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TITANIUM METAL POWDER PRODUCTION BY THE PLASMA QUENCH
PROCESS

FINAL REPORT
01/31/1997 – 12/31/1999

R. A. Cordes
A. Donaldson

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Prepared for the
U.S. Department of Energy
Assistant Secretary for
Energy Research
Washington, DC

Prepared by
Idaho Titanium Technologies, Inc.
Idaho Falls, ID

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Idaho Titanium Technologies, Inc.

***“Titanium Metal Powder Production
by the Plasma Quench Process”***

FY99 Final Technical Report

***This report has been prepared pursuant to U. S.
Department of Energy Cooperative Agreement
Number DE-FC07-97ID13511***

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Titanium Metal Powder Production by the Plasma Quench Process

Addendum to the Final Report

Subsequent to the end of the contract with the US Department of Energy and to the completion of the final report, but prior to the actual release of the final report, significant accomplishments occurred in the ongoing titanium project. These accomplishments are briefly set forth below.

Sintering Titanium Hydride Powder: Dr. Sarit Bhaduri, a professor at the University of Idaho and creator of the U of I Ceramic Processing Laboratory, demonstrated that the titanium hydride powder of Idaho Titanium Technologies, Inc. (ITT) can indeed be sintered into solid titanium metal. The photo on the left below shows the before and after of a sintered disk. The photo on the right shows the final polished disk.

Production/Sintering Titanium Carbide: Nano-crystalline titanium carbide has been produced by ITT using the same Rapid Plasma Quench process utilized to produce the titanium hydride powder. The particles are spherical, between 10 and 20 nanometers in diameter. Ordinary TiC requires temperatures over 2000 C for sintering, even with the addition of sintering aids such as silicon carbide. The TiC made by the ITT process can be sintered at 1500 C without sintering aids, which is a very significant distinction. The production rate is unique as well. ITT is currently producing the TiC powder at a rate of 25 pounds/hour and at a cost on the order of \$6 per pound. It is anticipated that the production rate can readily be increased to 100 pounds/hour.

Conclusions and Recommendations of Dr. Bhaduri:

"The microstructure analysis of the powders, Ti and TiC, clearly indicate that they are of nano-crystalline size. These powders allow for better densification due to the greater surface area associated with fine powders. The consolidation process carried out indicates that it is viable to obtain dense Ti/TiC samples via conventional sintering in a tube furnace as well as microwave sintering. The latter process, if fine-tuned, will allow for an economical and efficient technique to produce dense samples in an inert/controlled environment.

Initial results also indicate that there is some agglomeration present in the powder precursor that leads to the formation of porosity in the sintered sample. Ball-milling the powders prior to compaction, to break the agglomerated particles, can rectify this problem. Another source of these voids could be due to the evolution of gaseous phases in particular Cl₂ from residual TiCl₄ found in the powder. A viable method to rectify this problem has already been developed at ITT.

Furthermore, it was also found that by uni-axially compacting the powders with a die in an inert atmosphere resulted in dense green compacts. Therefore, a scale-up of the process to produce larger samples is viable. The prime concern or requirement would be the capability to sustain an inert atmosphere to work.

The above analysis of the preliminary results obtained from the Ti and TiC powders indicates that it is viable to achieve the necessary results with a few modifications to the processing of the powders."

Inquiries to Dr. Bhaduri can be made by contacting him by phone (208-885-7228) or by email (bhaduri@uidaho.edu).

Efforts are currently underway to identify possible sources of funding with which to continue the titanium/titanium carbide project.

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Idaho Titanium Technologies FY99 Final Report

Executive Summary

Introduction

Prior to obtaining funding from the U S Navy's Office of Naval Research (ONR), Idaho Titanium Technologies, Inc. (ITT) had developed a small-scale, experimental plasma reactor system, incorporating a proprietary rapid plasma quench step, to produce titanium hydride powder at a rate of one pound per hour with a purity level of 99%. This small system demonstrated the science behind the process, but substantial effort would be required to scale the process up to commercial production levels.

Program Goals

The goals of the Cooperative Agreement were very aggressive, including the scale-up of the titanium hydride production process to a production rate of 50 kg/hr at a purity level of 99+%. This goal was to be achieved by incrementally increasing the production capability of a series of reactor systems. This methodic approach was designed to allow ITT to systematically address the engineering issues associated with plasma torch design and operation, reactor system design and performance, quench system performance, and powder collection system design and performance. With quality powder available, actual fabrication with the titanium hydride was to be pursued. Finally, with a successful titanium production system in place, the production of titanium aluminide was to be pursued by the simultaneous injection of titanium and aluminum precursors into the reactor system.

Program Achievements

Iterating plasma system configuration turned out to be an extremely time consuming process, in particular the redesign and construction of new reactors to address specific issues as they emerged. Consequently there was insufficient time to examine the production of titanium aluminide. In spite of the inherently tedious process of reactor system design and fabrication, significant accomplishments were achieved as listed below.

- The design of a plasma torch capable of operating at 800 kW.
- The design of a plasma torch capable of operating in a highly corrosive environment.
- Demonstrated that the unique ITT torch/reactor concept to heat the reactants works.
- Demonstrated the continuous production of titanium hydride at 30 lbs./hr.
- Demonstrated that the subchloride content of the powder is extremely low, <0.5%.
- Demonstrated that the powder can indeed be sintered into solid metal.

Anticipated Benefits/Commercial Applications of the Research and Development

A critically significant benefit will be the decentralization and stabilization of titanium production. No longer will the US Navy and the defense and aerospace industries need to rely upon the traditionally unstable foreign supplies of titanium. In addition, the availability of relatively inexpensive titanium powder will enable the fabrication of titanium parts by such techniques as injection molding, parts that were heretofore too expensive to manufacture from titanium. This will enable new, cost-effective Navy applications. Other affected industries include national defense, oil & gas, aerospace, construction, medical, automotive, marine, and sports, among others.

Idaho Titanium Technologies FY99 Final Report

Introduction

Prior to the onset of the U S Navy-funded, U S Department of Energy administered Cooperative Agreement, Idaho Titanium Technologies Inc. (ITT) had successfully developed an experimental titanium metal powder production system utilizing a proprietary rapid plasma quench technology licensed from the Department of Energy Idaho National Engineering & Environmental Laboratory (INEEL). This experimental system operated at about 1-2 pounds per hour. The fundamental task at the heart of the Agreement was to scale this system to a production level of 100 pounds per hour. To do so, torch design and configuration, reactor design and configuration, and powder collection system design and configuration would need to be addressed.

The successful scale-up of the titanium hydride process has potentially profound ramifications. According to industry representatives, the ITT process literally has the potential to revolutionize the titanium industry. In so doing, great benefits accrue to both the federal government defense sector and to the private commercial sector. A stable titanium supply with stable costs will allow the automotive industry, the aerospace industry, the defense industry, and other current or potential users to commit to long-range applications of titanium heretofore unavailable. For example, the ability to use titanium cost-effectively in specific automotive engine parts means substantial increases in gas mileage, thereby promoting energy conservation on behalf of the entire nation. Aircraft and aircraft engine producers can commit to products requiring ever increasing amounts of titanium with the assurance that their needs can be met with prices remaining stable. The dramatically lower capital costs of an ITT production system relative to the traditional Kroll process for the production of titanium means that the ITT process will in fact displace the Kroll process and result in numerous production facilities world-wide capable of being operated cost-effectively on an as-needed basis.

Technical Objectives

Introduction

There were three overarching technical objectives at the heart of the Cooperative agreement – the development of a 1MW titanium production system, the demonstration of the ability to produce titanium aluminide, and the fabrication of parts from the titanium hydride powder.

Plasma Reactor System

The above objectives were to be achieved first by fabricating and operating a series of plasma reactor systems, each increasing in production capability. The insights gained by

this step-by-step evolutionary process would enable ITT ultimately to design, fabricate, and operate the target 1MW system. In particular such issues as reactor design and performance, plasma torch design, configuration and performance, and powder collection system design and performance would be addressed during this scale-up process.

Powder Collection System

Fundamental to the successful operation of a powder production system is the ability to collect the powder efficiently. To this end, a collection system had to be designed and maintained that could efficiently collect the powder regardless of the powder production rate.

Titanium Aluminide

With the successful design and operation of a 1MW-titanium production reactor system, the ability to produce titanium aluminide could be examined. This goal would involve the design and fabrication of an aluminum precursor feed system to use in conjunction with the existing operating reactor system. By feeding the titanium precursor (titanium tetrachloride) simultaneously with the aluminum precursor, it was anticipated that molecular level titanium aluminide would be produced. The same collection system utilized for the titanium powder would be used to capture the titanium aluminide.

Powder Fabrication

Having successfully produced titanium hydride powder, actual fabrication with that powder could be initiated. To that end, ITT intended to utilize a small in-house vacuum furnace to make small metal slugs. In addition, Penn State University was hired to examine fabricating with the titanium hydride powder in its powder metallurgy program.

Technical Outcome Overview

Introduction

ITT, in a relatively short period of time conducting true high-risk, cutting-edge research and development, demonstrated many significant accomplishments. A unique and revolutionary torch/reactor capable of withstanding temperatures up to 5000° C with high thermal efficiency has been operated. The dissociation of titanium tetrachloride into titanium powder and HCl has been demonstrated, and a one-megawatt reactor potentially capable of producing 100 pounds per hour has been built but not yet operated at that power level. The removal of residual subchlorides and adsorbed HCl and the sintering of powder to form solid bodies have been demonstrated. The production system has been operated at production rates up to 40 pounds per hour.

The ITT torch/reactor system is operational in two sizes. One operates at 125 kW, and with minor modifications will operate at about 400 kW. The other operates at 750 kW and with minor modifications will operate at over a megawatt. These torch/reactors are thermally efficient at temperatures as high as the 5000° C that is required for titanium

production. Very difficult problems with heat and corrosion were encountered during this development process and most have been successfully addressed.

The projected economies for achieving the ultimate goal of replacing the Kroll process are excellent. It appears that the Plasma Quench Process does indeed have the potential to replace the Kroll process and will as a result generate many new, long sought after applications for the use of titanium. The relative economics of the Kroll Process and the Rapid Plasma Quench Process are discussed later in this report.

Figure 1: Plasma Quench Reactor System

Unique Features of the Plasma Quench Reactor System

Tremendous technical changes have occurred in the process of evolving the Rapid Plasma Quench Reactor concept from the original bench scale to its current small commercial scale. The system today in fact bears little resemblance to the original bench-scale system. Numerous advancements have been made, the result of which is that the Rapid Plasma Quench Reactor System is quite likely unique in the world.

The characteristics that are responsible for the unique capabilities of this system are set forth below:

The arc directly heats the reactants. Most of the arc length is composed of the reactant species, or their dissociated ionized products. Very efficient heat transfer is accomplished by this innovation. As a result, even corrosive species such as chlorine can be directly heated to over 5000° K without corrosion problems arising for either the reactor or the electrodes.

Direct heating enables very short residence times in a very small reactor. At any given time there is only a gram or so of reactants in the reactor, even at commercial scale production rates. The Rapid Plasma Quench Reactor, with its small volume, operates at over a megawatt of power.

The Rapid Plasma Quench Reactor System can operate at several bar pressure because of its small size and water-cooled walls. This results in a relatively longer residence time for a very small reactor volume, increasing the probability of achieving complete reactions.

The patented Rapid Plasma Quench (US Patent 5,749,937) can cool the reactants at over a billion degrees Kelvin per second. This uniquely rapid quench is critical in that it prevents back reactions and permits the retention of otherwise unstable products.

Powder Collection System

The powder collection system, which consists of a series of cyclone separators designed and fabricated by ITT, has proven to be extremely efficient and has required no modification as the production rates have slowly increased. After entering the respective cyclones, the powder falls into containers that can be sealed and later purged with argon without any exposure to the air. The collection containers have been designed to integrate with the Post-Powder Collection Treatment System discussed below.

Figure 2: Powder Collection System

Post-Powder Collection Treatment System

The titanium hydride powder (TiH_2), produced by ITT's proprietary plasma quench method contains approximately 40% adsorbed dry hydrochloric acid (HCl). The possibility exists that some small percentage (1% or less) of titanium sub-chlorides (TiCl_3 and TiCl_2) might also appear in the powder. The removal of these constituents facilitates powder handling and subsequent processing.

Figure 3: Post-Powder Collection Treatment System

To address this issue, a "Post-Powder Collection Treatment System" shown above was designed consisting of a large-capacity glove box connected to a cylindrical vacuum furnace. Powder captured in the collection containers of the production system can be emptied into a series of trays residing in the glove box. This step occurs without any exposure of the powder to the air. The glove box has first been purged with argon. In addition a hot titanium-chip oxygen "getter" is used to ensure the purity of the inert atmosphere. These trays are then slid into the cylindrical vacuum furnace. The furnace is sealed and then evacuated to between 0.1 and 0.01 torr. The temperature is then slowly brought to 600°C . Heating continues until all impurities are stripped from the powder. The powder is then re-hydrogenated during the cool down.

This progression of gas stripping can be seen from the vapor pressure curves below. As indicated by Figure 4, adsorbed HCl is stripped from the powder at a very low temperature (165° to 185°C) once the vacuum is established. After HCl is removed from the powder, the temperature is increased until the TiCl_3 is stripped off. As indicated by Figure 5, TiCl_3 is stripped from the powder between 350° and 450°C at the vacuum levels present in the furnace. Following the removal of TiCl_3 , the temperature is

increased until TiCl_2 is stripped off. Figure 6 shows that TiCl_2 is stripped from the powder between 750° and 850° C at the indicated vacuum levels. A flow chart, which outlines this stripping process, is provided in Figure 7 below.

Figure 4. Adsorbed HCl Stripping

Figure 5. TiCl_3 Stripping

Figure 6. TiCl_2 Stripping

By flowing Argon over the powder, the effective temperature for TiCl_2 can be reduced to 600° C.

Figure 7. Stripping Flow Chart

Titanium Aluminide

Unfortunately the great amount of time required to evolve the necessary plasma reactor system precluded the actual production of titanium aluminide. An effort was made to identify a potential feed system, but insufficient resources remained at the end of the subject project to fabricate the feed system, test it, and ultimately operate the reactor system with the aluminum precursor feed system in place.

Parts Fabrication

The removal of the dry hydrogen chloride which is adsorbed by the titanium hydride powder is easily carried out given the appropriate equipment. It can be removed at 165°C to 185°C in the presence of flowing hydrogen gas or in a vacuum. Once the dry HCl is removed, the titanium hydride powder can indeed be sintered into solid metal bodies. ITT's vacuum furnace however was too small to prepare anything other than small disks, one of which is shown below. *Appendix A is devoted to an in-depth discussion of the metallurgical testing conducted by ITT and Penn State University.*

Sintered, Unpolished Disk

Patent Idea Disclosures

Three Patent Idea Disclosures were submitted to the DOE pursuant to the procedures set forth in the Cooperative Agreement. These disclosures addressed the plasma torch system, the plasma reactor, and the quench system.

Summary of Key Accomplishments

With a relatively small amount of funding and in a relatively short period of time, ITT has managed to go from a very small bench-scale system to a small-scale commercial system that in many respects represents a full-scale commercial system. In the course of this scale-up numerous significant accomplishments have occurred, some of which are set forth below:

- Three Patent Idea Disclosures filed with the DOE.
- Titanium metal powder can be produced with an extremely high yield at the 5000° C dissociation temperature.
- The titanium powder can be sintered in vacuum at 800 to 1300° C to form metal bodies.
- A torch/reactor system has been invented in which the reactants are in direct contact with the arc without creating corrosion problems with the electrodes. This is a particularly critical achievement in that it enables the continuous operation of the production system in a chlorine environment at 5000° C. Corrosion of the water-cooled nickel alloy reactor has only been a problem in high heat-loss reactor designs. Nickel base alloys corrode in dry chlorine at 500° C, so the inside wall of the reactor has to be kept below that temperature. Torch electrodes are a much tougher problem. Because the electrode surfaces are far above their corrosion temperature they must be shielded from chlorine. Properly placed injection of argon provides the necessary protection. Other parts of the torches required a more subtle design approach. Electrode shields are only millimeters from the arc and required very sophisticated design to prevent corrosion. ITT expects that more extensive development will be required for achieving maximum torch life in this demanding environment. Fortunately the torch parts are simple and very low cost. As long as they last at least a few hours, replacement will not be uneconomical.
- Rapid heat transfer and high thermal efficiency have been achieved. This achievement enables all of the reactants to reach the desired reaction temperature before exiting the reactor. In the ITT reactor system the plasma arc traverses the reactor from one side to the other. Since the arc can be 20,000° K to 30,000° K, and the water-cooled reactor walls are only inches away from the arc, radiant heat losses can be huge. Since the thermodynamic heat requirement to heat TiCl_4 to 5000° K and dissociate it is about 6 kW per pound and the Kroll process uses about 10 kW per pound, it is necessary to keep heat losses per pound below 4 kW to be competitive. For example, at 300 pounds per hour the heat losses would have to be no more than 1200 kW. At the present stage of development, heat losses are about 500 kW at a production rate of 25-30 pounds per hour for a total heat requirement of about 700 kW. This would be about 25

kW per pound. ITT estimates that a 3000 kW reactor would produce between 300 and 400 pounds per hour for a heat requirement of 10 kW per pound or less.

- Residual subchlorides, if any, can be removed by heating to 600° C.
- Adsorbed HCl can be removed at 165° C to 185°C in either flowing H₂ or in a vacuum.

Tests have demonstrated that subchlorides are not an operational problem. Powder produced at below target conditions, and thus containing high residual subchlorides in addition to the 40% HCl, has been successfully sintered into solid metal bodies, with no apparent residual chlorine.

