieved by introducing small additions of air to the cylinder. The patent also suggests that gasses other than air can be used as the passivating agent to manipulate the desired properties of the final subhydride powder. The suggest passivating agents are “carbon monoxide, ammonia, sulfur dioxide, ‘oxides of nitrogen,’ halogens, hydrogen chloride, hydrogen cyanide and various organic gases, such as methane or acetylene.”


<table>
<thead>
<tr>
<th>Example</th>
<th>Batch Size (g)</th>
<th>Composition</th>
<th>Reactor Temperature °C.</th>
<th>Length of Time During Which Gas Was Withdrawn From Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>TiH$_{0.030}$</td>
<td>449.8</td>
<td>20.0 hr</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>TiH$_{0.623}$</td>
<td>403.2</td>
<td>20.0 hr</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>TiH$_{1.026}$</td>
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<td>20.0 hr</td>
</tr>
<tr>
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<td>150</td>
<td>TiH$_{1.202}$</td>
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<tr>
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<td>TiH$_{1.043}$</td>
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<tr>
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<tr>
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<td>TiH$_{1.440}$</td>
<td>399.8</td>
<td>3 hr 35 min</td>
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<tr>
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<td>80</td>
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<td>4 hr 08 min</td>
</tr>
<tr>
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<td>150</td>
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<td>439.0</td>
<td>21 hr 00 min</td>
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<tr>
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<td>19 hr 55 min</td>
</tr>
<tr>
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<td>150</td>
<td>TiH$_{0.675}$</td>
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<td>20.0 hr</td>
</tr>
<tr>
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<td>441.2</td>
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</tr>
<tr>
<td>17</td>
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</tr>
<tr>
<td>18</td>
<td>1500</td>
<td>TiH$_{0.60}$</td>
<td>447.4*</td>
<td>20 hr 00 min</td>
</tr>
</tbody>
</table>

*Average of eight thermocouples.

Figure 3: Results of dehydriding trials reported by Richard Carlson.⁶

Mound Laboratories produced titanium subhydride for Sandia National Laboratories beginning in the early 1980's. The process used to produce TiH$_{1.65}$ closely resembles that described in the previously mentioned patent ⁶, with minor operation changes to increase the desired hydrogen stoichiometry. A simplified schematic of the reactor used by Mound Laboratories can be seen in Figure 4.
The process to produce titanium subhydride begins by filling the trays of the cylinder, within the furnace, with titanium hydride. The cylinder is evacuated via vacuum for 1-2 hours, until a desired pressure is reached. The cylinder is then heated to a range of 450 °C to 500 °C. As hydrogen is evacuated from the powder, the pressure inside the cylinder will rise. Once the pressure reaches a certain level, the gas within the cylinder is evacuated to a reservoir tank T. This reduces the pressure in the cylinder before it is again sealed. Tank T is then evacuated. The amount of hydrogen removed from the cylinder is recorded via a calculation of the pressure measurement. This process is repeated until an adequate amount of hydrogen has been removed to produce the desired subhydride composition. After the final evacuation of the cylinder, the system is allowed to cool before the subhydride is passivated.  

Figure 4: Schematic for the reactor used by Mound Laboratories to produce TiH$_{1.65}$.  

![Diagram of reactor](image_url)
The reactor originally used at Mound Laboratories is still in use and currently belongs to Northrop Grumman Innovation Systems (formerly Orbital ATK). Little modification has been made to the reactor, other than replacement of the manually controlled valves with computer controlled valves. Tank T may need to be evacuated multiple times to reach the desired subhydride composition. Figure 5 shows an in-situ pressure measurement from a recent batch operation in the reactor. Once the final pressure and desired subhydride composition has been reached, the cylinder remains sealed while the apparatus is turned off and allowed to cool overnight. Once cooled, the powder passivation procedure takes place.

![Figure 5: Hydrogen pressure measured during the dehydriding of a batch of TiH₂ at Northrup Grumman Innovation Systems](image)

The passivation procedure requires that a small portion of air be introduced to the cylinder, and the subsequent pressure decrease (from the oxygen reacting with the surface of the subhydride) monitored until and equilibrium is reached. This air introduction is repeated multiple times until no noticeable pressure decrease takes place. The lack of a pressure decrease indicates that the surface is fully passivated. The powder is then removed from the cylinder. Extensive passivation is a precaution to prevent pyrophoric ignition of the
subhydride powder, caused by the exothermic reaction of bare titanium with the atmosphere.\textsuperscript{6} An in-situ pressure measurement of the passivation of a recent batch operation in the reactor can be seen in Figure 6. Figure 6 demonstrates a decrease in pressure drop after each introduction of air, as the surface of the powder because less reactive with the atmosphere.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Air pressure measured during the passivation of a batch of TiH\textsubscript{x} at Northrup Grumman Innovation Systems\textsuperscript{8}}
\end{figure}

