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**Design of a Reactor System for
the Synthesis of Titanium Diboride**

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CHEMISTRY DIVISION

DESIGN OF A REACTOR SYSTEM FOR THE SYNTHESIS OF TITANIUM DIBORIDE

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1. SUMMARY

Titanium diboride is a hard, refractory material with potential wide industrial uses, including electrode coatings and machine-tool surfaces. For example, TiB_2 is being investigated as an inert carbon cathode coating for Hall cells, which are used in the production of aluminum. However, titanium diboride's utility is compromised by impurities such as oxides present in most commercial TiB_2 powder, which cause the coating to disintegrate at grain boundaries. Thus, a method to prepare high-purity TiB_2 is actively sought.

A laboratory-scale reactor system has been designed and is presented here to produce pure TiB_2 powder by chemical vapor decomposition according to the following reaction:

The system was designed to produce 4 g/h of TiB_2 and to retain maximum versatility of the operating variables over a wide variety of operating possibilities. An earlier thermodynamic study on the reaction (1) suggested that the reaction is favored at high temperature and reduced pressure, with excess hydrogen in the feed.

Based on the Besmann study (1), the reactor was designed to be an alumina tube 3-3/8 in. in ID x 30 in. long, capable of operating at a maximum temperature of 1700 K and at pressures ranging from 1 torr to atmospheric. The feed is preheated in the entry tube by an electrical resistance wire. A novel feature of this design is that Cl_2 gas in the feed provides a flame in the reactor, supplying the heat of reaction directly to the reactants. The region within the H_2 - Cl_2 flame will be at a substantially higher temperature than the surrounding gas or the reactor walls. Thus, it is anticipated that homogeneous nucleation will be favored.

Detailed sketches and equipment selection were completed in preparation for construction of the apparatus. The cost of the system, including feed and product collection systems, plus the reactor, was estimated to be about \$24,500 at current (1981) prices.

Finally, an experimental plan to evaluate the performance of the system is presented, along with a suggested analytical procedure for the powder product and suggested system startup and shutdown procedures.

2. INTRODUCTION

2.1 Background

Titanium diboride (TiB_2), a very hard, refractory material (melting point, $\sim 2800^\circ\text{C}$), has wide industrial application. Its resistance to corrosion and chemical attack and its hardness make it an excellent protective coating, for example, as a carbon-cathode coating in the Hall process of aluminum electrolysis (7). Possessing high thermal and electrical conductivities, the diboride coating reduces appreciably the electrical demand of the process, which governs the economics of the Hall process. However, the use of TiB_2 is limited by corrosion at the grain boundaries, which causes disintegration of the electrode. Oxide impurities present in all commercial TiB_2 powders may cause this corrosion. Other commercial applications include cutting-tool surfaces and the coating of parts which see erosive service, such as in coal-liquefaction plants. Currently it is commercially produced by a carbothermic reduction method in which the oxides of titanium and boron are reduced by carbon to give TiB_2 at high temperature by the following reaction:

This method leaves solid impurities such as titanium carbide, boron carbide, and unreacted oxides in the product.

Alternatively, it can be prepared by the thermochemical reduction of titanium tetrachloride and boron trichloride by hydrogen at elevated temperatures. Subsequent deposition of the product on a heated substrate by heterogeneous nucleation (1) occurs by the following overall reaction:

This method, known as chemical vapor deposition (CVD), is believed to produce a product of higher purity because only the solid diboride condenses from the gas. When powders are desired, the solid layer must be ground from the substrate to a powder. However, the extreme hardness of TiB_2 causes impurities to be introduced during the grinding step. This could be avoided if reaction (2) can be effected in the gas phase by homogeneous nucleation, thus forming TiB_2 powder directly. This method, which has been used successfully for producing UO_2 powder by chemical vapor decomposition (4), should produce high-purity TiB_2 . Since this approach has not been attempted, and since it shows substantial promise of being applicable, a design is required before a system can be built.

2.2 Objectives

The objective of this study was to design a reactor system to synthesize TiB_2 powder directly in the gas phase by homogeneous nucleation. Specific objectives included:

1. Design the reactor system, including all parts that are to be fabricated.
2. Compile a list of items to purchase, proposed vendors, and current prices.
3. Estimate the construction cost, including materials, fabrication, and assembly.
4. Determine operating limits for all the system variables and propose an experimental plan to test the system.
5. Investigate analytical methods for product examination.

3. DESIGN CRITERIA

The reactor system was designed to produce 4 g of TiB_2 per hour. Since the powder is to be produced by homogeneous nucleation in the gas phase, reaction methods must be found to enhance such homogeneous nucleation and minimize heterogeneous nucleation on a substrate, such as the reactor walls. In addition, the system must be sufficiently flexible to permit controlled variation of the independent variables over wide operating ranges. These constraints directed investigation to the areas described below.

3.1 Operating Variables

The operating variables include temperature, pressure, reactant feed rates, and feed compositions. Operating ranges for these variables were calculated from the given production rate and thermodynamic data. Figure 1 shows the results of a thermodynamic study performed by Besmann and Spear (1). In Fig. 1a, the equilibrium conversion to TiB_2 , defined as the mole percentage of TiCl_4 in the feed converted to TiB_2 , is plotted as a function of temperature at various pressures. Feed compositions are given in terms of the boron-to-titanium $[B/(B + Ti)]$ and the chlorine-to-hydrogen $[Cl/(Cl + H)]$ molar ratios. Percentage conversion increases with increasing temperature (constant pressure) and decreases with increasing pressure (constant temperature). Thus, equilibrium production of TiB_2 is favored by high temperature and low pressures. In Fig. 1b, the equilibrium conversion is plotted as a function of temperature at a fixed pressure and constant $B/(B + Ti)$ ratio for three values of $Cl/(Cl + H)$ ratio. Percentage conversion increases with increasing temperature [constant $Cl/(Cl+H)$]

Adapted from data by Besmann
and Spear (1)

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EQUILIBRIUM CONVERSION VS TEMPERATURE

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but decreases with increasing $\text{Cl}/(\text{Cl} + \text{H})$ ratio (constant temperature). Thus, equilibrium is favored at low $\text{Cl}/(\text{Cl} + \text{H})$ ratios, indicating that excess hydrogen should be added to the feed.

Besmann also showed that the $\text{B}/(\text{B} + \text{Ti})$ ratio in the feed affects the composition of the solid obtained. Any BCl_3 in excess of stoichiometric amount [$\text{B}/(\text{B} + \text{Ti}) > 2/3$] results in formation of elemental boron, which contaminates the product. Alternatively, any TiCl_4 in excess of the stoichiometric amount [$\text{B}/(\text{B} + \text{Ti}) < 2/3$] results in formation of TiCl_3 . TiCl_3 clogs operating equipment as the solid condenses when the product gases are cooled, but this property means that it can be easily be removed from TiB_2 product by vaporization. Of the two products it is obviously preferable to form small amounts of TiCl_3 , which will vaporize during subsequent powder processing. Therefore, the indication of a slight excess of TiCl_4 is probably prudent.

Using Besmann's thermodynamic considerations and considering the constraints imposed by construction material properties (Sect. 3.3), the following operating conditions were established as a design basis:

Temperature: 1700 K (maximum operating temperature)

Pressure: 0.3 atm

$\text{Cl}/(\text{Cl} + \text{H})$: 1/4 (three times molar excess hydrogen)

$\text{B}/(\text{B} + \text{Ti})$: 2/3 (stoichiometric ratio)

The system was designed so that the operating conditions could be adjusted over a wide range. For example, the operating temperature can be varied from room temperature to a maximum of 1700 K, and the pressure from 1 torr to atmospheric.

3.2 Preparation Methods

Flame processes have been used to produce refractory powders competitively with conventional methods using heated reactors (5, 6, 12). The latter favors heterogeneous nucleation on the heated reactor wall, which is hotter than the reactant gases. In flame processes, however, the reactant gases are directly heated by a flame produced from combustible feed gases. The reactor wall serves as insulation against heat loss and can be held at a lower temperature. Thus, homogeneous nucleation in the flame is kinetically favored. A unique feature of this design study is this flame-reactor concept, which uses a $\text{H}_2\text{-Cl}_2$ flame to provide the necessary heat of reaction to produce TiB_2 .

3.3 Choice of Structural Materials

Alumina was chosen as the structural material for the preheater-reactor system. Alumina resists high temperatures (up to 2100 K) and the corrosive gases used in the reaction. In addition, it is inexpensive and readily available. Stainless steel, which is corrosion resistant to the reaction materials at low temperatures, is specified for all piping and valves in the low-temperature portions of the equipment.

4. DESIGN RESULTS AND DISCUSSION

4.1 Overall Design

The reactor system is designed to produce TiB_2 powder at the rate of 4 g/h from gaseous TiCl_4 , BCl_3 , and H_2 . As shown in Fig. 2, the production system consists of four subsystems, including the reactor feed, product collection, and disposal systems. In the following sections, the design and operation of these subsystems is described in detail, along with cost and utility estimates. The remainder of the section is an overall description of the system.