Titanium Hydride

Titanium hydride, the form of titanium powder produced by the ITT plasma quench process, is much more resistant to oxidation than titanium metal powder. A review article by S. Froes, et al (Recent Advances in the Thermohydrogen Processing of Titanium Alloys, O. M. Senkov, J. J. Jonas, F. H. Froes, Journal of Metals, July 1996) indicated that titanium hydride is superior to metal powder for fabrication purposes. The hydrogen is completely removed from titanium simply by heating the titanium above 400° C.

Froes, et al, referenced above, stated that *"The addition of hydrogen as an alloying element has a beneficial effect on the hot workability because it leads to a significant increase in the ductility and a decrease in strength at high temperatures. Thus, operations involving hot processing (e.g., forging, hot pressing, superplastic forming, powder consolidation, and composite processing) are all facilitated. Temporary hydrogen alloying can have a beneficial effect on the microstructure and final properties of the alloys as well."*

Subchlorides

A reoccurring issue that arises during discussions with individuals unfamiliar with the ITT process is that of the presence of subchlorides, mainly TiCl₂. Both magnesium chloride and sodium chloride are known to have deleterious effects on powder metal. Concern therefore exists about the possible effects of the presence in the powder of titanium subchlorides. Subchlorides will be present if the temperature in the reactor is not high enough for complete dissociation or if recombination occurs during or after the gases have been cooled. TiCl₂ is the most likely subchloride because it has the highest dissociation temperature. The effect of pressure is not completely understood, although the thermodynamics is straightforward.

At the onset of ITT's development program, ITT's position was that it did not believe that there would be significant amounts of subchlorides in the product from ITT's plasma quench approach. However, because of the short residence time and steep temperature

gradients in the plasma reactor, concern did exist that it might not be possible to react all of the tetrachloride to titanium metal or titanium hydride. However, chemical analysis of titanium hydride powder produced by the plasma quench process during ITT's development program revealed that less than 0.5% of subchlorides existed. Due to the limitations of the analytical system, the actual amount may in fact be zero.

Operating conditions and reactor designs in place at the end of the subject Cooperative Agreement are even less likely to lead to the formation of subchlorides. However, if subchloride removal should, in fact, be required for powder produced at the higher production rates, the following scenario is anticipated. In the advanced Kroll process as practiced by Timet, magnesium chloride (MgCl_2) (80% of the product weight!) is easily removed by vacuum distillation after the Kroll reaction is complete. A similar approach would be used by ITT for subchloride removal from the plasma quench reaction product, if necessary. For example, the vapor pressure of TiCl_2 is sufficiently high at 1000°C for complete removal with a modest vacuum. Furthermore, complete removal could take place during the sintering operation for the production of parts from powder, although the vacuum system would have to be designed for the handling of subchloride vapor. For Kroll process replacement in which some form of preform is used to feed the melter, the subchloride could be removed in vacuum heat treatment of the preform or perhaps in the melter itself during melting. Major amounts of MgCl_2 are removed in the first vacuum arc remelt step for standard washed Kroll sponge. An EB melter might not be able to cope with large amounts of subchloride vapor, although a plasma hearth melter might.

Whether the subchloride contamination is less than 1% or in the ppm range, potential technology solutions are available which do not require intensive development or are beyond existing technology capability. The standard Kroll process in which the sponge was washed to remove MgCl_2 left large amounts of MgCl_2 to be removed in the VAR step. The advanced Kroll process uses vacuum distillation to remove all the byproduct MgCl_2 . Some modification of these approaches will be applicable to the plasma quench titanium process.

Modeling

ITT utilizes a modeling program based upon a variety of computer codes to calculate transport and thermodynamic properties, gas dynamics, equilibrium thermochemistry, and the statistical variation of various process parameters. Together these codes form the basis for modeling the plasma reactor used in the ITT production process.

Gas Dynamic Codes: Three separate computer codes are used to analyze gas dynamics. The PCOL computer program models transport processes in a free length dc plasma arc. The mass, momentum, and energy conservation equations are solved assuming a steady, two-dimensional, axisymmetric, fully coupled model. Turbulence is modeled with the k-epsilon model, while local thermodynamic equilibrium is assumed to prevail over the entire calculation domain. The fluid flow problem is assumed to be parabolic in nature, so downstream conditions do not affect upstream conditions.

The Pplume computer program models a free-expanding plasma jet (i.e., plume) which is

the main processing zone in applications such as plasma spraying or chemical synthesis. The assumptions and input used for the plasma column analysis also apply to the plume analysis. Output from the plasma column code at the nozzle exit is used as an initial condition to the plume code. The conservation equations used for the plume model are similar to those used for the column model.

Thermochemistry: The ACE81 computer program is an equilibrium thermochemistry code for high-temperature gas applications. It is an extremely versatile code for theoretical determination of transport and thermodynamic properties relevant to most thermodynamic processes. A variety of phenomena may be treated by this code, including the thermodynamic and chemical state in a reaction, shock state chemistry, and boundary layer composition. The ACE81 program utilizes standard relations and relatively conventional procedures to solve for the equilibrium thermodynamic state.

The chemical equilibrium code SOLGAS is widely used in the calculation of chemical equilibria, including calculation of predominance diagrams. The program uses Lagrange's method of undetermined multipliers and the method of steepest descent to find the minimum free energy of a constrained system, which is by definition the equilibrium composition. The program is capable of handling systems up to 14 elements, 84 species, and 19 phases. The code is used for calculation of coating phases and particle in-flight chemistry.

The HSC chemistry code is used for many kinds of chemical reactions and equilibria calculations. Calculations can include: reaction equations, heat and material balances, equilibrium compositions, electrochemical cell equilibria, formula weights, phase stability diagrams, and pH diagrams.

Statistics: The SADIE computer code is a general purpose statistics code using a Taguchi style, fractional factorial design of an experiment. The code statistically delineates the impact of each variable on measured coating characteristics across all combination of other factors. Thus, the effect of plasma processing variables on coating characteristics can be delineated.

The Design-Ease and Design-Expert codes calculate the factor coefficients for powder attribute effects analysis using least squares estimates for a variety of fractional and full-fractional designs, and central composite designs. The program first fits linear (main effects A, B, C only), quadratic (linear effects plus square of main effects, and two-factor interactions), and cubic polynomial (quadratic effects plus cube of main effects and cubed interactions to the data). ANOVA calculations are then conducted that provide a sequential comparison of models. Regression models are then determined for the responses.

The Minitab code is a highly functional statistical software package that provides a wide range of basic and advanced analysis capabilities. The code features the creative use of plots, application of standard statistical methods to real data, in-depth exploration of data, simulation as a learning tool, screening data for errors, manipulating data, transformations, and multiple regression capabilities.

General Purpose Modeling: The Compact 2D and 3D computer programs are general purpose computer programs designed to analyze fluid flow, heat and mass transfer,

chemical reaction, turbulence, radiation, and related phenomena. Compact 2D represents two-dimensional situations in the Cartesian, axisymmetric, or polar coordinate system. Compact 3D uses the Cartesian or cylindrical coordinate system.

Figure 9: HSC Reaction Equilibrium Diagram

The above HSC diagram illustrates the basic breakdown of titanium tetrachloride as a function of temperature. Note that it predicts that the reaction temperature should approach 5000° C to ensure that no subchlorides are present.

On the next page is an example of a set of diagrams resulting from reactor modeling. The modeling is preformed using a compact-3D program. Reactor slices can be taken at any angle and a temperature and velocity profile then shown along that slice. The white arrows on the OPPOSING model represent velocity vectors. The temperature profile is represented by the colors.

The Figures are as follows:

Figure 10a: Control Volumes for Temperature and Velocity Calculations

Figure 10b: 3-D Representation of a Plasma Reactor

Figure 10c: Temperature and Velocity Profiles

Figure 10a

Figure 10b

Figure 10c

A cost analysis is presented comparing the Kroll process with the ITT process. This analysis has been verified by an individual at Oak Ridge National Laboratory who did so on behalf of the US Department of Energy.

The Kroll Process for Titanium Metal Production

The Kroll process has two significant cost factors that prevent it from being sufficiently economic to support the potentially wide-ranging uses of titanium. First, a huge amount of capital is required for a Kroll plant: \$200,000,000 for a 20,000,000 lb. per year plant, or \$10 per annual pound. Second, magnesium is required in the Kroll process as a reducing agent. Consequently, all Kroll plants require an electrolytic magnesium plant onsite. Also, Kroll is a batch process that uses large expensive reactors for reduction.

In sharp contrast to the Kroll process, the Rapid Plasma Quench Process will require an order of magnitude less capital, and no metallic reducing agent. In addition, the Rapid Plasma Quench Process is continuous, with an essentially immediate startup and shutdown. Furthermore, unlike the complex equipment required by the Kroll process, the Rapid Plasma Quench system is made of off-the-shelf pipe and plate in modest sizes.

The following cost comparison is based upon a per pound cost analysis conducted by the International Titanium Association and based upon the assumption of a 20M pounds per year plant.

Table 1: Cost Analysis - The Kroll Process vs. The ITT Plasma Process

<i>Cost element</i>	Kroll	ITT
Rutile	0.18	0.18
Chlorination	0.41	0.41
Magnesium	1.13	0.00
Power	0.00	.30
Gas recovery	0.00	0.11
Hydrogen	0.00	0.34
Capital (20% per year)	2.00	0.20
Total	3.72	1.54

There is a great deal of simplification in the above analysis, but the key elements are present for both processes. Capital cost is included based on \$200M for a Kroll plant and \$20M for a ITT plant. Return on capital is assumed to be 20% per year.

Figure 11: The Rapid Plasma Quench Production Process

Appendix A

Metallurgical Testing

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TITANIUM METALLURGY

1.0 Introduction

Titanium and its alloys have various advantages over ferrous and other non-ferrous metallic materials, owing to their high strength-to-weight ratio and excellent corrosion resistance. Due to these superior qualities and recent efforts to move titanium into non-aerospace applications, future demand looks promising. There are estimations that in the year 2000, United States titanium metal demand will be approximately 45,000 short tons, equivalent to an average annual growth rate of 5.5% from 1983. The probable demand for titanium metal in 2000 in the rest of the world is expected to reach 160,000 short tons [1].

Recently, a widespread interest in powder injection molding (PIM) of titanium has generated concerns over two major issues – powder cost and product properties. These two issues are directly related to powder availability and powder attributes. The goal of Idaho Titanium Technologies LLC (ITT) is to reduce titanium powder price to a commercially acceptable level and to produce new, customized powders suitable for powder injection molding and titanium ingot production.

ITT produces an ultra-fine spherically-shaped titanium hydride powder using a plasma torch process followed by a rapid quenching step and then hydrogenation:

The ITT plasma system is made completely of nickel and inconel to resist corrosion by halogens. The 1.2 MW plasma reactor is only a few liters in volume in order to achieve high efficiency and a rapid reaction rate. In addition, a proprietary quench system (which cools uniformly at up to a billion K per second) is used to prevent back reactions.

Although the small, high purity, spherical titanium powder produced by ITT is ideally suited for the titanium injection molding industry, its use is not limited to that industry. Consolidation of titanium hydride powder into a pure ingot form is also of paramount interest. Titanium ingots can be formed by consolidating the powder into a pellet or sheet form, heat treating to remove volatile contaminants, and fed into a plasma or electron beam furnace for final melting and ingot formation. Other methods that are also being considered for powder consolidation are: vacuum hot pressing (VHP), hot isostatic pressing (HIP), cold isostatic pressing (CIP), and rapid omnidirectional compaction (ROC).

In order to appreciate the uniqueness of the ITT method for production of titanium hydride it is necessary to understand, at least in part, the historical approach to titanium production. Hence, brief discussions of the existing production methods are set forth below.

1.1 Plasma Quench Technology and the Kroll Process

The traditional method used in titanium ingot production has been the Kroll process. The Kroll process is based on the thermal reduction of titanium tetrachloride by molten magnesium:

The reaction is strongly exothermic and goes virtually to completion. Clean magnesium ingots are stacked inside a reactor vessel. The reactor is evacuated, warmed, and then brought slightly above atmospheric pressure. Magnesium ingots are melted and liquid titanium tetrachloride is introduced. Reaction temperatures are held between 800-900°C. The reaction is continued until on the order of 85 per cent of the magnesium is consumed. Residual magnesium salts are removed using either vacuum distillation or leaching.

After removal of the residual salts, the titanium chunks referred to as "sponge", are fed to a variety of melts. These melts commonly consist of either a vacuum arc re-melting furnace, a plasma arc-melting furnace, an electron beam melting furnace, or an induction skull-melting furnace. The varieties of melts produce the final titanium ingot desired.

The Kroll process has two significant cost factors that prevent it from being economically viable enough to support the potentially wide-ranging uses of titanium. First, a huge amount of capital is required for a Kroll Plant: \$200,000,000 for a 20,000,000 lb. per year plant, or \$10 per annual lb. Second, magnesium is required in the Kroll process as a reducing agent. Consequently, all Kroll plants require an electrolytic magnesium plant [2].

In sharp contrast to the Kroll process, the ITT process will require an order-of-magnitude less capital, and no metallic reducing agent. A simplified per pound cost analysis, conducted by the International Titanium Association, on the assumption of a titanium production facility producing 20M pounds per year, has been conducted. The results indicate a \$3.72/lb cost for the Kroll process as opposed to a \$1.54/lb cost for the ITT process. These results are based on the cost of rutile and chlorination (used in the production of titanium tetrachloride), magnesium (used in the Kroll process) and power, gas recovery, and hydrogen (used in the ITT process). A return on capital investment of 20% per year was also factored into the results.

1.2 Powder Metallurgy

There are several forms of powder metallurgy for which titanium hydride would be well suited. The list of possible candidates are powder injection molding (PIM), vacuum hot pressing (VHP), hot isostatic pressing (HIP), cold isostatic pressing (CIP), and rapid omnidirectional compaction (ROC). Each is discussed below to familiarize the reader.

Powder Injection Molding

A new technology known as powder injection molding (PIM) uses the shaping advantages of injection molding but is applicable to metals and ceramics. This process combines a small quantity of polymer with an inorganic powder to form a feedstock that can be molded. After shaping, the polymeric binder is extracted and the powder is sintered, often to near-theoretical densities. Accordingly, PIM delivers structural materials in a shaping technology previously restricted to polymers [13].

As stated previously, the characteristics of the TiH₂ powder produced at ITT (small particle sizes, spherical shape, and narrow size distribution) are ideally suited for the injection molding industry. The small particle size allows for faster sintering, smaller molding defects, and higher shape retention. The spherical shape promotes higher packing densities, lower mixture viscosity, and improved flow. In addition, the narrow size distribution of the powder allows for faster de-binding times, minimizes size segregation, and provides a more homogeneous microstructure [3].

PIM commonly uses fine titanium powder mixed with a variety of wax binders. The wax-metal mixture is extruded through a hot extrusion machine into molds. The wax is then burned off, chemically etched off, or wicked off and the final product is sintered to completion.

VHP, HIP, CIP, & ROC

Titanium powder in the hydrogenated form is advantageous in both vacuum hot pressing (VHP) and hot isostatic pressing (HIP). The hydrogenated powder allows a lower compaction pressure and/or temperature and has advantages in the control of microstructure. In the case of HIP, the hydrogen is retained in the titanium during compaction. In VHP, the hydrogen is removed during the compaction cycle. After both processes, a final vacuum anneal is required to bring the hydrogen content below specification levels (generally < 125 PPM.) onsite [4].

VHP applies pressure statically or dynamically to the heated powder in one or two opposing directions along a single axis or from all sides. A controlled atmosphere is required to protect the hot powders or prepared compacts from oxidation.

HIP is a technique in which high isostatic gas pressure (equal pressure from every side) is applied to a metal powder part or compact at elevated temperatures to produce particle bonding and sintering. Common pressures are in the range of 100 MPa and sintering temperatures for titanium of 1300°C are easily attainable.

CIP is a technique in which high fluid pressure is applied to a powder part at an ambient temperature to compact it into a predetermined shape. Powder parts are commonly densified between 60 and 80% of the theoretical density. Compaction pressures range from 210 to 410 MPa.

ROC utilizes a unique type of thick-walled powder container, a fluid die. The ROC method is comprised of a powder-filled cavity surrounded by a mass of fluid die material that is capable of plastic flow at the temperature and pressure of consolidation. The die acts as an incompressible fluid and transmits pressure to the powder uniformly.

Current Commercial Titanium Powder Production

The current method for production of fine, spherically-shaped titanium powder (used in the above-mentioned processes) uses a plasma rotating electrode process (PREP) technology. In the PREP process, an ingot formed from the Kroll process is rotated and brought to a positive potential (anode). A tungsten cathode is then used to transfer a helium plasma arc to the titanium anode. The molten titanium is flung off the anode (due to centrifugal forces) and the suspended titanium droplets solidify into fine spherically shaped powder particles of approximately 175 microns in diameter. This process is currently the only source for fine spherical titanium particles commercially available.

Unlike the PREP process, ITT's plasma process produces a small spherical titanium powder directly from the raw TiCl_4 feed material. Hence, production of a pure titanium ingot (used in the PREP process) is not required. This significantly reduces the cost of the ITT titanium powder as compared to powder produced by PREP. A recent quote from Starmet (a PREP titanium powder production facility located in Concord, Ma.) gave a wholesale titanium powder cost of \$40/lb for bulk quantities. A titanium powder production facility of the same size utilizing the plasma quench process could produce powder at \$5 to \$10/lb.

2.0 Analysis and Characterization of Titanium

On-going analysis of the titanium hydride powder is currently being conducted by ITT's in-house chemical engineer working in conjunction with a professor of physics at the University of Idaho. In addition, tests on injection molding of the titanium hydride powder have been conducted at Penn State's P/M laboratory.

A wide variety of tests are currently performed at the ITT facility including:

- Testing for hydrochloric acid (HCl) and the titanium sub-chloride (TiCl_2 & TiCl_3) content in the titanium hydride product.
- Vacuum sintering of titanium hydride compacts.
- HCl and sub-chloride stripping of titanium hydride powder using hot static degassing methodology.
- Injection molding of titanium powder.