1-5 Dehydriding Titanium Hydride

The titanium-hydrogen system has been exhaustively characterized to understand its behavior within an extensive range of temperatures, pressures, and physical manifestations. The process for producing pyrotechnic grade titanium subhydride for use in Sandia National Laboratories’ THKP formulation relies on low pressure, isothermal dehydrogenation of titanium hydride.\textsuperscript{3,6,7} This process is terminated without reaching equilibrium. Though equilibrium processing is mentioned in the patent as prior art, it is unknown whether an equilibrium process, taking advantage of known, low pressure titanium-hydrogen isotherms\textsuperscript{9,10}, would be successful in producing pyrotechnic grade titanium subhydride.

Isothermal operation of this process provides accurate control of the dehydrogenation rate of titanium hydride. Isothermal operation is also required to prevent sintering of the individual TiH\textsubscript{2} particles. Sintering of titanium hydride particles will severely alter their
material characteristics and can occur at temperatures well below 500°C.\textsuperscript{3,6,11-13} It is crucial to avoid sintering in the THKP process, as the BET surface area of the subhydride particles is known to be incredibly important to pyrotechnic performance.\textsuperscript{3}

![Figure 7: Data obtained from TiH\textsubscript{2} sintering experiments. (a) Heating profile in a vacuum furnace, (b) shrinkage in axial and radial directions, (c) weight loss percentage, (d) densification degree, (e) open porosity measurements.\textsuperscript{12}]

Fortunately, dehydrogenation can be performed effectively at temperatures under 400°C to avoid sintering.\textsuperscript{9-14} Low temperature dehydrogenation has been shown to be especially effective with material that has a smaller particle size (similar to the 2µm TiH\textsubscript{2} used in the THKP process).\textsuperscript{12,14} The correlation of smaller particle size with more efficient low temperature dehydrogenation is beneficial to an industrial process which is concerned with strict preservation of material characteristics.
Figure 8: TGA mass loss comparison of nano and micro size titanium hydride particles during dehydriding.\textsuperscript{14}

There are two distinct atmospheric conditions under which dehydrogenation is regularly performed. Dehydrogenation of TiH\textsubscript{2} under vacuum is commonly used as a method to remove hydrogen quickly, which is beneficial when processing bulk quantities of material.\textsuperscript{10,13,16} The THKP process is demonstrated to use dehydrogenation under vacuum.\textsuperscript{3,6,7,8} Dehydrogenation under an ultra high purity argon atmosphere removes hydrogen less rapidly, but has the benefit of greater prevention of atmospheric contamination of the highly reactive, bare titanium surface.\textsuperscript{12,14,15} The effective dehydrogenation provided by both methods stems from the minimization of partial pressure of hydrogen. Atmospheric hydrogen partial pressure is a determining factor of the hydrogen concentration in titanium subhydride. Titanium-hydrogen isotherms, like the one shown in Figure 9, provide equilibrium conditions to manipulate the amount of hydrogen in a given subhydride.\textsuperscript{9} As previously mentioned, it is unclear whether such a process would produce acceptable pyrotechnic titanium subhydride via these equilibrium conditions.
Surface passivation of the subhydride particles is an important processing step, as it prevents pyrophoric ignition upon first exposure to atmospheric oxygen.\textsuperscript{3,6,7} Titanium hydride is normally stable under atmospheric conditions due to the presences of a thin titanium oxide layer on the surface of each particle. The formation of this layer is rapid and can occur at low vacuum. The formation of this passivating layer occurs via the exothermic reaction between titanium and atmospheric oxygen. Titanium’s natural affinity for oxygen is so high that this surface reaction can become pyrophoric if a sufficient amount oxygen is present.\textsuperscript{17,18}

Dehydrogenation of titanium hydride has been shown to remove the passivating oxide layer from the surface of the material. This process occurs as hydrogen passes through the
surface of the material, reducing the various titanium oxides present in the layer. This reaction produces \( \text{H}_2\text{O} \) which is released along with hydrogen gas. The remaining material is titanium subhydride lacking a surface layer of titanium oxide.\textsuperscript{19,20,21}

![Figure 10: Composition of the efflux of titanium hydride during dehydriding.\textsuperscript{20}](image)