In the feed system, TiCl_4 , which is a liquid at room temperature, is vaporized and mixed with the gaseous Cl_2 and BCl_3 before it enters the preheater tube. Hydrogen gas flows through the annulus outside the preheater tube. The flow of each gas is monitored by a mass flow meter. All gases are heated to reaction temperature by an electrical resistance wire wrapped around the preheater tube. The gases meet at the preheater exit. Hydrogen, forming the exterior of the reaction flame, diffuses into the reaction mixture. This provides a protective blanket between the reactor wall and the reactant mixture. This suppresses heterogeneous nucleation and promotes homogeneous nucleation by preventing the reacting gases from contacting the reactor wall. The TiB_2 powder leaves the reaction chamber with the unreacted feed gases and HCl , while any TiCl_3 that is formed condenses as a solid on the cooled surfaces at the outlet end of the reactor. The product stream, at about 200°C , then enters the collection traps, where the solid TiB_2 is separated from the gases. Two interchangeable traps allow continuous operation while the powder is sampled or removed.

The remaining gases, mostly unreacted H_2 , HCl , and unreacted feed, pass through a mass flow meter, a vacuum pump (used to maintain the system pressure), and a packed-column scrubber. A gas-sample port is available in the line before the vacuum pump. The gas from the scrubber, which is mainly hydrogen, is mixed with methane and air and sent to a burner. The burner-product gases are vented.

4.2 Reaction System

The reaction system consists of a preheater, a reaction chamber, and a cooling section, which are shown in detail in Figs. 3 and 4. The system is contained in an alumina tube, 3-3/8 in. in ID (3-3/4 in. OD) by 55 in. long, the reactor portion of which is encased in an insulated furnace which provides a constant wall temperature. The portion of the tube containing the preheater is cooled by natural convection, while a water jacket cools the portion after the reaction chamber.

The material of choice for all tubes and internal parts of the reactor-preheater system is alumina, which can withstand the high temperature (1700 K) and corrosive attack by all the materials used or produced in this process. The tubing and fittings in the cooler sections at the ends of the reactor are of stainless steel, while Viton rubber is used for the vacuum seals at each end of the reactor.

4.2.1 Preheater

The preheater, located inside a cylindrical housing, 3-3/8 in. in ID, consists of two concentric tubes, the inner having a 7/16 in. ID and a 25-mil wall thickness, the outer having a 1 in. ID and a 25-mil wall thickness (see Figs. 4 and 5). Alumina tubes of this size are not commercially available; hence, they must be purchased as stock with the correct inside diameter and ground to the proper wall thickness. Hydrogen flows through the tube annulus, and the other three gases flow through the inner tube. The two tubes are sized such that the two streams have equal linear velocities to reduce eddies and turbulence at the point where the two streams meet (calculations are in Appendix 11.2.2). When the two streams enter the reactor, the hydrogen envelopes the chlorides, providing a gaseous blanket to prevent reaction on the wall of the reactor.

The preheater must supply 500 W of power to heat the gases to 1700 K (the maximum operating temperature) and to compensate for heat losses to the atmosphere within the preheater (Appendix 11.2.2). A 28-AWG (American wire gauge) molybdenum resistance heating element, wrapped around the last 6 in. of the outside wall of the inner preheater tube, provides this heat (Figs. 4 and 5). This constriction allows the molybdenum element to see only a H_2 atmosphere, preventing rapid oxidation at high temperature. The temperature of the preheater gas is approximately measured by a thermocouple placed in a well on the preheater wall. This temperature may be lower than the preheater gas temperature due to heat losses by radiation from the preheater wall.

Three concentric, cylindrical, alumina radiation shields reduce heat losses from the preheater (Figs. 4 and 5). In addition, thirteen disk-shaped alumina radiation shields are placed normal to the axis of the preheater anterior to the heating coil (Figs. 3 and 4). These shields protect the front inlet wall of the outer casing from reaching high

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EXPLODED VIEW OF REACTOR-PREHEATER			
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NOTE: All dimensions are in inches.
All tube dimensions refer to inside diameters.

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PREHEATER DIMENSIONS			
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temperatures. In addition, the outer casing is cooled by dissipating heat to the atmosphere by radiation and natural convection. This maintains the temperature of the end wall of the outer casing below 200°C. This low temperature is required to prevent degradation of the Viton rubber vacuum seals. Cooling jackets are placed on the inner and outer preheater tubes before they enter the outer casing to ensure that their temperatures are also below 200°C.

The preheater itself may be dismantled and removed from the outer casing (Fig. 4) and disassembled into four sections: the outer casing with a cylindrical radiation shield and entrance cone; an outer preheater tube with the end wall of the reactor housing, thirteen disk-shaped radiation shields, and a thermocouple well; an inner preheater tube with the preheater winding and cooling coil; and finally an outlet well to the reactor housing with its four radiation shields. The two-end walls are vacuum-sealed by removable Viton rubber seals. The seals may be O-rings or gaskets. The specification of the final item can be relatively simple and will take place during construction. Viton rubber is recommended for this purpose because it retains its sealing properties up to 200°C and will resist attack by the reactants in our system up to that temperature.

4.2.2 Reaction Chamber

The reaction chamber is contained in the same outer housing as the preheater, where the outer housing is the outer wall of the reactor. The hydrogen stream exits the preheater tube just before the chloride stream, thus creating a hydrogen blanket between the reactor wall and the chloride stream, preventing TiB_2 diffusion to the wall. This suppresses heterogeneous nucleation at the wall and enhances homogeneous nucleation in the gas phase.

A cone-shaped insert is placed at the reactor inlet to prevent the formation of a stagnant zone with a backflow eddy. Details are shown in Fig. 5. Holes 1/8 in. in diameter are drilled in the cone, near the outer edge, to allow evacuation of the preheater and to provide entrance for an extra hydrogen-gas blanket to protect the reactor wall, if necessary. This gas can be introduced into the port marked "Future Use" (Fig. 3).

The reaction zone is 31-5/8 in. long and 3-3/8 in. in ID (3-7/8 in. OD), and was sized using the kinetics of Besmann and Spear (Appendix 11.2.3). These kinetics apply for heterogeneous nucleation, and may not approximate the kinetics of homogeneous nucleation, thus the reactor was conservatively designed. The wall of the reaction zone will be maintained at a constant temperature by a tubular furnace around the reactor. The temperature inside the reactor wall will be measured by a thermocouple in a well cemented to the inside of the reactor wall.

NOTE: All dimensions are in inches.

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PREHEATER-REACTOR INTERFACE

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FIG.
6

Radiation shields are placed at the outlet of the reactor to reduce the heat loss from the furnace. The shields consist of four parallel plates, 3-3/4 in. long, attached to the end plate of the outer housing (see Figs. 3 and 7). This reactor end plate is also removable along with Viton rubber seals; hence a cooling coil is placed on the outer casing to cool the end plate to 200°C. This also permits condensation of any TiCl_3 which might be formed as a byproduct of the reaction onto the last 4 in. of the casing and radiation shields. Rapid cooling of the reaction mixture also stops the reaction, thus preventing the reverse reaction from occurring.

4.3 Reactant Feed System

The four reactants enter the preheater as gases. Since TiCl_4 is a liquid at ambient temperature, a vaporizer must be specified. The TiCl_4 vaporizer, a 1-liter stainless-steel container on a hot plate, will operate at an equilibrium pressure of 2 atm abs. and a temperature of 164°C. The 1-liter volume provides sufficient TiCl_4 for 10 h of operation while still allowing for a large vapor volume. This avoids significant pressure fluctuation of the system during vapor draw-off. The specified hot plate is rated at 800 W and is a standard laboratory item.

The feed rates of the four reactant gases are controlled by bellows-type metering valves and are monitored by mass flow meters. A transducer is placed on each of the four feed lines, and the flow rates are displayed and recorded continuously. The mass flow meters offer a distinct advantage over rotameters in that they measure the mass flow rate and require no compensation for gas temperature and pressure.

Both the hydrogen and chlorine feed lines will have flash arrestors to prevent propagation of any flame in the lines and to serve as check valves. The tubing, valves, and flow transducers are specified to be 1/4-in. stainless steel with Swagelok connections. If condensation of TiCl_4 should occur in the feed lines, as indicated by mass flow meter fluctuations, the feed lines will be wrapped with heating tape and insulation.

4.4 Collection System

It is expected that submicron size TiB_2 powder will be produced. This finely divided powder is removed from the gas stream in a low-pressure collector. The gas stream carrying the powder exits the reactor through a regulating valve. This valve maintains the reactor pressure typically near 200 torr and the collection-system pressure near 1 torr. Two solids collectors in parallel are used alternatively so that solids production can be monitored during continuous operation. The gas/solid product stream enters the collection trap (Fig. 8) through a tube

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END VIEW OF REACTOR OUTLET

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FIG.

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KAE

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COLLECTION TRAP

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FIG.
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extending to the bottom of the collector. The abrupt reversal of direction of the gas stream causes deposition of the powder by a combination of electrostatic and inertial forces. For particles in this size range, these forces become significant only if the pressure in the collectors is less than 20 torr. The exhaust gases exit through a recording mass flow meter, a vacuum pump, and another regulating valve.

A sample port, before the vacuum pump, allows gas sampling to be batch-wise with a collection bomb, or continuous using on-line instrumentation. The vacuum pump must be rated for 2800 liter/min at pressures less than 0.1 torr (Appendix 11.2.8). Two ball valves are used to isolate each collector and the vacuum pump or reactor during off-line operations concerning the collectors. A union between the two ball valves permits collector removal without contamination of either the reactor system or the collector. In addition, an inert-gas line can be used to overpressure each collector. This prevents leakage of air into the collector during transfer to a glove-box. The exit lines from the reactor are 0.5-in.-ID stainless steel tubing connected to stainless steel valves with TFE packing and Swagelok fittings. Efficient solids collection with this type of system has been demonstrated in previous studies (4).