2.1 Testing for HCl and TiCl_x

A recent article from "Journals of Metals" states that titanium hydride is preferred over plain titanium powder. Hydrogen use as a temporary alloying element in titanium alloys improves their processability, microstructure, and final properties [15]. Adsorbed HCl on the powder does not present a problem since it can be easily removed. Titanium sub-chlorides (TiCl_x) do, however, present a problem. TiCl_x content in the powder can contaminate the final product with unwanted chlorine if it is not first removed.

In determining the presence and the amounts of these previously mentioned products, ITT has developed an analytic method discussed in appendix AA1 of this report. As discussed in appendix AA1, a small sample of powder (thought to be contaminated due to a water leak in the system) was tested for adsorbed HCl content by placing a small amount of powder in an ultraclean-hydrogen purged furnace. The furnace was heated and the off gas was collected and measured for acid content. The titanium sample was then tested for sub-chloride content in the same manner with wet-hydrogen gas used to generate a titanium oxide residue and HCl off gas

2.2 Vacuum Sintering of TiH₂ Powder

Several samples of contaminated titanium hydride powders were tested for sinterability. The vacuum sintering experiments have been highly successful after initial problems with sub-chlorides coating the interior of the heater assembly were addressed. Titanium pellets were pressed at various pressures and brought to 1300°C (under a vacuum atmosphere) for various lengths of time. These pellets were then polished and photographed. Results include large porosity of the final sintered compact and obvious titanium metal formation. A photograph of a sintered titanium pellet, taken with a DC50 digital camera mounted on a microscope at 100x magnification, is shown below in figure 1.

Figure 1. Sintered titanium pellet 100x magnification.

2.3 Hot Static Degassing

Hydrochloric acid (HCl) and titanium sub-chlorides are potentially detrimental constituents in both the formation of titanium ingots and in the injection molding of titanium powders. During titanium ingot formation, a substantial amount of HCl would be detrimental to the plasma torches or electron beam guns used to liquefy and purify the titanium. A large concentration of HCl could potentially corrode the process guns and cause large pressure surges in the containment vessel. Sub-chloride affinity to coat surfaces combined with its electrical conductivity would cause obvious problems in a reactor containment vessel. During injection molding, the high vapor pressure of HCl would potentially make it difficult to maintain the integrity of a part in the initial sintering steps. In addition, sub-chlorides could cause electrical and coating problems in the containment vessel used for sintering. In light of these problems, ITT is developing a process for stripping both the sub-chlorides and hydrochloric acid from the titanium hydride powder.

To date, HCl has been successfully stripped from the TiH_2 powder using a hot static degassing method (which will be discussed later). The severe reactivity of titanium powder (after the hydrochloric acid was stripped away) required that the stripped titanium powder be handled in an inert atmosphere glove box. The reactivity of the stripped powder can be attributed to the presence of sub-chlorides in the samples tested.

2.4 Injection Molding

Injection molding methods have been pursued by both ITT and the Penn State P/M laboratories. While both entities performed press-sintering and powder coating experiments, they applied different methods and had different results. Penn State analyzed the powders for impurity content, particle size and distribution, various densities, and specific surface area with equipment that was not available at the ITT facility.

3.0 Penn State: Powder Metallurgy Testing and Results

Each ITT powder sample sent to Penn State was tested for particle size, distribution, and BET surface area at the Penn State metallurgical lab. In addition, Pycnometer, apparent, and tap densities were also measured.

The results from these tests are presented in the "Penn State: TiH_2 Powder Characteristics" section below. Many other measurements were proposed, including particle shape via scanning electron microscopy, dusting and autoignition temperature in air, and chaotic flow time distribution to identify uniformity. However, these tests were very difficult to conduct, since such tiny powders are very reactive, so that exposure to air for such tests proved to be impractical.

In order to test the sinterability of the TiH_2 powder, a series of experiments were performed involving loose powder sintering, pressing and sintering, hot hydrogen purging and sintering, and aluminum foam formation and sintering. The results from these tests are presented in the "Penn State: TiH_2 Powder Consolidation Experiments" section below.

In order to test the injection molding characteristics of the TiH_2 powder, a number of experiments were performed. These experiments included pre-treatment of the powder with a stripping fluid and filtering, applying a wax/polymer mixture to the powder and sintering, and stripping the powder of HCl followed by a wax coating in an inert atmosphere. The results from these experiments are presented in the "Penn State: Pre-Treatments and Injection Molding Experiments" section below.

It is important to note that Penn State was unfortunately not equipped to remove the adsorbed HCl from the powder before any of their experiments (with the exception of the hot static degassing / wax coating experiment illustrated in section 3.3). The presence of HCl (which coated the surface of the powder) created problems in the accuracy of particle size, surface area, and density experiments. In addition, due to the vapor pressure and corrosive properties of HCl, problems with loose powder sintering, pressing and sintering of a thin compact, and application of a wax / powder mixture occurred with results that were inconsistent with those of ITT, which were consistently successful.

3.1 Penn State: TiH_2 Powder Characteristics

Particle Size and Distribution for PIM

Powder injection molding (PIM) utilizes small particles (10-20 μm) with a relatively round shape to achieve high packing density. The following table gives some examples of typical sintering conditions for a titanium injection molding process, along with titanium particle sizes.

Table I: Typical particle size and sintering conditions for PIM

PROCESS	MEAN PARTICLE SIZE, μm		ALLOY	SINTERING		REF
	Ti	TiH_2		Temp, C	Vacuum	
PIM	38	-	Ti-Mo-Al	1296	Yes	5
PIM	22.9	16.7	Ti-Al-V	1250	Yes	6
PIM	30	30	Ti	1300	Yes	7
PIM	13-23	-	Ti	1250	Yes	8
PIM	23-25	16-17	Ti/Ti-Al-V	1250	Yes	9

Several samples of ITT's titanium hydride powder were measured for particle size and size distribution using a laser-scattering technique. A Horiba LA-920 laser scattering size analyzer was used to measure the particle size of as-received powders. Before each test, the analyzer

was calibrated. Sodium metaphosphate $[(\text{NaPO}_3)_{13} \cdot \text{Na}_2\text{O}]$ was used as a surfactant to prevent the powder from agglomerating. The powders were pre-dispersed into a liquid media in a glove box to avoid oxidation. De-ionized water and ethylene glycol were selected as the dispersing media. Ultrasonic agitation was also applied to de-agglomerate the powders. The following table gives the particle size and distribution of the as-received TiH_2 powder.

Table II: Particle size and distribution for as-received TiH_2 powders

SAMPLE	9/20/98	10/14/98	9/20/98	9/20/98	4/1/99 #1	4/1/99 #2
Dispersive Media	Ethylene glycol	De-ionized water	De-ionized water	De-ionized water	De-ionized water	De-ionized water
Ultrasonic	2 min	2 min	2 min	3 min	4 min	4 min
Particle Size & Distribution						
D ₁₀	.179 μm	.271 μm	.120 μm	.118 μm	.363 μm	.353 μm
D ₅₀	.459 μm	.531 μm	.398 μm	.387 μm	.834 μm	.779 μm
D ₉₀	.812 μm	1.126 μm	.865 μm	.749 μm	2.138 μm	2.044 μm
Mean	.505 μm	.603 μm	.495 μm	.460 μm	1.0918 μm	1.039 μm

BET Surface Area, Pycnometer, Apparent, and Tap Density

The BET surface area measurements were performed with a Quantachrome Autosorb-1, which measures the quantity of gas adsorbed onto and desorbed from a solid surface, at some equilibrium vapor pressure, by the static volumetric method. The results are shown on the following table.

Table III: BET surface area for as-received TiH_2 powders

POWDER	10/14/98	4/1/99 #2
BET specific surface area (m^2/g)	16.89	24.31

Pycnometer density gives a measurement of the true density of the powder. The actual density of a powder may be different from its theoretical density due to the presence of internal porosities and impurities such as oxides. The pycnometer density was measured using the Auto-sorb. The unit was calibrated prior to operation. The true volume of the powder is measured, and pycnometer density is calculated by dividing the weight of the powder by the true volume of the powder.

Apparent density gives a measure of the degree of packing of the powder in loose form. Apparent density provides an estimate of the total volume occupied by a loose (non-vibrated) powder mass.

Tap density provides a measure of the particle packing efficiency under vibration. The powder was tapped for 3000 cycles in a Quantichrome Dual Autotap. The tap density is obtained by dividing the weight of the powder by the final volume. Results are shown in the following table.

Table IV Pycnometer, apparent, and tap densities for as-received TiH_2 powders

POWDER	10/14/98	4/1/99 #2
Pycnometer density (g/cm^3)	3.67	2.81
Apparent density (g/cm^3)	.17	.09
Tap density (g/cm^3)	.22	.13

Powder Impurity Content

The TiH_2 powder was analyzed for impurity content. Because of its tendency to react and oxidize, many tests were very difficult to perform. However, both C and Cl content were obtained. The Cl content was 22.1% and the C content was .15%.

As stated previously, Penn State was not equipped to remove the adsorbed HCl from the powder before any of their experiments. This would account for the high chlorine concentration found. The chlorine concentration agrees well with the ITT analysis discussed in appendix AA1 of this report.

3.2 Penn State: TiH_2 Powder Consolidation Experiments / Results

Loose Powder-Sintering

Loose powder sintering was conducted to test the sinterability of the TiH_2 shipped by Idaho Titanium Technologies. Three samples of loose powder were loaded into ceramic crucibles and heated to sintering temperatures between 1025°C and 1150°C under an argon atmosphere. Results from these tests are shown in table V.

Hydrogen Purge-Sintering

Hot hydrogen was used to purge the powder by driving off HCl. Hydrogen provides a reducing atmosphere preventing the powder from oxidation. Experiments were conducted for both loose and pressed samples of powder. Various sintering cycles using hydrogen and argon were employed during the experiments. Results along with the test parameters are given in table V.

Press-Sintering

Thin disc samples were pressed in a glove box, to avoid oxidation, using a Parr Press. Due to very low apparent and tap densities, thicknesses of the resulting samples were very small. Two samples (approximately .3 cm thickness) were sintered in argon. Vacuum sintering was also conducted using pressed TiH_2 powder. Results along with the test parameters are given in table V.

Aluminum Foam-Sintering

In the foaming experiment, the idea was to employ the gases liberated from the TiH_2 to produce aluminum foams. First, the compact was sintered to nearly full density at a temperature below the TiH_2 decomposition temperature (550°C). The next step was to sinter the compact at a higher temperature (800°C). At 800°C , TiH_2 decomposes, releasing hydrogen gas to form an aluminum foam. Results from this experiment are shown in table V.

Table V: Penn State's powder consolidation results

PROCESS	POWDER	SINTERING ATM	SINTERING TEMP (C)	SINTERING TEMP HOLD (HR)	COMMENT	SINTER
Loose Powder	Loose	Argon	1025	3		NO
Loose Powder	Loose	Argon	1025	3		NO
Loose Powder	Loose	Argon	1025	3	1 hr hold at 600 C	NO
Hot Hydrogen Purge	Loose	Hydrogen	1300	2	Ar used only at 700 C during cooling.	NO
Hot Hydrogen Purge	Loose	Argon	1175	2	H2 used during heating/ Ar used at 1175 C.	NO
Hot Hydrogen Purge	Pressed	Argon	1300	2	H2 used during heating until HCl was removed.	NO
Press- Sinter	Pressed	Argon	1040	3	Pellet broke apart.	NO

Press-Sinter	Pressed	Argon	1040	3	Pellet broke apart.	NO
Press-Sinter	Pressed	Vacuum	1150	2	Pellet held shape	NO
Aluminum Foaming	Pressed	Argon	400	2	Pellet broke apart.	NO

Titanium powders, in most cases, must be compacted at room temperature in rigid dies or isostatically pressed in elastomeric tooling. There is one exception to this general rule. The exception pertains to prealloyed powder made from alloyed ingot by an ultraclean process such as the plasma rotating electrode process (PREP). Such powders are spherical and are not compactible at room temperature by ordinary means. These powders can however, be sintered in loose form to produce a porous structure or coating [11]. The loose powders sintered at Penn State contained between 20 to 40% HCl by weight, were non-alloyed, and were compactible at room temperature. Experiments that were conducted on sintering loose powder in the ITT laboratory indicated that loose titanium hydride powder was not sinterable (due to the low apparent density and HCl off gassing during the heating cycle).

As can be seen from table V, none of the experiments produced a sintered titanium part. However, the pressed TiH_2 pellet that was sintered under a vacuum atmosphere was the only experiment in which the pellet did not break apart. As can be seen from the table "Typical particle size and sintering conditions for PIM" on page AA2-7 of this report, titanium is always sintered in a vacuum atmosphere. ITT has found (from separate experiments on sintering TiH_2 in a vacuum and sintering TiH_2 in argon) sintering occurred in a vacuum atmosphere only.

Due to the titanium's low density and HCl content, ITT has found that a die system that produces a sufficiently thick green (pre-sintered) pellet is essential for sintering. When a green pellet of a thickness less than 1.3-cm was sintered, the residual sintered titanium product was extremely thin due to HCl off gassing during the sintering procedure. In addition, the small quantity of powder and large surface area of a thin green compact creates a contamination problem during the loading of the pellet into the sintering furnace. Penn State used a green pellet of .3-cm in thickness leading in part to their sintering difficulties.

3.3 Penn State: Pre-Treatment & Injection Molding Experiments / Results

Pre-Treatment of TiH_2 with a Fluid

To alleviate problems with small particle size, reactivity, and high impurity contents, pre-treatments of TiH_2 were conducted to clean and passivate the powders. The first process attempted was filtering. Since HCl can be dissolved in water, filtering experiments were conducted to wash out the acid. However, the powder passed through the .2 μm membrane used. The mean particle size is .387 μm by volume distribution. When converted into number distribution, the same powder has more than 90% particles smaller than .2 μm .

Applying a Wax/Polymer Mixture and Sintering

Several mixtures of wax, powder, and fusabond (a backbone polymer) were tested. Unfortunately, a useless solid body of material was produced. A second set of experiments, which involved coating the powder with a .01 to .1 μ m thick layer of paraffin wax, were conducted. Wax was dissolved in heptane and mixed with the powder. The mixture was then dried, pressed, and sintered in argon. Results from these tests show that coating of the powders was impractical since it was difficult to apply a thin, homogeneous polymer layer to the powder surface. Moreover, oxidation still occurred in air with coated powders. Another concern is the large amounts of wax needed to coat the powders, since wax could result in contamination during sintering. It was concluded that the sintering characteristics and wax powder interactions might benefit from removal of HCl before coating.

Hot Static Degassing / Wax Coating

A glassware assembly was designed for removal of the HCl and coating of the powder in the same equipment. Approximately 18 grams of powder and 42 grams of paraffin wax were used. The powder was heated up to 290 C and held for 1.5 hour, with no observable oxidation. The powder was then cooled down to 120 C and melted wax was added through the wax injector. However, approximately two minutes later, the stopper on the side of the flask was shot away 3 meters due to a rapid pressure build-up inside the flask. Subsequently, oxidation reaction occurred vigorously and the sample was destroyed. Subsequent tests were not performed.

ITT has had a great deal of success with the hot static degassing assembly previously mentioned. HCl stripping has doubled the size of the final sintered part and enabled faster cycling times for sintering when raw powder (without wax) was pressed and sintered. ITT wax coating procedures involve dissolving the wax in heptane (in order to achieve an even distribution of wax on the powder) and then boiling off the heptane (under vacuum) in the mixing flask. This procedure produced a wax-powder mixture that was slightly ductile and non-reactive in air.

4.0 ITT: TiH₂ Powder Consolidation Experiments / Results

A series of ongoing experiments are currently being performed in the ITT laboratory to test the sinterability of the titanium powder. These experiments involve loose powder sintering, pressing and sintering, and the use of hot static degassing equipment (designed by the ITT staff) that enables HCl stripping of the powder and subsequent pelletizing all in a super clean inert atmosphere. Several sintered titanium pellets have been formed at the ITT facility using both the press-sinter method and the HCl stripping (hot static degassing) press-sinter method.

Sintering titanium hydride compacts that contained adsorbed hydrochloric acid (HCl) and sub-chlorides (TiCl_x) presented major problems in the initial stages of experimentation. According to the data set forth in appendix AA1 of this report, the adsorbed HCl content of ITT's titanium powder ranges from 20 to 40%. This large volume of gas was liberated at a low temperature

(60 – 150 C). The off gassing of the powder produced cracked consolidated powder pellets and made it difficult to run tests on loose powder samples. After several runs at various temperature gradients, an optimum temperature-time procedure was adapted for sintering, in which a sintered consolidated titanium pellet could be formed without fracture.

Initial problems were also attributed to the tendency of TiCl_x to leave the pellet at elevated temperatures and then adhere to any surface below its boiling point temperature. Vapor pressure curves, illustrating the temperatures in which TiCl_3 and TiCl_2 are stripped from the pellet, are shown in figures 3 and 4 respectively.

Once a layer of sub-chloride was established it became electrically conductive. Initial sintering furnaces used at the ITT facility were resistive boron nitride heaters. The heaters possessed terminals located at the top (cooler section) of the unit. Titanium sub-chlorides would deposit on these terminals and create a constant problem with shorting out the furnace. In addition, shorting was experienced on the power feedthroughs at the base plate of the bell jar. To alleviate the problem, the furnace terminals were coated with a moldable aluminum ceramic paste and the feedthroughs were protected with a Teflon spacer. The heater was eventually replaced (due to the penetration of TiCl_x through the ceramic paste) with a clamshell molybdenum wire furnace encased in a refractive high temperature ceramic shell. The clamshell furnace was designed to prevent buildup of sub-chlorides along the power terminals. A diagram of the initial boron nitride furnace and the clamshell molybdenum furnace are shown in figure 2.