Due to titanium’s high affinity for oxygen, both pure \( \text{O}_2 \) and regular air will effectively passivate a bare titanium surface.\textsuperscript{3,6,7,22,23} This reaction will yield a thin film of titanium oxide on the surface of the material and will proceed rapidly at a wide range of temperatures and pressures.\textsuperscript{24,25,26} The reaction between oxygen and a bare titanium surface exhibits a logarithmic mass increase. The logarithmic nature of this reaction can be explained by the following mechanism: An initial, rapid mass uptake occurs as the bare titanium surface first reacts with atmospheric oxygen. This happens almost instantaneously due to the oxyphilic nature of titanium. Following this initial surface reaction, the rate of mass uptake rapidly decreases as oxygen diffuses through the now present oxide layer, to the bare titanium beneath. As the thickness of the oxide layer increases the mass uptake from oxidation
becomes negligible as oxygen will no longer be able to diffuse far enough to reach bare titanium. Increasing the temperature, pressure, or oxygen concentration gradient will increase the diffusivity of oxygen in the titanium, leading to a thicker surface oxide layer.\textsuperscript{22,23,24,25,26} Titanium is known to produce a powerful catalytic effect for certain hydrocarbon reactions. These reactions are normally performed over titanium which has an oxide layer present on the surface.\textsuperscript{27,28,29} It is also known that gas containing carbon will react with a bare titanium surface.\textsuperscript{30} Reactions with gasses containing carbon have the potential to create a passivating reaction layer of titanium carbide which would present significant differences in material properties compared to the common titanium oxide passivating layer.

Bare titanium also has an affinity for nitrogen, especially at high temperature.\textsuperscript{31,32,33} Titanium can be nitride completely or treated to create a surface layer similar to the process mentioned for oxidation.\textsuperscript{31,32,33,34,35} Unfortunately, nitrogen has a much lower diffusivity in titanium at low temperature compared to that of oxygen.\textsuperscript{34,35} This means at equal temperature and pressure. Nitrogen has a much lower passivating potential than oxygen. Titanium nitride is also susceptible to oxidation.\textsuperscript{34} This oxidation occurs rapidly at high temperatures but can progress even at room temperature.

The reactions of bare titanium subhydride with various passivating agents is of interest because of the opportunity for surface engineering. The possibility of manipulating the pyrotechnic characteristics of THKP via novel passivation was first suggested in the patent for the dehydrogenation process.\textsuperscript{6} Since it has been shown that ESD sensitivity is a surface property of titanium subhydride\textsuperscript{4}, then it is possible that ESD sensitivity can be manipulated by producing passivating layers other than titanium oxide on the fuel particles. Titanium oxide has considerably different material properties than titanium nitride and titanium.
carbide. If a passivation process were to produce a surface layer of titanium nitride or 
titanium carbide rather than titanium oxide, then the ESD sensitivity of the residual THKP 
formulation could possibly be improved. This possibility is of interest to Sandia National 
Laboratories in their ongoing effort to improve the safety of their employees and the 
materials they handle.

This work has been conducted with the main objective of observing the reaction kinetics 
of bare titanium subhydride with three passivating agents; nitrogen, oxygen, and propane. 
Following the measurement of reaction kinetics, the passivated titanium subhydride samples 
were characterized to observe the effect of each passivating agent on the surface of the fuel 
particles.
1-7 References


Chapter 2

Experimental Method for Producing Titanium Subhydride
2-1 Titanium Hydride Starting Material

The original Mound Laboratories process for creating TiH$_{1.65}$ for use THKP formulations, used TiH$_2$ powder with an average particle size of 2 µm as the starting material.$^{3,6,7}$ For this work, Sigma Aldrich 325 mesh (44 µm) titanium(II) hydride powder with an assay of 98% was used as the starting material. While this TiH$_2$ powder has a considerably larger particle size, it provides an economical supply choice which should acts as a strong representation of the chemical properties of the material used in Mound’s process. The comparative decrease in total surface area of the material also reduced the risk of a pyrophoric ignition throughout exponentiation.