4.5 Exhaust-Gas Disposal System

The exhaust gas (primarily H_2 and HCl) is disposed of by absorbing the hydrogen chloride in water and burning the hydrogen. The unconverted reactants $TiCl_4$ and BCl_3 will be absorbed in the scrubber. After leaving the vacuum pump, the gases pass through a packed column water scrubber, where the HCl and other water-soluble gases are removed. The water flow rate of 33 liter/h gives a 0.1 M HCl effluent if the maximum amount of HCl is formed and absorbed. The column diameter, allowing a safety factor for plugging and flooding, is 4 in. (10.2 cm); the column height is 18 in. (46 cm); and the column packing is 0.5-in. ceramic Raschig rings (see calculations in Appendix 11.2.7).

The absorption of $TiCl_4$ and BCl_3 is almost certainly associated with hydrolysis. Therefore fast complete absorption of these species is expected. Further study of the material balance on these compounds will be needed when the equipment is put into operation. The scrubber exhaust, primarily hydrogen, is mixed with methane and air and is oxidized in a burner. A platinum gauze placed on top of the burner ignites the hydrogen in the event that the air/methane pilot is extinguished. The burned gases are exhausted through a fume hood.

4.6 Utility Requirements

The utility requirements include exhaust-gas ventilation, cooling and scrubber water, methane for the exhaust burner, and electrical power. The TiB_2 production system must be adequately ventilated in a walk-in or standard

California fume hood. The exhaust gas is primarily air and water vapor, hence, special ventilation procedures are unnecessary; however, to ensure operator safety and to locate leaks, a chlorine detector should be installed in the hood.

Tap water can be used for cooling and scrubbing. The scrubber waste stream, mainly dilute HCl, can be drained into a laboratory sink. Methane for the exhaust burner is available in most laboratories, or bottled gas can be used. Two electrical power lines are required: a 120-V line to operate the flow controllers, and a 230-V line for the vacuum pump and furnace.

4.7 Cost Estimation

The purchase cost of the equipment, including fabrication, is \$24,500 (May 1981 dollars, as calculated in Appendix 11.3). As shown in Table 1, the preheater-reactor system is the most expensive subsystem at \$9900.

Table 1. Cost Estimate of Equipment

Feeding System	\$ 3,900
4 metering valves	
4 mass flow meters with recorders	
2 flash arresters	
vaporizer	
Preheater-Reactor System	9,900
1 furnace and controller	
1 Variac	
alumina tubes and parts	
construction	
Collection-Disposal System	8,500
1 vacuum pump	
1 mass flow meter with recorder	
3 pressure gauges	
valves	
Miscellaneous Parts and Contingency	<u>2,200</u>
Total System Cost	\$ 24,500

This will include parts and assembly, assuming that the parts are purchased ready to assemble with minimal fabrication required. Fabrication requires about 3 man-days for both an electrician and pipefitter. The feeding system costs \$3900 for the major pieces of equipment, including valves, mass flow meters, and the vaporizer. The collection and disposal system

costs \$8500, \$6000 of which is for the vacuum pump. The remainder is for valves, pressure gauges, flow transducer, and recorder. A contingency and miscellaneous parts cost of \$2200 is included to arrive at the total of \$24,500. Additional expenses may be incurred if a fume hood is not available [\$5000 purchase cost for a 6-ft California hood, plus \$2500 for installation (3)], or if a 240-V power line is not available [\$500 purchase cost for a transformer (3)]

Operating cost, excluding labor, is estimated from the feed-material cost, as shown in Table 2. The operating cost for a hundred 8-h runs at the design flow rate is \$4654 (ultra-high-purity chlorine) or \$7505 (research-grade chlorine). Ultra-high-purity chlorine is much less expensive, with a minimal loss in purity (99.96% vs 99.9%). The cost per 8-h run, crediting the excess feed materials, is \$42.96 (ultra-high purity) or \$70.39 (research grade).

Table 2. Cost of Reactants
(One hundred 8-h runs)

Feed	Unit Size/Unit Quantity		Total Cost	Cost/Run
H ₂ (Matheson purity)	215 ft ³	11	\$ 2244.00	\$ 21.23
BCl ₃	100 lb	1	1325.00	11.45
TiCl ₄	1.5 kg	22	936.10	9.04
Cl ₂ (research purity 99.96%)	100 liter	20	3000.00	28.67
Cl ₂ (ultra-high purity 99.9%)	15 lb	1	149.00	1.24
Total (research Cl ₂)			\$ 7505.10	\$ 70.39
Total (ultra-high Cl ₂)			\$ 4654.10	\$ 42.96

NOTES: All materials will be gases purchased from Matheson, except TiCl₄, which is a liquid and purchased from Aldrich.

Each run will use the design flow rate of gases, assuming that one hundred 8-h experiments are completed.

H ₂	3.20 mol/h
Cl ₂	0.10 mol/h
TiCl ₄	0.21 mol/h
BCl ₃	0.42 mol/h

5. OPERATING DETAILS OF THE SYSTEM

5.1 Procedure

To ensure operation safety and product purity, care must be taken during system startup and shutdown. To start up the system all the valves except the feed valves and those on the inert-gas lines are fully opened. The vacuum pump is then started to evacuate the system. Next, the methane flow is started and the exhaust burner lit. Then the scrubber and cooling-jacket water flows are started. This must be done before any heat is applied to the system to avoid damage to the vacuum seals. The furnace is then started, along with the H_2 feed and preheater. Hydrogen must be flowing whenever the preheater is hot to prevent rapid oxidation of the wire by any oxygen that might be present.

Once the entire system is up to temperature, one of the two collection traps is isolated from the system to prevent contamination during startup; then the feeds are started. The regulating valve on the outlet of the reactor should be adjusted to the desired reactor pressure. Overheating and melting of the reactor wall cannot occur because the heat losses through the reactor wall are much greater than the heat of reaction of H_2 and Cl_2 (Appendix 11.2.4). Finally, the $TiCl_4$ and BCl_3 flow are adjusted to the desired feed rates. When the system is at steady state, the collection traps are interchanged. Pure TiB_2 now collects in the fresh trap and the contaminated trap can be cleaned for later use. To prevent pressure surges in the system, a fresh collection trap should be first opened to vacuum, then opened to the reactor and the second trap isolated from the reactor and evacuated to remove gaseous impurities. The collector is then isolated from the vacuum pump and slightly overpressured with argon. Thus, a small leak in the system will result in an argon outflow from the collector, preventing contamination. It is imperative that the TiB_2 powder never be exposed to air. It is probably pyrophoric. Once isolated, the collector can be placed in a glove box with an argon atmosphere for examination and testing.

System shutdown is essentially the opposite of startup. The $TiCl_4$, BCl_3 , and Cl_2 feeds are stopped. The preheater is turned off and allowed to cool along with the reactor furnace. When the system is near room temperature, the cooling-jacket water, vacuum pump, and hydrogen are shut off. The vacuum pump, solids collectors, and reactor are isolated and overpressured with argon to prevent contamination from the atmosphere. The reactor is isolated, the scrubber water and burner gas are stopped, and the solids collectors removed. If it is necessary to clean $TiCl_3$ from the reactor, the argon flow may be stopped and the reactor opened, but only after the system is thoroughly cooled.

Since it takes a great deal of time to heat up the reactor wall furnace (up to 8 h), an alternate partial shutdown procedure should be used if the system is to be used in the next couple of days. All systems can

be shut down except the furnace. To do this, chlorine feeds and preheater should be shut down as before, keeping the hot molybdenum wire under an argon atmosphere. The scrubber water and burner gas are stopped, but the cooling-jacket water must be left on to prevent possible damage to the vacuum seals. The vacuum pump may be kept running to remove any impurities from the system, or it may be shut off if an argon overpressure exists. System startup time would be greatly reduced during subsequent experimentation. This method prevents impurities from accumulating during shutdown, thus reducing the possibility of contamination.

5.2 Safety Considerations

The safety hazards in this system fall into two categories: the flammability of the reactants and the toxicity of the reactants and products. Hydrogen is very flammable, so care is required during handling. The large excess of H_2 used in the reaction is burned before it is released to the atmosphere. For safety, a platinum gauze is placed before the burner head to ignite the H_2 if the burner flame is extinguished. In addition, an air flow rate through the hood of greater than 1.1 cfm would rapidly dilute the H_2 stream to below its lower explosive limit of 4.1% if the gauze failed to ignite it. As a worst case, this assumes that none of the H_2 reacts and all of it goes through the system into the hood. Check valves and flash arresters are placed on the H_2 and Cl_2 feed lines to protect the gas feed cylinders.

Hydrogen chloride and Cl_2 are both very toxic, so the entire apparatus must be placed in a fume hood. Escaping HCl can be detected before it causes serious harm. The odor of Cl_2 can be detected at above 3.5 ppm, and there is no immediate danger until the concentration reaches 15 ppm (11). At 15 ppm minor throat irritation occurs, while in the range of 30 ppm, coughing begins. The maximum chlorine concentration which can be breathed for 30 min without damage is 4 ppm. A level of 40-60 ppm is quite dangerous if breathed for 30 min, and 1000 ppm is fatal after a few breaths. These dosages are a concern only if a number of circumstances combine to cause a disaster. Certainly no experiment should be attempted without the hood running or with known system leaks.