The ITT molybdenum clamshell-sintering furnace is equipped with two temperature sensors to ensure accurate sintering. The first sensor monitors the temperature of the sintered pellet and the second monitors the temperature of the furnace wall. A hot ion gauge monitors the vacuum pressure. Both the pellet temperature sensor and the pressure sensor send an output signal to a strip chart recorder which monitors and records the pressure and temperature against time during sintering.

Figure 3. TiCl₃ vapor pressure curve

Figure 4. TiCl₂ vapor pressure curve

Three separate consolidation experiments involving the sintering furnaces were performed at the ITT facility. The experiments involved sintering of loose powder, sintering of a compact, and sintering of a compact stripped of HCl.

4.1 ITT: Loose Powder-Sintering

In order to test the sinterability of loose titanium powder, two separate experiments involving loose powder were performed. The first involved loading a ceramic crucible with TiH₂ powder in an inert atmosphere glove box and transporting the crucible to the sintering furnace in a jar purged with argon. The sintering furnace was evacuated to 10⁻⁶ torr. Temperature in the furnace was slowly brought to 1300°C over the course of one day. The sample was observed from an observation port located above the sample. This experiment produced a black non-sintered product.

A second experiment was conducted in much the same way. TiH₂ powder was loaded into a ceramic crucible and transported to the sintering furnace in an inert atmosphere. The sintering furnace was evacuated to 10⁻⁶ torr and argon was leaked in at one cubic foot an hour (bringing the final pressure up to 10 millitorr). Temperature in the furnace was slowly brought to 1300°C over the course of one day. The sample was observed from an observation port located above the sample. This experiment produced a black non-sintered product.

From these experiments, it was apparent that a higher packing density was required for sintering the TiH₂ powder.

4.2 ITT: Press-Sintering

Press-sintering constitutes the majority of the sintering tests performed at the ITT facility. There are two main reasons for the focus on press-sintering. First, "bugs" in the system (TiCl₄ coating and HCl off gassing) needed to be addressed. Second, press-sintering proved to be the most effective method.

Several samples of TiH_2 were pressed using a unidirectional Carver Press and die at pressures ranging from 2,000 psi to 15,000 psi. All pressing and powder handling was performed in an argon atmosphere. The samples were then transported to the sintering furnace in an argon-purged jar. Pressed samples were loaded onto a ceramic stand and a bell jar assembly was lowered and sealed over the sample and furnace. After the pressure was brought down to approximately 10^{-5} torr, the sintering furnace was turned on. A gradual heating between 25°C and 600°C was then commenced followed by a more rapid heating between 600°C and 1300°C . A flow diagram that depicts the various stages of compaction and sintering is given below.

Press-Sintering Flow Diagram

To ensure precise control over the heating rate of the pellet, power to the furnace was controlled in two ways. The main power lead to the system was controlled using a variable autotransformer. The stepped down power leaving the transformer was sent to a secondary PID controller that allowed a percentage of that power to be sent to the furnace. In this way, a precise amount of heat could be supplied to the non-sintered pellet during the critical initial degassing phase.

An operator data log was kept during the entire experiment. Table VI shows a typical ITT operator data log for sintering a titanium pellet.

Table VI: Operator data log 2/23/99

COMMENT:						
1) Weight of green pellet = .2311 g						
2) Pressed at 10,000 psi						
3) Pellet flaked slightly after extrusion from die						
Time	Auto Trans Power %	PID Power %	Temp Start (C)	Set Point Temp (C)	Pressure Start (Torr*10 ⁻⁵)	Comment During Heating
10:20	20	40	32	1500	6	Fraction of surface turned a whitish gray
11:10	30	40	132	1500	5.3	Some white spots on top, rest of sample is black
12:10	30	52	268	1500	4.5	OK
1:30	40	52	326	1500	4.6	Possible flaking on top
2:15	40	65	450	1500	12	Bell jar is getting coated with TiCl ₃
2:35	50	45	530	1500	10	OK
2:45	50	55	557	1500	12	OK
3:10	60	65	652	1500	4.5	OK
3:20	70	65	860	1500	4.9	OK
3:30	70	100	1055	1500	5.5	OK
4:30	off	off	1302	1500	6.4	OK

Once the pellet was brought to sintering temperature (1300 °C) it was gradually brought down to atmospheric temperature under vacuum. The pellet was then extracted from the furnace and encased in an epoxy mold for 12 hours. Once the epoxy hardened, the mold was extracted and the sintered pellet was polished (until shiny) using sanders with various grits.

To date, twelve sintered titanium pellets have been formed using the applied sintering methods. The pellets were pressed at various pressures, ranging from 2,000 psi to 15,000 psi, with pressures at 5,000 psi and 10,000 psi being the most successful.

The green (non-sintered) pressed titanium pellets, formed from pressing TiH₂ (containing around 40wt% HCl), retain their pressed shape extremely well. Example: a titanium hydride pellet that was pressed in March of 1998 was submerged in an oil bath immediately after ejection from the die. That pellet is intact today with no signs of degradation. Figure 5 shows a typical green pressed titanium pellet used in the sintering procedure.

Figure 5. TiH₂ green (before sintering) compact

To ensure repeatability and recording of off-gassing temperatures, a strip chart recorder logged the temperature and pressure against time during the entire sintering cycle. Figure 4 shows a strip chart recording for a sintered titanium pellet formed on 2/23/99. As can be seen by the following figure, the temperature (red line) was increased at a very slow rate during the initial heating of the pellet. This was done to prevent the rapid off gassing of HCl from the titanium pellet and a subsequent pellet fracture. The pressure (blue line), during initial heating, dropped off (due to HCl removal) and eventually stabilized once the HCl was removed. As the temperature was increased, the pressure eventually dropped off again due to TiCl₃ off gassing at 300°C. At 600°C, an increase in temperature without a dramatic pressure change is observed. TiCl₂ off gassing can be observed between 600°C and 800°C from the dip in the pressure at that temperature.

Figure 6. Strip chart of sintering TiH_2 with HCl

Once the pellet was brought to sintering temperature (1300 °C) it was gradually brought down to atmospheric temperature under vacuum. The pellet was then extracted from the furnace and encased in an epoxy mold for 12 hours. Figure 7 shows a sintered titanium pellet that was pressed at 10,000 psi and held at 1300 °C. This pellet is the product from the sintering test performed on 2/23/99 (reference to the above strip chart and operator data sheet). Figure 8 shows a sintered pellet that was pressed at 5,000 psi and held at 1300 °C.

Figure 7. Sintered Ti compact pressed at 10,000 psi.

Figure 8. Sintered Ti compact pressed at 5,000 psi.

The titanium compacts in the above photographs were taken with a DC 50 digital camera. The camera was adapted with special lenses to aid in close up photography. Unfortunately, the photo quality did not capture the true shiny metallic properties of the pellets.

4.3 ITT: Hot Static Degassing / Sintering

The engineering staff at ITT has developed a relatively new procedure for the sintering of titanium compacts. The procedure applies a hot static degassing methodology [10] on a small-scale system. In the past, titanium hydride powder (containing approximately 20 to 40% by weight HCl) were pressed in a unidirectional press and sintered. The HCl content of the powder presented three major problems. First, the adsorbed HCl was liberated from the pellet at a very rapid rate and a relatively low temperature causing fractures in the pellet. Second, shrinkage of the titanium pellet from the green state (non-sintered) to the sintered state was dramatic due to the large volume occupied by the HCl in the compact. Third, HCl removed from the pellet during the degassing stage was sent directly into the diffusion pump and then into the roughing pump. HCl in the pumps (mainly the roughing pump) caused internal damage, reduced efficiency, and caused a longer down times. It was apparent that removal of HCl before sintering would be very advantageous.

The apparatus for HCl removal consisted of a hot plate, a flat bottom flask, an injection unit (equipped with a large diameter rotary stopcock), and a magnetic stir bar. The flat bottom flask was adapted for a thermocouple. Additional ports were also provided for evacuating the flask and powder removal. The system was designed for easy loading and removal of TiH_2 powder. Equipment was loaded, unloaded, and operated inside of a glove box.

Argon, used in the glove box and the flat bottom degassing flask, was withdrawn from a liquid argon container and sent through an oxygen getter system in order to maintain ultra clean gas injection. The glove box was continually purged with the ultra clean gas to prevent any oxidation of the product during handling. The oxygen getter consisted of a packed bed of

titanium chips maintained at a constant temperature. The oxygen getter will be discussed in more length in section 6.1 "ITT: Powder Handling Equipment" of this text.

Inside the glove box, TiH_2 powder containing HCl and TiCl_x was loaded into the adapted flat bottom flask. A magnetic stir bar was then inserted into the flask, and the flask was sealed. A vacuum was applied to the flask and the temperature was increased to 400°C over a period of several hours. Periodic stirring of the powder was then applied to ensure that all HCl was stripped off. The flask was maintained at 400°C for two hours at which time the powder was cooled to atmospheric temperature. Argon was then permitted to leak in at a slow rate until the internal pressure equalized with the pressure in the glove box. Once the pressure was equalized, a side port on the flask was opened and the stripped powder was fed, by gravity, into the press die. The powder was compacted and the compact was coated in paraffin wax to prevent oxidation during the furnace loading stage. Sintering of the compact was carried out in the same manner as discussed in the previous "ITT: Press-Sintering" section. A flow diagram that depicts the various stages of compaction, stripping, and sintering is provided below.

Hot Static Degassing / Sintering Flow Diagram

Results from this experiment exceeded our expectations. During the vacuum distillation procedure, HCl was removed completely with an added bonus. Near the final heating cycle of the stripping process, the glass formed a brownish coating. The brown coating observed was caused from sub-chlorides being stripped from the powder.

The sintered pellets formed from the stripped powder were more than twice the size of the standard pellets. In addition, heating times were reduced due to the lack of off gassing.

A strip chart recording for this test was similar to the previously displayed strip chart with one exception. The increase in pressure between 30°C and 100°C was not observed. Pressure stabilization between 30°C and 100°C was observed due to a higher concentration of titanium in the green pellet and a negligible concentration of residual HCl (which would normally off-gas at this temperature range).

Figure 9 shows a size comparison of the standard sintered titanium compact and a compact that was sintered with pre-stripped powder. As you can see, the change is quite dramatic. The stripped sample shows less porosity and a larger shape due to pre treatment of the powder.

Figure 9. Comparison of sintered compacts with and without powder pre-treatment

The titanium compacts in the above photographs were taken with a DC 50 digital camera. The camera was adapted with special lenses to aid in close up photography. Unfortunately as stated previously, the photo quality did not capture the true shiny metallic properties of the pellets. The photo did however, capture the non-fractured surface of the treated titanium pellet. The brown discoloration in the epoxy on the pretreated titanium pellet was caused by removal of the epoxy sample before it had fully hardened.

The following table illustrates powder consolidation results achieved at the ITT laboratory.

Table VII: ITT's powder consolidation results

PROCESS	POWDER	SINTERING ATM	SINTERING TEMP (C)	SINTERING TEMP HOLD (HR)	COMMENT	SINTER
Loose Powder	Loose	Vacuum	1300	2		NO
Loose Powder	Loose	Vacuum /Argon	1300	2	Pressure was maintained at 10 millitorr	NO
Press-Sinter	Pressed 5,000 psi	Vacuum	1300	2	HCl, TiCl ₃ , and TiCl ₂ evolution can be seen on strip chart	YES
Press-Sinter	Pressed 10,000 psi	Vacuum	1300	2	HCl, TiCl ₃ , and TiCl ₂ evolution can be seen on strip ct.	YES
Vacuum Distillation & Press-Sinter	Pressed 5,000 psi	Vacuum	1300	2	Pellet was larger than standard sintered pellet, no off gassing of HCl in furnace	YES

5.0 ITT: Pre-Treatment & Injection Molding Experiments / Results

Titanium sub-chlorides (TiCl_x: TiCl₃ and TiCl₂) and HCl present a major problem with the injection molding characteristics of titanium. HCl reacts with the polymers creating detrimental affects in the stability. In addition, sub-chlorides present contamination problems. To address these problems, ITT has experimented with two "wet" stripping techniques and one "dry" stripping technique. The first "wet" technique involved stripping the HCl and TiCl_x with a fluid (acetone) and filtering. The second "wet" technique involved stripping the HCl and TiCl_x using an ether distillation procedure. The final "dry" technique involved stripping HCl and a fraction of the TiCl_x followed by the addition of molten wax in a well stirred heated inert vacuum atmosphere.

5.1 ITT: Pre-Treatment of TiH₂ with a Fluid

The purpose of this experiment was to chemically "wash out" HCl and sub-chlorides using acetone. Acetone was selected due to its affinity for HCl and its low reactivity with titanium. Both mixtures were filtered using a .2 µm membrane. A rough-vacuum water eductor pump aided in filtering.

In both tests, the majority of the powder passed through the .2 μm membrane. From the mean particle size, obtained from Penn State, it was determined that over 90% of the particles were smaller than .2 μm .

5.2 ITT: Ether Distillation

The purpose of this experiment was to use ether's polar affinity to chlorine combined with its non-reactivity with paraffin wax to create a wax coated titanium powder stripped of HCl and TiCl₄. In a glove box, a known amount of TiH₂ was placed in a round bottom flask. A volume of ether was added to the flask. The flask was then sealed and removed from the glove box. The TiH₂ / ether solution was mixed well and the powder was allowed to settle to the bottom. A known amount of paraffin wax was then added to the flask and the flask was then connected to a distillation column. The mixture was brought to 45°C and the ether was allowed to distill out over a period of several hours leaving a wax / TiH₂ mixture. The wax / TiH₂ mixture was poured into a mold and allowed to cool. Unfortunately, the titanium powder retained some of its original chlorine. The experiment was abandoned in favor of the less dangerous and cleaner option of hot static degassing.

5.3 ITT: Hot Static Degassing / Wax Coating / Sintering

The apparatus for HCl removal is the same as that described in "ITT: Hot Static Degassing / Sintering" section above, with a few exceptions. The injection unit, which was equipped with a large diameter rotary stopcock, was covered with a band heater and monitored with a thermocouple. Equipment was loaded, unloaded, and operated inside a glove box.

Inside the glove box, TiH₂ powder containing HCl and TiCl₄ was loaded into the adapted flat bottom flask. A magnetic stir bar was inserted and the flask was sealed. Vacuum was then applied to the flask and the temperature increased to 400°C over a period of several hours. Periodic stirring of the powder was commenced to ensure that all the HCl was stripped off. The flat bottom flask, containing only the TiH₂ powder, was maintained at 400°C for two hours at which time the powder was cooled to atmospheric temperature.

At this point, there were two separate methods for mixing wax with the stripped TiH₂ powder. The first method mixed the stripped titanium powder with pure molten wax through the wax injector unit positioned on top of the flask. The second method involved dissolving the wax in heptane under a slightly elevated temperature and adding the solution to the stripped titanium powder through the wax injector unit at atmospheric temperature.

Wax Injection Method #1

Wax was maintained in a molten state, in the wax injector unit, by a band heater. Argon was permitted to leak in at a slow rate until the internal pressure was equalized with the pressure in

the glove box. The molten wax was then added to the TiH_2 powder and the flask was resealed and re-evacuated. Temperature of the flask was increased until the wax in the flask became molten again. The mixture was agitated by a glass magnetic stir bar for two hours. After stirring, argon was again permitted to leak in at a slow rate until the internal pressure was equalized with the pressure in the glove box. Once the pressure was equalized, a side port on the flask was opened and the stripped powder / wax mixture was fed, by gravity, into a die assembly. The powder / wax mixture was held under pressure until it cooled and solidified. Sintering of the compact was carried out in the same manner as discussed in the previous "Press-Sintering" section.

Due to the small particle size and low apparent density of the titanium powder it was difficult to achieve an even coating of wax throughout the powder (the powder to wax volume ratio was too large).

Wax Injection Method #2

A known amount of wax was dissolved in heptane under a slightly elevated temperature. The solution was then added to the wax injector unit at atmospheric temperature. Argon was permitted to leak into the evacuated flat bottom flask until the internal pressure was equalized with the pressure in the glove box. The dissolved wax / heptane mixture was then added to the TiH_2 powder and the flask was resealed and re-evacuated. The temperature of the flask was increased slightly to allow the heptane to evaporate and leave the flask. Once the heptane was removed, the temperature in the flask was increased until the wax in the flask became molten again and the mixture was stirred for two hours. After stirring argon was again permitted to leak in at a slow rate until the internal pressure was equalized with the pressure in the glove box. Once the pressure was equalized, a side port on the flask was opened and the stripped powder / wax mixture is fed, by gravity, into the press die. The powder / wax mixture was held under pressure until it cooled and solidified.

The second method in which the wax was dissolved in heptane and then mixed with the titanium powder was more successful than the first method. Several solid, non-reactive, evenly mixed, titanium / wax pellets were formed in this fashion. The pellets were then sintered using two methods, discussed below.

TiH_2 / Wax Sintering Method #1

The first TiH_2 / wax sample was partially sintered in a packed bed of alumina ceramic to 900°C . This was done to wick the wax into the packed bed of ceramic and partially fuse the powder together in order to retain shape and particle density. The alumina ceramic was then removed from the partially fused pellet. The pellet was placed back into the sintering furnace and the temperature was driven to (1300°C) in a vacuum atmosphere.

TiH₂ / Wax Sintering Method #2

A second sample was placed in an alumina crucible, without the aid of a packed bed of ceramic. The TiH₂ / wax pellet was brought to sintering temperature (1300°C) in a vacuum atmosphere. The results from these tests are shown in table VIII.