To ensure a full understanding of the reaction kinetics for the surface reactions that takes place in this experimental work, the surface area of the starting material had to be determined. The surface area of the TiH$_2$ powder was measured via krypton gas sorption at 77.35 K in a Quantachrome ASiQwin automated gas sorption analyzer, using the Brunauer-Emmett-Teller (BET) model. Two separate samples of the TiH$_2$ starting material were analyzed via this method. The BET surfaces areas were 0.958 m$^2$/g and 0.918 m$^2$/g respectively. This analysis was conducted at Sandia National Laboratories and closely followed the procedures of similar analysis conducted for previous pyrotechnics projects.$^{36}$

2-2 Dehydriding and Passivation Under Thermogravimetric Analysis

In the interest of observing the reaction kinetics of passivation, the TiH$_2$ starting material was dehydrided in a similar fashion to the original production process. Individual samples (15-25 mg) of TiH$_2$ were heated under an argon atmosphere at 420°C with a Netzsch STA 449 F3 Jupiter Thermogravimetric Analyzer (TGA). The argon atmosphere was
produced from a source which was 99.999% pure and flowed at 100 mL/min while maintaining an internal pressure of 600 torr. This internal atmosphere was constantly removed by vacuum to prevent any accumulation of gas released from the starting material. The heating rate for the TGA was 5°C/min. Each sample was dehydrated under these conditions for a period ranging from 109 to 1159 minutes. Mass data was recorded as a relative percentage of the initial sample weight. This percentage is normalized with the assumption of stoichiometric TiH$_2$ and then converted to a corresponding molecular weight.

Upon completion of the predetermined dehydrating time period, the passivation time period commenced. Passivation was achieved by altering the internal TGA atmosphere from a 100 mL/min flow of argon (at a pressure of 600 torr) to a flow of a gas mixture which consisted of 20 mL/min of a passivating agent (creating a partial pressure of 120 torr) and 80 mL/min of argon (creating a partial pressure of 480 torr). Three separate passivating agents were used in these experimental trials; oxygen, nitrogen, and propane. The temperature remained at 420°C throughout the passivation period. Each sample was passivated under these conditions for a period ranging from 60 to 1500 minutes. During this period, the mass gain of each sample was recorded at a 4 Hz sampling rate.

Dehydrating and passivation trials showed that in the allotted time for each process, full dehydrogenation and full reaction with the passivating would not occur. This showed that the allotted time of treatment achieved the intended goal of surface reactions upon particles of titanium subhydride. This analysis was also conducted at Sandia National Laboratories and closely followed the procedures of a similar experiment conducted for previous pyrotechnics projects.$^{36}$
Chapter 3

Reaction Kinetics and Characterization of

Titanium Subhydride Passivation
3-1 Titanium Subhydride Stoichiometry

This work analyzed a total of 27 experimental trials. These trials began with a dehydriding period of either 109, 559, or 1159 minutes, during which the initial sample of titanium hydride was heated at 420°C under a flowing (100 mL/min at 600 torr) ultra high purity argon atmosphere. Samples dehydrided for 109 minutes showed minimal hydrogen evacuation, with a calculated hydrogen concentration range of TiH₅ X = 1.97 to X = 2. Samples dehydrided for 559 and 1159 minutes showed varied levels of hydrogen loss, with the calculated hydrogen concentration range of TiHₓ X = 1.13 to X = 1.89 and TiHₓ X = 0.94 to X = 1.81, respectively.

![Graph](image)

Figure 11: Hydride composition of each experimental sample calculated from TGA mass loss data versus the time of dehydriding.
3-2 Experimental Data from Thermogravimetric Analysis

Surface passivation with nitrogen was the first method to be examined. The initial mass loss from the dehydriding period varied significantly between these trials. The mass gain from the passivation period also varied significantly for these trials. The TGA data for the nitrogen passivated subset of samples can be seen in Figure 12.

Surface passivation with oxygen was the second method to be examined and served as a quasi-control because it is known that air passivation will produce a titanium oxide layer. The initial mass loss from the dehydriding period and the mass gain from the passivation period both showed more uniformity for these samples compared to the nitrogen passivated subset. The TGA data for the oxygen passivated subset of samples can be seen in Figure 13.

Surface passivation with propane was the third method to be examined. The initial mass loss from the dehydriding period was the most uniform for this subset of samples. However, the mass gain from the passivation period varied the most for these trials. The TGA data for the propane passivated subset of samples can be seen in Figure 14.

![Figure 12: TGA experimental data showing the dehydriding and passivation period for all samples passivated with nitrogen.](image)
Figure 13: TGA experimental data showing the dehydriding and passivation period for all samples passivated with oxygen.

Figure 14: TGA experimental data showing the dehydriding and passivation period for all samples passivated with propane.
3.3 Dehydriding Mass Gain Anomalies

Certain trials showed an apparent mass gain during the dehydriding period. A nitrogen trial exhibited an apparent mass gain of 0.2 Da while an oxygen trial showed an apparent mass gain of 0.26 Da. These dehydriding period mass gains can be seen in Figure 15 and Figure 16 respectively.