The major problems are associated with concentrations between 1.0 and 3.5 ppm. Chronic exposure to greater than 1 ppm day after day will cause damage. Since this low concentration is below the odor threshold, a chlorine detector should be placed in the room. A continuous sampling system would be the best; however, Matheson offers a manual system which detects concentration of chlorine below 1 ppm. During startup, sampling should be frequent. Subsequently, chlorine should be monitored every few hours since short exposures to low concentrations will not cause harm. Boron trichloride is corrosive but is considered much less toxic than Cl_2 (11). If the precautions discussed here are followed, there should be little danger to the operator. However, as a general precaution, two operators should be available for the startup phase of the experimental program.

6. PROPOSED EXPERIMENTAL PLAN

An experimental program to begin investigation is discussed below. The optimal conditions of temperature and pressure for powder formation should first be investigated. After locating the range of temperature and pressure over which powder is formed, the kinetics of the homogeneous nucleation can be studied by observing the effects of temperature, pressure, feed rates, and feed compositions on the mole % conversion and morphology of the powder. The mole % conversion to TiB_2 solid is defined as:

$$\% \text{ conversion} = \frac{\text{moles of } \text{TiB}_2 \text{ solid obtained}}{\text{stoichiometric moles of } \text{TiB}_2 \text{ to be obtained with the given feed conditions}} (100) \quad (3)$$

The moles of powder produced is determined by weighing the collection traps and using neutron-activation to determine the TiB_2 composition of the solid. It is possible that some of the TiB_2 deposits on the walls and other parts of the reactor system. This occurrence may be checked by a material balance on the reactants. A proposed experimental plan along with expected results from adjustment of the variables is presented in the following sections.

6.1 Optimal Conditions for Powder Formation

6.1.1 Temperature

The initial experiments are at constant pressure (0.3 atm) and different temperatures, ranging from 1200 to 1700 K. The expected rate of TiB_2 powder production, defined as the mass of TiB_2 powder collected in the collection trap per unit time (constant feed rate and composition), is plotted versus reciprocal temperature in Fig. 9a. The change in slope of the curve as temperature increases is due to a change in the rate-controlling mechanism. This behavior has been observed by Besmann for the case of heterogeneous nucleation (1), and we believe that homogeneous kinetics should follow similar behavior, except during initial formation of nuclei. At low temperatures, the reaction is kinetically limited, exhibiting a high activation energy (steeper slope); while at high temperatures, it becomes mass-transfer limited, exhibiting a lower activation energy. The temperature at which the transition between the two rate-controlling mechanisms occurs, however, may be different from that for the heterogeneous kinetics observed by Besmann. The production rate of TiB_2 is expected to approach a maximum with increasing temperature. This represents the optimal operating temperature.

x = conversion to TiB₂ Powder (%)

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AT			
OAK RIDGE NATIONAL LABORATORY			
PREDICTED SYSTEM BEHAVIOR			
DATE	DRAWN BY	FILE NO.	FIG.
5-25-81	MET	CEPS-X-333	9

However, if no or very little powder is formed in the range 1200-1700 K, the solids are likely forming on the reactor wall, which is kept at the same temperature as the preheater temperature. The experiments should be repeated over the same temperature range, but at a lower reactor wall temperature than that of the preheater, thus reducing the possibility of solids being formed on the wall. However, care should be exercised that the flame not be extinguished through heat loss to the wall by radiation. The extinction of the flame can be observed as a surge of Cl_2 in the product stream as measured by the in-line sampling port. To ensure flame ignition, a thin Pt wire should be installed at the tip of the preheater. If solid TiB_2 formation on the reactor wall persists after cooling the furnace, a blanket of hydrogen should be passed adjacent to the reactor wall through the opening in the reactor cone. This will deter the diffusion of reactants to the wall, suppressing heterogeneous nucleation.

After collection, the powder should be examined under a scanning electron microscope (SEM) to study its morphology as a function of temperature. As temperature increases, the particles are expected to increase in size as a result of the faster reaction rate and growth rate.

6.1.2 Pressure

Once an optimal temperature range has been established, pressure should be varied in the range of 0.01 to 0.3 atm. Figure 9b shows a plot of expected trend of mole % conversion to TiB_2 as a function of pressure at a given temperature, feed rate, and composition. The percentage conversion decreases with increasing pressure as predicted from thermodynamics. The upper dashed curve in Fig. 9b shows the corresponding behavior of the equilibrium conversion.

Again, the morphology of the powder should be examined by SEM as a function of pressure, even though pressure has not been found to affect the morphology of chemical-vapor-deposited TiB_2 significantly (2).

6.2 Kinetics Study

The preliminary scoping experiments should be followed by a study of the kinetics of the homogeneous reaction as a function of the system variables. A statistical experimental design should be used to increase statistical reliability while reducing the total number of experiments necessary.

The effects of temperature and pressure on the conversion have been discussed previously, so only the effects of feed rate and composition will be discussed here. All variables should be kept constant or adjusted systematically to isolate the particular variable being studied. Finally, a mass balance should be used to check the kinetic data obtained.

6.2.1 Total Feed Rate

Figure 9c shows a plot of conversion as a function of total feed rate for a given feed composition at constant temperature and pressure. Conversion should decrease with increasing feed rate due to a shorter residence time in the reactor, although overall powder production may increase.

The total feed rate is also believed to affect the morphology of the powder. The mean particle diameter decreases as residence time decreases, thus allowing less time for particle growth. This was observed by Formenti *et al.* for metal oxide particles prepared in a hydrogen-oxygen flame (5).

6.2.2 Feed Composition

Feed compositions can be characterized by the Cl_2 -to- H_2 feed ratio $[\text{Cl}/(\text{Cl} + \text{H})]$ and boron-to-titanium feed ratio $[\text{B}/(\text{B} + \text{Ti})]$. The effect of feed composition is studied by changing one of the ratios and keeping the other constant.

Figure 9d shows the variation of conversion versus $\text{Cl}/(\text{Cl} + \text{H})$ ratio in the feed. It should be noted that the ratio is defined on a gaseous- Cl_2 -free basis since Cl_2 gas in the feed participates in the overall reaction only to the extent that the flame it produces provides heat. As excess hydrogen in the feed decreases $\text{Cl}/(\text{Cl} + \text{H})$, the reaction will be shifted towards higher conversion to TiB_2 .

The $\text{Cl}/(\text{Cl} + \text{H})$ ratio affects the morphology of chemical-vapor-deposited TiB_2 , as observed by Besmann (2). The effect of this ratio on homogeneously produced TiB_2 should be made experimentally.

Figure 9e shows a plot of the conversion versus $\text{B}/(\text{B} + \text{Ti})$ feed ratio. At either low or high $\text{B}/(\text{B} + \text{Ti})$ feed ratio, conversion is high because of the excess TiCl_4 or BCl_3 , which shifts the equilibrium toward formation of diboride. The stoichiometric ratio, corresponding to a value of $2/3$, gives the lowest conversion.

The $\text{B}/(\text{B} + \text{Ti})$ ratio also affects the morphology of CVD TiB_2 (2) in the heterogeneous case. Although conversion is minimized at the stoichiometric ratio, it is important that impurity, especially boron, be avoided. Therefore, it is recommended that at least initially the stoichiometric ratio ($2/3$) be maintained.

6.2.3 Mass Balance Calculation

A product-gas flow meter and a sampling port, along with the feed-gas flow meters, permit calculation of an overall mass balance as well as individual-component balances. An overall mass balance on the system at the end of an experimental run gives:

$$\begin{array}{l} \text{mass of gases} \\ \text{fed in} \end{array} = \begin{array}{l} \text{mass of gases} \\ \text{leaving the} \\ \text{system} \end{array} + \begin{array}{l} \text{total mass of solids} \\ \text{deposited} \end{array} \quad (4)$$

where the total mass of solids deposited is that collected in the collection trap and that deposited on the reactor wall, tubes, and valves.

Based on the material balances, the mass of solids deposited on the reactor wall, tubes, and valves can be easily determined. A collection efficiency can be defined as:

$$\text{collection efficiency of powder formation} = \frac{\text{mass of solids collected in trap}}{\text{total mass of solids obtained}} \quad (5)$$

and a purity efficiency can be defined as:

$$\text{purity efficiency} = \frac{\text{mass of TiB}_2 \text{ collected}}{\text{mass of total solid collected}} \quad (6)$$

The mass of solids deposited can be determined by dismantling the reactor system and weighing the parts that come in contact with the reaction mixture. One potential problem, however, is that TiCl_3 collected on cold spots of the reactor wall and tubing may hydrolyze to give HCl and oxychlorides when exposed to moist air (10). This could introduce error in the mass balance. A component mass balance on the gaseous species at steady state provides an estimation of the reaction rates of individual gaseous species. From these balances, reaction rates can be followed as a function of changes in temperature, pressure, feed rates, and feed compositions, as described in the previous section.

7. PRODUCT ANALYSIS

Once the TiB_2 powder is obtained, it must be analyzed for purity and crystal morphology. The following discussion describes the purity analysis. The most accurate method, and for some elements the only method of analysis, is by neutron activation (NA). The sample is bombarded with neutrons to form unstable isotopes whose decay energies are monitored. In this way almost any solid element can be detected to the ppm range. Two important impurities which may be present are oxygen and chlorine. TiCl_3 is formed along with the TiB_2 ; however, it is not known to what extent the trichloride is formed. TiCl_3 can be sublimed above 425°C to purify the TiB_2 ; but, to determine reaction kinetics, it is important to measure the conversion to TiCl_3 . This is conveniently done using neutron activation. Oxides of titanium and boron, impurities which weaken TiB_2 grain boundaries, can be detected by neutron activation only. Characterization and control of these impurities is critical if high-strength TiB_2 is to be produced.