Table VIII: Hot static degassing / wax coating / sintering results

PROCESS SINTERING METHOD	POWDER	SINTERING ATM	SINTERING TEMP (C)	SINTERING TEMP HOLD (HR)	COMMENT	SINTER
#1) Packed Bed	Titanium / Wax Pellet	Vacuum	1300	2	A solid titanium pellet was not attainable	NO
#2) Alumina Crucible	Titanium / Wax Pellet	Vacuum	1300	2	A solid titanium pellet was not attainable	NO

To date, a solid titanium pellet has not been formed from a wax / powder mixture. There are two reasons for this failure. First, the agitation in stripping off the alumina ceramic from the small and partially sintered titanium pellet fractured and destroyed the sample. Second, the distance between titanium particles after the wax was removed (in sintering method #2) was too large for proper sintering. This non-sinterability of loose titanium powder can also be seen in section 4.1 "ITT: loose powder-sintering".

A binding agent for PIM commonly consists of two components – a backbone polymer (ex: polyethylene) that provides strength and a filler phase (ex: wax) that is easily extracted in the first phase of debinding. The powdered metal is mixed with the compositional binding agent in a heated high sheer mixer. The blended powder and binder is then extruded from the sheer mixer, pelletized, and hot pressure injected into a mold. After mold solidification, the filler phase of the binder (wax) is commonly removed by submerging the part in a solvent (ex: heptane). The porous metallic-polymer compound is transferred into a sintering furnace. The polymer holds the metallic particles close enough for particle adhesion during the initial heating stage. After the particles are adhered together the temperature is increased and the backbone polymer is burned off. The temperature is further increased until complete densification is achieved.

ITT currently has the capability of stripping HCl off the titanium powder and adding a filler phase binding agent to the powder. The method of using a packed bed of ceramic to wick out this filler agent is common practice with larger metallic PIM parts. Unfortunately, ITT is currently unable to evenly mix a backbone polymer with the TiH₂ powder. In order to mix ITT's TiH₂ powder with a polymer in the existing hot static degassing equipment the polymer must have a melting temperature around 100°C and readily dissolve in a solvent. A compound with the appropriate properties has yet to be found. ITT's PIM sintering results will improve

dramatically once a method of stripping the powder and mixing it with a backbone / filler binder is established.

6.0 ITT Equipment

This section is presented in order to provide the reader with a visual representation of the equipment used in the analytical testing of titanium powder. Titanium is very reactive, forming very stable oxides and nitrides. Unlike many metals, titanium is capable of dissolving its own surface oxides at sintering temperatures. The formation of additional oxides should be avoided. Consequently, the use of high vacuum or high-purity inert gas atmosphere is common practice [12]. The following section labeled "Powder Handling Equipment" describes the vacuum and high-purity inert gas equipment used in handling the ultra fine and reactive titanium powder.

ITT has developed a new procedure in the mixture and extrusion process for small-scale injection molding. The procedure applies hot static degassing methodology combined with wax mixing and vacuum distillation to produce a wax / powder pellet that is stable in the atmosphere and contains the least amount of wax possible. The following section labeled "Injection Molding Equipment" gives a visual representation and explanation of the equipment.

There are several forms of consolidation used in sintering metallic powders. One of the most common methods is CIP-Sinter-HIP. This procedure applies cold isostatic pressing (CIP) followed by a sintering procedure. In this fashion, a density between 90 and 97% of the theoretical density can be achieved. The part can then be hot isostatically pressed to 99 to 100% of theoretical density. Hot pressing is another method of powder consolidation commonly used in industrial practice. Hot pressing involves pressure, which is applied statically or dynamically to a heated powder in one direction along a single axis. A controlled atmosphere is required to protect the hot powders or prepressed compacts from oxidation or nitridation by air [14]. ITT performs a variation of hot pressing in which the metal powder is pressed in a unidirectional fashion (in a controlled atmosphere) and the extracted compact is placed in a vacuum furnace for final densification. Section 6.3 labeled "Powder Sintering Equipment" presents a visual representation and discussion of the equipment used in consolidation, treating, and sintering of the titanium powder.

6.1 ITT: Powder Handling Equipment

Glove Box

The engineers and technicians at ITT designed a large capacity glove box used for handling reactive titanium powder. The glove box was designed to house a Carver unidirectional press and die along with instrumentation for powder manipulation. The glove box is equipped with power feedthroughs, high-purity argon injection, withdrawal ports, a vacuum port, iron support

Figure 10. ITT glove box

High-purity argon (withdrawn from a heated oxygen getter assembly) is continuously flowing through the glove box and transfer port. This is done to ensure the lowest concentration of oxygen and nitrogen possible.

Oxygen Getter Assembly

The engineers and technicians at ITT working in conjunction with Len Hainz (consultant and manager of a titanium sponge processing division) designed a heated titanium chip oxygen getter assembly used for generating an ultra-pure argon gas. The oxygen getter was designed to facilitate the typical flows of argon gas while maintaining a reasonable useful life span. The oxygen getter is equipped with calcium silicate insulation, thermocouple, mica band heaters, titanium chips, and a Watlow 96 temperature controller. Materials of construction are stainless steel, titanium, calcium silicate, and copper.

Figure 11. ITT oxygen getter assembly

Argon is fed into the oxygen getter from a liquid argon container. The titanium chips (which fill the getter assembly) are heated to 450°C. The effluent high-purity argon is then fed into the bottom of the glove box. An exit port is located on the top of the glove box. The system is set up to either bubble the exit gas through a water bath or re-circulate the exit gas through the oxygen getter and back into the box.

Cad drawings of the vacuum distillation assembly are located later in this report. Section 7.1 describes the individual sections in a dimensional fashion.

Vacuum pump

A gas eductor unit (generating a moderate vacuum) is used to evacuate the powder distillation assembly (located inside the glove box). The gas eductor unit is equipped with a vacuum hose, tubing clamps, and a Swagelok ball valve. Materials of construction are stainless steel, copper, and rubber tubing.

Figure 12. ITT rough vacuum pump for glove box

Hot Static Degassing Assembly

The engineers at ITT in conjunction with Gary Gregston (glass blower employed by INEEL) designed a vacuum distillation and wax injection system to strip HCl from titanium powder. The apparatus consists of an adapted flat bottom flask and a wax injector unit. The flat bottom flask was adapted with vacuum fittings, a powder removal port, powder insertion port, stir bar insertion port, and a thermocouple well. A separate piece of equipment (wax injector) was designed to hold and disperse an incremental volume of molten or dissolved wax into the flask. In the powder distillation procedure, the wax injector is simply used as a plug valve. The flask is equipped with a glass magnetic stir bar, thermocouple, ground glass fittings, powder feeding funnel, and a hot plate that precisely controls both the temperature (based off thermocouple readout) and the rotational speed of the stir bar. The wax injector is equipped with a large diameter Teflon plug valve, ground glass fittings, band heater and band heater controller, thermocouple and display, wax injector funnel, and a support stand. Materials of construction are glass, stainless steel, and Teflon.

In the following figures, titanium powder is being statically degassed by heating the hot plate and evacuating the flask. Figure 13a displays the entire system in operation. Figure 13b displays the evacuated / heated flask with titanium powder inside.

Cad drawings of the vacuum distillation assembly are located later in this report. Section 7.2 describes the individual sections in a dimensional fashion.

Figure 13a. ITT powder distillation assembly

Figure 13b. ITT adapted flat bottom flask

6.2 ITT: Injection Molding Equipment

Hot Static Degassing / Wax Coating Assembly

The powder distillation and coating assembly is identical to the powder distillation system with one exception. The wax injector is used to hold and disperse an incremental volume of molten or dissolved wax into the flask.

Cad drawings of the vacuum distillation assembly are located later in this report. Section 7.2 describes the individual sections in a dimensional fashion.

6.3 ITT: Powder Sintering Equipment

Press Assembly

Due to the low apparent density of the powder, engineers at ITT designed a die system that allows for the maximum volume compaction possible. Materials of construction are stainless steel and heat treated H13.

Figure 14. ITT press and die assembly

The die sections consist of a stainless steel top piston support, small and large bottom piston support, and piston punch. The top and bottom pistons along with the titanium compaction piston support are made from heat treated H13. CAD drawings of the die are located later in this report in section 7.3.

Molybdenum Furnace Assembly

The initial sintering furnaces used at the ITT facility were resistive tubular boron nitride heaters. The heaters possessed terminals located at the top (cooler section) of the unit. Titanium sub-chlorides would deposit on these terminals and create a constant problem with shorting. The heater was eventually replaced with a clam shell molybdenum wire heater incased in a refractive high temperature ceramic shell. The clam shell heater was designed to prevent build up of sub-chlorides along the power terminals and enable sintering of multiple compacts.

The furnace assembly consists of a clam shell molybdenum / ceramic furnace (with power leads located on the bottom), molybdenum radiation heat shields, a boron nitride pedestal (which supports the titanium compact). In addition, two S type thermocouples with tantalum sheathes, ceramic heat shield spacers, a stainless steel support, and a boron nitride washer that separates the furnace from the support were used. The sintering furnace is equipped with two temperature sensors to ensure accurate sintering. The first sensor monitors the temperature of the sintered pellet and the second monitors the temperature of the furnace wall. Figure 15a below shows a top view of the furnace with the upper radiation shields removed.

Power to the furnace is controlled in two ways. First, the power is sent through a variable autotransformer in which the voltage can be dialed up at the operators discretion. Second,

when the power leaves the transformer it is sent through a solid state relay that is controlled by a series 96 Watlow temperature controller. The Watlow controller reads the temperature of the pellet and adjusts the power through put accordingly. The 96 controller also allows the operator to maintain a more precise control over the temperature rise of the compact. The series 96 comes with an option that allows the operator to adjust the amount of power sent through the relay. In essence, the autotransformer is used as a rough power adjustment and the controller is used as a fine adjustment. The to types of power control complement each other well. A third controller is placed in series with the preceding two, which reads the pressure output from an ion gauge and restricts the power if the pressure in the bell jar becomes too high. When the power leaves this final checkpoint it is channeled into power feedthroughs (that feeds the furnace) located on the base plate of the bell jar. Figure 15b illustrates the open system assembly.

Figure 15a. Molybdenum furnace assembly
(top view)

Figure 15b. Furnace, controllers,
& bell jar assembly

Strip Chart recorder

The strip chart recorder used in conjunction with the sintering furnace is the same piece of equipment used in the pH monitoring of impingers as described in appendix AA1. The recorder was adjusted to continuously monitor and record the pellet temperature and bell jar pressure. A print out of numerical value including; pressure, temperature, and time was set to print on the strip chart every thirty minutes.

7.0 ITT Equipment Assembly CAD Drawings

This section lays out the individual sections of equipment designed at the ITT facility. Dimensionalized drawings are presented for the oxygen getter, vacuum distillation assembly, Carver press die, and the sintering furnace.

7.1 ITT: Oxygen Getter Assembly

Oxygen Getter Assembly

Hot Static Degassing / Wax Coating Assembly

Magnetic Glass Stir Rod Configuration

Step #1

In an argon environment, melt or dissolve the wax in a separate container. Close the valve on the wax injector. Pour the melted wax into the injector and allow it to solidify.

Step #2

In an argon environment, place the glass coated magnetic stir bar in the bottom of the 1000ml flask. Purge the flask with argon for several minutes

Step #3

In an argon environment, pour a known amount of TiH_2 powder into the 1000ml flask.

Magnetic Glass Stir Rod Configuration

Step #4

Place the wax injector on the 1000 ml flask and secure. Wrap the injector with heat tape. Place the argon pressure head adapter on the unit and secure. Evacuate the flask and bring the powder temp. to 300C (for five min.) while agitating. Establish a pressure head of argon in the top of the wax injector.

Step #5

Cool the powder to 150C. While agitating the powder, open the injector valve. Heat the wax to the molten state and allow it to pass into the evacuated 1000 ml flask. Stop the wax flow before the entire volume has emptied into the evacuated flask. Continue agitation until uniformly mixed.

Step #6

Pour the molten wax-powder mixture into a pre-defined mold and allow solidification.

Glassware Assembly

7.3 ITT: Carver Press Die System

Press Die Assembly

Press Die Assembly Sections

Lower die support

MTRL: Stainless Stl.
Dim: Hole=+/- .005
Other=+/- .05
Quantity: 1

Upper & Lower die support 2

MTRL: Stainless Stl.
Dim: Hole=+/- .005
Other=+/- .05
Quantity: 2

Long die

MTRL: H13
Dim: +/- .001 between
long and short dies
Heat Treat After
Fabrication
Quantity: 1

Short die

MTRL: H13
Dim: +/- .001 between
long and short dies
Heat Treat After
Fabrication
Quantity: 1

Powder compaction die support

MTRL: H13
Dim: +/- .005
Bore to smaller
dimension - Heat treat-
polish out to very
tight dimensional fit to
die.
Quantity: 1

die ejection starter plate

MTRL: Stainless Steel
Dim: +/- .05
Quantity: 1

die ejection support plate

MTRL: Stainless Steel
Dim: +/- .005 on center
hole.
Other = +/- .05
Quantity: 1

Ejection die

MTRL: H13
Dim: +/- .005 on diameter

Heat Treat After
Fabrication
Quantity: 1

7.4 ITT: Sintering Furnace

Sintering Furnace Assembly

Molybdenum Sintering Furnace Assembly

Sintering Furnace Assembly Sections

Assembly Top View

Assembly Cross Section

Assembly Bottom View

ASSEMBLY

Sintering Oven Heat Shield Cap

Dim inner hole: +/- .005
 Dim other: +/- .05
 MTRL: .02" SS sheet
 Quantity: 1

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Appendix B

Analytical Chemistry

Analytical Chemistry Contents

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TESTING FOR ADSORBED HCl & TiCl_x IN TiH₂ SAMPLES

1.0 Introduction

Idaho Titanium Technologies utilizes a proprietary plasma quench technology to produce ultra-fine titanium hydride powder from titanium tetrachloride, a commodity precursor. The possible byproducts from this process are titanium hydride (desired), Hydrochloric acid (desired), and titanium sub-chlorides (TiCl_x-not desired).

A recent article from "Journals of Metals" [1] states that titanium hydride is preferred over plain titanium powder. Hydrogen use as a temporary alloying element in titanium alloys improves their processability, microstructure, and final properties. Adsorbed HCl on the powder does not present a problem since it can be easily removed. Titanium sub-chlorides are an un-wanted product of the TiH₂, and it is more difficult to remove due to its higher melting point and lower vapor pressure.

In order to determine the presence and the amounts of these afore mentioned products, ITT has developed an analytic method discussed below. The results of the examination of a recent sample (which was thought to be contaminated due to a water leak in the system) indicated a remarkably repeatable outcome.

Three small (.9 gram) individual samples were taken from one large container of contaminated TiH₂ powder. Different quantities of each of the three samples were then taken and analyzed. The results indicate a high repeatability of the measurable chlorine content in each sample. The results also indicate a maximum quantity (.5 gram) of sample in which the most accurate results are achieved.

2.0 Development of Product Analysis Methodology

Previously samples of TiH₂ had been sent to Desert Analytic (DA) located in Arizona. DA had the capability to determine the overall chlorine content in a TiH₂ powder sample. The normal minimum turn-around time for results was one week. DA was not, however, capable of distinguishing between TiCl_x and adsorbed HCl in a sample. Because of the long response time, the cost, and the overall inadequacy of merely identifying overall chlorine content, ITT developed a more comprehensive and timely analysis. This was accomplished by ITT's in-house chemical engineer working in conjunction with a professor of chemistry at the University of Idaho. A separate technique for testing the reliability of this analytical system was also developed.

3.0 Product Analysis Methodology

A schematic of the analytical testing system is set forth below. Two properties of the powder can be determined by this test. The first is the amount of adsorbed HCl on the powder. The second is the amount of TiCl_x in the TiH₂ powder sample.

Analytical Test System Schematic

3.1 Powder Handling

If the TiH₂ powder is exposed to the atmosphere the powder quickly oxidizes (due to the moisture in the air) and turns from a black to a light gray. The oxidation process creates TiO₂ according to the reactions:

This reaction eliminates the ability to determine the amount of adsorbed HCl and/or the amount of TiCl_x. To prevent this oxidation from occurring, a known amount of powder is placed into a glass boat under an argon atmosphere. This procedure is carried out in a glove bag attached to the glass tubing. Once the boat is in the oven, and the glassware is sealed air-tight, a purge is maintained on the sealed system using ultra-pure hydrogen (containing a very minute amount of moisture). A schematic of the procedure, using a glove bag, is shown below.

Powder Handling Schematic

3.2 Impingers

HCl Vapor is absorbed into water during the testing period. The absorption takes place in two impingers, which are connected in series. The impingers are packed with raschig rings (small sections of glass tubing). The glass raschig rings are used to hold up the bubbles to allow for greater residence time. The gas enters the bottom of the impinger through a glass frit. The frit is used to create small bubbles which provide a very large surface area to promote the absorption of the HCl into the H₂O.

One pH sensor is mounted in each of the two impingers. The sensor is attached to a strip chart recorder which records the pH as a function of time. The pH sensor is used to determine the point at which the water has ceased absorbing HCl. A pH strip chart line that does not decrease with time indicates this steady state point. The glass impinger schematic is given below.

Glass Impinger Schematic

3.3 HCl Concentration Test

The concentration of adsorbed HCl on the TiH₂ powder is determined using the system represented below in the "Analytical Test System Schematic". Ultra-pure hydrogen is passed over a thin bed, which consists of a .5-.8 gram sample of TiH₂ spread over a 2-foot length. The pure hydrogen is used during the entire HCl concentration test. An oven and controller maintains this bed at 300 C. The adsorbed HCl is vaporized and carried away by the "dry" hydrogen. This gas is then sent through the impinger system (described above) to be scrubbed for HCl. A schematic of the HCl analytical test is shown below.