Figure 15: TGA experimental data showing an apparent mass gain of the sample during the dehydriding period, prior to nitrogen passivation.

Figure 16: TGA experimental data showing an apparent mass gain of the sample during the dehydriding period, prior to oxygen passivation.
3-4 Passivation Reaction Kinetic Model

The reaction kinetic model that fit all of the passivation period mass gains from this work take the form of equation 1, where $w$ is the passivation mass gain, $k_L$ is the logarithmic constant, $C$ is the time constant, $t$ is time, and $k_P$ is the parabolic constant.

$$w = k_L \log(Ct + 1) + k_P\sqrt{t}$$

The time constant $C$ was found to alter the region of the curve where the transition from predominantly logarithmic mass gain to predominantly parabolic mass gain takes place. The kinetic model was found to best fit the experimental data when this constant was held at a value of 600. All variables of interest can be seen in Table 1.

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<th>Trial</th>
<th>Dehydrating Time (min)</th>
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<th>Passivation Time (min)</th>
<th>Passivation Agent</th>
<th>$k_L$</th>
<th>$C$</th>
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<td>C$_3$H$_8$</td>
<td>0.00026</td>
<td>600</td>
<td>0.03549</td>
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</table>
The smallest mass gain from nitrogen passivation was 0.42 Da or 0.85% of the initial sample weight while the largest mass gain from nitrogen passivation was 0.45 Da or 0.91% of the initial sample weight. The experimental data and corresponding kinetic models for these trials can be seen in Figure 17 A and 17 B respectively.

Figure 17: TGA experimental data showing nitrogen passivation trials with the smallest mass gain (A) and the largest mass gain (B) within the nitrogen passivation subset of samples.
The smallest mass gain from oxygen passivation was 0.31 Da or 0.62% of the initial sample weight while the largest mass gain from oxygen passivation was 0.55 Da or 1.1% of the initial sample weight. The experimental data and corresponding kinetic models for these trials can be seen in Figure 18 A and 18 B respectively.

![Figure 18: TGA experimental data showing oxygen passivation trials with the smallest mass gain (A) and the largest mass gain (B) within the oxygen passivation subset of samples.](image)
The smallest mass gain from propane passivation was 0.08 Da or 0.16% of the initial sample weight while the largest mass gain from propane passivation was 0.98 Da or 1.96% of the initial sample weight. The experimental data and corresponding kinetic models for these trials can be seen in Figure 19 A and 19 B respectively.

Figure 19: TGA experimental data showing propane passivation trials with the smallest mass gain (A) and the largest mass gain (B) within the propane passivation subset of samples.
3.5 Passivation Mass Gain Anomaly

One propane passivation trial showed an intriguing anomaly, with a drastic spike in mass gain during the middle of an otherwise routine passivation. No experimental difference were recorded, and the mass of the sample slightly decreased following the spike. This behavior can be seen in Figure 20.

Figure 20: TGA experimental data showing a propane passivation trial which exhibited an anomaly in the mass gain behavior.
3-6 Surface Characterization via X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy was conducted on a sample from each of the passivation subsets. Figure 21 shows the comparison of a propane-passivated sample with two reference spectra. It can be seen that the propane-passivated sample lacks a peak at 454 eV that is present in the reference spectra.

The comparison of XPS spectra of a nitrogen-passivated sample and an oxygen-passivated sample can be seen in Figure 22. These spectra are similar, but the oxygen-passivated sample exhibits a prominent peak at 461 eV that the nitrogen sample lacks.
Figure 22: XPS experimental data showing the surface characterization of samples passivated with oxygen (black) and nitrogen (green).

3-7 Scanning Electron Microscope Imaging

Scanning electron microscope imaging showed the characteristics of samples passivated by each passivating gas. Focused ion beam sectioning allowed for the imaging of the surface reaction layer of each of these samples. The sample passivated for the shortest time period (105 min) with nitrogen shows an apparent reaction layer thickness of up to 9.7 nm while the sample passivated for the intermediate time period (720 min) with nitrogen shows an apparent reaction layer thickness of up to 177 nm. The sample passivated for the shortest time period (129 min) with oxygen shows an apparent reaction layer thickness of up to 44.9 nm while the sample passivated for the intermediate time period (720 min) with oxygen shows an apparent reaction layer thickness of up to 111 nm. The sample passivated for the shortest time period (180 min) with propane shows an apparent reaction layer thickness of up to 41 nm while the sample passivated for the intermediate time period (720 min) with propane shows an apparent reaction layer thickness of up to 27.3 nm.
Figure 23: SEM images of a sample passivated with nitrogen showing: the surface of the particles (A), a FIB sectioned particle that was passivated for the shortest time period (B), and a FIB sectioned particle that was passivated for the intermediate time period (C).
Figure 2: SEM images of a sample passivated with oxygen showing: the surface of the particles (A), a FIB sectioned particle that was passivated for the shortest time period (B), and a FIB sectioned particle that was passivated for the intermediate time period (C).
Figure 25: SEM images of a sample passivated with propane showing: the surface of the particles (A), a FIB sectioned particle that was passivated for the shortest time period (B), and a FIB sectioned particle that was passivated for the intermediate time period (C).
Chapter 4