Samples to be analyzed by neutron activation should be stored under N_2 . Argon, the collection trap atmosphere, emits radiation upon neutron activation. Solid samples may be transferred from a glove box to a small

sample vial and analyzed. Care must be taken during handling because the powder is pyrophoric; however, once placed in a sample vial it is never removed during analysis. Lamont Bate, at the High Flux Isotope Reactor, is familiar with NA analysis of TiB_2 .

Another analytical technique is Scanning Electron Microscopy (SEM). Chlorine can be detected by this method; however, oxygen cannot. To achieve a quantitative estimate of the composition, standards of pure TiB_2 with known amounts of chloride must be prepared and then compared with an unknown sample. This method offers two advantages over neutron activation. It can be conducted in conjunction with examination of the morphology, and it is much less expensive than neutron activation. SEM indicates which species are present (atomic number greater than sodium) and approximate compositions.

8. CONCLUSIONS

A reactor system was designed to produce TiB_2 powder at the rate of 4 g/h directly by homogeneous nucleation. The production can be optimized by examining the TiB_2 powder properties, morphology, and compaction behavior as reaction conditions are changed. The system is expected to cost \$24,500 to build.

9. RECOMMENDATIONS

1. An accurate method for measuring reaction gas and flame temperature should be found in order to allow better understanding of the reaction kinetics.
2. If higher linear velocities are needed in the gas streams exiting the preheater, flame-burner jets can be made, using capped preheater tubes with drilled orifices.
3. If corrosion of the vacuum pump occurs, a cold-trap, using liquid nitrogen, can be installed before the pump to trap most of the corrosive gases. This is not expected to be a problem.
4. To minimize heterogeneous nucleation, a porous shell tube may be installed inside the reaction chamber so that excess hydrogen can be passed through the shell to diffuse into the center of the chamber, thus blanketing the reactor wall from the reactants.
5. Plasma enhancement using an RF induction coil may be added to the proposed design to electronically excite the gases without heating them, thus increasing reaction kinetics at lower temperature.

10. ACKNOWLEDGMENTS

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11. APPENDIX

11.1 Thermodynamic Properties of the Components

Thermodynamic properties for all chemical species involved in the reaction are given in Table 3 at 1700 K. Since the reaction is carried out at reduced pressures and elevated temperatures, ideal gas behavior may be assumed for all gaseous components.

Table 3. Thermodynamic Properties of Chemical Species (16)
T = 1700 K

Species	C_p (cal/mol-K)	$H^\circ - H^\circ_{298}$ (kcal/mol)	ΔH_f (kcal/mol)	ΔG_f (kcal/mol)
TiCl ₄ (g)	25.72	35.38	-183.02	-133.31
TiCl ₃ (g)	20.45	28.14	-130.54	-108.34
TiB ₂ (s)	21.60	25.09	-68.90	-59.38
BCl ₃ (g)	19.58	26.07	-96.85	-75.66
HCl (g)	8.31	10.61	-22.79	-25.09
H ₂ (g)	7.92	10.23	0.00	0.00
Cl ₂ (g)	9.10	12.44	0.00	0.00

11.2 Design Calculations

The original design calculations and data are on file at the MIT School of Chemical Engineering Practice, Bldg. 1505, ORNL. Appendices 11.2.1 through 11.2.8 detail the design calculations for all major equipment items.

11.2.1 Calculation of Feed Flow Rates

This system was designed to produce TiB₂ at the rate of 4 g/h. Conversion limits were obtained from equilibrium data; however, since little is known of the kinetics of the homogeneous reaction, a 30% approach to equilibrium was assumed.

An expression for the thermodynamic equilibrium constant as a function of temperature was given by Besmann and Spear (1) for the reaction:

the equilibrium constant is:

$$K = \frac{(P_{\text{HCl}})^{10}}{(P_{\text{TiCl}_4})(P_{\text{BCl}_3})^2(P_{\text{H}_2})^5} = P_{\text{tot}}^2 \frac{(x_{\text{HCl}})^{10}}{(x_{\text{TiCl}_4})(x_{\text{BCl}_3})^2(x_{\text{H}_2})^5} \quad (7)$$

where P is the pressure in atm, and x is the mole fraction.

Besmann and Spear (1) report that the equilibrium constant is:

$$\ln(K) = 31.32 - \frac{35,300}{T} \quad (8)$$

where T is in degrees Kelvin. At 1700 K the equilibrium constant $K = 3.77 \times 10^4$.

A total pressure of 0.30 atm was assumed. Hydrogen is three times stoichiometric and BCl_3 is stoichiometric. The following variables are defined, where f_{Ti} , f_{B} , and f_{H_2} are the molar feed rates of TiCl_4 , BCl_3 , and H_2 , respectively, and y is the molar rate of removal of TiCl_4 .

Based on the stoichiometry of the reaction [Eq. (2)], the following flow rates prevail in the gas phase at equilibrium: $\text{TiCl}_4 = f_{\text{Ti}} - y$, $\text{BCl}_3 = f_{\text{B}} - 2y$, $\text{H}_2 = f_{\text{H}_2} - 5y$, and $\text{HCl} = 10y$. The total molar flow rate in the gas phase then becomes:

$$f_{\text{tot}} = f_{\text{Ti}} + f_{\text{B}} + f_{\text{H}_2} + 2y \quad (9)$$

The equilibrium constant in terms of initial feed rates and changes in the number of moles now becomes:

$$K = \left(\frac{P_{\text{tot}}}{f_{\text{Ti}} + f_{\text{B}} + f_{\text{H}_2} + 2y} \right)^2 \left(\frac{(10y)^{10}}{(f_{\text{Ti}} - y)(f_{\text{B}} - 2y)^2(f_{\text{H}_2} - 5y)^5} \right) \quad (10)$$

An iterative solution of Eq. (10) is required to find y , the amount of TiCl_4 reacted at equilibrium. If a basis of 1 mole/unit time of TiCl_4 feed is assumed, then y becomes the equilibrium conversion.

The design conditions are: $P_{\text{tot}} = 0.30$ atm abs; $f_{\text{Ti}} = 1.0$ mol/h; $f_{\text{B}} = 2.0$ mol/h; $f_{\text{H}_2} = 15.0$ mol/h; $T = 1700$ K; and $K = 3.77 \times 10^4$. If these values are substituted into Eq. (10), the following results:

$$3.77 \times 10^4 = \left(\frac{0.30}{1.0 + 2.0 + 15.0 + 2y} \right)^2 \frac{(10y)^{10}}{(1.0-y)(2.0-2y)^2(15.0-5y)^5}$$

A trial-and-error solution yields:

$$y = 0.95$$

Since a 30% approach to equilibrium was assumed, the actual conversion in our system is 0.29.

To calculate the feed rate of TiCl_4 , it is assumed that no side reactions occur and that 4 g/h TiB_2 is produced. The molecular weight of TiB_2 is 69.522; hence, 4 g/h is 0.0575 gmol/h TiB_2 produced. Based on a 29% conversion of TiCl_4 , and assuming no side reactions, 0.21 gmol/h of TiCl_4 will be required.

A stoichiometric amount of BCl_3 is 0.42 mol/h, and a three-times molar excess of H_2 is 3.20 mol/h.

Chlorine will be added to provide the heat of reaction for the production of TiB_2 , as required by reactions (11) and (12):

$$\Delta H_{\text{ryn}} = 80 \text{ kcal at } 1700 \text{ K}$$

$$\Delta H_{\text{rxn}} = -45.5 \text{ kcal at } 1700 \text{ K}$$

The TiB_2 reaction was assumed with a conversion of 0.29, while the HCl reaction is assumed to have a conversion of 1.0. For each mole of TiCl_4 fed, 23.2 kcal of heat is required (0.29×80 kcal). Therefore, $23.2/45.5$ or 0.51 mole of Cl_2 is needed per mole of TiCl_4 fed.

Thus the molar flow of Cl_2 required is:

$$(0.21 \text{ mol TiCl}_4/\text{h})(0.51 \text{ mol Cl}_2/\text{mol TiCl}_4) = 0.10 \text{ mol Cl}_2/\text{h}$$

Obviously 0.1 mole of H_2 is added to react with the Cl_2 , bringing the total H_2 feed rate to 3.30 mol/hr. In summary, the feed rates for all four gases are: H_2 , 3.30 mol/h; TiCl_4 , 0.21 mol/h; BCl_3 , 0.42 mol/h; and Cl_2 , 0.10 mol/h.

11.2.2 Preheater Calculations

The physical dimensions as well as the heat duty of the preheater are calculated below. The energy required (kcal/mol) to heat the gases from 298 to 1700 K is shown in Table 4.

Table 4. Energy Required to Heat Feed Components

<u>Gas</u>	<u>ΔQ (kcal/mol)</u>
TiCl_4	35.375
BCl_3	26.072
Cl_2	12.441
H_2	10.233

The energy to heat the first stream, containing the H_2 , is:

$$Q = \dot{n} \Delta Q = (3.30 \text{ mol/h})(10.233 \text{ kcal/mol}) = 33.77 \text{ kcal/h} \quad (13)$$

or 39.26 W

Similarly, the energy to heat the other stream, containing the TiCl_4 , BCl_3 , and Cl_2 , is:

$$Q = \sum_i \dot{n}_i \Delta Q_i = 19.62 \text{ kcal/h or } 22.81 \text{ W} \quad (14)$$

A total duty of 500 W will be used to account for heat losses to the atmosphere.