HCl Analytical Test Schematic

3.4 TiCl_x Concentration Test

After the HCl concentration test is concluded (pH strip chart reaches steady state) the gas flow is switched over to the second set of impingers. The "dry" hydrogen is switched over to "wet" hydrogen. The wet H₂ is channeled through a nebulizer containing 5 ml of water. This super-saturated gas is passed over the thin bed of TiH₂ maintained at 300 C. The TiH₂ turns from a black powder (TiH₂, ?TiCl_x) to a light gray powder (TiO₂). The "wet" hydrogen carries away the HCl, generated from the reaction between Cl_x and H₂. This gas is then sent through the impinger system (described above) to be scrubbed for HCl. A schematic of the TiCl_x analytical test is shown below.

TiCl_x Analytical Test Schematic

3.5 pH Test

A simple pH test is performed to determine the presence of residual adsorbed HCl or TiCl_x left in the sample after the TiCl_x test. The residual powder left in the boat, after the TiCl_x test, is placed into a beaker of DI water (pH of 7) and agitated. Hydrochloric acid (HCl) is formed from the reaction between TiCl_x or HCl with water (H₂O). Due to the pH decreasing with increasing acidity, a pH of less than 7 indicates residual chlorine. Results of the pH test are given on the attached spreadsheet.

3.6 Determination of the HCl Concentration in the Impingers

Once the HCl gas is bubbled through the impingers and has reached steady state, the concentration of the acid needs to be determined. To determine the HCl concentration, water in both of the *used* impingers is collected. The impingers are then rinsed with DI water and the rinse is collected. The glassware (up to the valve directing flow to the impinger) is rinsed with DI water and the rinse is collected. All of the rinse water and impinger water is combined, agitated, and measured.

Three volumetric samples of the final solution are taken. A pre-calibrated pH meter (GLI 3150 Portable pH Meter) is placed in each sample. Using a buret, NaOH is added to each sample and the volume of NaOH is recorded against the pH.

The point at which just enough NaOH has been added to react with all of the HCl to form H₂O is called the equivalence point. The equivalence point, for the reaction between NaOH and HCl, is reached at a pH of seven.

A plot is constructed for the volume of NaOH added and the pH read. The amount of NaOH required to reach equivalence is determined by drawing a straight line from the 7 pH mark to the plotted line and then from *that* point to the volume of the corresponding NaOH.

The moles of NaOH are determined from the volume and molarity of the NaOH titrant. One mole of NaOH consumes one mole of HCl to form H₂O, hence the moles of HCl absorbed into the impingers can be calculated. From the volume of the sample and the volume of the collected rinse and impinger sample, the weight of the HCl can be determined. From this weight, a weight percent of Cl in the powder is calculated.

A spreadsheet showing the chlorine weight percent calculations for both the adsorbed HCl and the TiCl_x are presented in the back of this report.

4.0 Testing the Methods

4.1 Purpose

The method used in testing TiH₂ (described above) for TiCl_x and adsorbed HCl was created by ITT. This procedure is *not* a "cook book" method out of a chemistry handbook. Therefore, this method itself, must be tested for accuracy by some independent means.

Three procedures for testing the accuracy of our method have been developed. The three procedures are referred to as the Jell Capsule Test, 1 Molar (M) HCl Test, and a 9.1 Molar (M) TiCl₄ Test.

4.2 Jell Capsule Test

The jell capsule test is performed in order to determine the **total** chlorine content of the sample. The results from the TiCl_x and adsorbed HCl tests can then be compared to the jell capsule test to indicate whether or not all of the chlorine was captured. This test is the same test that Desert Analytic (DA) was performing for ITT before the previous method was developed.

Four pre-weighed "OOO" jell capsules are packed (in an argon atmosphere) with the TiH₂ powder being tested. After the weight of the powder has been determined, the four samples are held under a water solution. The capsules are packed in an argon atmosphere and held under a water bath to prevent the oxidation of TiH₂ and possible TiCl_x. The water is agitated until all four jell caps have completely dissolved. The sample is then titrated with NaOH and the weight percent of Cl in the powder is determined as stated above in "Determination of the HCl and TiCl_x Concentration". The concentration is then compared to the results obtained by the previously mentioned HCl and TiCl_x analytical tests. The Jell Capsule Test spreadsheet is included on the back of this report.

4.3 HCl 1 M Test

The 1 molar HCl test is used to simulate adsorbed HCl on TiH₂. This test indicates how much of the HCl, leaving the boat, is absorbed into the water-filled impingers.

A known volume of one molar HCl is placed in the boat shown in the "Analytical Test System Schematic" above. The *HCl Concentration Test* is conducted as stated above. The concentration of HCl in the sample is calculated from a titration with NaOH as described above in the *Determination of HCl and TiCl_x Concentration* section. The moles of chlorine calculated and the moles of chlorine used are then compared. The 1M HCl Test spreadsheet is included in the back of this report.

4.4 TiCl₄ 9.1 M Test

The 9.1 molar TiCl₄ test is used to simulate TiCl_x in the powder. This test indicates how much HCl, generated from the reaction between "wet" hydrogen and chlorine, is absorbed into the water filled impingers.

A known volume of 9.1 molar TiCl₄ is placed in the boat under an argon purge as shown in the "Powder Handling Schematic". The *TiCl_x Concentration Test* is conducted as stated above. The concentration of HCl in the sample is calculated from a titration with NaOH as described above in the *Determination of HCl and TiCl_x Concentration* section. The moles of chlorine calculated and the moles of chlorine used are then compared. The 9.1M TiCl₄ Test spreadsheet is included in the back of this report

5.0 Assumptions and Explanations

5.1 Assumptions

- 1) The majority of TiH₂ powder will come into contact with gas at 300 C.
- 2) The majority of the TiH₂ will not break up to form titanium and hydrogen at 300 C.
- 3) Water in the "wet" hydrogen gas will oxidize the TiH₂ to form TiO₂.
- 4) Water in the "wet" hydrogen gas will oxidize the TiCl_x to form TiO₂.
- 5) The majority of the TiCl_x's chlorine will combine with the "wet" H₂ to form gaseous HCl.
- 6) The majority of the gaseous HCl will be absorbed in water.
- 7) At 300 C the majority of adsorbed HCl will separate from the TiH₂.
- 8) The majority of the adsorbed HCl will be carried by the "ultra pure" H₂ gas.
- 9) The "wet" H₂ gas will carry the majority of the gaseous HCl generated.

5.2 Explanations

Gas Interaction With Powder

A .5 to .8 gram sample of TiH₂ powder is placed into a long boat (2 feet) in a very thin layer. Hydrogen gas at a rate of .05-.08 SCFM is sent over the sample for a period of several hours. This flow rate, thin layer of powder, and long running time assures a thorough gas to powder interaction.

Temperature Dependence of TiH₂

The TiH₂ sample is kept at a constant 300 degrees Celsius to retain the hydrogen on the titanium. The reason this is a critical issue is due to the extremely minute particle size of the TiH₂. A "non-coated" titanium particle (a particle without two hydrogen molecules attached) of a sufficiently small size has enough surface energy to sinter itself with the other titanium particles. A thermodynamic program (HSC) was used to show the degradation of TiH₂ at higher temperatures. HSC results are shown below.

TiH₂ Reaction with H₂O

When water is injected into the "wet" hydrogen gas and then passed over a bed of TiCl_x at 300 C, the reaction forms TiO₂ and HCl. The stoichiometric calculation for this reaction is:

A thermodynamic program (HSC) was used to show the reaction of TiCl_x . One mole of TiCl_x (TiCl_2 , TiCl_3 , TiCl_4) was heated to 300 C and water was applied starting with .5 mole and incrementing up in .1 mole steps. As seen below the reaction of H_2O with TiCl_x to form TiO_2 and HCl is evident.

Solubility of HCl in H_2O

According to the Handbook of Chemistry and Physics 32ed the solubility of HCl is 82.3 g / 100 ml cold water (0C). In the current ITT system, between .1 to .5 grams of TiH_2 are being tested and absorbed into 400 ml of ice water.

6.0 Results

6.1 Testing the Methods

1M HCl Test

The one molar HCl test indicates that around 94% of the HCl sent through the system was captured and recorded by the analytical method. This high percent of capture indicates that the analytical method for capturing and recording the amount of adsorbed HCl on the TiH₂ sample would be accurate.

Water was collected from both of the impingers and the rinse. Three, 150 milliliter samples were then taken. Each sample was tested separately and labeled 1a, 1b, and 1c. The results from the test indicate 94%, 93%, and 95% chlorine capture respectively.

<u>Test</u>	<u>WT% Recovered Cl</u>	<u>Comment</u>
3/11/98 1a	94%	The high chlorine WT% recovered indicates a reliable testing procedure.
3/11/98 1b	95%	The pH readings from the strip chart recorder indicate that the impingers had reached steady state.
3/11/98 1c	93%	The WT% from all three of the tests are very repeatable. This repeatability indicates an accurate titration test.

The spreadsheets indicating the results are shown on the following page.

1 M HCl Test For Collection Accuracy

PURE H2 / CHLORIDE SIMULATION / HCl RECOVERY / NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300

PH OF DI= 6.66

START TIME= 15:30
STOP TIME= 16:10
TIME OF TEST (HR)= 0.67

Date = 11-Mar

Test= 1a

Concentration NaOH (M)= 1

Sample Volume of Titrate HCl+H2O (mL)= 150

MAX FLOW RATE OF PURE H2 (SCFM)= 0.06

Total Collected

Test Vol 1M HCl (ml)	Vol Impingers HCl+H2O (ml)
25	680

Titrant		
Time	NaOH (mL)	pH
4:30	0	1.7
4:30	2	1.78
4:30	3	1.85
4:30	4	2.02
4:30	4.6	2.28
4:30	5	2.69
4:30	5.2	7.18

pH Vs. vol of NaOH -CHLORIDE TEST - HCl Recovery Calculation

Volume of NaOH (mL) @ Equivalence pt. (pH=7)=

5.176

Comment:

CHLORIDE Test Results from NaOH Titration

@Equivalence		Sample Conc.	Impinger	Impinger	Impinger
Mol NaOH	Mol HCl	Mol/L HCl	Mol HCl	Mol Cl	g Cl
0.005176	0.005176	0.035	0.0235	0.0235	0.832

MWCL=35.45

Recovered Wt % Cl (CHLORIDE) = 94 %

1 M HCl Test For Collection Accuracy

PURE H2 / CHLORIDE SIMULATION / HCl RECOVERY / NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300

PH OF DI= 6.66

START TIME= 15:30
STOP TIME= 16:10
TIME OF TEST (HR)= 0.67

Date = 11-Mar
Test= 1b

Concentration NaOH (M)= 1
Sample Volume of Titrate HCl+H2O (mL)= 150
MAX FLOW RATE OF PURE H2 (SCFM)= 0.06

Total Collected
Test Vol 1M HCl (mL) Vol Impingers HCl+H2O (mL)
25 680

Titrant		
Time	NaOH (mL)	pH
4:30	0	1.72
4:30	4	1.95
4:30	4.4	2.09
4:30	4.8	2.33
4:30	5	2.6
4:30	5.2	6.38
4:30	5.4	10.63

Volume of NaOH (mL) @ Equivalence pt. (pH=7)=

5.216

Comments:

CHLORIDE Test Results from NaOH Titration

@Equivalence		Sample Conc.	Impinger	Impinger	Impinger
Mol NaOH	Mol HCl	Mol HCl	Mol HCl	Mol Cl	g Cl
0.005216	0.005216	0.035	0.0236	0.0236	0.838

MWCL=35.45

Recovered Wt % Cl (CHLORIDE) = 95 %

96

9.1M TiCl₄ Test

The nine point one molar TiCl₄ test indicates that around 96.5% of the HCl sent through the system (due to the reaction between TiCl₄ and H₂O) was captured and recorded by the analytical method. This high percent of capture indicates that the analytical method for capturing and recording the amount of TiCl_x in the TiH₂ sample would be accurate.

Water was collected from both of the impingers and the rinse. Three, 150 milliliter samples were then taken. Each sample was tested separately and labeled 1a, 1b, and 1c. The results from the test indicate 98%, 96%, and 96% chlorine capture respectively.

<u>Test</u>	<u>WT% Recovered Cl</u>	<u>Comment</u>
3/11/98 1a	98%	The high chlorine WT% recovered indicates a reliable testing procedure.
3/11/98 1b	96%	The pH readings from the strip chart recorder indicate that the impingers had reached steady state.
3/11/98 1c	96%	The WT% from all three of the tests are very repeatable. This repeatability indicates an accurate titration test.

The spreadsheets indicating the results are shown on the following page.

9.1M TICl4 Test For Collection Accuracy

NON-PURE H2 / SUB-CHLORIDE SIMULATION / HCl RECOVERY / NaOH TITRATION EXPERIMENT

PH OF DI= 7

START TIME= 2:00
STOP TIME= 4:10
TIME OF TEST (HR)= 2.17

Heater Temperature (C)= 25-300

Date = 18-Mar

Test= 1a

Concentration NaOH (M)= 1

Sample Volume of Titrate HCl+H2O (mL)= 150

MAX FLOW RATE OF NON-PURE H2 (SCFM)= 0.06

Total Collected

Test Vol 9.1M TICl4 (ml) Vol Impingers (ml)

5 1262

pH Vs. vol of NaOH - SUB-CHLORIDE TEST - HCl Recovery Calculation

Volume of NaOH (mL) @ Equivalence pt. (pH=7)=

20.78

Comment: THE TEST WAS RUN AT 250 UNTIL 1/2 HIN IMPINGERS STABILIZED
THEN TEMP WAS RAISED TO 300C.

SUB-CHLORIDE Test Results from NaOH Titration

@ Equivalence @ Equivalence Sample Conc. Impinger Impinger Impinger

Mol NaOH Mol HCl Mol/L HCl Mol/L HCl Mol Cl g Cl

0.02078 0.02078 0.139 0.1776 0.1776 6.296

Recovered Wt % Cl (CHLORIDE) = 98 %

9.1M TiCl4 Test For Collection Accuracy

NON-PURE H2 / SUB-CHLORIDE SIMULATION / HCl RECOVERY / NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 25-300

PH OF DI= 7

START TIME= 2:00
STOP TIME= 4:10
TIME OF TEST (HR)= 2.17

Date = 18-Mar

Test= 1b

Concentration NaOH (M)= 1

Sample Volume of Titrate HCl+H2O (mL)= 150

MAX FLOW RATE OF NON-PURE H2 (SCFM)= 0.06

Test Vol 9.1M TiCl4 (ml) 5
Total Collected Vol Impingers (ml) 1262

Titrant		
Time	NaOH (mL)	pH
9:00	0	1.56
9:00	20	4.73
9:00	20.2	5.86
9:00	20.4	6.9
9:00	20.6	8.38

pH Vs. vol of NaOH - SUB-CHLORIDE TEST - HCl Recovery Calculation

Volume of NaOH (mL) @ Equivalence pt. (pH=7)=

20.41

Comment: THE TEST WAS RUN AT 250 UNTIL 7 MIN IMPINGERS STABILIZED
THEN TEMP WAS RAISED TO 300C.
SAMPLE SAT OVERNIGHT

SUB-CHLORIDE Test Results from NaOH Titration.

@ Equivalence		@ Equivalence	Sample Conc.	Impinger	Impinger	Impinger	MW CL: 35.45
Mol NaOH	Mol HCL	Mol/L HCL	Mol HCL	Mol Cl	g Cl		
0.02041	0.02041	0.136	0.1744	0.1744	6.184		

Recovered Wt % Cl (CHLORIDE) = 96 %

9.1M TiCl₄ Test For Collection Accuracy

NON-PURE H₂ / SUB-CHLORIDE SIMULATION / HCl RECOVERY / NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 25-300

PH OF DI= 7

START TIME= 2:00
STOP TIME= 4:10
TIME OF TEST (HR)= 2.17

Date = 18-Mar

Test= 1c

Concentration NaOH (M)= 1

Sample Volume of Titrate HCl+H₂O (mL) = 150

MAX FLOW RATE OF NON-PURE H₂ (SCFM)= 0.06

Test Vol 9.1M TiCl ₄ (ml)	Total Collected Vol Impingers (ml)
5	1282

Titration		
Time	NaOH (mL)	pH
11:20	0	1.44
11:20	20	4.81
11:20	20.2	5.91
11:20	20.4	6.89
11:20	20.6	8.34

Volume of NaOH (mL) @ Equivalence pt. (pH=7)=

20.42

Comment: THE TEST WAS RUN AT 25C UNTIL pH IN IMPINGERS STABILIZED
THEN TEMP WAS RAISED TO 300C.
SAMPLE SAT OVER NIGHT

SUB-CHLORIDE Test Results from NaOH Titration

@ Equivalence		Sample Conc.	Impinger	Impinger	Impinger
Mol NaOH	Mol HCl	Mol/L HCl	Mol HCl	Mol Cl	g Cl
0.02042	0.02042	0.136	0.1745	0.1745	6.187

Recovered Wt % Cl (CHLORIDE) = 96 %

6.2 Testing the TiH₂ Powder

HCl Concentration Test

Three small samples (.9 gram) were taken from one large (50 grams) quantity of contaminated TiH₂ powder. The powder was known to contain a large percentage of chlorine due to a water leak in the system at the time of collection. A different quantity of each small sample was tested for adsorbed HCl. Impinger water and rinse was collected from each run. Three 150-ml samples from each collection were taken and analyzed to insure repeatability of results. The results are as follows:

<u>Test</u>	<u>WT% Adsorbed Cl</u>	<u>WT TiH₂(g)</u>	<u>Comment</u>
3/30/98 1a	34%	.781	TiH ₂ had a depth of 1" in the boat. Leaving the possibility of buried HCl not leaving the powder.
3/30/98 1b	35%	.781	The pH readings from the strip chart recorder indicate that the impingers had reached steady state.
3/30/98 1c	35%	.781	The WT% from all three of the tests are very repeatable. This repeatability indicates an accurate titration test.
3/27/98 1a	32%	.341	TiH ₂ did not completely consume the bottom of the boat. Providing a thin barrier for desorption of HCl.
3/27/98 1b	30%	.341	The pH readings from the strip chart recorder indicate that the impingers had reached steady state.
3/27/98 1c	23%	.341	The WT% from the first two tests are very repeatable. The third test could be off due to miss calibration of the analytical pH sensor.
3/27/98 2a	30%	.217	TiH ₂ did not completely consume the bottom of the boat. Providing a thin barrier for desorption of HCl.
3/27/98 2b	30%	.217	The pH readings from the strip chart recorder indicate that the impingers had reached steady state.
3/27/98 2c	30%	.217	The WT% from all three of the tests are very repeatable. This repeatability indicates an accurate titration test.