Discussion of Titanium Subhydride Passivation

Experimental Results
Experimental Dehydriding

The dehydrogenation of titanium hydride samples conducted in this work was intended to closely resemble the dehydrogenation process described by in the 1980 patent, “PROCESS FOR REPRODUCIBLY PREPARING TITANIUM SUBHYDRIDE”. Unfortunately, the process of dehydrogenation under vacuum yielded sporadic mass loss data in the TGA. For this reason, the process was modified to dehydrogenate under a flowing Ultra High Purity argon atmosphere. This modification resulted in an observed mass loss which closely resembled the gradual, high temperature off gassing of hydrogen from bulk material in the subhydride manufacturing process, which can be seen in Figure 5. Given the non-reactive nature of argon, this modification should also yield a similar subhydride.

The observed mass loss of the 27 samples included in the analysis of this work showed a varied level of dehydrogenation. The overall trend of the dehydrogenation process showed that the longer a sample was held at temperature under a flowing argon atmosphere, the greater the mass loss of the sample would be. However, the observed mass loss of each sample varied greatly, even within identical time trials. This variation is likely due to inhomogeneity of the starting material. Although all 27 samples were taken from the same bottle of titanium hydride, their considerably small individual size (less than 30 mg each) likely led to variation of the microscopic characteristics between samples which were imperceivable to the human eye. It is likely that the behavior of this material during passivation would be more uniform if each trial were processing larger quantities, on the magnitude of grams or kilograms, negating the effects of material variability.
4-2 Passivating Gasses

This work focused on the reaction kinetics of titanium subhydride (which possessed a bare titanium surface after being dehydrided) with three passivating agents. The initial motivation to studying these reactions came from a suggestion from the 1980 patent, that novel passivation methods could be used to manipulate pyrotechnic characteristics of this material. The passivating agents were oxygen, nitrogen, and propane. Nitrogen was chosen as the first passivating agent because it is known that titanium nitride possesses different material characteristics than titanium oxide and that nitrogen will react with bare titanium. Additionally, the abundance of nitrogen would allow for low cost integration as a passivating agent in an industrial process. Oxygen was chosen as the second passivating agent because it provides a similar representation to air. This served as a quasi-control, as air is used to passivated titanium hydride in the commercial process that this work is meant to emulate. Although air only consists of about 21% oxygen, the oxyphilic nature of bare titanium suggests that pure oxygen and air would react near identically with the material of interest. This assumption has not been tested, so further analysis would be required for confirmation and to determine if bare titanium subhydride reacts with the nitrogen in air. Finally, propane was chosen as the third passivating agent. Propane was chosen for multiple reasons. The first reason was that it’s known that hydrocarbons will react with bare titanium and hydrocarbons were also a suggested a possible passivating agent in the 1980 patent. Propane was chosen as the specific hydrocarbon of interest because it is relatively inexpensive (making it a viable industrial passivating agent) and it contains no oxygen or nitrogen in its molecular structure.
4-3 Experimental Passivation

Nitrogen exhibited somewhat uniform surface passivation reaction kinetics. Each set of samples, identified by their respective passivation time periods, exhibited a mass gain behavior which was similar to the other samples in its set than samples with a different passivation time. The passivation mass gain for these samples fell within a range of 0.42 Da or 0.85% of the initial dehydrided sample weight to 0.45 Da or 0.91% of the initial dehydrided sample weight.

Oxygen exhibited the most uniform behavior of surface passivation reaction kinetics. The passivation mass gain for these samples fell within a range of 0.31 Da or 0.62% of the initial dehydrided sample weight to 0.55 Da or 1.1% of the initial dehydrided sample weight. It should be noted that these trials also exhibited remarkably similar dehydriding behaviors for each sample set. The initial uniformity of dehydriding may be, in part, responsible for the subsequent uniformity of passivation reaction kinetics.