The tube and annulus are sized to give equal linear velocities of the two streams when exiting the nozzle, thus reducing turbulence and eddies.

The volumetric flow rates of each gas at final conditions can be calculated from the ideal gas law:

$$\dot{V} = \frac{\dot{n} R T}{P} \quad (15)$$

The calculated volumetric flow rates for each gas at 1700 K, 0.30 atm is given in Table 5.

Table 5. Flow rates

Feed Component	$\dot{n}$ (mol/h)	$\dot{V}$ (cm ³ /min)
H ₂	3.30	25,587.0
Cl ₂	0.10	775.4
TiCl ₄	0.21	1,628.3
BCl ₃	0.42	3,256.6

If a linear velocity of 200 ft/min (6096 cm/min) is assumed, the total flow through the tube, which carries the TiCl₄, BCl₃, and Cl₂, is 5660.3 cm/min. Thus, the area of the tube A_T is 0.93 cm² or the radius is 0.54 cm. If a tube-wall thickness of 25 mils (0.0635 cm) is assumed (12), the outer radius of the tube is 0.6035 cm. By a similar calculation the outer tube area is 4.20 cm², or the outside radius is 1.30 cm, assuming a 0.0635-cm wall thickness. For these exit conditions, tapered tubes are unnecessary since the heating wire is 28 AWG (American Wire Gauge) (14), which is 0.032 cm in diameter and thus will not restrict the flow. If higher linear velocities are desired, the tubes, sealed at one end, should be purchased and holes drilled in the ends of them to give a smaller area for flow; alternatively, smaller tubes can be installed if adequate residence time for heating is maintained.

The length of the preheater to be wrapped by heating coil can be calculated, assuming that heat transfer occurs from the hot preheater wall to the gas by two processes: convection and radiation. The heat transfer rate Q is given by:

$$Q = h A(T_w - T_g) + \sigma \epsilon A(T_w^4 - T_g^4) \quad (16)$$

where: h = convective heat transfer coefficient = 2.78×10^{-4} cal/s-cm²-K,
 σ = Stefan-Boltzmann constant = 1.36×10^{-12} cal/cm²-s-K⁴, and ϵ = emissivity = 0.4.

The preheater is divided into small sections; a constant wall temperature is assumed for each section. The length of each section is calculated from the heat required to raise the gas temperature to the specified level. The length of the preheater is the sum of the subsection lengths. As an example, the heat duty required for the largest stream (H₂) is presented. The temperature rise in a section is 100 K, and the average temperature over the section is used to calculate the length. Equation (16) is used for the calculation.

$$\begin{aligned}
 Q \text{ (cal/s)} &= (2.78 \times 10^{-4}) 2\pi(0.5) L(1700 - T_g) \\
 &\quad + (1.36 \times 10^{-12})(0.4) 2\pi(0.5) L[(1700)^4 - T_g^4] \\
 &= \{8.73 \times 10^{-4}(1700 - T_g) + 1.71 \times 10^{-12}[(1700)^4 - T_g^4]\}L
 \end{aligned}
 \tag{17}$$

The heat duty and associated length of each section of the preheater is given in Table 6.

Table 6. Heat Duty and Preheater Length

Each Section		$T_{g,avg}$ (K)	Q (cal/s)	L (cm)
$T_{g,in}$ (K)	$T_{g,out}$ (K)			
300	400	350	0.636	0.041
400	500	450	0.641	0.042
500	600	550	0.642	0.042
600	700	650	0.644	0.043
700	800	750	0.650	0.045
800	900	850	0.653	0.046
900	1000	950	0.658	0.049
1000	1100	1050	0.666	0.052
1100	1200	1150	0.673	0.057
1200	1300	1250	0.682	0.065
1300	1400	1350	0.695	0.078
1400	1500	1450	0.702	0.101
1500	1600	1550	0.713	0.157
1600	1700	1650	0.721	0.437
			Total Length	1.255

The calculation of the preheater length is, of necessity, approximate. Indeed, the temperature of the gas can only approach the 1700°K wall temperature. Therefore 6 in. of preheater will be wrapped with resistance wire, which will provide any additional heat requirement.

11.2.3 Estimation of Reactor Volume

Since very little is known about the kinetics of the homogeneous nucleation process, Besmann's reactor residence time was used to get an initial estimate of the reactor volume (1). The volume of the reactor used in the Besmann study was 43.3 cm³, and the total flow rate was 462 cm³/min (STP). At T = 1700 K and P = 0.3 atm, the volumetric flow rate is:

$$F = 462 \left(\frac{1}{0.3} \right) \left(\frac{1700}{273} \right) = 9590 \text{ cm}^3/\text{min}$$

and the residence time is:

$$\tau = \frac{V}{F} = \frac{43.3}{9590} = 0.27 \text{ s} \quad (18)$$

For the molar flow rates given in Appendix 11.2.1, at T = 1700 K and P = 0.3 atm, the total flow is:

$$F = \sum_{i=1}^4 \dot{V}_i = 31,233 \text{ cm}^3/\text{min} \quad (19)$$

From Eq. (19) the reactor volume is calculated to be 140.5 cm³. This represents a lower limit of the reactor volume needed because homogeneous kinetics are believed to be slower than heterogeneous and thus may need a longer residence time. Thus both the reactor volume was oversized to provide adequate residence time and the furnace to minimize heat loss from the hot zone by radiation through the reactor outlet.

11.2.4 Calculation for Heat Losses Through Furnace Wall

Heat loss through the furnace wall was computed to determine whether it will be sufficient to dissipate the energy generated by the reaction of H₂ and Cl₂ if the reaction to form TiB₂ does not occur. The major resistance to heat transfer is the firebrick around the furnace. The firebrick is assumed to have a circular configuration. The outside temperature of the alumina tube and the inside temperature of the firebrick are assumed to be 1500 K. The outside temperature of the firebrick is 298 K with 18 in. of length. The heat transfer rate Q is:

$$Q = 2\pi k \frac{T_1 - T_2}{k(r_1/r_2)} \quad (20)$$

where:

$$k = 0.89 \text{ kcal/m-hr-}^\circ\text{C} \text{ (14)}$$

$$T_1 = 1500 \text{ K}$$

$$T_2 = 298 \text{ K}$$

$$r_1 = 0.505 \text{ m (firebrick OD)}$$

$$r_2 = 0.048 \text{ m (firebrick ID)}$$

$$\therefore Q = 2856 \text{ kcal/h-m furnace length}$$

Only 4.5 kcal/h of heat must be dissipated if the reaction to form TiB_2 fails to occur. Thus, overheating the reactor to the melting point cannot occur under the conditions for which the unit was designed.

11.2.5 Estimation of Theoretical Flame Temperature

The theoretical flame temperature is the maximum temperature the flame can attain under adiabatic conditions. For the combustion of H_2 in Cl_2 :

For the design flow rates, on a 1-h basis, assuming no TiB_2 formation, the products are: 0.21 mole TiCl_4 , 0.42 mole BCl_3 , 3.2 mole H_2 , and 0.2 mole HCl .

The energy balance becomes:

$$\sum_{\text{feed}} n_i \bar{c}_{p_i} (T_0 - T_{\text{ref}}) + n_{\text{Cl}_2} \Delta H_{\text{comb}} = \sum_{\text{product}} n_i \bar{c}_{p_i} (T_f - T_{\text{ref}}) \quad (21)$$

For $T_0 = 1700 \text{ K}$ and $T_{\text{ref}} = 1700$, Eq. (21) becomes:

$$0 + (0.1)(45,500) = (0.21 \bar{c}_{p_{\text{TiCl}_4}} + 0.42 \bar{c}_{p_{\text{BCl}_3}} + 3.2 \bar{c}_{p_{\text{H}_2}} + 0.2 \bar{c}_{p_{\text{HCl}}})(T_f - 1700)$$

Between 1700 and 2000 K, $\bar{C}_p$ can be obtained from JANAF Tables (16), where $\bar{C}_{p\text{BCl}_3}$ is 19.62 cal/gmol-K; $\bar{C}_{p\text{TiCl}_4}$ is 25.73 cal/gmol-K; $\bar{C}_{p\text{H}_2}$ is 8.06 cal/gmol-K; and $\bar{C}_{p\text{HCl}}$ is 8.41 cal/gmol-K. Thus, the theoretical flame temperature, T_f , is 1810 K.

11.2.6 Calculations for the Vaporizer

The vaporizer is a stainless-steel container on a hot plate; it holds enough TiCl_4 to operate for 10 h. In addition, it has a large vapor volume so that the vapor drawoff will not cause appreciable pressure fluctuations. The system operates at an equilibrium vapor pressure of 2 atm abs, to permit flow controls. The Antoine equation for TiCl_4 is given as follows (10):

$$\log P = 7.64433 - \frac{1947.6}{273.16 + T} \quad (22)$$

where P is in mm Hg, and t is in °C. The vapor pressure is 2 atm abs (1520 mm Hg) at 163.28 °C.

The volumetric flow rate of the vapor at the conditions inside the vaporizer is calculated from the ideal gas law:

$$\dot{V} = \frac{\dot{n} R T}{P}$$

where $\dot{n}$ is 0.21 mol/h, T is 436 K, P is 2 atm abs., and $R = 82.1 \text{ cm}^3\text{-atm/mol-K}$. Therefore the vapor flow rate is 3759 cm^3/h at 2 atm abs and 436 K.