The spreadsheets indicating the results are shown on the following page.

TiH2's Adsorbed HCl Concentration Test

PURE H2 - CHLORIDE TEST - HCl Recovery NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300
Date = 27-Mar
Test = 1a
Concentration NaOH (M)= 1
Sample Volume of Titrant HCl (mL)= 150
MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.15

Time	NaOH (mL)	pH
9:40	0	2.32
9:40	0.2	2.42
9:40	0.4	2.55
9:40	0.6	2.92
9:40	0.8	9.96

Discoloration of Glass ? Yes ☐
No ☒

START TIME= 7:40
STOP TIME= 8:40
TIME OF TEST (HR)= 1.00

Total Collected
Weight of TiH2 (g) 0.341
Vol Impingers (ml) 650

Weight of TiH2 Bottle Before (g)= 0
Weight of TiH2 Bottle After (g)= -0.341

pH Vs. vol of NaOH -CHLORIDE TEST - HCl Recovery Calculation

Volume of NaOH (mL) @ Equivalence pt. (pH=7)= 0.715

Comment: WORKED ON STABILIZING CONTINUOUS PH METER

CHLORIDE Test Results from NaOH Titration

Q Equiv. NaOH	Q Equiv. HCl	Sample Conc.	Impinger	TiH2's	TiH2's
Mol NaOH	Mol HCl	Mol/L HCl	Mol HCl	Mol HCl	g Cl
0.000715	0.000715	0.005	0.0031	0.0031	0.1098

TiH2's Wt % Cl (CHLORIDE) = 32 %

pH TEST

Date = 27-Mar
Test = 1a

Ph Of Water Before TiH2 Is Added= 4.92
Ph Of Water After TiH2 Is Added= 4.82

TiH2's Adsorbed HCl Concentration Test

PURE H2 - CHLORIDE TEST - HCl Recovery NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300

Discoloration of Glass ? Yes ☐ No ☒

START TIME= 7:40
STOP TIME= 8:40
TIME OF TEST (HR)= 1.00

Date = 27-Mar
Test= 1b
Concentration NaOH (M)= 1
Sample Volume of Titrant HCl (mL)= 150
MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.11

Total Collected
Weight of TiH2 (g) 0.341
Vol Impingers (mL) 650

Weight of TiH2 Bottle Before (q)= 0
Weight of TiH2 Bottle After (q)= -0.341

Concentration NaOH (M)= 1
Sample Volume of Titrant HCl (mL)= 150
MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.11

Time	NaOH (mL)	pH
10:30	0	2.31
10:30	0.2	2.44
10:30	0.4	2.7
10:30	0.6	5.13
10:30	0.8	10.51

Volume of NaOH (mL) @ Equivalence pt. (pH=7)= 0.67

General: WORKED ON STABILIZING CONTINUOUS PH METER

CHLORIDE Test Results from NaOH Titration

Q Equivalence	Q Equivalence	Sample Conc.	Impinger	TiH2's	TiH2's
Mol NaOH	Mol HCl	Mol/L HCl	Mol/L HCl	Mol/L HCl	g Cl
0.00067	0.00067	0.004	0.0029	0.0029	0.1029

TiH2's Wt % Cl (CHLORIDE) = 30 %

pH TEST

Date = 27-Mar
Test= 1b

pH Of Water Before TiH2 Is Added= 4.92
pH Of Water After TiH2 Is Added= 4.82

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TiH2's Adsorbed HCl Concentration Test

PURE H2 - CHLORIDE TEST - HCl Recovers NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300

Discoloration of Glass ? Yes ☐ No ☒

START TIME= 11:40
STOP TIME= 12:20
TIME OF TEST (min)= 0.67

Date = 27-Mar
Test= 2a
Concentration NaOH (M)= 1
Sample Volume of Titrate HCL (mL)= 150
MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.11

Total Collected
Vol Impingers (mL)
Weight of TiH2 (g) 0.217 842

Weight of TiH2 Bottle Before (g)= 0
Weight of TiH2 Bottle After (g)= -0.217

Titrant		
Time	NaOH (mL)	pH
1:50	0	2.27
1:50	0.2	2.4
1:50	0.4	9.66

Volume of NaOH (mL) @ Equivalence pt. (pH=7)= 0.328

CHLORIDE Test Results from NaOH Titration

Q Equivalence	Q Equivalence	Sample Conc.	Impinger	TiH2's	TiH2's
Mol NaOH	Mol HCL	Mol/L HCL	Mol HCL	Mol HCL	g Cl
0.000328	0.000328	0.002	0.0018	0.0018	0.0653

TiH2's Wt % Cl (CHLORIDE) = 30 %

pH TEST

Date = 27-Mar
Test= 2a

pH Of Water Before TiH2 Is Added= 4.64
pH Of Water After TiH2 Is Added= 4.25

TiH2's Adsorbed HCl Concentration Test

PURE H2 - CHLORIDE TEST - HCl Recovery NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300

Discoloration of Glass ? Yes ☐ No ☒

START TIME= 11:40

STOP TIME= 12:20

TIME OF TEST (HR)= 0.67

Date = 27-Mar

Test= 2b

Concentration NaOH (M)= 1

Sample Volume of Titrate HCl (mL)= 150

MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.11

Total Collected
Weight of TiH2 (g) 0.217
Vol Impingers (mL) 842

Weight of TiH2 Bottle Before (g)= 0
Weight of TiH2 Bottle After (g)= -0.217

Titrant		
Time	NaOH (mL)	pH
2:00	0	1.96
2:00	0.2	2.27
2:00	0.4	9.94

Volume of NaOH (mL) @ Equivalence pt. (pH=7)= 0.328

CHLORIDE Test Results from NaOH Titration

Q Equivalent	Q Equivalent	Sample Conc.	Impinger	TiH2's	TiH2's
Mol NaOH	Mol HCl	Mol HCl	Mol HCl	Mol HCl	g Cl
0.000328	0.000328	0.002	0.0018	0.0018	0.0653

TiH2's Wt % Cl (CHLORIDE) = 30 %

pH TEST

Date = 27-Mar
Test= 2b

pH Of Water Before TiH2 Is Added= 4.64
pH Of Water After TiH2 Is Added= 4.25

TiH2's Adsorbed HCl Concentration Test

PURE H2 - CHLORIDE TEST - HCl Recovery NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300

Discoloration of Glass ? Yes ☐ No ☒

START TIME= 11:40
STOP TIME= 12:20
TIME OF TEST (HR)= 0.67

Date = 27-Mar

Test= 2c

Concentration NaOH (M)= 1

Sample Volume of Titrate HCl (mL)= 150

MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.15

Titrant		
Time	NaOH (mL)	pH
2:10	0	2.1
2:10	0.2	2.23
2:10	0.4	9.53

Total Collected
Weight of TiH2 (g) 0.217
Vol Impingers (mL) 842

Weight of TiH2 Bottle Before (g)= 0
Weight of TiH2 Bottle After (g)= -0.217

Volume of NaOH (mL) @ Equivalence pt. (pH=7)= 0.33

CHLORIDE Test Results from NaOH Titration

Q Equivalence	Q Equivalence	Sample Conc.	Impinger	TiH2's	TiH2's
Mol NaOH	Mol HCl	Mol/L HCl	Mol HCl	Mol HCl	g Cl
0.00033	0.00033	0.002	0.0019	0.0019	0.0657

TiH2's Wt % Cl (CHLORIDE) = 30 %

pH TEST

Date = 27-Mar
Test= 2c

Pk Of Water Before TiH2 Is Added= 4.64
Pk Of Water After TiH2 Is Added= 4.25

TiH2's Adsorbed HCl Concentration Test

PURE H2 - CHLORIDE TEST - HCl Recovery NaOH TITRATION EXPERIMENT

START TIME= 7:40
STOP TIME= 8:40
TIME OF TEST (hr)= 1.00

Discoloration of Glass ? Yes ☐ No ☒

Weight of TiH2 Bottle Before (g)= 0
Weight of TiH2 Bottle After (g)= -0.781

Total Collected
Weight of TiH2 (g) 0.781
Vol. Impurities (ml) 772

Heater Temperature (C)= 300

Date = 30-Mar
Test = 1a
Concentration NaOH (M)= 1
Sample Volume of Titrant HCl (ml) = 150
MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.15

Sample Volume of Titrant HCl (ml) = 150
MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.15

pH Vs. vol of NaOH - CHLORIDE TEST - HCl Recovery Calculation

Time	NaOH (ml)	pH
11:30	0	1.79
11:30	0.2	1.85
11:30	0.4	1.93
11:30	0.6	2.02
11:30	0.8	2.12
11:30	1	2.26
11:30	1.2	2.55
11:30	1.4	4.59
11:30	1.6	10.87

Volume of NaOH (ml) @ Equivalence pt. (pH=7)= 1.475

CHLORIDE Test Results from NaOH Titration.

Equivalents	Q Equivalents	Sample Conc.	Impinger	TiH2's	MoHCL	MoHCL	g Cl
0.00148	0.001475	0.010	0.0076	0.0076	0.0076	0.2691	

TiH2's Wt % Cl (CHLORIDE) = 34 %

pH TEST

Date = 30-Mar
Test = 1a

pH of Water Before TiH2 Is Added= 7.65
pH of Water After TiH2 Is Added= 5.65

TiH2's Adsorbed HCl Concentration Test

PURE H2 - CHLORIDE TEST - HCl Recovery NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300
 Date = 30-Mar
 Test= 1b
 Concentration NaOH (M)= 1
 Sample Volume of Titrant HCl (mL)= 150
 MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.15

Discoloration of Glass ? Yes ☐
 No ☒

START TIME= 7:40
 STOP TIME= 8:40
 TIME OF TEST (HR)= 1.00

Total Collected
 Weight of TiH2 (g) 0.781
 Vol Impingers (ml) 772

Weight of TiH2 Bottle Before (g)= 0
 Weight of TiH2 Bottle After (g)= -0.781

Time	NaOH (mL)	pH
11:45	0	1.61
11:45	0.4	1.71
11:45	0.8	1.85
11:45	1	2.07
11:45	1.2	2.23
11:45	1.4	2.94
11:45	1.6	10.89

Volume of NaOH (mL) @ Equivalence pt. (pH=7)= 1.502

Control:

CHLORIDE Test Results from NaOH Titration

Q Equivalent	Q Equivalent	Sample Conc.	Impinger	TiH2's	TiH2's
Mol NaOH	Mol HCl	Mol/L HCl	Mol HCl	Mol HCl	g Cl
0.001502	0.001502	0.010	0.0077	0.0077	0.2740

TiH2's Wt % Cl (CHLORIDE) = 35 %

pH TEST

Date = 30-Mar
 Test= 1b

pH Of Water Before TiH2 Is Added= 7.65
 pH Of Water After TiH2 Is Added= 5.65

TiH2's Adsorbed HCl Concentration Test

PURE H2 - CHLORIDE TEST - HCl Recovery NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300

Discoloration of Glass ? Yes ☐ No ☒

START TIME= 7:40
STOP TIME= 8:40
TIME OF TEST (HR)= 1.00

Date = 30-Mar
Test= 1c
Concentration NaOH (M)= 1
Sample Volume of Titrate HCl (mL)= 150
MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.11

Total Collected
Weight of TiH2 (g) 0.781
Vol Impingers (ml) 772

Weight of TiH2 Bottle Before (g)= 0
Weight of TiH2 Bottle After (g)= -0.781

Time	NaOH (ml)	pH
11:50	0	1.5
11:50	0.4	1.57
11:50	0.8	1.8
11:50	1.2	2.18
11:50	1.4	4.06
11:50	1.6	10.95

pH Vs. vol of NaOH - CHLORIDE TEST - HCl Recovery Calculation

Volume of NaOH (mL) @ Equivalence pt. (pH=7)= 1.486

General:

CHLORIDE Test Results from NaOH Titration

Q Equivalent	Q Equivalent	Sample Conc.	Impinger	TiH2's	TiH2's
Mol NaOH	Mol HCl	Mol HCl	Mol HCl	Mol HCl	g Cl
0.001486	0.001486	0.010	0.0076	0.0076	0.2711

TiH2's Wt % Cl (CHLORIDE) = 35 %

pH TEST

Date = 30-Mar
Test= 1c

pH Of Water Before TiH2 Is Added= 7.65
pH Of Water After TiH2 Is Added= 5.65

TiClx Concentration Test

Three small samples (.9 gram) were taken from one large (50 grams) quantity of contaminated TiH₂ powder. The powder was known to contain a large percentage of chlorine due to a water leak in the system at the time of collection. A different quantity of each small sample was tested for TiCl_x. Impinger water and rinse was collected from each run. Three 150 ml samples from each collection were taken and analyzed to insure repeatability of results. The results are as follows:

Test	WT% Adsorbed Cl	WT TiH₂(g)	Comment
3/30/98 1a	4%	.781	TiH ₂ had a depth of 1" in the boat. Leaving the possibility of buried TiCl _x not reacting to form HCl.
3/30/98 1b	4%	.781	The pH readings from the strip chart recorder indicate that the impingers had reached steady state.
3/30/98 1c	4%	.781	The WT% from all three of the tests are very repeatable. This repeatability indicates an accurate titration test.
3/27/98 1a	8%	.341	TiH ₂ did not completely consume the bottom of the boat. Providing a thin barrier for TiCl _x -H ₂ O interaction.
3/27/98 1b	9%	.341	The pH readings from the strip chart recorder indicate that the impingers had reached steady state.
3/27/98 1c	9%	.341	The WT% from all three of the tests are very repeatable. This repeatability indicates an accurate titration test.
3/27/98 2a	14%	.217	TiH ₂ did not completely consume the bottom of the boat. Providing a thin barrier for TiCl _x -H ₂ O interaction.
3/27/98 2b	14%	.217	The pH readings from the strip chart recorder indicate that the impingers had reached steady state.
3/27/98 2c	14%	.217	The WT% from all three of the tests are very repeatable. This repeatability indicates an accurate titration test.

The results from the TiCl_x test indicate a rise in the *detectable* Wt% of sub-chlorides, from the same powder, with decreasing sample size. There are two explanations for this occurrence. The first of which being, the large quantity of TiH₂ used in sample 3/30/98 1 a, b, and c and the second being the small amount of TiH₂ used in sample 3/27/98 2 a, b, and c.

Test 3/30/98 1 a, b, and c tested the largest sample of TiH₂ out of all three tests performed. This large sample resulted in a depth of TiH₂ (one inch) in the sample boat. This depth prevented possible sub-chlorides from interacting with the wet gas. This hypothesis was confirmed with the pH test, which indicated that residual chlorine was left over after the impingers (absorbing the HCl from the reaction between TiCl₃ and H₂O) had come to steady state. This occurrence of residual chlorine was not found in the two smaller samples.

Test 3/27/98 2 a, b, and c tested the smallest sample out of all three tests performed. The large amount of water collected from the impingers and rinse coupled with the small amount of powder tested decreased the accuracy of the test. Due to such a small amount of chlorine absorbed in the water only three titration points (0, .2, and .4 ml NaOH) were attained before all of the HCl had reacted. The chlorine WT% was shown to go down with sample 3/27/98 1 a, b, and c in which, consequently, four titration points (0, .2, .4, and .6 ml NaOH) occurred.

Test 3/27/98 1 a, b, and c presented the most accurate result out of the three. However, the powder in test 3/27/98 1 a, b, and c did not completely cover the surface of the containment boat. An even more accurate result can be obtained by adding enough powder to the boat to coat the entire inner surface while maintaining a thin layer. From the previous information it can be concluded that a .4 to .5 gram sample is a sufficient sample size for creating an accurate test.

The spreadsheets indicating the results are shown on the following page.