Propane exhibited the most unpredictable surface passivation reaction kinetics. There was little correlation between the mass gain of each sample and the respective passivation time. The passivation mass gain for these samples fell within a range of 0.08 Da or 0.16% of the initial dehydrided sample weight to 0.98 Da or 1.96% of the initial dehydrided sample weight.

4-4 Reaction Kinetic Model

The reaction kinetics of the surface passivation of all samples analyzed in this work fit the kinetic model demonstrated by Equation 1. This kinetic model is the result of the combination of two independent terms, the first of which being a logarithmic term and the
second being a parabolic term. The logarithmic term represents the Fehlner-Mott (F-M) model of oxide layer growth. This model represents thin film growth where the assumed rate limiting step is interstitial transport of anions through the surface reaction layer.\textsuperscript{37} This logarithmic reaction model can be seen in equation 2, where \( w \) is the passivation mass gain, \( k_L \) is the logarithmic constant, \( C \) is the time constant, and \( t \) is time. The parabolic term represents the Wagner model for oxide layer growth. This model represents thick film growth where the assumed rate limiting step is also diffusion of charged particles through the surface reaction layer.\textsuperscript{37} This reaction model can be seen in equation 3, where \( w \) is the passivation mass gain, \( t \) is time, and \( k_P \) is the parabolic constant.

\begin{equation}
[2] \quad w = k_L \log(Ct + 1)
\end{equation}

\begin{equation}
[3] \quad w = k_P \sqrt{t}
\end{equation}

The transition from the initial F-M (logarithmic) term to the Wagner (parabolic) term in the kinetic model observed in this work suggests the following mechanism. Following dehydriding, the titanium subhydride particles have a surface of bare titanium which lacks both an oxide layer and a fully hydrided lattice. Upon exposure to a passivating gas, the surface is rapidly oxidized, forming a thin film. Since the material remains at a high temperature (420°) the diffusivity of the material also remains high, allow the passivating agent to diffuse quickly through the initial thin reaction layer (increased diffusivity of oxygen in titanium subhydride at elevated temperatures (>350°) has been previously demonstrated.\textsuperscript{38}). However as the reaction layer grows thicker, the diffusion of the passivating agent slows from a logarithmic rate to a parabolic rate. This mechanism includes the assumption that each of the passivating gasses dissociates at the surface of the reaction
layer before diffusing toward the active titanium beneath. The optimized rate constants for the kinetic model of each sample can be seen in Table 1.

**4-5 Experimental Anomalies**

The *in-situ* measurements recording via TGA presented anomalies which remain unexplained at the time of this work. A common anomaly was recorded during the longest dehydriding time period, where the sample’s mass loss seems to reach an apparent minimum, followed by a gradual mass increase. This behavior is illustrated in Figure 15 and Figure 16. This may suggest that these samples slowly oxidized despite a flowing argon atmosphere. It is possible that this pre-passivation mass gain was due to oxygen contamination. However, this anomaly has not been investigated at the time of this work, and the cause of this mass gain could be attributable to multiple factors including measurement drift of the instrument over time. The second anomaly was present in only one trial but is noteworthy. One propane passivation trial, shown in Figure 20, exhibited an abnormal mass increase followed by an erratic measurement which eventually stabilized to the parabolic behavior of mass gain similar to the other samples examined in this work. The cause of this anomaly is unexplained but could be the result of instrument error or internal disturbance of the sample.

**4-6 Material Characterization**

Following passivation, representative samples were analyzed to characterize their surface and determine the effect of each passivating agent. The first method of surface analysis was X-ray photoelectron spectroscopy (XPS). The second method was scanning electron microscope (SEM) imaging before and after sectioning via a focused ion beam (FIB).
XPS analysis was performed at Sandia National. The results can be seen in Figure 21 & Figure 22. Each of the samples were oxidized to the maximum depth of XPS analysis, which is about 5 nm. Figure 21 shows a sample passivated with propane (purple) compared to reference spectra of titanium (red) and titanium oxide (yellow). The propane passivated sample lacks a peak at the 455eV that is present on the reference spectra, suggesting a chemical difference. However, this spectra is still indicative of an oxidized (TiO$_x$) surface. Figure 22 shows a comparison of a sample passivated with oxygen (O$_2$) and a sample passivated nitrogen (N$_2$). The samples were similar suggesting both surfaces were oxidized (TiO$_x$). The propane and nitrogen passivated samples showed nearly identical XPS spectra, while the oxygen passivated sample exhibited an additional peak at 462 eV which indicates Ti 2p O 1s. The staff member performing the XPS analysis suggested that this may be a hydroxide. This difference may suggest that there is a different oxidation mechanism taking place when the sample is passivated with oxygen compared to when the sample is passivated with propane or nitrogen. This could mean that passivation via nitrogen and propane forms a titanium nitride and titanium carbide surface layer (respectively) in-situ, but that layer is quickly oxidized upon exposure to the atmosphere. This mechanism obviously differs from a sample which has bare titanium directly reacting with pure oxygen (oxygen passivation). These differing mechanisms of forming an oxide layer (TiO$_x$) may prove useful in manipulating pyrotechnic properties, given the minor chemical difference they exhibit.