The volumetric depletion rate of the liquid phase is 22.5 cm^3/h ; thus 225 cm^3 of liquid must be charged to the vaporizer for a 10-h run. A total vaporizer volume of 1 liter provides adequate vapor space.

The heat duty of the vaporizer at steady state consists of the energy to vaporize the liquid and that required to make up for heat losses to the atmosphere. The former is approximately 2.05 W, while the latter is calculated to be 46.7 W for conservative conditions (see calculation file). Since the smallest available hot plate is rated at 840 W, it was selected.

11.2.7 Scrubber Dimensions

The scrubber designed was based on a flooding correlation discussed in the Chemical Engineers' Handbook (15). Calculations are based on the following conservative assumptions:

1. All of the BCl_3 and TiCl_4 is converted to TiB_2 . In actuality we expect only 29% with the remaining $\text{TiCl}_4 + \text{BCl}_3$ being absorbed in the scrubber.

2. Two moles of Cl_2 are burned per mole TiCl_4 to provide the heat of reaction.

3. A three-times excess of H_2 over that needed to convert the TiCl_4 plus any hydrogen needed to burn the chlorine is used in the process.

4. The feed of TiCl_4 is that needed to produce the desired amount of TiB_2 using a conversion of TiCl_4 equal to 0.29.

With these assumptions the scrubber will be designed to handle the maximum gas flow rate.

The water flow rate was chosen so that if a maximum amount of HCl were formed and all of it were absorbed in the water, the resulting solution would be 0.1 M HCl . For these conditions the gas flow rates are given in Table 7.

Table 7. Reactor Feed and Product Flow Rates
Based on Total Conversion Assumption

<u>Gas</u>	<u>Feed (mol/h)</u>	<u>Product (mol/h)</u>
TiCl_4	0.237	-
BCl_3	0.474	-
Cl_2	0.474	-
H_2	4.029	2.370
HCl	-	3.318

The required water flow rate is calculated from:

$$0.1 \text{ mol/liter HCl} = \frac{3.318 \text{ moles HCl/h}}{L}$$

where L , the liquid flow rate, is 33.18 liter/h = 0.0203 lb/s. Since the gas flow rate is the highest at the bottom, the column will be sized based on flooding at that point.

The gas flow rate G is given by the following expression:

$$G = \dot{n}_1 (mw_1) + \dot{n}_2 (mw_2) \quad (23)$$

where n_1 (H_2 flow rate) = 2.37 mol/h and n_2 (HCl flow rate) = 3.318 mol/h. Equation (23) yields the following results:

$$G = 125.77 \text{ g/h and } mw_{avg} = 21.88 \text{ g/gmol}$$

The density of the gas stream is calculated from the ideal gas law:

$$\rho_g = \frac{(mw)_{avg} P}{RT} = \frac{(21.88)(1)}{(0.7302)(536)} = 0.0558 \text{ lb}_m/\text{ft}^3 \quad (24)$$

The flooding velocity is obtained from Fig. 18-38 (15). The following abscissa is required:

$$\frac{L}{G} \left(\frac{\rho_g}{\rho_l} \right)^{\frac{1}{2}} = \left(\frac{0.0203}{7.7 \times 10^{-5}} \right) \left(\frac{0.0558}{62.4} \right)^{\frac{1}{2}} = 7.9 \quad (25)$$

Since the rings will be dumped rather than stacked in the column, the ordinate read from Fig. 18-38 (15) is:

$$\frac{U_T a_p}{g \epsilon^3} \left(\frac{\rho_g}{\rho_l} \right) \mu^{0.2} = 0.0018 \quad (26)$$

where

U_T = superficial gas velocity, ft/s

a_p = total area of packing, ft^2/ft^3 bed

ϵ = void fraction of dry packing

g = 32.2 ft/s^2

ρ_g, ρ_l = gas, liquid densities, lb/ft^3 = 62.4 and 0.0558, respectively

μ = liquid viscosity, cp = 0.89 cp for water at 25°C

The one-half inch Raschig rings which are used as packing have the following characteristics: the area of the packing a_p is $112 \text{ ft}^2/\text{ft}^3$ of bed, and the void fraction of the packing ϵ is 0.64. From these values one may calculate U_T , the superficial gas velocity, as 0.267 ft/s (8.14

cm/s), above which gas velocity flooding may occur. The volumetric flow rate of the gas at the bottom of the column is 38.66 cm³/s.

The area of the column is then calculated by dividing the volumetric flow rate by the area and setting it equal to the linear flow rate. The minimum area is 4.25 cm², yielding a diameter of 2.46 cm. Thus, a column of 10-cm diameter is substantially removed from the flooding velocity. The column height, 45 cm, was selected to ensure total removal of the HCl.

11.2.8 Calculation of the Vacuum Pump Capacity

The desired collection-trap pressure is approximately 1 torr. The gas flow rate into the scrubber, V_2 , is 38.66 cm³/s (2.28 liter/min) at 1 atm pressure (P_1) and 298 K. At lower pressures, P_2 , the volumetric flow rate changes so that the molar flow rate is constant.

$$\dot{V}_2 = \dot{V}_1 \left(\frac{P_1}{P_2} \right) = 2.28 \left(\frac{760}{1} \right) = 1732 \text{ liter/min}$$

If liquid-nitrogen cold traps are placed before the vacuum pump, only the H₂ will be pumped out of the system. This would reduce the pumping-rate requirement to 1023 liter/min to maintain a pressure of 1 torr in the collectors. Sargent-Welch suggests that the pump capacity be double the actual requirement (8). Thus a pump which will maintain a 1-torr vacuum and a pumping capacity of ~2800 liter/m atom torr is required.

11.3 Equipment List and Cost

The following is a list of the major pieces of equipment and services to be purchased. Also listed are the suggested vendor and current prices as well as the use of the equipment. This list is the basis for the overall cost estimate and is given in May 1981 dollars.

Unit - Preheater-Reactor

1.	1 each	Furnace (Lindberg)
1500 °C maximum temperature
4-in-ID tube
30-in. heated zone
controller and transformer (240 V)
USE: reactor wall heater	\$ 7000.00 each ¹
2.	1 each	Variac (Union Carbide Stores)
7.5 KVA
20 amp
USE: preheater temperature controller	250.00 each

3. Alumina tubes (McDanel)

998 alumina (99.8% Al_2O_3)
gas tight

a)	1 each	3-3/8 in. ID
3-3/4 in. length
55 in. length
open both ends
USE: outer housing and reactor vessel	\$ 700.00 each
b)	1 each	7/16 in. ID ²
11/16 in. OD
23½ in. length
open both ends
USE: inner preheater tube	43.00 each
c)	1 each	1 in. ID ²
1¼ in. ID
21-11/16 in. length
open both ends
USE: outer preheater tube	55.00 each
d)	1 each	¼ in. ID
3/8 in. OD
48½ in. length
closed one end
USE: reactor wall thermocouple well	78.00 each
e)	1 each	3/16 in. ID
¼ in. OD
17-3/4 in. length
closed one end
USE: preheater wall thermocouple well	27.00 each
f)	1 each	1-5/8 in. ID
1-7/8 in. OD
7-7/8 in. length
open both ends
USE: radiation shield	39.00 each
g)	1 each	2-1/8 in. ID
2-3/8 in. OD
7-7/8 in. length
open both ends
USE: radiation shield	49.00 each
h)	1 each	2-3/4 in. ID
3 in. OD
10¼ in. length
open both ends
USE: radiation shield	67.00 each

4. Alumina flats (McDanel)

998 alumina (99.8% Al_2O_3)

a)	2 each	3-3/4 in. long 2-1/8 in. wide 1/8 in. thick USE: reactor outlet radiation shields	\$ 9.00 each
b)	2 each	3-3/4 in. long 3 in. wide 1/8 in. thick USE: reactor outlet radiation shields	9.00 each
c)	3 each	2-3/16 in. diam, circular 1/8 in. thick USE: preheater radiation shields	9.00 each
d)	13 each	2-3/4 in. diam, circular 1/8 in. thick USE: preheater radiation shields	9.00 each
e)	1 each	3-3/8 in. diam, cylindrical 2 in. thick USE: cone at the entrance of reactor	50.00 each
5.	Miscellaneous parts		300.00
6.	Construction Costs (Union Carbide craftsmen) 3 man/days		1000.00 (3)
Total Reactor Preheater Cost			\$ 9838.00

Unit - Feed System1. Mass flow meter (Matheson)³

a)	1 each	Power supply and readout box Handles up to 5 transducers Model 8143	750.00 each
b)	4 each	Flow transducers 316 stainless steel 1 each capable of handling 1230 cc/min H_2 78.5 cc/min TiCl_4 157 cc/min BCl_3 37.3 cc/min Cl_2 All flows are at 273 K, 1 atm pressure USE: flow measurement on all feed lines	525.00 each

2.	4 each	Valves (Nu Pro)
Bellows metering valves
Type "BMG"
stainless steel
1/4 in. Swagelok fittings
Cat #SS-4 BMG
USE: control the feed flow rates	\$ 212.30 each
3.	each	Hot plate (Cole-Parmer)
840 W capacity
700°F maximum temperature
Cat #4659-00
USE: vaporizer heat source	73.00 each
4.	2 each	Flash arrestors (Matheson)
Check valve and stops
flash back
1/4 in. x 1/4 in. NPT
Model 6103
USE: H ₂ and Cl ₂ feed lines	53.00 each