TiH2's TiClx Concentration Test - Sub-Chloride Test

NON-PURE H2 - SUB-CHLORIDE TEST - HCl Recovers NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300

Discoloration of Glass ? Yes ☐ No ☒

START TIME= 8:40
STOP TIME= 9:10
TIME OF TEST (HR)= 0.50

Date = 27-Mar
Test= 1a
Concentration NaOH (M)= 1
Sample Volume of Titrate HCl (mL)= 150
MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.11

Total Collected
Weight of TiH2 (g) 0.341 Vol Impingers (ml) 1036
Weight of TiH2 Bottle Before (g)= 0
Weight of TiH2 Bottle After (g)= -0.341

Time	NaOH (mL)	pH
11:30	0	3.05
11:30	0.2	10.37

Volume of NaOH (mL) @ Equivalence pt. (pH=7)= 0.106

SUB-CHLORIDE Test Results from NaOH Titration

Q Equivalence	Q Equivalence	Sample Conc.	Impinger	TiH2's	TiH2's
Mol NaOH	Mol HCl	Mol/L HCl	Mol HCl	Mol HCl	g Cl
0.000106	0.000106	0.001	0.0007	0.0007	0.0260

TiH2's Wt % Cl (SUB-CHLORIDE) = 8 %

pH TEST

Date = 27-Mar
Test= 1a

pH Of Water Before TiH2 Is Added= 4.92
pH Of Water After TiH2 Is Added= 4.82

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START TIME=	8:40
STOP TIME=	9:10
TIME #1 TEST INRI-	0.50

Date = 27-Mar

Test=	1b
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Concentration NaOH (M)= 1

Sample Volume of Titrate HCL (mL) =	150
-------------------------------------	-----

MAX FLOW RATE OF NON-PURE N2 [SCFM]-	0.15
--------------------------------------	------

Titrant

Weight of Till2 (g)	Total Collected Vol Impingers (ml)
0.341	1036

Weight of TiH2 Bottle Before (g)=	0
Weight of TiH2 Bottle After (g)=	-0.341

Volume of NaOH [mL] @ Equivalence pt. [pH=7]= 0.126

Comment: WORKED ON STABILIZING CONTINUOUS PLMETER

HW CL-35.45

<u>Equidissar</u>	<u>Equidissar</u>	<u>Sample Conc.</u>	<u>Impinger</u>	<u>TiH2's</u>	<u>TiH2's</u>
<u>Mol NaOH</u>	<u>Mol HCl</u>	<u>Mol/L HCl</u>	<u>Mol HCl</u>	<u>Mol HCl</u>	<u>g Cl</u>
0.000126	0.000126	0.001	0.0009	0.0009	0.0309

TiH2's Wt % Cl (SUB-CHLORIDE) = 9 %

Date =	27-Mar
Test=	1b

Ph Of Water Before TiH2 Is Added=	4.92
Ph Of Water After TiH2 Is Added=	4.82

TiH2's TiClx Concentration Test - Sub-Chloride Test

NON-PURE H2 - SUB-CHLORIDE TEST - HCl Recovery NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300

Date = 27-Mar

Test= 1c

Concentration NaOH (M)= 1

Sample Volume of Titrant HCL (mL)= 150

MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.15

Discoloration of Glass ? Yes ☐ No ☒

START TIME= 8:40

STOP TIME= 9:10

TIME OF TEST (HR)= 0.50

Total Collected

Weight of TiH2 (g) 0.341

Vol Impingers (ml) 1036

Weight of TiH2 Bottle Before (g)= 0

Weight of TiH2 Bottle After (g)= -0.341

Titration

Time	NaOH (mL)	pH
12:20	0	2.65
12:20	0.2	9.91

Volume of NaOH (mL) @ Equivalence pt. (pH=7)= 0.12

Comment: WORKED ON STABILIZING CONTINUOUS PH METER

SUB-CHLORIDE Test Results from NaOH Titration

Q Equivalence	Q Equivalence	Sample Conc.	Impinger	TiH2's	MW Cl-35.45
Mol NaOH	Mol HCL	Mol/L HCL	Mol HCL	Mol HCL	g Cl
0.00012	0.00012	0.001	0.0003	0.0003	0.0294

TiH2's Wt % Cl (SUB-CHLORIDE) = 9 %

pH TEST

Date = 27-Mar

Test= 1c

Ph Of Water Before TiH2 Is Added= 4.92

Ph Of Water After TiH2 Is Added= 4.82

TiH2's TiClx Concentration Test - Sub-Chloride Test

NON-PURE H2 - SUB-CHLORIDE TEST - HCl Recovery NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300

Discoloration of Glass ? Yes ☐ No ☒

START TIME= 12:20
STOP TIME= 13:00
TIME OF TEST (HR)= 0.67

Date = 27-Mar

Test= 2a

Concentration NaOH (M)= 1

Sample Volume of Titrate HCl (mL)= 150

MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.11

Total Collected
Weight of TiH2 (g) 0.217
Vol Impingers (ml) 1058

Weight of TiH2 Bottle Before (g)= 0
Weight of TiH2 Bottle After (g)= -0.217

Time	NaOH (mL)	pH
2:45	0	1.99
2:45	0.2	10.13

pH Vs. vol of NaOH - SUB-CHLORIDE TEST - HCl Recovery Calculation

Volume of NaOH (mL) @ Equivalence pt. (pH=7)= 0.125

Control:

SUB-CHLORIDE Test Results from NaOH Titration

Q Equivalence	Q Equivalence	Sample Conc.	Impinger	TiH2's	TiH2's
Mol NaOH	Mol HCl	Mol/L HCl	Mol HCl	Mol HCl	g Cl
0.000125	0.000125	0.001	0.0009	0.0009	0.0313

TiH2's Wt % Cl (SUB-CHLORIDE) = 14 %

pH TEST

Date = 27-Mar
Test= 2a

pH Of Water Before TiH2 Is Added= 4.64
pH Of Water After TiH2 Is Added= 4.25

TiH2's TiClx Concentration Test - Sub-Chloride Test

NON-PURE H2 - SUB-CHLORIDE TEST - HCl Recovers NaOH TITRATION EXPERIMENT

Heater Temperature (C)=	300	Discoloration of Glass ?	Yes	No	START TIME=	12:20
Date =	27-Mar			X	STOP TIME=	13:00
Test=	2b				TIME OF TEST (HR)=	0.67
Concentration NaOH (M)=	1	Total Collected			Weight of TiH2 Bottle Before (g)=	0
Sample Volume of Titrate HCl (mL)=	150	Weight of TiH2 for	Vol Impingers (ml)		Weight of TiH2 Bottle After (g)=	-0.217
MAX FLOW RATE OF NON-PURE H2 (SCFH)=	1.15	0.217	1058			

Titrant		
Time	NaOH (ml)	pH
2:30	0	2.06
2:30	0.2	10.13

Volume of NaOH (mL) @ Equivalence pt. (pH=7)= 0.125

SUB-CHLORIDE Test Results from NaOH Titration.

Q Equivalents	Q Equivalents	Sample Conc.	Impinger	TiH2's	TiH2's
Mol NaOH	Mol HCl	Mol/L HCl	Mol HCl	Mol HCl	g Cl
0.000125	0.000125	0.001	0.0009	0.0009	0.0313

TiH2's Wt % Cl (SUB-CHLORIDE) = 14 %

pH TEST

Date =	27-Mar
Test=	2b
pH Of Water Before TiH2 Is Added=	4.64
pH Of Water After TiH2 Is Added=	4.25

TiH2's TiClx Concentration Test - Sub-Chloride Test

NON-PURE H2 - SUB-CHLORIDE TEST - HCl Recovery NaOH TITRATION EXPERIMENT

Heater Temperature (C)=	300	Discoloration of Glass ?	Yes ☐ No ☒	START TIME=	12:20
Date =	27-Mar			STOP TIME=	13:00
Test=	2c			TIME OF TEST (HR)=	0.67
Concentration NaOH (M)=	1	Total Collected		Weight of TiH2 Bottle Before (g)=	0
Sample Volume of Titrant HCL (mL)=	150	Weight of TiH2 (g)	0.217	Weight of TiH2 Bottle After (g)=	-0.217
MAX FLOW RATE OF NON-PURE H2 (SCFH)=	1.15	Vol Impingers (ml)	1058		

Titrant		
Time	NaOH (ml)	pH
2:20	0	2.34
2:20	0.2	9.85

Volume of NaOH (ml) @ Equivalence pt. (pH=7)= 0.125

SUB-CHLORIDE Test Results from NaOH Titration

Q Equivalence	Q Equivalence	Sample Conc.	Impinger	TiH2's	TiH2's
Mol NaOH	Mol HCL	Mol/L HCL	Mol HCL	Mol HCL	g Cl
0.000125	0.000125	0.001	0.0009	0.0009	0.0313

TiH2's Wt % Cl (SUB-CHLORIDE) = 14 %

pH TEST

Date =	27-Mar
Test=	2c
pH Of Water Before TiH2 Is Added=	4.64
pH Of Water After TiH2 Is Added=	4.25

TIH2's TiClx Concentration Test - Sub-Chloride Test

NON-PURE H₂ - SUB-CHLORIDE TEST - HCl Recovery, H₂OH TITRATION EXPERIMENT

Discoloration of Glass? Yes No

START TIME=	11:06
STOP TIME=	12:06
TIME OF TEST INEL-	1.00

Total Collected	
Weight of TiH ₂ (g)	Vol Impingers (ml)
0.781	1152

Weight of TiH2 Bottle Before [q]=	0
Weight of TiH2 Bottle After [q]=	-0.781

pH Ys. vol of NaOH - SUB-CHLORIDE TEST - HCl Recovery Calculation

Volume of H_2O (mL) @ Equivalence pt. (pH=7)=

Comment: SLIGHT AMOUNT OF NON-BEASTED TIME LEFT IN THE BOAT.

PH TEST ON THE POWDER, AFTER SUB-CHLORIDE TEST, RESULTED IN A DROP FROM 11.55 TO 11.555

SUB-CHLORIDE Test Results from NaOH Titration.

5.2.HIL

THI2.3

Impinger

170131Z JUL 67

31 Feb 1965

Prüfungsausschuss

www.pearsoned.com

$$\text{TiH}_2\text{'s Wt \% Cl (SUB-CHLORIDE)} = \frac{4}{4} \%$$

ISAIL HO

Date =	30-Mar
Test=	1a

ppm of Water Before TmH2 Is Added=	7.65
ppm of Water After TmH2 Is Added=	5.65

App B-38

TiH2's TiClx Concentration Test - Sub-Chloride Test

NON-PURE H2 - SUB-CHLORIDE TEST - HCl Recovery NaOH TITRATION EXPERIMENT

Heater Temperature (C)= 300

Date = 30-Mar

Test= 1c

Concentration NaOH (M)= 1

Sample Volume of Titrant HCL (ml)= 150

MAX FLOW RATE OF NON-PURE H2 (SCFH)= 1.15

Discoloration of Glass? Yes ☐ No ☒

START TIME= 11:06

STOP TIME= 12:06

TIME OF TEST (HR)= 1.00

Total Collected

Weight of TiH2 (g) 0.781

Vol Impingers (ml) 1152

Weight of TiH2 Bottle Before (g)= 0

Weight of TiH2 Bottle After (g)= -0.781

Time	NaOH (ml)	pH
1:50	0	2.14
1:50	0.2	10.25

pH Vs. vol of NaOH - SUB-CHLORIDE TEST - HCl Recovery Calculation

Volume of NaOH (ml) @ Equivalence pt. (pH=7)= 0.121

SUB-CHLORIDE Test Results from NaOH Titration.

Q Equivalence	Q Equivalence	Sample Conc.	Impinger	TiH2's	MW Cl-35.45	TiH2's
Mol NaOH	Mol HCL	Mol/L HCL	Mol HCL	Mol HCL		g Cl
0.000121	0.000121	0.001	0.0009	0.0009		0.0329

TiH2's Wt % Cl (SUB-CHLORIDE) = 4 %

pH TEST

Date = 30-Mar

Test= 1c

pH Of Water Before TiH2 Is Added= 7.65

pH Of Water After TiH2 Is Added= 5.65

Comment: SLIGHT AMOUNT OF NON-REACTED TiH2 LEFT IN THE BOAT.

pH TEST ON TiH2 POWDER, AFTER SUB-CHLORIDE TEST, RESULTED IN A DROP FROM PH-7.65

TOP1-5.65

pH Test

A simple pH test was performed on the powder of each sample after the powder was allowed to completely react with the wet gas. A real time pH strip chart connected to the impingers indicated this point. The results are as follows.

<u>Test</u>	<u>Water pH Before TiH₂ Was Added</u>	<u>Water pH After TiH₂ Was Added</u>	<u>Comment</u>
3/30/98 1 a, b, & c	7.65	5.65	The drop in pH indicates possible residual sub-chlorides or adsorbed HCl.
3/27/98 1 a, b, & c	4.92	4.82	There was virtually no change in pH indicating that all of the chlorine has been removed.
3/27/98 2 a, b, & c	4.64	4.25	There was virtually no change in pH indicating that all of the chlorine has been removed.

The results are indicated on the spreadsheets containing the adsorbed HCl and the sub-chloride tests.

Jell Capsule Test

The jell capsule test indicates that the weight percent of chlorine (from sub-chlorides and adsorbed HCl) is around 42%. This coincides with the 30 to 35 WT% adsorbed HCl and 8 to 9 additional WT% TiCl₄.

The spreadsheet indicating the result is shown on the following page.

TiH2's TiClx, Clx Concentration - NaOH Titration Test

Total Chlorine Concentration Jell Cap NaOH Titration Experiment

Date = 1-Apr
 Test= 1
 Concentration NaOH (M)= 1

Weight of Jell Cap (g)= 0
 Weight of Jell Cap + TiH2 (g)= 0.102
 Weight of TiH2 (g)= 0.102

Time	Titrant NaOH (mL)	pH
4:30	0	2.2
4:30	0.2	2.32
4:30	0.4	2.48
4:30	0.6	2.88
4:30	0.8	4.55
4:30	1	4.7
4:30	1.2	6.44
4:30	1.4	9.73

Volume of NaOH (mL) @ Equivalence pt. (pH=7)= 1.23

Test Results from NaOH Titration Test

@ Equivalence @ Equivalence MW Cl= 35.45

Mole NaOH	Mole HCL	g Cl
0.00123	0.00123	0.044

Wt % Cl (TOTAL CHLORIDES) = 42.7 %

7.0 Glass Ware and Instrumentation

7.1 Assembly

The assembly drawing and the top and side view drawings on the next three pages lay out all of the glass ware and instrumentation used in the testing procedure for the TiH_2 powder. Many of the individual parts were made by a glass blower and cannot be found in a catalog. For this reason, each individual part in the assembly drawing has been labeled with letters A through T. Cad drawings and/or manufacturers with a part number have been listed in alphabetical order according to the letter designated to that specific part by the assembly drawing. With this information a complete and accurate re-creation of the assembly can be achieved.

IMPINGERS, Ph PROBES, & STRIP CHART

TOP VIEW

OVEN AND CONTROLLER

ASSEMBLY

Assembly Components

Assembly Top View

Assembly Side View

PURPOSE: USED TO AID IN DRAINING
IMPINGER.

RETAINS RASCHING RINGS WHILE
LETTING THE WATER DRAIN OUT

Rasching Rings Retainer View

PURPOSE: USED TO AID IN DRAINING
IMPINGER.

RETAINS WATER IN IMPINGER STEM
DURING DRAINING.

Impinger Stem Plug View

PURPOSE: USED TO CONNECT IMPINGERS.

FITS ONTO THE SECOND IMPINGER INLET
STEM.

#2 Impinger Connector View

PURPOSE: USED TO CONNECT IMPINGERS.

FITS ONTO THE FIRST IMPINGER OUTLET
STEM.

#1 Impinger Connector View

PURPOSE: USED TO CONNECT FIRST
IMPINGER TO INLET TUBE.

FITS ONTO THE FIRST IMPINGER INLET
STEM.

#1 Impinger Inlet Tube Connector View

PURPOSE: USED TO BUBBLE GAS THROUGH A WATER SAMPLE.

FITS AND SECOND IMPINGER ARE IDENTICAL.

#1 & #2 Impinger View

G

PURPOSE: USED TO SUPPORT pH
SENSOR ONTO IMPINGER.

FIRST AND SECOND IMPINGER SENSOR
SUPPORTS ARE IDENTICAL.

PROBE IS SEALED WITH SILICONE
RUBBER.

#1 & #2 Impinger pH Sensor Support View

pH Sensor and Strip Chart Recorder View

PURPOSE: USED TO AID IN DRAINING
IMPINGER.

RETAINS WATER IN THE PROBE INSERT
SECTION OF THE IMPINGER DURING
DRAINING.

pH Sensor Impinger Support View

PURPOSE: TO HOLD UP THE
GAS BUBBLES AND INCREASE
RESONANCE TIME.

THE RINGS ARE PACKED
INTO BOTH IMPINGERS UP
TO BOTTOM OF THE pH
PROBE.

Rasching Rings View

Dry H2 Gas Cooling Chamber View

PURPOSE: USED AS A COOLING CHAMBER FOR THE WET H₂ GAS - NO MEL.
 THE 3" BUSH LOCATED IN THE MIDDLE ARE FILLED WITH WATER AND ARE USED
 TO COOL THE SUB-CHAMBERS AND PROVIDE A LONGER RESIDENCE TIME FOR
 THE GAS.

Wet H₂ Gas Cooling Chamber View

PURPOSE: TO SWITCH GAS FLOWS FROM ONE SET OF IMPINGERS TO THE OTHER.

Bi-directional Valve View

PURPOSE: USED TO SIZE THE CYLINDRICAL REACTOR TO HOLD THE POWDER ON A BOAT AND THE GAS

Reactor View

PURPOSE: TO SUPPORT AND ELEVATE OVEN TO
ALLOW CONDENSATION IN THE FOLLOWING TUBING
TO RUN INTO IMPINGERS.

Cylindrical Heater Support View

P

SIDE

TOP

PURPOSE: TO HOLD THE TiH_2 SAMPLE IN THE OVEN.

ALSO USED TO HOLD 1M HCl & 9.1M TiCl_4 DURING CALIBRATION.

TiH₂ Boat View

PURPOSE: TO RAISE THE POWDER AND SURROUNDING ATMOSPHERE TO 300 C. ALLOWS FOR HOT TiH_2 , HCl , TiCl_x + WET AND DRY H_2 INTERACTION.

MARSHALL HELIUM DIFFUSION FURNACE
 MODEL # SLM-1
 SERIAL # 189
 T MAX=400C

Cylindrical Heater View

R

PURPOSE: TO MAINTAIN TEMPERATURE AT
300 C IN THE OVEN.

WATLOW SERIES 965 CONTROLLER

Watlow 965 Controller View

PURPOSE: ALLOWS AN INLET FOR WET H₂
NEBULIZED WITH WATER.

Wet Hydrogen Injection Port View

PURPOSE: ALLOWS ARGON PURGE AND DRY HYDROGEN INTO THE SYSTEM.

Dry Hydrogen & Argon Injection Port View

References

- [1] Journal of Metals "*Recent Advances in the Thermohydrogen Processing of Titanium Alloys*" (Overview), O.N. Senkov, J.J. Jonas, and F.H. Froes, July 1996, pp. 42-47.