SEM imaging was also performed at Sandia National Laboratories. Imaging of samples passivated with nitrogen, oxygen, and propane, shown in Figures 23 A, 24 A, and 25 A (respectively), did not show any apparent physical differences. However, imaging after
sectioning via FIB revealed differences in the reaction layers of samples passivated by each passivating agent with different passivation times.

Six samples were analyzed with SEM after FIB bisection. There were two samples for each passivation agent, one of these samples being treated for the shortest passivation time (<180 min) and the other being treated for the intermediate passivation time (720 min). There was an observed trend, showing that a longer passivation time would lead to a thicker apparent reaction layer. Figure 26 B shows a sample passivated with nitrogen for the short time period, demonstrating a single apparent reaction layer with a thickness in the range of 7.8 nm to 9.8 nm at the surface of the particle. Figure 23 C shows a sample passivated with nitrogen for the intermediate time period, demonstrating an apparent reaction layer with a thickness in the range of 13.6 nm to 15.6 nm at the surface of the particle, and a noticeably separate reaction layer with a thickness in the range of 164 nm to 177 nm below the surface layer. This physical difference, where samples passivated for the short time show a single reaction layer while samples passivated for the intermediate time period show two separate reaction layers, was also observed in the samples passivated with Oxygen. This trend can be observed by comparing Figure 23 B to Figure 23 C (nitrogen passivation), and Figure 24 B to Figure 24 C (oxygen passivation). However, the samples passivated with propane both showed a single reaction layer, despite differences in passivation time. This can be seen by comparing Figure 25 B to Figure 25 C (propane passivation). Propane passivated samples also showed an inconsistent difference in the overall thickness of the reaction layer between the short and intermediate passivation periods. XPS analysis suggests that composition of the surface reaction layer of each sample is a form of titanium oxide (TiO$_x$).
4-7 References


Chapter 5

Conclusion
5-1 Conclusion

The observed mass gain (following exposure to a passivating gas) of each titanium subhydride sample is strong evidence that the sample is directly reacting with the passivating gas. A reaction between the titanium subhydride and each passivating gas would likely produce a titanium nitride, titanium oxide, and titanium carbide / titanium hydride surface reaction layer (for nitrogen, oxygen, and propane respectively). However, the observed reaction layer composition for each sample sub set was a form of titanium oxide (TiO$_x$). The most reasonable explanation for this outcome is that whatever reaction layer is formed during passivation will be immediately oxidized once the sample is exposed to the air. This outcome makes sense because titanium has a higher chemical affinity for oxygen than nitrogen, carbon, or hydrogen. The slight difference in XPS data for the directly oxidized sample of titanium subhydride seems to support this explanation as well.

This work showed that titanium subhydride will react with nitrogen, oxygen, and propane directly following dehydriding. The kinetic model for these reactions shows that an immediate surface passivation takes place, followed by a prolonged diffusion of the passivating gas into the bulk material. The end result of each of these passivation methods is a titanium subhydride with a titanium oxide surface layer.

5-2 Future Work

The scope of this work was relatively narrow as a result of it being conducted under a project topic which had previously experienced a multiple decade hiatus at Sandia National Laboratories. Multiple areas of interest have been illuminated by this work and the suggested research topics to follow are discussed below.
The isothermal conditions of the passivation experiments conducted in this work were chosen based on the temperature (420°) suggested in the 1980 patent. Passivation with nitrogen, oxygen, and propane should be conducted at a range of temperatures to observe the effect on the kinetic model.

Passivation should also be attempted with a wider range of passivating agents. Characterization of the resulting materials may provide insight to possible surface engineering techniques which can be employed on the industrial scale of this process.

The passivation methods (via nitrogen, oxygen, and propane) performed in this work should be implemented on a larger quantity of titanium subhydride. This will allow for mixture with potassium perchlorate, making the study of the resulting pyrotechnic performance feasible. These passivation techniques may result in unforeseen benefits (or detriments) to the pyrotechnic mixture compared to using the traditional titanium subhydride.