Total Feed System Cost

\$ 3878.20

Unit - Collection/Disposal System

1.	1 each	Vacuum pump (Sargent-Welch) ⁴
Ultimate vacuum < 1 torr
Flow rate 2600 liter/min at 1 torr, 298 K
Pump motor and drive
Model 1396
USE: to maintain the system pressure	6132.00 each
2. Valves (Whitey)			
	a) 11 each	Ball valves
stainless steel
1/4 in. Swagelok fittings
Cat #22-45S-8
USE: shut off and isolation of collection traps	104.49 each
	b) 2 each	Vee stem valves
stainless steel
1/4 in. Swagelok fittings
Cat #SS-7VS-8
USE: regulate reactor and collector pressure	100.50 each
3.	3 each	Pressure gauges (Matheson)
0-760 torr abs
316 stainless steel
0.25% full-scale accuracy
Model 63-5601	175.00 each

4. 1 each	Mass flow transducer 316 stainless steel Capable of handling the product flow, mostly H ₂ Approximately 1200 scfm with a pressure of ~200 torr and temperature of 200°C To be used with the readout box for the feeds	\$ 525.00 each
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Total Collection/Disposal System Cost

\$ 8499.39

NOTES FOR EQUIPMENT LIST:

1. This furnace must be special-ordered. The specifications must be sent to Lindberg and firm price is requested. To bracket the cost of this furnace, two units were priced, one larger than required and one smaller.

a) Smaller Unit

4-in. ID	\$3685	
24-in. heated length		
Single-zone furnace		
Controller and transformer (240 V)	<u>970</u>	
Total		\$4655

b) Larger Unit

4-in. ID	\$5675	
36-in. heated length		
Three-zone furnace		
Controller and transformer (240 V)	<u>2590</u>	
Total		\$8265

A \$7000 price estimate was selected.

2. These two tubes must be ground to a wall thickness of 25 mils. Since the inside diameter is correct, grinding of the exterior will be required to arrive at the desired wall thickness. McDanel is capable of performing this work, but it is not included in the cost. All other tubes may be used as received.
3. The mass flow meter could be converted to a mass flow controller. This is accomplished by substituting the power supply and controller box Model 8249 (at \$1500 each) for Model 8143. Four control valves must be added at \$250 each.
4. The flow rate of the vacuum pump is very pressure-dependent. In our case it is given by $F = 1732/P$, where F is the flow rate in liter/min at a given pressure P torr. If an ultimate vacuum of only 5 torr is to be obtained in any part of the system rather than the 1 torr which was specified, then the pump capacity must be $F = 1732/5$ or 346.4 liter/min. The pump which is specified should be 1.5 to 2 times the

capacity actually required (8). Thus a pump with a 692.8 liter/min pumping rate could be specified if a Storr vacuum is used rather than the 1-torr pressure specified in the original calculations. The smaller pump for the Storr pressure system could represent a substantial cost reduction.

11.4 List of Vendors

The following is a list of vendors whose product information was used in calculating the costs. In some cases, contact was made to ascertain technical information on the product in question.

Cole-Parmer
7425 N. Oak Park Ave.
Chicago, IL 60648
phone: (800)323-4340
Product: hot plate

Lindberg, Inc.
2450 W. Hubbard St.
Chicago, IL 60612
phone: (312)942-2600
Product: furnace

Matheson
1805 Southland Dr.
Gonzales, LA 70737
phone: (504)644-5303
Products: mass flow meters, pressure gauges, gases

McDaniel Refractory Co.
510 Ninth Ave.
Beaver Falls, PA 15010
phone: (412)843-8300
Products: alumina parts and tubes

National Element
422 Oliver Ave.
Troy, MI 48084
phone: (313)362-0950
Products: molybdenum heating elements

Omega Engineering
One Omega Drive
Box 4047
Stamford, CT 06907
phone: (203)359-1660
Products: thermocouples and accessories

Ridge Valve and Fitting Co.

P.O. Box 10086

Knoxville, TN 37919

phone: (615)588-2414

from Oak Ridge: 483-0211

Products: Nupro and Whitey valves and Swagelok fittings

Sargent-Welch

7306 N. Linden Ave.

Skokie, IL 60076

phone: (312)677-0600

Product: vacuum pumps

11.5 Nomenclature

a	total area per unit volume, ft^3/ft^2
A	area, cm^2
C_p	heat capacity, cal/gmol-K , $\text{Btu/lb-}^\circ\text{F}$
d	diameter, cm
D	diameter, cm
f	molar feed rate, mol/h
F	total volumetric flow rate, cm^3/min
g	acceleration due to gravity, cm/s^2 or ft/s^2
G	mass gas flow rate, g/h or lb/s
h	convective heat transfer coefficient, $\text{cal/s-cm}^2\text{-K}$ or $\text{Btu/h-ft}^2\text{-}^\circ\text{F}$
H	enthalpy, kcal/mole , cal/mole
k	thermal conductivity, $\text{Btu/h-ft-}^\circ\text{F}$
K	equilibrium constant, atm^2
L	mass liquid flow rate, lb/s ; length, cm or ft
m_w	molecular weight, g/gmole or lb/lb_m
n	number of moles, mole
$\dot{n}$	molar flow rate, moles/h
N	dimensionless quantity

P	pressure, atm or mm Hg
Q	heat duty, kcal/mole, or W, or cal/s, or kcal/h-min, or kcal/h-in.
R	gas law constant, $\text{cm}^3\text{-atm/mol-K}$ or liter-atm/mol-K or $\text{ft}^3\text{-atm/lb}_m\text{-}^\circ\text{R}$
R	radius, cm
t	temperature, $^\circ\text{F}$
T	temperature, K or $^\circ\text{C}$
U	superficial mass velocity, ft/s or cm/s
$\dot{V}$	volumetric flow rate, cm^3/min or cm^3/h , or liter/min, or cm^3/sec
V	reactor volume, cm^3
x	mole fraction, dimensionless
y	equilibrium conversion, moles

Greek Symbols

β	coefficient of thermal expansion, $^\circ\text{F}^{-1}$
ϵ	void fraction, dimensionless; emissivity, dimensionless
τ	residence time, s
ρ	density, g/cm^3 or lb/ft^3
σ	Stefan-Boltzmann constant, $\text{cal/cm}^2\text{-s-K}^4$
μ	viscosity, lb/ft-h or cp

Subscripts

1,2,3 ..	components or states
298	at 298 K
B	boron trichloride
f	flame, theoretical
g	gas
Gr	Grashoff number
H ₂	hydrogen
i	species i

ℓ liquid
 Nu Nusselt number
 o feed conditions
 p pressure
 Pr Prandtl number
 ref reference state
 t at flooding
 T tube
 Ti titanium tetrachloride
 tot total
 vap vaporization
 w wall

Superscript

o standard state

11.6 Literature References

1. Besmann, T.M., and K.E. Spear, "Analysis of the Chemical Vapor Deposition of Titanium Diboride," Parts I and II, J. Electrochem. Soc., 124, 786 (1977).
2. Besmann, T.M., and K.E. Spear, "Morphology of Chemical Vapor Deposited TiB₂," J. Crystal Growth, 31, 60 (1975).
3. Earley, E.L., personal communication, ORNL, May 1981.
4. Federer, J.I., W.C. Robinson, Jr., and F.H. Patterson, "Conversion of UF₆ to UO₂ in a Flame Reactor," Nucl. Applications, 6, 298 (1969).
5. Formenti, M., F. Juillet, P. Meriaudeau, S.J. Teichner, and P. Vergnon, "Preparation in a Hydrogen-Oxygen Flame of Ultrafine Metal Oxide Particles," J. Coll. Sur. Sci., 39(1), 79 (1972).
6. George, A.P., R.D. Murley, and E.R. Place, "Formation of TiO₂ Aerosol from the Combustion Supported Reaction of TiCl₄ and O₂," Faraday Soc. Symp., No. 7 (1973).

7. Grjotheim, K., C. Krohn, M. Malinovsky, K. Mathiakovsky, and J. Thonstad, "Aluminum Electrolysis," Aluminum Verlag GmH, Dusseldorf, p. 333 (1977).
8. Hansen, D., Sargent-Welch Scientific Co., Skokie, IL., May, 1981.
9. Heestand, R.L., and C.F. Leitten, "Thermochemical Reduction of Uranium Hexafluoride for the Direct Fabrication of Uranium Dioxide Ceramic Fuels," Nuclear Applications, 1(6), 584 (1965).
10. Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd ed., Vol. 20, Wiley, New York, 1963.
11. Matheson Gas Products, Matheson Gas Data Book, Milwaukee, Wis. (1970).
12. McDanel Refractory Co., personal communication, Beaver Falls, Pa., May 1981.
13. Merriman, J.R., S.H. Smiley, and H.L. Kaufman, "Preparation of Unusual Refractory Powders by Flame Processes," Proc. Conf. Chemical Vapor Deposition of Refractory Metals, Alloys, and Compounds, Gatlinburg, TN, Sept. 12-14-1967, pp. 229-242, American Nuclear Society, Hinsdale, IL (1967).
14. National Element, personal communication, Troy, MI, May 1981.
15. Perry, R.H., and C.H. Chilton, Chemical Engineers' Handbook, 5th ed., Sect. 18, McGraw-Hill, New York (1969).
16. Stull, D.R., and H. Prophet, JANAF Thermochemical Tables, 2nd ed., U.S. Govt. Printing Office, Washington, D.C. (1971).
17. Tek, M.R., and J.O. Wilkes, "Notes and Problems in Fluid Flow and Heat Transfer," Univ. of Michigan, Ann Arbor (1974).